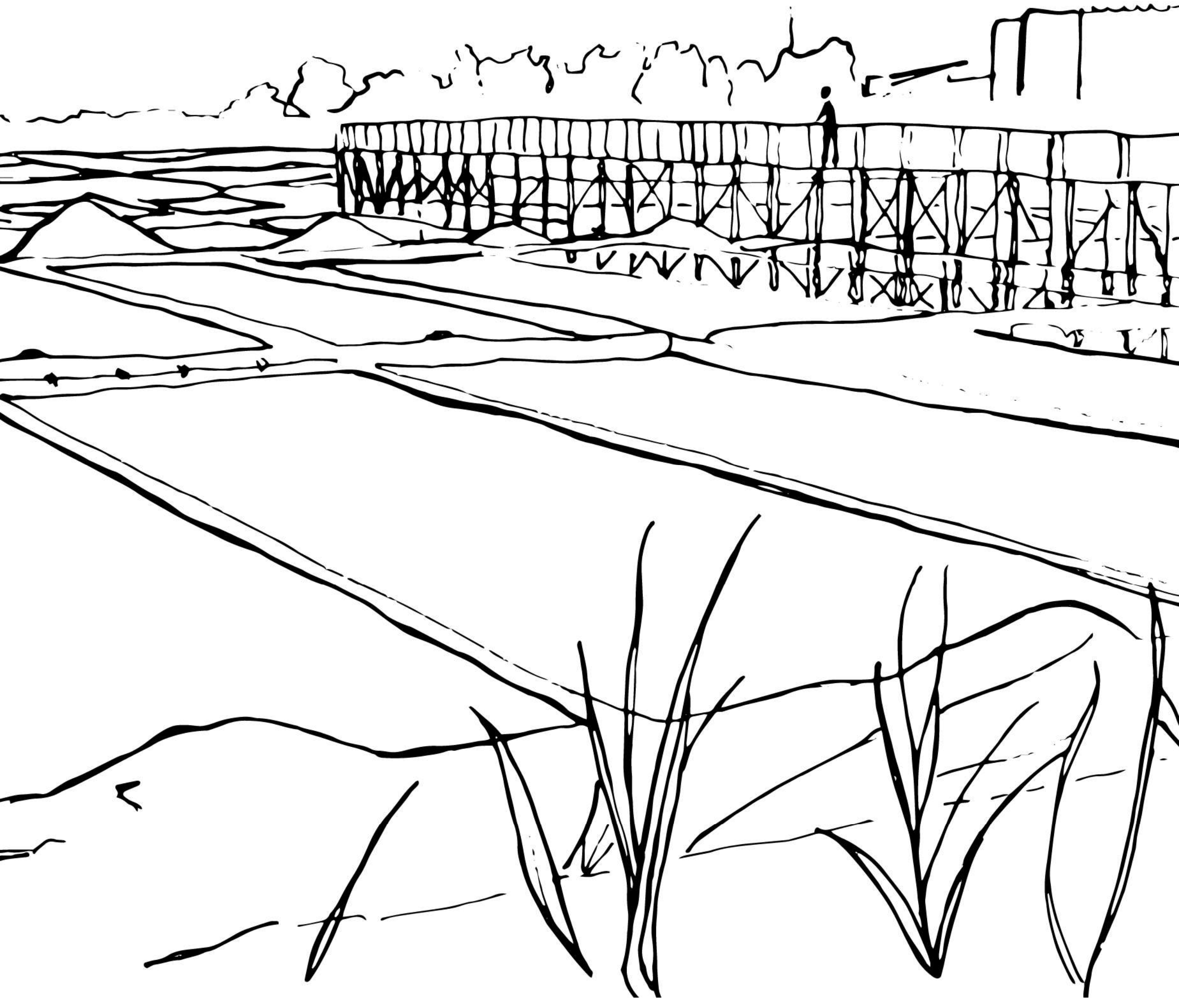
13th
IBCC
29 | 30
MARÇO
2022
AVEIRO
Inorganic & Bioinorganic
Chemistry Conference

Book of Abstracts



WELCOME MESSAGE

Dear Colleagues,

Under the auspices of the Portuguese Chemical Society (SPQ), and on behalf of the Organizing Committee, it is my pleasure to invite you to attend the 13th Inorganic & Bioinorganic Chemistry Conference which will be held in the 29th and 30th of March 2022 in Aveiro. After successive delays because of the (still) on-going COVID-19 pandemic, it is with great pleasure that we finally announce the realization of this event that will occur in a presential mode.

The aim of this biennial Conference is to provide a forum to discuss inorganic and bioinorganic chemistry topics. The importance of inorganic chemistry in catalysis, energy, materials, nanotechnology, biology and medicine is immense and current research challenges require active discussions among the inorganic chemistry community.

The preliminar scientific programme is already completed with remarkable line-up of invited scientists that include the recipient of the 5th edition of the Alberto Romão Dias Prize, Professor João Rocha (University of Aveiro), and two plenary lectures (videoconference) from Professor Omar Yaghi (University of Berkeley) and Professor Konstantinos Demadis (University of Creete). The programme will further include oral and poster presentations, in a good balance while promoting mostly the interaction between scientists.

We very much look forward to welcoming you in Aveiro.

COMMITTEES

Organizing Committee

Filipe A. Almeida Paz

CICECO, Depart. Chemistry, Univ. Aveiro, Portugal

🖂 filipe.paz@ua.pt

Manuel Souto

CICECO, Depart. Chemistry, Univ. Aveiro, Portugal

🖂 manuel.souto@ua.pt

Ana Luisa Daniel da Silva

CICECO, Depart. Chemistry, Univ. Aveiro, Portugal

🖂 ana.luisa@ua.pt

Flávio Figueira

CICECO, Depart. Chemistry, Univ. Aveiro, Portugal

🖂 ffigueira@ua.pt

Ricardo Faria Mendes

CICECO, Depart. Chemistry, Univ. Aveiro, Portugal

🖂 rfmendes@ua.pt

Isabel Vieira

CICECO, Depart. Chemistry, Univ. Aveiro, Portugal

🖂 ivieira@ua.pt

Bárbara Ferreira

CICECO, Depart. Chemistry, Univ. Aveiro, Portugal

🖂 barbaraferreira@ua.pt

Tatiana Amarante

CICECO, Depart. Chemistry, Univ. Aveiro, Portugal

🖂 tatiana.amarante@ua.pt

Luís Cunha Silva

Depart. Chemistry and Biochemistry, Fac. Ciências, Univ. Porto, Portugal

🖂 l.cunha.silva@fc.up.pt

Vânia André

Centro de Quimica Estrutural, Instituto Superior Técnico, Portugal

✉ vaniandre@tecnico.ulisboa.pt

Bernardo Monteiro

Instituto Superior Técnico, Universidade de Lisboa, Campus Tecnológico e Nuclear✉
bernardo.monteiro@ctn.tecnico.ulisboa.pt

Cláudia Pereira

Universidade Nova de Lisboa✉ ccl.pereira@fct.unl.pt

Scientific Committee

Filipe A. Almeida Paz

CICECO, Depart. Chemistry, Univ. Aveiro, Portugal

Maria da Conceição Rangel

Universidade do Porto – ICBAS

Cristina Freire

Universidade do Porto – Faculdade de Ciências

Baltazar de Castro

Universidade do Porto – Faculdade de Ciências

António Pires de Matos

Universidade Nova de Lisboa e Instituto Tecnológico e Nuclear

Maria José Calhorda

Universidade de Lisboa – Faculdade de Ciências

José G. Moura

Universidade Nova de Lisboa – Faculdade de Ciências e Tecnologia

Joaquim Marçalo

Instituto Superior Técnico, Universidade de Lisboa, Campus Tecnológico e Nuclear

Tito Trindade

CICECO, Depart. Chemistry, Univ. Aveiro, Portugal

Secretariat SPQ

Cristina Campos

Leonardo Mendes

GENERAL INFORMATION

Registration

The registration fee includes:

- Admission to all the Meeting's scientific sessions
- Conference materials
- Lunches (both days)
- Coffee Break(s)

Please note: Due to the COVID-19 pandemic, food at coffee breaks may not be served by the Organisation

Poster and oral presentations (technical information)

Oral Presentations

Participants giving an oral presentation are strongly encouraged to send the presentation at least one day before the beginning of the conference so it can be uploaded into the available computer in the room. Each participant will have the chance to test his/her presentation before the beginning of each session.

An Apple Macintosh with Keynote and the latest version of Microsoft Office will be available so all presentation formats can easily be used. Presentations in PDF can also be used. A laser pointer will also be available to each presenter.

Please note:

Plenary Lectures will have a total duration of 50 minutes (45 + 5 for discussion) while normal presentations are of 20 minutes (15 + 5 for discussion).

Posters

We would like to encourage the participants with an accepted communication as a poster to mount them during the registration period. Materials to fix the posters will be provided at the registration desk. The location of the poster presentation will be in Galeria multiusos - Zona ZTC

Please note:

Posters should be printed with a maximum dimension of 90 x 110 cm (width x height) and preferably in paper.

Official language

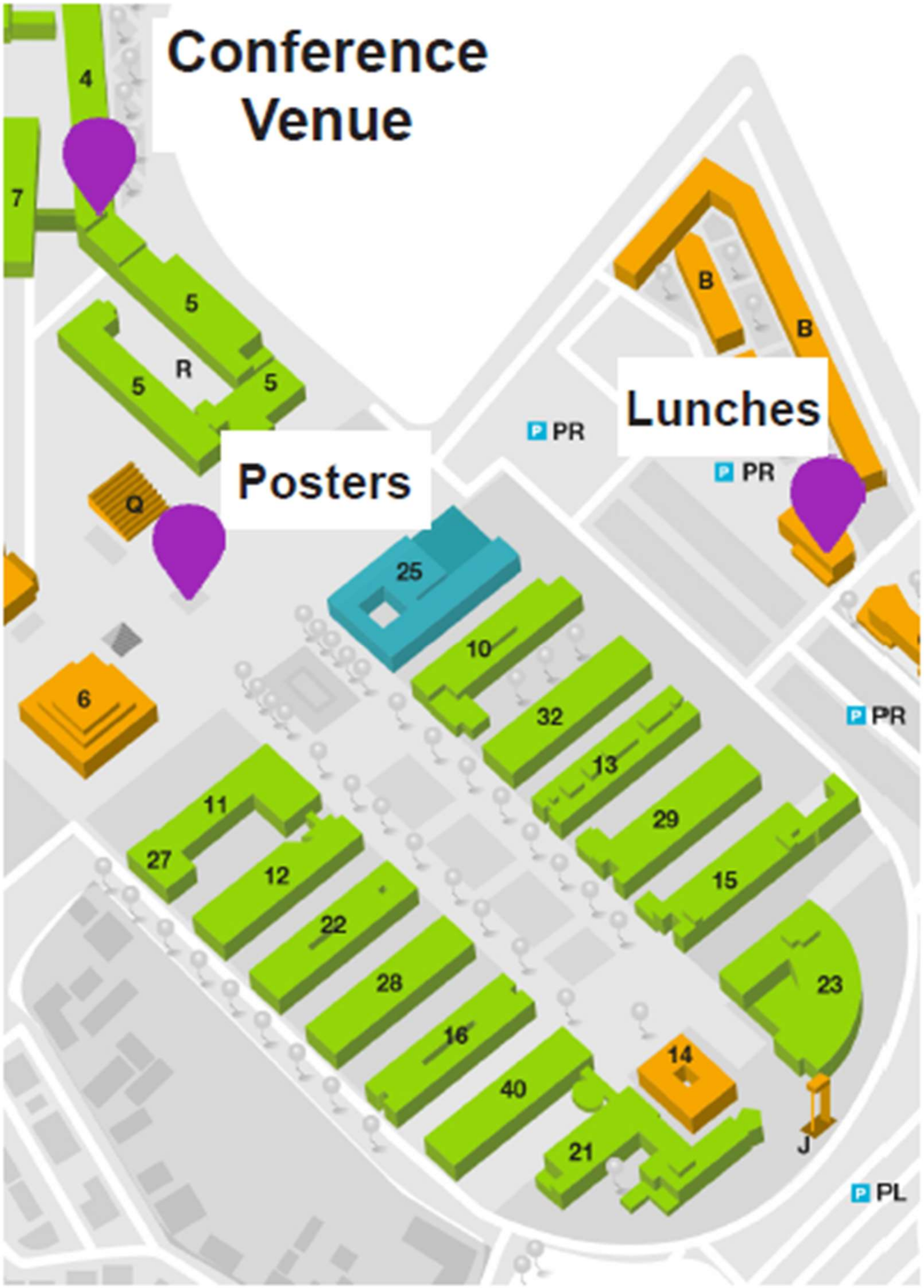
The official language of the Workshop is English. No simultaneous translation will be provided.

Badges and Security

It is essential that you wear your personal badge at all times while in the Workshop venue and during all the Events, as it is the official entrance pass to scientific sessions and other activities.

VENUE MAP

The 13th Inorganic & Bioinorganic Chemistry Conference will be held at the University of Aveiro, at Anfiteatro Carlos Borrego ((building number 7)



Reach the university campus from Aveiro train station

Aveiro railway station is located at about 15 minutes walking distance or 5 minutes taxi ride from the University Campus or 10 minutes bus (line 4) which departs from outside the railway station.

Reach the university campus by car

From the north using the A1 motorway or from the east using the A25: Take the A1 motorway headed to Lisbon. Exit the A1 in the direction of Aveiro and take the A25. There are two exits to the city from the A25, first "Aveiro-Norte" and some kilometers further on, the "Aveiro" exit. This second exit is the best for reaching the University of Aveiro campus.

From the south using the A1 motorway: Take the A1 motorway in the direction of Porto, exit the motorway at "Aveiro-Sul/Águeda" (exit 15) and follow the EN235 road directly to the University Campus. From the south, using the A8 and A17 motorways: Exit the motorway at "Aveiro-Sul" and follow the EN235 road directly to the University campus.

SCIENTIFIC PROGRAMM

Time	Tuesday (29 March)
08h30	**REGISTRATION**
09h30	**OPENING SESSION** with **Filipe Almeida Paz** (Conference Chair), **Professor Artur Silva** (President of SPQ and Vice-Rector of the University of Aveiro), **Professor João Coutinho** (Director of CICECO) and **Professor Armando Silvestre** (Director of the Chemistry Department of the University of Aveiro)
	Chair: Tito Trindade
10h00	**PL1 - B Royo -** "The Impact of N-Heterocyclic Carbenes in Manganese Catalysis"
11h00	**OC1 - L Maia** - "Molybdenum: a single metal, multiple oxygen and hydrogen atom transfer options"
11h20	**OC2 - A Brás** - "Novel ruthenium-cyclopentadienyl agents targeting KRAS mutated colorectal cancer"
11h40	**OC3 - G Francescato** - "Nickel N-Heterocyclic Carbene Complexes based on Xanthines: Synthesis and Antifungal Activity on *Candida sp.*"
12h00	**OC4 - S Jaros** - "Silver(I) and copper(I) aminophosphine coordination polymers for sensing and biological applications"
	LUNCH (12h30 - 14h00) *Location* : University Restaurant
	Coffee Break & Poster Session (14h00 - 15h00) *Location* : Galeria Multiusos – ZTC
	Chair: Artur Silva. Co-Chair: Filipe A. Almeida Paz
15h00	**Prémio Alberto Romão Dias.** *Recipient* **: Professor João Rocha**, University of Aveiro
15h30	**PL2 - J Rocha** - "Still here having fun with porous silicates & Metal-Organic Frameworks"
16h30	**PL3 - O Yaghi** - "Reticular Chemistry for a Sustainable Future"

Time	Wednesday (30 March)
	Chair: José Moura
09h00	**PL4 - K D Demadis -** "Phosphonates and metal-phosphonates: A short journey through their chemistry, technology and applications"
10h00	**OC5 - M Souto** - "Perylene-based Metal-Organic Frameworks:Tunable Electrical and Optical Properties"
10h20	**OC6 - V André** - "Antibiotic coordination frameworks for enhanced activity"
10h40	**Break and Elections**
	Chair: Teresa Duarte
11h00	**OC7 - S Balula** - "Polyoxometalates: a decade of success applications for effective sustainable catalytic systems"
11h20	**OC8 - M Pacheco** - "The role of structure-directing agents in photochromic WO3 (nano)materials"
11h40	**OC9 - T Fernandes** - "Dendrimer-based Metal Nanoalloys for Optical Detection of Pesticides"
12h00	**OC10 - N Bandeira** - "Remarks on Noble Gas Tetroxides: Insights and Predictions"
	LUNCH (12h30 - 14h00) *Location* : University Restaurant
	Coffee Break & Poster Session (14h00 - 15h30) *Location* : Galeria Multiusos – ZTC
	Chair: Baltazar Castro
15h30	**PL5 - E Pereira** - "Biological macromolecules and metal nanoparticles: applications and new properties"
16h30	**CLOSING CEREMONY** - Poster prizes and final remarks

INSTITUTIONAL SUPPORT

SOCIEDADE PORTUGUESA DE QUÍMICA

universidade de aveiro

CICECO
AVEIRO INSTITUTE OF MATERIALS

SPONSORS

sarspec
At light speed!

Qlabo
Quality Driven

LABOR
SPIRIT, Lda.

HIDEN
ISOCHEMA

CASA DE VINHAGO

paralab

riaparque

INDEX

Plenary Sessions

Oral Presentations

POSTER PRESENTATION

Plenary Sessions


13th IBCC 29 | 30 MARÇO 2022

PL1

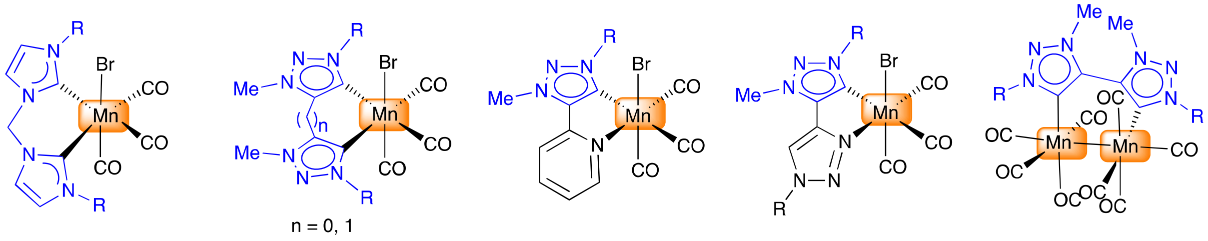
The Impact of N-Heterocyclic Carbenes in Manganese Catalysis

B. Royo*

ITQB NOVA, Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Avenida da República, 2780-157 Oeiras, Portugal
** E-mail: broyo@itqb.unl.pt*

Manganese has recently emerged as an excellent metal for catalysis. The vast natural abundance of manganese-it is the third most abundant transition metal in Earth´s crust-together with its low price and non-toxicity render it a particularly attractive metal for catalysis. Recent advances have shown the impressive reactivity of this metal in various important organic transformations, including (de)hydrogenation, hydrosilylation, and transfer hydrogenation reactions. Compared to the extensively employed pincer phosphine-derived ligands in Mn catalysis, the development of phosphine-free Mn catalytic systems remains poorly developed.[1]

We have recently disclosed the excellent catalytic performances in reduction reactions of Mn complexes bearing N-heterocyclic carbene (NHC) ligands, a key class of inexpensive and readily available ligands.[2] In this seminar, our recent work on manganese with mesoionic carbenes of 1,2,3-triazolylidene type, an interesting subclass of NHCs, will be presented. Up to date, the Mn chemistry of mesoionic carbenes have remained elusive. Here we present the first examples of Mn(I) complexes with bidentate ligands featuring combinations of pyridine, triazole, and 1,2,3-triazolylidene ligands (Scheme 1).[3] In addition, the synthesis of Mn(0) complexes containing a bridging 1,2,3-triazolylidene will be discussed. Having this complexes with varying electronic and steric properties, we have investigated their activity in a number of catalytic processes, including hydrosilylation, oxidation, borrowing hydrogen processes, and CO_2 reduction. The impact of the introduction of NHC ligands in the catalytic efficiency of the Mn complexes will be discussed.



Scheme 1: Mn-NHC complexes applied in catalysis

Acknowledgements
We thank the Fundação para a Ciência e a Tecnologia for financial support through projects PTDC/QUI-QIN/0359/2021, MOSTMICRO-ITQB UIDB/04612/2020, UIPD/04612/2020, CERMAX Project No.022162, UIDB-UIDP/50006/2020 and UIDB-UIDP/04378/2020.

References

1 J. R. Carney, B. R. Dillon and S. P. Thomas, *Eur. J. Chem.*, 2016, 3912–3929.
2 M. F. Pinto, S. Friães, F. Franco, J. Lloret-Fillol and B. Royo, *ChemCatChem.*, 2018, **10**, 2734-2740; S. C. A. Sousa, S. Realista and B. Royo, *Adv. Synth. Catal.,* 2020, **362**, 2437-2443.
3 M. F. Pinto, M. Olivares, A. Vivancos, G. Guisado-Barros, M. Albrecht and B. Royo, *Catal. Sci. Technol.*, 2019, **9**, 2421-2425. S. Friães, S. Realista, C. S. B. Gomes, P. N. Martinho, L. Veiros, M. Albrecht and B. Royo, *Dalton Trans.*, 2021, **50**, 5911-5920.

PL2

Still here having fun with porous silicates & Metal-Organic Frameworks

João Rocha[1,*]

[1] *CICECO-Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal,*
** E-mail: rocha@ua.pt*

In the past quarter century, I had a lot of fun designing and building up nanoporous transition metal and lanthanide silicates, and Metal-Organic Frameworks (MOFs), in the form of powders (Figure 1), films and membranes, studying their structures and properties and looking for promising real-world applications. I'm still here and having fun with these chemical zoo, and this talk will show you why.

Without fully unveiling the story (for more impact, I hope), I shall explain how the porous silicates my lab has been producing are essentially different from conventional zeolites. Even if some of their putative properties and applications (including catalysis ion exchange, gas storage and separation) are like zeolites', other are unprecedented, for example, intriguing light emission or deployment as a drug (already on the market) to treat hyperkalemia (excess K^+ in serum).

MOFs materials are much 'softer' than silicates, but both exhibit nanoporosity and are, thus, complementary gadgets in the toolbox of chemists. I shall highlight my work on lanthanide-bearing MOFs and their application in sensing of molecules, pH and temperature. MOFs can also be explored for the betterment of people in developing countries, and I shall illustrate this point with an example of mosquito nets. I have been concerned with potential applications of MOFs to clean the environment and here I shall present an example of UO_2^{2+} capture from waters. The talk will close with some examples of my recent research on electrically conductive MOFs and photoresponsive organic-inorganic ferroelectrics.

Figure 1: Still having fun with porous powders.

Acknowledgements

This work received financial support from PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior (PIDDAC)) through CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020. The NMR spectrometers are part of the National NMR Network (PTNMR) and are partially supported by Infrastructure Project Nº 022161 (co-financed by FEDER through COMPETE 2020, POCI and PORL and FCT through PIDDAC.

PL3

Reticular Chemistry for a Sustainable Future

Omar Yaghi

University of California, Berkeley, CA, 94720
Yaghi@berkeley.edu

The clean air, clean energy, and clean water challenges facing our planet today impact our health, wealth, happiness, and future. These three stresses present difficult science and engineering problems to solve as they require, among many aspects, the selective capture of small molecules (e.g. hydrogen, methane, carbon dioxide, and water). Our ability to capture, store, manipulate, and harness the power of these molecules in an efficient and economical manner is paramount to our success in building a sustainable future. The emerging field of reticular chemistry and materials has yielded extensive classes of nanoporous metal-organic frameworks and covalent organic frameworks. The flexibility with which these materials can be made, modified, and scaled bodes well for their integration into devices and providing robust solutions to these challenges. In this presentation, I will highlight how efforts in establishing the basic science of reticular materials that has led us to carbon capture from air and flue gas, and harvesting water from air to produce drinking water in various parts of the world regardless of temperature and humidity levels. Our efforts in taking this technology from the laboratory to the field including the design and engineering of prototypes will be discussed and the results presented.

PL4

Phosphonates and metal-phosphonates: A short journey through their chemistry, technology and applications

K.D. Demadis*, E. Chachlaki, A. Fanourgiakis, A. Moschona, M. Vassaki, K. Xanthopoulos

Crystal Engineering, Growth & Design Laboratory, Department of Chemistry
University of Crete, Voutes, Heraklion GR-71003, Crete, Greece
** E-mail: demadis@uoc.gr*

(Poly)phosphonic acids constitute an exciting family of phosphorus compounds. One of the attractive attributes of these molecules is the rich chemistry of the phosphonate moiety, and, in particular, its high affinity for metal ions and mineral surfaces. Whether the phosphonate group belongs to a “small” molecule or to a polymeric matrix, phosphonate-containing compounds have found a phalanx of real-life applications.

Herein, we address all the attractive attributes of molecules that are endowed with phosphonate moieties, and some derivatives with other functional groups (carboxylates, amines, sulfonates, heterocyclics, etc.). Moreover, a mention is made on phosphonate-containing polymers. Last, but not least a general overview is given on the growing field of metal-phosphonate materials, their basic structural architectures and how their structural features can affect their properties.

Phosphonates (as organic molecules) and metal-phosphonates (as solid MOF-type materials) have seen a tremendous growth in the past decades. There are several reasons for that: (a) there have been important advances in the synthesis of several types of phosphonic acids, esters and phosphonate-containing polymers, (b) virtually the metal ions from the entire Periodic Table have been mapped regarding their coordination with phosphonate linkers, (c) The metal-phosphonate compounds that have been synthesized and structurally characterized have been evaluated for their utility in several technological and pharmaceutical applications.

Since the latter have been the principal drivers for the observed growth, we will present the applications that use (or could potentially use) the attributes of phosphonates and metal phosphonates:
(1) Phosphonic acids as scale inhibitors or scale/deposit dissolvers in water treatment applications
(2) Phosphonic acids and metal-phosphonates as corrosion inhibitors in water treatment applications
(3) Phosphonic acids and metal-phosphonates as controlled release and drug delivery systems
(4) Phosphonic acids and metal-phosphonates as novel consolidants in Archaeology, for the preservation of Cultural Heritage elements.

This presentation has the ambition to convince even the most skeptical observer that phosphonate chemistry is not just a curiosity-driven exercise, but a true problem solver.

Acknowledgements
We thank the Hellenic Foundation for Research and Innovation (HFRI) for financial support of the PhD Candidates A.M. and M.V., through Research Fellowships (KA 10439 and KA 10440), and the Special Account for Research Grants of the University of Crete for funding the work of the PhD Candidates E.C. and K.X. in the research project “Innovative Materials and Applications” (INNOVAMAT, KA 10694).

Biological macromolecules and metal nanoparticles: applications and new properties

E. Pereira

LAQV/REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto; Rya do Campo Alegre, s/n, 4169-007 Porto, Portugal
** E-mail: eulalia.pereira@fc.up.pt*

Metal nanoparticles are well known to have useful optical properties that can be used in biosensors and other applications in bionanotechnology. These optical properties arise from the Localized Surface Plasmon Resonance (LSPR), and include extremely high absorption and scattering of visible light, enhancement of Raman signals of molecules adsorbed to their surface, and fluorescence quenching/enhancement. As such, they are excellent reporters in (bio)sensing applications, opening the way to new types of biosensors, and improving the performance and sensitivity of well-known detection methods.

Our research team is studying bionanoconjugates containing metal nanoparticles in biosensing and biocatalysis applications, in particular studying the effect of size/shape of nanoparticles (Figure 1). Selected examples will be presented including (i) the use of silver and gold nanostars in disposable platforms for Surface Enhanced Raman Spectroscopy (SERS);[1] (ii) gold nanoparticles for immunosensors;[2] (iii) gold nanoparticles as activity modulators of enzymes;[3] and gold nanoparticles for genosensors.

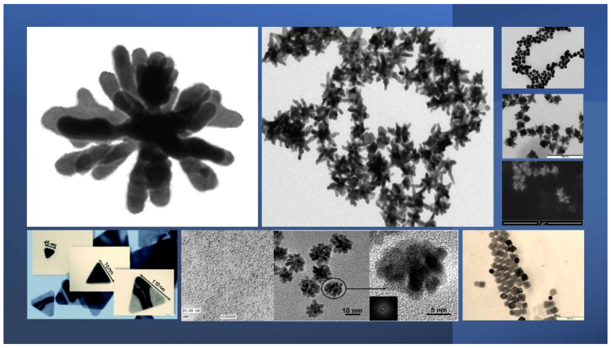


Figure 1: Selected electron microscopy images of metal nanoparticles synthesized and used: From top left (clockwise direction): silver nanostar; gold nanostars; gold nanospheres and nanostars; gold nanocubes; platinum nanodendrites; gold nanotriangles.

Acknowledgements

The work was supported through the project UIDB/50006/2020 | UIDP/50006/2020, funded by FCT/MCTES through national funds, and through National Funds (FCT, Fundação para a Ciência e Tecnologia) through project PTDC/NAN-MAT/30589/2017.

References

1. a) M. J. Oliveira, I. Cunha, M. P. de Almeida, T. Calmeiro, E. Fortunato, R. Martins, L. Pereira, H. J. Byrne, E. Pereira, H. Águas, and R. Franco, *J. Mater. Chem. B,* 2021, **9**, 7516-7529; b) M. J. Oliveira, M. P. de Almeida, D. Nunes, E. Fortunato, R. Martins, E. Pereira, H. J. Byrne, H. Águas; R. Franco *Nanomaterials* **2019**, *9*, 1561;
2. a) L. J. Bessa, M. P. de Almeida, P. Eaton, E. Pereira, P. Gameiro P. *Int. J. Environ. Res. Public Health* 2020, **17**, 7891; b) C. M. Silveira, R. Zumpano, M. Moreira, M. P. de Almeida, M. J. Oliveira, M. Bento, C. Montez, I. Paixão, R. Franco, E. Pereira, G. Almeida *ChemElectroChem* 2019, **6**, 4696; c) M. P. de Almeida; P. Quaresma; S. Sousa; S. Couto; I. Gomes, L. Krippahl, R. Franco, E. Pereira, *Phys. Chem. Chem. Phys.*, 2018, **20**, 16761.

ORAL PRESENTATIONS

Molybdenum: a single metal, multiple oxygen and hydrogen atom transfer options

L. Maia[1,*], J.J.G. Moura[1]

[1] *LAQV, REQUIMTE, NOVA School of Science and Technology | FCT NOVA, Campus de Caparica, Portugal*
* *E-mail: luisa.maia@fct.unl.pt*

Molybdenum biological relevance is poorly recognised and largely disregarded. Yet, molybdenum is essential to all forms of life, being found in the active site of enzymes that catalyse redox reactions involving carbon, nitrogen and sulfur atoms of key metabolites (Figure 1).[1] Some of the molybdenum-dependent reactions constitute key steps in the global biogeochemical cycles of carbon, nitrogen and sulfur, while in humans they play several carbon- and nitrogen-related roles and are vital for the sulfur metabolism.[2,3] The recent explosive growth in understanding the structure and function of molybdoenzymes is helping us to grasp the biochemical versatility of this transition metal and in this communication some key molybdoenzymes reactions will be thoroughly discussed.

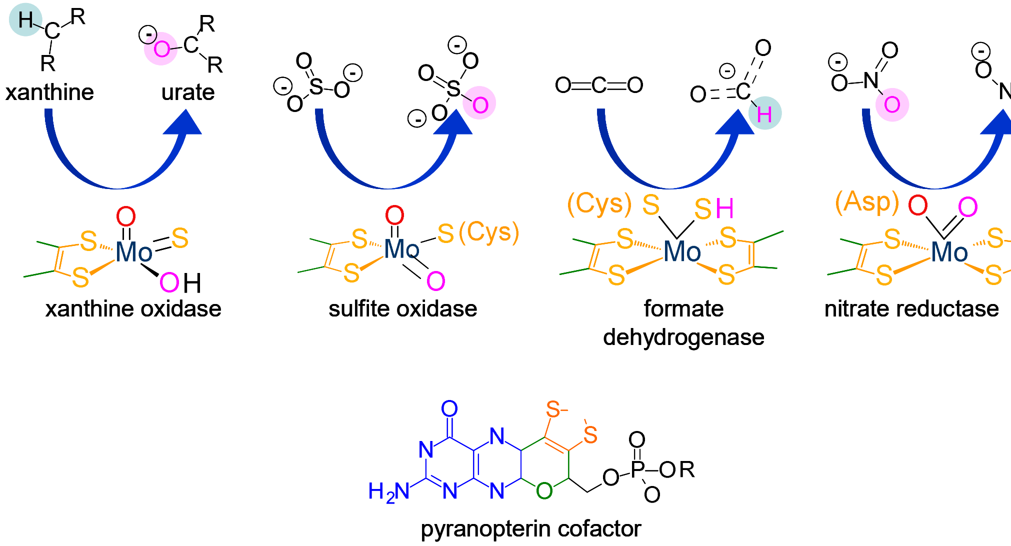


Figure 1: In biological systems, molybdenum is mainly found associated with one or two pyranopterin molecules that coordinate the metal by a *cis*-dithiolene group. The metal coordination sphere is completed by a diverse array of groups that allowed the evolution of enzymes with different physiological functions, such as xanthine oxidase and sulfite oxidase (involved in human health and disease), formate dehydrogenase (responsible for the biological carbon dioxide and formate handling and an interesting biotechnological target for the development of devices for atmospheric carbon dioxide utilization) or nitrate reductase (responsible for the biological nitrate utilisation and also a biotechnological target to mitigate soils and aquifers contamination). Bottom: structure of the pyranopterin molecule; top: active site structure of key molybdoenzymes (for simplicity, only the dithiolene moiety of the pyranopterin molecules(s) is(are) represented).

Acknowledgements

This work was supported by the PTDC/BTA-BTA/0935/2020 project and also by the Associate Laboratory for Green Chemistry - LAQV (UIDB/50006/2020 and UIDP/50006/2020), which are financed by national funds from Fundacão para a Ciência e a Tecnologia, MCTES (FCT/MCTES). LBM also thanks to FCT/MCTES, for the CEEC-Individual Program Contract (CEECIND/03810/2017).

References

1. Maia L., Moura I., Moura J.J.G., Molybdenum and Tungsten Enzymes: Biochemistry, The Royal Society of Chemistry, Cambridge, pp 1-80, 2017 (DOI: 10.1039/9781782623915-00001).
2. a) Maia L., Moura J.J.G., Chem. Rev. 2014, 114, 5273 (DOI: 10.1021/cr400518y). b) Maia L., Moura, J.J.G., Redox Biol. 2018, 19, 274 (DOI: 10.1016/j.redox.2018.08.020).
3. a) Maia L., Fonseca L., Moura I., Moura J.J.G., J. Am. Chem. Soc. 2016, 138, 8834 (DOI: 10.1021/jacs.6b03941). b) Maia L., Moura I., Moura J.J.G., Carbon Dioxide Utilisation - The Formate Route, Springer International Publishing, pp 29-81, 2021 (DOI: 10.1007/978-3-030-58315-6_2).

OC2

Novel ruthenium-cyclopentadienyl agents targeting KRAS mutated colorectal cancer

Ana Rita Brás[1,2,3]*, Pedro Fernandes[1,2], Tiago Moreira, Andreia Valente[3#], Ana Preto[1,2#]

[1] *CBMA – Centre of Molecular and Environmental Biology, University of Minho, Braga, Portugal*
[2] *IBS - Institute of Science and Innovation for Bio-Sustainability, University of Minho, Braga, Portugal*
[3] *CQE – Centro de Química Estrutural, Institute of Molecular Sciences and Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Lisbon, Portugal*
#Co-senior authorship
** E-mail: pg31015@alunos.uminho.pt*

Colorectal cancer (CRC) is an important cause of global morbidity and mortality however, limited therapeutic drugs are available[1,2]. CRC harboring KRAS and BRAF mutations (the most frequent mutations present in CRC) make this type of cancer resistant to available inhibitors, which constitutes a clinically relevant problem that needs to be overcome[3]. Moreover, targeting KRAS mutations are being difficult to achieve highlighting the need of developing new specific target drugs. Ruthenium (Ru) drugs had arisen as one of the most promising metallodrugs with features that increase their specificity and selectivity toward cancer cells[4].

In this work, a new family of Ru-cyclopentadienyl agents was designed using macromolecules and/or biomolecules to increase the targeting for CRC cells. Here, we aimed to unravel the anticancer effects and mechanism of action of these new Ru agents in CRC cells. For that purpose, we used two CRC-derived cell lines with KRAS and BRAF mutations and a normal colon cell line to evaluate cell viability, proliferation, cell death mechanism, migration, intracellular distribution, actin cytoskeleton alterations, and KRAS signaling pathways expression (the most important signaling pathways for CRC carcinogenesis).

Our results revealed that the new Ru-cyclopentadienyl agents present promising anticancer activity. We found that all Ru agents are selective to CRC cells, decrease proliferation, induce apoptosis, decrease migration, and have different distributions in CRC cells (Figure 1). The lead agent, PMC79, also affects the actin cytoskeleton and inhibits KRAS signaling pathways in CRC, only in the cell line with KRAS mutation. This result suggests that PMC79 has a noticeable effect on CRCs harboring KRAS mutation. Overall, the new Ru-cyclopentadienyl agents are promising drugs for CRC therapy, which could bring new exciting therapeutic avenues in CRC harboring KRAS mutations.

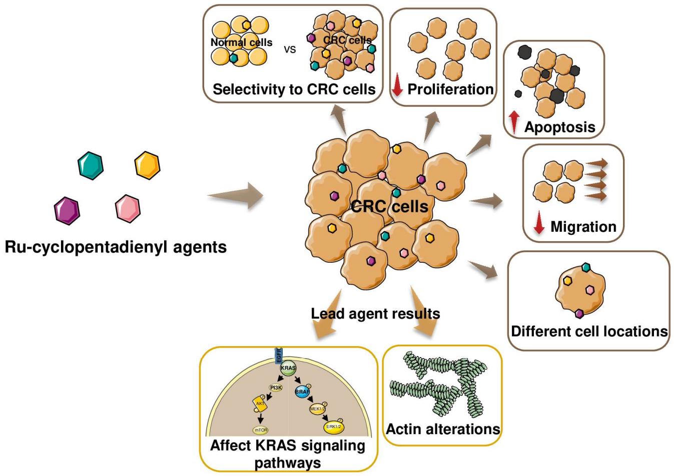


Figure 1: Results of Ru-cyclopentadienyl agents in CRC cell lines.

Acknowledgments

We thank the Fundação para a Ciência e a Tecnologia (FCT) for Ana Rita Brás PhD grant (SFRH/BD/139271/2018) and Andreia Valente's CEECIND 2017 Initiative (CEECCIND/01974/2017). This work was funded by FCT, I.P./MCTES through national funds (PIDDAC) - UIDB/00100/2020 and UID/BIA/04050/2019, and through PTDC/QUI-QIN/28662/2017.

References

1 H. Sung, J. Ferlay, R. L. Siegel, M. Laversanne, I. Soerjomataram, A. Jemal and F. Bray, *CA. Cancer J. Clin.*, 2021, **71**, 209–249; 2 G. Cazzanelli, T. Moreira, S. Ferro, J. Azevedo-Silva, E. Nogueira and A. Preto, in *Frontiers in Anti-Cancer Drug Discovery*, 2016; 3 L. László, A. Kurilla, T. Takács, G. Kudlik, K. Koprivanacz, L. Buday and V. Vas, *Cells*, 2021, **10**, 1–19; 4 S. Thota, D. A. Rodrigues, D. C. Crans and E. J. Barreiro, *J. Med. Chem.*, 2018, **61**, 5805–5821.

OC3

Nickel N-Heterocyclic Carbene Complexes based on Xanthines: Synthesis and Antifungal Activity on *Candida sp.*

Giulia Francescato[1]*, Sofia Marques da Silva[1], Maria Inês P.S. Leitão[1], Carolina Cordeiro[1], Nicolaus Giannopoulos[1], Clara S. B. Gomes[2,3], Catarina Pimentel[1], and Ana Petronilho[1]

[1]*Instituto de Tecnologia Química e Biológica António Xavier, Avd Republica, 2780-157 Oeiras, Portugal. Tel. (+351) 21 4469716, Fax: (+351) 21 441 12 77*

[2]*LAQV-REQUIMTE, Department of Chemistry, NOVA School of Science and Technology, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal.*

[3]*UCIBIO – Applied Molecular Biosciences Unit, Department of Chemistry, School of Science and Technology, NOVA University Lisbon, 2819-516 Caparica, Portugal*

** E-mail: giulia@itqb.unl.pt*

Invasive fungal diseases affect more than two million people worldwide. The increasing incidence of invasive fungal infections is the result of many factors, including an increase in the resistance to current drugs[1]. There is as such an urgent need to obtain new drugs that are efficient, selective and able to overcome existing resistance mechanisms. Candida yeasts are responsible for more than 70% of all Invasive fungal diseases and *Candida Glabrata* infections are among the most concerning as it is a species resistant to the classic azole based antifungals[2].

Nickel compounds have been recently reported to be active antifungal agents against candida strains[3]. Inspired by this, we have developed a set of nickel NHCs based on xanthines. Xanthine derivatives are excellent ligand precursors for the formation of N-heterocyclic carbenes (NHCs) complexes[4].

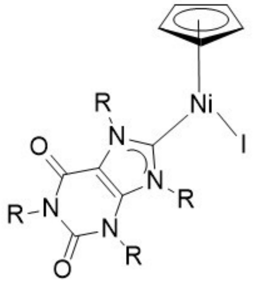


Figure 1: General structure of Nickel(II)(NHC) complexes based on xanthines

Acknowledgements

This work was financially supported by: Project LISBOA-01-0145-FEDER-007660 (Microbiologia Molecular, Estrutural e Celular) funded by FEDER funds through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI).

References

1 D. W. Denning, M. J. Bromley, *Science*, 2015, **347**, 1414-1416.
2 P.G. Pappas, M.S. Lionakis, M.C. Arendrup, L. Ostrosky-Zeichner, B.J. Kullberg, *Nat. Rev. Dis. Prim.*, 2018, **4**, 1.
3 A. Akbari, H. Ghateazadeh, R. Takjoo, B. Sadeghi-Nejad, M. Mehrvar, J. T. Mague, *J. of Mol. Structure*, 2019, **1181**, 1181, 287.
4 A. Kascatan-Nebioglu, M. J. Panzner, J. C. Garrison, C. A. Tessier, W.J. Youngs, *Organometallics*, 2004, **23**, 1928-1931.

OC4

Silver(I) and copper(I) aminophosphine coordination polymers for sensing and biological applications

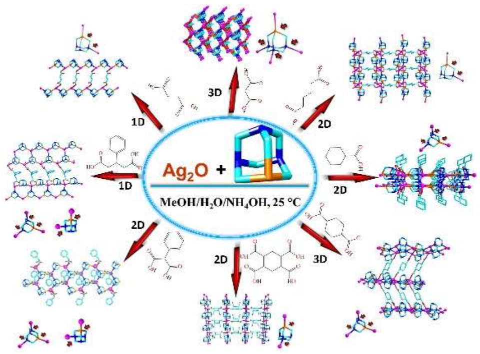
S. W. Jaros[1,*], M. Florek[2], B. Bażanów[2], J. Sokolnicki[1], M. Haukka[3], D. Paradowski[2], A. Krogul-Sobczak[4], D. S. Nesterov[5], A. M. Kirillov[5], P. Smoleński[1]

[1] Faculty of Chemistry, University of Wrocław, Poland
[2] University of Environmental and Life Sciences, Poland
[3] Department of Chemistry, University of Joensuu, Finland
[4] Faculty of Chemistry, University of Warsaw, Poland
[5] CQE, IST, Universidade de Lisboa, Portugal
** E-mail:sabina.jaros@chem.uni.wroc.pl*

The design and synthesis of silver(I) and copper(I) coordination compounds have seen a sweeping development in recent years due to their rich structural diversity and many different applications, including luminescence, electrical conductivity, catalysis, and biological activity. In particular, bioactive coordination polymers (bioCPs) have emerged as a promising class of compounds that feature high porosity, structural tunability, proper stability, versatile host-guest interactions, sorption, and ion release properties, along with an interesting sensing capability and therapeutic outcome.[1-3]

Thus, an increasing effort has been paid toward the design of new antimicrobial materials and luminescent "turn-on" sensors based on coordination polymers. Among many parameters that influence the self-assembly formation, stability, water solubility, and antimicrobial and sensing properties of Cu(I) and Ag(I) coordination networks, the choice of the multidentate ligands with both homo and heteroatom donor systems is a particularly important factor.[1-3]

Hence, we highlight herein our recent results on the synthesis and characterization of rare aqua-soluble bioactive or luminescent silver(I)- and copper(I)-organic networks, derived from a cagelike aminophosphine (1,3,5-triaza-7-phospaadamantane) and its derived ligands, as well as various carboxylic acids and/or supporting ligands. These products exhibit significant antimicrobial activity and stimuli-responsive photoluminescence, thus opening up their potential exploration as novel bioactive and sensing materials.[1-3]



Scheme 1: Simplified representation for the self-assembly synthesis of Ag(I)-based bioCPs.

Acknowledgments
We thank the National Science Center (Grant No. 2019/35/D/ST5/01155, Poland) and FCT (PhD grant SFRH/BD/77024/2011 and projects LISBOA-01-0145-FEDER-029697, UIDB/00100/2020, Portugal) for financial support.

References

S. W. Jaros, A. Krogul-Sobczak B. Bażanów, M. Florek, D. Poradowski, D. S. Nesterov, U. Śliwińska-Hill, A. M. Kirillov, P. Smoleński, *Inorg. Chem.* 2021, **60**, 15435–15444.
S. W. Jaros, J. Król, B. Bażanów, D. Poradowski, A. Chrószcz, D. S. Nesterov, A. M. Kirillov, P. Smoleński, *Molecules*, 2020, **25**, 2119/1-2119/13.
S. W. Jaros, J. Sokolnicki, A. Wołoszyn, M. Haukka, A. M. Kirillov, P. Smoleński, *J. Mater. Chem. C*, 2018, **6**, 1670-1678.

Perylene-based Metal-Organic Frameworks: Tunable Electrical and Optical Properties

Gonçalo Valente,[1] Ana Paracana,[2] Miguel Hernández-Rodríguez,[2] Antonio Rodríguez Diéguez,[3]
Joaquín Calbo,[4] Helena Alves,[2] João Rocha[1] and Manuel Souto[1,*]

[1] Department of Chemistry, CICECO-Aveiro Institute of Materials, University of Aveiro, Aveiro, Portugal
[2] Department of Physics, CICECO-Aveiro Institute of Materials, University of Aveiro, Aveiro, Portugal
[3] Department of Inorganic Chemistry, University of Granada, 18071, Granada, Spain
[4] Instituto de Ciencia Molecular (ICMol), Universidad de Valencia, c/Catedrático José Beltrán, 2, 46980 Paterna, Spain
** E-mail: manuel.souto@ua.pt*

Electrically conductive Metal-Organic Frameworks (MOFs) have emerged in the past few years as promising materials towards applications in (opto)electronics, electrocatalysis or energy storage, among others.[1] One of the most common strategies for the design of conductive MOFs is based on the use of electroactive organic ligands and their partial oxidation/reduction to increase the number of charge carriers.[2] Although perylene salts were reported as the first molecular conductors, they have been scarcely explored as building block for the construction of conductive MOFs. In the first part of the talk, I will present the electrical conductivity enhancement of a perylene-based MOF upon partial ligand oxidation by using two-probe single-crystal devices.[3] The origin of the conductivity enhancement is rationalized by means of spectroscopic studies and quantum-chemical calculations. In the second part of the talk, I will present a new family of perylene-based MOF with different transition metals (Co, Ni, Zn) to study the influence of the metal on the MOF's optical properties. These results highlight the great versatility of perylenes as building blocks for the construction of electroactive MOFs.

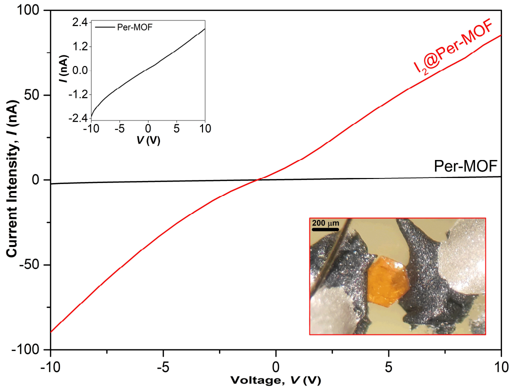


Figure 1: Representative Current (*I*)–Voltage (*V*) plot for crystal devices of Per-MOF (black) and I_2@Per-MOF (red) at 300 K.

Acknowledgements
This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, Grants UIDB/50011/2020 and UIDP/50011/2020, financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. We thank FCT for funding the project PTDC/QUI-ELT/2593/2021.

References

[1] M. D. Allendorf, R. Dong, X. Feng, S. Kaskel, D. Matoga and V. Stavila, *Chem. Rev.*, **2020**, *120*, 8581.
[2] M. Souto, K. Strutyński, M. Melle-Franco and J. Rocha, *Chem. Eur. J.*, **2020**, *26*, 10912.
[3] G. Valente *et al. submitted*.

Antibiotic coordination frameworks for enhanced activity

V. André[1,2*], M. M. Alves[1,2], P. C. Alves[1,2], P. Rijo[3,4], J. Mota[1,2], D. R. Ferreira[1,2], C. Bravo[1,2]

[1] 1Centro de Química Estrutural, Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal; [2] IST-ID, Av. Rovisco Pais, 1049-003, Lisboa, Portugal; [3]Universidade Lusófona's Research Center for Biosciences and Health Technologies, Lisboa, Portugal; [4]Research Institute for Medicines, Faculty of Pharmacy, Universidade de Lisboa, Lisboa, Portugal

** E-mail: vaniandre@tecnico.ulisboa.pt*

Antibiotics largely contributed to reduce the number of deaths associated with microbial infections in the last century, but over the last years their efficacy has been compromised, making imperative to find more efficient forms. Metal-organic frameworks (MOFs) and hydrogen bonded frameworks exploring antibiotics as ligands (antibiotic coordination frameworks, ACFs) are presented herein as auspicious alternatives to enhance the antimicrobial activity of commercially available active pharmaceutical ingredients[1]. Mechanochemistry, a sustainable technique[2], has been used as the main synthetic technique to unveil these novel ACFs.
Biological assays using Gram-positive and Gram-negative bacteria, as well as yeasts have shown that new ACFs with different drugs, as nalidixic acid, pipemidic acid or tazobactam, making use of different metal sites are more active against specific microorganisms than the free antibiotics used in their synthesis[3,4,5].

Figure 1: Antibiotic coordination frameworks

Acknowledgements
Fundação para a Ciência e a Tecnologia (FCT, Portugal) (projects PTDC/QUI-OUT/30988/2017, UIDB/00100/2020, UIDP/00100/2020, and contract CEECIND/00283/2018) and FEDER, Portugal 2020 and Lisboa2020 (project LISBOA-01-0145-FEDER-030988 and contract under DL No. 57/2016 regulation) are acknowledged for funding.

References

[1] V. André, P.C. Alves, M.T. Duarte, *Inorganica Chimica Acta*, 2021, **525**, 120474.
[2] J.G. Hernández, I. Halasz, D. Crawford, M. Krupicka, M. Baláž, V. André, L. Vella-Zarb, A. Niidu, F. García, L. Maini, E. Colacino, *European Journal of Organic Chemistry* 2020, **2020**, 8-9.
[3] V. André, A. Silva, A. Fernandes, R. Frade, P. Rijo, C. Garcia, A.M.M. Antunes, J. Rocha, M.T. Duarte, *ACS Applied BioMaterials*, 2019, **2**(6), 2347.
[4] P.C. Alves, P. Rijo, C. Bravo, A.M.M. Antunes, V. André, *Molecules*, 2020, **25**, 2374.
[5] D.R. Ferreira, P.C. Alves, A.M. Kirillov, P. Rijo, V. André, *Frontiers in Chemistry*, 2022, **9**, 815827.

OC7

Polyoxometalates: a decade of success applications for effective sustainable catalytic systems

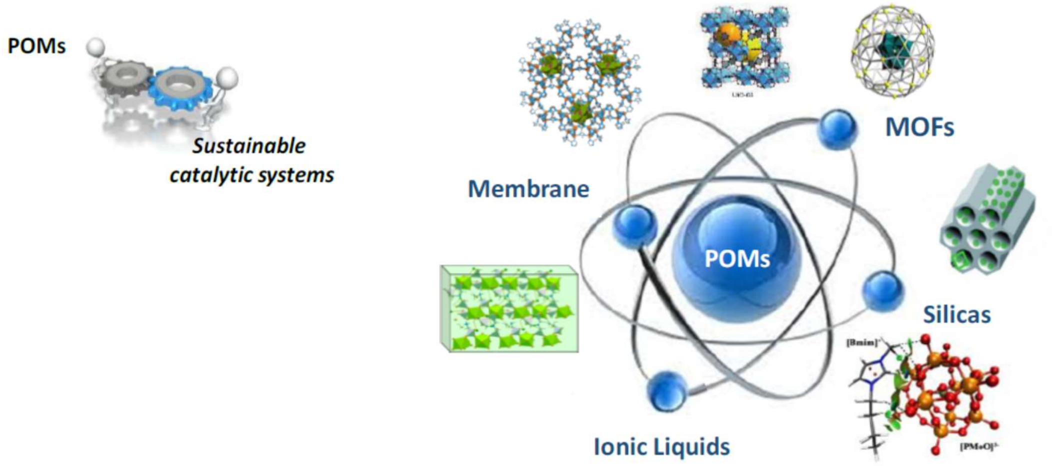
Salete Balula*, Alexandre Viana, Rui Faria, Carlos Granadeiro, Fátima Mirante, Luís Cunha-Silva

REQUIMTE/LAQV & Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal

Early-transition metal oxygen anion clusters, also known as polyoxometalates (POMs), are a class of compounds with high interest as catalysts due to their unusual versatility and compatibility with environmental friendly conditions and operations, being designated by "green catalysts". Despite their good activity in various catalytic systems, their solubility in polar media became a disadvantage, precluding their application at industrial scale where efficiency, robustness and recycling are required. To overcome this drawback, considerable efforts to promote their recovering and recycling have been made through the immobilization of POMs using various solids supports.

The POMOF group from LAQV/REQUIMTE have been using the POMs as active center in different sustainable catalytic systems: olefins epoxidation, glycerol acetalization, desulfurization of fuels, ring opening epoxides, Isomerization of glucose, among others. 1-4 The conciliation of sustainability and catalytic efficiency has been the main target. Therefore, POMs structural modifications and their incorporation in different solids has been largely investigated. The most success support materials found are mainly silica, Metal-Organic Frameworks and polymeric membrane. Strategic functionalization and support design have been strong focus of research.

POMs MOFs Silicas Membrane Ionic Liquids



Acknowledgements

The work received financial support from Portuguese national funds (FCT/MCTES) through the strategic project UIDB/50006/2020 (for LAQV-REQUIMTE); it was also funded by the European Union (FEDER funds through COMPETE POCI-01-0145-FEDER-031983) and FCT/MCTES to the R&D project GlyGold (PTDC/CTM-CTM/31983/2017). LCS and SSB thank FCT/MCTES for funding the Individual Call to Scientific Employment Stimulus (CEECIND/00793/2018 and EECIND/03877/2018, respectively). AMV and RGF thank FCT/MCTES and ESF (European Social Fund) for their PhD grants (Refs. SFRH/BD/150659/2020 and UI/BD/151277/2021, respectively) through POCH (Programa Operacional Capital Humano).

References

1) Granadeiro, C. M.; Barbosa, A. D. S.; Silva, P.; Paz, F. A. A.; Saini, V. K.; Fires, J.; de Castro, B.; Balula, S. S.; Cunha-Silva, L. *Applied Catalysis a-General* **2013**, *453*, 316.
2) Juliao, D.; Barbosa, A. D. S.; Peixoto, A. F.; Freire, C.; de Castro, B.; Balula, S. S.; Cunha-Silva, L. *Crystengcomm* **2017**, *19*, 4219.
3) Lara-Serrano, M.; Morales-delaRosa, S.; Campos-Martin, J. M.; Abdelkader-Fernandez, V. K.; Cunha-Silva, L.; Balula, S. S. *Sustainable Energy & Fuels* **2021**, *5*, 3847.
4) Fernandes, S. C.; Viana, A. M.; de Castro, B.; Cunha-Silva, L.; Balula, S. S. *Sustainable Energy & Fuels* **2021**, *5*, 4032.

The role of structure-directing agents in photochromic WO_3 (nano)materials

Marlene L. Pacheco[1*], Tânia V. Pinto[1], Céu M. Sousa[2], Alexandra Guedes[3], Ginesa Blanco[4], J. M. Pintado[4], Paulo J. Coelho[2], Cristina Freire[1], Clara Pereira[1]

[1] REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal

[2] Departamento de Química e CQ-VR, Universidade de Trás-os-Montes e Alto Douro, 5001-801 Vila Real, Portugal

[3] Instituto de Ciências da Terra e Departamento de Geociências, Ambiente e Ordenamento do Território, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal

[4] Departamento de Ciencia de Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, 11510 Puerto Real, Cádiz, Spain

** E-mail: up201811988@edu.fc.up.pt*

Photoresponsive textiles are increasingly needed for applications such as anti-counterfeiting, UV-protection, fashion, and camouflage for military purposes.[1] Inorganic materials, such as tungsten(VI) oxide, are promising for the production of light-responsive textiles, demonstrating fast response to light stimulus (sunlight/UV radiation), high color reversibility, good coloration, cyclability and resistance to high temperatures, although the bleaching can take several days.[2] The processes used for the synthesis of such materials need to be simple, low-cost and easy to scale-up in order to be used in industry.

In this work, several WO_3-based photochromic materials were produced through a cost-effective single-step solvothermal reaction using different types of structure-directing agents to be subsequently used for the production of advanced light-responsive textiles. The role of the structure-directing agent on the morphological, structural, chemical and photochromic properties of the as-prepared materials was evaluated by electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, diffuse reflectance UV−vis spectroscopy and colorimetry. Two distinct classes of materials were obtained: WO_3 Lindqvist-type polyoxometalates involved in a network of polyvinylpyrrolidone (PVP), and WO_3/H_2WO_4-based materials, where H_2WO_4 was the predominant phase. The WO_3 Lindqvist-type polyoxometalates presented better photochromic response, reaching higher total color difference (ΔE = 21.4 up to 50.6 *vs.* ΔE = 1.9 up to 15.2 for the WO_3/H_2WO_4 materials). Moreover, distinct colors were achieved for both sets of materials (Figure 1A).

The Lindqvist-type WO_3 materials with the best photochromic performance, prepared using PVP with different molecular weights, were incorporated on cotton substrates by screen-printing to create three photoresponsive fabrics: WO_3_PVP_L@cot, WO_3_PVP_M@cot and WO_3_PVP_H@cot. The smart fabric WO_3_PVP_L@cot presented remarkable coloration from white to blue in 5 min, when irradiated with UV light, and bleached in 5 hours after being placed in the dark (Figure 1B), with ΔE = 28.4. The WO_3_PVP_H@cot revealed an impressive dual chromism (photochromism and hydrochromism), rapidly changing its color when irradiated with UV light for 4 min, and returning to the initial color when placed in the dark for 3 h or when immersed in water for 10 s. The obtained results confirmed that the as-prepared WO_3 materials accomplished the features necessary to be implemented in the textile industry.

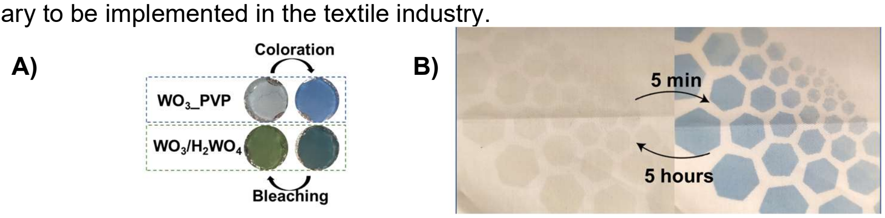


Figure 1: A) Photochromic response of WO_3_PVP and WO_3/H_2WO_4 materials before and after UV light irradiation (λ = 360 nm). B) Photographs of the light-responsive cotton fabric WO_3_PVP_L@cot before and after UV light irradiation (λ = 360 nm).

Acknowledgements

Work funded by Portuguese funds through Fundação para a Ciência e a Tecnologia (FCT)/MCTES in the framework of the projects UIDB/50006/2020 and UIDP/50006/2020. Marlene Pacheco thanks FCT for PhD grant (SFRH/PB/BD/144240/2019) and the Doctoral Programme ChemMat.

References

1 T. V Pinto, D. M. Fernandes, A. Guedes, N. Cardoso, N. F. Durães, C. Silva, C. Pereira and C. Freire, *Chem. Eng. J.*, 2018, **350**, 856–866.

2 S. Wang, W. Fan, Z. Liu, A. Yu and X. Jiang, *J. Mater. Chem. C*, 2017, **6**, 191–212.

Dendrimer-based Metal Nanoalloys for Optical Detection of Pesticides

T. Fernandes[1,*], N.C.T. Martins[1], S. Fateixa[1], H.I.S Nogueira[1], A.L. Daniel-da-Silva[1], T. Trindade[1]

[1] *Department of Chemistry, CICECO- Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal*
** E-mail: jtfernandes@ua.pt*

The distinctive nanoarchitecture of poly(amidoamine) (PAMAM) dendrimers offers a set of interesting features for the design of dendrimer-metal hybrids suitable for sensing applications[1, 2]. Our research group has explored the characteristics of such hybrid systems in the optical detection of aqueous analytes, by using surface enhanced Raman scattering (SERS) methods[3-5]. Herein, the chemistry of PAMAM dendrimers is explored to produce a series of gold and silver colloidal nanoalloys of variable chemical composition. Colloids of metal nanoalloys of tunable size, surface chemistry and shape were obtained by carefully selecting the reaction conditions. By taking advantage of the dendrimer's architecture, which was used as the sole reducing and stabilizing agent, we have prepared metal colloids showing long-term colloidal stability and tunable optical response. In addition, the *in situ* synthesis of the Au/Ag nanoparticles in the presence of PAMAM, led to nanoassemblies having the dendrimer as a macromolecular "glue". In these nanoassemblies, interparticle plasmon coupling between neighboring nanoparticles was observed, resulting in better SERS response as compared to their monometallic counterparts. As such, the dendrimer stabilized metal hybrids were explored in SERS studies aiming at probing vestigial pesticides in spiked water samples. To achieve this goal, the Au:Ag-PAMAM nanostructures were explored in the design of multiple SERS sensing substrates that were then applied using variable operational conditions. To this end, SERS studies were accomplished either in the colloidal form (**Figure 1-A**) or hydrophobic paper substrates by the controlled deposition of the Au:Ag-PAMAM hybrids through inkjet printing (**Figure 1-B**). The SERS substrates presented here allowed the screening of thiram and ziram for concentrations as low as 1×10^{-7} M. Both, the colloids and the paper-based substrates displayed good SERS signal homogeneity, high repeatability and long-term stability. The strategies described in this research demonstrate the versatility of the reported methods to prepare efficient dendrimer-based SERS substrates, which can be used for water quality monitoring in multiple analytical contexts.

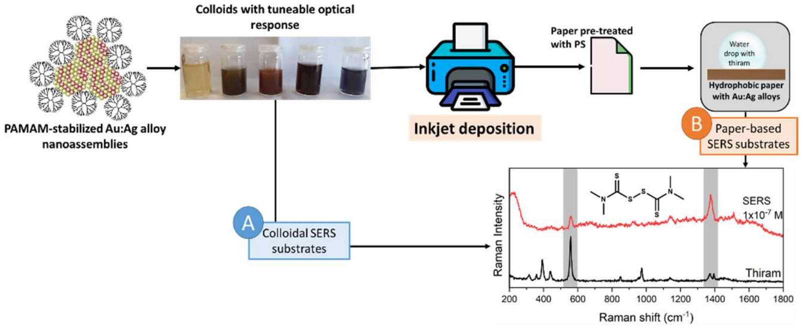


Figure 1: Au:Ag-PAMAM nanoalloys as SERS substrates by using distinct operational conditions.

Acknowledgements
This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC).Tiago Fernandes thanks the Fundação para a Ciência e Tecnologia (FCT) for the PhD grant SFRH/BD/130934/2017. The costs resulting from the FCT hirings is funded by national funds (OE), through FCT, I.P. in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, of August 29.

References

1. H. Viltres, Y. C. López, C. Leyva, N. K. Gupta, A. G. Naranjo, P. Acevedo–Peña, A. Sanchez-Diaz, J. Bae and K. S. Kim, *Journal of Molecular Liquids*, 2021, **334**, 116017.
2. T. Fernandes, A. L. Daniel-da-Silva and T. Trindade, *Coordination Chemistry Reviews*, 2022, **460**, 214483.
3. T. Fernandes, S. Fateixa, H. I. S. Nogueira, A. L. Daniel-da-Silva and T. Trindade, *European Journal of Inorganic Chemistry*, 2020, **2020**, 1153-1162.
4. T. Fernandes, S. Fateixa, M. Ferro, H. I. S. Nogueira, A. L. Daniel-da-Silva and T. Trindade, *Journal of Molecular Liquids*, 2021, **337**, 116608.
5. T. Fernandes, N. C. T. Martins, S. Fateixa, H. I. S. Nogueira, A. L. Daniel-da-Silva and T. Trindade, *Journal of Colloid and Interface Science*, 2022, **612**, 342-354.

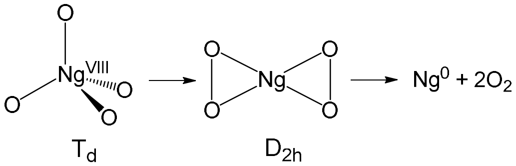
Remarks on Noble Gas Tetroxides: Insights and Predictions

Nuno A. G. Bandeira[1,*], Sandrina Oliveira, Joaquim Marçalo[2]

[1] BioISI, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal
[2] Centro de Química Estrutural, Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa, Estrada Nacional 10, 2695-066 Bobadela LRS, Portugal
** E-mail: nuno.bandeira@ciencias.ulisboa.pt*

The chemistry of Radon is still largely unknown, and due to its radioactive character is difficult to handle and study in conventional laboratory conditions. By and large the most widely studied congener is xenon which displays a rich chemistry[1] with the most electronegative elements fluorine and oxygen. More than a decade ago an extensive computational study by Slepkov and others[2] was published on the decomposition reaction of xenon tetroxide (XeO_4). The latter is a violently explosive gas that is greatly endothermic ($\Delta_f H^{\ominus}_{298.15}$=+643 kJ mol^{-1}), however the rate of decomposition is slow enough to make it stable even at room temperature. Their main findings were that this explosive decomposition instead of being stepwise as initially thought would occur in a concerted fashion by formation of a 'bow tie' intermediate species $Xe(\eta^2\text{-}O_2)$ giving way to the respective elements (Scheme 1).

In this communication the existence of RnO_4 (Td) is predicted based on comparisons with the known xenon analogue. In addition, we re-analyze this curious $Xe(\eta^2\text{-}O_2)$ structure under the lens of wavefunction methods and draw comparisons with the likely heavier tetroxide $Rn(\eta^2\text{-}O_2)_2$. These D_{2h} isomers will be shown to have partial multiconfigurational character (Figure 1) and an enquiry is made into the formal oxidation state of the noble gas atom in these species.



Scheme 1: Decomposition reaction of late noble gas tetroxides (Ng=Xe,Rn).

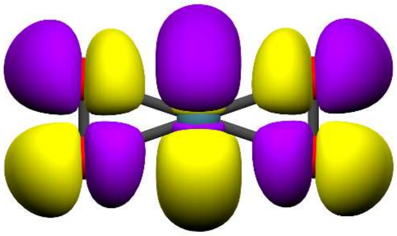


Figure 1: CASPT2 Natural Orbital that is partially occupied in $Rn(\eta^2\text{-}O_2)_2$.

Acknowledgements
We thank the Fundação para a Ciência e a Tecnologia for project RadonChem PTDC/QUI-QFI/31896/2017 and unit funding UIDB/04046/2020-UIDP/04046/2020 (BioISI), UIDB/00100/2020-UIDP/00100/2020 (CQE) and LA/P/0056/2020 (IMS).

References

1. F. Grandinetti, *Noble Gas Chemistry: Structure, Bonding, and Gas-Phase Chemistry*, Wiley, 1st edn., 2018.
2. V. Slepkov, S. Kozlova and S. Gabuda, *J. Phys. Chem. A*, 2011, **115**, 7811-7814.

POSTERS

Detection of galectin-3 biomarker through UV-Vis spectroscopy

Maria António[1*], Tânia Lima[2,3], Rita Ferreira[4,5], Margarida Fardilha[2], Rui Vitorino[2,5,6] and Ana L. Daniel-da-Silva[1]

[1] CICECO-Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal;
[2] iBiMED-Institute of Biomedicine, Department of Medical Sciences, University of Aveiro, Aveiro, 3810-193, Portugal
[3]Cancer Biology and Epigenetics Group, Research Center of Portuguese Oncology Institute of Porto (GEBC CI-IPOP) & Porto Comprehensive Cancer Center (P.CCC), 4200-072 Porto, Portugal.
[4]QOPNA, Department of Chemistry, University of Aveiro, 3810-193, Aveiro, Portugal
[5]LAQV-REQUIMTE, Chemistry Department, University of Aveiro, 3810-193, Aveiro, Portugal
[6]UnIC@RISE, Department of Surgery and Physiology, Cardiovascular R&D Center, Faculty of Medicine of the University of Porto, Alameda Professor Hernâni Monteiro, 4200-319 Porto, Portugal
* E-mail: maantonio@ua.pt

Galectin-3 (Gal-3) is a carbohydrate-binding protein[1] related to the development and progress of heart failure [2,3]. In this work, we developed a colorimetric method for detecting Gal-3 using modified gold nanoparticles (AuNPs) as probes. The surface of AuNPs was modified and covalently bonded to Gal-3 antibody. The resulting probes were blocked with BSA and set in contact with Gal-3 in buffer, spiked into diluted saliva (1:10) and diluted fetal bovine serum (1:100). The alterations in the localized surface plasmon resonance of AuNPs were monitored using UV–VIS spectroscopy. A linear relationship between the aggregation ratio (A_{750nm}/A_{526nm}) and the Gal-3 concentration was found. The sensing range and LOD values were 0 - 200 μg.L^{-1} and 10.8 - 31.5 μg.L^{-1}, respectively, depending on the matrix complexity. Yet, the sensing range and LOD can be compared to the Gal-3 typical cut-off of 17.7 μg.L^{-1} [4]. The specificity of AuNPs probes was confirmed and their colloidal stability was ensured for 10 days. The strategy was tested in human plasma samples and evaluated with the western blot technique (Figure 1). This method uses a simple UV-Vis spectrometer for analysis, providing a low-cost approach for Gal-3 detection and easier transition to point-of-care test.

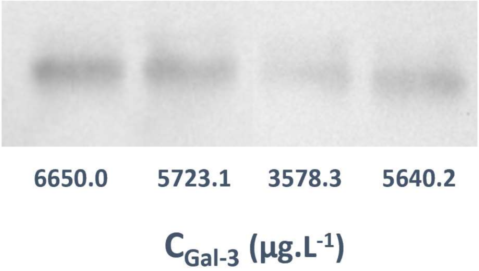


Figure 1: Western blot results of the plasma samples analysis, at different Gal-3 concentrations.

Acknowledgements

We thank the Fundação para a Ciência e a Tecnologia (FCT), FCT/MEC (PIDDAC), European Union, QREN, FEDER, and COMPETE for the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020 & LA/P/0006/2020, the project iBiMED (UIDB/04501/2020, POCI-01-0145-FEDER-007628), UnIC (UID/IC/00051/2019) and the project LAQV- REQUIMTE (UIDB/50006/2020). M.A. thanks FCT for the PhD grant (SFRH/BD/136881/2018). T. L. thanks FCT for the PhD grant (SFRH/BD/136904/2018). A.L.D.-d.-S. acknowledges FCT for the contract (IF/00405/2014). R.V. thanks the FCT for the Investigator Grant (IF/00286/2015).

References

1 A. Krześlak and A. Lipińska, *Cell Mol Biol Lett*, 2004, **9**, 305–328.
2 U. C. Sharma, S. Pokharel, T. J. Van Brakel, J. H. Van Berlo, J. P. M. Cleutjens, B. Schroen, S. André, H. J. G. M. Crijns, H. J. Gabius, J. Maessen and Y. M. Pinto, *Circulation*, 2004, **110**, 3121–3128.
3 R. R. van Kimmenade, J. L. Januzzi, P. T. Ellinor, U. C. Sharma, J. A. Bakker, A. F. Low, A. Martinez, H. J. Crijns, C. A. MacRae, P. P. Menheere and Y. M. Pinto, *J. Am. Coll. Cardiol.*, 2006, **48**, 1217–1224.

P2

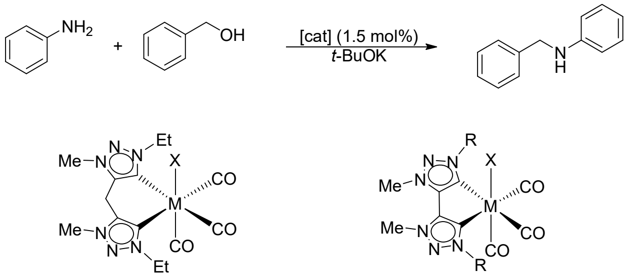
4 D. J. A. Lok, P. Van Der Meer, P. W. B. A. De La Porte, E. Lipsic, J. Van Wijngaarden, H. L. Hillege and D. J. Van Veldhuisen, *Clin. Res. Cardiol.*, 2010, **99**, 323–328.

Manganese and Rhenium Triazolylidene Complexes for N-Alkylation of Amines with Alcohols

S. Friães[1,*], C.S.B. Gomes[2], B. Royo[1]

[1]*ITQB NOVA, Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Avenida da República, 2780-157 Oeiras, Portugal*
[2]*REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516, Caparica, Portugal*
**E-mail: sofiafriaes@itqb.unl.pt*

N-alkylation of amines with alcohols *via* borrowing hydrogen approach has emerged as an atom economical and waste-free strategy to provide N-alkylated amines. Various catalytic systems have been developed for these transformations. However, the traditional ones are based on precious metals, such as Ir, Ru and Rh.[1] Due to their high cost, toxicity and limited availability, numerous efforts have been done to developing non-noble metal catalysts with Fe, Mn, Co and Ni. Nonetheless, the majority of these catalytic systems are based on phosphine ligands. With the aim of developing phosphine-free catalytic systems with cheap metals, our research team has recently focused on the preparation of active Mn catalysts using N-heterocyclic carbene ligands (NHCs).[2] Mesoionic carbenes (MICs), especially those derived from 1,2,3-triazolylidenes, are an interesting subclass of NHCs that have advanced to prominent class of ligands in catalysis. In many cases, their strong σ-donor and weak π-acceptor properties yield metal complexes with enhanced catalytic activities and stability.[3] Despite these interesting features, the chemistry and catalysis of Mn has remained elusive.[4] Herein we describe the synthesis of a new family of tricarbonyl Mn(I) complexes bearing ditriazolylidenes of general formula *fac*-[Mn(MIC^MIC)(CO)$_3$Br] and their catalytic activity in the N-alkylation of amines. For comparison, their Re counterparts have also been investigated (Scheme 1). Interestingly, we showed for the first time, that Mn and Re triazolylidenes are efficient catalysts for the alkylation of aniline with benzyl alcohol in the presence of a base.



1 (M = Mn, X = Br)
2 (M = Re, X = Cl)

3 (R = Et, M = Mn, X = Br)
4 (R = n-Bu, M = Mn, X = Br)
5 (R = Et, M = Re, X = Cl)
6 (R = n-Bu, M = Re, X = Cl)

Scheme 1: Catalytic N-alkylation of aniline with benzyl alcohol by Mn and Re triazolylidenes.

Acknowledgements

We thank the Fundação para a Ciência e a Tecnologia for financial support of PhD grant SFRH/BD/131955/2017 (S.F.) and projects PTDC/QUI-QIN/0359/2021, MOSTMICRO-ITQB UIDB/04612/2020, UIPD/04612/2020, CERMAX Project No.022162, UIDB-UIDP/50006/2020 and UIDB-UIDP/04378/2020. We also thank C. Almeida for elemental analysis at ITQB NOVA.

References

1 A. Corma, J. Navas and M. J. Sabater, *Chem. Rev.*, 2018, **118**, 1410–1459.
2 S. C. A. Sousa, S. Realista, B. Royo, *Adv. Synth. Catal.*, 2020, **362**, 2437-2443.
3 M. Pinto, M. Olivares, Á. Vivancos, G. Guisado-Barros, M. Albrecht, B. Royo, *Catal. Sci.Technol.*, 2019, **9**, 2421–2425.
4 S. Friães, S. Realista, H. Mourão and B. Royo, *Eur. J. Inorg. Chem.*, 2022, DOI: 10.1002/ejic.202100884.

Dawson Sandwich-type POMs@MWCNT as efficient electrocatalysts for O_2 reactions

Inês S. Marques[1,*], Diana M. Fernandes[1], Cristina Freire[1],Israël-Martyr[2],Anne-Lucie Teillout[2], Pedro de Oliveira[2]

[1] REQUIMTE/LAQV, department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal
[2] Laboratoire l´Institut de Chimie Physique – ICP Université Paris-Saclay –CNRS UMR 800, Paris, France
** up201608306@edu.fc.up.pt*

The incessant and drastic growth of global energy demand makes it imperative to develop new affordable high-quality materials at a large scale to act as powerful electrocatalysts (ECs) on clean energy storage and conversion devices.[1] Among these, fuel cells (FC) and water splitting devices have emerged as strong candidates however, their application has been hampered due to the use of noble metal-based electrocatalysts. In the reactions of oxygen - the O_2 reduction (ORR) and evolution (OER) reactions, conventional electrocatalysts are based on noble metals and their oxides, such as Pt, Pd, RuO_2, and IrO_2. However, in addition to being scarce and having a high cost these have poor stability under operating conditions.

This work involves the preparation of electrocatalysts based on Dawson Sandwich-type polyoxometalates and multi-walled carbon nanotubes doped with melamine. All materials prepared demonstrated moderate ORR electrocatalytic performance in alkaline medium with diffusion-limiting current densities between -4.68 and -3.06 mA cm^{-2} and potential onset values of $0.94 \geq E_{onset} \geq 0.74$ V vs. RHE. Additionally, the materials tested showed selectivity towards a mixed-regime mechanism of 2- and 4-electron, between 2.7 and 3.5. The materials also presented moderate to good OER electrocatalytic performances in alkaline medium, with overpotential values between 0.39 and 0.56 V vs. RHE and maximum current densities between 8.9 and 183.8 mA cm^{-2}.

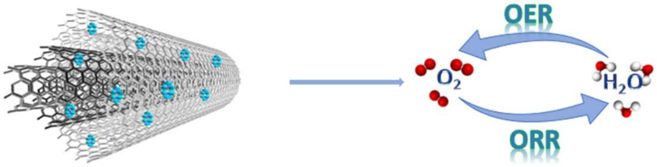


Figure 1: Schematic illustration of application of hybrids.

[1] Freire, C.; Fernandes, D. M.; Nunes, M.; Abdelkader, V.K.; *ChemCatChem*, 2018, *10*, 1703.

P4

Carbon-Silica Composite Nanoparticles With Enhanced Fluorescence Emission

J. Nogueira[1,*], T. Trindade[1], A.L. Daniel-da-Silva[1]

[1] CICECO – Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal
** E-mail: jh.nogueira@ua.pt*

Inorganic nanoparticles present several advantages compared to organic dyes in developing fluorescent probes, such as better photostability, narrow emission bands and wider wavelength range for the excitation source. Semiconductor quantum dots and carbon dots are among the colloidal systems exhibiting such properties, together with the ability for exploring surface chemistry envisaging stable fluorescent properties and biocompatibility. These features make them suitable for fluorescence probing of a variety of biological and organic analytes.[1,2] Carbon-based nanoparticles obtained by hydrothermal methods have gained prominence in the past years,[3] namely due to the low cost and wide variety of carbon sources used in the synthesis.[4] In this work, novel fluorescent carbon-silica composite nanoparticles were prepared via the hydrothermal treatment of previously synthesized carrageenan/silica hybrid nanoparticles (Figure 1). The resulting composite nanoparticles display a distinct emission spectrum and enhanced fluorescence emission compared to nanoparticles prepared by hydrothermal treatment of carrageenan in similar experimental conditions. The amorphous silica network is expected to confer chemical robustness to the material and to protect the fluorescence centers from quenching. Due to the general affinity of carbon-silica nanomaterials towards organic contaminants,[5] these novel composites might be explored as fluorescence probes for such analytes through changes in the fluorescence behavior after interaction with the contaminant molecules.

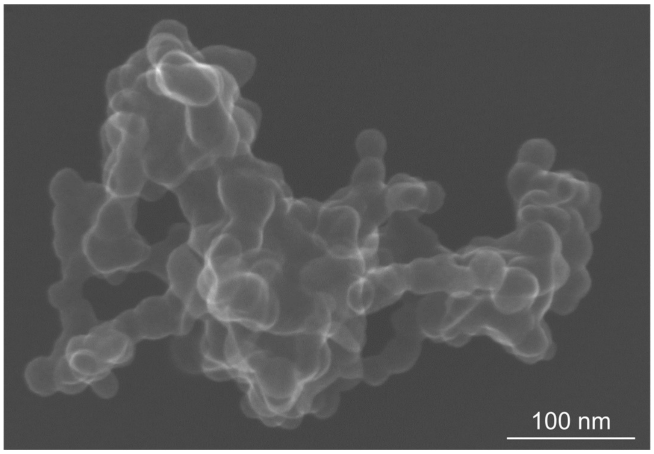


Figure 1: Scanning Electron Microscopy image of fluorescent composite of carbon and silica.

Acknowledgements

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC). J. Nogueira thanks the Fundação para a Ciência e a Tecnologia (FCT) for the PhD Scholarship SFRH/BD/146249/2019.

References

1 A. Chandra, S. Prasad, G. Gigli and L. L. del Mercato, in *Colloids for Nanobiotechnology*, eds. W. J. Parak and N. B. T.-F. of N. Feliu, Elsevier, 2020, vol. 16, pp. 117–149.
2 M. Jorns and D. Pappas, A review of fluorescent carbon dots, their synthesis, physical and chemical characteristics, and applications, *Nanomaterials*, 2021, **11**, 1448.
3 J. Nogueira, M. António, S. Mikhalev, S. Fateixa, T. Trindade and A. Daniel-da-Silva, Porous Carrageenan-Derived Carbons for Efficient Ciprofloxacin Removal from Water, *Nanomaterials*, 2018, **8**, 1004.
4 Y. Tian, Z. Ran and W. Yang, Carbon dot-silica composite nanoparticle: An excitation-independent fluorescence material with tunable fluorescence, *RSC Adv.*, 2017, **7**, 43839–43844.
5 S. F. Soares, M. I. Rodrigues, T. Trindade and A. L. Daniel-da-Silva, Chitosan-silica hybrid nanosorbents for oil removal from water, *Colloids Surfaces A Physicochem. Eng. Asp.*, 2017, **532**, 305–313.

Perylene-based Metal-Organic Frameworks: Synthesis, Tunable Optical Properties and Electrochemical Studies

Gonçalo Valente[1*], Filipe A. Almeida Paz[1], João Rocha[1], Manuel Souto[1]

[1] Department of Chemistry, CICECO – Aveiro Institute of Materials, University of Aveiro, Aveiro, Portugal
** E-mail: goncalovalente@ua.pt*

Besides their inherent porosity, Metal-Organic Frameworks (MOFs) may also incorporate tunable electronic properties (electrical and optical) which strongly depend on the selected building blocks, becoming very attractive for their implementation as integral components in electronic devices.[1] In recent years, electroactive organic molecules have emerged as promising building blocks for the design and construction of crystalline porous frameworks such as MOFs for different applications in electronics.[2] In this direction, the construction of new perylene-based MOFs is encouraged due to their remarkable luminescence and promising electrical properties.

Herein, we report a detailed study on the electrical conductivity enhancement of a perylene-based MOF upon partial ligand oxidation by iodine doping using two-probe single-crystal devices. In addition, a new family of perylene-based MOF with different transition metals (Co, Ni, Zn) has been synthesized exhibiting tunable optical properties depending on the nature of the metal. This study highlights the great versatility of perylenes as building blocks for the construction of electroactive MOFs.

In summary, we have reported the first evidence of increased conductivity in a perylene-based MOF upon iodine doping. This conductivity is ascribed to the partial oxidation of the perylene ligands, as witnessed by EPR and emission spectroscopy, and supported by theoretical calculations. The charge transport is described by means of a through-space hopping mechanism along the herringbone perylene packing, with highest conductivities of the order of 10^{-5} S·cm^{-1} measured in two-contact single-crystal devices.[3] For these reasons, we highlight the potential of perylene building blocks for the design of electrically conductive and photoresponsive MOFs. In addition, we have presented a new synthetic route to prepare a novel family of isostructural MOFs based on PTC and TM exhibiting high crystallinity and stability. These studies on PTC-TM indicate that it is possible to tune the optical properties by switching the TM while the electrochemical properties of perylene are preserved, demonstrates by solid-state cyclic voltammetry of PTC-TM.[3]

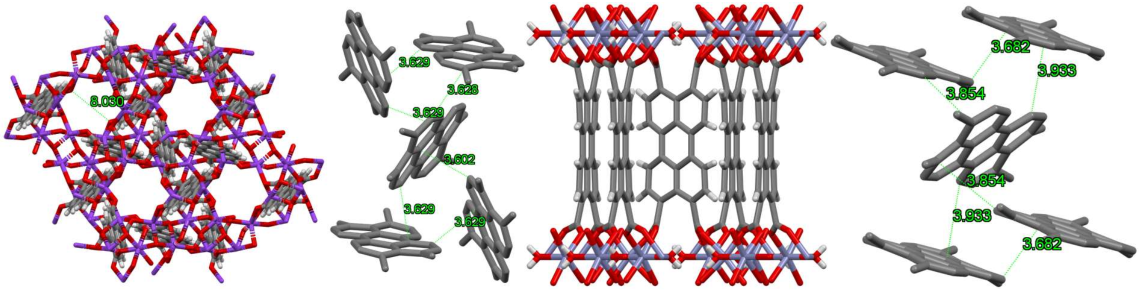


Figure 1. Partial views of the crystals structures of Per-MOF and PTC-TM MOF on the *ac* and *bc* planes showing the arrangement of the metal ion and PTC linkers. Color code: C (grey), H (white), O (red), K (purple) and Zn (blue).

Acknowledgements
This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, Grants UIDB/50011/2020 and UIDP/50011/2020, financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. We thank FCT for funding the project PTDC/QUI-ELT/2593/2021.

References
[1] M. D. Allendorf, R. Dong, X. Feng, S. Kaskel, D. Matoga and V. Stavila, *Chem. Rev.*, 2020, *120*, 8581. [2] M. Souto, K. Strutyński, M. Melle-Franco and J. Rocha, *Chem. Eur. J.*, 2020, *26*, 10912. [3] G. Valente et al. 2022, submitted.

P6

Magnetic MoS_2 based nanocomposites for the removal of pesticides

L. O. Amaral [1,*], J. Nogueira [1], A. Estrada [1], T. Trindade[1], A. L. Daniel-da-Silva [1]

[1] CICECO-Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
** E-mail: leonardoa@ua.pt*

The agro-food industry produces large amounts of water namely in fruit and vegetables' washing and cleaning processes.[1] Due to the high concentration of pesticides, the wastewater can no longer be reused and is discharged into wastewater treatment units, where the treatments employed might be non-effective in removing such contaminants.[1] Acetamiprid is an insecticide commonly used in this context, namely to control *Hemiptera spp.* proliferation in fruit, vegetables and ornamental plants and flowers. Several methods have been developed to remediate the presence of acetamiprid and other pesticides in wastewater discharged into treatment units.[1] Adsorption is a simple, low-cost and easy scaled-up process. In this sense, nanomaterials have been explored due to their potential superior effectiveness of adsorption owing to the large specific surface area, as compared to conventional materials.[2] Among the transition metal dichalcogenides, MoS_2 nanomaterials have proved to be effective in removing water contaminants by adsorption processes.[3] Moreover, the combination of these materials with magnetic particles impart to the ensuing nanocomposites the ability for easy, fast and cost-less recovery of the sorbents by magnetic separation.[4]

In this work, composite nanostructures of MoS_2-Fe_3O_4 were produced by a hydrothermal method.[5] The nanostructures were characterized by transmission electron microscopy and powder X-ray diffraction. The uptake of acetamiprid spiked in water samples was investigated by using variable operational conditions, namely the insecticide concentration and contact times. The concentration of acetamiprid in the aqueous samples was monitored using UV-VIS spectroscopy by measuring the absorption at λ=245 nm, due to the analyte. The MoS_2-Fe_3O_4 materials assessed in this research decreased the concentration of acetamiprid by 48%, after 3 h contact time in the dark. The performance of the MoS_2-Fe_3O_4 nanomaterials as multifunctional sorbents is discussed based on these results and their potential for subsequent regeneration.

Acknowledgements

L. Amaral thanks the Fundação para a Ciência e a Tecnologia (FCT) for the PhD Grant UI/BD/151138/2021 J. Nogueira thanks the FCT for the PhD Scholarship SFRH/BD/146249/2019. A.C. Estrada also acknowledge their research position funded by national funds (OE), through FCT-Fundação para a Ciência e a Tecnologia, I.P., in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19. This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC).

References

1 M. C. Campos-Mañas, P. Plaza-Bolaños, A. B. Martínez-Piernas, J. A. Sánchez-Pérez and A. Agüera, *Chemosphere*, 2019, **232**, 152–163.
2 S. F. Soares, T. Fernandes, T. Trindade and A. L. Daniel-da-Silva, *Environmental Chemistry Letters*, 2020, 18, 151–164.
3 Y. Wu, M. Su, J. Chen, Z. Xu, J. Tang, X. Chang and D. Chen, *Dyes and Pigments*, 2019, **170**, 1–8.
4 J. Guo, C. Yang, Z. Sun, Z. Yang, L. Wang, C. Lu, Z. Ma and F. Guo, *Journal of Materials Science: Materials in Electronics*, 2020, **31**, 16746–16758.
5 H. J. Song, S. You, X. H. Jia and J. Yang, *Ceramics International*, 2015, **41**, 13896–13902.

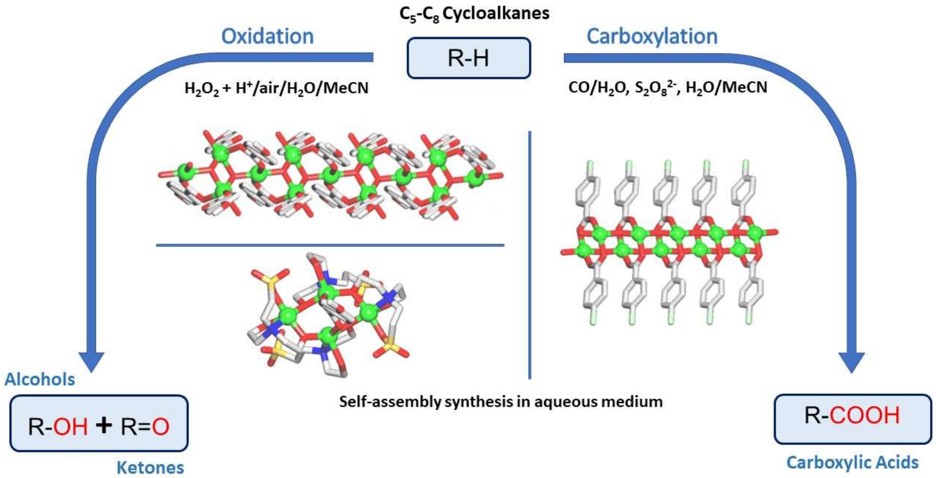
Time-dependent Self-Assembly of Copper(II) Coordination Compounds: New Catalysts for Oxidative Functionalization of Alkanes

Inês F. M. Costa*, Marina V. Kirillova, Vânia André, Tiago A. Fernandes, Alexander M. Kirillov

Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001, Lisboa, Portugal

** E-mail: inesfmcosta@tecnico.ulisboa.pt*

The present study reports a time-dependent self-assembly formation of new copper(II) coordination compounds from an aqueous-medium reaction mixture composed from copper(II) nitrate, H_3bes biobuffer (*N*,*N*-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid), ammonium hydroxide and benzenecarboxylic acid, namely 4-methoxybenzoic (Hfmba) or 4-chlorobenzoic (Hfcba) acids. Two products were isolated from each reaction: 1D coordination polymers $[Cu_3(\mu_3\text{-}OH)_2(\mu\text{fmba})_2(\text{fmba})_2(H_2O)_2]_n$ (**1**) or $[Cu_2(\mu\text{-}OH)_2(\mu\text{-fcba})_2]_n$ (**2**) and discrete tetracopper(II) rings $[Cu_4(\mu\text{-}H\text{bes})_3(\mu\text{-}H_2\text{bes})(\mu\text{-fmba})]\cdot 2H_2O$ (**3**) or $[Cu_4(\mu\text{-}H\text{bes})_3(\mu\text{-}H_2\text{bes})(\mu\text{-fcba})]\cdot 4H_2O$ (**4**), respectively. The compounds were obtained as stable crystalline solids in relatively good yields and characterized by standard methods, including single-crystal X-ray diffraction.[1] The structures of **1** and **2** feature distinct types of metal-organic chains driven by the μ_3- or μ-OH^- ligands along with the μ-benzenecarboxylate linkers. The structures of **3** and **4** disclose the chair-like Cu_4 rings assembled from four μ-bridging and chelating aminoalcoholate ligands along with μ-benzenecarboxylate moieties. To evaluate a catalytic activity of **1**−**4**, two model reactions were explored, namely (a) the mild oxidation of saturated hydrocarbons with hydrogen peroxide to form alcohols and ketones, and (b) the mild carboxylation of alkanes with carbon monoxide, water and peroxodisulfate to generate carboxylic acids. For these reactions, effects of different parameters were studied, including an influence of acid co-catalyst and selectivity characteristics. Apart from notable catalytic activity and widening the family of Cu-based catalytic systems, this study showcases a novel time-dependent synthetic strategy for the self-assembly of two different Cu(II) coordination compounds from the same reaction mixture.



Scheme 1: Model Cu-catalyzed hydrocarbon oxidation and carboxylation reactions.

Acknowledgements
This work has been supported by the Foundation for Science and Technology (FCT) (grant PD/BD/150418/2019 and projects UIDB/00100/2020, PTDC/QUI-QIN/3898/2020, CEECIND/03708/2017, LISBOA-01-0145-FEDER-029697, UIDP/00100/2020, and REM2013).

References

1. Costa, I.F.M.; Kirillova, M.V.; André, V.; Fernandes, T.A.; Kirillov, A.M.; Time-dependent Self-Assembly of Copper(II) Coordination Polymers and Tetranuclear Rings: New Catalysts for Oxidative Functionalization of Saturated Hydrocarbons, *Inorg. Chem.* **2021**, 60, 14491-14503.

Synthesis and Characterization of Violet/Blue-Emitting Ce(III) Bis(aryloxide) Cyclam Halide Complexes

L. Maria[1,*], P. M. R. Paulo[2], M. F. N. N. Carvalho[2], J. Marçalo[1], I. C. Santos[3], S. Oliveira[1]

[1]CQE/IMS & [3]C²TN, Instituto Superior Técnico, U. Lisboa, Bobadela, Portugal
[2]CQE/IMS, Instituto Superior Técnico, U. Lisboa, Lisboa, Portugal
** E-mail: leonorm@ctn.tecnico.ulisboa.pt*

Cerium is the most abundant of the rare earth elements and is one of the most inexpensive. It displays low-to-moderate toxicity and plays an important role in organic synthesis [1]. Although, the Ce^{3+} ions exhibit intrinsic 4f → 5d optical absorption transitions, the corresponding luminescence has not typically been observed in molecular cerium(III) compounds, likely due to rapid deactivation of their excited states by non-radiative relaxation pathways. Nevertheless, the number of reported luminescent Ce^{3+} complexes has increased in the last years, with a large variation in the luminescence properties; *e.g.* the emission wavelength could be adjusted by varying the coordination environment [2,3]. Some of these complexes have demonstrated to be photocatalytically active [3]. Furthermore, cerium(III) complexes are expected to be more stable in OLEDs since their excited-state lifetimes are generally in the order of nanoseconds [4].

Herein, we report the synthesis and characterization of two violet-blue emissive cerium(III) halide complexes supported by a bis(aryloxide) cyclam ligand, with the general formula $[Ce\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}X]$ (X = Cl (**1**), I (**2**)). The compounds were characterized by ^1H NMR spectroscopy, ESI-MS and single-crystal X-ray diffraction analysis.

The two Ce(III) compounds exhibit, in thf, intense absorption bands in the UV region and emission spectra with maxima centered at *ca.* 415 nm. Initial photophysical studies in tetrahydrofuran showed that **2** (39%) exhibits a photoluminescence quantum yield higher than **1** (4%).

In order to evaluate the redox properties of the complexes, their electrochemical behavior was studied by cyclic voltammetry in thf. The preliminary results show that the Ce(III)/Ce(IV) oxidation potential is lower (*ca.* 250 mV) for complex **2** than for complex **1**.

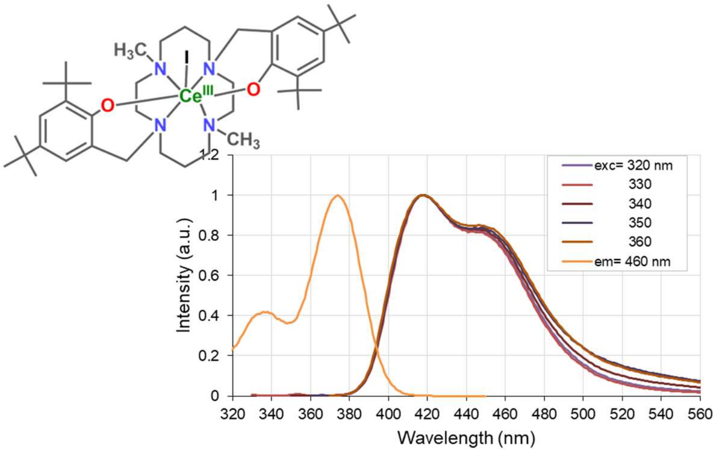


Figure 1: Normalized excitation and emission spectra of **2** in thf solution (0.5 mM) at room temperature.

Acknowledgements
We thank the Fundação para a Ciência e a Tecnologia for financial support through the Projects UIDB/00100/2020 (CQE), LA/P/0056/2020 (IMS) and UIDB/04349/2020 (C²TN).

References

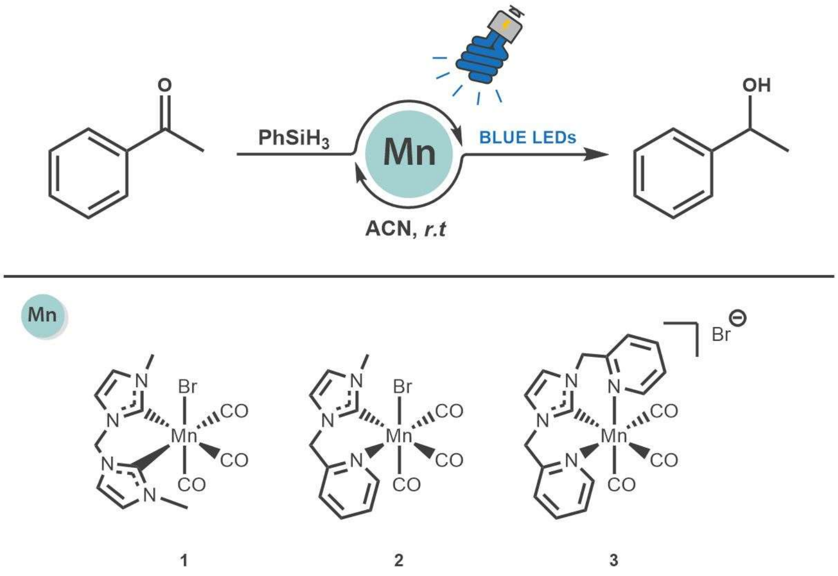
[1] H. Tsurugi and K, Mashima, *J. Am. Chem. Soc*., 2021, **143**, 7879−7890.
[2] Y. Qiao, D.-C. Sergentu, H. Yin, A. V. Zabula, T. Cheisson, A. McSkimming, B. C. Manor, P. J. Carroll, J. M. Anna, J. Autschbach, E. J. Schelter, *J. Am. Chem. Soc*., 2018, **140**, 4588−4595.
[3] Y. Qiao, E. J. Schelter, *Acc. Chem. Res.*, 2018, **51**, 2926−2936.
[4] L. Wang, Z. Zhao, G. Zhan, H. Fang, H. Yang, T. Huang, Y. Zhang, N. Jiang, L. Duan, Z. Liu, Z. Bian, Z. Lu, C. Huang, *Light Sci. Appl.*, 2020, **9**, 157.

Visible-Light Hydrosilylation of Ketones Mediated by Mn N-Heterocyclic Carbene Complexes

H. Mourão[1,*], C. S. B. Gomes[2], B. Royo[3]

[1] ITQB NOVA, Instituto de Tecnologia Química e Biológica António Xavier, Avenida da República, 2780-157 Oeiras, Portugal
[2] LAQV- and UCIBIO-Requimte, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
** E-mail: henrique.mourao@itqb.unl.pt*

Recently, the employment of simple transition metals as photocatalysts (PC) has led to the discovery of unprecedented chemical transformations. Compared to the conventional cooperative dual catalysis, which combines a photocatalyst (PC) and a transition metal catalyst working in synergy, this new class of unconventional PCs operate through a single catalytic cycle. In this case, the transition metal photocatalyst plays a double role, harvesting light and catalyzing the chemical transformation.[1] This new area of photocatalysis represents a very attractive approach of promoting chemical reactions, using visible light and avoiding the need of expensive photosensitizers. In continuation with our work devoted to sustainable catalytic methods for the functionalization of organic molecules,[2,3] we describe here the excellent catalytic activity of a Manganese N-heterocyclic carbene (NHC) complex working as a photocatalyst for the hydrosilylation of ketones with phenyl silane (Scheme 1). The catalytic system operates at room temperature and under visible-light irradiation (blue LED), enabling the conversion of a wide variety of functionalized ketones to the corresponding alcohols in excellent yields. The Mn-NHC complexes have been fully characterized by spectroscopic and analytical methods, including the crystal X-ray diffraction studies. Experimental essays performed for the elucidation of the reaction mechanism will be presented.



Scheme 1: Photocatalytic hydrosilylation of ketones mediated by Mn-NHC complexes

Acknowledgements
We thank the Fundação para a Ciência e a Tecnologia for financial support of PhD grant SFRH/BD/XXXX (H.M.) and projects PTDC/QUI-QIN/0359/2021, MOSTMICRO-ITQB UIDB/04612/2020, UIPD/04612/2020, CERMAX Project No.022162, UIDB-UIDP/50006/2020 and UIDB-UIDP/04378/2020. We also thank C. Almeida for elemental analysis at ITQB NOVA.

References

1 M. Parasram and V. Gevorgyan, *Chem. Soc. Rev.*, 2017, **46**, 6227–6240.
2 S. C. A. Sousa, S. Realista and B. Royo, *Adv. Synth. Catal.*, 2020, **362**, 2437-2443.
3 S. Friães, S. Realista, H. Mourão and B. Royo, *Eur. J. Inorg. Chem.*, 2022, DOI: 10.1002/ejic.202100884.

Gas-Phase Reactions of Ionic Gold Complexes with Small Molecules: Potential New Gold-Based Catalysts

<u>Sandrina Oliveira</u>[1]*, Joaquim Marçalo[1], M. Conceição Oliveira[2], Leonor Maria[1], Rafaela A. L. Silva[3], Nuno A. G. Bandeira[4]
[1] CQE/IMS, Instituto Superior Técnico, U. Lisboa, Bobadela, Portugal
[2] CQE/IMS, Instituto Superior Técnico, U. Lisboa, Lisboa, Portugal
[3] C^2TN, Instituto Superior Técnico, U. Lisboa, Bobadela, Portugal
[4] BioISI, Faculdade de Ciências, U. Lisboa, Lisboa, Portugal
**e-mail: sandrina@ctn.tecnico.ulisboa.pt*

Gas-phase reactions of metal ions with small molecules have been extensively studied.[1,2] Research in this area has focused predominantly on the interactions of naked and ligated transition metals ions with small molecules because these systems are good models for understanding the fundamentals of catalytic processes.[3]

In this work, gas-phase ion chemistry studies are being performed using quadrupole ion trap (QIT) mass spectrometry (MS) with electrospray ionization (ESI). QIT-MS is a technique that is especially suited for studies of ion/molecule reactions (IMR) at room temperature, due to the ability to perform complex sequences of ion manipulation, and provide detailed kinetic, mechanistic, and energetic information.

We have previously prepared in the gas-phase, gold(I) bis(dithiolene) complexes, $[Au(qdt)]^-$ (qdt = quinoxaline-2,3-dithiolate) and $[Au(mnt)]^-$ (mnt = 1,1-dicyanoethylene-2,2'-dithiolate), from the correspondent gold(III) salts, $(TPP)[Au(qdt)_2]$ and $(TBA)[Au(mnt)_2]$ in CH_3CN solutions, directly injected into the ESI source of the QIT. CID (collision-induced dissociation) of $[Au(qdt)_2]^-$ and $[Au(mnt)_2]^-$ formed by ESI also showed the formation of $[Au(qdt)]^-$ and $[Au(mnt)]^-$, respectively.[4]

We will present examples of the reactivity of these Au(I) (bis)dithiolene complexes with different small molecules. We observed so far that $[Au(X)(L)]^-$ (X=qdt, mnt) complexes are formed with L= NO, NO_2 and O_2 but not with N_2 and N_2O. As shown on Fig. 1, $[Au(qdt)]^-$ is clearly more reactive than $[Au(mnt)]^-$ and NO more reactive than O_2.

Theoretical studies of these systems, using DFT methods, are being conducted to evaluate the experimental observations, address electronic structures and energetics, tackle the nature of bonding and give rise to ideas, concepts and strategies for condensed-phase chemistry and catalysis.

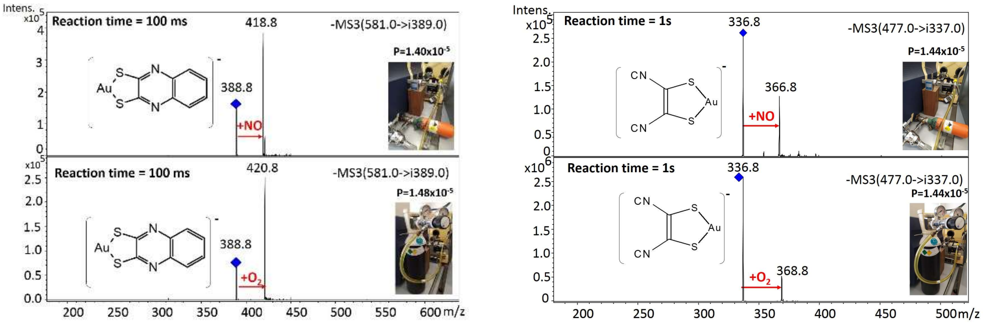


Figure 1: Mass spectra showing coordination of NO and O_2 to $[Au(qdt)]^-$ (left) and $[Au(mnt)]^-$ (right).

Acknowledgements
This work was supported by Fundação para a Ciência e a Tecnologia (FCT) through projects PTDC/QUI-QFI/31896/2017, UIDB/00100/2020 (CQE), LA/P/0056/2020 (IMS), UIDB/04349/2020 (C2TN) and UIDB/04046/2020 (BioISI), and through RNEM– Portuguese Mass Spectrometry Network, ref. LISBOA-01-0145-FEDER-022125, also supported by the Lisboa Regional Operational Programme (Lisboa2020), under the PT2020 Partnership Agreement, via the European Regional Development Fund (ERDF).

References

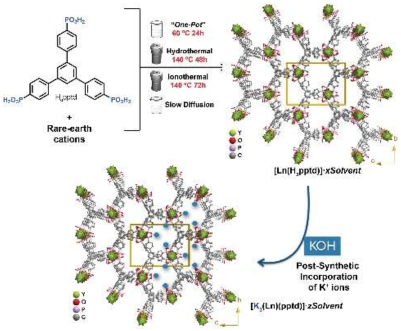
[1] K. Eller, H. Schwarz, *Chem. Rev.,* 1991, **91**, 1121–1177.
[2] P. B. Armentrout, *Mass Spectrom Rev*., 2021, 1–21, https://doi.org/10.1002/mas.21703.
[3] D. K. Bohme, H. Schwarz, *Angew. Chem. Int. Ed.,* 2005, **44**, 2336–2354.
[4] S. Oliveira, J. Marçalo, M. C. Oliveira, L. Maria, R. A. L. Silva, N. A. G. Bandeira, Reactivity of dithiolate gold(I) complexes with molecular O2 in the gas-phase, CQE Days – Spring Meeting, Lisboa, May 27-28, 2021.

Enhancing MOF Properties by Cationic Incorporation

Ricardo F. Mendes,[1] Sérgio M. F. Vilela,[1,2] Jorge A. R. Navarro,[3] Duarte Ananias,[1,4] Paula Barbosa,[5] Harriott Nowell,[6] Germán Pérez-Sánchez,[1] José R. B. Gomes,[1] Filipe Figueiredo,[5] João P. C. Tomé,[7] Filipe A. Almeida Paz[1]

[1] Department of Chemistry, CICECO – Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal;
[2] Department of Chemistry, LAQV-REQUIMTE, University of Aveiro, 3810-193 Aveiro, Portugal
[3] Department of Inorganic Chemistry, University of Granada, 18071 Granada, Spain;
[4] Department of Physics, CICECO – Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal;
[5] Department of Materials & Ceramic Engineering, CICECO – Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal;
[6] Diamond Light Source, Didcot OX11 0DE, Oxon, Oxfordshire, United Kingdom;
[7] Departamento de Engenharia Química, Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal
** E-mail: rfmendes@ua.pt*

Research on Metal-Organic Frameworks (MOFs) and Coordination Polymers (CPs) is currently driven towards the need to employ such materials in technological areas. Our research group has focused on the design of novel networks based on polyphosphonic acid ligands and rare-earth cations. With these building units we obtained highly robust dense networks exhibiting, in many cases, multifunctionality (*e.g.*, photoluminescence combined with catalytic activity). In this manuscript we report a new series of isotypical porous rare-earth-phosphonate MOFs whose properties are significantly boosted by a simple acid-base post-synthetic modification of the parent materials: $[Ln(H_3pptd)]\cdot$*zSolvent* [where $Ln^{3+} = Y^{3+}$ (1) and $(Y_{0.95}Eu_{0.05})^{3+}$ (1_Eu)] are converted into $[K_3Ln(pptd)]\cdot$*zSolvent* [where $Ln^{3+} = Y^{3+}$ (1K) and $(Y_{0.95}Eu_{0.05})^{3+}$ (1K_Eu)] by immersing the powder of 1 and 1K_Eu into an ethanolic solution of KOH for 48 h. The K^+-exchanged Eu-based material is photoluminescent, do not show photobleaching under several harsh conditions, and exhibits a considerable boost in CO_2 adsorption being capable of being reused for several consecutive cycles. They can further separate C_2H_2 from CO_2 from a complex ternary gas mixture composed of CH_4, CO_2 and C_2H_2. Moreover, the incorporation of K^+ ions increases the conductivity by 4 orders of magnitude, rendering this material as one of the best conducting MOFs reported to date.[1]



Scheme or Figure 1: Legend here

Acknowledgements
This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC), UniRCell (Ref. SAICTPAC-0032-2015, POCI-01- 0145-FEDER-016422) and CQE (UIDB/00100/2020), financed by national funds through the FCT/MEC and when appropriate cofinanced by FEDER under the PT2020 Partnership Agreement. FCT is also gratefully acknowledged for the postdoctoral grants SFRH/BPD/94381/2013 (to S.M.F.V.) and for the Junior Research Position CEECIND/00553/2017 (to R.F.M.). J.A.R.N. thanks Spanish MINECO(CTQ2017-84692-R), Junta de Andalucia (P18-RT-612) and EU FEDER Funding. The research contract of P.B. is funded by National Funds (OE), through FCT−Fundação para a Ciência e a Tecnologia, I.P., in the scope of the framework contract foreseen in the numbers 4, 5, and 6 of article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/ 2017, of July 19.

References

1. S. M. F. Vilela, J. A. R. Navarro, P.Barbosa, R. F. Mendes, G. Pérez-Sánchez, H.Nowell, D. Ananias, F. Figueiredo, J. R. B. Gomes, J. P. C. Tomé, and F. A. Almeida Paz, Journal American Chemical Society (2021), Volume 143, 1365−1376; DOI 10.1021/jacs.0c10421

P12

Hybrid Silver(I)-Doped Biopolymer Films to tackle Bacterial Biofilms

Tiago A. Fernandes,[1] Inês F.M. Costa,[1] Ana Catarina Sousa,[1,2] Paula Jorge,[3] Rafaela G. Cabral,[1,2] Vânia André,[1] Nuno Cerca,[3] Alexander M. Kirillov[1]

[1]Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
[3]Área Departamental de Engenharia Química, ISEL - Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, R. Conselheiro Emídio Navarro, 1, 1959-007 Lisboa, Portugal
[3]Centre of Biological Engineering, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal
** E-mail:tiago.a.fernandes@tecnico.ulisboa.pt*

This study outlines the synthesis, characterization, and antibacterial properties of new hybrid biopolymer materials doped with bioactive silver(I) coordination polymers (bioCPs).[1,2] Four new bioCPs, $[\mathrm{Ag_4(\mu_8\text{-}H_2pma)_2}]_n\cdot 4n\mathrm{H_2O}$ (**1**), $[\mathrm{Ag_5(\mu_6\text{-}H_{0.5}tma)_2(H_2O)_4}]_n\cdot 2n\mathrm{H_2O}$ (**2**), $[\mathrm{Ag_2(\mu_6\text{-}hfa)}]_n$ (**3**), and $[\mathrm{Ag_2(\mu_4\text{-}nda)(H_2O)_2}]_n$ (**4**) were assembled from Ag sources ($\mathrm{AgNO_3}$ or $\mathrm{Ag_2O}$) and pyromellitic ($\mathrm{H_4pma}$), trimesic ($\mathrm{H_3tma}$), homophthalic ($\mathrm{H_2hfa}$), or 2,6-naphthalenedicarboxylic ($\mathrm{H_2nda}$) acids as building blocks. These compounds were used as active antimicrobial agents (dopants) in the development of bioCP-doped biopolymer films, based on epoxidized soybean oil acrylate (ESOA) or potato starch (PS) as model biopolymer materials, which can be adjusted to exhibit various rates of degradability/silver release. Both bioCPs and their hybrid biopolymer films (**1**@[ESOA]$_n$, **2**@[ESOA]$_n$, **3**@[ESOA]$_n$, **4**@[ESOA]$_n$, **3**@[PS]$_n$, and **4**@[PS]$_n$) with a very low loading of bioCP (0.05−0.5 wt%) showed a remarkable antimicrobial activity against Gram-positive (*S. epidermidis* and *S. aure*us) and Gram-negative (*P. aeruginosa* and *E. coli*) bacteria. The biopolymer films produced also inhibited the development of bacterial biofilms (Figure 1). Overall, **1**@[ESOA]$_n$ revealed greater antibacterial effect when compared to other doped films; **3**@[PS]$_n$ showed higher efficacy than **3**@[ESOA]$_n$, while **4**@[ESOA]$_n$ and **4**@[PS]$_n$ had similar antimicrobial and biofilm inhibition performance. This multidisciplinary study not only combines several important research areas, but also expands an antimicrobial application of bioactive coordination polymers and hybrid biopolymer materials obtained from renewable biofeedstocks such as soybean oil and potato starch.

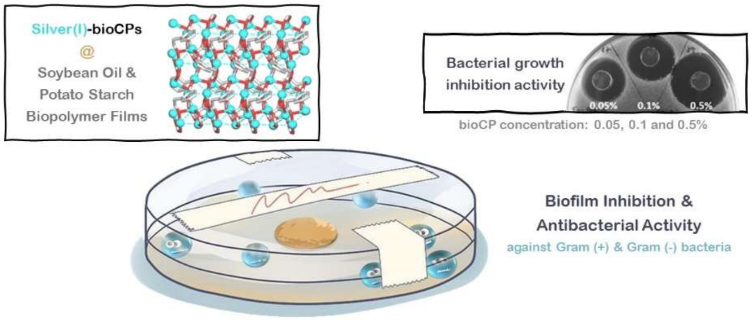


Figure 1: Illustration of biofilm inhibition and antibacterial activity of hybrid biopolymer materials doped with bioactive silver(I) coordination polymers.

Acknowledgements
This work was supported by the Foundation for Science and Technology (FCT) and Portugal 2020 (projects PTDC/QUI-QIN/29697/2017, LISBOA-01-0145-FEDER-029697, UIDB/00100/2020, UIDP/00100/2020, LA/P/0056/2020, IPL/2021/Naf4Med3D_ISEL, and REM2013), contracts under DL No. 57/2016, CEECIND/02725/2018, and CEECIND/00194/2020.

References

[1] T. A. Fernandes, I. F. M. Costa, P. Jorge, A. C. Sousa, V. André, N. Cerca, A. M. Kirillov, *ACS Appl. Mater. Interfaces*, 2021, **13**, 12836–12844.
[2] T. A. Fernandes, I. F. M. Costa, P. Jorge, A. C. Sousa, R. G. Cabral, V. André, N. Cerca, A. M. Kirillov, *ACS Appl. Mater. Interfaces*, 2022.

P13

Metallodrugs with antibacterial activity and their incorporation into nanocellulose membranes for wound healing applications

A. Gomes[1,*], C. Pereira[2], R. Mendes[1], F. Paz[1], A. Almeida[2], T. Santos[1], C. S. R. Freire[1], B. J. M. Leite Ferreira[1]

[1]*Department of Chemistry and CICECO, University of Aveiro, 3810-193, Aveiro, Portugal*
[2]*Department of Biology and CESAM, University of Aveiro, 3810-193, Aveiro, Portugal*
**E-mail: adrianagomes@ua.pt*

Wounds have a significant impact on society, not only on those who suffer from them but also on the health care system. Moreover, wounds do not always follow the expected healing process. The incidence of complications, such as infections, can inhibit wound healing and increase the cost of health care. Therefore, wound dressings emerge as a possible solution since they are crucial in promoting wound healing.[1]

In an increasingly environmentally conscious society, biopolymers-based wound dressings are becoming more eminent because of their abundance, renewable character, exudates' absorption capacity, and non-cytotoxicity.[2] Cellulose is an example of a widely studied polysaccharide, being increasingly used in wound healing applications. In particular, bacterial cellulose (BC) has a unique morphology and unique physicochemical, mechanical, and biological properties. In addition, BC can be modified and functionalized in order to have better performances. Moreover, bacterial cellulose has a nanofibrillar structure that provides ideal conditions for wound healing, and BC-based materials can act as drug delivery systems due to their ability to incorporate and release bioactive molecules.[3]

On the other hand, antibiotic resistance is one of the biggest threats to global health since it is reducing the ability to treat common infectious diseases. Metallodrugs with antibacterial activity emerge as a possible alternative to antibiotics. These pharmacologically active metal complexes display new properties and might have enhanced biological activity due to the synergistic combination between the ligands and the metal. Besides, metallodrugs possess different geometries and three-dimensional structures that are generally associated with higher clinical success rates.[4]

This work presents the synthesis and characterization of metallodrugs with antibacterial activity, and their incorporation into BC membranes for wound healing applications. Cobalt(II), copper(II), nickel(II), and zinc(II) complexes of levofloxacin and ciprofloxacin, in the presence and absence of N-donor ligands, were synthesized and characterized. All complexes exhibited antibacterial activity against *Staphylococcus aureus*, and one was successfully incorporated into BC membranes, increasing their thermal stability. A rapid release profile, suitable for topical administration, was obtained.

Acknowledgements

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC).

References

1. C. Lindholm and R. Searle, *Int. Wound J.*, 2016, **13**, 5-15.
2. M. P. Sikka and V. K. Midha, *Advanced Textiles for Wound Care*, Woodhead Publishing, Cambridge, 2019.
3. M. Jorfi and E. J. Foster, *J. Appl. Polym. Sci.*, 2015, **132**, 41719-41739.
4. L. Viganor, O. Howe, P. McCarron, M. McCann and M. Devereux, *Curr. Top. Med. Chem.*, 2017, **17**, 1280-1302

A Copper(II) Dicarboxylate Coordination Polymer with Antibacterial Activity

Chris H. J. Franco[1,*], Filipa Macedo[2], Rafaela G. Cabral[1,3], Tiago A. Fernandes[1], Ana C. Sousa[1,3], Nuno Cerca[2], Alexander M. Kirillov[1].

[1]Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
[2]Centre of Biological Engineering, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal
[3]Área Departamental de Engenharia Química, ISEL - Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, R. Conselheiro Emídio Navarro, 1, 1959-007 Lisboa, Portugal
** E-mail: chris.franco@tecnico.ulisboa.pt*

The search for new antimicrobial compounds represents an important research direction to combat microbial resistance. Bioactive coordination polymers are a promising class of antimicrobial materials.[1,2] The present study highlights the synthesis, characterization and antibacterial activity of a novel Cu(II) coordination polymer, $\{[Cu(dda)(NH_3)_2]\cdot H_2O\}_n$ (CP **1**). This compound was generated by self-assembly from a copper(II) salt, dodecanedioic acid ($HO_2C–C_{10}H_{20}–CO_2H$, H_2dda) and aqueous ammonia, followed by characterization by standard methods (elemental analysis, FTIR, single-crystal and powder X-ray diffraction). Optimization conditions to increase yield of CP **1** were explored, resulting in up to 90% yields in a single crystal phase. Single-crystal X-ray diffraction shows that the crystal is twinned with contribution of two domains (0.38:0.62) and has a transformation matrix of 180°. CP **1** crystallizes in the monoclinic system, space group $P2_1/c$, and is composed of copper(II) centers lying in a special position (center of inversion), which are coordinated by μ-dda^{2-} linkers and NH_3 ligands building an infinite linear 1D chain. The copper centers are 5-coordinated and adopt a trigonal *bipyramid* $\{CuN_2O_3\}$ geometry (Figure 1). Antibacterial activity of **1** was evaluated against Gram-positive and Gram-negative bacteria, showing a pronounced activity for *E. coli* and *S. epidermidis* (Figure 1). H_2dda also revealed some minor antibacterial activity against *S. epidermidis* and *S. aureus*. The obtained results are promising and the research on constructing hybrid polymer materials with CP **1** as an antimicrobial dopant is currently in progress.[2]

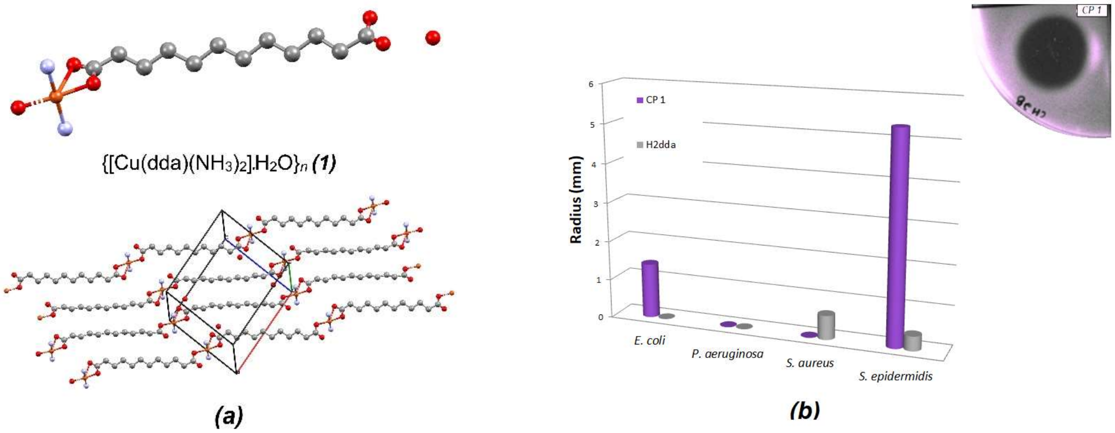


Figure 1: (a) Crystal structure and packing pattern of coordination polymer **1**. (b) Antibacterial activity data (inset shows an example of inhibition halo).

Acknowledgements

This work was supported by the Foundation for Science and Technology (FCT) (projects UIDB/00100/2020, UIDP/00100/2020, LA/P/0056/2020, PTDC/QUI-QIN/29697/2017, LISBOA-01-0145-FEDER-029697; contracts under DL No. 57/2016 and CEECIND/00194/2020) and IPL (IPL/2021/Naf4Med3D_ISEL).

References

[1] C. Pettinari,, R. Pettinari, C. Nicola, A. Tombesi, S. Scuri, F. Marchetti. *Coord. Chem. Rev.,* 2021, **446**, 214121.
[2] R. Li, T. Chen, X. Pan. *ACS nano*., 2021, **15**, 3, 3808-3848.
[3] T. A. Fernandes, I. F. M. Costa, P. Jorge, A. C. Sousa, V. André, N. Cerca, A. M. Kirillov, *ACS Appl. Mater. Interfaces*, 2021, **13**, 12836–12844.

P15

How does culture media in nanototoxicity assessment affect the size, shape, and composition of TiO_2 and CeO_2 engineered nanomaterials?

C. B. Lopes[1,*], A. C. Estrada[1], F. Rosário[2, 3, 4], C. Costa[2, 3, 4], J.P. Teixeira[2, 3, 4], A. T. Reis[2, 3, 4]

[1]CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal;
[2]EPIUnit, Institute of Public Health, University of Porto, Porto, Portugal;
[3]Laboratory for Integrative and Translational Research in Population Health (ITR) Porto, Portugal;
[4]Institute of Public Health (ISPUP), Porto University, Porto, Portugal
** E-mail: claudia.b.lopes@ua.pt*

Nowadays, humans are constantly exposed to nanoparticles, and their effects and impact on the human body are still not completely known.[1] Due to the widespread use of titanium dioxide nanoparticles (TiO_2NP) and the use of cerium oxide nanoparticles (CeO_2NP) in nanomedicine, the NanoLegaTox project aims to explore the toxicological effect of these nanoparticles on human lungs, brain, and liver, alone and co-exposed with arsenic and mercury, at environmental realistic concentrations. Therefore, nanoparticle characterization (Figure 1) is key to the project's success as it plays an important role to understand their interaction with the metals and the biological behavior of these nanomaterials.

Size and shape were given particular attention, as these parameters have been shown to alter cellular uptake, protein adsorption, accumulation in organelles and distribution throughout the body. At first instance, and due to the analytical challenges associated with characterization in culture media and during exposure, the characterization of TiO_2NP and CeO_2NP was performed in its pristine state, i.e. in the commercially available suspensions. However, some of the culture media properties, such as ionic strength, pH, or even the high protein content may alter the nanomaterials physicochemical characteristics.

Here, we investigate and compare the size and shape, the XRD pattern and the surface composition of pristine TiO_2NP and CeO_2NP, with the ones obtained upon addition of the nanoparticles to cell culture media with added fetal bovine serum. This helps to identify the effect of true size and shape, and NPs composition during in vitro nanotoxicity assessment.

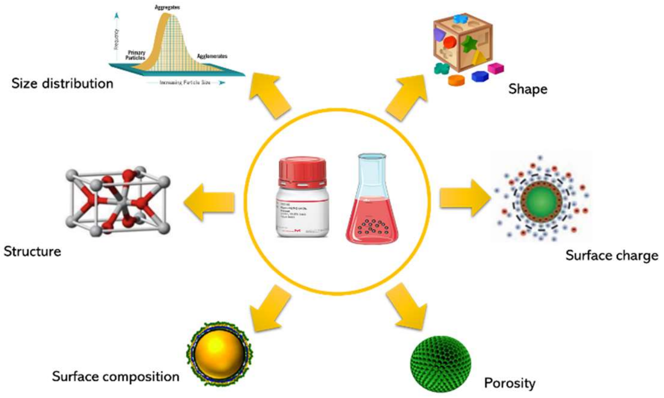


Figure 1: Nanoparticle's characterization scheme.

Acknowledgements

Project NanoLegaTox (POCI-01-0145-FEDER-029651) was cofinanced by COMPETE 2020, Portugal 2020 and European Union, through FEDER. A.T. Reis thanks the financial support of Fundação para a Ciência e Tecnologia through Grant SFRH/BPD/122112/2016. A.C. Estrada and C.B. Lopes are funded by national funds (OE), through FCT – Fundação para a Ciência e a Tecnologia, I.P., in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19.

References

1 Ray P. C.; Yu H.; Fu P. P. J. Environ. Sci. Health C 2009


13th IBCC 29 | 30 MARÇO 2022

P16

Synthesis of Platinum Complexes based on Uracil

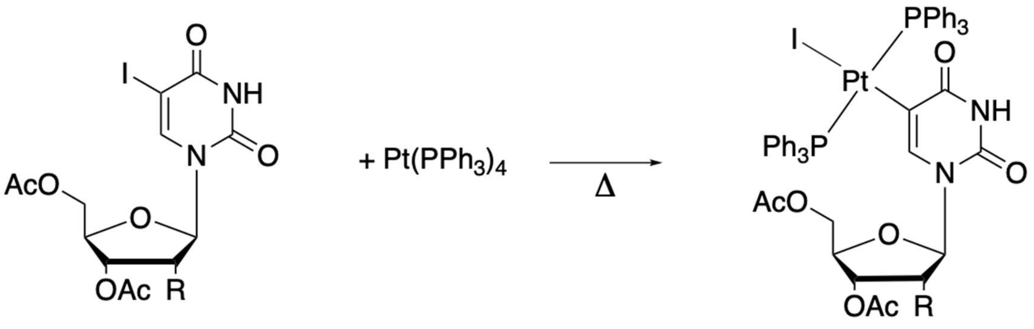
G. Orsini[1], M.I.P.S. Leitão[1], A. Petronilho[1*]

ITQB NOVA Av. da República, 2780-157 Oeiras, Portugal
giulia.orsini@itqb.unl.pt

Modified nucleosides are widely used in chemotherapy, acting as antimetabolites that disrupt the synthesis of nucleic acids. Currently, and similarly to cisplatin[1], they can be applied as a standalone treatment or in combination chemotherapies, to improve effectiveness in treatment by the dual mode of action that each drug provides. However, combination therapies are often problematic due to the different pharmacokinetics of individual drugs. To circumvent these issues, one promising strategy is to combine cytotoxic functionalities in one single drug.

In line with this, we have developed synthetic methodologies to obtain nucleosides functionalized with platinum complexes. We have recently reported the synthesis of complexes based on guanosine[2] and adenosine[3]. These complexes are formed by means of C-X oxidative addition to Pt(0) precursors, in good yields. More recently, we have focused our attention on synthesis of organometallic nucleosides based on pyrimidine bases. Specifically, we have examined the reactivity of uridine.

We synthesized complex **3** via C-I oxidative addition of the pyrimidine-based ligand **I** to the Pt(0) precursor (Scheme 1). Compound **3** can be easily deprotected under basic conditions. Similar reactivity was observed for deoxyuridine (compound **II**) leading to complex **4** (Scheme 1). In this poster communication, we will discuss aspects of this reactivity.



I R: OAc
II R: H

3 R: OAc
4 R: H

Scheme 1: Metallation of pyrimidine-based ligand precursors.

Acknowledgements
This work was financially supported by: Project LISBOA-01-0145-FEDER-007660 (Microbiologia Molecular, Estrutural e Celular) funded by FEDER funds through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI). A special thanks to the PhD fellowship UI/BD/152076/2021 funded by FCT and to my supervisor Ana Petronilho.

References

1. B. Swanepoel, G. M. Nitulescu, O. T. Olaru, L. Venables, and M.van de Venter, *Int. J. Mol. Sci.*, 2019, **20**, 5559.
2. M.I. Leitão, F. Herrera, A. Petronilho, *ACS Omega*, 2018, **3**, 15653-15656.
3. M.I. Leitão, G. Francescato, C. Gomes, A. Petronilho, *Molecules*, 2021, **26**, 5384.

Porphyrin Coordination Polymers for Catechol Oxidation

F. Figueira[1]*, K. A. D. F. Castro[2], J. A. S. Cavaleiro[2], M. G. P. M. S. Neves[b], F. A. A. Paz[1], J. P. C. Tomé[3], M. M. Q. Simões[2]

[1]CICECO - Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.
[2]LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.
[3]Centro de Química Estrutural & Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.
** E-mail: ffigueira@ua.pt*

The rational design of porphyrin coordination polymer catalysts offers several advantages over their homogeneous counterparts, including recyclability and reusability, as well as facile post-reaction removal of the catalytic components from the organic products.[1] In this regard, the construction of metalloporphyrin-based nanoscopic cages in a highly organized manner with rich π-electron density can provide favorable interactions with targeted guests while containing multiple active metal centers that can facilitate synergistic interactions with the substrates enhancing the catalytic activities.[2]

Herein the strategies used to obtain novel coordination polymers from the reaction of 5,10,15,20-tetrakis[2,3,5,6-tetrafluoro-4-(4-pyridylsulfanyl)phenyl]porphyrins and 5,10,15,20-tetrakis(4-pyridyl)porphyrins with copper(II) acetate are presented.[3,4] The new materials exhibit high heterogeneous catalytic activity for catechol oxidation in the presence of air (O_2) or H_2O_2 (30 %) (Scheme 1).

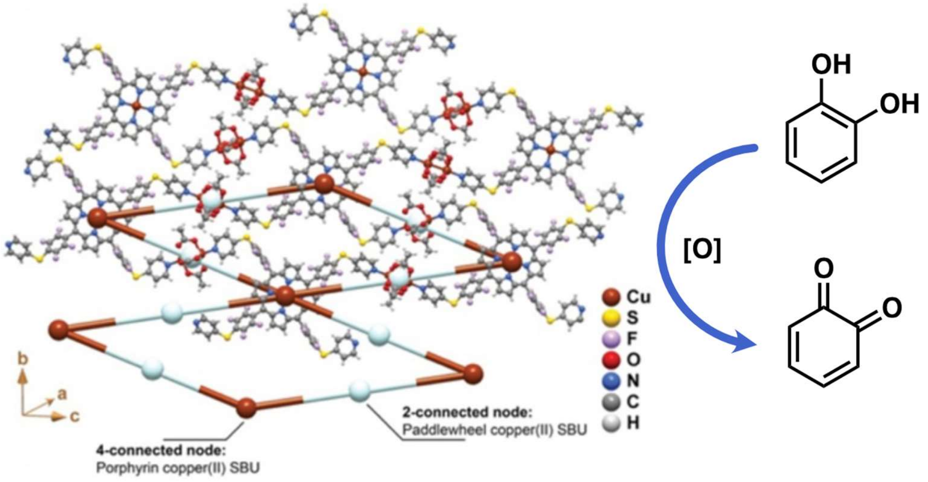


Figure 1: Catechol oxidation by porphyrin coordination polymers.

Acknowledgements

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, and LAQV-REQUIMTE *UIDB/50006/2020 & UIDP/50006/2020* financed by national funds through the FCT/MEC (PIDDAC).*The research contract of FF (REF-168-89-ARH/2018) is supported by national funds (OE), through FCT, in the scope of the framework contract foreseen in Nos. 4, 5 and 6 of article 23 of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19.*

References

[1] Firmino, A. D. G.; Figueira, F.; Tomé, J. P. C.; Paz, F. A. A.; Rocha, J.; *Coord. Chem. Rev.*, **2018**, *355,* 133. [2] Pereira, C.F.; Simões, M.M.Q.; Tomé, J.P.C.; Almeida Paz, F.A.; *Molecules,* **2016**, *21*, 1348. [3] Castro, K. A. D. F.; Figueira, F.; Mendes, R. F.; Cavaleiro, J. A. S.; Neves, M. G. P. M. S.; Simões, M. M. Q.; Paz, F. A. A.; Tomé, J. P. C.; Nakagaki, S.; *ChemCatChem* **2017**, *9*, 2939. [4] Castro, K. A. D. F.; Figueira, F.; Mendes, R. F.; Paz, F. A. A.; Neves, M. G. P. M. S.; Cavaleiro, J. A. S.; Nakagaki, S.; Tomé, J. P.C.; Simões, M.M.Q.; *Polyhedron*, **2019**, *158*, 478.

P18

The antioxidant activity of 3-hydroxy-4-pyridinone chelators

Sílvia Vinhas[1], Maria Rangel[2*]

[1] LAQV-REQUIMTE, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, 4169-007, Porto, Portugal

[2] LAQV-REQUIMTE Instituto de Ciências Biomédicas Abel Salazar, Rua Jorge Viterbo Ferreira 228, 4050-313, Porto, Portugal E-mail: mrangel@icbas.up.pt*

Reactive oxygen species (ROSs) are generated during normal cellular metabolism, participating in cellular signalling. However, if the concentration of ROSs increases beyond the healthier limit, their presence can be harmful. Once the generated free radicals are usually unstable, their excess tend to react quickly, usually with biomolecules, which is believed to be the principal cause of several diseases, like Alzheimer's or cancer.[1]
Iron is well-known as contributing for hydroxyl radical's production, through Fenton and Haber-Weiss reactions, meaning that the presence of redox active iron in the organism, can enhance ROSs concentration.[2]
ROSs reactivity can be neutralized by compounds with the capacity to donate an electron and stabilize their resulting radical. These compounds, known as antioxidants, play a crucial role in ROSs neutralization and are considered an ally to preserve a healthy body.[3]
3-Hydroxy-4-pyridinones (3,4-HPO) are N-heterocyclic compounds, bearing hydroxyl and ketonic oxygen atoms in the 3rd and 4th position of the hexagonal ring. These compounds are widely known for their chelating properties towards M (III) and M(II) and biocompatibility. The delocalisation of the nitrogen's electrons, affords aromaticity to the hexagonal ring, which is responsible for the increase of the acidity of the hydroxyl group, at the 3rd position, achieving phenolic properties.[4] All these characteristics suggests that 3,4-HPO derivatives can be good candidates to neutralize reactive oxygen species, congregating chelating properties and radical scavenging behaviour in the same molecule.[5]

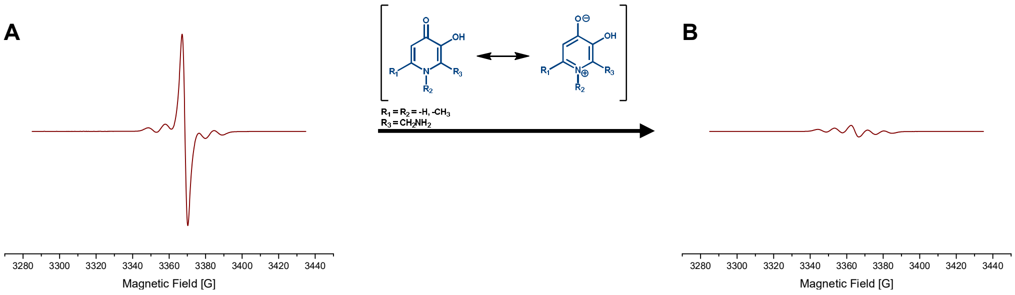


Figure 1: DPPH EPR signal in the absent (A) and in the presence of an hexadentate chelator (B).

The present work is focused on the synthesis and evaluation of antioxidant activity of 3,4-HPO compounds and compares four bidentate units and an hexadentate chelator. The antioxidant activity was evaluated through DPPH free radical scavenging method, using Electron Paramagnetic Resonance (Figure 1) and UV-Vis spectroscopies. From the experimental data, we could confirm that beyond 3,4-HPO derivatives chelating ability, these molecules also can donate electrons to reactive oxygen species revealing strong antioxidant potency.

Acknowledgements

This work received financial support from PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through the project UIDB/50006/2020 | UIDP/50006/2020. SV gratefully acknowledges NORTE-08-5369-FSE-000050 for her PhD grant.

References

1. A. Fassihi, F. Hasanzadeh, A. M. Attar, L. Saghaie and M. Mohammadpour, *Res Pharm Sci*, 2020, **15**, 515-528.
2. T. Kanti Das, M. R. Wati and K. Fatima-Shad, *Archives of Neuroscience*, 2014, **2**.
3. S. Mathew, T. E. Abraham and Z. A. Zakaria, *J Food Sci Technol*, 2015, **52**, 5790-5798.
4. C. S. Santos, A. Leite, S. Vinhas, S. Ferreira, T. Moniz, M. W. Vasconcelos and M. Rangel, *Plant Direct*, 2020, **4**, e00256.
5. V. M. Nurchi, R. Cappai, K. Chand, S. Chaves, L. Gano, G. Crisponi, M. Peana, M. A. Zoroddu and M. A. Santos, *Dalton Trans*, 2019, **48**, 16167-16183.

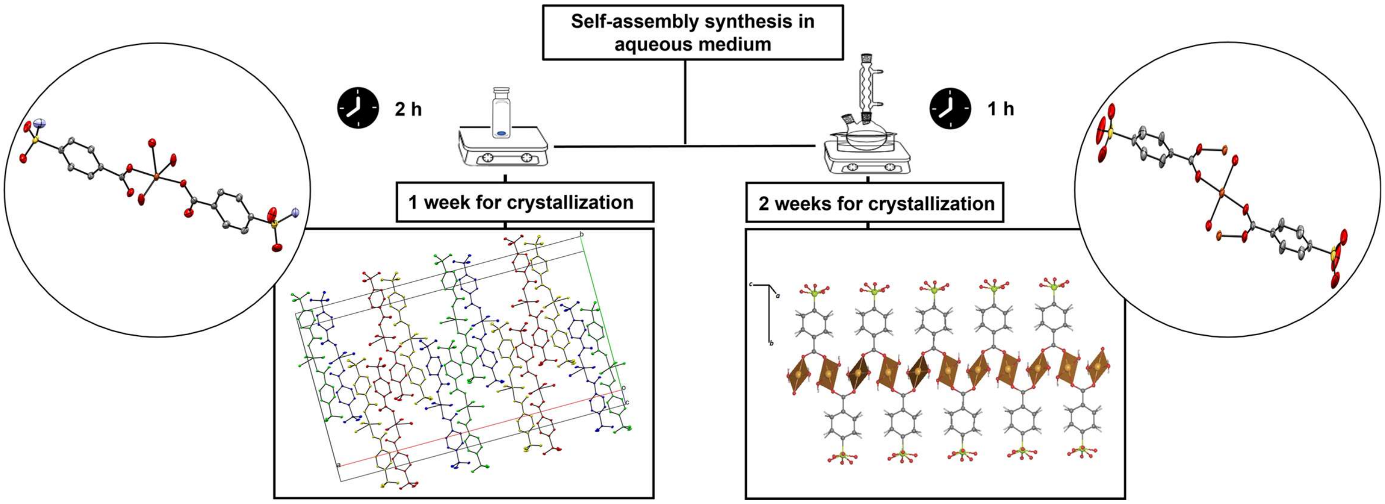
Synthesis and Structural Characterization of Copper(II) 4-Sulfobenzoate and 4-Sulfamoylbenzoate Coordination Compounds

Gilvan A. Correia*, Chris H. J. Franco, Marina V. Kirillova, Tiago A. Fernandes, Alexander M. Kirillov

Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001, Lisboa, Portugal

** E-mail: gilvan.correia@tecnico.ulisboa.pt*

In pursuit of our general interest in the synthesis of copper(II) coordination compounds and their catalytic exploration toward mild C−H functionalization of alkanes and other substrates,[1] in the present study we describe some recent synthetic strategies to obtain novel Cu(II) complexes and coordination polymers driven by 4-sulfamoylbenzoate and 4-sulfobenzoate blocks. Two slightly different synthetic strategies and ligand precursors were explored, resulting in the generation of a discrete complex $[Cu(pab)_2(H_2O)_3]$ (**1**) and a 1D coordination polymer $\{[Cu(\mu\text{-psb})(H_2O)_2]\cdot(H_2O)\}_n$ (**2**). Both compounds were synthetized in aqueous medium by reacting Cu^{2+} ions with 4-sulfamoylbenzoic acid (Hpab, for **1**) or 4-sulfobenzoate monopotassium salt (Kpsb, for **2**), and sodium hydroxide. While compound **1** was obtained by self-assembly at room temperature, the synthesis of **2** required refluxing, followed by crystallization (Scheme 1). The products were obtained as stable crystalline solids in relatively good yields and characterized by standard methods, including single-crystal X-ray diffraction. The structures of **1** and **2** feature distinct coordination modes of ligands (pab^- or psb^-) and their carboxylate moieties (terminal monodentate or μ-bridging bidentate), as well as different coordination environments around Cu(II) centers (trigonal bipyramidal or square pyramidal), respectively. The use of distinct reaction and crystallization conditions is a decisive factor for the control and synthesis of these copper(II) coordination compounds. Regarding the reactivity of **2**, some strategies are currently in progress to extend this 1D coordination polymer into 2D or 3D metal-organic architectures by introducing an additional linker ligand. The exploration of the obtained compounds as potential catalysts[1] in mild oxidative functionalization of hydrocarbons is currently being investigated.



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

Acknowledgements
This work has been supported by the FCT (UIDB/00100/2020, LA/P/0056/2020, PTDC/QUI-QIN/3898/2020, CEECIND/03708/2017, LISBOA-01-0145-FEDER-029697). This work has also received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No 860762 (CHAIR project).

References

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

Recycling industrial Coal Fly Ashes for catalytic reduction of nitroarenes

J. Mendes[1], A.C. Santos[2], B. Valentim[2], I. Kuźniarska-Biernacka[1*], A.F. Peixoto[1], C. Freire[1]

[1] *REQUIMTE/LAQV, Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal*
[2] *Earth Science Institute – Porto pole, Department of Geosciences, Environment and Spatial Plannings, Faculty of Sciences, University of Porto, Rua do Campo Alegre s/n, 4169– 007 Porto, Portugal*
** E-mail: iwonakb@fc.up.pt*

Renewable energies have been garnering increasing attention in the past decades owing to the increased awareness of sustainable development and environmental challenges, but coal still plays an important role in power generation. The main byproduct of its combustion is coal fly ash (CFA). Annually, about 750 million tons of CFA are produced worldwide[1] and several efforts have been made in order to convert into valuable products as: ceramics tiles, zeolites, alumina etc. More recently, the CFA has been used as a supporting material for transition metal oxides of Mn(II), Co(II), and Ni(II) to environmental applications (catalytic degradation of 4-chlorophenol).[2]

Nitrophenol (NPh) is frequently detected in wastewater from many industries (pharmaceutical, foundry, rubber processing, etc.) and it is proven that are toxic to the environment and may cause diseases to human beings. Furthermore, other anthropogenic chemicals such as toluene, benzene and nitrobenzene can be transformed into NPhs with nitrogen oxides and photochemical reactions in the air. To date, a variety of techniques have been developed to effectively remove NPh from waters, including coagulation, adsorption, microbial degradation, electrochemical oxidation and advanced oxidation, photocatalytic oxidation, and advanced reduction.[3, 4] Among these methods, catalytic reduction stands out because aminophenol (APh) is the only reaction product. The APh are value added products as they intermediate the synthesis of pharmaceuticals, dyes, and can be used as a corrosion inhibitor and an antioxidant.

In this work the Fe-rich fraction collected from the economizer CFA by magnetic separation (ferrite magnet), named as bulk ECOM, without any further chemical functionalization was tested as catalysts for 2-NPh or 4-NPh reduction in the presence of $NaBH_4$ (reductant) in water at room temperature. Furthermore, the effect on the ECOM of a previous treatment with NaOH and $NaBH_4$ was also evaluated. All the samples are active in NPh reduction, a complete reduction of 4-NPh was observed in 90 min using ECOM washed with NaOH, while only 92% of 2-NPh was reduced in 75 min using the same catalyst. In the case of bulk ECOA 81% of 4-\NPh and 100% of 2-NPh was reduced in 120 min. This indicated that some surface changes caused by washing with NaOH or $NaBH_4$ allow easier access of substrate to active sites.

Acknowledgements

We thank the Fundação para a Ciência e a Tecnologia for financial support through the projects UIDB/50006/2020, UIDB/04683/2020 and UIDP/04683/2020 CHARPHITE of the 3rd ERA-MIN Program 2015 (FCT ref. ERA-MIN/0005/2015) and PhotoBioTrans (ref. EXPL/CTM-CTM/0790/2021). I.K.-B. thanks FCT for funding through program DL 57/2016 – Norma transitória REQUIMTE/EEC2018/14, A.C.S. thanks FCT for PhD scholarship Ref: SFRH/BD/131713/2017 and COVID/BD/151941/2021). A.F.P. thanks FCT for funding under the Scientific Employment Stimulus ref: 2020.01614.CEECIND/CP1596/CT0007.

References

1. R. S. Blissett and N. A. Rowson, *Fuel*, 2012, **97**, 1-23.
2. M. Kim and S. Bae, *Chemosphere*, 2018, **212**, 1020-1029.
3. J. Park and S. Bae, *Journal of Hazardous Materials*, 2019, **371**, 72-82.
4. J. Park, G. Dattatraya Saratale, S.-K. Cho and S. Bae, *Science of The Total Environment*, 2020, **705**, 134544.

Ruthenium(II) Triazole Complexes as Potential Anticancer Agents

O. A. Lenis-Rojas[1]*, R. Cabral[2], B. Carvalho[2], S. Friaẽs[1], C. Roma-Rodrigues[2], J. A. A. Fernández[3,4], S. F. Vila[4], L. Sanchez[4], C. S. B. Gomes[5], A. R. Fernandes[2], and B. Royo[1]

[1]ITQB NOVA, Av. da República, 2780-157 Oeiras, Portugal. [2]UCIBIO, Dept. Ciências da Vida, FCT-UNL, Campus de Caparica, 2829-516, Portugal. [3]Laboratory of Zebrafish, Dept. Medical Genetics and Genomic Medicine School of Medical Sciences, UNICAMP, Sao Paulo, Brazil. [4]Dept. Zoología Genética y Antropología Física, Facultad de Veterinaria, USC, 27002 Lugo, Spain. [5]LAQV- and UCIBIO-REQUIMTE, Dept. Química, FCT-UNL, 2829-516 Caparica, Portugal.
*E-mail: oscar.rojas@itqb.unl.pt

Cancer is a leading cause of death worldwide, accounting for nearly 10 million deaths in 2020. One of the most effective and broadly used treatments for cancer are based on chemotherapy. Since the introduction of cisplatin and other platinum drugs, the cure rate improved in most types of cancer. However, the severe toxic effects associated with Pt-based drugs and the inherent resistance of tumors to this treatment have led to the scientific community to search for alternative metallodrugs that can overcome these drawbacks.

Herein, we present our results on the development of a new family of Ru complexes with interesting properties as anticancer agents. A series of half-sandwich Ru(II) compounds bearing 1,2,3-triazole-derived ligands have been synthesized and fully characterized (Figure 1), including the X-ray diffraction studies. The cytotoxic activity of these complexes has been evaluated against human tumor cells, namely ovarian carcinoma (A2780), colorectal carcinoma (HCT116), and colorectal carcinoma resistant to doxorubicin (HCT116dox), and against normal primary fibroblasts. Among the Ru complexes tested, those bearing triazole-pyridine fragments displayed good activity as anticancer agents in A2780 cancer cell lines, while showed no antiproliferative effect in human normal dermal fibroblasts.[1] Interestingly, exposure of ovarian carcinoma cells to IC50 concentrations of these complexes led to an accumulation of reactive oxygen species, and an increase of apoptotic and autophagic cells. Moreover, in vivo toxicity studies of these complexes using zebrafish and chicken embryos probed that they were non-toxic. Thus, it has been demonstrated that the newly synthesized Ru complexes containing triazole-pyridine ligands are promising candidates as anticancer agents against ovarian cancer[1].

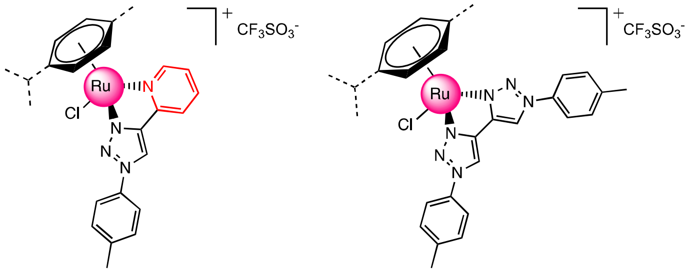


Figure 1: Half-sandwich Ru(II) compounds tested as anticancer drugs

Acknowledgements
We are grateful to FCT for projects MostMicro unit Project LISBOA-01-0145-FEDER-007660 of Portugal. Oscar A. Lenis-Rojas acknowledge national funds through FCT, POPH-Programa Operacional Potencial Humano, and FSE (European Social Fund) for the CEEC 2017 Initiative. Also, to FCT Project MOSTMICRO-ITQB with refs UIDB/04612/2020 and UIDP/04612/2020 and Applied Molecular Biosciences Unit - UCIBIO with refs FCT (UIDP/04378/2020 and UIDB/04378/2020).

References

1. Lenis-Rojas, O. A. *et al.* Triazole-Based Half-Sandwich Ruthenium(II) Compounds: From in Vitro Antiproliferative Potential to in Vivo Toxicity Evaluation. *Inorg. Chem.* **60**, 8011–8026 (2021).

Sustainable fuel desulfurization and denitrogenation using coordination defective Zr- and Hf-UiO-66s

R. G. Faria*, Alexandre M. Viana, Fátima Mirante, Salete S. Balula, Luís Cunha-Silva

[a]LAQV REQUIMTE, Department of Chemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal
** E-mail: up201202396@edu.fc.up.pt*

The harmful environmental and health effects arising from the combustion of fossil fuels have been widely recognized as one the current days' major global crises. The presence of N- and S-containing compounds in fuels leads to the emission of their corresponding oxides, contributing to worldwide climate change phenomena. Currently, the petroleum industry resorts to the injection of hydrogen at high temperatures and pressures to remove these compounds from fuel streams. With strict legislation being introduced to limit S in fuels, the development of new technologies encompassing desulfurization and denitrogenation with superior sustainability claims is a priority. Simultaneous catalytic oxidative desulfurization (ODS) and denitrogenation (ODN) processes display high efficiency for the removal of S and N-content in fuels. This technology allows to produce cleaner fuels under energetically sustainable conditions, using environmentally benign oxidants and recyclable catalysts[1]. Metal-organic frameworks (MOF), 3D porous materials, comprised of organic bridging ligands and metallic centres, have emerged as promising catalysts, due to their structural diversities and unique properties, such as high porosity, large surface areas and remarkable stabilities.

Pristine UiO-66, a MOF family composed by the self-assembly of 12-connected Zr_6 or Hf_6 nodes bridged by 1,4-benzene-dicarboxylate linkers, were prepared, thoroughly characterized, and tested as heterogenous catalysts in ODN and ODS systems. Both materials exhibited good catalytic activity for the ODN system (80% and 94% denitrogenation for the Zr and Hf-based MOF, respectively); ODS performance, however, was lacking, and thus, a straightforward activation was performed. Post-synthetic treatment of the pristine MOF with titanium chloride introduces coordination defect centres into the rigid UiO-66 structures, boosting the catalytic activity of UiO-66(Zr) from 62% to 97% and doubling that of UiO-66(Hf) (from 40% to 80% desulfurization) (Figure 1).

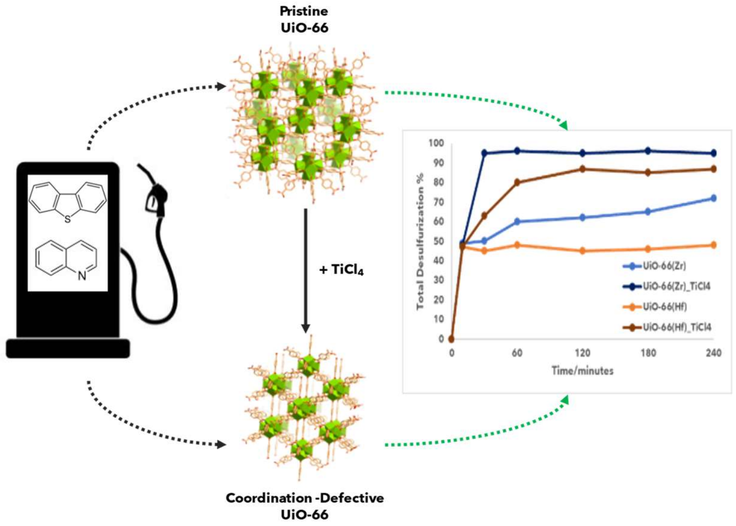


Figure 1: ODS performance of pristine and coordination defective UiO-66s.

Acknowledgements

This work received financial support from Portuguese national funds (FCT/MCTES) through the strategic project UIDB/50006/2020 (for LAQV-REQUIMTE) and was also funded by the European Union (FEDER funds through COMPETE POCI-01-0145-FEDER-031983) and FCT/MCTES to the R&D project GlyGold (PTDC/CTM-CTM/31983/2017). LCS and SSB thank FCT/MCTES for funding the Individual Call to Scientific Employment Stimulus (CEECIND/00793/2018 and EECIND/03877/2018, respectively). RGF and AMV thank FCT/MCTES for the PhD grants (/BD/151277/2021 and SFRH/BD/150659/2020, respectively).

References

1. F. Mirante, R.F. Mendes, F.A.A. Paz, S.S. Balula, *Catalysts*, 2020, **10**, 731

P23

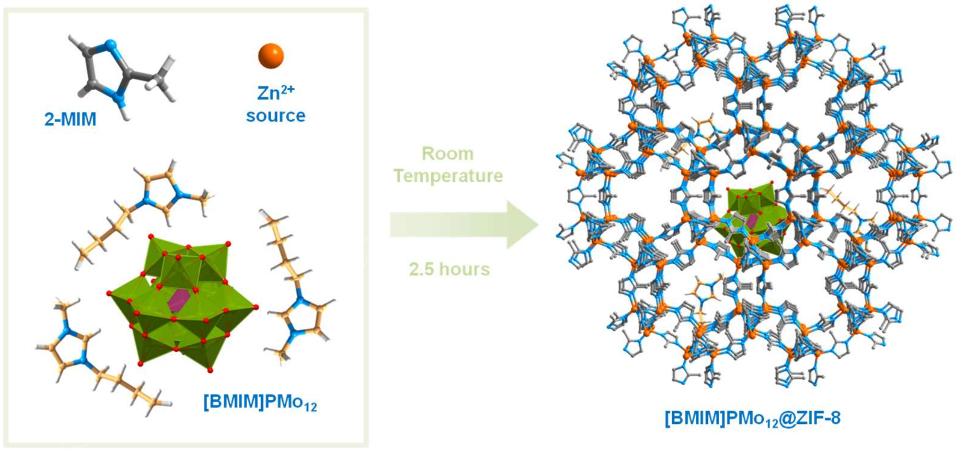
Recent advances in porous MOF-derived materials towards eco-sustainable catalytic systems

L. Cunha-Silva*, S. C. Fernandes, D. F. Silva, A. M. Viana, R. G. Faria,
F. Mirante, C. M. Granadeiro, S. S. Balula

LAQV / REQUIMTE, Department of Chemistry, Faculty of Sciences - University of Porto,
Rua do Campo Alegre, 4169-007 Porto, Portugal
** E-mail: l.cunha.silva@fc.up.pt*

Metal–organic frameworks (MOFs), also known as porous coordination polymers, have been proven to be outstanding candidates for bridging the gap between zeolites and mesoporous silica. MOFs are constituted by metal ions/clusters interconnected by organic linkers and have captured widespread interest, achieving an explosive development over the past two decades. The crystalline nature, structural diversity, and tailorability, as well as ultrahigh surface area make MOFs find their potential applications in diverse areas, such as gas sorption and separation, chemical sensing, proton conductivity, biomedicine and catalysis. However, in numerous MOFs the structural stability and performance limits their practical applications, relatively to other porous materials. Consequently, distinct strategies have been used to prepare MOF based materials and overcome these disadvantages.[1,2]

The modification and derivation of MOFs, and their utilization as platform, opens an avenue to the preparation of diversified porous materials with unique advantages in comparison to traditional pristine materials. Following our interest in the development and application of functional MOFs towards catalytic sustainable processes an overview of more interesting functional porous MOF-based materials prepared and investigated as heterogeneous catalysts in our research group is reported (Scheme 1).[3]



Scheme 1: representation of the preparation of the POM/MOF composite material by a “bottle-around-the ship” approach and using a sustainable room temperature synthetic strategy (one-pot and in situ).[3]

Acknowledgements

The work received financial support from Portuguese national funds (FCT/MCTES) through the strategic project UIDB/50006/2020 (for LAQV-REQUIMTE); it was also funded by the European Union (FEDER funds through COMPETE POCI-01-0145-FEDER-031983) and FCT/MCTES to the R&D project GlyGold (PTDC/CTM-CTM/31983/2017). LCS and SSB thank FCT/MCTES for funding the Individual Call to Scientific Employment Stimulus (CEECIND/00793/2018 and EECIND/03877/2018, respectively). AMV and RGF thank FCT/MCTES and ESF (European Social Fund) for their PhD grants (Refs. SFRH/BD/150659/2020 and UI/BD/151277/2021, respectively) through POCH (Programa Operacional Capital Humano).

References

1. L. Jiao, Y. Wang, H.-L. Jiang, Q. Xu, *Adv. Mater.* **2018**, 30, 1260.
2. Y.-Z. Chen, R. Zhang, L. Jiao, H.L. Jiang, *Coord. Chem. Rev.* **2018**, *362*, 1.
3. D. F. Silva, A. M. Viana, I. Santos-Vieira, S. S. Balula, L. Cunha-Silva, *Molecules* **2022**, 27, 1711.

Encapsulation of catalytic active PMo_{12} in MOF-808 for simultaneous desulfurization and denitrogenation of fuel

S. C. Fernandes,*, A. Viana, L. Cunha-Silva, S. S. Balula,

LAQV / REQUIMTE, Department of Chemistry, Faculty of Sciences - University of Porto, 4169-007 Porto, Portugal
** E-mail: up201603496@fc.up.pt*

The combustion of S- and N-based compounds present in fuels is associated with the emission of hazardous gases, namely, S and N oxides (SO_x and NO_x), which leads to environmental and industrial problems. Therefore, strict legislation demanding low sulfur limits have been stablished for road fuels (S < 10 ppm) and for marine fuel (S < 500 ppm). The legislation to control N content in fuels is not regulated yet; however, the European standards for global emission of NOx have been tightened.

Hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) are the traditional methods used by petroleum refineries for the removal of S and N from fuels, but these processes are based on expensive technology, requiring severe experimental conditions to achieve high efficiency. Oxidative desulfurization (ODS) and oxidative denitrogenation (ODN) are alternative and/or complementary methods to the HDS and HDN processes. Through ODS and ODN, S- and N-based refractory compounds can be effectively removed from liquid fuels using moderate temperature and atmospheric pressure. However, reports of success simultaneous ODS and ODN processes are scarce.[1] ODS and ODN occurs in in two main steps: oxidation and extraction. The oxidation step requires the activation of the oxidant, such as H_2O_2, by a catalyst. Polyoxometalates (POMs), such as phosphomolybdic acid $H_3PMo_{12}O_{40}$ (PMo_{12}) show high catalytic performance in oxidative reactions.[2] Nevertheless, these compounds are highly soluble in catalytic media behaving as homogeneous catalysts, with difficult removal at the end of the reaction. Therefore, their heterogenization by immobilization in adequate solids supports, such as metal-organic frameworks (MOFs), provides the preparation of active heterogeneous catalysts with robustness and easy recovery from reaction. MOF-808 presents two types of cavities: a smaller tetrahedral pore and an adamantane shaped pore.

In this work, a novel heterogeneous catalyst was prepared by the encapsulation of an active center PMo_{12} on to MOF-808 framework by "bottle-around-the-ship" approach (Figure 1). The composite PMo_{12}@MOF-808 was tested as catalyst for simultaneous ODS and ODN of a multicomponent model fuel containing various refractory S and N-compounds. In these catalytic studies, H_2O_2 was used as oxidant and the ionic liquid [BMIM]PF_6 as extraction solvent since this combination has shown great performance in ODS.[3] The recycling capacity and stability of the heterogeneous catalyst were also investigated.

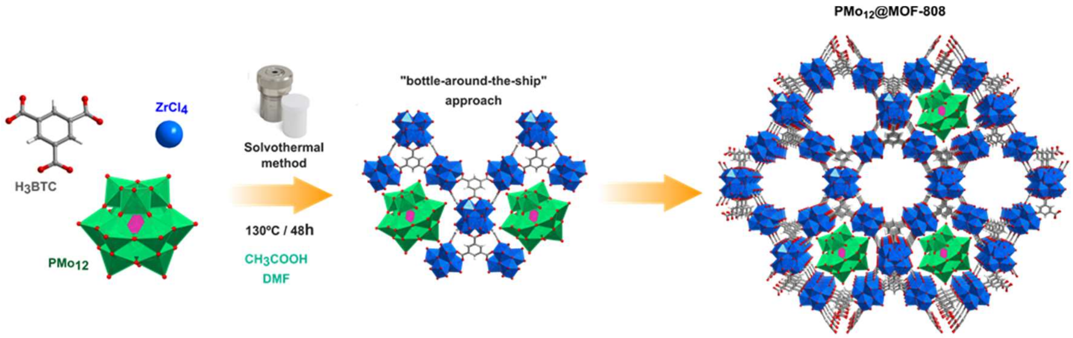


Figure 1: Representation of the preparation of PMo_{12}@MOF-808 by the "bottle-around-the ship" approach.[1]

Acknowledgements

The work received financial support from Portuguese national funds (FCT/MCTES) through the strategic project UIDB/50006/2020 (for LAQV-REQUIMTE); it was also funded by the European Union (FEDER funds through COMPETE POCI-01-0145-FEDER-031983) and FCT/MCTES to the R&D project GlyGold (PTDC/CTM-CTM/31983/2017). AMV thanks FCT/MCTES and ESF (European Social Fund) for his PhD grants (Refs. SFRH/BD/150659/2020) through POCH (Programa Operacional Capital Humano).

References

1. S. C. Fernandes, A. M. Viana, B. Castro, L. Cunha-Silva and S. S. Balula, *Sustain. Energ. Fuels*, 2021, **5**, 4032-4040.
2. F. Mirante, N. Gomes, L. C. Branco, L. Cunha-Silva, P. L. Almeida, M. Pillinger, S. Gago, C. M. Granadeiro and S. S. Balula, *Microporous Mesoporous Mater.*, 2019, **275**, 163-171.
3. Z. Yao, H. N. Miras and Y.-F. Song, *Inorg. Chem. Front.*, 2016, **3**, 1007-1013.

Development of tailored mesoporous silica-based materials for water remediation

D. Flores[1,*], C. M. Granadeiro[1]

[1] LAQV-REQUIMTE, Department of Chemistry and Biochemistry, University of Porto, 4169-007, Porto, Portugal
** E-mail: up201503782@up.pt*

The prevention of water contamination and/or its remediation are fundamental, since water is an extremely important and indispensable natural resource for life.[1] Toxic metal ions and organic dyes are two of the most alarming water pollutants, which can lead to adverse effects on human health or even carcinogenicity.[2] Several studies have been focusing on the development of effective procedures and technologies for environmental remediation.[3] Adsorption is regarded as one of the most promising methods, from an economic and energetic point of view, exhibiting the advantages of simplicity and practicability for the efficient removal of a wide range of water pollutants, namely toxic metal ions, pesticides, organic dyes, and antibiotics.[4] A wide variety of adsorbents have been tested and silica has received enormous attention due to its structural and economic characteristics and advantages, namely fast adsorption of metal ions, high surface area, remarkable chemical, thermal and mechanical stabilities, and uniformity of pore distribution.[3,5]

In the present work, two different types of mesoporous silica-based materials, spherical silica particles and periodic mesoporous organosilicas, were synthesized and tailored with different functional groups and/or porosities. The adsorptive capacity of the prepared materials was evaluated in the removal of some of the most common organic and inorganic pollutants. The effect of adsorption kinetics and recycling ability were also assessed.

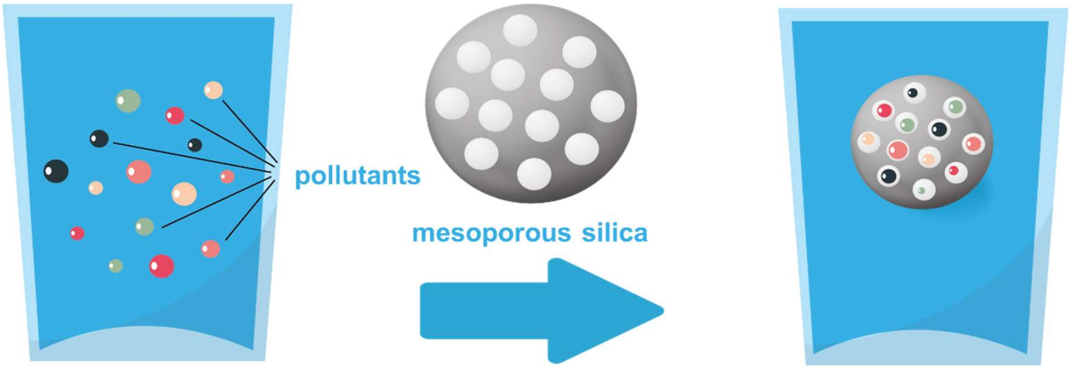


Figure 1: Schematic representation of pollutants adsorbed on silica-based materials.

References

1. Q. Gao, J. Xu, X. H. Bu, *Coord. Chem. Rev.* **378** (2019) 17.
2. J. Li, X. Wang, G. Zhao, C. Chen, Z. Chai, A. Alsaedi, T. Hayat, *Chem. Soc. Rev.* **47** (2018) 2322.
3. S. Radi, C. Abiad, A. P. Carvalho, S. M. Santos, M. A. F. Faustino, M. G. P. M. S. Neves, N. M. M. Moura, *J. Mater. Chem. A* **6** (2018) 13096.
4. F. D. Guerra, M. F. Attia, D. C. Whitehead, F. Alexis, *Molecules* **23** (2018) 17.
5. F. Mirante, A. C. Alves, D. Julião, P. L. Almeida, S. Gago, R. Valença, J. C. Ribeiro, B. Castro, C. M. Granadeiro, S. S. Balula, *Fuel* **259** (2020) 116.

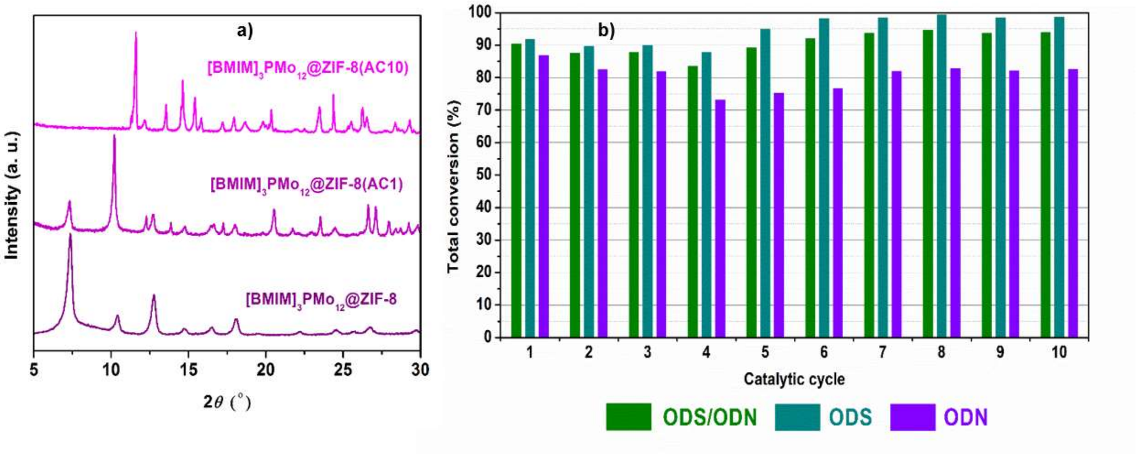
P26

Ionic Liquid-based Polyoxometalate incorporated at ZIF-8 for Oxidative Desulfurization and Denitrogenation Processes

Dinis F.Silva[1,*], A. M. Viana[1], I. Santos-Vieira,[2], S. S. Balula[1], L. Cunha-Silva[1]

[1] LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal
[2] CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal
** E-mail: josedinis.silva@fc.up.pt*

An effective and sustainable process capable to execute simultaneously desulfurization and denitrogenation of fuels is in fact an actual need for the refinery industry. The key to achieve this goal is the parallel oxidation of sulfur and nitrogen compounds present in fuels, by the utilization of active and recyclable catalysts.[1] Polyoxometalates are described for their high catalytic efficiency as homogeneous catalysts in simultaneous oxidative desulfurization and denitrogenation of model fuel oils.[2] This work presents a novel heterogeneous catalyst prepared via encapsulation of an imidazolium-based polyoxometalate (POM) into ZIF-8 framework ([BMIM]PMo12@ZIF-8). This composite material has shown exceptional catalytic efficiency towards the oxidative desulfurization and denitrogenation of a model fuel containing various sulfur and nitrogen compounds. The catalyst was able to completely remove all these compounds after only 60 minutes and the catalytic system was able to be reused for ten consecutive cycles without loss of efficiency. This work presents the first incorporation of an ionic liquid POM in to ZIF-8. The novel material was successfully used as catalyst to simultaneous remove sulfur and nitrogen from a multicomponent model fuel.



Scheme 1: Scheme of a) PXRD patterns of [BMIM]PMo$_{12}$@ZIF-8 material before catalytic utilization, isolated after 1st cycle (AC1) and after the 10th catalytic cycle (AC10) and b) Reutilization performance of [BMIM]PMo$_{12}$@ZIF-8 over 10 cycles combining desulfurization and denitrogenation processes to treat a multicomponent model fuel.[3]

Acknowledgements
The work was financed through the project UIDB/50006/2020, through COMPETE POCI-01-0145-FEDER-031983 and FCT/MCTES to the R&D project PTDC/CTM-CTM/31983/2017. LCS and SSB thank FCT/MCTES for funding the Individual Call to Scientific Employment Stimulus (CEECIND/00793/2018 and EECIND/03877/2018, respectively). AMV thank FCT/MCTES for the PhD grants SFRH/BD/150659/2020.

References

1. S.C. Fernandes, A. M. Viana, B. de Castro, L. Cunha-Silva, S. S. Balula, *Sust. Ener. & Fuels,* 2021, **5**, 4032-4040
2. D.F. Silva, A. M. Viana, F. Mirante, B. de Castro, L. Cunha-Silva, S.S. Balula, *Sustain. Chem.,* 2021, **2**, 382-391
3. D.F. Silva, A. M. Viana, I. Santos-Vieira, S. S. Balula, L. Cunha-Silva, *Mol.*, 2022, **5**, 1711.

P27

Nanostructured drug delivery systems for melanoma treatment

C. Cunha[1], D. Marinheiro[2], R. Afonso[1], J. Nogueira[2], S. F. Soares[2], F. Brás[2], P. Oskoei[1], M. Saleh[3], E. Andresen[3], B. Rühle[3], U. Resch-Genger[3], V. Bastos[1], B.J.M.L. Ferreira[2], A. L. Daniel-da-Silva[2], H. Oliveira[1]

[1]CESAM & Department of Biology, University of Aveiro, Aveiro, Portugal
[2]CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Aveiro, Portugal
[3]Federal Institute for Material Research Testing (BAM), Berlin, Germany
** E-mail: catarinafilipacunha@ua.pt*

Melanoma is one of the most aggressive forms of skin cancer, that occurs as a result of malignant transformation of melanocytes giving rise to a diverse set of clinical features [1–3]. Melanoma revealed some resistance to the conventional therapies [2,4], so is the major importance the development of new mechanisms of therapeutics to improve cancer treatment enhancing patients' quality of life. Nanotechnology provides an opportunity to encapsulate antitumor drugs into nanostructured drug delivery systems, which allows a controlled and prolonged release pattern, ensures a targeted action, and enhances the biological potential of the drugs[4–6]. Nanoparticles can be combined with different targeting ligands to reduce the off-target effect. This will not only increase the bioavailability of the drug, but also reduce the adverse effects associated with compounds used in conventional therapies [4]. In the present work, we present three different approaches for the development of nanostructured drug delivery systems for melanoma therapy: i) mesoporous silica NaYF4:Yb,Er (NaYF4:Yb,Er@mSiO2) were functionalized with folic acid (FA) and loaded with doxorubicin (DOX); ii) mesoporous silica nanoparticles (MSN) were loaded with resveratrol (RES) [7]; iii) fluorescent carbon dots are being prepared for the loading of drugs (e.g doxorubicin, active phytocompounds). Our results showed that NaYF4:Yb,Er@mSiO2 functionalization with FA enhanced the DOX release. A slight pH-dependence of DOX release at acidic pH was observed. The polyphenol RES was successfully encapsulated onto MSNs which promoted the amorphization of RES desirable to increase the solubility of this drug. A pH-dependence of RES release was also observed. In both nanostructures, the pH-sensitive behavior is of high interest and may benefit drug delivery to tumor cells because the intracellular pH in tumor cells is lower than in healthy cells. Both DOX loaded-NaYF4UCNPs@mSiO2-FA and RES-loaded MSNs showed cytotoxicity to melanoma cancer lines. In conclusion, our results demonstrated that the developed nanostructured systems could serve as drug delivery systems for melanoma therapy.

Acknowledgements

This work was developed within the scope of the projects CESAM UIDB/50017/2020 & UIDP/50017/2020, CICECO-UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC). and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. This work was supported by the project PTDC/BTM-MAT/31794/2017 (POCI-01-0145-FEDER-031794) funded by FEDER, through COMPETE2020—Programa Operacional Competitividade e Internacionalização (POCI), and by national funds (OE), through FCT/MCTES. J. Nogueira thanks the FCT for the PhD Scholarship SFRH/BD/146249/2019. B. Ferreira also acknowledge their research position funded by national funds (OE), through FCT-Fundação para a Ciência e a Tecnologia, I.P., in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19.

References

1 R. A. Akasov, N. v. Sholina, D. A. Khochenkov, A. v. Alova, P. v. Gorelkin, A. S. Erofeev, A. N. Generalova and E. v. Khaydukov, *Scientific Reports*, , DOI:10.1038/s41598-019-46115-w.
2 B. Domingues, J. Lopes, P. Soares and H. Populo, *ImmunoTargets and Therapy*, 2018, Volume 7, 35–49.
3 C. Garbe, T. Amaral, K. Peris, A. Hauschild, P. Arenberger, L. Bastholt, V. Bataille, V. del Marmol, B. Dréno, M. C. Fargnoli, J. J. Grob, C. Höller, R. Kaufmann, A. Lallas, C. Lebbé, J. Malvehy, M. Middleton, D. Moreno-Ramirez, G. Pellacani, P. Saiag, A. J. Stratigos, R. Vieira, I. Zalaudek and A. M. M. Eggermont, *European Journal of Cancer*, 2020, 126, 141–158.
4 H. Kaur and P. Kesharwani, *Journal of Controlled Release*, 2021, 337, 589–611.
5 S. Bayda, E. Amadio, S. Cailotto, Y. Frión-Herrera, A. Perosa and F. Rizzolio, *Nanoscale Advances*, 2021, 3, 5183–5221.
6 A. Wicki, D. Witzigmann, V. Balasubramanian and J. Huwyler, *Journal of Controlled Release*, 2015, 200, 138–157.
7 D. Marinheiro, B. J. M. L. Ferreira, P. Oskoei, H. Oliveira and A. L. Daniel-da-silva, *Materials*, 2021, 14, 1–18.

P28

A novel bioactive Cu(II) complex with ibuprofen: Synthesis, characterization, binding capacity and antitumoral properties

B. J. M. Leite Ferreira[1,*], L. P. Monteiro[1], F. Martel[2], R. Mendes[1], F. Paz[1], T. M. Santos[1],

[1]*Department of Chemistry and CICECO – Aveiro Institute of Materials, University of Aveiro, Aveiro, Portugal*
[2]*Unit of Biochemistry - Department of Biomedicine, Faculty of Medicine of Porto, University of Porto, and Instituto de Investigação e Inovação em Saúde (i3S), Porto, Portugal*
**E-mail: barbaraferreira@ua.pt*

Non-steroidal anti-inflammatory drugs (NSAIDs) are an important class of therapeutic molecules, discovered more than 100 years ago, that are nowadays extensively used as analgesic, anti-inflammatory, and antipyretic agents. NSAIDs general mode of action involves the inhibition of cyclooxygenase (COX) enzyme, which takes part in the biosynthesis of prostaglandins and thromboxane. However, their use is usually associated with several side effects such as kidney failure and gastrointestinal problems.[1] Transition metals are crucial to human health and have structural and functional roles comprising the maintenance of cellular functions involved in a wide range of essential physiological activities in human organism. Moreover, transition metals exhibit different oxidation states and can interact with a number of negatively charged molecules.[2] This capacity has been explored for the development of metal-based (metallodrugs) with promising pharmacological application and may offer unique therapeutic opportunities.[3] The synthesis of metallodrugs involving transition metal ions and NSAIDs as ligands started with the preparation of an acetylsalicylic acid (commercially known as aspirin) copper(II) complex. Posterior studies revealed that the Cu(II)-aspirin complex presented a more effective anti-inflammatory effect and lower ulcerogenicity and irritation in the digestive tract compared to parent drug (free aspirin).[4] This study was an important breakthrough because free aspirin has no COX specificity, meaning that blocks the conversion of arachidonic acid into endoperoxide, stopping some steps of the inflammatory process, but also inhibit COX-1 which is present in almost all tissues (stomach, kidneys, intestine, etc.) causing an increase in the risk of gastrointestinal bleeding and damage.[1] Therefore, coordination with Cu(II) brought many advantages, both in the mitigation of aspirin side effects and on its biological activity.

This work describe the synthesis (using two methodologies, one pot and microwave-assisted synthesis) and characterization of a novel Cu(II) complex coordinated with ibuprofen and 2,2'-dipyridylamine. Binding studies (with DNA and BSA), MTT (against MDA-MB-231, a triple negative cancer cell line) and TBARS assays tested the metallodrug potential for future antitumoral applications.

Acknowledgements

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC). The position held by B.J.M.Leite Ferreira was funded by national funds (OE), through FCT—Fundação para a Ciência e a Tecnologia, I.P., in the scope of the framework contract foreseen in numbers 4, 5 and 6 of Article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, July 19.

References

1. I. Ghlichloo; V. Gerriets. Nonsteroidal Anti-inflammatory Drugs (NSAIDs), 1st ed.; StatPearls Publishing: Florida, USA, 2020.
2. A.C.F Santos; L.P.G. Monteiro; A.C.C. Gomes; F. Martel; T.M. Santos; B.J.M.L. Ferreira. NSAID-Based Coordination Compounds for Biomedical Applications: Recent Advances and Developments. *Int. J. Mol. Sci.* 2022, **23**, 2855.
3. S. Rafique; M. Idrees; A. Nasim; H. Akbar; A. Athar. Transition metal complexes as potential therapeutic agents. *Biotechnology and Molecular Biology Reviews* 2010, **5**, 38-45.
4. Chohan ZH, Iqbal MS, Iqbal HS, Scozzafava A, Supuran CT. Transition metal acetylsalicylates and their antiinflammatory activity. *J Enzyme Inhib Med Chem*. 2002, 17, 87-91.

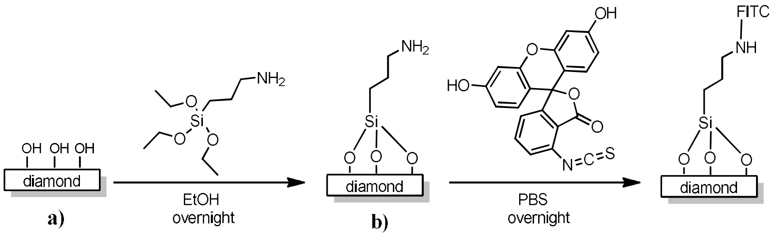
Functionalization of HFCVD diamond with (3-aminopropyl)triethoxysilane and fluorescein isothiocyanate (FITC)

Nádia E. Santos[1,2,*], Leandro Felício[3], Susana Santos Braga[1], Joana C. Mendes[2], Flávio Figueira[3], Miguel Neto[3], Jonas Deuermeier[4]

[1] LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193, Aveiro, Portugal
[2] Instituto de Telecomunicações e Departamento de Eletrónica, Telecomunicações e Informática, Universidade de Aveiro, 3810-193 Aveiro, Portugal
[3] CICECO—Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[4] CENIMAT/I3N, Centro de Investigação de Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516, Caparica, Portugal
** E-mail: nadiaasantos@ua.pt*

As-grown hot-filament chemical vapor deposition (HFCVD) diamond can be easily functionalised through a variety of physical and/or chemical methods to feature amine groups that are an ideal platform for the subsequent binding of enzymes, DNA or proteins.[1]

In the present work, we use boron-doped HFCVD diamond films as the substrate to demonstrate our functionalization approach. Firstly, the samples were exposed to oxygen plasma, in order to create active O-terminated surfaces. In a second step, the surface was used to react with a solution of 5% of (*3*-aminopropyl)triethoxysilane (APTES) in ethanol overnight (Scheme 1a). This step was important to create a spacer between the diamond surface and the amine group, with enough distance to the surface to attach a wide variety recognition units. Herein, as a proof of concept we used fluorescein isothiocyanate (FITC) to modify the diamond surface with a simple immersion procedure in a 0.1 mg/ml solution of FITC in PBS with 10% DMSO (Scheme 1b).



Scheme 1 – Functionalization of O-terminated diamond films

After each step, the samples were tested for the contact angle, which showed expected alterations in the hydrophobicity of the surfaces. X-ray Photoelectron Spectroscopy (XPS) with calculation of sulfur/carbon (S/C) and nitrogen/carbon (N/C) ratios confirmed the presence of both molecules attached onto the surface. We expect to expand this procedure to other recognition units in order to produce highly specific sensors for infectious diseases.

Acknowledgements

We acknowledge University of Aveiro and FCT/MCTES (Fundação para a Ciência e a Tecnologia, Ministério da Ciência, da Tecnologia e do Ensino Superior) for financial support to LAQV-REQUIMTE (Ref. UIDB/50006/2020), and to CICECO—Aveiro Institute of Materials (Refs. UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020) through national founds (PIDDAC) and, where applicable, co-financed by the European Regional Development Fund (FEDER), within the PT2020 Partnership Agreement. The work of Instituto de Telecomunicações was funded by FCT/MCTES through national funds and when applicable co-funded by FEDER–PT2020 partnership and EU funds under the projects UID/EEA/50008/2019 and UIDB/50008/2020-UIDP/50008/2020. The research contract of FF (REF-168-89-ARH/2018) is funded by national funds (OE), through FCT, in the scope of the framework contract foreseen in Nos. 4, 5 and 6 of article 23 of the Decree-Law 57/2016, of 29 August, changed by Law 57/2017, of 19 July. This work is funded by National Funds through the FCT - Fundação para a Ciência e a Tecnologia, I.P., under the scope of the project UIDB/50025/2020-2023

References

1. N. E. Santos, F. Figueira, M. Neto, F. A. Almeida Paz, S.S. Braga, J. C. Mendes, *Appl. Sci.* 2022, **12, 3000**; https://doi.org/10.3390/app12063000

P30

Characterization of functionalized magnetite nanoparticles produced by three methodologies

Gabriela T. A. D. Santos[1, *], Ana C. Estrada[2], C. O. Amorim[3], J. S. Amaral[3], Patrícia S. M. Santos[1], Armando C. Duarte[1]

[1]CESAM & Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal
[2]CICECO & Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193, Aveiro, Portugal
[3]CICECO & Physics Department, University of Aveiro, Campus Universitário de Santiago, 3810-193, Aveiro, Portugal
**gtads@ua.pt*

Magnetic nanoparticles have been studied to remove contaminants from aqueous matrices due to its advantages, such as, tuning size, particle shape, magnetic properties allowing their recovered and reused, high surface-to-volume ratio, and the possibility of being coated or surface functionalized[1]. Magnetite nanoparticles have been also coated with silica (SiO_2) shells since it prevents oxidation and nanoparticles aggregation, as well as provides stability and a versatile surface for subsequent chemical functionalization[2]. In addition, N-(trimethoxysilylpropyl)ethylendiaminetriacetate, trisodium salt (TMS-EDTA) has been used for coating silica shell due to its ability as chelating agent to capture contaminants, such as metals, or to the possibility of further functionalization for contaminants sorption[3,4].

In this work three methodologies were investigated to produce core/shell nanoparticles, comprising magnetite cores coated with amorphous silica functionalized with EDTA (Fe_3O_4/SiO_2-EDTA). Thus, after the synthesis of magnetite nanoparticles two ways were used to obtain Fe_3O_4/SiO_2-EDTA. One methodology consisted of coating the magnetite with silica and subsequent functionalization with EDTA, in a two-step procedure[5]; the other two methodologies comprised of coating and modifying the magnetite nanoparticles with silica and EDTA simultaneously, performing the procedure in one step[6,7]. Different characteristics were observed for Fe_3O_4/SiO_2-EDTA nanoparticles obtained by the three different methodologies, in what concerns to the SiO_2 coating and SiO_2-EDTA shell dimension, colloidal stability, and magnetic properties.

Acknowledgements

Thanks are due to FCT/MCTES for the financial support to CESAM (UIDP/50017/2020+UIDB/50017/2020), through national funds. Gabriela Santos thanks FCT for the doctoral grant SFRH/BD/137755/2018. A.C. Estrada is funded by national funds (OE), through FCT – Fundação para a Ciência e a Tecnologia, I.P., in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19. Patrícia S.M. Santos thanks support by the FCT Scientific Employment Stimulus – Individual 2017 (CEECIND/01835/2017).

References

1 A. H. Lu, E. L. Salabas and F. Schüth, *Angew. Chemie - Int. Ed.*, 2007, **46**, 1222–1244.
2 E. S. D. T. Mendonça, A. C. B. de Faria, S. C. L. Dias, F. F. H. Aragón, J. C. Mantilla, J. A. H. Coaquira and J. A. Dias, *Surfaces and Interfaces*, 2019, **14**, 34–43.
3 Y. Huang and A. A. Keller, *Water Res.*, 2015, **80**, 159–168.
4 T. Gong and Y. Tang, *Water Sci. Technol.*, 2020, **81**, 170–177.
5 D. Dupont, W. Brullot, M. Bloemen, T. Verbiest and K. Binnemans, *ACS Appl. Mater. Interfaces*, 2014, **6**, 4980–4988.
6 D. S. Tavares, A. L. Daniel-Da-Silva, C. B. Lopes, N. J. O. Silva, V. S. Amaral, J. Rocha, E. Pereira and T. Trindade, *J. Mater. Chem. A*, 2013, **1**, 8134–8143.
7 Y. Liu, R. Fu, Y. Sun, X. Zhou, S. A. Baig and X. Xu, *Appl. Surf. Sci.*, 2016, **369**, 267–276.

Biologically active Ag(I) and Au(I) camphorimine complexes

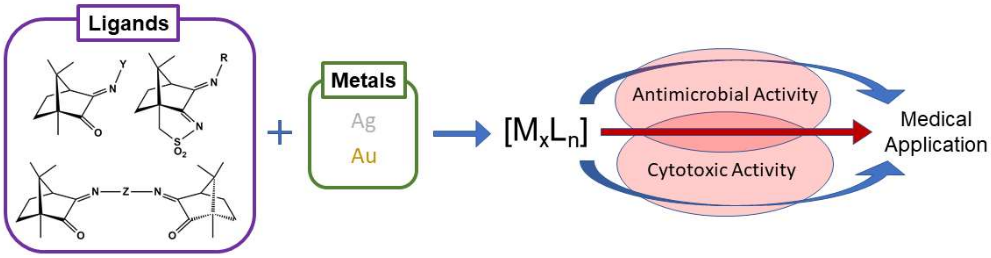
Joana P. Costa, M. Fernanda N. N. Carvalho

CQE Instituto Superior Técnico, Institute of Molecular Sciences, Universidade de Lisboa, Portugal
E-mail: joanavcosta@tecnico.ulisboa.pt

New antimicrobials are urgent and necessary to treat infections resistant to currently used antibiotics and antifungals. In the end of 2021, the World Health Organization (WHO) declared the antibiotics microbial resistance (AMR) as one of the ten global human health threats.[1] According to estimates,[2] in 2050 the worldwide mortality due to AMR may reach 10 million persons *per* year and the related costs ca. 1 trillion dollars. Such numbers clearly show the need for new efficient antimicrobial agents able to treat infections and overcome microorganisms (bacteria or fungi) resistance.

Complexes are potentially efficient alternatives to existing antimicrobials since the specific characteristics of the metal and the ligands may prompt mechanisms of action different from the organic molecules in use. Aiming at the identification of complexes with biological properties, in particular combining antimicrobial and anticancer activity we have synthesized a variety of complexes based on silver ($Ag(NO_3)$, Ag(OAc)) and gold ($KAu(CN)_2$, AuCl) precursors, using camphorimine ligands with distinct electronic and steric properties. Two pathways were followed to assess the biological properties (antimicrobial, anticancer) of the camphorimine complexes. The evaluation of the antibacterial activity was based on the calcularion of the MIC values towards Gram-positive (S. *aureus* Newman) and Gram-negative (B. *contaminans*, E. *coli*, P. *aeruginosa*) bacteria. The antifungal activity was evaluated towards the *Candida* species (C. *albicans* and C. *glabrata*). The anticancer properties were assessed by evaluation of the Inhibition Concentration (IC_{50}) through the MTT assay towards cancer (A2780, A2780cisR, other) and non-tumoral (V79, HEK 293, other) cell lines. Results obtained until now show that the gold complexes have neglectable fungal activity but they have high cytotoxic and antimicrobial activity.[3] The silver complexes, especially those of the type [Ag(OH)L] display very good antimicrobial activity.[4,5]

Aiming at applications in surgical remediation, two selected camphorimine complexes were used to functionalize PCL coating and their ability to prevent the colonization and inhibit microfilm formation by *Candida* strains evaluated.[6]



Scheme 1: Synthesis of different complexes, selection of the ones with best activity for medical application.

Acknowledgements
Financial support by FCT - Fundação para a Ciência e a Tecnologia through project UIDB/0100/2020 and a PhD Grant to Joana Costa (UI/BD/152244/2021).

References

[1] WHO, Antimicrobial resistance, 17th November 2021, https://www.who.int/news-ro]om/fact-sheets/detail/antimicrobial-resistance. Acceded on the 18th February

[2] Dadgostar, P. Antimicrobial Resistance: Implications and Costs. Infection and Drug Resistance 2019, 12, 3903-3910.

[3] Costa, J.P.; Sousa, A.S.; Soeiro, C.; Leitão, J.H.; Galvão, A.M.; Marques F.; Carvalho, M.F.N.N.; Synthesis and Characterization of Camphorimine Au(I) Complexes with a Remarkably High Antibacterial Activity towards B. *contaminans* and P. *aeruginosa*, Antibiotics, 2021, 10, 1272.

[4] Costa, J.P.; Sousa, S.A.; Galvão, A.M.; Mata, J.M.; Leitão, J.H.; Carvalho, M.F.N.N.; Key Parameters on the Antibacterial Activity of Silver Camphor Complexes, Antibiotics, 2021, 10, 135.

[5] Costa, J.P.; Pinheiro, M.J.F.; Sousa, S.A.; Rego, A.M.B.; Marques, F.; Oliveira, M.C.; Leitão, J.H.; Mira, N.P.; Carvalho, M.F.N.N.; Antimicrobial Activity of Silver Camphorimine Complexes against *Candida* Strains, Antibiotics, 2019, 8, 144.

[6] Pinheiro, M.J.F.; Costa, J.P; Marques, F.; Mira, N.P.; Carvalho, M.F.N.N; Alves, M.M; Bioactive Coatings with Ag-Camphorimine Complexes to Prevent Surface Colonization by the Pathogenic Yeast *Candida albicans*, Antibiotics, 2021, 10, 638.

P32

Layer-by-layer assembly of graphene/lanthanopolyoxometalates into luminescent thin films

Maria J. Martins[1,*], Tito Trindade[1], Helena Nogueira[1]

[1] *CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal*
** E-mail: mariacmartins@ua.pt*

The layer-by-layer (LbL) electrostatic assembly is a procedure that consists of alternately exposing a substrate to solutions of oppositely charged chemical species, such as polyelectrolytes. The interactions between the oppositely charged layers are dominated, though not exclusively, by electrostatic attractive forces. Thin films fabrication by LbL methods has a strong potential in a wide range of applications, such as coatings, photonics, and sensors. Due to the important mechanical, thermal, chemical and electronic properties, the integration of graphene-based materials into LbL assemblies overcomes some limitations on the physical and chemical properties. Furthermore, the incorporation of lanthanopolyoxometalates (LnPOMs) will confer photoluminescent properties that can be explored in the development of optical devices. It has been described that LnPOMs containing the Eu^{3+} ion exhibit photoluminescent properties due to excitation paths that involve ligand-to-metal charge-transfer states associated with O-Ln and O-M (M = Mo, W) transitions[1,2].

In this work, a graphene oxide functionalized with an ionic liquid was decorated with LnPOMs to produce a hybrid nanocomposite with luminescent behaviour (rGO-IL-LnPOM). Then, the nanocomposite was attached to a quartz substrate which was previously prepared by a layer-by-layer process, alternating a layer of positively charged polyelectrolyte (poly(allylamine hydrochloride), PAH) and a layer of negatively charged polyelectrolyte (poly(4-styrenesulfonate), PSS) (Figure 1). Due to the presence of negative LnPOM species in the hybrid nanocomposite (rGO-IL-LnPOM), the latter negatively charged species can be attached onto the positive PAH top layer of the quartz substrate. The resulting multilayered structure exhibit photoluminescence behaviour showing that the LnPOMs emission is maintained in the nanohybrid film, with a good potential for application in nanosensors. We have tested these nanohybrid films for the detection of metals ions in aqueous solutions. The nanohybrid film showed a good response for Cr^{3+} in aqueous solution, with selectivity and linearity between 1-10 μM, associated to the luminescence quenching of Cr^{3+}. Our strategy to construct luminescent graphene/lanthanopolyoxometalate nanohybrid films is expected to provide a new methodology to develop economical, fast and sensitive nanosensors for environmental pollutants monitoring.

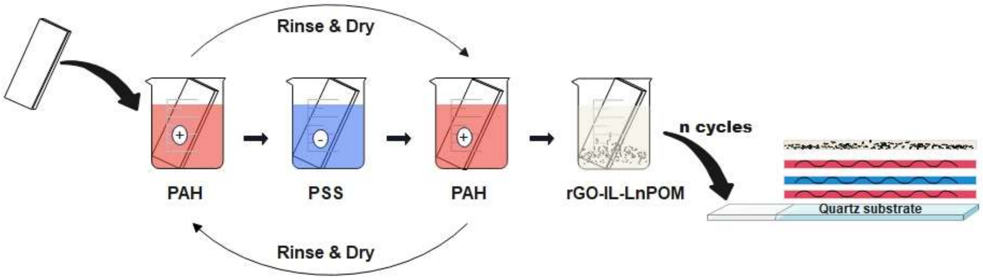


Figure 1: Schematic illustration of LbL electrostatic assembly of luminescent graphene/lanthanopolyoxometalates.

Acknowledgements
This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC). Maria João Martins thanks Fundação para a Ciência e a Tecnologia for the PhD Grant COVID/BD/151933/2021.

References
1. Fateixa, S., Carvalho, R.S., Daniel-da-Silva, A.L., Nogueira, H.I.S. and Trindade, T., *Eur. J. Inorg. Chem.*, 2017, DOI: 10.1002/ejic.201700888.
2. Nogueira, H. I. S., Bornes, C., Fateixa, S. and Trindade, T., *Eur. J. Inorg. Chem.*, 2019, DOI: 10.1002/ejic.201801157.

Functional/Hybrid Carbon-based Nanomaterials as Building Blocks for Innovative Multi-Tasking Energy Storage Textiles

Clara Pereira[1,*], Rui S. Costa[1,2], Joana S. Teixeira[1,2], Ana L. Pires[2], André M. Pereira[2]

[1] *REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal*

[2] *IFIMUP – Instituto de Física dos Materiais Avançados, Nanotecnologia e Fotónica da Universidade do Porto, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal*

** E-mail: clara.pereira@fc.up.pt*

Over the years, the design of high-performance functional and smart textiles with innovative properties has been a major quest, boosted by the market trends and consumer requirements.[1] The growth of the markets of IoT and wearable electronics led to a demand for advanced energy storage technologies integrated on clothing, with a myriad of applications ranging from Healthcare, Sports and Protection to Fashion and Defense. Supercapacitors are a clean and safe energy storage solution to produce wearable energy storage clothing, owing to their high power density, fast charging, long cycle life and robustness.[2]

Nanotechnology fostered new opportunities in the Textile and Clothing industry, to endow new functionalities on fabrics, while preserving their intrinsic aesthetic properties, comfort and lightness.[1] The combination of carbon-based nanomaterials with redox-active transition metal oxides is a promising route for the development of high-performance textile supercapacitors with synergistically-enhanced energy density and power density by enabling the occurrence of both non-faradaic and pseudocapacitive charge storage mechanisms.[1,3,4]

In this work, we will provide an overview of the progress on the development of innovative smart textile supercapacitors with multifunctional properties (Figure 1):[1,3,4] (i) energy storage/fluorescent textiles; (ii) magnetically-responsive energy storage textiles and (iii) an innovative all-in-one self-powered energy harvesting & storage technology. The remarkable role of functional carbon-based nanomaterials and hybrid carbon/metal oxides as building blocks for the development of such smart systems will be highlighted. The journey from the concept and design of these engineered nanomaterials through eco-sustainable and scalable routes, their incorporation on textile substrates and assembly of multi-tasking systems will be presented. Finally, the assessment of the electrochemical performance and feasibility of the developed technologies to power electronic devices will be demonstrated.

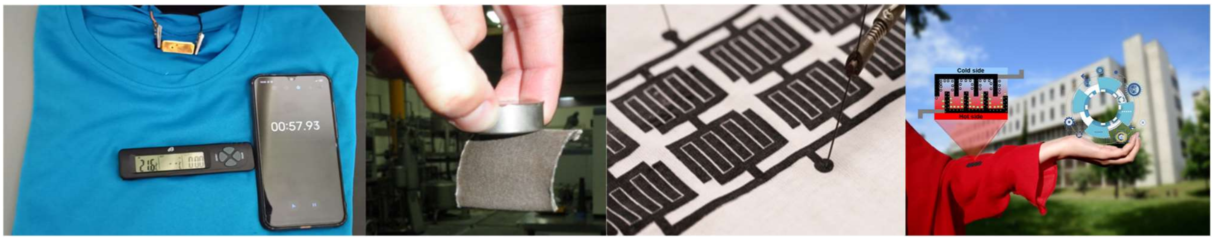


Figure 1: Multifunctional energy storage textiles.

Acknowledgements

Work funded by Portuguese funds through Fundação para a Ciência e a Tecnologia (FCT)/MCTES in the framework of the projects PTDC/CTM-TEX/4126/2021, UIDB/50006/2020 and UIDP/50006/2020. Work also supported by the project PTDC/CTM-TEX/31271/2017 with funding from FEDER through COMPETE 2020 (POCI) and from Portuguese funds through FCT/MCTES under Program PT2020. JST thanks FCT for the PhD scholarship with ref. SFRH/BD/145513/2019.

References

[1] A. K. Yetisen, H. Qu, A. Manbachi, H. Butt, M. R. Dokmeci, J. P. Hinestroza, M. Skorobogatiy, A. Khademhossein and S. H. Yun, *ACS Nano*, 2016, **10**, 3042.

[2] J. S. Teixeira, R. S. Costa, A. L. Pires, A. M. Pereira and C. Pereira, *Dalton Trans*., 2021, **50**, 9983.

[3] J. S. Teixeira, A. M. Pereira and C. Pereira, *Chem. Eng. J.*, 2021, **426**, 131274.

[4] A. L. Pires, R. S. Costa, C. Pereira and A. M. Pereira, *ACS Appl. Electron. Mater.*, 2021, **3**, 696.

P34

Taking inspiration from molybdoenzymes: Electron transfer between oxo-molybdenum(IV) dithiolene and iron porphyrin

N. Paul[1,2*], R. Sarkar[2], S. Sarkar[2] , J.J.G. Moura[1]

[1] LAQV, REQUIMTE, NOVA School of Science and Technology | FCT NOVA, Campus de Caparica, Portugal
[2] Department of Chemistry, Indian Institute of Engineering Science and Technology Shibpur. West Bengal, Kolkata, India
** E-mail: n.paul@fct.unl.pt*

Molybdoenzymes play numerous catalytic roles in biological systems. The molybdoenzyme sulfite oxidase (SO) transforms the toxic sulfite to sulfate using water as the oxygen atom source and cytochrome ***c*** as the physiological oxidizing partner.**[1,2]** In animals, each subunit of this dimeric enzyme holds a Mo-cofactor (Moco) linked by a flexible dangling peptide chain to a *b*-type heme (Fig. 1a).**[3]** In the reductive half cycle, the active site [$Mo^{VI}O_2$] center oxidizes sulfite to sulfate, yielding a reduced [$Mo^{IV}O$] center. This is then oxidized through intramolecular electron transfer to the heme *b*, by two consecutive intramolecular proton coupled one-electron transfer steps, to regenerate the resting state [$Mo^{VI}O_2$].[2,4] In this study, to mimic the intramolecular electron transfer in native SO, an oxo-molybdenum (dithiolene) complex covalently linked to iron porphyrin (Fig.1 b) was synthesized to exhibit metal centered electron transfer between the two model prosthetic groups. This bimetallic model complex, D1, (characterized by UV-Vis, IR, and ESI Mass spectroscopy) responds to such electron transfer. The D1 EPR signal clearly indicates such electron transfer with the intermediate generation of Mo(V) signal (Fig. 1c).

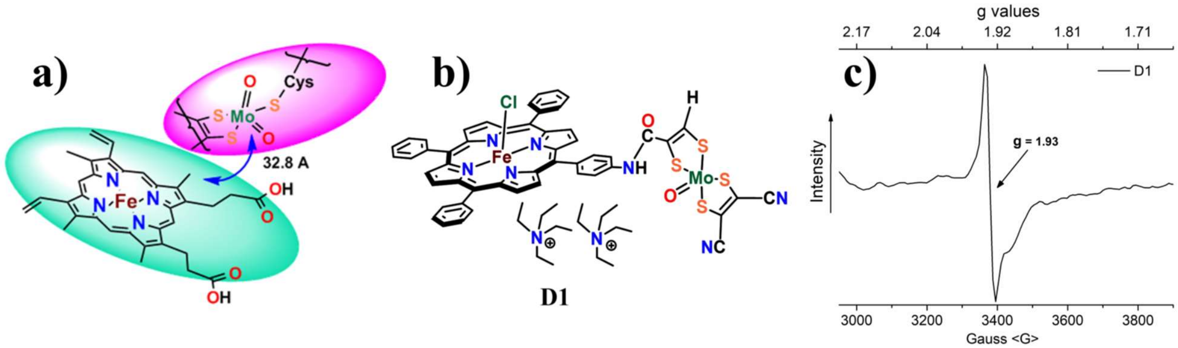


Figure 1: a) Schematic representation of SO Moco and heme centers; **b)** Chemical structure of Fe···Mo bimetallic model complex D1; **c)** X-band EPR spectra of D1 at 120K in polycrystalline KBr matrix showing the Mo(V) signal.

Acknowledgements
This work was supported by CSIR New Delhi, DST India and by the PTDC/BTA-BTA/0935/2020 project and also by the Associate Laboratory for Green Chemistry - LAQV (UIDB/50006/2020 and UIDP/50006/2020), which are financed by national funds from Fundacão para a Ciência e a Tecnologia, MCTES (FCT/MCTES).

References

1. C. Kisker, H. Schindelin and D. C. Rees, Annu. Rev. Biochem, 1997, 66, 233-267.
2. (a) R. Hille, Chem. Rev., 1996, 96, 2757-2816; (b) R. Hille, T. Nishino and F. Bittner, Coord. Chem. Rev, 2011, 255, 1179-1205; (c) L. B. Maia, I. Moura and J. J. G. Moura, in Molybdenum and Tungsten Enzymes: Biochemistry, The Royal Society of Chemistry, 2017, pp. 1-80.
3. C. Kisker, H. Schindelin, A. Pacheco, W. A. Wehbi, R. M. Garrett, K. V. Rajagopalan, J. H. Enemark and D. C. Rees, Cell, 1997, 91, 973-983.
4. B. Pakhira, R. Sarkar and S. Sarkar, in Molybdenum and Tungsten Enzymes: Bioinorganic Chemistry, The Royal Society of Chemistry, 2017, pp. 68-93.

P35

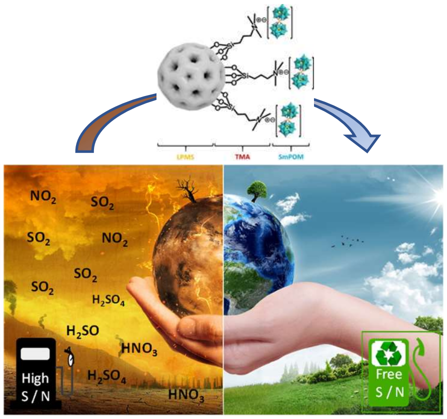
Sustainable Desulfurization of Diesel using Efficient Heterogeneous Catalyst based in Polyoxomolybdate Supported in Large-Pore Silica Spheres

F. Mirante,[a] S. Gago,[b] R. Valença,[c] J. C. Ribeiro,[c] B. de Castro,[a] C. M. Granadeiro,[a] and S. S. Balula [a]

[a]LAQV / REQUIMTE, Department of Chemistry, Faculty of Sciences - University of Porto,
Rua do Campo Alegre, 4169-007 Porto, Portugal
[b]LAQV-REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa,
2829-516, Monte da Caparica, Portugal
[c]Galp, Refinaria de Matosinhos, 4452-852 Leça da Palmeira, Matosinhos, Portugal
** E-mail: fatima.mirante@fc.up.pt*

Polyoxometalates (POMs) belong to a class of metal–oxygen cluster anions that have been applied in several fields, one of the most important being the acid and oxidative catalysis. [1] However, in order to prepare stable heterogeneous catalysts, it is convenient to immobilize POMs in solid supports that allow their recovery and reuse. Mesoporous silica nanoparticles possess ordered porosity, high surface area-to-volume ratio, controllable pore size and can be easily functionalized. These properties may even improve the performance of materials in terms of energy and power density, lifetime and stability, make them ideal for use as supports for adsorption, catalysis, chemical separations and fuel cells.[2]

A novel composite has been synthetized and characterized through the immobilization of the Keggin sandwich-type $[Sm(PMo_{11}O_{39})_2]^{11-}$ anion (SmPOM) on large-pore silica spheres (LPMS), previously functionalized with trimethylammonium groups (TMA) (Scheme 1).[3] The material SmPOM@TMA-LPMS has been evaluated as heterogeneous catalyst in a biphasic desulfurization system using acetonitrile or the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6) as extraction solvents and H_2O_2 as oxidant. The optimized extractive and catalytic oxidative desulfurization system (ECODS) with [BMIM]PF_6 was able to reach complete sulfur removal from a model diesel containing 2100 ppm S in just 60 min.[1] The desulfurization performance of the heterogeneous catalyst was compared with the corresponding homogeneous SmPOM.[1] The reusability and stability of the composite were also investigated for consecutive ECODS cycles without loss of desulfurization efficiency, turning the process more sustainable and cost-effective. The remarkable results with simulated diesel have motivated the application of the catalyst in the desulfurization of untreated real diesel.



Scheme 1:
The SmPOM@TMA-LPMS composite used in ECODS.

Acknowledgements
The work received financial support from Portuguese national funds (FCT/MCTES) through the strategic project UIDB/50006/2020 (for LAQV-REQUIMTE); it was also funded by the European Union (FEDER funds through COMPETE POCI-01-0145-FEDER-031983). LCS and SSB thank FCT/MCTES for funding the Individual Call to Scientific Employment Stimulus (CEECIND/00793/2018 and EECIND/03877/2018, respectively). C.M.G acknowledges FCT/MCTES for funding through DL 57/2016 program contract – Norma transitória.

References
1. S.-S. Wang, *et al.*, Chem. Rev. **2015**, 115, 4893-4962
2. F. Mirante, *et al.*, Microporous Mesoporous Mater. **2019**, 275, 163-171.
3. F. Mirante, *et al.*, Fuel **2020**, 259, 116213.

P36

Chartergellus-CP1 peptide from *Chartergellus communis* wasp venom with activity against breast cancer cell lines

Susana Soares[1*], Kamila Soares Lopes[2], Márcia Mortari[2], Helena Oliveira[1] and Verónica Bastos[1]

[1] CESAM & Department of Biology, University of Aveiro, 3810-193 Aveiro, Portugal

[2] Department of Physiological Sciences, Institute of Biological Sciences, University of Brasília, Brasília, Brazil

* *e-mail: susanasoares98@ua.pt*

Abstract

Cancer is the second leading cause of mortality and morbidity worldwide and one of the most common diseases in society. Breast cancer represents the most incident cancer in all words by 2020, with about 30% of breast cancer cases resulting in patient death[1]. Surgery, chemotherapy, radiation therapy, and hormone therapy remain the main treatments for this type of cancer[2]. Cancer subtypes directly influence the treatment to be applied [3]. Triple-negative breast cancer has the worst prognosis of all breast cancers and has the lowest survival rate, once this cancer does not respond to anti-hormonal therapy [4,5]. However, increasing resistance to anti-cancer drugs through poor response for some types of breast cancer to treatments highlights the need to develop new therapeutic agents to fight the disease[6]. In this context, venoms of arthropods such as scorpions, bees, and wasps, in the last decades, have shown a high potential against cancer [7]. Wasp venom is one of the most variable venoms and consists of complex mixtures of biologically active compounds, mostly peptides, proteins, and other small molecular mass compounds that may have antimicrobial, anti-inflammatory, and/or antitumor activity [8].

In this study, we evaluated the anti-tumor potential of the Chartergellus-CP1 peptide isolated from the wasp venom of *Chartergellus communis* in human breast cancer cell lines MCF-7 (HR+) and MDA-MB-231 (triple-negative). Cell viability, morphology and reactive oxygen species (ROS) production were assessed for both cell lines after exposure to Chartergellus-CP1 during 24 and 48 h.

The results showed that Chartergellus-CP1 peptide proved to be highly cytotoxic against both cell lines, promoting a high dose-dependent antitumor action. Chartergellus-CP1 leaded to a high generation of ROS (this was more evident in the MCF-7 cell line). This work demonstrates, for the first time, the cytotoxic effects of Chatergellus-CP1 on human breast cancer cell lines showing the potential of Chatergellus-CP1 as an antitumor peptide.

Acknowledgments

The authors acknowledge the financial support to CESAM by FCT/MCTES (UIDP/50017/2020 &UIDB/50017/2020 & LA/P/0094/2020), through national funds, and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. The Portuguese Foundation for Science and Technology (FCT) is also acknowledged for the research contract of V. Bastos (CDL-CTTRI-161-ARH/2018) funded by the FCT project (POCI-01-0145-FEDER-031794) and H. Oliveira for the research contract under the Scientific Employment Stimulus (CEECIND/04050/2017). The authors would like to express their sincere gratitude to the following Brazilian funding agencies: FAP-DF (project number 00193-00001343/2019-53 e 00193-00000724/2021-30) and CNPq (project number 306547/2020-1 and 403543/2021-5) for their financial support.

References

2 Cancer Today, https://gco.iarc.fr/today/home, (accessed Feb 8, 2021).
3 T. A. Moo, R. Sanford, C. Dang and M. Morrow, *PET Clinics*, 2018, 13, 339–354.
4 C. W. S. Tong, M. Wu, W. C. S. Cho and K. K. W. To, *Frontiers in Oncology*, 2018, 8, 227.
5 A. Bardia, I. A. Mayer, J. R. Diamond, R. L. Moroose, S. J. Isakoff, A. N. Starodub, N. C. Shah, J. O'shaughnessy, K. Kalinsky, M. Guarino, V. Abramson, D. Juric, S. M. Tolaney, J. Berlin, W. A. Messersmith, A. J. Ocean, W. Awegener, P. Maliakal, R. M. Sharkey, S. v. Govindan, D. M. Goldenberg and L. T. Vahdat, *Journal of Clinical Oncology*, 2017, **35**, 2141–2148.
6 G. Stockmans, K. Deraedt, H. Wildiers, P. Moerman and R. Paridaens, *Current Opinion in Oncology*, 2008, 20, 614–620.
7 K. O. Alfarouk, C. M. Stock, S. Taylor, M. Walsh, A. K. Muddathir, D. Verduzco, A. H. H. Bashir, O. Y. Mohammed, G. O. Elhassan, S. Harguindey, S. J. Reshkin, M. E. Ibrahim and C. Rauch, *Cancer Cell International*, 2015, **15**, 71.
8 M. W. Pennington, A. Czerwinski and R. S. Norton, *Bioorganic and Medicinal Chemistry*, 2018, **26**, 2738–2758

AUTHOR
INDEX

AUTHORS