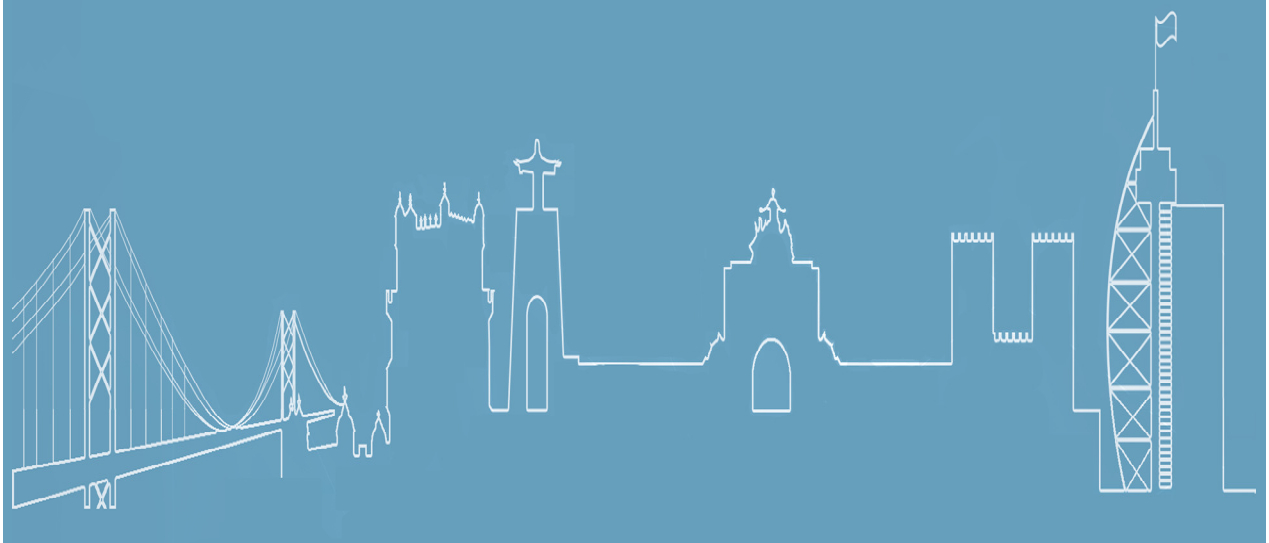
2024 IBiCC



Inorganic & Bioinorganic Chemistry Conference

Lisboa | May 16 - 18, 2024

Welcome

The Division of Inorganic and Bioinorganic Chemistry of the Portuguese Chemical Society and the Associação para a Inovação e Desenvolvimento da FCT (NOVA.ID.FCT), NOVA School of Science and Technology (NOVA FCT), are pleased and honoured to welcome you at the 14th edition of the Inorganic & Bioinorganic Chemistry Conference, held May 16 to 18, 2024, at the Retorate of NOVA University of Lisbon, Portugal.

The 2024IBiCC aims to provide a forum to discuss all Inorganic and Bioinorganic Chemistry topics, particularly those on the frontier with Catalysis, Energy, Materials, Nanotechnology, Biology and Medicine. The challenges humankind currently faces require joint discussions and the 2024IBiCC will foster collaboration and scientific exchange in a stimulating, scientifically rewarding and friendly environment. Young researchers (students and young PhDs) are strongly encouraged to present their work and interact with renowned established researchers.

On behalf of the Organising Committee, I welcome you to this
Inorganic & Bioinorganic family reunion,

Luisa Maia
Chair of the #2024IBiCC
President of the SPQ Division of Inorganic and Bioinorganic Chemistry

Acknowledgments and Sponsors

Institutional

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Program at a Glance

	Thursday, May 16	Friday, May 17	Saturday, May 18	
09:00 - 09:15		KN 4 D'Autréaux	KN 9 Rangel	09:00 - 09:15
09:15 - 09:30		IL 1 Silveira	IL 9 Realista	09:15 - 09:30
09:30 - 09:45		IL 2 Morais	IL 10 Rosa	09:30 - 09:45
09:45 - 10:00		IL 3 Mota	IL 11 Balula	09:45 - 10:00
10:00 - 10:15		IL 4 Conzuelo	IL 12 Figueira	10:00 - 10:15
10:15 - 10:30		Coffee Break	Coffee Break	10:15 - 10:30
10:30 - 10:45		IL 5 Côrte-Real	IL 13 Maria	10:30 - 10:45
10:45 - 11:00		KN 5 Louro	IL 14 Pinto	10:45 - 11:00
11:00 - 11:15		OC 1 - 3 Romão, Engrola, Bacchella	IL 15 Gonçalves	11:00 - 11:15
11:15 - 11:30		KN 6 Walburger	OC 7 - 9 Pereira, Monteiro, Šivickytė	11:15 - 11:30
11:30 - 11:45			KN 10 Branco	11:30 - 11:45
11:45 - 12:00				11:45 - 12:00
12:00 - 12:15	Registration	***Group Photo*** Lunch	Lunch	12:00 - 12:15
12:15 - 12:30				12:15 - 12:30
12:30 - 12:45				12:30 - 12:45
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13:15 - 13:30				13:15 - 13:30
13:30 - 13:45				13:30 - 13:45
13:45 - 14:00		Posters Session	Posters Session	13:45 - 14:00
14:00 - 14:15	Opening Session			14:00 - 14:15
14:15 - 14:30			SPQ Division Meeting	14:15 - 14:30
14:30 - 14:45	PL 1 Garcia Martinez	OC 4 - 6 Matias, Kirin, Garcia	OC 10 - 12 Batista, Santos, Fernandes	14:30 - 14:45
14:45 - 15:00		IL 6 Mahmudov	IL 16 Duarte	14:45 - 15:00
15:00 - 15:15		IL 7 Geraldes	IL 17 Pauleta	15:00 - 15:15
15:15 - 15:30	KN 1 Kulak	KN 7 Lodeiro	KN 11 Cavazza	15:30 - 15:45
15:30 - 15:45				15:45 - 16:00
15:45 - 16:00	KN 2 Gallo	Coffee Break	Coffee Break	16:00 - 16:15
16:00 - 16:15				16:15 - 16:30
16:15 - 16:30	KN 3 Murgida	IL 8 Rocha	IL 18 Aureliano	16:30 - 16:45
16:30 - 16:45		KN 8 Kirillov	KN 12 Salgueiro	16:45 - 17:00
16:45 - 17:00	Welcome			17:00 - 17:15
17:00 - 17:15		Award A. Romão Dias Pereira Moura	PL 2 Hausinger	17:15 - 17:30
17:15 - 17:30	Posters Session			17:30 - 17:45
17:30 - 17:45				17:45 18:00
17:45 18:00				18:00 - 18:15
18:00 - 18:15			Closing Session Poster Prizes	18:15 - 18:30
18:15 - 18:30				
20:30 22:30		Conference Dinner		20:30 22:30

Detailed Program

Time	Thursday, May 16	
12h00 - 14h00	**Registration**	
14h00 - 14h30	**Opening Session** José Júlio Alferes (Dean of NOVA FCT, Lisbon, Portugal) Ana Isabel Aguiar-Ricardo (Head of the Chemistry Department of NOVA FCT, Lisbon, Portugal) Jorge Parola (Portuguese Chemical Society, Portugal) Luisa Maia (NOVA FCT, Lisbon, Portugal)	
14h30 - 16h45	Chair: José Moura (NOVA FCT, Lisbon, Portugal)	
14h30 - 15h15	PL 1 - Javier Garcia Martinez (Universidad de Alicante, Spain) Catalyzing the green revolution: unlocking previously inaccessible processes	
15h15 - 15h45	KN 1 - Nora Kulak (Faculty of Science, Universität Potsdam, Germany) Copper instead of platinum: metal-containing compounds for applications from medicine to catalysis	
15h45 - 16h15	KN 2 - Emma Gallo (University of Milan, Italy) Non-reductive CO_2 valorization promoted by eco-friendly porphyrin species	
16h15 - 16h45	KN 3 - Daniel Murgida (Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Argentina) Improving the performance of heme peroxidases and peroxigenases by $O_2^{\bullet-}$ / $HO^{\bullet}$ activation	
16h45 - 18h30	Welcome Reception	Posters Session

Time	**Friday, May 17**		
09h00 - 10h30	Chair: Teresa Santos-Silva (NOVA FCT, Lisbon, Portugal)		
09h00 - 09h30	KN 4 - Benoit D'Autréaux (Université Paris-Saclay, CEA, CNRS, Paris, France) Biosynthesis of [2Fe-2S] clusters via formation and fusion of [1Fe-1S] precursors by the ISC machinery		
09h30 - 09h45	IL 1 - Célia Silveira (NOVA ITQB, Lisbon, Portugal) Dye-decolorizing peroxidases: insights into their role as immobilized biocatalysts		
9h45 - 10h00	IL 2 - Tânia Morais (Faculty of Sciences, University of Lisbon, Portugal) Smart metallodrugs for precision therapy of FGFR breast cancer		
10h00 - 10h15	IL 3 - Cristiano Mota (NOVA FCT, Lisbon, Portugal) Oxidative damage of Mo/W formate dehydrogenases		
10h15 - 10h30	IL 4 - Felipe Conzuelo (NOVA ITQB, Lisbon, Portugal) Electrochemical characterizations of new multicopper oxidases		
10h30 - 11h00	Coffee Break		
11h00 - 12h45	Chair: Leonor Morgado (NOVA FCT, Lisbon, Portugal)		
11h00 - 11h15	IL 5 - Leonor Côrte-Real (IST, ULisbon, Portugal) The anticancer potential of 8-hydroxyquinoline schiff base metal complexes containing N-heterocycles		
11h15 - 11h45	*Talk sponsored by Dias de Sousa* KN 5 - Ricardo Louro (NOVA ITQB, Lisbon, Portugal) Known unknowns, unknown unknowns, and unknown knowns: a brief report from the survey of the Desulfuromonadia "cytochromome"		
11h45 - 11h55	OC 1 - Célia Romão (NOVA ITQB, Lisbon, Portugal) Unveiling metal distribution from bacterial nano-compartments after stress exposure		
11h55 - 12h05	OC 2 - Filipa Engrola (NOVA FCT, Lisbon, Portugal) Molybdenum cofactor adducts unveiling arsenite oxidase catalytic mechanism		
12h05 - 12h15	OC 3 - Chiara Bacchella (Università di Pavia, Italy) How cysteine directs metal-mediated TAU toxicity		
12h15 - 12h45	KN 6 - Anne Walburger (CNRS, Aix Marseille Université, France) Draw me an oxidoreductase that reacts with menaquinones: the case of the formate dehydrogenase force from *Bacillus subtilis*		
12h45 - 14h30	Group Photo	Lunch	Posters Session
14h30 - 16h00	Chair: Luis Branco (NOVA FCT, Lisbon, Portugal)		
14h30 - 14h40	OC 4 - Inês Matias (IST, ULisbon, Portugal) CO_2-driven *N*-formylation/-methylation of amines using *C*-scorpionate metal complexes		
14h40 - 14h50	OC 5 - Srecko Kirin (Ruđer Bošković Institute, Zagreb, Croatia) Synthesis and characterization of transition metal complexes with chiral monodenate oxazoline ligands		
14h50 - 15h00	OC 6 - Beatriz Garcia (NOVA ITQB, Lisbon, Portugal) Molybdenum catalyzed acceptorless dehydrogenation of alcohols for the synthesis of quinolines		
15h00 - 15h15	IL 6 - Kamran T. Mahmudov (IST, ULisbon, Portugal & Baku State University, Azerbaijan) Modulating the primary and secondary coordination spheres of metal ions		
15h15 - 15h30	IL 7 - Carlos Geraldes (Faculty of Science and Technology, University of Coimbra, Portugal) Paramagnetic complexes as sensors for biomedical MRS and MRI		
15h30 - 16h00	KN 7 - Carlos Lodeiro (NOVA FCT, Lisbon, Portugal) Metallic nanoparticles: from metal complexes to anisotropic nanostructures and materials		
16h00 - 16h30	Coffee Break		
16h30 - 17h15	Chair: Carla Nunes (Faculty of Sciences, University of Lisbon, Portugal)		
16h30 - 16h45	IL 8 - João Rocha (Aveiro Institute of Materials - CICECO, Portugal) Advances in photoresponsive ferroelectrics: designing hybrid and metal-nitrosyl crystals		
16h45 - 17h15	KN 8 - Alexander Kirillov (IST, ULisbon, Portugal) Antimicrobial coordination polymers: from self-assembly to biomaterials		
17h15 - 18h15	Chair: Luisa Maia (NOVA FCT, Lisbon, Portugal) Jorge Parola (NOVA FCT, Lisbon, Portugal)		
17h15 - 18h15	Award Alberto Romão Dias Inês Cardoso Pereira (NOVA ITQB, Lisbon, Portugal) From Chemistry to Biology, and back Isabel Moura (NOVA FCT, Lisbon, Portugal) A Bioinorganic tour to Denitrification		
20h30 - 22h30	Conference Dinner		

Time	**Saturday, May 18**		
09h00 - 10h30	Chair: Clara Gomes (NOVA FCT, Lisbon, Portugal)		
09h00 - 09h30	*Talk sponsored by Dias de Sousa* KN 9 - Maria C. Rangel (ICBAS, University of Porto, Portugal) Iron is master of them all		
09h30 - 09h45	IL 9 - Sara Realista (Faculty of Sciences, University of Lisbon, Portugal) Electrosynthesis of metal-organic framework films		
9h45 - 10h00	IL 10 - Vitor Rosa (NOVA FCT, Lisbon, Portugal) Metal coinage heteroleptic complexes: structure and reactivity		
10h00 - 10h15	IL 11 - Salete Balula (Faculty of Sciences, University of Porto, Portugal) Clever strategies to broaden polyoxometalates functionalities: from molecules to composites		
10h15 - 10h30	IL 12 - Flávio Figueira (Aveiro Institute of Materials - CICECO, Portugal) Metal-organic frameworks for anion detection		
10h30 - 11h00	Coffee Break		
11h00 - 12h45	Chair: Isabel Correia (IST, ULisbon, Portugal)		
11h00 - 11h15	IL 13 - Leonor Maria (IST, ULisbon, Portugal) Multi-electron transfer reactions of uranium bis(aryloxide) cyclam complexes		
11h15 - 11h30	IL 14 - Sara Pinto (University of Coimbra, Portugal) Manganese(II/III)-water soluble fluorinated tetrapyrrolic macrocycles as potencial redox MRI probes		
11h30 - 11h45	IL 15 - Nuno Gonçalves (Aveiro Institute of Materials - CICECO, Portugal) 3D-printed ceramic-like residue-containing materials for water remediation		
11h45 - 11h55	OC 7 - Clara Pereira (Faculty of Sciences, University of Porto, Portugal) Hybridization of MWCNTS and nano ferrites for high-performance electromagnetic shielding textiles		
11h55 - 12h05	OC 8 - Rodrigo Monteiro (Aveiro Institute of Materials - CICECO, Portugal) Effect of inclusion of $CpFe(Co)_2L$ complexes in cucurbit[7]uril on their CO-release profiles		
12h05 - 12h15	OC 9 - Ona Šivickytė (Faculty of Sciences, University of Lisbon, Portugal) Photocatalytic CO_2 reduction: mechanistic DFT study		
12h15 - 12h45	KN 10 - Luis Branco (NOVA FCT, Lisbon, Portugal) Development of magnetic and luminescent ionic systems as MRI contrast agents		
12h45 - 14h30	Lunch	Posters Session	SPQ Division Meet.
14h30 - 16h00	Chair: Vânia André (IST, ULisbon, Portugal)		
14h30 - 14h40	OC 10 - Alzir Batista (Federal University of São Carlos, SP, Brazil) On the activity of Ru(II)/natural products complexes against cancer cells		
14h40 - 14h50	OC 11 - Ariana Santos (Aveiro Institute of Materials - CICECO, Portugal) Development of a novel coordination polymer comprising Cu(II) and chrysin with anticancer potential		
14h50 - 15h00	OC 12 - Tomás Fernandes (NOVA FCT, Lisbon, Portugal) Unraveling a class of stretchable cytochromes: functional mechanisms of PgcA from *Geobacter sulfurreducens*		
15h00 - 15h15	IL 16 - Américo Duarte (NOVA ITQB, Lisbon, Portugal) Elucidating electron transfer chains in the electroactive *Geobacter sulfurreducens*		
15h15 - 15h30	IL 17 - Sofia Pauleta (NOVA FCT, Lisbon, Portugal) Bacterial peroxidases from pathogenic bacteria		
15h30 - 16h00	KN 11 - Christine Cavazza (Laboratoire Chimie et Biologie des Métaux, Grenoble, France) Carbon monoxide dehydrogenase: an interesting electrocatalyst for reversible CO_2/CO interconversion		
16h00 - 16h30	Coffee Break		
16h30 - 17h15	Chair: Célia Romão (NOVA ITQB, Lisbon, Portugal)		
16h30 - 16h45	IL 18 - Manuel Aureliano (Faculty of Sciences and Technology University of Algarve, Faro, Portugal) P_5W_{30} presents agonist-like properties on purinergic receptors		
16h45 - 17h15	*Talk sponsored by Dias de Sousa* KN 12 - Carlos Salgueiro (NOVA FCT, Lisbon, Portugal) What happens when Biophysics and Microbiology/Genetics meet?		
17h15 - 18h30	Chair: Isabel Moura (NOVA FCT, Lisbon, Portugal)		
17h15 - 18h00	*Talk sponsored by The American Corners Portugal* PL 2 - Robert P. Hausinger (Michigan State University, USA) Biosynthesis and functions of the nickel-pincer nucleotide (NPN) cofactor		
18h00 - 18h30	**Poster Prizes & Closing Session** Luisa Maia (NOVA FCT, Lisbon, Portugal)		

Posters List

Only the presenter name is indicated.

P01 - Vusala Aliyeva (IST, ULisbon, Portugal)
Synthesis of cyclic carbonates from CO_2 and epoxides using transition metal complex catalysts

P02 - Pedro Alvim (Faculty of Sciences, University of Lisbon, Portugal)
The role of anion symmetry in the magnetic switching of iron(III) complexes

P03 - André Amador (NOVA FCT, Lisbon, Portugal)
Formate and nitrate: how promiscuous is formate dehydrogenase?

P04 - Vânia André (IST, ULisbon, Portugal)
Silver-antibiotics synergy: unveiling the power of coordination frameworks for enhanced activity

P05 - Jorge Antunes (NOVA FCT, Lisbon, Portugal)
Deciphering the role of cytochrome $C_{BC}A$ in *geobacter* extracellular electron transfer pathways

P06 - Nuno Bandeira (Faculty of Sciences, University of Lisbon, Portugal)
Oxygen activation through a biomimetic tungsten(IV) complex

P07 - Catarina Barbosa (NOVA ITQB, Lisbon, Portugal)
Miniaturized DYP peroxidase-based biosensor for H_2O_2 detection

P08 - Marcos Bento (Faculty of Sciences, University of Lisbon, Portugal)
CO_2 photoreduction studies with Fe(II) complexes

P09 - Agnese Bertinelli (NOVA FCT, Lisbon, Portugal)
CO_2 reduction by formate dehydrogenase: kinetic characterisation

P10 - Isabel Calhau (Aveiro Institute of Materials - CICECO, Portugal)
Antibacterial activity and CO release studies of [(η3-Allyl)(CO)2(X)(pyrazolylpyridine)] complexes

P11 - Silvia de Caro (IUSS Pavia, Italy)
Synthetic models of nitrated neuromelanin: structural characterization and reactivity studies

P12 - Nuno Conceição (IST, ULisbon, Portugal)
Catalytic and anticancer activity of gold(I) complexes bearing PTA and derived ligands

P13 - Gilvan Correia (IST, ULisbon, Portugal)
Copper(II) coordination polymers driven by 3,4-pyridinedicarboxylic acid: synthesis, crystal structures, and catalytic oxidation of α-pinene

P14 - Henrique Costa (Faculty of Sciences, University of Lisbon, Portugal)

Enhancing photocatalytic performance of titanate nanowires through modification with carbon dots

P15 - Frederico Duarte (NOVA FCT, Lisbon, Portugal)

Sensing copper(II) and mercury(II) ions by a solvent modulated emission sulfur bridged dansyl dyes as molecular probes

P16 - Sandra Fernández-Fariña (Universidade de Santiago de Compostela, Spain)

Advances in the study of metallohelicates via cluster helicates with biological properties

P17 - Ana C. Fernandes (IST, ULisbon, Portugal)

Reductive depolymerization of plastic waste catalyzed by earth-abundant metal catalysts

P18 - Bárbara Leite Ferreira (Aveiro Institute of Materials - CICECO, Portugal)

Enhanced antidiabetic effect of chrysin by complexation with Cu(II) and Co(II) ions

P19 - Mariana Ferreira (Faculty of Sciences, University of Lisbon, Portugal)

CO_2 conversion with supramolecular structures

P20 - Filipe Figueiredo (IST, ULisbon, Portugal)

Recovering of the rare earth elements Y and Eu from phosphors

P21 - Bruno Fonseca (NOVA ITQB, Lisbon, Portugal)

Deciphering azo dye binding: Probing exoelectrogenic cytochrome-mediated bioremediation pathways

P22 - Vusala Aliyeva (IST, ULisbon, Portugal)

Chalcogen bonding in the decoration of [1,2,5]selenadiazole dyes

P23 - Adriana Gomes (University of Aveiro, Portugal)

Unravelling the biological potential of two novel flavonoid-based Zn(II) complexes

P24 - Clara Gomes (NOVA FCT, Lisbon, Portugal)

Unveiling the potential of MOFs: from crystalline sponges to sustainable hydrogen production

P25 - Ana C. Henriques (Faculty of Sciences, University of Lisbon, Portugal)

Catalytic oxidative desulfurization of fuels: a green way to stop air pollution

P26 - Luis Lima (NOVA ITQB, Lisbon, Portugal)

New copper(II)-binding azoles as potential antifungals

P27 - Frederico Lourenço (NOVA ITQB, Lisbon, Portugal)

Structural relevance of the interaction between *E.coli* YTFE with *e.coli* ISC proteins

P28 - Beatriz Machado (NOVA FCT, Lisbon, Portugal)

Chemoselective oxidation of primary alcohol catalysed by well-defined copper(I) catalysts

P29 - Luisa Maia (NOVA FCT, Lisbon, Portugal)

Metal-dependent formate dehydrogenases: how do they catalyse the reduction of CO_2?

P30 - Cláudia Malta-Luís (NOVA ITQB, Lisbon, Portugal)

Forging new paths for the treatment of invasive infections caused by fungi: the potential of a nickel N-heterocyclic biscarbene complex

P31 - Carolina Mariano (NOVA ITQB, Lisbon, Portugal)

Iron attenuates fluconazole activity against *Candida glabrata*

P32 - Bárbara Marques (Faculty of Sciences, University of Lisbon, Portugal)

Ruthenium-antibiotic conjugates as new potential anticancer agents

P33 - Rafaela Tenera Marques (Faculty of Sciences, University of Lisbon, Portugal)

Photoreduction of CO_2 with cryptate catalysts

P34 - Francisco Mendes (NOVA ITQB, Lisbon, Portugal)

New metal complexes of a fluconazole derivative with antifungal activity

P35 - Vitor Mordido (NOVA FCT, Lisbon, Portugal)

Characterization of recombinant cytochrome c_{552} from *Wolinella succinogenes* and nitrous oxide reductase from *Pseudomonas stutzeri*

P36 - Pedro Moreira (Faculty of Sciences, University of Lisbon, Portugal)

Supported molybdenum catalysts for oxidative desulfurization of sulfur compounds

P37 - Leonor Morgado (NOVA FCT, Lisbon, Portugal)

NMR interaction studies between cytochromes unveil electron transfer network in *geobacter*'s periplasm

P38 - Carla Nunes (Faculty of Sciences, University of Lisbon, Portugal)

Oxidative desulfurization of sulfur compounds with supported MoO_2 nanoparticles

P39 - Margarida Nunes (University of Évora, Portugal)

Analytical study of religious simulacra

P40 - Elisabete Oliveira (NOVA FCT, Lisbon, Portugal)

Mesoporous inorganic silica nanomaterials as innovative synergistic tools against antimicrobial resistance

P41 - Giulia Orsini (NOVA ITQB, Lisbon, Portugal)

Novel 2-chloro-adenosine based on platinum: synthesis and anti-proliferative assessment

P42 - Navendu Paul (NOVA FCT, Lisbon, Portugal)

Interaction of split-soret cytochrome with formate dehydrogenase

P43 - Joana Pereira (IST, ULisbon, Portugal)

Extraction of thorium and uranium from aqueous solutions with functionalized ionic liquids

P44 - Inês Pereira-Gomes (NOVA FCT, Lisbon, Portugal)

Two new tetrasubstituted macrocycles with dansyl dyes as fluorescent and solvatochromic systems for metal ion detection

P45 - Luis Pereira (NOVA FCT, Lisbon, Portugal)

Bacteria to fight CO_2: exploiting formate dehydrogenases to reduce CO_2 to formate

P46 - Zeljko Petrovski (NOVA FCT, Lisbon, Portugal)

Novel materials with transition metal complexes for efficient catalytic epoxidation

P47 - Carlos Romão (NOVA ITQB, Lisbon, Portugal)

Antimicrobial and anticancer properties of carbon monoxide releasing molecules of the fac-$[Re(CO)_3(N\text{-}N)L]^+$ family

P48 - Giulia Romeo (NOVA ITQB, Lisbon, Portugal)

Synthesis of nickel bis-N-heterocyclic carbenes as antifungal agents

P49 - Catarina Roque (NOVA ITQB, Lisbon, Portugal)

Stressing out: promoting antifungal activity by fostering reductive stress with metal complexes

P50 - Marco Sá (Faculty of Sciences, University of Lisbon, Portugal)

Developing new ruthenium-peptide conjugates for targeting metastatic breast cancer

P51 - Catarina Silva (IST, ULisbon, Portugal)

Indium-111 radiocomplexes carrying a DNA intercalator for auger therapy of prostate cancer

P52 - Ricardo Soares (NOVA ITQB, Lisbon, Portugal)

One step backwards to take two steps forward into the evolution of multiheme cytochromes

P53 - Joana Teixeira (Faculty of Sciences, University of Porto, Portugal)

Enhancing thermal charging of textile supercapacitors through CNT/metal sulfide materials

P54 - Tito Trindade (University of Aveiro, Portugal)

Exploring 2D inorganic materials through surface chemistry probes

P55 - Gabriel Valério (NOVA FCT, Lisbon, Portugal)

Development of artificial enzymes able to reduce CO2 and NO_x based on copper enzymes

P56 - Isabel Velo-Heleno (University of Santiago de Compostela, Spain)

A route to iron(III) helical complexes from bisthiosemicarbazones

P57 - Isabel Santos Vieira (University of Aveiro, Portugal)

Acidic zeolites as heterogeneous catalysts for solvent-free glycerol acetalization

P58 - Khurram Tahir (NOVA ITQB, Lisbon, Portugal)

Microbially catalyzed anode and cathode microbial electrosynthesis system for efficient carbon dioxide sequestration and volatile fatty acid production

Abstracts of Oral Presentations

By chronological order.

PL 1

Catalyzing the Green Revolution: Unlocking Previously Inaccessible Processes

Prof. Javier García-Martínez

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During the presentation, I will describe a new strategy we have devloped for the synthesis of superior hierarchical catalysts, which lack long-range order but at local scale contain zeolite building units. [1,2] In fact, they are made out of fragments of one or even various zeolite structures and display improved accessibility, strong acidity, and excellent stability. Because of these features, they effectively catalyze reactions involving very bulky molecules, which currently are produced using highly corrosive homogenous catalysts. To achieve this goal, we built on a well-known technique, namely the interconversion of zeolites, which we interrupted at different times to yield the desired amounts of building units of the zeolites involved. The addition of quaternary ammonium surfactants during their preparation allows the development of well-defined mesoporosity and large surface areas. Using this simple procedure, we were able to produce families of materials with controlled amounts of different zeolitic building units and, consequently, optimize their catalytic performance for various reactions. Our surfactant-templated zeolites are now commercially available [3].

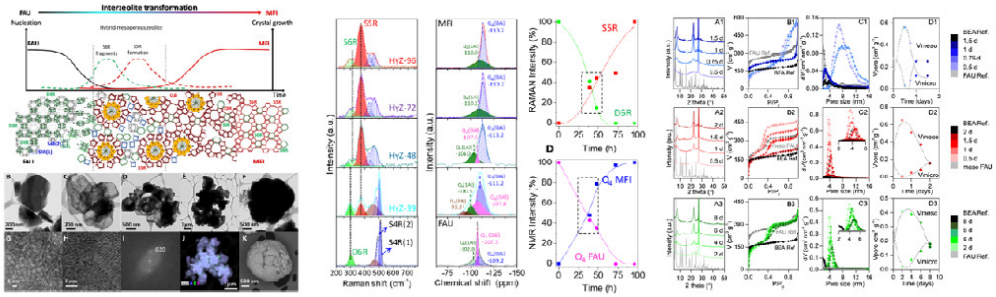

Figure 1. Textural, structural, and morphological characterization of some intermediates of the interconversion of zeolite FAU into MFI and BEA structures.

References:

[1] M. Mendoza-Castro, Z. Qie, N. Linares, J. García-Martínez, *Nat. Comm.* **2023,** (14) 1256

[2] M. Mendoza-Castro, E. De Oliveira-Jardim, N.T Ramírez-Márquez, C. A. Trujillo, N. Linares, J. García-Martínez, *J. Am. Chem. Soc.* **2022**, 144, 11, 5163–5171

[3] A. Sachse, J. García-Martínez, *J.; Chem. Mater.* **2017**, 29 (9), 3827– 3853

KN 1

COPPER INSTEAD OF PLATINUM: METAL-CONTAINING COMPOUNDS FOR APPLICATIONS FROM MEDICINE TO CATALYSIS

J. Heinrich, I. Prediger, N. Kulak*

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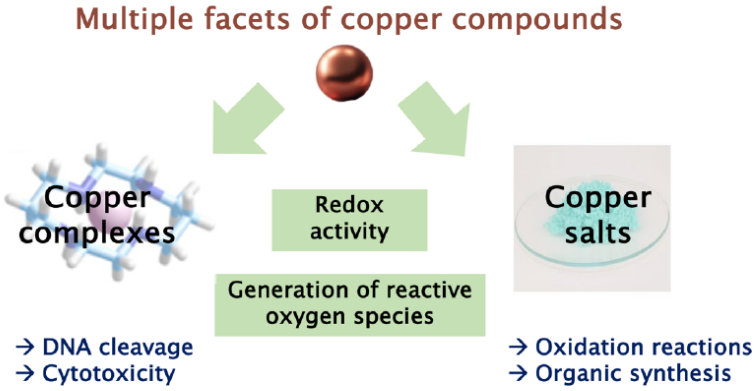
Precious metals are of importance and in widespread use in industry and daily life. For instance, Pt and Ru compounds are used or being developed as anticancer drugs, and Pd and Ir compounds are used as catalysts in industry. Precious metals, however, are not very abundant in the earth crust, and mining is thus expensive. Additionally, the amount of CO_2 produced through mining and purification is relatively high.[1] This is our motivation for aiming to apply compounds based on earth-abundant metals for applications in medicine as well as catalysis.

I will present strategies for using earth-abundant metals by exploiting their redox properties in two different fields: Copper complexes have been designed for efficiently generating reactive oxygen species (ROS) and thus killing cancer cells.[2] On the other hand, simple salts of copper have been applied for oxidation reactions that are of importance in industry.



References:

[1] R. M. Bullock, Science, 2020, 369, eabc3183.

[2] J. Heinrich, N. Kulak et al., Chem. Eur. J., 2021, 27, 18093–18102.

Acknowledgements:

This work was supported by the German Research Foundation (DFG) FOR 5538.

KN 2

NON-REDUCTIVE CO_2 VALORIZATION PROMOTED BY ECO-FRIENDLY PORPHYRIN SPECIES

E. Gallo*[1], C. Damiano[1], M. Cavalleri[1], L. Invernizzi[1]

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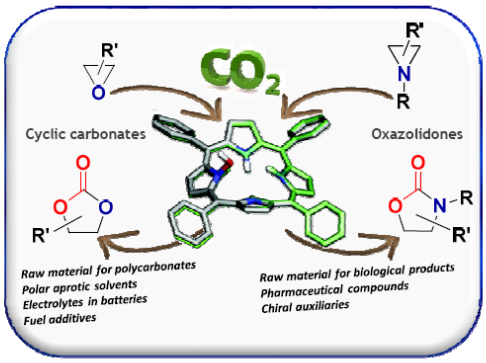
The design of accessible synthetic strategies for using CO_2 as a C1 source in the production of valuable compounds is a 'hot topic' both at academic and industrial levels. Alongside efforts to mitigate and store greenhouse emissions, the conversion of CO_2 into chemicals can contribute for achieving carbon neutrality by 2050. In addition, the use of low-cost, widely accessible waste as a reagent can furnish undeniable economic benefits in alignment with circular economy principles [1]. In this regard, the conversion of CO_2 into oxazolidinones and cyclic carbonates offers the additional advantage of being a 100% atom-economical reaction.



This presentation will offer an overview of porphyrin-promoted catalytic methodologies developed by our group in recent years [2]. Special emphasis will be placed on discussing the catalysts nature, including various binary and bifunctional porphyrin-based systems [3], alongside the electronic/steric properties of starting materials and experimental conditions employed. These factors are crucial for assessing the environmental impact of the processes and envisaging practical applications of synthetic procedures. Furthermore, catalytic mechanisms will be proposed based on spectroscopic and theoretical studies, taking into account the identification of active intermediates [4].

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KN 3

IMPROVING THE PERFORMANCE OF HEME PEROXIDASES AND PEROXIGENASES BY $O_2^{\cdot-}$ / $^{\cdot}OH$ ACTIVATION

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Heme peroxidases and peroxygenases are two families of enzymes that catalyse the oxidation and hydroxylation, respectively, of a broad variety of substrates of industrial interest. Despite their structural and functional differences, both types of enzymes rely on the H_2O_2-mediated generation of highly reactive oxoferryl intermediates to perform their function. In this talk I will show that the catalytic activity and operational pH range of plant peroxidases, bacterial dye decolorizing peroxidases and fungal peroxygenases can be drastically boosted without the need for complex molecular biology procedures by simply activating the enzymes electrochemically in the absence of externally added H_2O_2 [1] The method is based on the in situ generation of $O_2^{\bullet-}$, $^{\bullet}OH$ and H_2O_2, which bind the heme iron to form catalytically competent oxoiron intermediates [2]. Moreover, the enzymes can be successfully immobilized on biocompatible electrodes and actuated as efficient electrocatalysts.

Preferential $O_2^{\bullet-}$, $^{\bullet}OH$ or H_2O_2 activation of the enzymes is determined by the protein scaffold and by specific residues at the distal heme side [3].

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Acknowledgments:

This work was supported by CONICET, ANPCyT, UBACyT and the European Commission.

KN 4

BIOSYNTHESIS OF [2FE2S] CLUSTERS VIA FORMATION AND FUSION OF [1FE1S] PRECURSORS BY THE ISC MACHINERY

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Iron-sulfur (Fe-S) cluster are essential and ubiquitous prosthetic groups of proteins, biosynthesized by multi-protein machineries via a still elusive mechanism.[**1**] The Iron-Sulfur Cluster assembly (ISC) machinery synthesizes [2Fe2S] cluster on the scaffold protein IscU using sulfur provided in the form of a cysteine-bound persulfide by the cysteine desulfurase IscS, and electrons delivered by the ferredoxin-ferredoxin reductase couple Fdx-FdxR. Here, we report the characterization of the intermediates formed during the Fe-S cluster assembly process by the *E. coli* ISC machinery. Using an *in vitro* reconstituted machinery, our data revealed that the assembly of [2Fe2S] clusters is initiated by binding of a ferrous iron to IscU, followed by persulfide provided by IscS that is reduced into sulfide by the Fdx-FdxR couple, as reported for the murine ISC system.[**2,3**] Sulfide quantification, EPR and real-time electronic absorption kinetics indicate that persulfide reduction by Fdx-FdxR leads to a [1Fe1S] intermediate. NMR and native mass spectrometry analysis showed that IscU carrying the [1Fe1S] precursor dissociates from IscS and dimerizes to generate a bridging [2Fe2S] cluster. These data provide the first evidence of the formation of [1Fe1S] precursors fusing into a bridging [2Fe2S] cluster during the Fe-S cluster assembly process.

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Acknowledgments: This work was supported by the "Agence Nationale de la Recherche"

IL 1

DYE-DECOLORIZING PEROXIDASES: INSIGHTS INTO THEIR ROLE AS IMMOBILIZED BIOCATALYSTS

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Dye-decolorizing peroxidases (DyPs) are heme *b*-containing enzymes that couple the oxidation of a variety of structurally different substrates, with reduction of hydrogen peroxide to water. They are recognized for their potential in biotechnological applications, including lignin degradation and detoxification of synthetic dyes and environmental pollutants [1]. Despite similarities in the heme cavity architectures, DyPs from different sources exhibit significant variations in specific activities, which influences their suitability for diverse applications [1,2]. We investigate the structural and electrocatalytic properties of DyPs, focusing on their potential as immobilized biocatalysts in electrochemical biosensors for H_2O_2 detection and in electrocatalytic degradation of environmental pollutants. Using resonance Raman (RR) and surface-enhanced RR (SERR) spectroscopy we have characterized the heme active site architecture of a number of bacterial DyPs and evaluated their structural integrity upon immobilization on electrode surfaces [2,3]. Our work demonstrates the efficiency of combined SERR spectroscopy and electrochemistry for the rapid screening and selection of promising enzyme candidates for construction of biosensors and other applications. In particular, we have demonstrated that, among almost a dozen candidates, the DyP from *Pseudomonas putida* (PpDyP), retains its solution configuration upon immobilization on biocompatible electrodes, while exhibiting high catalytic efficiency, and is therefore an excellent candidate for the development of 3rd generation H_2O_2 biosensors [3,4].

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IL 2

SMART METALLODRUGS FOR PRECISION THERAPY OF FGFR BREAST CANCER

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Metastatic breast cancer (MBC) remains one of the most common and lethal types of tumors worldwide. The median survival time of patients with MBC is merely 2 years, mostly due to the lack of effective drugs capable of reaching metastases and the inadequate selectivity of current treatments toward cancer cells that result in severe adverse effects[1].
Recently, we have been dedicated to developing an innovative family of smart metallodrug delivery systems capable of targeting with high precision MBC cells, therefore sparing the healthy tissues. These systems consist of novel ruthenium-peptide conjugates (RuPCs) that selectively recognize the fibroblast growth factor receptor (FGFR) overexpressed by MBC cells[2], and controllably release a highly cytotoxic organometallic ruthenium complex upon the stimulus of the acidic tumor microenvironment. Thus, these RuPCs may promote enhanced therapeutic efficacy with reduced side effects.

Herein, we report the synthesis, structural characterization, and *in silico*/*in vitro* biological evaluation of new RuPCs. The interaction with their molecular target (cell membrane) was studied by molecular dynamics simulations. The drug release profile in aqueous solution was evaluated at pH values that mimic both the tumor microenvironment and the healthy tissues/bloodstream. The cytotoxicity and selectivity were determined in a panel of human breast cancer cells and non-tumoral fibroblasts with different levels of FGFR expression at the referred pH values.

The lead RuPC showed controlled release of the Ru complex in its active form allied to selective antiproliferative activity against FGFR(+) MBC cells, suggesting its potential use as a novel agent for the precision therapy of MBC.

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Acknowledgments:

This work was funded by Fundação para a Ciência e Tecnologia (FCT), I.P./MCTES through the projects PTDC/QUI-QIN/0146/2020 (Arrows2cancer, DOI 10.54499/PTDC/QUI-QIN/0146/2020), UIDB/00100/2020 (CQE, DOI 10.54499/UIDB/00100/2020), LA/P/0056/2020 (IMS, DOI 10.54499/LA/P/0056/2020). FCT, POPH and FSE- European Social Funds are acknowledged for the Individual Call to Scientific Employment Stimulus 2022.00028.CEECIND/CP1722/CT0005 (DOI 10.54499/2022.00028.CEECIND/CP1722/CT0005) project.

IL 3

OXIDATIVE DAMAGE OF MO/W FORMATE DEHYDROGENASES

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Mo- and W-Formate dehydrogenases (Mo/W-Fdhs) catalyse the reversible reduction of CO_2 to formate. The sensitivity of these enzymes to O_2 hampers their industrial use as biocatalysts. However, the chemical/structural implications of O_2-induced damage remain unknown yet are crucial for devising protective mechanisms. Our focus is on studying W-FdhAB from *D. vulgaris*, which serves as a suitable model for biocatalytic applications in CO_2 reduction due to its robustness and high catalytic activity[1, 2].

Our recent study[3], which combines biochemical, spectroscopic, and structural analyses of *Dv*FdhAB, reveals that O_2 inactivation is promoted by the presence of substrate and results in the formation of a new active site species, consistently captured in the crystal structures. This process involves the displacement of the catalytic SeCys from tungsten coordination, replaced by a O_2 or H_2O_2 molecule (Fig. 1). In addition, we proved that oxidative inactivation does not require Mo/W reduction, as widely assumed, occurring in the oxidized state in the presence of CO_2.

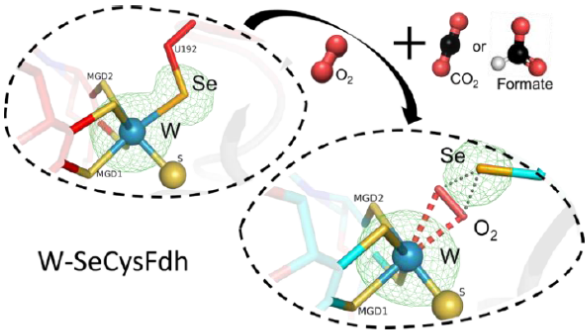

Fig. 1 - SeCys displacement on W-FdhAB. Anomalous difference Fourier map in green mesh (contoured at 5σ).

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IL 4

ELECTROCHEMICAL CHARACTERIZATIONS OF NEW MULTICOPPER OXIDASES

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Multicopper oxidases (MCOs) are broadly extended enzymes in nature, coupling the oxidation of a variety of organic and inorganic substrates to the catalytic reduction of O_2. These enzymes are of particular interest for diverse biotechnological applications and consequently have been widely investigated to gain a better understanding of the intricate bioelectrocatalytic reactions taking place during redox conversion, serving also as molecular blueprints for the design of synthetic catalysts. While various MCOs have been already studied, the attributes of metallo-oxidases remain mostly unexplored. The particular structural and catalytic features exhibited by metallo-oxidases make them of great interest for detailed bioelectrochemical studies. In particular, the multicopper oxidase from *Aquifex aeolicus* (McoA) presents a highly compact structure, which translates into remarkable stability. The study of redox proteins confined over an electrode surface is a powerful approach enabling precise modulation of the driving force for interfacial electron transfer through the control of the electrode potential. The possibility of using an electrode to replace substrate oxidation for the supply of electrons facilitates the investigation of redox enzymes that are in direct electron transfer with the electrode. Simultaneously, different experimental parameters such as the pH of the solution and substrate availability can be easily investigated. As will be shown, a comparison of the bioelectrocatalytic currents for O_2 reduction under different conditions allows us to gain further insights into the catalytic properties of wild-type McoA and variants obtained through directed evolution.

Acknowledgments:

This work was supported by FCT - Fundação para a Ciência e a Tecnologia, I.P., through grant 2022.02027.PTDC, MOSTMICRO-ITQB R&D Unit (UIDB/04612/2020, UIDP/04612/2020) and LS4FUTURE Associated Laboratory (LA/P/0087/2020).

IL 5

THE ANTICANCER POTENTIAL OF 8-HYDROXYQUINOLINE SCHIFF BASE METAL COMPLEXES CONTAINING N-HETEROCYCLES

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Given their pharmacological properties, Schiff bases have been considered interesting scaffolds in medicinal chemistry. Our group has recently reported the anticancer potential of Zn(II)- and Cu(II)-complexes derived from 8-hydroxyquinoline (8HQ) Schiff bases containing piperidine/morpholine units.[1] Encouraged by their promising results, other complexes containing different *n*-heterocycles (imidazole) or transition metals (Ni(II)/V(IV)O) were also prepared. Preliminary biological results indicate that the Cu(II)-compounds with a morpholine unit have the highest anticancer activity, while the Zn(II)-complexes with the imidazole unit present relevant selectivity. Ni(II)- and V(IV)O-complexes with the morpholine unit are also cytotoxic and present a synergistic effect with 5-Fluorouracil (5FU). The selected Cu(II)- and Ni(II)-complexes were nanoformulated in lipid-based systems to overcome solubility/selectivity problems. *In vitro* results demonstrated that liposomal formulations potentiated cytotoxic properties of loaded compounds. The proof of concept in appropriate murine models constitutes ongoing studies.

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Acknowledgments:

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KN 5

KNOWN UNKNOWNS, UNKNOWN UNKNOWNS, AND UNKNOWN KNOWNS: A BRIEF REPORT FROM THE SURVEY OF THE DESULFUROMONADIA "CYTOCHROMOME"

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Multiheme cytochromes *c* (MHC) provide prokaryotes with a metabolic versatility that contributes to their role in the biogeochemical cycling of the elements and the operation of bioelectrochemical systems. However, MHC were only isolated and studied in detail from a limited number of species. Among these, members of the Desulfuromonadia class are particularly MHC-rich, and for that reason, we employed bioinformatic tools to study the cytochromome encoded in their genomes to obtain a broad view of the diversity of MHC.

We found that the most prevalent MHC have homologues already characterized, but nearly half of the MHC families in the Desulforomonadia class have no known homologues. Using AlphaFold2 we predicted their 3D structures and generated an atlas of novel MHC, including examples with high beta-sheet content and nanowire MHC with unprecedented high numbers of putative heme cofactors per polypeptide.

This work illuminates for the first time the universe of experimentally uncharacterized MHC that are likely to contribute to the metabolic versatility and the fitness of Desulfuromonadia in diverse environmental conditions, and to their potential use in biotechnological applications.

Acknowledgments:

This work was supported by European EC Horizon2020 TIMB3 (Project 810856); MOSTMICRO-ITQB with references UIDB/04612/2020 and UIDP/04612/2020; Fundação para a Ciência e a Tecnologia (FCT) Portugal (project PTDC/BIA-BQM/4143/2021).

OC 1

UNVEILING METAL DISTRIBUTION FROM BACTERIAL NANO-COMPARTMENTS AFTER STRESS EXPOSURE

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Bacterial nano-compartments are known to exist within bacteria. We have studied the electron dense granules (EDG), from the radiation resistant bacteria *Deinococcus radiodurans* and the involvement of both DNA-binding proteins Dps1 (*dr2263*) and Dps2 (*drb0092*) [1-3] on these cellular substructures. *Dr*Dps are ferritin-like proteins, with the ability to store Mn and Fe as well as to bind/protect DNA under *in vitro* conditions [3]. The formation of EDG in *Dr*Dps knockout mutants is abolished, suggesting that these proteins play an important role in the formation and regulation of these bacterial nano-compartments. Using X-ray fluorescence nano-imaging data (ID16A-NI and ID16-B ESRF), we have investigated the metal content in these nano-compartments. Our results show that these are element-rich regions, particularly with phosphorous, calcium and manganese [4]. Therefore, these nano-compartments act as element-rich regions under control conditions, which are triggered to release the different elements when cells are subject to stress [4]. To further increase our molecular and structural insights into these regions, we performed STEM analysis coupled with Electron Dispersive X-ray Spectroscopy (EDS) on the *Dr* cells. Our data reveals a heterogeneous metal composition across different cells, suggesting an important mechanism in response to stress.

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Acknowledgments:

This work was supported by INSTRUCT-ERIC-Access Proposal, PID: 19879. FCT Project: PTDC/BIA-BQM/31317/2017. European Union's Horizon 2020 research and innovation programme under grant agreement No 857203- IMpaCT - Imaging life from Molecules to cells - building knowledge on Cryo-electron microscopy methodologies at ITQB NOVA – www.itqb.unl.pt/impact. *ESRF proposal LS3037.*

OC 2

MOLYBDENUM COFACTOR ADDUCTS UNVEILING ARSENITE OXIDASE CATALYTIC MECHANISM

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Water contamination with arsenic presents a global threat both to the environment and to public health. A recent study [1] identified that up to 220 million people are at risk due to groundwater consumption. The arsenite oxidase (Aio) [2-4], a complex metalloenzyme, can be used as a biosensor and, putatively, in bioremediation since it oxidizes arsenite (As^{III}) and antimonite (Sb^{III}) [5], to less toxic and easier to remove species As^{V}/Sb^{V}. Our goal is to unravel Aio's catalytic mechanism for the development of new effective and economically sustainable bioengineered solutions [6]. Recently, we obtained 4 high-resolution structures (up to 1.44 Å) of Aio with As/Sb oxyanions bound to the active site. These allowed us to revisit the catalytic mechanism of As^{III} oxidation which combined with site-directed mutagenesis and activity assays, provide information on important catalytic-relevant residues [7]. Additionally, we observed for the first time, the initiation step of the reaction, corresponding to Aio in its oxidised state (1.87 Å, *unpublished data*).

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Acknowledgments:

This work was supported by the Applied Molecular Biosciences Unit which is financed by FCT (UIDP/04378/2020 and UIDB/04378/2020 and Engrola PhD student grant UI/BD/151155/2021).

OC 3

HOW CYSTEINE DIRECTS METAL-MEDIATED TAU TOXICITY

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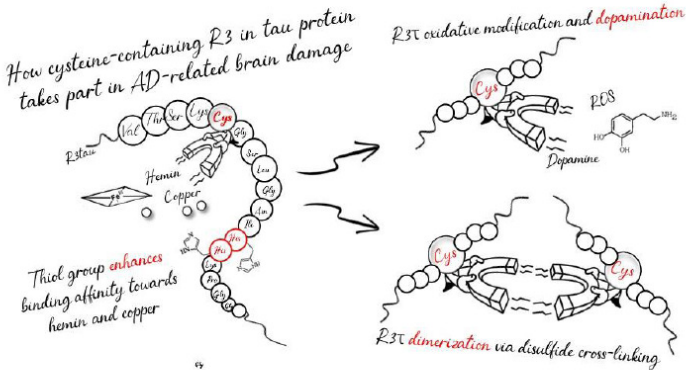
Tau protein is a neuronal component involved in the axonal stabilization but, in pathological conditions, it is dissociated from the microtubule and generates insoluble neurofibrillary tangles.[1] Tau comprises four pseudorepeats (R1–R4),[2] containing one (R1, R2, R4) or two (R3) histidines, that potentially act as metal binding sites. Moreover, the presence of two cysteine residues in R2 and R3 might have a crucial role in protein aggregation, through possible disulfide bond formation, and/or affecting the binding and reactivity of redox-active metal ions, as copper or hemin.[3-5]



We, therefore, compare the interaction of copper and hemin with octadeca-R3-peptide (R3C) and with its mutant containing an alanine residue (R3A) to assess the role of thiol group. In the spectrophotometric titrations of complexes with copper and hemin, a remarkable strong interaction was observed only in the case of R3C;[6] moreover, copper-R3C and hemin-R3C complexes display a particular oxidative mechanism triggered by the presence of cysteine. In both cases, HPLC-MS analysis shows that cysteine can form disulfide bonds and dopamine-Cys covalent adducts, with potential implication in tau aggregation process.

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KN 6

DRAW ME AN OXIDOREDUCTASE THAT REACTS WITH MENAQUINONES: THE CASE OF THE FORMATE DEHYDROGENASE FORCE FROM *BACILLUS SUBTILIS*

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Formate production is a means by which many anaerobic microorganisms clear out reducing equivalents during fermentation. However, with a redox potential of -420 mV, formate is also a valuable source of energy. Its integration in microbial metabolism relies on metal-dependent Formate Dehydrogenases (FDHs) that are exclusively found in prokaryotes and were already present in the last universal common ancestor (LUCA) [1]. By using phylogenetic analysis, we have identified a new class of FDHs, the so-called ForCE, and characterize them in *Bacillus subtilis* [2]. The ForC catalytic subunit couples formate oxidation to menaquinone reduction. While the ForE subunit is of unknow function and includes a conserved domain. First, we have solved the Cryo-EM structure of the ForCE complex that unveiled an unprecedent structural arrangement with lipids and menaquinones, enhancing its functional understanding. Secondly, we have demonstrated that ForCEs are part of the aerobic respiratory chain of *B. subtilis* coupling formate oxidation to oxygen reduction. Moreover, we have found that the complex ForCE is connected to the membrane thanks to the ForE subunit through the conserved domain. Finally, we have identified that genes encoding proteins with a such a conserved domain are found in synteny with genes encoding several types of oxidoreductases reacting with quinones, both in archaeal and bacterial phyla. Overall, the ForCE organization is conserved across the microbial world and such kind of organization connects a panel of redox reactions to respiratory processes.

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OC 4

CO_2-DRIVEN N-FORMYLATION/-METHYLATION OF AMINES USING C-SCORPIONATE METAL COMPLEXES

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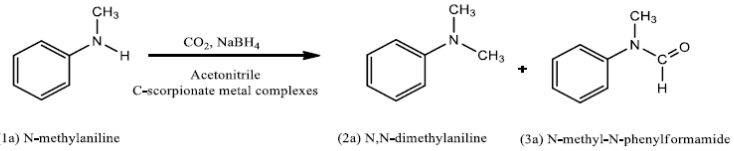
Conversion of CO_2 into added-value products has recently received great attention, from both academia and industry, once it is considered as a sustainable solution to reduce global warming, fossil fuel depletion and energy storage problems [1].

Herein, we report the high catalytic potential use of C-scorpionate metal complexes, specifically, $[NiCl_2(tpm)].3H_2O$, $[CoCl_2(tpm)].3H_2O$ and $[PdCl_2(tpm)]$ [tpm = hydrotris(1H-pyrazol-1-yl)methane] in the N-formylation/N-methylation of amines using ($NaBH_4$/MeCN/CO_2) as catalytic system (Scheme 1).



(1a) N-methylaniline (2a) N,N-dimethylaniline (3a) N-methyl-N-phenylformamide

Scheme 1 - N-formylation and N-methylation of N-methylaniline with CO_2 and $NaBH_4$, catalyzed by C-scorpionate metal complexes.

Different parameters were studied, revealing a significant impact on the selectivity of the product. Interestingly, monitoring the reaction course by ^1H NMR revealed the presence of an intermediate species that influenced product formation, which was later identified.

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OC 5

SYNTHESIS AND CHARACTERIZATION OF TRANSITION METAL COMPLEXES WITH CHIRAL MONODENATE OXAZOLINE LIGANDS

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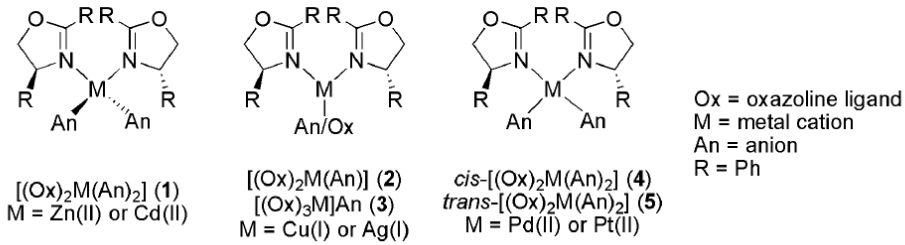
Chiral bisoxazolines are prominent examples of privileged ligands with C_2-symmetry; their transition metal complexes have been successfully used as selective catalysts in a number of asymmetric reactions [1]. On the other hand, chiral monodentate oxazolines are significantly less explored as ligands for transition metal catalysis [2, 3].

Following our interest in inorganic stereochemistry [4, 5], chiral tetrahedral complexes $[(Ox)_2M(An)_2]$ (**1**) with M = Zn(II) or Cd(II), trigonal complexes $[(Ox)_2M(An)]$ (**2**) and $[(Ox)_3M]An$ (**3**) with M = Cu(I) or Ag(I) and square planar complexes *cis*-$[(Ox)_2M(An)_2]$ (**4**) and *trans*-$[(Ox)_2M(An)_2]$ (**5**) with Pd(II) or Pt(II) have been synthesized (Ox = oxazoline, An = anion), see the Figure below. The characterization of complexes **1** - **5** by spectroscopic and crystallographic techniques as well as by DFT calculations will be presented.



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Support by Croatian Science Foundation (CSF) projects IP-2022-10-8456 and DOK-2021-02-7366 is gratefully acknowledged.

OC 6

MOLYBDENUM CATALYZED ACCEPTORLESS DEHYDROGENATION OF ALCOHOLS FOR THE SYNTHESIS OF QUINOLINES

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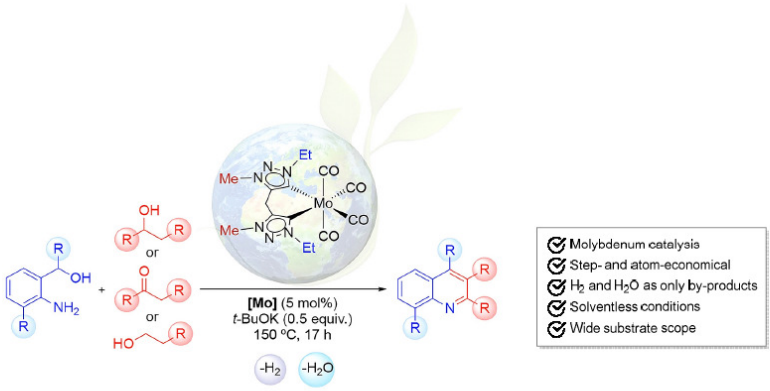
Mesoionic 1,2,3-triazolylidenes represents a prominent class of ligands in organometallic chemistry. Extensive catalytic applications of these ligands with noble metals can be found in the literature.[1] In contrast, the chemistry and catalysis of 1,2,3-triazol-5-ylidenes with molybdenum has remained poorly developed. We present here the first Mo triazolylidene complexes catalyzing the atom-economical synthesis of quinolines through acceptorless dehydrogenative coupling (ADC) of alcohols.[2] A new family of bis-triazolylidene Mo(0) complexes have been prepared and applied as catalysts for the synthesis of a wide variety of substituted quinolines from 2-aminobenzylalcohols and readily available secondary alcohols (Scheme 1). Interestingly, variation of the wingtips of the triazolylidenes in $[Mo(CO)_4(bis\text{-}trz)]$ complexes has a significative impact in the catalytic efficiency of their Mo complexes.



Scheme 1. Synthesis of substituted quinolines mediated by a Mo(0)-trz complex

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IL 6

MODULATING THE PRIMARY AND SECONDARY COORDINATION SPHERES OF METAL IONS

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Besides the metal itself, the functional properties of metal complexes are also controlled/directed by the ligands, and traditionally a strong focus has been addressed on ligand design/development in coordination chemistry. For instance, often simple metal salts do not show an appreciable or high catalytic activity in metal complex catalysis, whereas coordination compounds with noncovalent interactions and coordination activation modes able to promote efficiently a variety of catalytic transformations. In a regio-, site- or stereo-selective reaction, decoration of organic ligands with noncovalent bond donor or acceptor sites is one of the useful strategies in metal complex or cooperative catalysis [1].

The role of noncovalent interactions is not limited to their contribution in catalysis, since the application and function of coordination compounds in molecular recognition, crystal engineering, material chemistry, etc. are also dependent on intermolecular interactions at the primary or secondary coordination sphere of metal complexes [2-5].

In this lecture, we discuss the structural aspects of the weak interactions in coordination compounds.

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Acknowledgments:
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IL 7

Paramagnetic complexes as sensors for biomedical MRS and MRI

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The presence of paramagnetic metal ions in small complexes or bound to biomacromolecules proteins leads to induced shift and relaxation effects in their neighboring NMR-active nuclei, such as ^{1}H, ^{13}C, ^{15}N ^{17}O and ^{19}F, which depend mainly on the magnetic anisotropy and electronic spin relaxation of the metal center, as well as on geometrical factors linking it with the observed nuclei. Examples of this are the use of Ln^{3+} ions as NMR shift and relaxation probes in structural biology and of Gd^{3+}chelates as contrast agents in clinical MRI. Here, the use of paramagnetic NMR effects as sensors of important biological parameters is illustrated by several examples, namely: a) an Yb^{3+}macrocyclic complex as a pH-responsive paraCEST agent for *in vivo* MRI [1], b) the detection of glucose-derived D- and L-lactate in erythrocytes and cancer cells by use of a Yb^{3+}-based chiral NMR shift reagent [2], and c) the use of fluorinated $Mn^{3+/2+}$-porphyrins as redox-responsive ^{19}F and ^{1}H NMR relaxation probes, including ^{19}F-MRI [3,4].

Acknowledgements
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KN 7

METALLIC NANOPARTICLES: FROM METAL COMPLEXES TO ANISOTROPIC NANOSTRUCTURES AND MATERIALS

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Metallic nanoparticles of noble metals have a wide range of applications across diverse fields, making them essential materials with significant impact on technology, healthcare, and environmental sustainability [1]. In our group we have been working with nanostructures for catalysis [2], proteomics [3], electronics and optoelectronics [4], plasmonics [5] and antibacterial [6] applications. As examples I will discuss a seed-mediated strategy for synthesizing uniform Au nanostars with tunable optical properties using adenosine monophosphate (AMP) as a capping ligand. [7]. Same methodology has been applying in the preparation of AgNPs with antimicrobial properties supported in polymers.[8] Moreover, to introduce luminescent properties, Silver-Telluride 2D organometallic nanofibers [9] were successfully synthesized using diphenyl ditelluride (DPDT) as a precursor and $AgNO_3$. Tetracoordinate complexes starts the reaction, the Treatment with oleylamine under ultrasound induced an aggregation emission effect (AIE), transforming non-emissive nanofibers into highly red emissive fluorescent nanomaterial.

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Acknowledgments:

This work was supported by the Associate Laboratory for Green Chemistry – LAQV which is financed by national funds from FCT/MCTES (UIDB/50006/2020 and UIDP/50006/2020) as well as the Scientific Society PROTEOMASS (Portugal) for funding support (General Funding 2023-2024 Grants). S.N. and F.D. thanks to FCT/MEC (Portugal) for theirs doctoral grants SFRH/BD/144618/2019 and 2021.05161.BD. J.F-. L. thanks the individual research contract DL57/2016 NT. The work was carried out partially through the INL User Facilities (Braga, Portugal). Authors thank the FCT-MEC grant SiSi4Bacter (PTDC/QUI-COL/1517/2020).

IL 8

ADVANCES IN PHOTORESPONSIVE FERROELECTRICS: DESIGNING HYBRID AND METAL-NITROSYL CRYSTALS

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In the quest for next-generation smart materials, the development of photoresponsive ferroelectrics stands as a pivotal advancement, offering unprecedented opportunities in memory storage, sensing, and optoelectronic devices. Here, I will present pioneering work in this field through the molecular-level design and synthesis of organic-inorganic hybrid materials and metal-nitrosyl ferroelectric crystals. I start by introducing a novel hybrid high-temperature ferroelectric, $(Me_2NH_2)[NaFe(CN)_5(NO)]$, constructed by incorporating an inorganic photochromic nitroprusside anion with the polar organic cation dimethylammonium ($Me_2NH_2^+$), to achieve ferroelectricity via synergistic dipole ordering below 408 K [1]. The material exhibits reversible photoswitching between ferroelectric ground and metastable states, enabled by light-induced isomerization of the N-bound nitrosyl ligand. Building upon this, further research led to the development of a new metal-nitrosyl ferroelectric crystal, (DMA)(PIP)[$Fe(CN)_5(NO)$] (DMA = dimethylammonium, PIP = piperidinium), achieved by employing a dual-organic-cation approach [2]. This strategy not only reduces crystal symmetry to enable robust ferroelectric properties but also introduces a novel mechanism for reversible photoisomerization, allowing for the external control of ferroelectric polarization states through light irradiation. Both studies highlight the significant potential of molecular engineering in creating advanced materials with tuneable photoresponsive behaviours, paving the way for innovations in photostimulated ferroelectric devices and optoelectronics.

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Acknowledgments:

I wish to thank all my collaborators in this work, in particular Dr. Wei-Jian Xu, Dr. Andrei Kholkin, Luís Veríssimo (University of Aveiro) and Prof. José M. G. Martinho (IST). This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020, and LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC).

KN 8

ANTIMICROBIAL COORDINATION POLYMERS: FROM SELF-ASSEMBLY TO BIOMATERIALS

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To address increasing antimicrobial resistance, the search for new bioactive molecules and sustainable materials is currently in high demand. This presentation will highlight our recent research on the self-assembly synthesis, crystallization methods, structural features and applications of a wide diversity of functional metal-organic architectures, including bioactive metal-organic frameworks (MOFs), coordination polymers (CPs), metal complexes and derived materials with potent antibacterial, antiviral, and biofilm inhibition properties [1-3]. The following topics will be discussed.

(1) Self-assembly generation and structural diversity of silver(I) and copper(II) coordination polymers derived from carboxylic acids, aminoalcohols, aminophosphines, and other ligands.

(2) Application of these compounds as efficient antimicrobials against different types of Gram-positive and Gram-negative bacteria, bacterial biofilms, and fungi.

(3) Design of CP-doped biopolymer films based on soybean oil, potato starch or cellulose.

(4) Antibacterial and biofilm inhibition activity of the obtained biopolymer films as a function of dopant type and loading, biopolymer matrix, and metal ion release rates.

(5) Antiviral and cytotoxic activity of silver(I) coordination polymers bearing bioactive ligands.

This multidisciplinary study expands the antimicrobial use of bioactive coordination polymers and hybrid biopolymer materials obtained from renewable biofeedstock sources.

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All the coauthors of the cited references are gratefully acknowledged. Financial support is provided by the FCT (PTDC/QUI-QIN/3898/2020, LA/P/0056/2020, and UIDB/00100/2020; Portugal).

Award Alberto Romão Dias 1

FROM CHEMISTRY TO BIOLOGY, AND BACK

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The focus of my lab is on understanding the chemistry behind biological processes, with a special emphasis on understanding proteins. Proteins are the molecular machines that drive most cellular processes and display an outstanding and exquisite control of the chemistry they perform. We study mostly metalloproteins, where one or more metal ions expand proteins' functionalities and allow them to perform very challenging chemical reactions. Our main focus is on metalloproteins involved in the energy metabolism of anaerobic bacteria and on the mechanism and engineering of some of these enzymes for biotechnologically relevant biocatalysis. In this talk I will briefly present a few selected highlights from the work carried out in my lab in these two areas, trying to showcase our contribution to the area of Bioinorganic Chemistry.

I am very thankful to the Jury of the Prémio Alberto Romão Dias and Sociedade Portuguesa de Química for this award, which stems from the hard work of many students and collaborators, for which I am deeply grateful. This award is for all of us.

Award Alberto Romão Dias 2

A BIOINORGANIC GUIDE TO DENITRIFICATION

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A concise updated review of the bioinorganic aspects of denitrification is presented, with emphasis on structural and mechanistic aspects of the relevant enzymes involved in this stepwise complex pathway. The metal diversity detected in this pathway is also acknowledged. Denitrification, or dissimilative nitrate reduction, is an anaerobic process used by some bacteria for energy generation. This process is important in many aspects, but its environmental implications have been given relevance. Nitrate accumulation and release of nitrous oxide in the atmosphere due to excess use of fertilizers in agriculture are examples of two environmental problems where denitrification plays a central role. The reduction of nitrate to nitrogen gas is accomplished by four different types of metalloenzymes in four simple steps: nitrate is reduced to nitrite, then to nitric oxide, followed by the reduction to nitrous oxide and by a final reduction to dinitrogen. These four steps are catalysed by four different metalloenzymes with catalytic centres containing Mo, Cu and Fe. This pathway has been extensively studied by Bio and Bioinorganic chemistry, with emphasis on definition of the metal active centres, as well of the mechanisms involved. The structures of these enzymes have been solved, and unique metal centres have been revealed, such as the ”CuZ” centre. The application of spectroscopic, bio-electrochemical / biophysical techniques and kinetic studies enabled the identification of catalytic intermediates, and to obtain structural information on the operating electron transfer complexes.

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The work was suported by the project from FCT UIDB/50006/2020 and UIDP/50006/2020 from the Associated Laboratory of Green Chemistry-LAQV and the projects PTDC/QUI-BIQ/116481/2010, PTDC/BBB-BIQ/0129/2014 and PTDC/2022.01152.

KN 9

IRON IS MASTER OF THEM ALL

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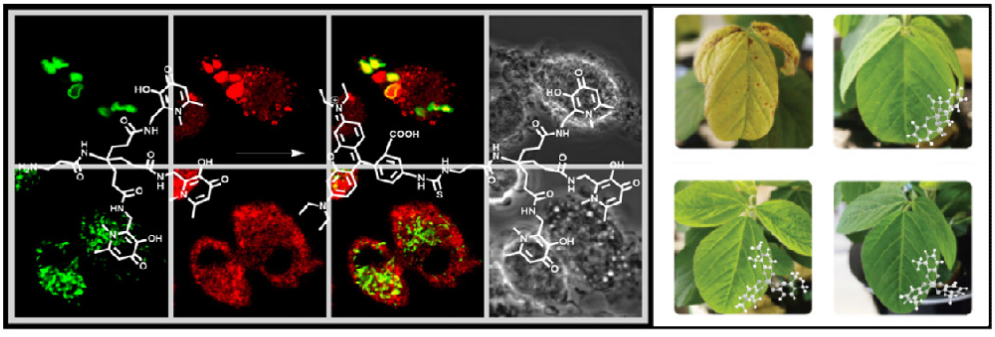
Iron is an essential element for life and throughout Earth's geological history, the decrease in its bioavailability worked as an evolutionary stimulus. Currently, iron is a scarce nutrient for which most organisms have to compete.

The work in our group shows that access or deprivation of iron is a field of intervention in various societal issues, such as infectious diseases or agronomic production. The importance of several molecular frameworks has been demonstrated and our choice has been focused on ligands of the 3,4-HPO class. The latter molecules have an enormous potential in diverse fields of application, including the development of new antimicrobials and iron fertilizers. The strong chelating properties of 3,4-HPO ligands associated with their versatility in synthesis clearly constitutes an enormous advantage to fine-tune properties of ligands and complexes according to the function desired. An overview of the most important achievements of the group in the areas of infectious diseases and crop production will be delivered.



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Acknowledgments:

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IL 9

ELECTROSYNTHESIS OF METAL-ORGANIC FRAMEWORK FILMS

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New functionalised surfaces are crucial for the development of materials science. Namely, the deposition of materials yielding thin films is urgently needed in all modern technologies. This allows fine-tuning the properties of several common substrates (eg. carbon-based materials, metal oxides, etc.) overcoming their intrinsic limitations. Many candidates have been used and metal-organic materials (MOMs) started to attract attention. MOMs are built from the self-assembly of metal ions (nodes) and organic ligands (linkers) offering an infinite number of combinations and properties such as crystallinity, permanent porosity, high surface area and available active sites.[1] Recently, electrochemical techniques have emerged as alternatives for high-quality film formation, with shorter synthesis times under milder conditions and the ability to fine-tune morphology as key advantages.[2]

This discussion will cover cathodic deposition (direct method) and electrophoretic deposition (indirect method) for creating MOM coatings. Moreover, it will be discussed the main challenges and the resultant film properties, assessed through several characterisation techniques like X-ray diffraction, infrared spectroscopy, and scanning electron microscopy, depending on the chosen method.

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IL 10

METAL COINAGE HETEROLEPTIC COMPLEXES: STRUCTURE AND REACTIVITY

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NHC heterocyclic carbene complexes have been used with great success as catalysts in various reactions over the last two decades. In order to broaden their scope, the development of new complexes bearing two different types of ligands has been intensively pursued in order to induce new electronic or steric properties and to improve their stability or reactivity. Here we present the synthesis and structural characterisation of a new family of diimine-NHC complexes bearing Cu(I), Ag(I) and Au(I) as metal centres [2]. Their reactivity as catalysts in the synthesis of propargylamines and enynes is also reported..

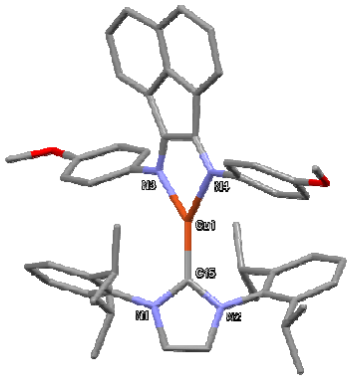

Figure 1: Mercury representation of an NHC-Diimine Cu(I) complex (PF_6 and hydrogens omitted for clarity).

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IL 11

CLEVER STRATEGIES TO BROADEN POLYOXOMETALATES FUNCTIONALITIES: FROM MOLECULES TO COMPOSITES

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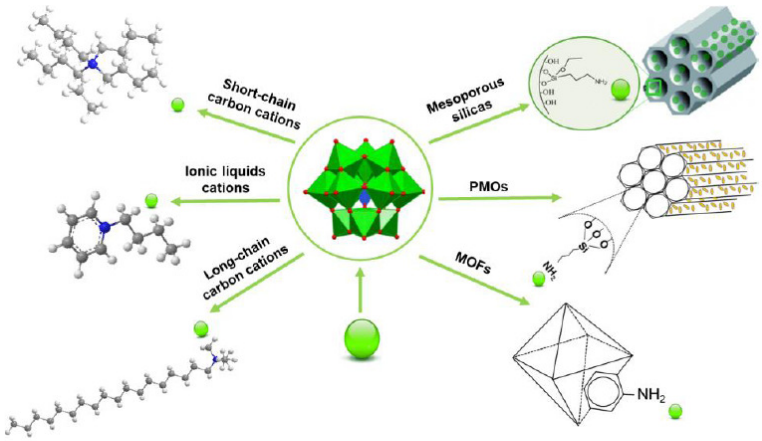
In the last two decades, the POMOF group from LAQV/REQUIMTE has been dedicated to investigate polyoxometalates (POMs) and their structural modification, modulation and functionalization.[1] Various structures, integrating different transition metals and lanthanides, have been prepared according with the required application. POM structures have been associated with various organic units, integrated into different porous solid supports, and encapsulated in distinct inorganic materials and, more recently, combined in polymeric membranes. A straight bridge between inorganic chemistry and materials science was built to activate and modulate the application of POMs, with an aim to increase the sustainability and cost-efficiency of their systems.



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Funding:

This work received financial support from FCT/MCTES (UIDB/50006/2020 DOI 10.54499/UIDB/50006/2020) through national funds

IL 12

METAL-ORGANIC FRAMEWORKS FOR ANION DETECTION

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Metal-organic frameworks (MOFs), renowned for their porosity, structural variety, and extensive surface areas, have established a solid footing in the realm of anion detection, including biological relevant anions and environmental contaminants [1, 2]. These crystalline materials, characterized by their tunability and diversity, excel in the selective recognition of anionic species, thanks to tailored ligand design, functional group integration, and post-synthetic modifications [3]. Our research is primarily focused on leveraging MOFs for the sensitive and selective identification of anionic targets such as phosphate and hydrogen phosphate, emblematic of our broader goal to address environmental and safety concerns [4, 5]. By strategically designing porphyrin-based metal-organic frameworks (MOFs), we have made significant progress in optical detection systems, demonstrating the potential of MOFs as receptors in sensor devices [5]. This communication showcases our latest efforts in synthesizing MOFs specifically designed for anion recognition, representing a significant advancement in the field of sensor technologies.

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IL 13

MULTI-ELECTRON TRANSFER REACTIONS OF URANIUM BIS(ARYLOXIDE) CYCLAM COMPLEXES

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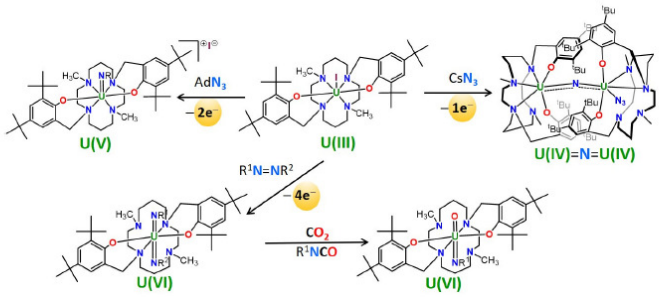
Uranium has a unique history closely connected to applications in nuclear energy that have determined the evolution of its research. Its exceptional and diverse chemical reactivity has fascinated inorganic chemists. Low-valent uranium species exhibit rich reductive chemistry and have been applied in the activation of small molecules and in the formation of uranium–ligand multiple bonds [1]. We have successfully isolated a well-defined U(III) complex, [ULI], supported by a bulky bis(aryloxide) cyclam ligand (L), that is capable of reducing azides and azobenzenes and form U-N multiple bond complexes with uranium in +4 to +6 oxidation states [2-4]. A *trans*-oxo-imido U(VI) complex was also obtained by activation of CO_2 [3]. Preliminary studies on the reduction of [ULI] with KC_8 in n-hexane led to a new compound, which reacted with benzene to form a arene-bridged diuranium(III) complex with a benzene dianion. This seems to be consistent with the formation of a formal U(II) complex. The reactivity of this "masked U(II)" compound with other substrates is under study and these results will be also discussed in this presentation.



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IL 14

MANGANESE(II/III)-WATER SOLUBLE FLUORINATED TETRAPYRROLIC MACROCYCLES AS POTENCIAL REDOX MRI PROBES

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Early diagnosis significantly enhances survival rates and facilitates simpler and more cost-effective treatment modalities. One promising approach to enhancing early detection involves the development of MRI contrast agents capable of detecting alterations in the cellular environment, typically indicative of disease, as healthy cells typically maintain highly regulated cellular environments. [1-3] Herein, we present the synthesis of fluorinated porphyrins [4,5] coordinated with manganese and their physical-chemical characterization. The choice of manganese as paramagnetic metal was devised to address the recent association of certain diseases, namely NSF, with the physiological presence of free gadolinium (the paramagnetic atom typically used in clinical contrast agents). Results obtained using various techniques including UV-Vis, ^{19}F and ^{1}H NMR and NMRD are also presented, demonstrating the potential of these porphyrins as potential $^{19}F/^{1}H$ MRI redox probes.

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IL 15

3D-PRINTED CERAMIC-LIKE RESIDUE-CONTAINING MATERIALS FOR WATER REMEDIATION

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Additive manufacturing (AM), or 3D-printing, is revolutionizing water treatment by enabling the creation of intricate structures with precise pore characteristics while minimizing waste. Inorganic polymers (IPs), or geopolymers, are ceramic-like, cost-effective, and eco-friendly materials obtained through alkaline activation of aluminosilicate sources (e.g., metakaolin). [1] IPs have gained attention for environmental applications, serving as efficient dyes [2] and metal sorbents [3] in polluted wastewater. Their environmental potential is amplified when incorporating residues such as bauxite residue, in line with circular economy. RM is a highly alkaline, generated in large amounts (>4 Bt globally) during alumina production.

This work reports the preparation of 3D-printed IPs with controlled porosity through direct ink writing (DIW), an extrusion-based 3D printing approach, with post-surface modification with synthesis and growth of carbon nanotubes (CNTs), produced by thermal chemical vapor deposition (TCVD) on metallic iron (derived from the hematite in the bauxite residue), followed by coating with TiO_2 by atomic layer deposition. The photocatalytic activity of the CNTs/TiO_2 composites im-mobilized in the 3D-printed porous was evaluated in the degradation of selected contaminants of emerging concern (CECs), using aqueous samples under near-visible and UV light irradiation.

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OC 7

HYBRIDIZATION OF MWCNTS AND NANO FERRITES FOR HIGH-PERFORMANCE ELECTROMAGNETIC SHIELDING TEXTILES

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Electromagnetic (EM) radiation has seen a significant rise, driven by the swift progress in electronic and telecommunication technologies. The increasing exposure to EM radiation poses health risks and threatens the functionality of electronic devices, pressing the demand for efficient EM shielding materials [1]. The hybridization of carbon-based materials with transition metal ferrites is a promising route for achieving enhanced EM shielding properties through complementary reflection and absorption mechanisms.

In this work, hybrid nanomaterials of multiwalled carbon nanotubes (MWCNTs) functionalized with magnetic ferrite nanoparticles ($A_xB_yC_zFe_2O_4$, where A, B, C = Zn(II), Ni(II) and/or Bi(III)) were fabricated and used to produce effective EM shielding textiles by coating. The morphological, structural, chemical and magnetic properties of the hybrids were examined by TEM, XRD, Raman spectroscopy, chemical analyses and magnetometry. The Ni- and Zn-containing hybrids led to functional textiles with shielding effectiveness (SE) above 30 dB in the frequency range of 5.85–18 GHz, corresponding to an excellent rating for general use textiles [2], and up to 2× higher SE normalized by coating thickness than the fabric coated with MWCNTs. These findings underscore the potentialities of hybrid MWCNT/ferrite materials to boost the SE, opening avenues for everyday clothing and military equipment.

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Acknowledgments: FCT/MCTES through national funds in the scope of the projects LA/P/0008/2020 (DOI: 10.54499/LA/P/0008/2020), UIDP/50006/2020 (DOI: 10.54499/UIDP/50006/2020), UIDB/04968/2020 (DOI: 10.54499/UIDB/04968/2020) and UIDP/04968/2020 (DOI: 10.54499/UIDP/04968/2020). CRP thanks FCT for funding through Individual Call to Scientific Employment Stimulus, ref. 2021.04120.CEECIND/CP1662/CT0008 (DOI: 10.54499/2021.04120.CEECIND/CP1662/CT0008).

OC 8

EFFECT OF INCLUSION OF $CpFe(CO)_2L$ COMPLEXES IN CUCURBIT[7]URIL ON THEIR CO-RELEASE PROFILES

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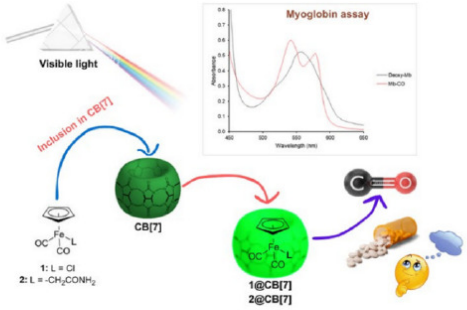
Besides its negative side, carbon monoxide (CO) has a therapeutic effect and it is in this context that CO-releasing molecules (CORMs) were developed. Most CORMs are constituted by metal-carbonyl groups, including iron (Fe), where $CpFe(CO)_2L$ derivatives are included[1], and these can release CO under light irradiation. In this work, inclusion compounds of cucurbit[7]uril with $CpFe(CO)_2Cl$ and $CpFe(CO)_2CH_2CONH_2$ were prepared to obtain products with improved pharmacokinetic properties and a controlled CO-release rate. The products were studied in relation to their CO-release profile through the myoglobin (Mb) assay, with absorption spectroscopy (Q-band region), under visible light irradiation.



According to the obtained results, the products show therapeutic potential as prodrugs for CO delivery.

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OC 9

PHOTOCATALYTIC CO_2 REDUCTION: MECHANISTIC DFT STUDY

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Photocatalytic reduction is an appealing tool to recycle continuously increasing amounts of CO_2, CO, CH_4 and other compounds, mainly due to its sustainability [1]. There are numerous examples of photocatalytic systems for CO_2 activation [2], however, many of them are developed employing precious metals making them costly. Additionally, poor mechanistic understanding of newly-developed transformations hinders their design and catalytic improvement. In this work, we focus on a dinuclear Co(II)Zn(II) cryptate (**Figure 1)** with demonstrated catalytic activity and explore the role of the catalyst in the reaction. Through *in silico* re-evaluation of the proposed mechanism of CO_2 reduction and conversion to CO [3,4], we propose a detailed reaction pathway, explain the formation of key intermediates and discuss the contributions of Co and Zn in the reaction.

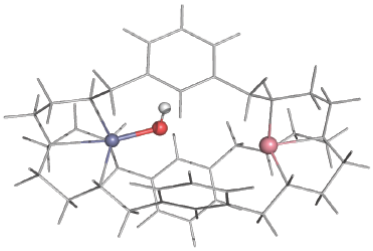

Figure 1. Dinuclear Co(II)Zn(II) cryptate used a a catalyst in the CO_2 activation, Zn(II) shown in purple, Co(II) – in pink.

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Acknowledgments:

This work was supported by FCT through project grant PTDC/QUI-QIN/0252/2021.

KN 10

DEVELOPMENT OF MAGNETIC AND LUMINESCENT IONIC SYSTEMS AS MRI CONTRAST AGENTS

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Neurodegenerative diseases are incurable and highly debilitating conditions marked by the progressive deterioration and death of neural tissues [1]. One major challenge associated with these pathologies is the late detection stage, resulting in less effective treatment options. In recent years, Magnetic Resonance Imaging (MRI) has garnered significant attention as a potential solution [2]. In this context, our work is focused in the development of biocompatible magnetic and luminescent ionic systems (ionic liquids and organic salts) composed by choline derivative cations and Mn(II), Gd(III), or Tb(III) anion complexes with potential applications as MRI contrast agents [3]. In parallel, some selected analogues of these compounds were functionalized in Mesoporous Silica Nanoparticles (MSNs) to evaluate the impact of this immobilization in their toxicity profile. Magnetic salts and MSN materials were characterized by spectroscopy, magnetic susceptibility; thermal properties and their toxicity [4]. Finally, relaxation studies were performed in order to evaluate their applicability as contrast agents for MRI technique (see Figure 1).

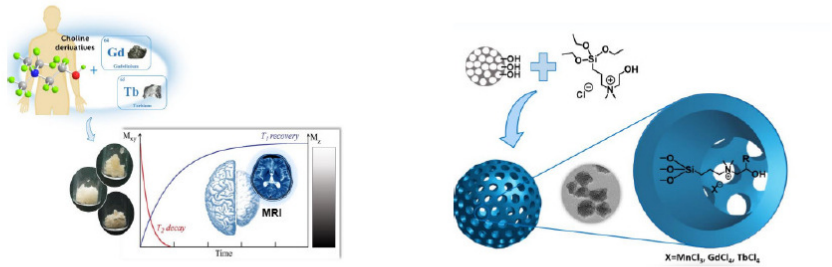

Figure 1 – Strategies for development of Magnetic Ionic and MSNs Systems for Imaging (MRI).

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OC 10

ON THE ACTIVITY OF Ru(II)/NATURAL PRODUCTS COMPLEXES AGAINST CANCER CELLS

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Lawsone (2-hydroxy-1,4-naphthoquinone) (NQ2) and lapachol (2-hydroxy-3-(3-methylbut-2-en-1-yl)naphthalene-1,4-dione) (NQ3) belong to the naphthoquinone class, which can be from natural or synthetic origin. These naphthoquinones exhibit antibacterial, antiparasitic, and anticancer biological properties, among others [1-2]. The complexes [Ru(NQ2)(dppen)(bipy)]PF6 and [Ru(NQ3)(dppen)(bipy)]PF6 (dppen = *cis*-1,2-bis(diphenylphosphino)ethylene; bipy = 2,2`-bipyridine (bipy) were synthesized by refluxing the precursor *cis*-[$RuCl_2$(dppen)(bipy)] complex, with the respective NQ2 and NQ3 ligands, in MeOH/DCM and presence of triethylamine. The obtained complexes were characterized by several techniques: molar conductivity, FTIR and UV/Vis spectroscopies, cyclic voltammetry, 1H, 13C, and 31P{1H} NMR, and monocrystal X-ray diffraction. Conductance measurements in dichloromethane indicated that the complexes are 1: 1 electrolytes, confirming the presence of PF_6^- counter ion in the compounds. Based on the $^{31}P\{^1H\}$ NMR spectra, it is possible to observe the expected doublets, confirming the presence of complexes of AX systems. The cytotoxicity assays (IC50, μM), *in vitro*, of the complexes, tested against breast human tumor cell lines (MDA-MB-231, MCF-7, and SKBR-3), were carried out by the MTT method. The complexes were also tested against the non-cancer cells MCF-10A. The selectivity indexes showed for the complexes are higher than those shown for the cisplatin, used as a positive control.

The complexes were shown to be more cytotoxic than the free ligands and than the widely used anticancer drug, cisplatin, under identical conditions, with much better selectivity indexes.

In addition, the effect of the complexes on the mechanism of cell death was analyzed.

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OC 11

DEVELOPMENT OF A NOVEL COORDINATION POLYMER COMPRISING Cu(II) AND CHRYSIN WITH ANTICANCER POTENTIAL

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The development of cisplatin marked a significant milestone in cancer treatment [1]. However, its effectiveness is often limited not only by its adverse side effects, but also by the development of drug resistance [2]. Flavonoid-based metallodrugs represent a strategy for the development of novel and more effective anticancer compounds. In particular chrysin, with important chelating sites, can synergistically interact with metal ions and enhance its anticancer or anti-inflammatory activities [3]. In this work, we were able to synthesize and structurally characterize the first flavonoid-based one-dimensional coordination polymer (CP). The compound was obtained by combining chrysin, 1,10-phenanthroline and Cu(II) ion employing three synthetic methodologies, namely the traditional heating reflux, solvothermal, and microwave-assisted synthesis. The CP was further characterized by powder/single crystal XRD, FTIR, FT-Raman and UV-vis spectroscopy, elemental and thermogravimetric analysis. Antitumoral studies against malignant human cell lines (Caco-2 and AsPC-1) proved that the CP reduces the viability and proliferation of Caco-2 cells, by about 70% and 100% at 10 μM, respectively, and reduces the viability of AsPC-1 cells by 18% at 5 μM, which indicates that it may be a promising candidate towards colorectal cancer therapy.

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OC 12

Unraveling a Class of Stretchable Cytochromes: Functional Mechanisms of PgcA from *Geobacter sulfurreducens*

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In Nature, the majority of triheme cytochromes contain heme groups fixed within a certain structural frame, which limits the distances at which these can transfer electrons, while providing other important functional features [1]. Recently, the AlphaFold model of PgcA, an extracellular cytochrome that contributes to Fe(III) oxides reduction in the electroactive bacterium *Geobacter sulfurreducens* [2], showed a fuzzy arrangement with three monoheme cytochrome domains linked by unstructured stretches. A similar arrangement was found in proteins from other organisms, revealing a new class of cytochromes, which we termed "microbial heme-tethered redox strings" [3].

The cytochrome domains of PgcA were produced and studied by complementary biophysical techniques. The domains are structurally homologous, but their heme groups show variable axial coordination and reduction potential values. Electron transfer experiments monitored by NMR and visible spectroscopies showed that the domains exchange electrons promiscuously, while reducing different electron acceptors. These results, which were reproducible in the full-length cytochrome, show that PgcA uses flexible low-complexity protein stretches to adopt multiple conformations that promote intra- and intermolecular electron transfer events at variable distances, providing functional advantages over other cytochromes.

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This work was supported by Fundação para a Ciência e a Tecnologia (FCT) through the following grants: SFRH/BD/145039/2019 and COVID/BD/153449/2023 (TMF), PTDC/BIA-BQM/4967/2020

IL 16

ELUCIDATING ELECTRON TRANSFER CHAINS IN THE ELECTROACTIVE *Geobacter sulfurreducens*

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Electroactive bacteria combine the oxidation of carbon substrates with an extracellular electron transfer (EET) process that discharges electrons to an electron acceptor outside the cell. This process involves electron transfer through consecutive redox proteins that efficiently connect the inner membrane to the cell exterior. In this study, we isolated and characterized the quinone-interacting membrane cytochrome *c* ImcH from *Geobacter sulfurreducens*, which is involved in the EET process to high redox potential acceptors. Spectroscopic and electrochemical studies show that ImcH hemes have low midpoint redox potentials, ranging from - 150 to -358 mV, and connect the oxidation of the quinol-pool to EET, transferring electrons to the highly abundant periplasmic cytochrome PpcA with higher affinity than to its homologues. Despite the larger number of hemes and transmembrane helices, the ImcH structural model has similarities with the NapC/NirT/NrfH superfamily, namely the presence of a quinone-binding site on the P-side of the membrane. In addition, the first heme, likely involved in the quinol oxidation, may have an unusual His/Gln coordination. Our work suggests that ImcH is electroneutral and transfers electrons and protons to the same side of the membrane, contributing to the maintenance of a proton motive force and playing a central role in recycling the menaquinone pool.

Acknowledgments:

This work was supported by Fundaçao para a Ciência e Tecnologia through project PTDC.07024.2022, R&D units MOSTMICRO-ITQB (UIDB/04612/2020 and UIDP/04612/2020) and associated laboratory LS4FUTURE (LA/P/0087/2020)

IL 17

BACTERIAL PEROXIDASES FROM PATHOGENIC BACTERIA

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The emergence of pathogenic bacterial strains that are resistant to most available antibiotics is a concern for public health. Thus, there is a need to develop new antimicrobial compounds but also to identify novel molecular systems that are unique to the bacteria and can be the target for these compounds. Under this scope, we are studying metalloenzymes that are responsible for the anaerobic respiration and detoxification of copper, mechanisms that are important for infection and contribute to its virulence.

In *Neisseria gonorrhoeae*, a bacterial peroxidase, detoxifies H_2O_2 and uses it as an alternative electron acceptor under anaerobic conditions.[1] This enzyme has been characterized using different spectroscopic and biophysical techniques.[2] The bacterial peroxidase has been structurally characterized in the active state and with azide, an inhibitor, bound to the active site.[2] In addition, we will show for the first time that this enzyme is also catalytically active towards peroxynitrite, with a high affinity.

In *Escherichia coli*, a quinol bacterial peroxidase, a non-classical bacterial peroxidase,[1] has been characterized biochemically and its kinetic parameters determined.[3] The role of the additional haem at the N-terminal has been assessed by mutating its axial ligand, which changes its reduction potential. This variant enzyme has lower catalytic activity, and it is less thermostable than the wild-type.[4] The model structure obtained using AlphaFold2 has been used to identify residues involved in the catalysis and electron transfer pathway.

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Acknowledgements:
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KN 11

CARBON MONOXIDE DEHYDROGENASE: AN INTERESTING ELECTROCATALYST FOR REVERSIBLE CO_2/CO INTERCONVERSION

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Carbon monoxide dehydrogenase (CODH) plays a central role in carbon metabolism in anaerobic microorganisms by reversibly catalyzing the reduction of CO_2 to CO. A remarkable feature of CODH is the presence of a mulitmetallic NiFeS active site, unique in biology. Given its complexity, its assembly and insertion into CODH requires an elaborated maturation pathway [1]. In the search for new sustainable catalytic devices, CODH are of great interest: they work under mild conditions, with earth-abundant metals and minimal overpotential. They are therefore good candidates to develop efficient bio-electrocatalytic devices, despite their oxygen-sensitivity and complexity. In order to achieve an efficient CO_2-to-CO conversion, we have developed a multidisciplinary approach, combining structural and biophysical studies, site-directed mutagenesis, custom electrode design and the use of ionic liquids. Recently, we optimized the production and purification of CODH from *Rhodospirillum rubrum* (RrCODH), which has been spectroscopically and structurally characterized [2]. We carried out a comparative study of RrCODH with the thermophilic CODH-II from *Carboxydothermus hydrogenoformans* (ChCODH-II) by electrochemistry. Selective CO_2/CO interconversion with maximum turnover frequencies of 150 s^{-1} for CO oxidation (1.5 mA cm^{-2} at 250 mV overpotential) and 420 s^{-1} for CO_2 reduction (4.2 mA cm^{-2} at 180 mV overpotential) are catalyzed by a recombinant CODH immobilized on modified MWCNT electrodes [], either in classic three-electrode cell or in specifically-designed CO_2/CO-diffusing electrodes

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IL 18

P_5W_{30} PRESENTS AGONIST-LIKE PROPERTIES ON PURINERGIC RECEPTORS

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The application of polyoxometalates (POMs) in chemistry and biological sciences has been rapidly growing [1]. POMs are a family of polyanionic metal-oxides formed by group V and VI metals, such as V, Mo and W. POMs have been shown to inhibit a significant number of ATP-binding proteins and to affect several cellular processes [1]. Purinergic receptors are activated by adenine nucleotides (ATP and ADP) and can be divided into ionotropic P2X and metabotropic P2Y receptors. Herein, we observed that P_5W_{30} induce the activation of P2Y receptors that affords about 80% contribution to the increase of cytosolic Ca^{2+} concentration, in immortalized mouse hippocampal neuronal HT-22 cells, whereas P2X contributes, at most, with 20%. ^{31}P-NMR measurements indicate that P_5W_{30} is stable in the medium. Once P_5W_{30} presents agonist like properties for purinergic P2 receptors, it might be useful for understanding several physiological and pathological processes.

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Acknowledgments:

This work was supported by Portuguese national funding from the Foundation for Science and Technology (FCT) through projects UIDB/04326/2020, UIDP/04326/2020, LA/P/0101/2020 (M.A.)

KN 12

WHAT HAPPENS WHEN BIOPHYSICS AND MICROBIOLOGY/GENETICS MEET?

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Cytochromes are electron transfer (ET) proteins essential in various biological systems, playing crucial roles in the respiratory chains of bacteria. They are particularly abundant in electrogenic microorganisms [1] and responsible for the efficient ET to the cells' exterior, a feature that opened new avenues to be explored for emerging biotechnological applications in bioremediation, microbial electrosynthesis, and bioenergy fields. However, to develop these applications, it is critical to unequivocally identify the redox partners and, hence, elucidate the ET along the respiratory paths. Genomic and proteomics studies have identified several *c*-type cytochromes from *Geobacter sulfurreducens* as key players in different cell compartments [2]. However, investigating direct ET events between proteins with identical features in nearly all spectroscopic techniques is extremely challenging. To overcome this, we developed an NMR-based methodology that explores the uniqueness of each protein heme resonances in both reduced and oxidized states [3]. By exploring this new methodology, and by keeping the proteins in their natural state, we were able to monitor direct ET reactions within the redox partners and to fully elucidate an extracellular electron transfer pathway within the intricate redox networks of *G. sulfurreducens* [4,5].

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Acknowledgments:

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PL 2

BIOSYNTHESIS AND FUNCTIONS OF THE NICKEL-PINCER NUCLEOTIDE (NPN) COFACTOR

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The nickel-pincer nucleotide (NPN) cofactor catalyzes the proton-coupled hydride-transfer reactions of selected racemases and epimerases [1, 2]. This novel organometallic molecule has a square-planar nickel atom that is tri-coordinated by a modified pyridinium mononucleotide, forming C-Ni and two S-Ni bonds [3]. Within the active site of enzyme, the nickel is additionally bound by a histidyl residue and in some cases the NPN cofactor is covalently tethered to a lysyl group. Biosynthesis of NPN is a three-step process [4]. LarB catalyzes C5-carboxylation and phosphoanhydride hydrolysis of nicotinic acid adenine dinucleotide to produce the dicarboxylated pyridine mononucleotide (P2CMN) [5]. LarE catalyzes an ATP-dependent sulfur insertion reaction that converts P2CMN into a species with two thiocarboxylic acids (P2TMN) [6]. LarC is a CTP-dependent nickel insertase or cyclometallase that transforms P2TMN into NPN [7, 8]. Recent developments in understanding the biosynthesis and utilization of the NPN cofactor will be described.

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Acknowledgments: This work was supported by the National Institutes of Health (GM128959).

Abstracts of
Poster Presentations

P 01

SYNTHESIS OF CYCLIC CARBONATES FROM CO_2 AND EPOXIDES USING TRANSITION METAL COMPLEX CATALYSTS

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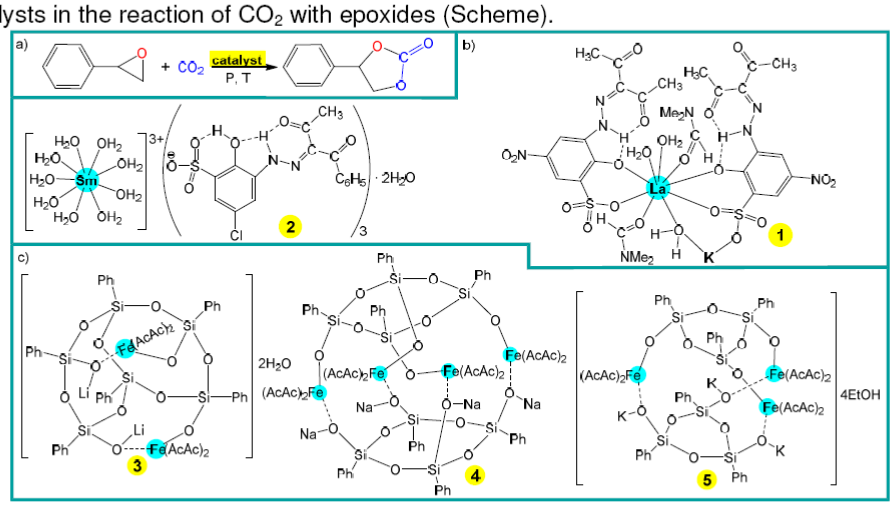
Cyclic carbonates have a variety of applications and commercial value for the synthesis of important industrial intermediates to produce polyurethanes and polycarbonates, as polar aprotic organic solvents for electrolytes in lithium-ion batteries and fuel additives, as well as fine chemicals for agricultural compounds and preparation of pharmaceuticals [1,2]. The most atom-economy efficient, greenest and cheapest method for the preparation of cyclic carbonates is the catalytic coupling of carbon dioxide with epoxides, which can take place on a large industrial scale (Scheme 1a, for the particular case of 2-phenyloxirane as a model epoxide) [1,2]. To date, many homogeneous and heterogeneous catalytic systems have already been developed, including organocatalysts, metal complex catalysts or their cooperations. Herein, we have applied several lanthanide [3] and iron(III) [4] complexes as catalysts in the reaction of CO_2 with epoxides (Scheme).



Scheme. Molecular structure of complexes used as catalysts (b,c) for the coupling reaction (a).

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P 02

THE ROLE OF ANION SYMMETRY IN THE MAGNETIC SWITCHING OF IRON(III) COMPLEXES

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The miniaturization of information storage devices and the search for new materials capable of supporting this evolution is one of the many contemporary challenges in materials science, here, spincrossover (SCO) based molecular materials rise as a promising field. The abrupt type of thermal transition, defined by its quick reversibility between the two different spin states can be exploited for molecular switch applications. However, identifying materials that exhibit such transitions is far from straightforward, but by tweaking the SCO system (e.g. changes in the ligand backbone or the anion used) we can achieve this switching ability, with the counter anion being of particular significance to our research. The interactions between magnetic center and anion play an important role in the cooperativity and the type of transition due to the different types of intermolecular bonds that can be formed (π-π stacking, hydrogen bonding and van der Waals interactions) [1]. By modifying these interactions, we can design multicomponent materials provided with novel and intriguing properties, ranging from conductive SCO materials [2] to compounds that exhibit magnetoelectric coupling through SCO [3]. In this work we have continued the search for novel multicomponent SCO compounds with abrupt thermal transition by coupling Fe(III) complexes with different ligands with symmetrical and asymmetrical bisdithiolate and chiral boron anions, capable of different types of interactions in the crystal structure.

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P 03

FORMATE AND NITRATE: HOW PROMISCUOUS IS FORMATE DEHYDROGENASE?

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Formate dehydrogenases (FDHs) are enzymes that catalyse the reversible two-electron interconversion of formate and CO_2 (eq. 1) [1,2].

$$CO_2 + 2e^- + H^+ \rightleftharpoons HCOO^- \quad (1)$$

The active site of the metal-dependent FDHs harbours one molybdenum (or one tungsten) ion coordinated by the *cis*-dithiolene group of two pyranopterin cofactor molecules, one terminal sulfido group and one sulfur or selenium atom from a cysteine or a selenocysteine residue (depending on the enzyme source) (Fig. 1). Remarkably, nitrate reductase, an enzyme that catalyses instead an oxygen-atom abstraction reaction (eq. 2), harbours an active site with the same structure and, in fact, some FDHs (for example the enzyme from *Rhodobacter capsulatus* [3]) were described to have nitrate reductase activity.

$$ONO_2^- + 2e^- + 2H^+ \rightleftharpoons NO_2^- + H_2O \quad (2)$$

In this communication, the ability of the *Desulfovibrio desulfuricans* FDH (a selenocysteine-containing FDH) to handle nitrate will be revisited.

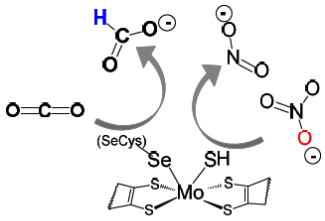

Fig. 1. Schematic representation of the metal active centre structure of a selenocysteine-containing FDH and the possibility of reactivity with both CO_2/formate and nitrate.

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P 04

SILVER-ANTIBIOTICS SYNERGY: UNVEILING THE POWER OF COORDINATION FRAMEWORKS FOR ENHANCED ACTIVITY

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In the context of global health, addressing the pressing issue of antimicrobial resistance (AMR) has become a paramount concern. In this pursuit, leveraging the synergistic effects between silver and commonly used antibiotics has emerged as a promising avenue. Following our research line on antibiotic coordination frameworks [1], this work investigates the innovative domain of silver-antibiotic coordination frameworks (Ag-ACFs), [2, 3] tapping into the potential of readily available antibiotics. Through systematic exploration, we uncover the dynamic interactions between silver ions and antibiotics, leading to the formation of robust antibiotic coordination frameworks that outperform conventional approaches, yielding novel forms with enhanced antimicrobial efficacy. Employing mechanochemistry [4] as a novel synthetic technique, Ag-ACFs present a sustainable and efficient pathway for combating microbial resistance, heralding transformative strides in antimicrobial therapy.

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P 05

DECIPHERING THE ROLE OF CYTOCHROME CBCA IN *GEOBACTER* EXTRACELLULAR ELECTRON TRANSFER PATHWAYS

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Geobacter sulfurreducens has a unique respiratory mechanism that allows the bacterium to survive in the absence of oxygen or other soluble electron acceptors, termed extracellular electron transfer (EET). This distinctive feature that involves the transfer of electrons through consecutive redox partners connecting the inner membrane to external electron acceptors has potential applications in several biotechnological areas, namely bioremediation, bioenergy production and microbial electrosynthesis [1]. One key player is the CbcBA complex. CbcBA is an inner membrane quinone cytochrome *c* oxidoreductase complex essential for electron transfer to extracellular electron acceptors with a low redox potential, as Fe(III) minerals or electrodes poised between –210 mV and –280 mV [2]. The complex is formed by CbcA, a cytochrome containing 7 *c*-type heme groups anchored to the membrane by a C-terminal α-helix, and CbcB, an integral membrane di-heme *b*-type cytochrome.

The periplasmic domain of CbcA was heterologously produced and characterized using complementary spectroscopic techniques at both the structural and functional levels. CbcA crystal structure was determined by the multi-wavelength anomalous dispersion (MAD) technique, and the crystals diffracted up to 1.9 Å resolution. Circular Dichroism was used for determination of the protein´s thermodynamic parameters. The apparent midpoint reduction potential of the protein was measured by UV-visible potentiometric redox titrations and is the most negative ever reported for *G. sulfurreducens'* inner-membrane oxidoreductases. Finally, Nuclear Magnetic Resonance was used to probe biomolecular interactions with putative periplasmic redox partners. The results obtained contribute to the understanding of the complex networks for EET in *Geobacter.*

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P 06

OXYGEN ACTIVATION THROUGH A BIOMIMETIC TUNGSTEN(IV) COMPLEX

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Biology offers a source of inspiration for transformations of special relevance namely the activation of small molecules like O_2, CO_2, N_2, etc. One such example is acetylene hydratase which contains a formally W(IV) active site containing aromatic 1,2-dithiolate ligands, a cysteine residue, and an aqua ligand. This active site is generally called metallopterin, or specifically in this case tungstopterin.

Recently,[1] a stoichiometric oxygen activation was reported by Mösch-Zanetti and co-workers wherein a formally W(IV) complex {$WO(6\text{-}MePyS)_2[P(CH_3)_3]$} (6-MePyS = 6-methylpyridine-2-thiolate) can effect a stoichiometric di-oxygen activation and cleavage. This complex is inspired by acetylene hydratase but instead of the aromatic dithiolate coordination, it contains a pyridine-thiolate as a ligand.

In this talk, a mechanistic proposal will be given for this reaction. A density functional protocol [DKH2-PBE0-D4/x2c-TZVP(x2c-SVP)] will be used as a quantitative tool to evaluate barrier heights and free energies of intermediates in order to put forward quantum chemically viable routes for this transformation.

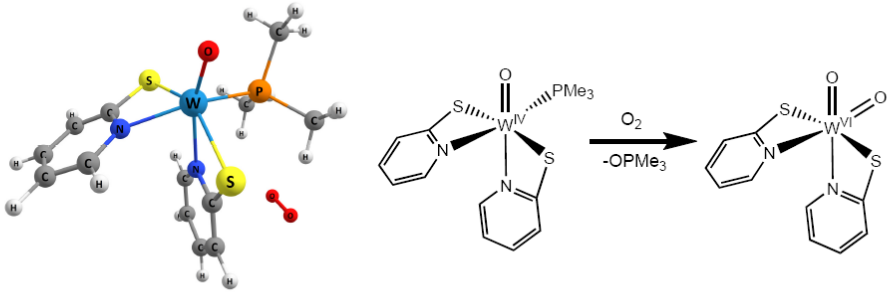

Figure 1 - Tungsten complex used for oxygen capture and activation.

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P 07

MINIATURIZED DYP PEROXIDASE-BASED BIOSENSOR FOR H_2O_2 DETECTION

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Dye-decolorizing peroxidases (DyPs) are heme-containing enzymes that couple the oxidation of structurally different substrates, such as phenolic and azo dyes and lignin-related compounds, with the reduction of H_2O_2 to water. DyPs are a promising target for biotechnological applications [1] due to broad substrate range, high purification yields and easy genetic engineering that facilitates production of variants with improved properties.

We have previously demonstrated that DyP from *Pseudomonas putida* MET94 (wt PpDyP) represents a great candidate for the construction of 3rd generation H_2O_2 biosensors [2], which are based on direct electron transfer between the immobilised enzyme and an electrode [3].

In this work, we developed a miniaturised, user-friendly H_2O_2 biosensor by immobilising wt PpDyP and its variant, engineered following *in silico* design to achieve higher stability, in screen-printed electrodes modified with biocompatible gold nanostructures. The electrocatalytic H_2O_2 reduction and the structural features of the adsorbed PpDyPs were evaluated using electrochemistry and Resonance Raman, respectively. Both biosensors displayed good sensitivity, dynamic response range, long-term stability and capacity to detect H_2O_2 in human serum and urine samples in open-air configuration, thus being appropriate for rapid on-site measurements.

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P 08

CO_2 PHOTOREDUCTION STUDIES WITH Fe(II) COMPLEXES

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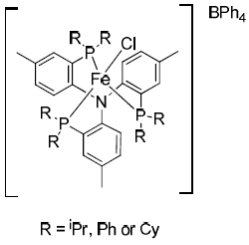
CO_2 is one of the primary greenhouse gases in Earth's atmosphere. There is currently a significant interest in developing strategies for capturing and converting it into chemicals with economical value. [1] Photoreduction is considered a promising method for CO_2 conversion operating at ambient pressure and temperature, transforming CO_2 into products such as CO, CH_4, and CH_3OH. [2] In CO_2 conversion, different types of molecular complexes can be used as catalysts based in different metal centres. [3] Here we present our preliminary results on the photoreduction of CO_2 to CO using visible light and Fe(II) catalysts.



R = ^{i}Pr, Ph or Cy

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

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P 09

CO_2 REDUCTION BY FORMATE DEHYDROGENASE: KINETIC CHARACTERISATION

Agnese Bertinelli*[1], Luis Pereira[1], André Amador[1], Isabel Moura, José J.G. Moura, Luisa B. Maia

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Formate dehydrogenases (FDH) are enzymes that catalyse the reversible two-electron interconversion of formate and CO_2 (eq. 1) [1,2]. The class of metal-dependent FDHs comprises only prokaryotic enzymes that hold different redox-active centres and whose active site harbours one molybdenum or one tungsten atom that mediates the formate oxidation/CO_2 reduction. Due to their ability to reduce CO_2, FDH have been the centre of intense research to develop innovative, "greener" and more efficient devices to convert the problematic CO_2 into added-value compounds [2,3].

$$CO_2 + 2e^- + H^+ \rightleftharpoons HCOO^- \qquad (1)$$

In this communication, the kinetic properties of the FDH from the sulfate reducing bacterium *Desulfovibrio desulfuricans* (Dd FDH) will be described.

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(read it here: https://docentes.fct.unl.pt/lblm/files/co2_utilisation-formatedehydrogenases-maia.pdf).

Acknowledgements:

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P 10

ANTIBACTERIAL ACTIVITY AND CO RELEASE STUDIES OF [(η³-Allyl)(CO)₂(X)(pyrazolylpyridine)] COMPLEXES

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In this work, two molybdenum dicarbonyl complexes with the general formula [(η³-Allyl)(CO)₂(X)(pypzH)] (X = Cl (**1**), Br (**2**); pypzH = 2-[3(5)-pyrazolyl]pyridine) were synthesized and characterized by elemental analysis, ATR FT-IR, FT-Raman and ^{1}H NMR spectroscopies. The CO release profile was investigated for both complexes using the standard UV-vis myoglobin assay. **1** and **2** act as CO-releasing molecules in the dark under physiological conditions (10 mM PBS, pH 7.4, 37 ºC). The antibacterial activity was evaluated for **1** and **2** using the broth microdilution method to determine the minimum bactericidal concentration (MBC) against *Escherichia coli* and methicillin-resistant *Staphylococcus aureus* (MRSA)[1]. Both complexes showed a strong antibacterial profile, reducing the viable cell count in a short period. Overall, these octahedral compounds could be an alternative to general antibiotics.

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P 11

SYNTHETIC MODELS OF NITRATED NEUROMELANIN: STRUCTURAL CHARACTERIZATION AND REACTIVITY STUDIES

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Parkinson's disease (PD) is a neurodegenerative condition related with mitochondrial dysfunction and oxidative and nitrative stress and characterized by progressive loss of dopaminergic neurons. Despite the PD arising mechanism has not been fully clarified yet, it has been established that PD is associated to high levels of neuromelanins (NMs), that are dark pigments found in dopaminergic neurons, formed by melanic, lipidic, protein, and inorganic moieties [1]. NM biosynthesis occurs in the neurons' cytosol as a consequence of accumulation of dopamine (DA), which can be oxidized and then polymerize [2]. NMs accumulate during aging and exhibit both neuroprotective and neurodegenerative effects [1]. Only a small amount of NM can be isolated from the human brain [1], so synthetic models of NM can be developed for research purposes.

In this study, we prepare synthetic NMs from DA and β-lactoglobulin (BLG), a whey and milk protein of ruminants. Moreover, we take into consideration the nitrative stress, which is related to PD. In fact, under pathological conditions, nitric oxide, a signaling molecule, can interact with reactive oxygen species to generate reactive nitrogen species [1].

We evaluated the effects on the melanization process of the nitration of either BLG, turning its Tyr residues into 3-nitrotyrosine, and DA, adding to the reaction mixture its nitrated derivate, 6-nitrodopamine. Synthetic NMs were prepared both in presence and absence of Fe(II) and characterized by HPLC-MS/MS, ^{1}H-NMR, and UV-vis analysis. The reactivity of the synthetic NMs was investigated as well, studying the DA catalytic oxidation in presence of Cu(II).

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Acknowledgments:
The authors acknowledge support from the Ministero dell'Università e della Ricerca (MUR) and the University of Pavia through the program "Dipartimenti di Eccellenza 2023–2027".

P 12

CATALYTIC AND ANTICANCER ACTIVITY OF GOLD(I) COMPLEXES BEARING PTA AND DERIVED LIGANDS

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The neutral gold(I) complexes [AuCl(L)] [where L = 1,3,5-triaza-7-phosphaadamantane, PTA (**1**); 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane, DAPTA (**2**); or 1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane-3,7-diylbisphenylmethanone, DBPTA (**3**)] and the cationic complexes [AuCl(L)]X [where L is either PTA-CH_2-C_6H_4-*p*-COOH and X = Br (**4**) or PTA-CH_2-C_6H_3-*p*-OH-*m*-CHO and X = Cl (**5**)] were synthesized and tested as homogeneous and heterogenized catalysts in the peroxidative oxidation of cyclohexane in a CH_3CN/H_2O medium under mild conditions. Their cytotoxicity towards a selection of ovarian, lung and colon cancer cell lines was also evaluated.

Acknowledgments:

Centro de Química Estrutural (CQE) acknowledges the financial support of Fundação para a Ciência e Tecnologia (FCT) (projects UIDB/00100/2020, UIDP/00100/2020 and LA/P/0056/2020). FCT/MCTES is also acknowledged for projects UIDB/50006/2020 and UIDP/50006/2020 (LAQV) and bilateral project Portugal-Germany 5625-DRI-DAAD-2020/21. As far as concerned the biological part, this

P 13

COPPER(II) COORDINATION POLYMERS DRIVEN BY 3,4-PYRIDINEDICARBOXYLIC ACID: SYNTHESIS, CRYSTAL STRUCTURES, AND CATALYTIC OXIDATION OF α-PINENE

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Terpenes are abundant natural products and useful substrates for the synthesis of diverse value-added molecules for cosmetic, fragrance, and pharma industry. Although various catalytic systems have been developed for the oxidation of terpenes, these catalysts often incorporate expensive metals and are unrecoverable in many cases. Hence, there is a demand for more efficient and sustainable catalysts.

In this work, two new isostructural 2D coordination polymers were synthesized via self-assembly method and fully characterized. The products were formulated as $\{[Cu_2(pdc)_2(H_2mdea)(H_2O)_2]\cdot 2H_2O\}_n$ (Cu-mdea) and $\{[Cu_2(pdc)_2(H_3tipa)(H_2O)_2]\cdot 4H_2O\}_n$ (Cu-tipa) {H_2pdc, 3,4-pyridinedicarboxylic acid; H_2mdea, methyldiethanolamine; H_3tipa, triisopropanolamine}. Their 2D structures revealed 4-connected nets with the **sql** topology type made by 5-coordinated copper(II) units $\{CuO_3N_2\}$ and μ_3-pdc^{2-} linkers (Figure 1). Both compounds were explored as heterogeneous catalysts for the oxidation of α-pinene into value-added C−H functionalized products, namely 4-*tert*-butilperoxy-2-pinene and verbenone. Catalytic studies were carried out in a small batch reactor (2 mL) at atmospheric pressure with *tert*-butylhydroperoxide as oxidant. Both Cu-mdea and Cu-tipa catalyze the allylic α-pinene oxidation and display similar efficiency. Under optimized conditions (~93% of α-pinene conversion), 4-*tert*-butylperoxy-2-pinene (42%) and verbenone (25%) were obtained as major products. PXRD and FTIR analyses revealed that both catalysts are stable and can be recovered after catalytic tests. These findings highlight the potential of these coordination polymers as catalysts for the oxidation of α-pinene. Further tests and optimization studies are in progress.

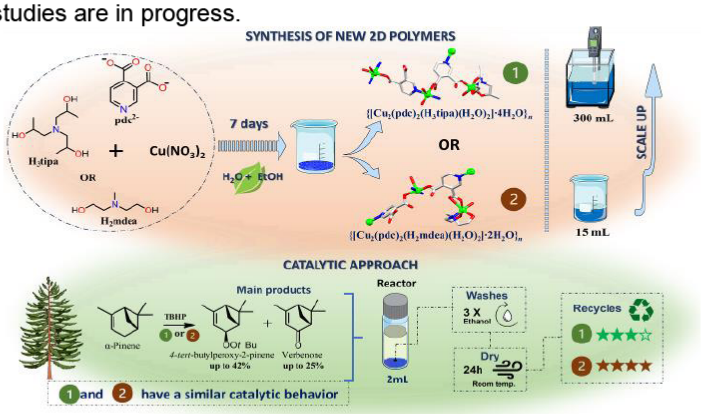

Figure 1. Synthesis of Cu-mdea and Cu-tipa and their catalytic application.

Acknowledgments: This work was supported by the Programme MARIE CURIE of the European Union (grant 1018.P.05917.1.01) CHAIR 860762 and the FCT projects UIDB/00100/2020, PTDC/QUI-QIN/3898/2020, CEECIND/03708/2017, and UIDP/00100/2020.

P 14

ENHANCING PHOTOCATALYTIC PERFORMANCE OF TITANATE NANOWIRES THROUGH MODIFICATION WITH CARBON DOTS

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Climate change and environmental degradation pose significant threats to the sustainability of humanity. In the *European Green Deal*, the European Commission presents ambitious actions and strategies to preserve biodiversity in aquatic systems and to mitigate particularly harmful pollution from microplastics to pharmaceuticals. In this context, advanced inorganic semiconductor nanomaterials with enhanced optical and photocatalytic properties have been proposed for the photodegradation of organic pollutants, specifically pharmaceuticals and personal care products. [1]

In this study, hybrid titanate nanowires (TNWs) modified with carbon dots (C-dots) were synthesized via a hydrothermal method. C-dots were produced using wastewater form a cork industry as carbon source, promoting a more circular economy. Different hybrid nanoparticles were obtained using either a one-pot or step-by-step procedure. Structural, morphological, and optical properties of the produced samples were analysed using XRD, TEM, UV-Vis diffuse reflectance, and photoluminescence spectroscopies. As intended, the hybrid nanomaterials (C-dots/TNWs) exhibited extended light absorption into the red spectrum compared to pristine TNWs, making them more promising for visible light photo-assisted applications. C-dots/TNWs samples were evaluated in the photodegradation of a model pollutant, demonstrating enhanced photocatalytic activity compared to pristine TNWs.

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SENSING COPPER(II) AND MERCURY(II) IONS BY A SOLVENT MODULATED EMISSION SULFUR BRIDGED DANSYL DYES AS MOLECULAR PROBES

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Five novel bis-dansyl derivatives featuring a sulfur bridge have been successfully synthesized, fully characterized, and subjected to photophysical analysis both in solution and in the solid state. In recent years, our research team has been dedicated to the development of fluorescent organic and inorganic dyes capable of effectively responding to various factors such as metal ions, temperature fluctuations, and solvent conditions. [1-4] This communication focuses on the investigation of compounds L1 to L5 across different solvent environments to explore their solvatochromic behavior in both ground and excited states. These compounds exhibit a color range spanning from blue to yellow.

Given the intrinsic properties of these compounds, efforts were directed towards understanding their potential utility in environmental remediation, leading to investigations into metal ion sensing capabilities. Remarkably, all compounds except L5 demonstrated high sensitivity towards Cu(II) and Hg(II) ions, showcasing extensive modulation of their emission characteristics in response. This study underscores the multifaceted properties of dansyl derivatives and their promising applications in biomedicine and environmental sciences.

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Acknowledgments:
This work was supported by the Associate Laboratory for Green Chemistry – LAQV which is financed by national funds from FCT/MCTES (UIDB/50006/2020 and UIDP/50006/2020) as well as the Scientific Society PROTEOMASS (Portugal) for funding support (General Funding 2023-2024 Grant)s. F.D. thanks to FCT/MEC (Portugal) for his doctoral grant 2021.05161.BD. E.O. thanks FCT/MEC (Portugal) for the individual contract, CEECIND/00648/2017.

P 16

ADVANCES IN THE STUDY OF METALLOHELICATES VIA CLUSTER HELICATES WITH BIOLOGICAL PROPERTIES

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Helicates stand out as versatile metal-based platforms with numerous applications, particularly in biomedicine [1]. In 2005, our research group pioneered cluster helicates, a novel type of metallo-helicates achieved through an electrochemical approach. Since then, numerous examples of cluster helicates have been reported [2]. To achieved this, we designed a thiosemicarbazone ligand, H_2L, with flexible bidentate [NS] domains separated by a rigid aromatic spacer, meeting the requirements for helical structure assembly. Employing an electrochemical methodology, we successfully synthesized a tetranuclear Ag^+ cluster helicate (Figure 1). Further investigations into the biological activity of this silver cluster helicate revealed promising potential in the field of biomedicine.

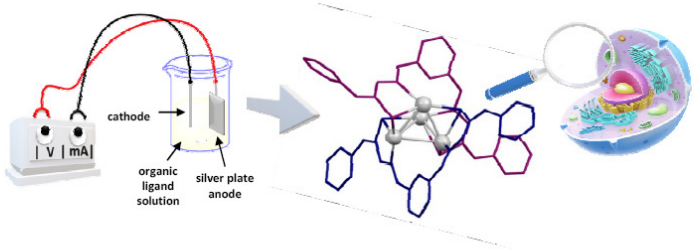

Figure 1. Synthesis of the silver(I) cluster helicate $[Ag_4(L)_2]\cdot 4DMSO\cdot 0.3H_2O$.

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This work was supported by the following FEDER co-funded grants. From Consellería de Cultura, Educación e Ordenación Universitaria, Xunta de Galicia GRC GI-1584 (ED431C 2023/02), MetalBIONetwork (ED431D2017/01). From Ministerio de Ciencia e Innovación, Project PID2021-127531NB-I00 (AEI/10.13039/501100011033/ FEDER, UE).

P 17

REDUCTIVE DEPOLYMERIZATION OF PLASTIC WASTE CATALYZED BY EARTH-ABUNDANT METAL CATALYSTS

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Plastic waste is being generated at alarming rates, posing as a major environmental issue and human health hazard. To combat this problem, the scientific community has dedicated efforts to developing new methodologies for converting plastic waste into value-added compounds. In recent years, reductive depolymerization has emerged as an effective protocol for converting plastic waste into valuable compounds and raw materials for industry.[1]

In continuation of our work,[2-7] in this communication we describe the reductive depolymerization of polyester and polycarbonate plastic waste into value-added compounds catalyzed by Earth-abundant catalysts (Figure 1).

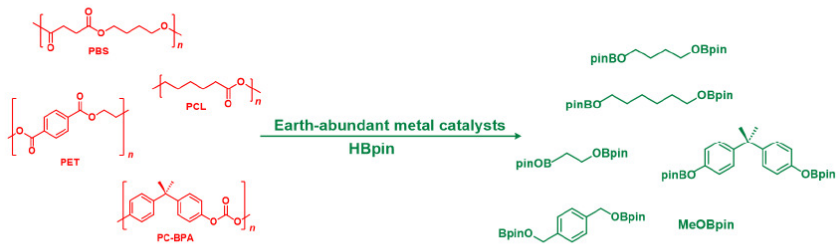

Figure 1 – Reductive depolymerization of plastic waste using Earth-abundant metal catalysts.

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P 18

ENHANCED ANTIDIABETIC EFFECT OF CHRYSIN BY COMPLEXATION WITH Cu(II) AND Co(II) IONS

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Diabetes mellitus is a high-prevalence chronic metabolic disease associated with severe health risks. Given its growing incidence, the development of innovative therapeutic agents is imperative [1]. Chrysin naturally possesses antidiabetic properties [2], that we hypothesized could be further enhanced by its complexation with metal ions, taking advantage of the known therapeutic potential of coordination compounds [3]. Herein we report the synthesis, characterization, and biological evaluation of Cu(II)- and Co(II)-chrysin metal complexes, prepared via solvothermal methodology. Techniques including XRD, TGA, FTIR and UV-VIS spectroscopy were employed to assess their structural integrity and composition. Biological assays on Caco-2 and Hep-G2 cell lines revealed promising antidiabetic potential with minimal cytotoxicity. Specifically, assessment of glucose and fructose cellular uptake demonstrated the capacity of the compounds to significantly reduce the intestinal absorption of both sugars and to increase the hepatic uptake of glucose. Currently, studies are being performed to assess their impact on the genes involved in glucose and lipid metabolism, as well as their effects at the adipocyte level. Overall, our findings suggest that the antidiabetic effect of chrysin can be potentiated through coordination with Cu(II) and Co(II) ions.

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CO_2 CONVERSION WITH SUPRAMOLECULAR STRUCTURES

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Over the last few decades, the greenhouse effect that we often hear about and that it is crucial to our survival, has become a risk. Carbon dioxide is one of the gases that most contributes to this effect. Consequently, many methods for converting CO_2 have been explored, including the electrochemical reduction of CO_2 (eCO_2RR). Metal-Organic Frameworks (MOFs) are porous and crystalline 3D structures made of metals and organic ligands, that have shown to be effective catalysts for the eCO_2RR, yielding useful chemical compounds, such as hydrocarbons and alcohols [1]. This work is focused on the synthesis of various MOFs that contain different metals, including copper, iron, nickel, and zirconium, and their catalytic activity regarding the eCO_2RR. Both the direct (cathodic deposition) and indirect (electrophoretic deposition) synthesis methods have been investigated, as well as the efficiency of the eCO_2RR for the MOFs Cu-MOF-74, Cu-ade, Fe-MIL-101 and NH_2-UiO-66.

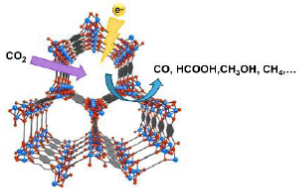

Figure 1. Scheme of the structure of a MOF (Cu-MOF-74) and several possible products of the eCO_2RR. Adapted from [2].

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CQE is a Research Unit funded by Fundação para a Ciência e a Tecnologia (FCT) through projects UIDB/00100/2020 and UIDP/00100/2020. IMS is an Associate Laboratory funded by FCT through project LA/P/0056/2020. We are grateful to FCT for Project PTDC/QUI-QIN/0252/2021. S.R. acknowledges FTC for financial support (2020.02134.CEECIND). P.N.M. acknowledges FTC for financial support (CEECIND/00509/2017).

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RECOVERING OF THE RARE EARTH ELEMENTS Y AND EU FROM PHOSPHORS

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Rare earth elements (REEs) are essential components in numerous specialized applications because of their unique optical and magnetic characteristics. REE are considered critical materials mainly due to the high supply risk [1]. Mining REE ores causes severe environmental impacts, including release of radioactive dust, acidification of soil and water courses, photochemical oxidation, ozone layer depletion, increasing eutrophication potential, and destruction of ecosystems. Further, mining leads to debilitating health conditions that affects the exposed miners and nearby villages [2]. Presently, only a small fraction of these elements is recycled [3]. Recover and reuse of these elements is a critical issue whose implementation will help stabilizing prices and reduce environmental damages.

Y-Eu-based phosphors are crucial components in various electrical and electronic devices, including televisions, and other monitors, fluorescent lamps and LEDs. This study evaluates the recovery of Y and Eu in a REE-rich phosphor fine size fraction using acid leaching (H_2SO_4 or HNO_3) in the presence of H_2O_2 as co-lixiviant. Experimental design and response surface methodology were applied to model and optimize the leaching process. Several combinations between solid-liquid ratio, temperature and leaching acid were evaluated. Results showed that the recovery of REE increases with temperature and solid/liquid ratio, being in general above 70%, and that Y and Eu show a similar profile, as expected. Leaching at 25 ºC increases selectivity towards zinc, which could assist further downstream processing. The leaching kinetics was modelled suggesting that at lower temperature (25ºC), for Zn, Y and Eu, the chemical reaction is the rate-limiting step, whereas at 40ºC and 55ºC ash diffusion plays an important role. Further, results revealed that Zn leaching is more temperature sensitive than the REEs. Results obtained provided as well important data to the development of a pilot unit for the recovery of REE from waste phosphors.

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Acknowledgments:

This work was supported by Agência Nacional de Inovação Portugal (ANI) through project PT2020 nº 33576. Filipe Figueiredo grateful acknowledges support from ANI for the individual granted fellowship.

P 21

Deciphering azo dye binding: Probing exoelectrogenic cytochrome-mediated bioremediation pathways

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Wastewater containing azo dyes remains a prominent environmental concern in developing countries, particularly those hosting extensive textile industries. Despite the affordability of azo dyes commonly used for coloring textile fibers, their poor fixation characteristics result in a substantial presence of these dyes in the effluent. The large water requirements of textile processing contribute to the generation of significant volumes of wastewater contaminated with azo dyes. The direct release of this wastewater into water bodies poses immediate threats to both human and aquatic life due to the considerable toxicity, mutagenicity, and carcinogenicity of these dyes.

Addressing the challenge of eliminating azo dyes from wastewater is crucial, and various measures have been implemented to mitigate their environmental impact. Presently, physicochemical methods used for dye treatment are not highly cost-effective. Bioremediation processes have emerged as a viable alternative due to their cost-effectiveness and eco-friendliness. However, the stable and less biodegradable nature of azo dyes, characterized by an aromatic molecular structure and electron-deficient azo linkage, presents a significant hurdle. Additionally, the presence of polar groups, such as sulfonate groups, further complicates the bioprocess by hindering the passage of these dyes through cell membranes.

Biodegradation of azo dyes involves a two-step process: bio-reduction into amines under anaerobic conditions and subsequent oxidation and degradation under aerobic conditions. Microorganisms capable of extracellular electron transfer (EET), particularly exoelectrogen organisms like *Shewanella oneidensis* and *Geobacter sulfurreducens*, are promising candidates for azo dye biodegradation. These organisms, with their versatile multiheme cytochrome-based respiratory pathways, are also utilized in bioelectrochemical systems (BESs) as self-regenerating catalysts producing electrical current or valuable compounds.

Studies have shown that outer-membrane multiheme cytochromes (OMCs) involved in EET processes in BESs also participate in the reduction of azo dyes. Therefore, exoelectrogens with efficient EET capacity are likely to be effective azo dye reducers. However, relying solely on colorimetric methods, such as the reduction of methyl orange (MO), to study and optimize EET in these microorganisms may lead to misinterpretations. These methods, while suitable for direct EET to azo dyes, may not accurately reflect the optimization of BESs, potentially perpetuating studies with exoelectrogen variants biased towards azo dye reduction.

This work seeks to elucidate the binding mechanism of MO with two crucial EET OMCs (OmcA and MtrC) belonging to the Mtr (metal-reducing) respiratory pathway of *S. oneidensis*. For this purpose, binding studies were performed in order to obtain binding constants and epitope maps and also theoretical calculations were done to find possible binding pockets for MO. The data obtained was compared to what is known for the native extracellular substrates of these OMCs.

P 22

CHALCOGEN BONDING IN THE DECORATION OF [1,2,5]SELENADIAZOLE DYES

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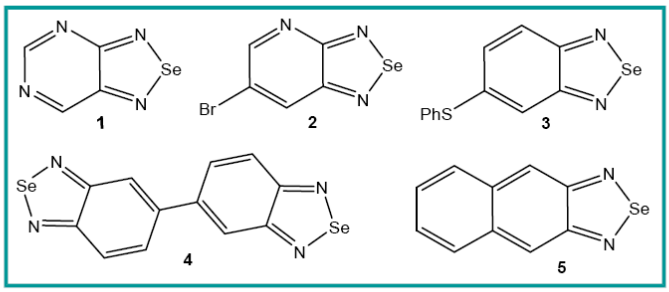
Organochalcogens have attracted much interest owing to their applications as photo- and semiconducting materials, substrates in organic synthesis, sensors, pharmaceuticals (*e.g.,* ebselen), etc. The functional properties as well as expected performances of these materials can be effectively tuned by the decoration of synthons or tectons by π-conjugated system or noncovalent bond donor and acceptor substituents. Due to the involvement in intermolecular chalcogen bonding a [1,2,5]selenadiazole synthon has widely used in the design of new materials [1-3]. Herein, we report a series of [1,2,5]selenadiazoles (Scheme), *i,e.,* [1,2,5]selenadiazolo[3,4-d]pyrimidine (**1**), 6-bromo-[1,2,5]selenadiazolo[3,4-b]pyridine (**2**), 5-(phenylthio)benzo[c][1,2,5]selenadiazole (**3**), 5,5'-bibenzo[c][1,2,5]selenadiazole (**4**) and naphtho[2,3-c][1,2,5]selenadiazole (**5**), which were synthesized *via* the reaction of selenium dioxide with the corresponding diamines in dichloromethane, and characterized by spectroscopic methods.



Scheme. [1,2,5]selenadiazoles.

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P 23

UNRAVELLING THE BIOLOGICAL POTENTIAL OF TWO NOVEL FLAVONOID-BASED Zn(II) COMPLEXES

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The healthcare system is currently facing major challenges, such as the increase in antibiotic resistance. In this scenario, there is an urgent need for the development of innovative and efficient therapeutic agents. Metal complexes could represent a good alternative as they can exhibit 3D structures, mechanisms of action that cannot be achieved with organic molecules alone, as well as unique electronic, magnetic, and spectroscopic properties [1]. In particular, flavonoid-based metal complexes represent a promising class of inorganic compounds as they exhibit many interesting properties, especially in terms of their biological activity, which includes antioxidant and antimicrobial effects that are often stronger than those of the parent flavonoids [2]. In this work, we developed two novel flavonoid-based metal complexes, specifically zinc(II) complexes with quercetin or morin and the N-donor ligand 1,10-phenanthroline. These complexes were synthesized by two less explored methodologies, namely solvothermal and microwave-assisted synthesis. The complexes have been structurally characterized and their biological potential is currently being investigated regarding their antioxidant activity and antibacterial effect.

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P 24

UNVEILING THE POTENTIAL OF MOFs: FROM CRYSTALLINE SPONGES TO SUSTAINABLE HYDROGEN PRODUCTION

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Single-crystal X-ray diffraction (SCXRD) is essential in chemistry, but it relies on high-quality single crystals, which can be difficult to obtain. In 2013, Fujita and co-workers introduced the Crystalline Sponge Method (CSM) to determine the structures of non-crystalline compounds using SCXRD [1]. In CSM, guest molecules are encapsulated in a crystalline metal-organic framework (MOF) for analysis. Fujita's most versatile crystalline sponge has limitations that currently hinder its wider applicability and efficiency. On the other hand, due to their intrinsic properties, MOFs are also being used as photocatalysts to produce hydrogen from the photocatalytic splitting of water.

Herein, we report the development of Zn-MOFs for applications as crystalline sponges for structure elucidation of non-crystalline samples by SCXRD and as photocatalysts for H_2 production. All synthesised materials were characterised by infrared and diffuse reflectance spectroscopy and single crystal X-ray diffraction.

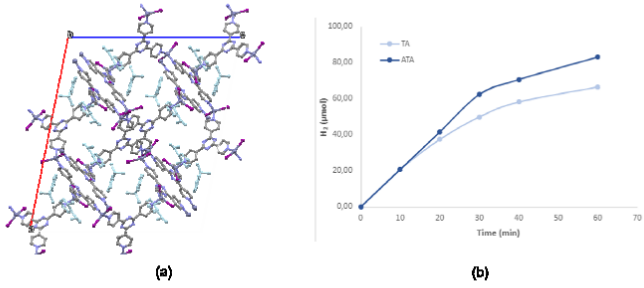

Figure 1. (a) Determination of the molecular structure of *o*-iPr-aniline using the CSM. (b) Production of H_2 from water splitting, using a 300 W Xe lamp and $[Zn(tpt)_2(L)I]_n$ (L=TA, ATA) as photocatalyst.

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P 25

CATALYTIC OXIDATIVE DESULFURIZATION OF FUELS: A GREEN WAY TO STOP AIR POLLUTION

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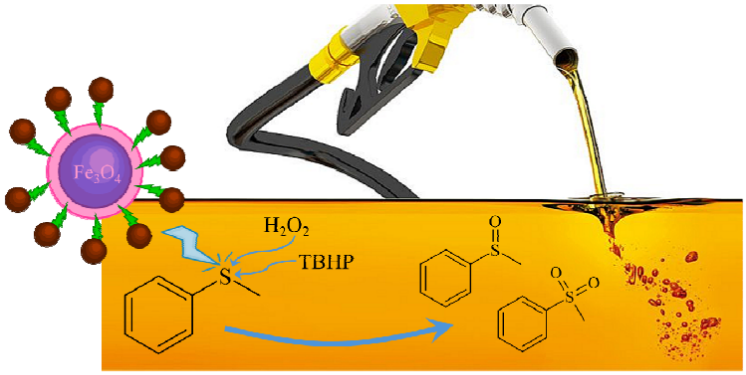
Air pollution has always been a problem due to its consequences on human health and the environment. The combustion of fossil fuels is its main source because it releases sulfur oxides from the sulfur compounds present in the fuel, such as thiophene and derivatives, which mainly causes acid rains, cardiovascular and asthmatic diseases, and cancer. It is imperative to remove these compounds and one way to do that is to submit the fuels to a green process known as oxidative desulfurization (ODS) using heterogeneous catalysts to promote the reaction. [1] The present work aimed the use of MoO_3 nanoparticles anchored to Fe_3O_4 magnetic nanoparticles as a catalyst to the ODS of methyl phenyl sulfide, diphenyl sulfide, dibenzothiophene and 1-benzothiophene, using TBHP and H_2O_2 as oxidants. The results obtained turned out to be very promising, yielding sulfoxides and sulfones which are often used in pharmaceuticals, organic chemistry, agrochemicals, etc. A reaction with a mixture of all 4 substrates was also successfully performed, opening a door to test this system with real fuel samples.



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P 26

NEW COPPER(II)-BINDING AZOLES AS POTENTIAL ANTIFUNGALS

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Invasive fungal infections are a rising problem due to the growing resistance developed by pathogenic fungi to the limited number of drugs and drug classes currently available, and also to the sluggish antifungal drug pipeline. Azole compounds are the most used antifungal drug class, working by inhibiting the biosynthesis of ergosterol that is an essential component of fungal cell membranes [1]. Interestingly, the recent discovery of a synergistic antifungal effect between several antifungal azoles and copper(II) has raised the interest in copper-binding azole compounds [2]. In this regard, we have previously found that a metal-binding azole is able to show antifungal activity through different mechanisms [3].

We set out to develop a family of new azole compounds containing different copper(II)-binding functions in order to explore their potential as antifungal agents. Here, we present the synthesis of a range of target compounds based on three related azole scaffolds. We have studied the copper(II)-binding ability of these azole compounds as well as their antifungal activity towards *Candida glabrata*, an opportunistic pathogen.

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P 27

STRUCTURAL RELEVANCE OF THE INTERACTION BETWEEN *E.COLI* YTFE WITH *E.COLI* ISC PROTEINS

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When a pathogen invades the host, the cells of the innate immune system produce Reactive Oxygen Species (ROS) and Reactive Nitrogen Species (RNS) which damage several pathogens components including the Fe-S cluster containing proteins. To survive in this harsh condition, pathogens have developed detoxifying and repair proteins [1].

Repair of iron centre (RIC) protein was first found in E. coli [2]. But these proteins are widely spread in the bacterial and in some eukaryotic pathogens [3][4]. *Escherichia coli* YtfE contains a di-iron centre with the capacity to donor iron to the ISC system for the assembly of the novo Fe-S clusters, restoring the activity of the damaged Fe-S proteins [5][6][7].

Since we previously showed that YtfE interacts with IscU and IscS [8], we are now charactering structurally the formation of the complexes. We isolated the complex YtfE- IscU (ratio 1:1), which was analysed by small angle X-ray scattering (SAXS) and NMR methodologies. These results are herein presented and discussed.

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P 28

CHEMOSELECTIVE OXIDATION OF PRIMARY ALCOHOLS CATALYSED BY WELL-DEFINED COPPER(I) CATALYSTS

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The chemoselective and regioselective oxidation of primary alcohols to yield only aldehydes is a reaction of significant interest in organic chemistry. Primary alcohols, abundant in biomass, can be used as renewable starting materials. However, current methods use harsh conditions and toxic compounds which are not ideal [1]. This study aims to find a sustainable and cost-effective catalytic system for the oxidation reaction under mild conditions and with high selectivity. Built upon the groundbreaking research of S. Stahl and co-workers, our research group has discovered a new family of copper(I) complexes, which may serve as catalysts for the aerobic oxidation of benzyl alcohol, bearing diazabutadiene (DAB) and bis(imino) acenaphthene (BIAN) as ligands (**Figure 1**). The synthesized compounds allowed us to study the impact of the counter-ion (OTf^- and BF_4^-) and the effect of the chelating solvents on the stability and activity of the complex.

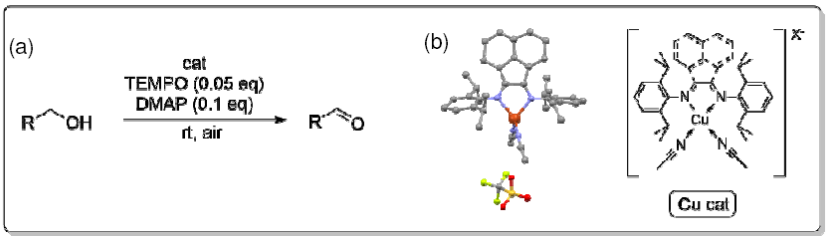

Figure 1. (a) – general conditions for the oxidation reaction. (b) – X-ray image by Mercury (left) and structure representation (right).

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P 29

METAL-DEPENDENT FORMATE DEHYDROGENASES: HOW DO THEY CATALYSE THE REDUCTION OF CO_2?

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Biocatalysis is attracting the attention of scientists and engineers eager to develop greener, more sustainable, processes to maintain our modern lifestyle without further destroying the Planet. Enzymes operate under truly green conditions, at ambient temperature and pressure, in water, close to neutral pH; they offer exceptional substrate and product selectivities and specificities, coupled with high specific activity (only a very low percentage of catalyst/enzyme is needed) and an excellent kinetic performance. Hence, enzymes can teach us important chemical lessons to design improved artificial, bio or hybrid catalytic systems for CO_2 activation and conversion into added-value compounds.

In this communication, the reaction mechanism of metal-dependent formate dehydrogenase will be reviewed, highlighting the different lines of evidence that support the metal-sulfido-dependent, hydride transfer mechanism of CO_2 and formate interconversion.

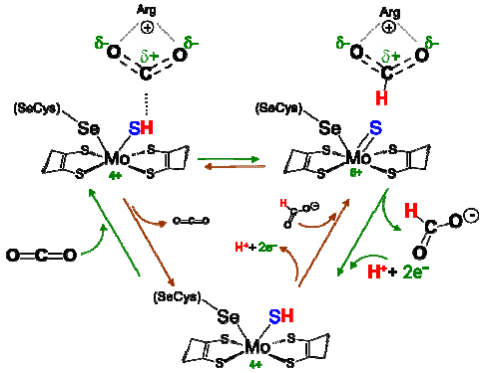

Figure 1: Proposed FDH reaction mechanism.

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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 (DOI: 10.54499/UIDB/50006/2020) and UIDP/50006/2020 (DOI: 10.54499/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-Ind Program Contract.

P 30

FORGING NEW PATHS FOR THE TREATMENT OF INVASIVE INFECTIONS CAUSED BY FUNGI: THE POTENTIAL OF A NICKEL N-HETEROCYCLIC BISCARBENE COMPLEX

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Fungal infections range from superficial skin rashes to health threatening invasive infections. *Candida*, an opportunistic yeast, is the leading cause of invasive fungal infections in hospitals. These infections are associated with high rates of morbidity and mortality, and have a strong impact on both patients and healthcare systems. The lack of swift diagnosis and effective therapeutics is acknowledged to greatly contribute to their severity. The situation has worsened over the last few years due to the emergence of *Candida* spp that are resistant to current antifungals. This scenario has prompted the intensive search for alternative antifungals. In this work, we assessed the efficacy and mode of action of a nickel N-heterocyclic biscarbene complex, against medically relevant fungi. The complex exhibited high selectivity for *Candida glabrata*, one of the most prevalent causes of hospital acquired bloodstream fungal infections worldwide. Using ICP-AES, we detected intracellular metal accumulation, suggesting that the compound can enter the cells. We evaluated its impact on established antifungal targets (ergosterol biosynthesis and cell wall) and their potential to induce oxidative damage. Our results clearly indicate a new mode of action of this drug, which is currently under investigation. Notably, the nickel complex showed a synergistic interaction with fluconazole, transforming this widely used fungistatic drug into a fungicidal agent. Importantly, this compound exhibited low *in vivo* toxicity and is effective in decreasing fungal burden in the *Galleria mellonella* animal model.

Acknowledgments:

This work was supported by FCT - Fundação para a Ciência e a Tecnologia, I. P., through MOSTMICRO-ITQB R&D Unit (UIDB/04612/2020, UIDP/04612/2020), LS4FUTURE Associated Laboratory (LA/P/0087/2020) and through the Municipality of Oeiras (IOVPoC-2021-06). CML is the recipient of a PhD fellowship funded by FCT (UI/ 153387 2022).

P 31

IRON ATTENUATES FLUCONAZOLE ACTIVITY AGAINST *CANDIDA GLABRATA*

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Invasive fungal infections (IFIs) represent a significant health concern worldwide, as recently acknowledged by the World Health Organization upon the release of the first priority list of fungal pathogens [1]. Fluconazole, a triazole, stands as the most frequently prescribed antifungal for treating IFIs, due to its affordability, oral bioavailability, broad spectrum of activity, and safety profile [2]. At the molecular level, fluconazole targets lanosterol 14-α-demethylase, an enzyme that catalyzes the conversion of lanosterol to ergosterol, a key component of fungal cell membranes. The inhibition of ergosterol biosynthesis arrests cell growth, due to the accumulation of toxic sterol species and disruption of membrane integrity [2]. We have recently found that when in excess, iron decreases the antifungal activity of fluconazole against *Candida glabrata*, the second most prevalent causative agent of nosocomial IFIs. Iron excess is associated with many medical conditions or treatments, and therefore, this finding can have important clinical implications regarding the treatment of IFIs caused by *Candida glabrata* in such contexts. In this work, we explored the mechanisms underlying the antagonistic interaction between iron and fluconazole, having identified key molecular players.

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P 32

RUTHENIUM-ANTIBIOTIC CONJUGATES AS NEW POTENTIAL ANTICANCER AGENTS

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Cancer is a predominant cause of death, with more than 10 million deaths reported in 2020. Most currently available treatments exhibit limited efficacy and high adverse effects, presenting a critical need for innovative therapeutic strategies [1]. Moreover, bacterial infections are responsible for the development of several tumors and are often more prevalent and life-threatening in cancer patients due to their lowered immunity induced by cancer itself and chemotherapeutic treatment. The microbiome is characteristic of each tumor and highly influences its progression, metastasis, and drug sensitivity [2]. Striving for an improved therapeutic strategy, we conjugated one of our Ru(II)-(η^5-C_5H_5) complexes, which has proved to be active against several types of cancer *in vitro* and *in vivo* [3], to two antibiotics, aiming at a modulation of the anticancer properties. Herein we report the synthesis and characterization (NMR, FT-IR, UV-vis spectroscopies) of the two new ruthenium-antibiotic conjugates containing a linker sensitive to tumor microenvironment for controlled release of the cytotoxic complex and antibiotic moieties. Their isomeric structure was assessed by density functional theory calculations and their stability in aqueous/organic solutions was studied over time via UV-vis and NMR spectroscopies. Their *in vitro* cytotoxic activity in A375, A431, A549, and MDA-MB2 31 cancer cell lines will also be discussed.

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Acknowledgments:
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PHOTOREDUCTION OF CO_2 WITH CRYPTATE CATALYSTS

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CO_2 plays a crucial role in the carbon cycle, which keeps the Earth's temperature stable. The expansion of the human population and the energy demand, increased Earth's CO_2 concentration unbalancing the carbon cycle, affecting our planet's energy balance. Molecular activation is crucial in chemical and biological systems, where CO_2 is an important player. Thus, researchers and industries had a deep interest in producing catalysts that, by photoreduction, can convert CO_2 either into liquid fuel precursors or directly to liquid fuels

The photoconversion of CO_2 can be made in homogeneous media and requires three components: the catalyst (which in the active form, converts CO_2), the sacrificial donor (donates electrons and is consumed) and the photosensitiser (absorbs light and mediates the electronic transfer between the catalyst and the sacrificial donor).

We present the synthesis and characterisation of Co(II)/Co(II),[1] Co(II)/Zn(II) and Fe(III)/Fe(III) dinuclear cryptates with -Br as a substituent in the aromatic ring. The photoreduction of CO_2 and the optimisation of the photocatalytic system and setup was also investigated.

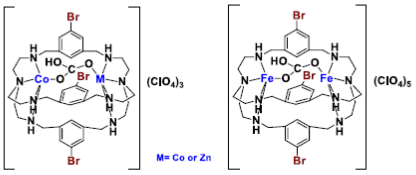

Figure 1. Dinuclear Co(II)/Co(II), Co(II)/Zn(II) or Fe(III)/Fe(III) cryptate with ClO_4^- as anion.

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Acknowledgments:

Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e a Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. We are grateful to Fundação da Ciência e a Tecnologia, FCT, for Project PTDC/QUI-QIN/0252/2021. P.N.M. (CEECIND/00509/2017) and S. R. (2020.02134.CEECIND) acknowledge FTC for financial support.

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NEW METAL COMPLEXES OF A FLUCONAZOLE DERIVATIVE WITH ANTIFUNGAL ACTIVITY

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The emergence of antifungal resistance, allied with a lack of new drugs, is leading the scientific community to look for new ways to fight fungal infections. Metal complexes have recently attracted great interest since they can provide additional mechanisms of action compared with organic compounds alone.[1] Fluconazole, a model triazole antifungal drug, has recently been modified with different metal-binding moieties and the antimicrobial activity of such compounds was tested in the presence of increasing amounts of supplemental copper(II) with interesting results.[2] In our previous work, we synthetized an azole compound with a chelating function, which when coordinated to copper(II) showed promising antifungal activity.[3]

In this work, we have developed a new fluconazole derivative modified by appending a particular chelating function replacing a triazole moiety on the fluconazole structure. This compound was used as a ligand to prepare complexes with selected metal cations, which were studied regarding their antifungal activity against *Candida* spp. Preliminary results point to an excellent antifungal activity of all complexes against several *Candida* species, with minimal toxicity found for human cells.

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P 35

Characterization of recombinant cytochrome c_{552} from *Wolinella succinogenes* and nitrous oxide reductase from *Pseudomonas stutzeri*

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Cytochrome c_{552} from *Wolinella succinogenes* is one of the few examples of a low reduction potential class I *c*-type cytochrome with a mixture of high/low spin state populations observed in its visible spectrum. Analysis of its structural model suggests that the Met/His coordinated heme is highly solvent-exposed. The visible spectra obtained at different pH values reveal the presence of a protonable group with a p*K*a of 7.3, which also influences the reduction potential of this small cytochrome c_{552} ($Em^{0'}$ of 97 ± 5 mV, pH 7.0) and can be either an H_2O/OH^- group distantly coordinating the heme iron, or one of the propionate groups. The thermostability of cytochrome c_{552} has been studied by circular dichroism and differential scanning calorimetry, indicating a highly stable protein at pH 5-7 (90 ºC to 77 ºC).

Recombinant nitrous oxide reductase from *Pseudomonas stutzeri* was isolated, and its thermostability and activation mechanisms were characterized.

Acknowledgments:

This work was supported by by Fundação para a Ciência e a Tecnologia, I.P. (FCT), through a project grant to IM (2022.01152.PTDC). This work was also supported by national funds from FCT in the scope of the project UIDP/04378/2020 and UIDB/04378/2020 of the Research Unit on Applied Molecular Biosciences-UCIBIO and the project LA/P/0140/2020 of the Associate Laboratory Institute for Health and Bioeconomy-i4HB, and projects UIDB/50006/2020 and UIDP/50006/2020 of the Associated Laboratory for Green Chemistry (LAQV).

P 36

SUPPORTED MOLYBDENUM CATALYSTS FOR OXIDATIVE DESULFURIZATION OF SULFUR COMPOUNDS

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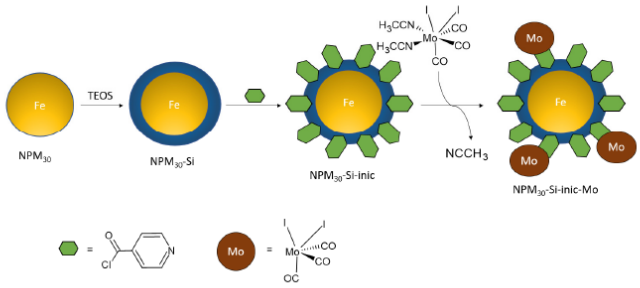
Growing awareness of the harmful effects of sulfur-containing fuels and new requirements of sulfur standard contents has driven the need for green fuel production. [1][2] Oxidative desulfurization (ODS) offers a promising solution, involving oxidation of sulfur compounds to sulfoxides and sulfones followed by their removal. In this study, a new catalyst, NPM_{30}-Si-inic-Mo, was developed for ODS. It showed effective oxidation of sulfides, with *tert*-butyl hydroperoxide as the most efficient oxidant. Four compounds were tested (methyl phenyl sulfide, diphenyl sulfide, 1-benzothiophene and benzothiophene). Catalytic tests demonstrated high yields, particularly with methyl phenyl sulfide and diphenyl sulfide, achieving 98% and 34% yields, respectively, using 2 mmol of oxidant. Moreover, the feasibility of catalyst recovery via magnetic separation was explored, revealing clear solutions post-removal, and suggesting potential for practical application.



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This work was supported by Fundação para a Ciência e Tecnologia through project with DOI 10.54499/2022.03236.PTDC, Centro de Química Estrutural, by UIDB/00100/2020 and

P 37

NMR INTERACTION STUDIES BETWEEN CYTOCHROMES UNVEIL ELECTRON TRANSFER NETWORK IN *GEOBACTER*'S PERIPLASM

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The analysis of several *Geobacter* genome's revealed abundant cytochromes with multiple duplications for some families of proteins [1]. *G. sulfurreducens* has been the model organism for the study of the complex electron transfer networks of exoelectrogens, and several studies identified key players in different cell compartments for each metabolic pathway. In these studies, the apparent redundancy was shown to be necessary since the proteins were found to be involved in distinct electron transfer routes depending on the terminal electron acceptor. For the family of triheme periplasmic cytochromes PpcA-E, knockout and complementation mutants revealed that in the absence of all other homologs, any of the proteins was able to support wild-type levels of Fe(III) reduction [2]. However, in contrast, RNA transcriptomics showed that the five triheme cytochromes are differently expressed depending on the final acceptor [3]. The combination of both studies suggests that despite the specificity found for other cytochromes, the periplasmic cytochromes are promiscuous and able to interact with different redox partners.

Pairwise interactions and electron transfer reactions between PpcA-E were performed by exploring the distinctive Nuclear Magnetic Resonance (NMR) spectroscopic signatures of each cytochrome [4]. The results revealed that the five proteins are able to exchange electrons between each other, while forming transient and unspecific redox complexes. This suggests that the constitutively expressed pool of cytochromes in *Geobacter* cells can establish and maintain a proper redox potential in the periplasm, providing reducing power to the cell to ensure electron transfer across the periplasm independently of the terminal acceptor or even a specific redox partner.

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OXIDATIVE DESULFURIZATION OF SULFUR COMPOUNDS WITH SUPPORTED MoO_2 NANOPARTICLES

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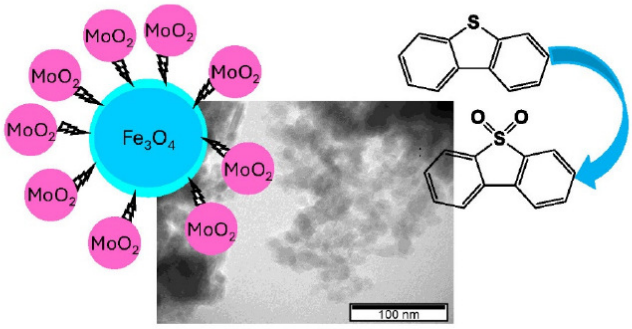
Producing green fuels is of utmost importance due to increased awareness of the adverse effects on human health and the environment. The removal of sulfur compounds is imperative to meet the new requirements of sulfur standard contents (10–15 ppm).[1][2] Oxidative desulfurization (ODS) is considered a promising and highly efficient method owing to its mild operation conditions and high efficiency. In this work, the catalyst was prepared by supporting MoO_2 nanoparticles (NP's) on Fe_3O_4 NP's and was tested in the oxidation of sulfides (diphenyl and methyl phenyl sulfide, dibenzothiophene and 1-benzothiophene). Reactions were carried out at 80 °C, with oxidant *tert*-butyl hydroperoxide or H_2O_2, and different substrate:oxidant ratio 1:1 or 1:2 mmol.



In general, it was found that the oxidation to sulfoxide and sulfone occurred successfully. The most promising oxidant to obtain the sulfone was *tert*-butyl hydroperoxide, with 100% yield when 2 mmol of oxidant was used. In the test where all substrates were mixed, very good results were obtained, although no conversion of 1-benzothiophene substrate was observed.

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ANALYTICAL STUDY OF RELIGIOUS SIMULACRA

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St Clementina and St Simplício, presumably mother and son, are two examples of over fifty simulacra recently identified in Portugal. According to archival sources, the skeletons found in the catacombs of Rome after discovering the burial galleries in 1578 were sent to different Catholic countries inside life-sized figurative reliquaries representing the martyr saints [1]. These simulacra, mounted with metallic structures and dressed in luxurious fabrics of the time, were intended to expose the sacred bones for veneration. In-situ characterisation with digital radiography and optical microscopy, and sampling of different materials, including fibres, wax, and metal threads, was carried out during the campaigns. In this work, the morphological and chemical characterisation of these simulacra was conducted through Fourier transformed infrared spectroscopy (ATR-FT-IR), liquid chromatography coupled with diode-array detection and mass spectrometry (LC/DAD/MS), pyrolysis coupled to gas chromatography and mass spectrometry (Py-GC/MS), and scanning electron microscopy coupled with X-rays microanalysis (SEM/EDS). The osteological evaluation was performed based on the bones that could be accessed. This study offered valuable insight into these religious simulacra contributing to the knowledge of the production procedures and materials used.

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Acknowledgments:
The authors thank Dra Ana Paula Costa and Santa Casa da Misericórdia de Almada for the access to the simulacra. They also acknowledge FCT for funding through the "Holy Bodies" Project (10.54499/2022.01486.PTDC) (J. Palmeirão and M. Nunes research fellowship and studentship) and Strategic Projects 10.54499/UIDP/04449/2020, 10.54499/UIDB/04449/2020 and IN2Past 10.54499/LA/P/0132/2020 (HERCULES Laboratory), and UIDB/0622/2020 and UIDP/0622/2020 (CITAR).

P 40

MESOPOROUS INORGANIC SILICA NANOMATERIALS AS INNOVATIVE SYNERGISTIC TOOLS AGAINST ANTIMICROBIAL RESISTANCE.

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Efforts to combat antibacterial resistance have extended from the discovery of novel antibiotics to the chemical modification of existing ones. However, the emergence of new antibiotics does not guarantee a permanent solution to resistance issues [1]. Currently, antibacterial nanomaterials have being addressed as a solution to this problem, showing remarkable efficiency against antimicrobial resistance. The strategic integration of antimicrobial nanomaterials with conventional antibiotics and/or other drugs presents a crucial approach to bypass the development of bacterial resistance mechanisms [2, 3].

Inorganic silica mesoporous nanoparticles (MNs) emerged as a promising new generation of nanocarriers because they have low toxicity, high specific surface area, large pore volume, tunable pore structures, and size, allowing the transportation of multiple drugs and analytes [1-3]. Moreover, the wide range of possible known surface modifications adds stability, biocompatibility, solubility, therapeutic effects and optoelectronic properties to these nanomaterials, while extending their biomedical applications [1-3].

Inspired by recent advances in this area, the multiple applications of mesoporous of silica nanoparticles combined with metal nanoparticles, antibiotics and other drugs are herein addressed and evaluated as drug delivery systems in several bacterial strains.

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This work was supported by the Associate Laboratory for Green Chemistry - LAQV which is financed by national funds from FCT/MCTES (LA/P/0008/2020 DOI 10.54499/LA/P/0008/2020, UIDP/50006/2020 DOI 10.54499/UIDP/50006/2020 and UIDB/50006/2020 DOI 10.54499/UIDB/50006/2020) as well as the PROTEOMASS Scientific Society (Portugal) for funding support (General Funding Grant 2022-2023). J.G. thanks FCT/MEC (Portugal) for her doctoral grant 2022.09495.BD. EO thanks FCT/MEC (Portugal) for the individual contract, CEECIND/05280/2022.

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NOVEL 2-CHLORO-ADENOSINE BASED ON PLATINUM: SYNTHESIS AND ANTI-PROLIFERATIVE ASSESSMENT

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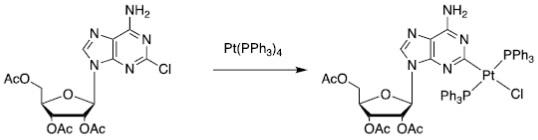
The issue of resistance to cisplatin poses a significant challenge in cancer treatment.[1] A promising strategy to address this problem consists in combining multiple mechanisms of action within a molecule. For example, the combination of a metal complex with a modified nucleoside is a promising approach to achieve this goal.[2]

Inspired by this, we employed 2-Chloroadenosine, known for its antiproliferative properties, as ligand precursor to develop new platinum (II) complexes through oxidative addition to Pt(0). The resulting complex was further functionalized in order to obtain the corresponding N-heterocyclic carbene.

The antitumor activity of the synthesized compounds was evaluated on different cell lines upon their encapsulation in NPs[3], performed with the aim of increasing selectivity for tumor cells and consequently reduce side effects. The synthesis and biological activity of 2-Cl-adenosine derivatives will be discussed in this poster communication.



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Acknowledgments:

This work was financially supported by: Project LISBOA-01-0145-FEDER-007660) funded by FEDER funds hrough COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI).

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INTERACTION OF SPLIT-SORET CYTHOCROME WITH FORMATE DEHYDROGENASE

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The class of metal-dependent Formate dehydrogenases (FDHs) comprises prokaryotic enzymes holding redox-active centres and a catalytic site, containing either molybdenum or tungsten, mediating the reversible two electron reaction of formate/carbon dioxide interconversion. The carbon dioxide reduction is of particular interest, since is a possible route for its atmospheric mitigation with simultaneous production of added-value products, such as hydrogenated-derived compounds. In particular, the periplasmic formate dehydrogenase from *Desulfovibrio desulfuricans* (Dd), a molybdenum-containing enzyme, was proven to be a particularly efficient enzyme for the CO_2 reduction to formate [1,2]. The immobilized DdFDH direct electrochemical behaviour was attained in the presence and absence of substrates and the corresponding catalytic currents were observed [3]. Further studies have now been extended on the catalytic performance of FDH in the absence and presence of the Split-Soret cytochrome (DdSS) from the same organism [4], a candidate physiological redox partner. A wide range of DdSS concentrations were tested with different ratios of DdFDH/DdSS in order to probe the specific interaction between the two proteins.

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P 43

EXTRACTION OF THORIUM AND URANIUM FROM AQUEOUS SOLUTIONS WITH FUNCTIONALIZED IONIC LIQUIDS

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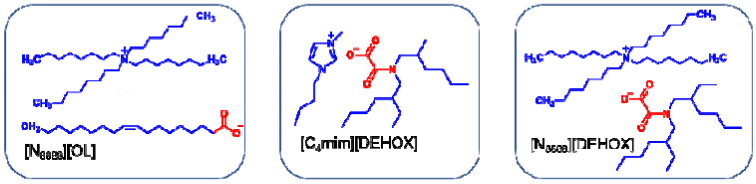
Thorium is tagged to be a next-generation nuclear fuel since it is more abundant than uranium and produces less long-lived nuclear waste compared to uranium fuel [1]. Fertile ^{232}Th is converted to fissile ^{233}U in the nuclear reactor and, to accomplish a closed fuel cycle, reprocessing of spent nuclear fuel and separation of thorium and uranium are required. As a separation technology, liquid-liquid extraction with ionic liquids (ILs) is a promising strategy for advanced nuclear fuel cycles. ILs have tunable physical properties such as water miscibility, viscosity and polarity. Additionally, the introduction of binding groups in the cationic or anionic unit with high affinity for metals is expected to enhance extraction efficiency and selectivity.

Three functionalized ILs (FILs) with a carboxylate or an oxamate moiety (see Fig.) were previously used by us with success to extract lanthanides from aqueous solutions, with $[N_{8888}][DEHOX]$ showing a high selectivity along the lanthanide series [2]. In this work, we are evaluating the ability of these FILs, dissolved in toluene, to extract selectively thorium and uranium from acidic aqueous solutions. Several parameters are under study, namely M:IL ratio, pH and contact time, in order to optimize efficiency and selectivity. Preliminary studies with thorium and uranium solutions at pH 3 and M:IL ratio of 1:4 showed that $[N_{8888}][OL]$ has a preference for extracting U(VI) ions and $[C_4mim][DEHOX]$ for extracting Th(IV) ions, while $[N_{8888}][DEHOX]$ extracts both actinide ions. These results are based on X-ray fluorescence (XRF) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis.



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Acknowledgments: This work was supported by FCT (UIDB/00100/2020 (CQE), LA/P/0056/2020 (IMS), UIDB/04349/2020 (C[2]TN).

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TWO NEW TETRASUBSTITUTED MACROCYCLES WITH DANSYL DYES AS FLUORESCENT AND SOLVATOCHROMIC SYSTEMS FOR METAL ION DETECTION

Inês Pereira-Gomes*[1], Frederico Duarte[1], Georgi Dobrikov[2], Atanas Kurutos[2,3], Jose Luis Capelo-Martinez[1,4], Hugo M. Santos [1,4], Carlos Lodeiro[1,4]

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In the last years, multiple researches highlight the important role of fluorescence systems to detect and monitors metal ions at environmental and biological fields due to their high toxicity.[1–4] In light of this, two novel dansyl derivatives bearing a cyclen, **L1**, and cyclam, **L2**, units were synthesized and their photophysical characterization were investigated in solution and in the solid state, as well as their ability to sense pollutant metal ions. Moreover, L1-2 demonstrate positive solvatofluorochromic behavior, emitting from turquoise to yellow. Both macrocyclic systems exhibit high sensitivity towards Cu^{2+} and Hg^{2+} metal ions leading to the suppression of fluorescence emission with a minimal addition of each metal ion. Therefore, the synthesis of the mercury (II) complexes was performed and studied. Thermostability studies were also conducted by considering the emission in the solid state, where both compounds were found to quench its emission according to a linear behavior on certain ranges of temperature which suggest their potential application as molecular thermometers.

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Acknowledgments:

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BACTERIA TO FIGHT CO_2: EXPLOITING FORMATE DEHYDROGENASES TO REDUCE CO_2 TO FORMATE — PREPARATION OF PERIPLASMIC FRACTIONS TO PURIFY THE ENZYMES

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The atmospheric levels of CO_2 are causing huge and unpredictable impacts on Earth's climate due to its significant greenhouse effect. To stop the catastrophic consequences caused by climate change, CO_2 emissions must be greatly reduced. Additionally, it is necessary to develop new and more effective ways to convert this compound into added-value products [1,2]. In this context, the conversion of CO_2 into formate (eq. 1) offers significant benefits for carbon recycling, since formate can be easily stored, transported and converted into various products highly interesting for the energy and chemical industry. To achieve the CO_2 conversion into formate, enzymes offer significant advantages, namely the selectivity and specificity of substrate and product, as well as the ability to run reactions at room temperature and pressure, in water, at neutral pH.

$$CO_2 + 2e^- + H^+ \rightleftharpoons HCOO^- \qquad (1)$$

Our main goal is to exploit formate dehydrogenase (FDH) [3] enzymes to develop photochemical and electrochemical devices for the conversion of CO_2 into added-value compounds. Presently, we are interested in studying the periplasmic FDH from the *Desulfovibrio desulfuricans* bacterium [4]. To this end, it is necessary to first prepare a *D. desulfuricans* periplasmic fraction free of cytoplasmic protein contamination. In this communication, different steps to prepare the periplasmic fraction will be compared.

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P 46

NOVEL MATERIALS WITH TRANSITION METAL COMPLEXES FOR EFFICIENT CATALYTIC EPOXIDATION

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Diverse transition metal complexes can be successfully used as catalysts for olefin epoxidations with *tert*-butyl hydroperoxide achieving very high selectivity for epoxidation product [1]. They can be also successfully applied as catalysts when incorporated into novel materials such as ionic liquids and porous materials such as metal organic frameworks. Particularly in this form oxodiperoxomolybdenum complexes recently proved as successful and highly active catalysts providing also further opportunities for improvement in catalysis and catalysts reusability [2,3].

Some recent results as well as advances in preparation and use of ionic liquids and covalent organic frameworks for the purpose of transition metal catalysed epoxidation will be presented.

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P 47

ANTIMICROBIAL AND ANTICANCER PROPERTIES OF CARBON MONOXIDE RELEASING MOLECULES OF THE *fac*-[Re(CO)$_3$(N-N)L]$^+$ FAMILY

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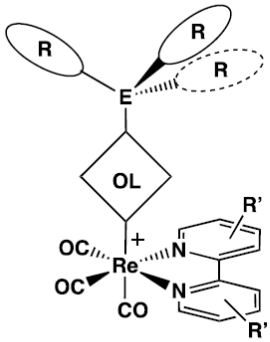
The optimization of the toxicity profile of *fac*-[Re(CO)$_3$(N-N)L]$^+$ complexes against microbial and tumoral cells has involved many ligand modifications mostly on the diimine ligand (N-N). Following our previous work on the bactericidal profile of *fac*-[Re(CO)$_3$(bpy)(Ctz)]$^+$ (**A**) (Ctz= clotrimazole = Ph$_2$(C$_6$H$_4$Cl)C-Imidazole; bpy = bipyridyl) [1], we are now reporting on the effect of ligand modifications to the axial clotrimazole ligand: the high cytotoxicity of the conjugate (**A**) seems to be due to the influence of the trityl based (Ph$_2$(C$_6$H$_4$Cl)C) substituent in Ctz. While the conjugate of *fac*-[Re(CO)$_3$(bpy)]$^+$ with 1-Ph$_3$C-Imidazole maintained the activity of (**A**) towards *S. aureus*, replacing Ctz with Ph$_2$HC-Im, PhH$_2$C-Im, PhIm, tBuIm and HIm led to an abrupt loss of toxicity in all cases. In contrast, high activity was kept when replacing Ctz with Ph$_3$P or Cy$_3$P, both with a similar lipophilic C$_{3v}$ structure. The Ctz, 1-Ph$_3$C-Im and PPh$_3$ derivatives of *fac*-[Re(CO)$_3$(bpy)]$^+$ are also 10 times more potent anti-tumorals than the other imidazole derivatives or cisplatin against colon (HT-29) and breast (MDA-MB-231) cancer cell lines. Intracellular CO release accompanies the antimicrobial and anti-tumoral cytotoxicity, confirming our former report in [1]. These results suggest further research is warranted into the use of this type of structures (Figure) as potent antimicrobial and anti-tumoral drugs.



E = C, B, N, P; R = Bulky group
R' = Substituent; OL = Optional Linker

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Acknowledgments:
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P 48

SYNTHESIS OF NICKEL BIS-N-HETEROCYCLIC CARBENES AS ANTIFUNGAL AGENTS

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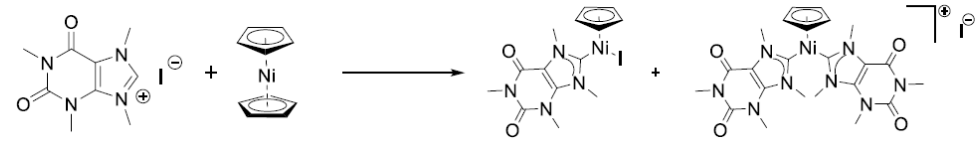
Fungal infections represent a significant global health burden, requiring the development of novel antifungal agents, more selective and with the ability to overcome existing resistance mechanisms. Metal complexes have emerged as promising candidates to achieve this purpose. We have reported a library of nickel complexes based on xanthines that are active as antifungals on candida strains. Specifically, the biscarbene complex **4** $[NiCp(NHC)_2]^+$ (Sheme 1) and monocarbene **3** are active for *Candida albicans*, while complex **4** demonstrated a high selectivity for *Candida glabrata*. [1]

Following on this, we performed the direct coordination of other imidazolium salts to nickelocene ($NiCp_2$), to yield [NiCpI(NHC)] complexes, aiming to expand this class of compounds, specifically of biscarbenes, to evaluate their efficiency and selectiveness. The results will be further discussed in this communication.



1 2 3 4

Scheme 1 – Synthesis of Ni(II)(NHC) monocarbene **3** and biscarbene complex **4**.

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Acknowledgments:

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

P 49

STRESSING OUT: PROMOTING ANTIFUNGAL ACTIVITY BY FOSTERING REDUCTIVE STRESS WITH METAL COMPLEXES

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Infectious diseases, especially among disadvantaged populations without easy access to health care, have increased significantly in recent decades. [1] This problem has been exacerbated by antifungal drug resistance, created by the fungi's metabolic pathways, making it necessary to develop new drugs able to operate through different modus operandi. [2] One of the possible ways of killing fungi is by altering the homeostatic balance of the cell. Focusing on this, we envisaged the development of new compounds able to disrupt redox balance by fostering reductive stress inside the cell, by reducing NAD+ and GSSH, which are essential for maintaining cellular redox homeostasis. [3]

In this work, new complexes based on Iridium and ruthenium have been developed for this purpose. The compounds were synthesized employing an uracil-imidazole ligand, for which transfer hydrogenation reactions have been reported (Figure 1).

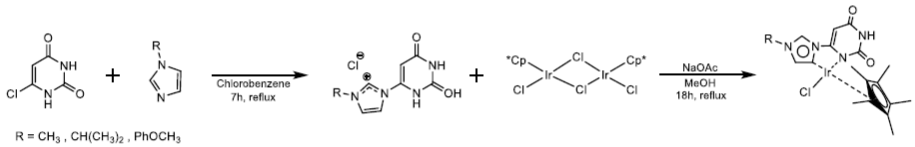

Figure 1. Example of a metal complex synthesis reaction.

All the complexes synthesized were tested for their ability to reduce NAD to NADH, aiming to predict their behaviour at the cellular level. The compounds with the best catalytic results progressed to the evaluation of reductive stress in *Candida albicans* and *Candida glabrata*. These results will be reported in this communication.

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P 50

DEVELOPING NEW RUTHENIUM-PEPTIDE CONJUGATES FOR TARGETING METASTATIC BREAST CANCER

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Metastatic breast cancer (MBC) is a highly aggressive subtype that accounts for 15-20% of all breast cancer cases. There is still no clinical cure for MBC, and available treatments have limited effectiveness and often cause severe side effects due to their lack of specificity [1]. To overcome these limitations, our group is currently developing novel ruthenium smart metallodrug delivery systems capable of targeting both primary tumor and metastases of breast cancer [2]. These systems comprise a peptide that recognizes with high affinity the fibroblast growth factor receptor (FGFR), often overexpressed by MBC cells, linked to a cytotoxic Ru(II)-(η^5-C_5H_5) complex through an entity sensitive to the slightly acidic tumor microenvironment. These systems allow accumulation, site- and time-specific release of the active species into the tumor. Herein we report the synthesis, characterization, and biological evaluation of two new pH-responsive ruthenium-peptide conjugates (RuPCs) intended to be used as a smart metallodrug delivery system for MBC therapy. Three new cytotoxic units, with the general formula [RuCp(PPh_3)(NN)][CF_3SO_3] (NN: new monofunctionalized bipyridine ligands), were synthesized and fully characterized. The drug release profile and preliminary biological evaluation were evaluated at pH values that mimic the tumor microenvironment and bloodstream.

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INDIUM-111 RADIOCOMPLEXES CARRYING A DNA INTERCALATOR FOR AUGER THERAPY OF PROSTATE CANCER

Joana F. Santos[1], Catarina D. Silva[*1], Ana Rita Julião[1], Célia Fernandes[1,2], Paula Raposinho[1,2], Filipa Mendes[1,2], Margarida Sobral[3,4], Rafael P. Silveira[3], Ana M. Urbano[3,5], Paulo J. Oliveira[3], António Paulo[1,2]

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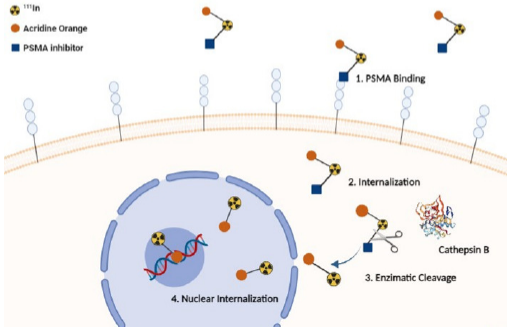
Currently, Targeted Radionuclide Therapy (TRT) of prostate cancer (PCa) relies on the use of ^{177}Lu-PSMA-617 (Pluvicto^{TM}), a prostate specific membrane antigen (PSMA) inhibitor labelled with the β^- emitter ^{177}Lu [1]. However, β^- emitters have some limitations, such as nephrotoxicity and β^- radiation resistance. To overcome these issues, Auger electron (AE) emitters can be a good alternative due to their high linear energy transfer (LET) within a nanometric range, which can lead to highly lethal and selective effects in target tumor cells particularly if the AE-emitter is placed near the DNA in the cell nucleus [2,3].

Towards this goal, we have designed dual-targeting ^{111}In-complexes carrying a PSMA inhibitor and an acridine orange (AO) intercalator to promote specific uptake by PCa cells and selective accumulation in the nucleus. DOTA-based chelators bearing PSMA-617 and AO groups were synthesized and labelled with the AE-emitter ^{111}In. The preclinical studies of the resulting radioconjugates included cellular uptake, internalization and PSMA-blocking assays in cell lines expressing different PSMA levels, and the evaluation of radiobiological effects (e.g., clonogenic assay). The dual-targeted ^{111}In-complexes showed a PSMA-mediated uptake in PSMA(+) PC3 PIP cells, being able to compromise the cell survival in a dose-dependent manner with enhanced radiobiological effects compared to the single-targeted congeners. These results give promising prospects to proceed with therapeutic assays in PSMA(+) tumor-bearing mice.



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Acknowledgments:

This work was funded by Fundação para a Ciência e Tecnologia, Portugal (projects UID/Multi/04349/2019 and PTDC /MED-QUI/1554/2020). The authors acknowledge Prof M. Pomper (Johns Hopkins Medical School, Baltimore, USA) for the kind gift of the PC3 PIP-Flu cell lines. Joana F. Santos acknowledges the PhD grant PRT/BD/154612/2023; Catarina D. Silva acknowledges the PhD grant PRT/BD/154625/2023.

P 52

ONE STEP BACKWARDS TO TAKE TWO STEPS FORWARD INTO THE EVOLUTION OF MULTIHEME CYTOCHROMES

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Multiheme *c* type cytochrome (MHC) contain a wide range of numbers of covalently bound heme *c* cofactors and catalyze diverse chemical reactions. These include reactions that are pivotal to many biogeochemical cycles, including those of nitrogen, sulfur and iron. This was made possible by the evolution of MHC in different microbial organisms that diversified to different ecological niches. Understanding the evolution of MHC has been a challenge due to the low preserved amino acid sequence across time and limited available 3D structures. MHC were initially proposed to evolve solely by fusion of redox modules, going from simple MHC to more complex and containing more heme cofactors per polypeptide chain. In this work we focused our attention in the largest group of homologous MHC that contain MHC from 4 to 11 hemes and are involved in the nitrogen, sulfur and iron biogeochemical cycles. We gathered data from sequence phylogenetic reconstruction, structural comparison and minimal functional site characterization of the hemes that suggests that the evolution of MHC is more dynamic and follows a process of grafting and pruning of protein modules [1]. Altogether, this work shifts the paradigm of MHC evolution and helps us understand their evolution and role across large timescales.

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Acknowledgments:
This work was supported by European EC Horizon2020 TIMB3 (Project 810856); MOSTMICRO-ITQB with references UIDB/04612/2020 and UIDP/04612/2020; Fundação para a Ciência e a Tecnologia (FCT) Portugal (project PTDC/BIA-BQM/4143/2021).

P 53

ENHANCING THERMAL CHARGING OF TEXTILE SUPERCAPACITORS THROUGH CNT/METAL SULFIDE MATERIALS

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The fast innovation of wearable technologies has spurred a growing demand for self-powered devices capable of capturing thermal energy (e.g., body heat), converting it into electrical energy and efficiently storing it [1]. Thermally-chargeable supercapacitors (TCSCs) appeared as a solution; but, challenges remain such as the role of the electrode materials.

Herein, innovative hybrid carbon nanotubes (CNT)@bi-/trimetallic sulfide electrode materials (Bi, Zn, Mo-based variants) were prepared and used in smart textile TCSCs. Textile electrodes were produced by coating cotton fabrics with the produced materials. Asymmetric TCSCs were fabricated by stacking two textile electrodes with distinct compositions (CNT and hybrid materials) with an ionic solid-gel electrolyte in between. BiMoZnS-based asymmetric TCSC showed one of the best electrochemical performances, with an energy density of 4.96 μW h/cm^2 at 360.51 μW/cm^2 (vs. 3.10 μW h/cm^2 at 107.69 mW/cm^2 for a reference CNT-based TCSC). The thermal energy harvesting studies are ongoing but already demonstrated the simultaneous energy harvesting/storage functionalities of the devices.

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Funding: This work received financial support from FCT/MCTES (UIDB/50006/2020 DOI: 10.54499/UIDB/50006/2020) through national funds.

Acknowledgments: FCT/MCTES is acknowledged in the framework of the projects LA/P/0008/2020, UIDP/50006/2020, UIDB/50006/2020, PTDC/CTM-TEX/4126/2021, UIDB/04968/2020, and UIDP/04968/2020 (DOI: 10.54499/LA/P/0008/2020, 10.54499/UIDP/50006/2020, 10.54499/UIDB/50006/2020, 10.54499/PTDC/CTM-TEX/4126/2021, 10.54499/UIDB/04968/2020 and 10.54499/UDIP/04968/2020), through national funds. JST thanks FCT/MCTES and European Social Fund through POCH for PhD grant SFRH/BD/145513/2019 (DOI: 10.54499/SFRH/BD/145513/2019). CRP thanks FCT for funding through the Individual Call to Scientific Employment Stimulus ref. 2021.04120.CEECIND/CP1662/CT0008 (DOI: 10.54499/2021.04120.CEECIND/CP1662/CT0008).

P 54

EXPLORING 2D INORGANIC MATERIALS THROUGH SURFACE CHEMISTRY PROBES

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There has been a growing interest in two-dimensional (2D) inorganic materials, very often with announcements of new entries into the field of flatland chemistry. This research area has been dominated by graphene since the groundbreaking experiments performed by the Nobel laureates Geim and Novoselov (2010). A deep understanding of the surface chemistry of other mono- and few-layered materials is required for the advancement of diverse applications using such 2D nanosystems. Our research in this topic led us to explore the properties of 2D inorganic materials and their metal nanocomposites, particularly for applications in surface-enhanced Raman spectroscopy (SERS). In this communication, we discuss selected 2D materials (e.g. GO, MoS_2) that act as Raman signal amplifiers when interacting with colloids and specific molecules at their surfaces. Through our findings, we aim to demonstrate that this approach provides valuable insights into the interaction between inorganic surfaces and chemisorbed species. Furthermore, our research shows the potential of such 2D materials as analytical platforms for Raman spectroscopy in the context of trace molecular detection.

Acknowledgments

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI 10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC).

P 55

DEVELOPMENT OF ARTIFICIAL ENZYMES ABLE TO REDUCE CO_2 AND NO_X BASED ON COPPER ENZYMES

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Carbon dioxide (CO_2) and nitrogen oxides (NOx) are a barrier between the present and a healthier planet, being nowadays the highest responsible for the climate change. However, these abundant and low-cost compounds also make them interesting to produce valuable products, bringing together two important needs, first their mitigation and second the production of other high-valued chemicals. Nature developed various ways of use CO_2 and NOx, such has Ribulose-1,5-biphosphate Carboxylase for CO_2 fixation [1], and others such as nitrate reductases in the denitrification route [2]. In this work the goal is to construct an efficient artificial enzyme, through proper catalytic site mutations, with the ability to catalyse CO_2 and NOx. A screening revealed a promising type-3 copper (T3Cu) enzyme, identified as a tyrosinase. Initial biochemical characterization was attained together with its Alphafold2 structure. The active centre holds the typical copper coordinating histidines. Considering it as a tyrosinase, the native L-Dopa oxidase activity was tested. Preliminary electrochemical assays allowed to calculate the redox center formal potential.

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Acknowledgments:

GNV acknowledge FCT/MCTES for funding through grant number 2021.06216.BD. This work was supported by the Associate Laboratory for Green Chemistry—LAQV which is financed by national funds from FCT/MCTES (UIDB/50006/2020 (DOI 10.54499/UIDB/50006/2020)), the Research council of Norway, grant number 301022 and UIDP/50006/2020 (DOI 10.54499/UIDP/50006/2020)) through national funds.

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A ROUTE TO IRON(III) HELICAL COMPLEXES FROM *BIS*THIOSEMICARBAZONES

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Designing artificial helical complexes from metal ions is a major goal of Metallosupramolecular Chemistry. Recently, these compounds have received a great deal of attention due to their important properties in fields such as Pharmacology, Biology or Materials Chemistry [1]. In this context, several iron(II) helicates have been published which are able to interact with DNA and have anti-cancer and anti-microbial properties [2].

In the light of these previous results, we have designed a route to prepare iron(III) helical complexes, called helicates, using *bis*thiosemicarbazone ligands. Here we report four neutral iron(III) helicates, obtained by an electrochemical methodology, and the study of their interaction with DNA.

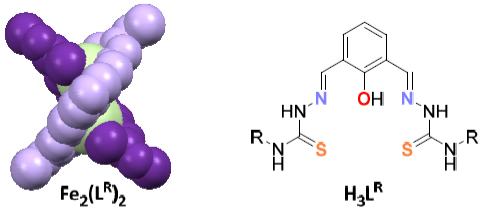

Figure 1. Fe(III) helical complexes (left) derived from *bis*thiosemicarbazone ligands (right).

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Acknowledgments:

This research was funded by the following FEDER co-funded grants. From Consellería de Cultura, Educación e Ordenación Universitaria, Xunta de Galicia GRC GI-1584 (ED431C 2023/02) and from Ministerio de Ciencia e Innovación, Project PID2021-127531NB-I00 (AEI/10.13039/501100011033/ FEDER, UE).

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ACIDIC ZEOLITES AS HETEROGENEOUS CATALYSTS FOR SOLVENT-FREE GLYCEROL ACETALIZATION

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Fossil fuels have significantly contributed to the ongoing climate crisis. One potential alternative for the short to medium term is biodiesel [1]. Despite its growth in recent decades, biodiesel production remains economically challenging compared to petrodiesel. To enhance the economic feasibility, researchers have turned to glycerol, a major by-product of biodiesel production, as a precursor for synthesizing valuable compounds through various pathways. One promising avenue involves the acid-catalyzed acetalization reaction, which can produce alternative fuel additives. While much research has focused on using acetone to selectively synthesize solketal, other aldehydes and ketones can undergo similar reactions, yielding products with potential as fuel additives [2,3]. This study aims to optimize the acetalization of glycerol with alternative ketones and aldehydes, employing zeolites as heterogeneous catalysts. Key reaction parameters, including reagent/glycerol molar ratio, temperature, time, and catalyst concentration, will be investigated. Glycerol conversion and product selectivity will be determined via gas chromatography (GC) analysis, with a focus on the recovery, stability, and reusability of the catalysts.

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Acknowledgments:

This work received financial support from PT national funds (FCT/MCTES) through LAQV-REQUIMTE (UIDB/50006/2020 & UIDP/50006/2020) and CICECO-Aveiro Institute of Materials (UIDB/50011/2020 & UIDP/50011/2020). The position held by I.C.M.S.S.-V. (Ref. 197_97_ARH-2018) was 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 article 23 of the Decree-Law 57/2016 of 29 August, changed by Law 57/2017 of 19 July.

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MICROBIALLY CATALYZED ANODE AND CATHODE MICROBIAL ELECTROSYNTHESIS SYSTEM FOR EFFICIENT CARBONDIOXIDE SEQUESTATION AND VOLATILE FATTY ACID PRODUCTION

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The on-going climate crisis and accelerating production of greenhouse gases such as carbon dioxide has sparked a sense of urgency in the scientific community to come up with solutions to sequestrate and/or recycle CO_2 [1]. Microbial electrosynthesis (MES) has emerged as a renewable and green technology that uses electroactive microbial catalysts to mineralize and treat different wastes/pollutants such as CO_2 [2]. This study aims to develop a novel dual biocatalyzed MES consisting of an efficient gas diffusion biocathode for CO_2 sequestration in combination with a bioanode for simultaneous product valorization. The use of biocatalysts both at the anode and cathode in a dual biocatalytic MES can simultaneously treat CO_2 and waste pollutants along with bio production of chemicals making the process more energy and cost efficient. The developed system will minimize the carbon footprint mitigating climate change with a significant scientific and societal impact. The decreasing CO_2 emissions and simultaneous biotransformation of wastes in the bioanode will have a great societal impact resolving not only the long going carbon capture crisis but at the same time presenting a sustainable platform for environmental remediation and chemical production. The use of dual bio-catalysed MES will create new knowledge in biosynthesis, power and fuel generation along with persistent pollutant treatment with bioelectrochemical systems using microbes.

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Acknowledgments:
This work was supported by This research is supported by the Marie Skłodowska-Curie Actions Postdoctoral Fellowships 2021 (Project: 101068836 — BIOELECTRO-CO2, HORIZON-MSCA-2021-PF-01-01). and Fundação para a Ciência e Tecnologia (Portugal) through the Research Unit MOSTMICRO – UIDB/04612/2020 and UIDP/04612/2020, and Associate Laboratory LS4FUTURE – LA/P/0087/2020.

P

RUTHENIUM(II) PHOSPHINE COMPLEXES WITH MERCAPTO LIGAND AS NEW POTENTIAL ANTIMELANOMA AGENTS

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Ruthenium has become a popular metal used in the pursuit of anticancer agents because of its special characteristics such as hexavalent coordination, easy modulation by different ligands and the accessible oxidation states (II and III) in physiological solutions[1]. The coordination of ligands with prior biological activity to ruthenium is an intriguing strategy to obtain new compounds that are more cytotoxic than individual compounds, due the synergistic effects[2].Therefore, in this work we have synthesized, characterized and evaluated the biological properties of new ruthenium complexes with the general formula $[Ru(N\text{-}S)(P\text{-}P)_2]PF_6$, and $[Ru(N\text{-}S)(N\text{-}N)_2]PF_6$, where N-S represents H2mq = 2-mercapto-4(3H)-quinazoline, P-P can be either dppe (1,2'-*bis*(diphenylphosphine)ethane), dppm (1,1'-*bis*(diphenylphosphine)methane), dppen (1,2'-*bis*(diphenylphosphine)ethene) and N-N signifies bipy (2,2'-bipyridine). All complexes containing phosphinic ligands displayed an inhibition of melanoma cell growth in a dose-dependent manner. The IC_{50} values of the complex containing the dppen phosphine exhibited four times greater activity against the A-375 (human melanoma) compared to the non-tumor HaCat (keratinocyte cells) cells. Moreover, this complex demonstrated the capacity to inhibit colony formation in both HaCat and A-375 cells, with a more pronounced effect on the A-375 cells. Also, alter the morphology of A-375 cells, as well as inhibit cell migration at concentrations of 0.2 and 0.4 μM. The interaction between ruthenium complexes and the biomolecules DNA and Human Serum Albumin (HSA), was also investigated. All complexes exhibited weak interaction with DNA, possibly through the grooves. The interaction of the complexes with HSA was also evaluated using the fluorescence technique, which allowed to verify that the interaction of the complexes with HSA is moderate. In light of the obtained results, it is observed that ruthenium phosphine complexes containing the ligand mercapto H2mq exhibit promising cytotoxic properties against melanoma.

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Acknowledgments:

This work was supported by the Brazilian Agencies of Research: CAPES, CNPq, FAPESP (grant number 2021/14210-3) and FAPDF (grant number 00193-00002088/2023-42).

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