12th IBCC

INORGANIC & BIOINORGANIC Chemistry Conference

PORTO
5|6 JULY 2018
INSTITUTO DE CIÊNCIAS
BIOMÉDICAS DE ABEL SALAZAR
SALÃO NOBRE › COMPLEXO ICBAS/FFUP

ABSTRACTS ›

SOCIEDADE PORTUGUESA DE QUÍMICA
DIVISÃO DE QUÍMICA INORGÂNICA E BIOINORGÂNICA

TITLE

Book of Abstracts 12th IBCC – Inorganic and Bioinorganic Chemistry Conference of the Division of Inorganic and Bioinorganic Chemistry of SPQ

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COVER ART DESIGN

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Sociedade Portuguesa de Química
Av. da República, 45 - 3º Esq
1050-187 Lisboa - Portugal

DATE

July 2018

12th IBCC

INORGANIC & BIOINORGANIC Chemistry Conference

Organized under the auspices of Sociedade Portuguesa de Química (SPQ)

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ORGANIZING ENTITIES

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GENERAL INFORMATION

CONFERENCE VENUE

Salão Nobre
Complexo ICBAS/FFUP
Instituto de Ciências Biomédicas de Abel Salazar - ICBAS
Rua Jorge de Viterbo Ferreira 228,
4050-313 Porto
Portugal

GPS: Lat.=41,148; Lon.=-8.626

REGISTRATION

All attendees must register at the registration/information desk located at the foyer of the Main Auditorium (Salão Nobre) that will be open from 9h00 through the course of the scientific program.

AUDIO-VISUAL EQUIPMENT

The conference room is equipped with a computer and standard audio-visual equipment namely a data projector, projection screen, a laser pointer, and a microphone. Each speaker should upload and review his/her presentation as far in advance as possible, being advised for it to be placed in the previous session. Speakers at Poster Pitch/Flash communication sessions are required to provide their presentation upon registration.

Please take note of the following: All presentations must use a PowerPoint (Microsoft) or PDF format. A USB memory stick should be used for uploading the presentation. Personal laptops cannot be used for presentations.

ORAL PRESENTATIONS

Keynote Lectures (KL) will last 30 minutes, including the discussion. Oral Communications (OC) will last 10 minutes, including discussion. Poster Pitch/Flash communications will be strictly kept to 3 minutes, no time for discussion will be considered; discussion is expected to occur during the poster sessions.

All speakers are requested to carefully plan the presentation in order to respect the schedule avoiding delays in the program.

POSTER SESSIONS

Posters should be affixed upon registration and should be held in the stands throughout the scientific program. Members of the organizing committee will be available to assist attendees during poster set-up.

LUNCHS AND COFFEE-BREAKS

There are several restaurants near the conference venue, and there is a canteen and cafeteria inside the FFUP/ICBAS building (building 2, ground floor). Do not hesitate in contacting organizing committee members for more details and advice.

Morning and afternoon sessions will be interrupted for Coffee-Breaks, which will be simultaneous with Poster Sessions. Coffee and nibbles will be available at near the poster stands at the foyer of the conference auditorium.

SOCIAL EVENT

The Conference dinner will be held at Restaurante **Casa da Música** on July 5th at 20H30. **Casa da Música** kindly offered us the opportunity to perform a **guided tour** of this beautiful building designed by Rem Koolhaas. If you are interested in visiting this landmark of our city, please make sure to arrive on time.

Casa da Música - Piso 7
Avenida da Boavista, 604-610,
4149-071, Porto

GPS: Lat.=41.158, Lon.=-8.631
(http://www.casadamusica.com/informacoes/como-chegar/)

12th IBCC Program			
Time	05/07/2018_Quinta-feira	Time	06/07/2018_Sexta-feira
8:30	Registration		
9:30	Opening Session	9:00	**KL5:** Ana Daniel-da-Silva *"Surface Functionalization in Engineered Nanoparticle Design for Bioapplications"* ***Chair:*** *Tito Trindade*
10:00	**KL1:** Ricardo Franco *"Metal Nanoparticle-based Bionanosensors"* ***Chair:*** *Maria Rangel*	9:30	Oral communications OC9 – OC12 ***Chair:*** *Tito Trindade*
10:30	**KL2:** Diana Fernandes *"Carbon-based Nanomaterials for Electrocatalysis"* ***Chair:*** *Baltazar de Castro*	10:30	Coffee-break & Posters
11:00	Coffee-break & Posters	11:00	**KL6:** Carla Nunes *"Molybdenum Nanomaterials as Versatile Catalysts"* ***Chair:*** *Maria José Calhorda*
11:30	Oral communications OC1 – OC4 ***Chair:*** *Carla Nunes*	11:30	Flash communications ***Chair:*** *André Silva*
12:30	Lunch	12:30	Lunch Meeting of the Division of Inorganic and Bioinorganic Chemistry of SPQ
14:30	**KL3:** Filipe Paz *"Structural Flexibility in Phosphonate-Based Metal-Organic Frameworks"* ***Chair:*** *Joaquim Marçalo*	14:30	Oral communications OC13 – OC16 ***Chair:*** *Pedro Vaz*
15:00	Flash communications ***Chair:*** *André Silva*	15:30	**KL7:** Prémio Alberto Romão Dias Cristina Freire ***Chairs:*** *Maria Rangel; Carlos Romão*
16:00	Coffee-break & Posters	16:00	Coffee-break & Posters
16:30	**KL4:** Isabel Correia *"Speciation and Cytotoxicity of Phenanthroline Metal Complexes"* ***Chair:*** *José Moura*	17:00	Silver Anniversary celebration ***Chairs:*** *Maria Rangel; Baltazar de Castro*
17:00-18:00	Oral communications OC5 – OC8 ***Chair:*** *Ricardo Franco*	17:45-18:00	Closing Session
20:30	Casa da Música		
	Visit and Conference Dinner		

12th IBCC Extended Program

Time	05/07/2018
8:30	Registration
9:30	Opening Session
10:00	**KL1:** Ricardo Franco *"Metal Nanoparticle-based Bionanosensors"* ***Chair:*** *Maria Rangel*
10:30	**KL2:** Diana Fernandes *"Carbon-based Nanomaterials for Electrocatalysis"* ***Chair:*** *Baltazar de Castro*
11:00	Coffee-break & Posters
11:30	**Oral communications: OC1 – OC4** **OC1:** Carla Queirós: *"The influence of structural features in the catalytic activity of cobalt(II) based coordination polymers"* **OC2:** Filipe Monteiro-Silva: *"Behaviour of catechol-based rosamine chemosensor in the presence of copper(II)"* **OC3:** Mani Outis: *"Photoluminescence and thermochemical properties of highly emissive Eu(III) ionic liquids"* **OC4:** Ana C. Fernandes: *"One-pot synthesis of amines from biomass resources"* ***Chair:*** *Carla Nunes*
12:30	Lunch
14:30	**KL3:** Filipe Paz *"Structural Flexibility in Phosphonate-Based Metal-Organic Frameworks"* ***Chair:*** *Joaquim Marçalo*
15:00	Flash communications Posters: P1 to P20 ***Chair:*** *André Silva*
16:00	Coffee-break & Posters
16:30	**KL4:** Isabel Correia *"Speciation and Cytotoxicity of Phenanthroline Metal Complexes"* ***Chair:*** *José Moura*
17:00-18:00	**Oral communications: OC5 – OC8** **OC5:** Luísa Maia: *"Biological CO_2 reduction: aiming to develop a catalyst for the utilization of the abundant atmospheric CO_2"* **OC6:** Cristina M. Cordas: *"Characterization of the Desulfovibrio desulfuricans formate dehydrogenase direct electrochemical behaviour"* **OC7:** Susana L. H. Rebelo: *"Biomimetic catalysis by Fe(III) and Mn(III) porphyrins: new nanomaterials and new mechanistic insights"* **OC8:** Tânia Soares: *"Potential pro-inflammatory hazard of low size and citrate-coated silver nanoparticles for human neutrophils"* ***Chair:*** *Ricardo Franco*
20:30	Casa da Música
	Visit and Conference Dinner

12th IBCC Extended Program

Time	06/07/2018
9:00	**KL5:** Ana Daniel-da-Silva *"Surface Functionalization in Engineered Nanoparticle Design for Bioapplications"* ***Chair:*** *Tito Trindade*
9:30	**Oral communications: OC9 – OC12** **OC9:** Cláudia C.L. Pereira: *"Carbon dioxide as building block in the synthesis of the anti-infective agent hexamine"* **OC10:** Andreia Valente: *"Ruthenium cyclopentadienyl compounds: cytotoxic agents against resistant cancer cells"* **OC11:** Ana Petronilho: *"Guanine based N-heterocyclic carbenes: synthesis and base pairing properties"* **OC12:** Ana I. Tomaz: *"Ruthenium complexes as cancer metallodrugs"* ***Chair:*** *Tito Trindade*
10:30	Coffee-break & Posters
11:00	**KL6:** Carla Nunes *"Molybdenum Nanomaterials as Versatile Catalysts"* ***Chair:*** *Maria José Calhorda*
11:30	Flash communications Posters: P21 to 35 & **Qlabo** presentation ***Chair:*** *André Silva*
12:30	Lunch Meeting of the Division of Inorganic and Bioinorganic Chemistry of SPQ
14:30	**Oral communications: OC13 – OC16** **OC13:** Andreia F. Peixoto: *"Highly active sulfonic acid aryl-silica nanoparticles catalysts for FFA esterification"* **OC14:** Beatriz Royo: *"Manganese organometallic complexes in catalytic reductions"* **OC15:** Tânia V. Pinto: *"Designing novel X-ray shielding bismuth oxide-coated textiles"* **OC16:** Joana S. Teixeira: *"New intelligent textiles for energy storage: from hybrid nanomaterials to supercapacitor devices"* ***Chair:*** *Pedro Vaz*
15:30	**KL7:** Prémio Alberto Romão Dias Cristina Freire ***Chairs:*** *Maria Rangel; Carlos Romão*
16:00	Coffee-break & Posters
17:00	Silver Anniversary celebration ***Chairs:*** *Maria Rangel; Baltazar de Castro*
17:45-18:00	Closing Session

	List of Keynote Lectures
KL1	*Metal Nanoparticle-based Bionanosensors* Ricardo Franco and Eulália Pereira
KL2	*Carbon-based Nanomaterials for Electrocatalysis* Diana Fernandes
KL3	*Structural Flexibility in Phosphonate-Based Metal-Organic Frameworks* Filipe A. A. Paz
KL4	*Speciation and Cytotoxicity of Phenanthroline Metal Complexes* Isabel Correia, Patrique Nunes, Cristina P. Matos, Nádia Ribeiro, Sofia Gama, Fernanda Marques, João Costa Pessoa
KL5	*Surface Functionalization in Engineered Nanoparticle Design for Bioapplications* Ana Daniel-da-Silva
KL6	*Molybdenum Nanomaterials as Versatile Catalysts* Carla Nunes
KL7	Prémio Alberto Romão Dias A. Cristina Freire
	List of Oral Communications
OC1	*The influence of structural features in the catalytic activity of cobalt(II) based coordination polymers* Carla Queirós, Baltazar de Castro, Ana M. G. Silva, Salete Balula, Luís Cunha Silva
OC2	*Behaviour of catechol-based rosamine chemosensor in the presence of copper(II)* Filipe Monteiro-Silva, Alberto Diez-Varga, Maria Rangel, Ana M. G. Silva, Tomás Torroba
OC3	*Photoluminescence and thermochemical properties of highly emissive Eu(III) ionic liquids* Mani Outis, João P.Leal, Hugo Cruz, M. Helena Casimiro, Luis M. Ferreira, Fábio Fernandes, Bernardo Monteiro, César A.T.Laia, Cláudia C.L.Pereira
OC4	*One-pot synthesis of amines from biomass resources* João A. T. Caetano, Ana C. Fernandes
OC5	*Biological CO_2 reduction: aiming to develop a catalyst for the utilization of the abundant atmospheric CO_2* Luísa Maia, Isabel Moura, José J. G. Moura
OC6	*Characterization of the Desulfovibrio desulfuricans formate dehydrogenase direct electrochemical behaviour* Cristina M. Cordas, M. Campaniço, R. Baptista, L. Maia, J.J.G. Moura, I. Moura
OC7	*Biomimetic catalysis by Fe(III) and Mn(III) porphyrins: new nanomaterials and new mechanistic insights* Susana L. H. Rebelo, Tânia Moniz, Maria Rangel, Baltazar de Castro, Craig J. Medforth
OC8	*Potential pro-inflammatory hazard of low size and citrate-coated silver nanoparticles for human neutrophils* Tânia Soares, Félix Carvalho, Eduarda Fernandes, Marisa Freitas
OC9	*Carbon dioxide as building block in the synthesis of the anti-infective agent hexamine* Cláudia C.L.Pereira, Marco R. Gomes da Silva, João P. Leal, Bernardo Monteiro

OC10	*Ruthenium cyclopentadienyl compounds: cytotoxic agents against resistant cancer cells* Andreia Valente, Leonor Côrte-Real, Helena Garcia
OC11	*Guanine based N-heterocyclic carbenes: synthesis and base pairing properties* Maria Inês P.S. Leitão, Carmen Gonzalez, Zuzanna Filipiak, Ana Petronilho
OC12	*Ruthenium complexes as cancer metallodrugs* Ana Isabel Tomaz, R. F. M. de Almeida, C. Roma-Rodrigues, F. Marques, A. D. de Sousa, O. Rojas, C. Matos, A. R. Fernandes, M. H. Garcia
OC13	*Highly active sulfonic acid aryl-silica nanoparticles catalysts for FFA esterification* Andreia F. Peixoto, Mohamed M. Aboelhassan, Sónia M. Silva, Cristina Freire
OC14	*Manganese organometallic complexes in catalytic reductions* Mara Pinto, Sofia Friães, Federico Franco, Julio LLoret-Fillol, Beatriz Royo
OC15	*Designing novel X-ray shielding bismuth oxide-coated textiles* Tânia V. Pinto, P.S.F. Ramalho, C. Brito, A.L. Gonçalves, A. Barros, G. Santos, J. Morgado, O.S.G.P. Soares, M.F.R. Pereira, C. Freire, C. Pereira
OC16	*New intelligent textiles for energy storage: from hybrid nanomaterials to supercapacitor devices* Joana S. Teixeira, Rui S. Costa, André M. Pereira, Clara Pereira
	List of Poster Communications *List of Flash Communications
P1*	*Microwave-assisted synthesis of functional pyrrolidine-fused chlorins for medicinal applications* Alexandre Seabra, José Almeida, Andreia Leite, Maria Rangel, Augusto C. Tomé, Ana M. G. Silva
P2*	*Sustainable catalytic systems based on UiO-66(Zr) for oxidative desulfurization of diesel fuels* Alexandre Viana, Susana Ribeiro, Baltazar de Castro, Salete Balula, Luís Cunha Silva
P3*	*Design of molecular wires based on organometallic iron (II) and ruthenium (II) complexes* Ana Catarina Sousa, M. F. M. M. Piedade, M. Paula Robalo
P4	*Serum transferrin glycation and the occurrence of non-transferrin-bound iron in type 1 Diabetes Mellitus* Cláudia S. Cardoso, Davide Carvalho, Maria Rangel, André M. N. Silva
P5*	*Photoluminescent composite based on decatungstoeuropate@periodic mesoporous organosilica* Carlos M. Granadeiro, Susana O. Ribeiro, Anna M. Kaczmarek, Luís Cunha-Silva, Pedro L. Almeida, Sandra Gago, Rik Van Deun,Baltazar de Castro, Salete S. Balula
P6*	*Ternary iron and ruthenium complexes for cancer therapy: cytotoxicity and dna interaction* Cristina P. Matos, Zelal Adiguzel, Yasemin Yildizhan, Patrique Nunes, Luis Raposo, A. R. Fernandes, M. Helena Garcia, João Costa Pessoa, Ceyda Acilan, Ana Isabel Tomaz, Isabel Correia
P7	*Green desulfurization systems using a peroxophosphomolybdate as catalyst* Diana Julião, Ana C. Gomes, Martyn Pillinger, Rita Valença, Jorge C. Ribeiro, Luís Cunha-Silva, Isabel S. Gonçalves, Salete S. Balula
P8	*The potential role of soil application of a tris(3-hydroxy-4-pyridinonate) iron (III) complex in iron deficiency chlorosis treatment* Elsa Rodrigues, Sofia Ferreira, Andreia Leite, Tânia Moniz, Maria Rangel, Marta W. Vasconcelos, Susana M. P. Carvalho, Carla S. Santos

P9	*Efficient titanium-polyoxometalate supported by SBA-15-TM as catalysts and its performance in oxidative desulfurization* Fátima Mirante, Susana O. Ribeiro, Baltazar de Castro, Carlos M. Granadeiro, Salete S. Balula
P10	*MoS$_2$ Nanomaterials as heterogenenous catalyst in nitroarene reduction* Filipe Gaspar, Carla Nunes
P11	*Bifunctional porphyrin-based Nano-Metal-Organic Frameworks: catalytic and chemosensing studies* Flávio Figueira, Carla F. Pereira, Ricardo F. Mendes, João Rocha, Mário M. Q. Simões, João P. C. Tomé, Filipe A. Almeida Paz
P12*	*Design of new bio-MOFs as multidelivery systems for osteoporosis treatment* Jéssica Silva Barbosa, Susana S. Braga, Filipe A. Almeida Paz
P13*	*Magnetic bio-hybrid nanocarriers for pH-responsive release of doxorubicin* João Nogueira, Sofia Soares, Tito Trindade, Ana Luísa Daniel da Silva
P14	*The f-elements in the gas phase – inorganic chemistry chalanges at the bottom of the periodic table* Bernardo Monteiro, João P. Leal, Joaquim B. Branco, Joaquim Marçalo, José M. Carretas, Leonor Maria
P15*	*Antitumor agent–porphyrin conjugates for targeted photodynamic therapy* José Almeida, Carla Queirós, Andreia Leite, Maria Rangel, Philipp Stockmann, Marta Gozzi, Sara Durini, Evamarie Hey-Hawkins, Ana M. G. Silva
P16	*Uranium(III) complexes supported by hydrobis(mercaptoimidazolyl)borates: synthesis and oxidation chemistry* Leonor Maria, Isabel C. Santos, Joaquim Marçalo, Isabel Santos
P17*	*Layered MOF-based materials prepared in ionic liquids: oxidative catalysis activity* André D. S. Barbosa, Baltazar de Castro, Salete S. Balula, Luís Cunha-Silva
P18*	*Caffeine based nickel(II) n-heterocyclic carbenes: synthesis and catalytic applications* Maria Inês P.S. Leitão, Nicolaus Giannopoulos, Ana Petronilho
P19*	*A highly active n-heterocyclic carbene Mn(I) complex for selective electrocatalytic CO$_2$ reduction to CO* Mara Pinto, Federico Franco, Beatriz Royo, Julio Lloret-Fillol
P20*	*Detection of C-reactive protein using functionalized gold nanoparticles* Maria António, Rui Vitorino, Ana L. Daniel-da-Silva
P21*	*Design of functionalized materials for application in analytical methods for determination of Fe(III)* Maria Inês Oliveira, Andreia Leite, André Silva, Ana M. G. Silva, Maria Rangel
P22	*Synthesis and evaluation of fluorescence properties of a europium-functionalized MOF* Mário Luís C. G. Pinho, Carla Queirós, Andreia Leite, Baltazar de Castro, Maria Rangel, Luís Cunha-Silva, Ana M. G. Silva
P23*	*Evaluation of the antibacterial activity against Gram-positive and Gram-negative strains of bis(3-hydroxy-4-pyridinonato) copper(II) complexes.* Andreia Leite, Lucinda J. Bessa, Ana M. G. Silva, Paula Gameiro, Maria Rangel

P24*	*Efficient graphene-based electrocatalysts for emerging pollutants determination* Paula Teixeira, Diana M. Fernandes, Penny Mathumba, Emmanuel I. Iwuoha, C. M. Delerue-Matos, Cristina Freire
P25*	*Co/Al hydrotalcite with Au_{NP} for environmental catalytic applications* Inês J. Marques, Ruben Torres, Pedro D. Vaz, Carla D. Nunes
P26*	*Microfluidic paper-based analytical device for the determination of salivary calcium* Mafalda T. S. Silva, Karina C. Acciainoli, Raquel B. R. Mesquita, António O. S: S. Rangel
P27	*Lamellar coordination polymer with a remarkable catalytic activity* Ricardo F. Mendes, Margarida M. Antunes, Patrícia Silva, Paula Barbosa, Filipe Figueiredo, Anthony Linden, João Rocha, Anabela A. Valente, Filipe A. Almeida Paz
P28	*Structure, electrochemistry and anticancer activity of novel thiosemicarbazone complexes of ruthenium(II)* Ricardo G. Teixeira, Andreia Valente, Fernando Avecilla, M. Paula Robalo, Susana Santos, Ana Isabel Tomaz, M. Helena Garcia
P29*	*Microwave enhanced synthesis of azide substituted porphyrins* Rodrigo P. Monteiro, José Almeida, Cátia Teixeira, Paula Gomes, Maria Rangel, Ana M. G. Silva
P30*	*New generation of energy storage devices: carbon-based microsupercapacitors* Rui S. Costa, André M. Pereira, Clara Pereira
P31*	*The influence of polyoxometalate structures in oxidative catalytic systems: activation strategies* Salete Balula, Susana Ribeiro, Diana Julião, Fátima Mirante, Isabel Gonçalves, Martyn Pillinger, Luís Cunha-Silva, Baltazar de Castro, Carlos Granadeiro
P32	*Micro-structural characterization of ultrasonically welded wires* Sandra Matos, Fernando Veloso, Carlos Santos, Emanuel Carvalho, Leonardo Gonçalves
P33*	*Multi-elemental characterization and differentiation of portuguese wines according to their protected geographic indications* Sílvia Rocha, Edgar Pinto, Agostinho Almeida, Eduarda Fernandes
P34*	*Improvement of the synthesis of 3-hydroxy-4-pyridinone chelators: a comparative study using conventional, microwave and ohmic heating* Sílvia Vinhas, Ana M. G. Silva, Tânia Moniz, Andreia Leite, Baltazar de Castro, Maria Rangel
P35*	*The potential role of three tris(3-hydroxy-4-pyridinonate) iron(iii) complexes on iron deficiency chlorosis prevention* Sofia Ferreira, Carla S. Santos, Andreia Leite, Tânia Moniz, Marta W. Vasconcelos, Maria Rangel
P36	*Design of a new fluorescent carboxyrosamine labelled 3-hydroxy-4-pyridinone iron(III) chelator with potential antibacterial activity* Tânia Moniz, Ana M. G. Silva, Baltazar de Castro, Maria Rangel
P37	*Zinc(II), copper(II), nickel(II) and cobalto(II/III) mixed ligand complexes as multi-purpose metallodrugs* Teresa M. Santos, B. L. Ferreira, R. Mendes, F. A. Paz, A. L. D.-da-Silva

*will present a Flash Communication

Flash Communications schedule will follow poster order:

P1 to P20 will be on July 5th

P21 to P35 will be on July 6th

Keynote Lectures

KN1

METAL NANOPARTICLE-BASED BIONANOSENSORS

Ricardo Franco[1] and Eulália Pereira[2]
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4169-007 Porto, Portugal

Gold and silver nanoparticles (NPs) with different morphologies exhibit interesting and innovative chemical, optical and electrical nanoscale properties. These can be explored in the context of sensitivity improvement for biosensing applications [1]. The motivation for our work has been key bio-/non-bio interactions occurring at the surface of these nanoparticles when they are conjugated with detecting biomolecules (e.g., oligonucleotides, enzymes and antibodies/antigens) [1,2]. The techniques used in these studies are a mixture of spectroscopic (UV/visible, fluorescence, light dispersion, Raman/SERS) and biochemical (agarose gel electrophoresis, column chromatography) techniques, that are especially suited to study alterations of nanoscale properties, namely the ones related to optical/plasmonic effects. Examples from our own research include DNA-detection systems based on either Au nanospheres or Au nanotriangular plates; enzymatic oxidase activity enhancement induced by Au nanospheres; and an immunodetection system for malaria antigens. This latter system is based on Au nanospheres-monoclonal antibodies conjugates, that specifically recognize malaria antigens in clinical samples, on a competitive fluorescence-based format [3]. The application of the same AuNP-antibodies conjugates on a point-of-care paper-based immunochromatographic assay for malaria detection, is under development. Still in early stages of development, AuNP-synthetic antigen conjugates are intended to detect circulating antibodies, for the non-invasive detection of pneumonia in plasma samples. Our first steps on the use of Ag nanostars drop-casted on paper, as an innovative and ultra-sensitive plasmonic surface for SERS (Surface Enhanced Raman Spectroscopy)-based detection [4], pave the way for a future platform for SERS-based immunodetection.

Acknowledgements: This work was supported by the Applied Molecular Biosciences Unit-UCIBIO and by the Associate Laboratory for Green Chemistry-LAQV, which are financed by national funds from FCT/MCTES (UID/QUI/50006/2013 and UID/Multi/04378/2013) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER - 007265), and also under the project DISERTOX PTDC/CTM-NAN/2912/2014, financed by national funds from FCT/MCTES.

[1] Peixoto de Almeida, M., *et al*. *Gold Nanoparticles in Analytical Chemistry* 2014 Valcárcel M, López-Lorente A.I. (eds.), 1st ed., *66*, 529–567, Elsevier
[2] Franco, R. and Pereira, E. *Encyclopedia of Metalloproteins*. 2013, 908-915, Kretsinger, R.H.; Uversky, V.N.; Permyakov, E.A. (eds.), Springer Science+Business Media
[3] Cavadas, M.A.S., *et al*. *Part. Part. Syst. Charact.* 2016 *33(12)*, 906–915
[4] Oliveira, M.J., *et al*. *Sci. Rep.* 2017 *7*, 2480

KN2

CARBON-BASED NANOMATERIALS FOR ELECTROCATALYSIS

Diana M. Fernandes

Requimte/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Portugal, diana.fernandes@fc.up.pt

Since their discovery, carbon nanomaterials (CMs) have been attracting considerable experimental and theoretical interest because of their exceptional structures and properties. Due to their unique structural diversity and the ease of tuning their chemical, electronic and crystalline properties, CMs are attractive for a wide range of electrochemical applications, such as electrocatalysis, fuel cells, batteries and supercapacitors [1,2]. CMs such as carbon nanotubes and graphene have also attracted considerable interest in the field of modified electrodes, due to low residual current and readily renewable surfaces, providing an important and feasible platform for electroanalysis [3]. Also, their properties, such as fast electron transportation, excellent mechanical strength and high surface area, suggest their ability to detect analytes and to promote a fast electron transfer between the electrode and the analyte, which make them promising ECs. CMs have also been presented as effective electrocatalysts that fulfill the requirements for several electrochemical reactions of massive importance in energy conversion systems. Additionally, the possibility of chemical modification and/or functionalization broadens their utility and gives rise to favourable electrocatalytic properties with regard to several electrochemical processes.

Here, the electrocatalytic applications of several carbon-based ECs developed by our group in two major areas of high current impact, electrochemical sensing and renewable energy, are overviewed.

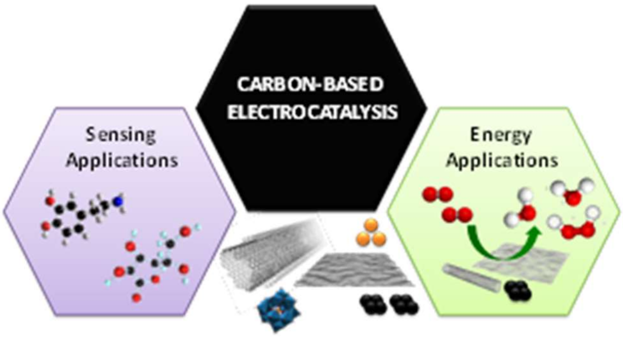

Figure 1: Electrochemical applications of carbon-based ECs.

Acknowledgements: Thanks are due to: Project UNIRCELL (POCI-01-0145-FEDER-016422) funded by FEEI through Programa Operacional Competitividade e Internacionalização (COMPETE2020) and by national funds through FCT; FCT/MEC and EU under FEDER funds (POCI/01/0145/FEDER/007265), Program PT2020 (UID/QUI/50006/2013) and Program FCT–UT Austin, Emerging Technologies (Project UTAP-ICDT/CTM-AN/0025/2014).

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KN3

STRUCTURAL FLEXIBILITY IN PHOSPHONATE-BASED METAL-ORGANIC FRAMEWORKS

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The quest for novel zeo-type compounds remains intensive research area in Inorganic Chemistry (and Materials Science) because to their importance in the global chemical economy. Though Metal-Organic Frameworks (MOFs) have been known for decades, it was Omar Yaghi's vision [1] that showed that these crystalline compounds could sustain permanent porosity and being used as functional materials. Countless new MOFs are reported on a daily basis. However, scientific reports are usually based on slow, time-consuming methods, using hazardous solvents, with MOFs exhibiting poor thermal and mechanical stabilities, which also hinders their use in practical applications.

Our research group is walking into almost two decades of experience in MOF chemistry and applications, with focus on the use of phosphonate-based linkers (-PO_3) connected to lanthanides (Ln), yielding functional lanthanide-polyphosphonate MOFs (LnMOFs): while tetrahedral -PO_3 linkers mimic the connectivity found in zeolites, promoting structural robustness and thermal stability, Ln cations induce photoluminescence (PL) boosted by the linkers (*i.e.*, antenna effect) [2]. In addition, the presence of various phosphonic acid groups lining the surface of the crystallites confers to the materials the great ability to catalyse a number of reactions of industrial interest.

The present keynote will summarize some of our key achievements in the design of such functional materials [3] while also showing their great potential concerning structural flexibility [4].

Acknowledgments

I wish to give a personal and heartfelt "thank you" to all the collaborators and students involved in the research in my group over the past years. All contributed immensely with work and discussions to the great body of results. This body of work was developed within the scope of the project CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID /CTM /50011/2013), financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. Fundação para a Ciência e a Tecnologia (FCT, Portugal) is also gratefully acknowledged for funding this research and dissemination of the results.

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KN4

SPECIATION AND CYTOTOXICITY OF PHENANTHROLINE METAL COMPLEXES

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Phenanthrolines are a class of heterocyclic bioactive molecules that have attracted great interest due to their structural and chemical properties, such as aromaticity, basicity and chelating ability. Metvan, a vanadium 4,7-dimethyl-1,10-phenanthroline complex, has been recognized as one of the most promising anticancer V-compounds, active against several cancer cell types, with apoptosis-inducing activity at nanomolar concentrations.[1] Casiopeinas® are antineoplastic heteroleptic Cu-phenanthroline complexes, currently in phase I clinical trials.[2]

Metal complexes undergo speciation *in vitro* and *in vivo* conditions, which implies that the active species may be the bioactive free ligand, a synergistic effect of the ligand and metal ion, or a new metal species formed with other ligands present in the biological environment. This introduces complexity in the identification of the active species and the evaluation of the biological effects. Hence, speciation studies in biological media are a critical step in the evaluation of the therapeutic potential of a metal compound.

We report studies involving the preparation and characterization of a family of metal complexes [Cu(II), V(IV), Zn(II) and Fe(III)] of the type ML_2 with L = 2,2'-bipyridine, 1,10-phenanthroline, 1,10-phenanthrolin-5-amine and 4,7-dimethyl-1,10-phenanthroline. The photophysical properties of the complexes and ligands were determined, as well as their ability to interact with nucleic acids and serum proteins. Their cytotoxicity was evaluated towards ovarian (A2780), breast (MCF7) and prostate (PC3) cancer cell lines, under different incubation conditions. Their speciation in different environments was screened: in aqueous media to evaluate hydrolytic stability, in incubation cellular media in the presence and absence of albumin to evaluate stability and ability to bind proteins and other ligands and inside cells. With this account we aim to highlight the importance and the role speciation plays in the biological activity of metal-based drugs, so that we can begin to systematically exploit the therapeutic potential of metallodrugs.

Acknowledgements: FCT (projects UID/QUI/00100/2013, grants SFRH/BD/101214/2014 and SFRH/BD/108743/2015), Programa Operacional Regional de Lisboa (LISBOA-01-0145-FEDER-007317) and programme *Investigador* FCT.

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KN5

SURFACE FUNCTIONALIZATION IN ENGINEERED NANOPARTICLE DESIGN FOR BIOAPPLICATIONS

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Inorganic nanoparticles (NPs) exhibit unique size-dependent physical, optical, electronic and chemical properties that make them especially suited to be used as part of biomolecular composites. These include the localized plasmon resonances of gold NPs, valuable for biosensing, and the magnetic features of some metal oxide NPs, which are of interest for applications requiring magnetic guidance and separation. Nanoparticles also exhibit high surface-to-volume ratios, providing a high reactive surface available for the display of multiple biological components at their surface that can contribute to increased avidity and multifunctionality. The surface chemistry of colloidal inorganic NPs plays a crucial role in key aspects for bioapplications such as the colloidal stability in buffers or physiological fluids, targeting ability, *in vitro*/*in vivo* performance, and biocompatibility, among others. [1,2] Herein novel chemical strategies for the surface modification and bioconjugation of magnetic iron oxide NPs and gold NPs are discussed, through several examples of systems developed for specific applications in protein enrichment and detection, and drug delivery.

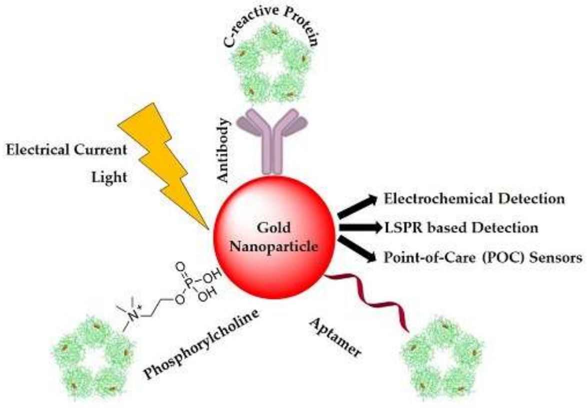

Figure 1: Strategies for the surface functionalization of gold nanoparticles aiming *in vitro* detection of C-reactive protein, which is a biomarker of cardiovascular diseases. [1]

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (UID/CTM/50011/2013), financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. A.L. Daniel-da-Silva acknowledges FCT for the IF-2014 FCT Investigator Programme.

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KN6

MOLYBDENUM NANOMATERIALS AS VERSATILE CATALYSTS

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Nanoscale materials with different morphologies have stimulated great interest due to unique properties and wide range of potential applications in contrast to their bulky counterparts [1]. The search for new catalytic materials and processes has a strong requirement in the selectivity of the chemical transformations and is thus a challenge. Molybdenum nanomaterials are one of the most attractive metals due to their special structural characteristics. Mo nanomaterials (MoO_3, MoO_2) can be assessed by different methods delivering different morphologies (nanowires, nanotubes, nanobelts or nanofibers) with diverse catalytic performances concerning both substrate conversion and product selectivity.

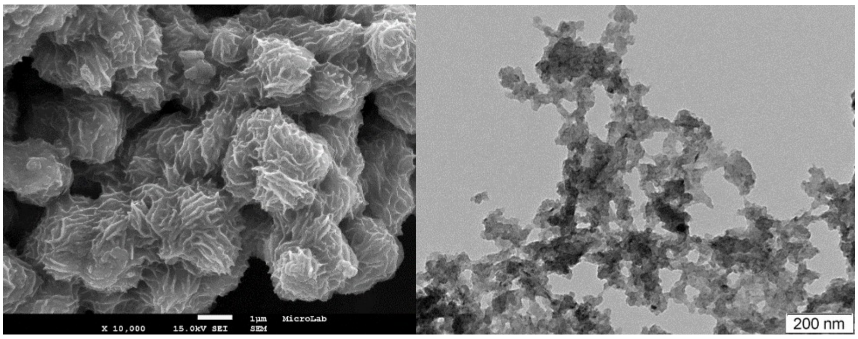

Figure 1: SEM (right) and TEM (left) images of MoO_x (x = 2, 3) materials.

In this talk, a tour on the preparation of nanosized MoO_x (x = 2, 3) materials and their catalytic applications will be shown [1-3]. This will cover relevant issues such as different synthesis procedures and their impact in morphology and catalytic activity. Concerning the catalytic testing the materials were efficient in the oxidation of olefins, sulfoxides and alcohols using *tert*-butylhydroperoxide (tbhp) and H_2O_2 as oxygen sources. The results from the catalytic experiments showed that these catalysts were very active leading to very high levels of substrate conversion and product selectivity. Efficiency tests evidence that for some transformations the nanoparticles can work under olefin:oxidant stoichiometric ratios, which is an advantage, although induction periods are observed under these conditions, found to be dependent on the synthesis process and the amount of oxidant. The catalysts were also recyclable without major loss of activity or structural changes.

Acknowledgements: Fundação para a Ciência e Tecnologia (FCT), POCI and FEDER Portugal projects EXPL/QEQ-QIN/1137/2013 and PEst–OE/QUI/UI0612/2013, are acknowledged for financial support.

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Oral Communications

OC1

THE INFLUENCE OF STRUCTURAL FEATURES IN THE CATALYTIC ACTIVITY OF COBALT(II) BASED COORDINATION POLYMERS

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Coordination polymers (CPs) can be highly organized compounds with remarkable relevance in the development of materials science and modern chemistry [1,2]. Considering the enormous interest in the synthesis of stable CP materials that can be used in heterogeneous catalysis we are exploring the 5-aminoisophthalic acid (H_2aip) to prepare new functional CPs with catalytic activity.

Two cobalt(II) based CPs (Co-CPs) were prepared in water, using two heating methods: hydrothermal and microwave-assisted synthesis. Attempts of preparing the materials using ohmic heating were performed [3]. The main goal of this work is to evaluate the effect of the synthetic methodology in the preparation of CPs with differences in the particles size, pore distribution and catalytic activity. The structural features of the two Co-CPs were determined using several techniques, such as X-ray diffraction and elemental analysis. The Co-CPs, **Co-aip_CP1** and **Co-aip_CP1**, revealed to be 2D structures, formulated as $[Co_2(aip)_2(4,4'\text{-bipy})(H_2O)_2].4H_2O$ and [Co(aip)(1,10-phen)] where: both extend to 3D supramolecular structures - **Co-aip_CP1** extends to essentially due to H-bonds while **Co-aip_CP2** extends through π–π interactions and H-bonds; **Co-aip_CP1** reveals 1D channels partially occupied by the lattice water molecules and in **Co-aip_CP2** the pores are partially occupied by the co-ligand molecules (*phen*; Figure 1). The catalytic activity of the two Co-CPs towards olefins (*cis*-cyclooctene and styrene) oxidation was studied and the performance of both catalysts was compared.

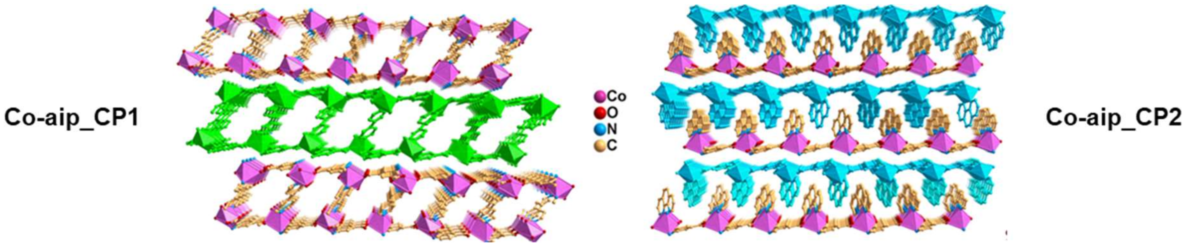

Figure 1: Representation of the extended crystalline structures for **Co-aip_CP1** and **Co-aip_CP2**, where different layers are distinguished by different coloration schemes.

Acknowledgements: The authors gratefully acknowledge the COST action CM1302 (SIPs). The work was financed by European Union, FEDER (Fundo Europeu de Desenvolvimento Regional) through PT2020 and by national funds through the FCT (Fundação para a Ciência e a Tecnologia), QREN, and COMPETE, NORTE-07-0162-FEDER-000048, UID/QUI/50006/2013 (LAQV/REQUIMTE), project M-ERA-NET/0005/2014, the post-graduation SFRH/BPD/111899/2015 (to LCS) and the PhD SFRH/BD/79702/2011 (to CQ) fellowships.

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OC2

BEHAVIOUR OF CATECHOL-BASED ROSAMINE CHEMOSENSOR IN THE PRESENCE OF COPPER(II)

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Two catechol-based rosamines – Ros2,3-OH and Ros3,4-OH – containing a catechol ligand that is part of the π-system of the fluorophore, were synthesized and characterized. Catechol derivatives have found usefulness as Fe(III) probes featuring high affinity and selectivity provided by the catechol unit [1] as well as pH sensors, in combination with other pH-responsive groups [2]. Besides the already known behaviour towards specific biogenic amines, pH and select metal ions, further studies on possible selective Cu(II) sensing abilities were performed.

Synthetic route optimization, reaction methodologies, as well as photophysical studies will be presented. Furthermore, behavior in the presence of Cu(II) was assessed and possible physiological/non-physiological interfering cationic and anionic species, as well as high-affinity metal-ion chelators, including EDTA and cyclam, were tested.

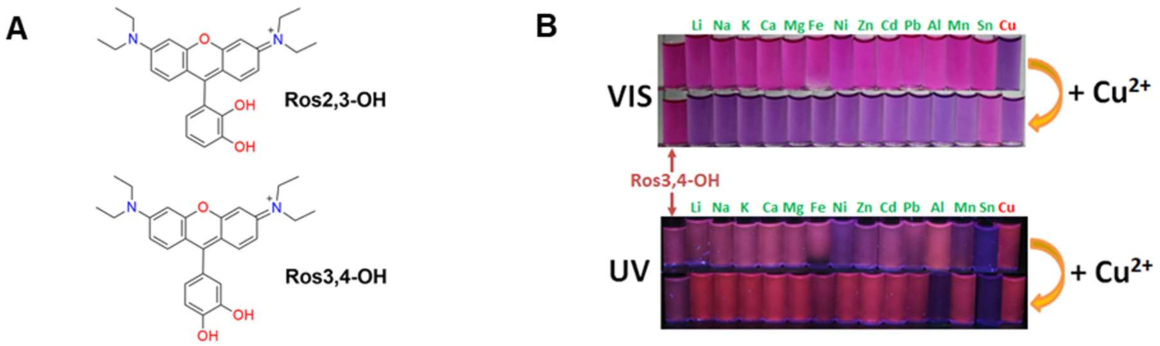

Figure 1: A) Catechol-based rosamines Ros2,3-OH and Ros3,4-OH; B) Ros3,4-OH behavior in the presence of different metal cations.

Acknowledgements: This work is financed by WaterJPI/0001/2016 within project “AGRINUPES – Integrated Monitoring and Control of Water, Nutrients and Plant Protection Products Towards a Sustainable Agricultural Sector” as well as by the European Union, FEDER through PT2020 and by national funds through the FCT (Fundação para a Ciência e a Tecnologia), QREN, and COMPETE, NORTE-07-0162-FEDER-000048, UID/QUI/50006/2013 (LAQV/REQUIMTE) and the project M-ERA-NET/0005/2014. We also gratefully acknowledge financial support from the “Ministerio de Economía y Competitividad” of Spain (Project CTQ2015-71353-R) and the “Junta de Castilla y León” of Spain (Project BU051U16).

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OC3

PHOTOLUMINESCENCE AND THERMOCHEMICAL PROPERTIES OF HIGHLY EMISSIVE Eu(III) IONIC LIQUIDS

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Combination of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionate (fod), a highly fluorinated betadiketonate, with Eu(fod)3 yielded [Eu(fod)$_4$] a simetric tetrakis europate anion with four fod units bonded to the Eu(III) centre. This anion combined with [P$_{6,6,6,14}$] cation yields [P$_{6,6,6,14}$][Eu(fod)$_4$], a Room Temperature Ionic Liquid(RTIL). During heating of this RTIL a gradual colour change was observed, from the familiar light yellow to a deep red at temperatures close to 80°C with a more intense emission at 579 nm. This phenomenon displayed visible colour reversibility [1] Also, the photoluminescence and thermochemical properties of similar complexes were investigated in detail and the influence of the long chain tetraalkylphosphonium counterion, together with the aromatic diketone ligand, on the unusual thermal behavior is presented [2]

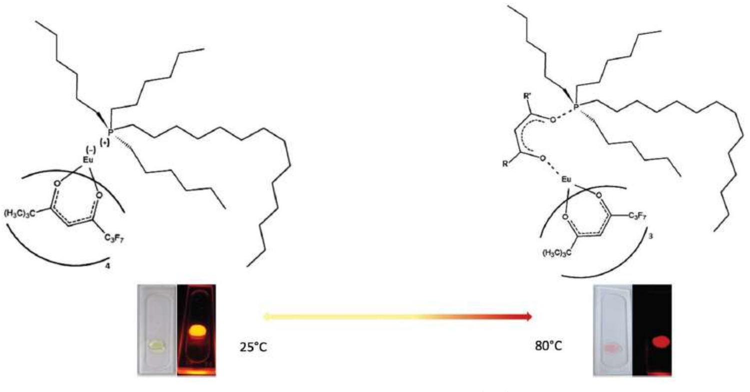

Figure 1: Possible structure of the complex Eu(III) formed upon heating to 80 ^{o}C.

Acknowledgements: This work was supported by REQUIMTE-LAQV and C2TN/IST both financed by FCT under UID/QUI/50006/2013 and UID/Multi/04349/2013 projects, respectivly. This work was also co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER - 007265).

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OC4

ONE-POT SYNTHESIS OF AMINES FROM BIOMASS RESOURCES

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Conversion of carbohydrates into valuable nitrogen compounds represents an interesting possibility for the sustainable synthesis of biologically active amines, which has been achieved with limited success. Amines derived from furfural (furfurylamines) have diverse applications, including in the preparation of polymers, biologically active compounds and as intermediates in the synthesis of pharmaceuticals such as antiseptic agents, antihypertensives and diuretics (e.g. furosemide).

This communication describes the first methodology for the direct conversion of mono- and polysaccharides into furfurylamines catalyzed by $HReO_4$.[1] These *one-pot three-reaction* and *four-reaction processes* allow the conversion of xylose and xylan, respectively, into a large variety of secondary and tertiary amines with good overall yields and chemoselectivity (Figure 1).

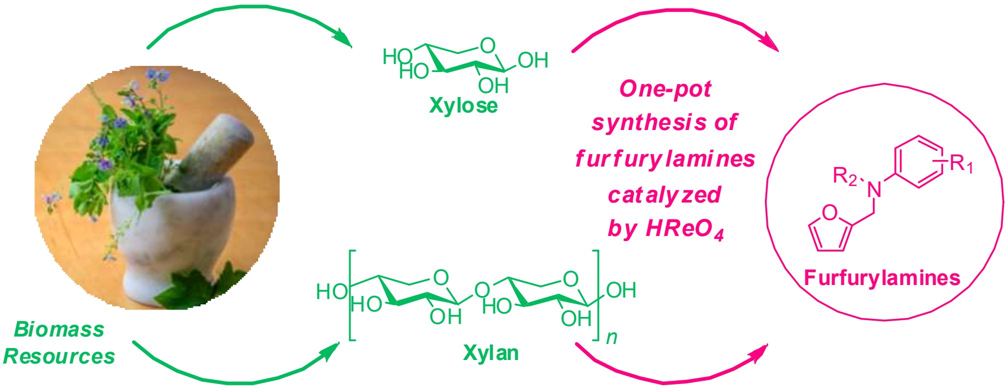

Figure 1: One-pot synthesis of amines from biomass resources.

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OC5

BIOLOGICAL CO2 REDUCTION: AIMING TO DEVELOP A CATALYST FOR THE UTILIZATION OF THE ABUNDANT ATMOSPHERIC CO2

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Formate dehydrogenases (FDH) are enzymes that catalyze the reversible two-electron oxidation of formate to carbon dioxide (eq. 1) [1-3]. The group of metal-dependent FDHs comprises only prokaryotic enzymes that hold different redox-active centers and whose active site harbors one molybdenum (or one tungsten) atom that mediates the formate oxidation/carbon dioxide reduction.

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

In this communication, the ability of the molybdenum-containing FDH from *Desulfovibrio desulfuricans* (Dd FDH) to reduce carbon dioxide to formate will be discussed. The Dd FDH was found to be one of the most efficient carbon dioxide reducers so far described in the literature, with a k_{cat} of $47s^{-1}$ and a K_m^{CO2} of 16µM [4] and a novel FDH reaction mechanism was proposed [4,5]: both formate oxidation and carbon dioxide reduction proceed through hydride transfer, through a mechanism where the sulfo group of the oxidized (Mo^{6+}=S) and reduced (Mo^{4+}-SH) molybdenum center are suggested to be the direct hydride acceptor and donor, respectively (Fig. 1).

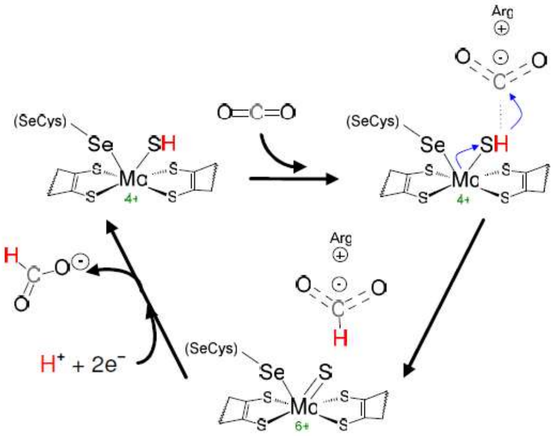

Figure 1: FDH reaction mechanism proposed by Maia et al. [4]
(the mechanism is reversible, but, for simplicity, only the carbon dioxide reduction is shown).

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OC6

CHARACTERISATION OF THE *Desulfovibrio desulfuricans* FORMATE DEHYDROGENASE DIRECT ELECTROCHEMICAL BEHAVIOR

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Formate dehydrogenase (FDH) enzymes catalyse the reversible two-electron oxidation of formate to CO_2 [1, 3]. The class of metal-dependent FDHs comprises only prokaryotic enzymes holding different redox-active centres with a catalytic site containing either one molybdenum or tungsten atom that mediates the formate oxidation or the CO_2 reduction. This reduction reaction has particular interest, since it may be a route for atmospheric CO_2 mitigation, with the simultaneous production of added-value compounds (chemical feedstocks and fuels) as formate-derived compounds.

Recently, it was found that the periplasmic FDH from *Desulfovibrio desulfuricans* (DdFDH), a molybdenum-containing FDH, is one of the most efficient enzymes for the reduction of CO_2 to formate [4]. In this work, the direct electrochemical behaviour of immobilized DdFDH was characterised. The catalytic centre redox transitions' potentials were determined in non-turnover conditions and preliminary results of the electrocatalytic activity of DdFDH towards CO_2 reduction was attained using direct electrochemical methods.

Acknowledgements: This work was supported by the LAQV, which is financed by national funds from FCT/MCTES (UID/QUI/50006/2013) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER - 007265). LM thanks to FCT/MCTES, for the fellowship grant, SFRH/BPD/111404/2015, which is financed by national funds and co-financed by FSE.

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OC7

BIOMIMETIC CATALYSIS BY Fe^{III} AND Mn^{III} PORPHYRINS: NEW NANOMATERIALS AND NEW MECHANISTIC INSIGHTS

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Heme-containing enzymes such as catalases and P450 monooxygenases have provided inspiration for a diverse range of biomimetic applications. For example, oxygenation reactions catalyzed by Fe^{III} and Mn^{III} porphyrins have been developed for a broad spectrum of substrates, providing a green production method for value-added chemicals [1,2]. In addition, synthetic metaloporphyrins can catalyze H_2O_2 dismutation or scavenge reactive oxygen species and have been studied as antioxidants.

We are currently developing novel metaloporphyrin nanostructures by ionic self-assembly of oppositely charged porphyrins [3] with the goal of using these materials as oxygenation catalysts and antioxidants (Figure 1). Studies for the evaluation of antioxidant activity by an EPR spin-trapping study have also provided new mechanistic insights into the catalase and monooxygenase activities of synthetic metaloporphyrins.

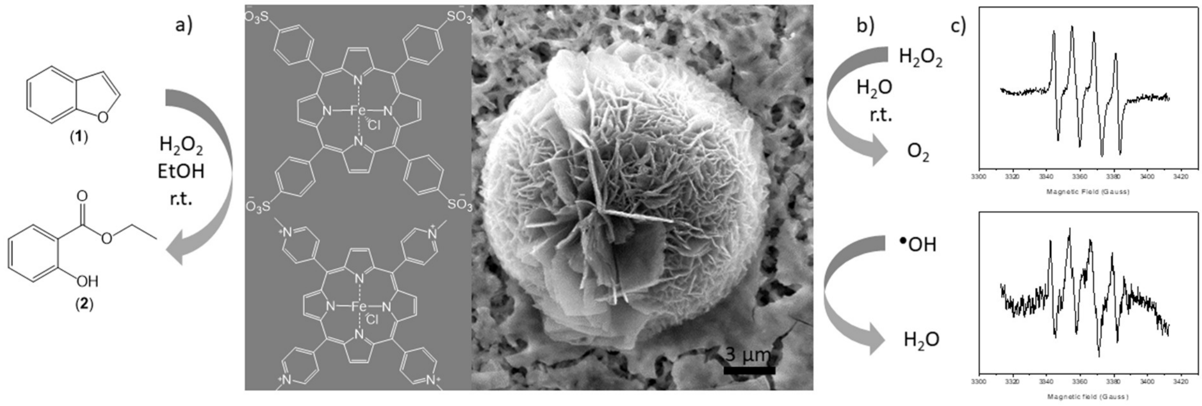

Figure 1: Centre: Nanostructured material prepared by ionic self-assembly of Fe^{III} porphyrin ions to be tested as: a) monooxygenase catalyst for benzofuran oxidation and b) catalase and antioxidant model; c) EPR spectra obtained for different catalytic systems.

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OC8

POTENCIAL PRO-INFLAMMATORY HAZZARD OF LOW SIZE AND CITRATE-COATED SILVER NANOPARTICLES FOR HUMAN NEUTROPHILS

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Silver nanoparticles (AgNPs) are among the most widely used nanomaterials. Humans may be exposed to AgNPs via water, food, cosmetics, drugs, medical devices, etc. Therefore, nonvoluntary human contact with AgNPs is unavoidable, leading to systemic exposure and consequent interaction with immune cells. Neutrophils, as host defense cells, play a key role in recognizing, ingesting, digesting, and eliminating foreign agents, including nanoparticles (especially those with a low size). Therefore, it is very important to carefully understand how a given AgNP coated with different agents [citrate *versus* polyvinylpyrrolidone (PVP)], interact with human neutrophils. The main objective of this study was to evaluate the effect of three different sizes of citrate and PVP–coated AgNPs (5, 10 and 50 nm) in human neutrophils' oxidative burst (evaluated by the fluorescent probe dihydrorhodamine 123) and intracellular calcium levels (measured with the fluorescent probe FLUO-4/AM). It was observed that the effects of AgNPs were size and coating-dependent. The citrate-coated and 5 nm AgNPs were the most cytotoxic and potent inducers of human neutrophils' oxidative burst, also causing significant increase in intracellular calcium levels. These data corroborate the higher interaction of low size nanoparticles with human neutrophils, and highlights the potential pro-inflammatory hazard of using citrate coating AgNPs.

Acknowledgements: This work received financial support from the European Union (FEDER funds POCI/01/0145/FEDER/007265) and National Funds (FCT/MEC, Fundação para a Ciência e Tecnologia and Ministério da Educação e Ciência) under the Partnership Agreement PT2020 UID/QUI/50006/2013, and "Programa Operacional Competitividade e Internacionalização" (COMPETE) (POCI-01-0145-FEDER-029248), and under the framework of QREN (NORTE-01-0145-FEDER-000024). Tânia Soares acknowledges FCT the financial support for the PhD grant (SFRH/BD/128647/2017), in the ambit of "QREN - POPH - Tipologia 4.1 - Formação Avançada", co-sponsored by Fundo Social Europeu (FSE) and by national funds of Ministério da Ciência, Tecnologia e Ensino Superior (MCTES).

OC9

CARBON DIOXIDE AS BUILDING BLOCK IN THE SYNTHESIS OF THE ANTI-INFECTIVEAGENT HEXAMINE

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Electrochemical reduction of CO_2 in a $EMIMBF_4$ saturated solution in the presence of small amounts of the ionic liquidtetramethylguanidiniumazide ($TMGHN_3$) yield as major product the nonvolatile hexamethylenetetramine (HMT) also known as hexamine or methenamine.

Figure 1, shows the evolution of the copper electrode surface during contact with $TMGHN_3$. $TMGHN_3$ allow continuous Cu removal from the electrode during the applied overpotential, ensuring also deposition, as a fresh electrode, of Cu-nanoparticles on the surface.

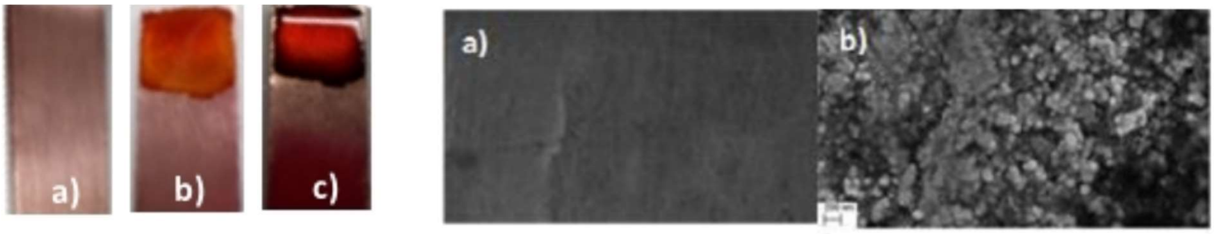

Figure 1. Copper electrode surface evolution upon contact with $TMGHN_3$ and scanning electron micrographs of Cu electrode (a) before and (b) after electrolysis of CO2. Cu-NPs were deposited during CO_2 electrolysis.

Using this experimental methodology, hexamine is indirectly obtained from reaction of ammonium with formaldehyde, or an intermediate, of CO_2 electro-reduction. Also, carboxylic acids, such as formic and acetic acid were found in low amounts when $TMGHN_3$ additive was used with the copper electrode.

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This work was also supported by the Associate Laboratory for Green Chemistry-LAQV which is financed by national funds from FCT/MCTES (UID/QUI/50006/2013) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER - 007265), Fundação para a Ciência e a Tecnologia and Portugal 2020 to the Portuguese Mass Spectrometry Network (LISBOA-01-0145-FEDER-402-022125) and C2TN (UID/Multi/04349/2013).

OC10

RUTHENIUM CYCLOPENTADIENYL COMPOUNDS: CYTOTOXIC AGENTS AGAINST RESISTANT CANCER CELLS

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One of the major concerns regarding chemotherapy is drug resistance that considerably limits the efficiency of the drugs. Multidrug resistance (MDR) can be inherent or acquired (i.e. after subsequent treatments) and is responsible for more than 90 % of treatments failure of metastatic cancers using adjuvant chemotherapy.[1] Thus, the finding of new cytotoxic and MDR inhibitors is a relevant clinical challenge. Ruthenium compounds are seen as valid option to the chemotherapeutics in clinical use due to their general low toxicity, good tolerability and stability under physiological conditions. In this frame, our research group has been engaged in the discovery of new anticancer agents with different mechanisms of action from the traditional chemotherapeutic agents.[2] Here we will present our newest findings regarding "Ru-cyclopentadienyl bipyridine" compounds that showed concomitant cytotoxicity and inhibition for MDR ABC exporters.[3] These proteins are overexpressed in cancer cells, pump drugs out of the cells and confer resistance to drugs. Our studies involving the syntheses of new compounds, molecular docking and biological assessment show the potential of these new compounds to treat aggressive and resistant cancers.

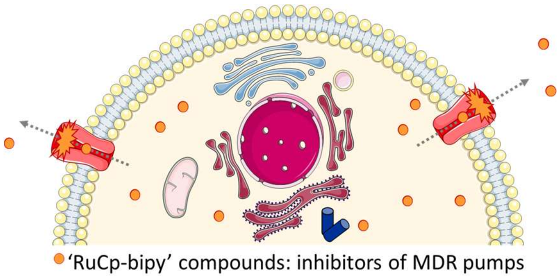

Figure 1: "Ru-cyclopentadienyl bipyridine" compounds are inhibitors of MDR pumps

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OC11

GUANINE BASED N-HETEROCYCLIC CARBENES: SYNTHESIS AND BASE PAIRING PROPERTIES

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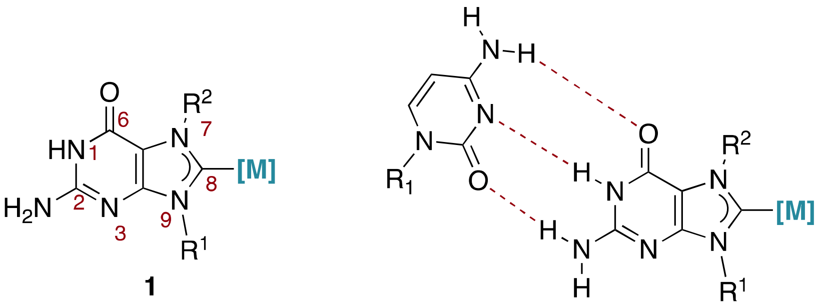
The N7of guanine is the most nucleophilic atom within DNA, and thus one of the main targets for methylating agents[1]. Once formed, 7-Methyl Guanine (7-MeG) derivatives bear a positive charge, due to the quaternization of N7, and have an increased lability of C8-H bond, attributed to the formation of an ylide upon proton loss[2]. In addition, the positive charge associated with N7 of 7-MeG decreases the pKa of N1 by two units and facilitate the formation of the enolic tautomer[3]. Thus, although the methylation does not block any available sites for base pairing, the sterics and electronic variations associated with methylation can alter base pairing patterns. In fact, the positive charge associated with N7 of 7-MeG decreases the pKa of N1 by two units and facilitates the formation of the enolic tautomer, and can alter base pairing properties.

We have recently developed methodologies for synthesis of NHCs derived from 7-methylguanine stabilized by transition metals, via direct and unsupported C-H activation. These results will be discussed in this communication.



1

R^1= ribose, desoxyribose
R^2= H, Me
[M]= $Pt(L_2)X$

Figure 1: Guanine based NHCs and the corresponding base pairs.

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OC12

RUTHENIUM COMPLEXES AS CANCER METALLODRUGS

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The increasing impact of Cancer worldwide and the efficiency of platinum-based chemotherapy available in the Clinic has stimulated the search for new effective alternatives to overcome noxious side effects and other drawbacks. Ruthenium-based compounds, exhibiting a wider spectrum of action and lower toxicity, have emerged as very promising candidates. Ruthenium complexes that combine stability and suitable solubility with a large spectrum of action are a hot topic in metallodrug research, and we have identified some complexes with high chemotherapeutic potential [1-4]. Despite the effort on this filed, the mechanism of action of Ru-based candidates is still not well understood.

In this work different aspects of the mode of action of some of our prospective agents are addressed. These complexes exhibit high cytotoxicity *in vitro*, are active against cisplatin resistant cell lines, interact strongly with DNA and the mechanism of cytotoxic action induced can be traced to apoptosis and autophagy. Their sub-cellular distribution indicates major accumulation at the cell membrane. Membrane lipid domains (with crucial roles in cell signaling) have markedly different lipid composition and organization in cancer versus non-cancer cells [5]. Complexes tested in liposomes mimicking different domains in human cell membranes showed a high affinity for the fluid lipid bilayer and increased the leakiness of the membrane without compromising the liposome integrity. In membrane models of mammalian healthy/cancer cells, complexes modified the hydration and the membrane dipole potential, and disordered the lipid bilayer to a greater extent in the cancer cell model. Our findings suggest that, besides the DNA damage at the nucleus, key targets for these ruthenium complexes might possibly be located at the cell membrane.

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OC13

HIGHLY ACTIVE SULFONIC ACID ARYL-SILICA NANOPARTICLES CATALYSTS FOR FFA ESTERIFICATION

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Esterification of free fatty acids (FFA) in the presence of an alcohol is an important reaction for transformation of low grade and cheap feedstock (waste) into biodiesel.[1,2] Mesoporous silica with alkyl or aryl-sulfonic acids have been widely used in esterification of FFA, although the limits of the pore size and long channels tend to allow slow in-pore diffusion and consequently lower catalytic activity.[3] Although the effort to enlarge the pore size of mesoporous materials the diffusion problem is still unsolved.[4] To overcome this problem silica nanoparticles (SiO_2NPs) with different sizes (~10 and ~100 nm) were functionalized by different post-grafting methodologies[3] as a strategy to prepare sulfonic acid SiO_2NPs (SO_3H-aryl-SiO_2NPs) potential highly active heterogeneous acid nanocatalysts, Fig. 1. Physicochemical characterization of the functionalized SiO_2NPs was carried out by, FTIR, XPS, EA and potentiometric titration (acid strength). The acid catalytic activity was evaluated in the esterification reaction of different size chain FFA including lauric, palmitic, oleic, linoleic and stearic acids in the presence of methanol. SiO_2NPs(10)_CSPTMS showed to be the most active and stable catalyst giving almost 100 % conversion after 1 hr reaction, for oleic and linoleic acid, without no significant loss of activity until the fifth cycle reaction. The kinetic profiles and TOF values for all the catalysts and FFAs studied will be presented and discussed in detail in this communication.

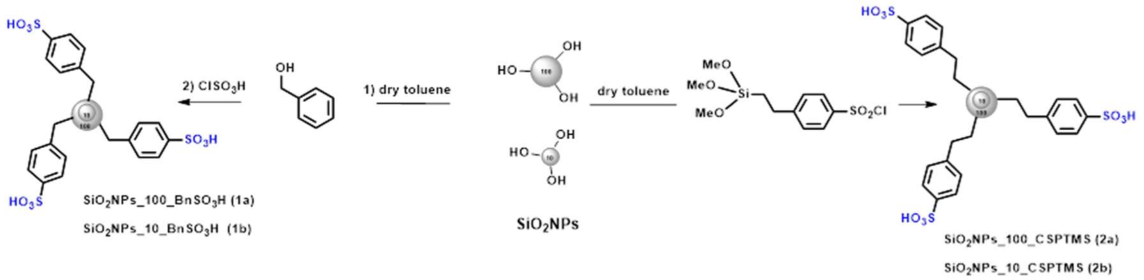

Figure 1: Schematic representation of the SiO_2NPs functionalization

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OC14

MANGANESE ORGANOMETALLIC COMPLEXES IN CATALYTIC REDUCTIONS

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In recent years, the development of catalysts based on first-row transition metals has become a central topic in catalysis. Among 3d metals, manganese is a particular attractive candidate for catalysis due to its natural abundance and non-toxicity. Catalytic applications with manganese compounds featuring N- and O-based ligands are well established, whereas organometallic compounds have been poorly developed.[1] In this work, we present the synthesis of new manganese complexes bearing N-heterocyclic carbene (NHC) ligands, and their application as catalysts for the reduction of carbonyl groups. Well-defined manganese(I) carbonyl complexes bearing bis-NHC ligands (Figure 1) showed to be effective catalysts for the reduction of carbonyl groups through hydrosilylation reactions.[2] A wide variety of ketones were selectively reduced to the corresponding alcohols using phenylsilane and the cheap and readily available polymethylhydrosiloxane (PMHS) in the presence of catalytic amounts of manganese(I) compounds. In addition, we have also proved the excellent efficiency of Mn-bis-NHC complexes in the selective electrocatalytic reduction of CO_2 to CO.[3] The mechanistic insights of these catalytic reactions will be discussed.

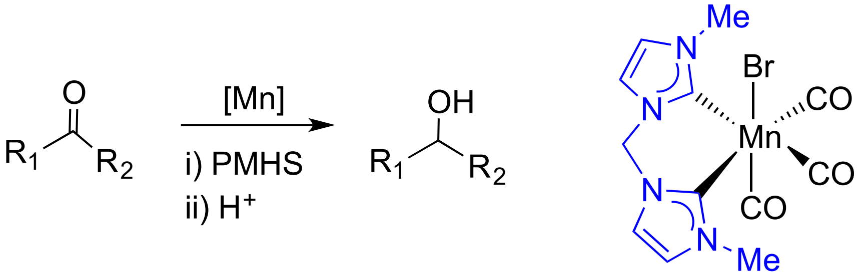

Figure 1: Catalytic reduction of ketones with silanes and Mn-NHC complexes.

Acknowledgements: We thank FCT from Portugal for projects UID/Multi/04551/2013 and RECI/BBB-BQB/0230/2012 (NMR facilities), and for grant PD/BD/105994/2014 (M.P.) and contract IF/00346/2013 (B.R.). We also thank CERCA Programme (Generalitat de Catalunya), the MINECO CTQ2016-80038-R project, ICIQ-IPMP program (F.F.) and Severo Ochoa Excellence Accreditation 2014–2018 (SEV-2013-0319).

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OC15

DESIGNING NOVEL X-RAY SHIELDING BISMUTH OXIDE-COATED TEXTILES

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Lead aprons have been extensively used in medical fields to protect and shield medical personnel and patients from the harmful effects of ionizing radiation during diagnostic and therapeutic procedures. However, lead is not a desirable material for wearable radiation protection due to its heavy weight, inflexibility, poor durability, and toxicity [1]. Alternatively, metals/metal oxides with high atomic number and high density, such as Bi, W, Sb, Sn or their combinations, can impart higher shielding protection with the advantage of lower toxicity when compared to lead [2]. Furthermore, protective clothing with the incorporation of appropriate metallic/composite materials can be designed to be lead-free, in addition to being lightweight, comfortable, cost-effective, and potentially capable of significantly attenuating X-ray radiation [3].

In this work, a set of cotton fabrics coated with different weight percentages (wt%) of Bi_2O_3 were prepared (Figure 1A). Both the parent Bi_2O_3 and coated fabrics were characterized by infrared spectroscopy and X-ray diffraction. In addition, the X-ray attenuation properties of the Bi_2O_3-coated textiles were evaluated. The results showed a radiation attenuation ratio (RAR) higher than 99 % for the fabrics coated with ≥50 wt% of Bi_2O_3 (Figure 1B).

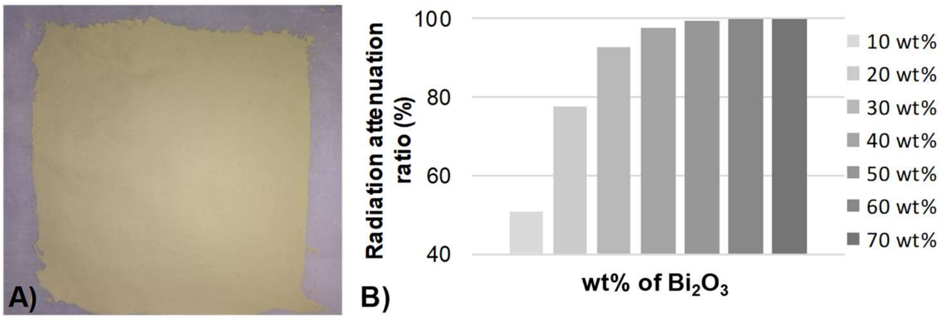

Figure 1. A) Photograph of cotton fabric coated with Bi_2O_3 and B) radiation attenuation ratio of the coated fabric *vs.* Bi_2O_3 weight percentage.

Acknowledgements: The work was funded by FEDER and COMPETE 2020 – POCI (Mobilizing Project TexBoost – Less Commodities more Specialities) and by FCT/MEC under FEDER in the framework of Program PT2020 (project UID/QUI/50006/2013-POCI/01/0145/FEDER/007265, POCI-01-0145-FEDER-006984) and by NORTE-01-0145-FEDER-000006. T.V. Pinto, P.S.F. Ramalho and A.L. Gonçalves thank the Mobilizing Project TexBoost for postdoctoral and research fellow grants, respectively. C. Pereira thanks FCT for the FCT Investigator contract IF/01080/2015.

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OC16

New Intelligent Textiles for Energy Storage: from Hybrid Nanomaterials to Supercapacitor Devices

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Nowadays, the worldwide population is increasingly using electronic and intelligent devices and, if we think about the new technologies, we really want all devices to be connected intermittently [1]. The problem is that there is not enough energy to meet the current devices' requirements. To address this issue, energy storage systems are required, namely supercapacitors (SCs). One of the main concerns on energy storage is to develop new SC technologies that have higher energy storage capacity and a shorter charging time to load electronic devices. In the context of wearable technologies, the design of textile supercapacitors (TSCs) is a promising strategy to provide all these characteristics. With the help of nanotechnology, TSCs performance can be improved, while maintaining their flexibility, lightness and comfort [2].

This work is focused on the preparation of hybrid nanomaterials of doped nanocarbon (DNC) functionalized with manganese oxide nanoparticles (~17 nm, as aggregates) and their incorporation onto cotton textile substrates in order to produce new smart TSCs for energy storage (Fig.1). The hybrid nanomaterials were successfully prepared (as confirmed by X-ray diffraction, Fourier transform infrared spectroscopy and scanning electron microscopy-energy dispersive spectroscopy) and symmetric and asymmetric TSCs were fabricated on cotton substrates. The electrochemical measurements demonstrated that the asymmetric hybrid@fabric//DNC@fabric SC presented the highest specific capacitance, energy density and power density values and a behavior of hybrid SC with the simultaneous occurrence of oxidation-reduction reactions and non-faradaic charge storage. These TSC-type energy storage devices are a revolutionary promise for the technological world.

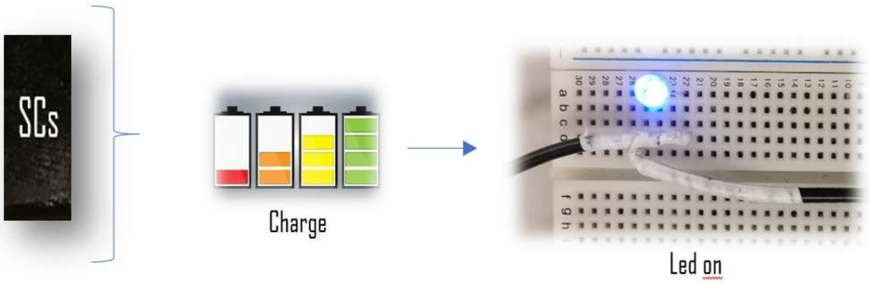

Figure 1: LED lighting resulting from energy stored on textile SCs.

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Posters

*Flash Communications

P1*

MICROWAVE-ASSISTED SYNTHESIS OF FUNCTIONAL PYRROLIDINE-FUSED CHLORINS FOR MEDICINAL APPLICATIONS

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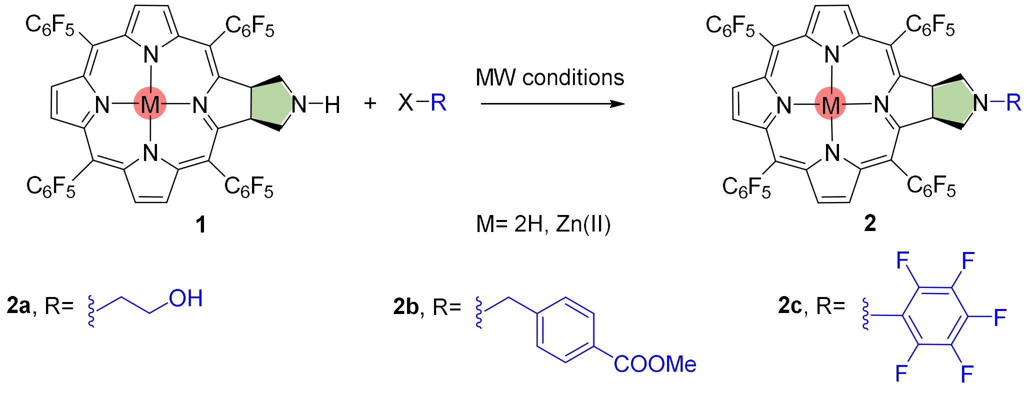
Porphyrin macrocycles (particularly hydroporphyrins), are promising photosensitizers (PS) for the photodiagnostic and photodynamic therapy (PDT) of cancer [1]. PDT's mechanism of action is based on the destruction of cancerous and microbial cells by reactive oxygen species generated by energy-transfer from a light-activated PS to molecular oxygen. Among PSs, chlorins (7,8-dihydroporphyrins) demonstrate great potential for medicinal use, mainly due to their high phototoxicity, low dark toxicity and strong absorption bands at ca. 650 nm, making them suitable for the diagnosis and therapy of deeply seated tumors [2].

Herein we describe our latest results involving the *N*-alkylation and *N*-arylation of the pyrrolidine-fused chlorin 1 (and its corresponding Zn(II) complex) with 2-bromoethanol, methyl 4-(bromomethyl)benzoate and hexafluorobenzene, respectively, in order to obtain functional pyrrolidine-fused chlorins 2a-c (Scheme 1). Synthetic protocols employing microwave heating conditions and photophysical properties of the most promising PSs will be presented and discussed.



Scheme 1: Microwave-assisted synthesis of functional pyrrolidine-fused chlorins 2a-c.

Acknowledgements: The authors gratefully acknowledge the COST action CM1302 (SIPs) and the "Cooperação Científica e Tecnologica FCT/DAAD-2017/2018" through the project "Novel ligand-porphyrin conjugates for targeted photodynamic therapy of cancer". The work was financed by European Union, FEDER (Fundo Europeu de Desenvolvimento Regional) through PT2020 and by national funds through the FCT (Fundação para a Ciência e a Tecnologia), QREN, and COMPETE, NORTE-07-0162-FEDER-000048, UID/QUI/50006/2013 (LAQV/REQUIMTE), project M-ERA-NET/0005/2014, QOPNA research project (FCT UID/QUI/00062/2013), project PTDC/QEQ-QOR/6160/2014, and the post-graduation fellowship SFRH/BPD/85793/2012 (to AL).

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P2*

SUSTAINABLE CATALYTIC SYSTEMS BASED ON UiO-66(Zr) FOR OXIDATIVE DESULFURIZATION OF DIESEL FUELS

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Oxidative desulfurization (ODS) is one of the most promising cost-effective methods for the deep desulfurization of diesel fuel, corresponding to the need for lower emission of sulfur which results from its combustion.[1] ODS process allows the efficient removal of the most refractory sulfur-containing compounds leading to near zero sulfur fuels under mild conditions (low temperature and pressure). Following our research activity on functional crystalline materials, we have been developing novel catalytic systems for efficient ODS processes resorting on Metal-Organic Frameworks (MOFs) as active heterogeneous catalysts. MOFs are highly organized coordination polymers that are often be crystalline and porous. UiO-66(Zr) is a highly stable MOF based on $Zr_6O_4(OH)_4(CO_2)_{12}$ secondary building units and, due to its high surface area and exceptional chemical, thermal and mechanical stability, was applied as heterogeneous catalyst in ODS processes. Active catalysts were prepared following solvothermic and microwave-assisted synthesis.[2] Using strategic economical preparative methodologies, active MOFs were obtained after only 15 minutes. All the materials were characterized by various techniques, such as PXRD, FTIR-ATR spectroscopy and SEM. High catalytic efficiency was found for some of the prepared MOFs, ensuring near total desulfurization of model diesels and relevant results for real diesel samples after few hours, under sustainable conditions.

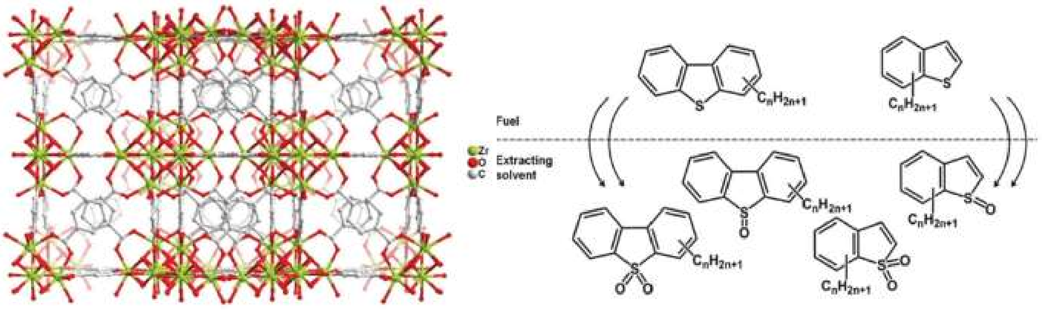

Figure 1: 3D framework of UiO-66(Zr) (left) and the ODS process in a diesel fuel (right).

Acknowledgements: the work was co-financed by UE, FEDER - Fundo Europeu de Desenvolvimento Regional and COMPETE 2020 – POCI (POCI-01-0145-FEDER-007265) through PT 2020 and by national funds through the FCT / MCTES for the research centre REQUIMTE - LAQV (UID/QUI/50006/2013); additional thanks to the FCT/MCTES for the PhD fellowship SFRH/BD/95571/2013 (to SR), and the Post-doctoral grant SFRH/BPD/111899/2015 (to LCS).

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P3*

DESIGN OF MOLECULAR WIRES BASED ON ORGANOMETALLIC IRON (II) AND RUTHENIUM (II) COMPLEXES

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The search for suitable molecular structures and a fundamental understanding of their function in nanoscale devices play a key role in the emerging field of molecular electronics such as optoelectronics, solar energy conversion, molecular switches, and transistors.[1,2] Single molecule devices are essential components for molecular electronics. In particular, organometallic complexes with two redox active metal units linked by a *p*-conjugated spacer are considered to be nano-scale conducting wires.

In order to construct an efficient organometallic wire, M-Spacer-M (Figure 1), different transition metal fragments (M) and bridging ligands (spacers) have been examined and the effect of varying parameters such as the nature of the bridging unit, the redox potentials of the end groups, intramolecular distances (*i.e.* length of the bridge) and chemical functionalization of the different building blocks (*i.e.* linkage) are discussed.

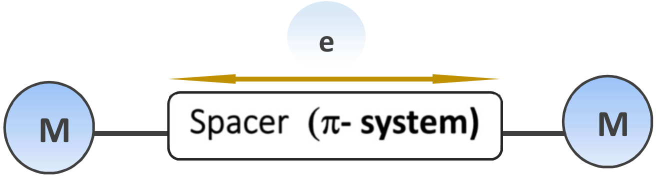

Figure 1: Generic 1D organometallic wire with a bifunctional spacer

Here, we report, the synthesis and characterization of several mono and dinuclear iron(II) and ruthenium(II) complexes based on different organic bridging units ($N\equiv C-CH_2-C\equiv N$, $N\equiv C-CH=CH-C\equiv N$, $Y\equiv C-C_6H_4-C\equiv Y$ (Y=N or C), etc) and different metallic fragments ($[CpM(dppe)]^+$ (M=Fe, Ru), ($[CpFe(CO)_2]^+$), connected by nitrile and/or acetylide groups. These organometallic binuclear systems, allowing the communication between redox-active terminal end groups through delocalized bonds, can be used as molecular wires.

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P4

SERUM TRANSFERRIN GLYCATION AND THE OCCURRENCE OF NON-TRANSFERRIN-BOUND IRON IN TYPE 1 *DIABETES MELLITUS*.

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The cross-talk between *diabetes mellitus* (DM) and iron metabolism has long been described [1], but the molecular mechanism involving iron in the pathophysiology of DM is not completely understood. A particular aspect which may contribute to explain iron toxicity in DM is the common presence of toxic non-transferrin-bound iron (NTBI) species in the blood serum of diabetic patients [2]. Transferrin (Tf) is the blood plasma iron transporter, presenting a higher iron affinity than all alternative plasma ligands. Being so, the presence of NTBI at low Tf saturation values (< 50%) is surprising and remains unexplained. We hypothesise that glycation, the non-enzymatic modification of proteins by glucose during hyperglycaemia, of serum Tf may account for this phenomenon [3].

Here in, modifications occurring to serum transferrin in a small cohort of type 1 DM patients were characterized in detail, using mass spectrometry based proteomics. Participants were 36 ambulatory individuals diagnosed with type 1 DM. All participants provided informed consent for the study. NTBI values were assessed with the ultrafiltration assay developed by Singh *et al*. [4]; iron detection was performed with ferrozine reagent.

32 patients were shown to have positive NTBI values, ranging between 0.06 and 1.84 µM. Considering all samples, 17 different Tf amino acid residues were confirmed to undergo glycation, but no individual presented more than 5 modification sites. No correlation was found between the number of glycation sites and NTBI level. The most frequently modified residues were K206 (n=15), K534 (n=9) and K657 (n=12). K206 and K534 lay at the entrance of the two Tf iron binding pockets and we have previously shown that their modification by glucose hinders Tf iron-binding capacity [3].

Acknowledgements: This work received financial support from the European Union (FEDER funds through COMPETE) and National Funds (FCT, Fundação para a Ciência e Tecnologia), under the Partnership Agreement PT2020 through project UID/QUI/50006/2013-POCI/01/0145/FEDER/007265 (LAQV/REQUIMTE). Programa Operacional Regional do Norte (ON.2 - O Novo Norte), under the Quadro de Referência Estratégico Nacional (QREN) and funded by Fundo Europeu de Desenvolvimento Regional (Feder) NORTE-07-0124-FEDER-000066 and NORTE-01-0145-FEDER-000024.

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P5*

PHOTOLUMINESCENT COMPOSITE BASED ON DECATUNGSTOEUROPATE@PERIODIC MESOPOROUS ORGANOSILICA

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The peculiar features of lanthanide-based luminescence, namely resistance to photobleaching and line-like emission resulting in a high color purity of the emitted light, has led to their extensive use in optical applications, such as lasers, cell imaging and luminescent chemical sensing.[1] The weak light absorption of lanthanide ions can be overcome by the so-called antenna effect using efficient sensitizers, including polyoxometalates (POMs).[2] In this work, the $[Eu(W_5O_{18})_2]^{9-}$ POM was immobilized on a bifunctional periodic mesoporous organosilica (BPMO).[3] The resulting composite exhibits intense red emission and the photoluminescent studies show an efficient energy transfer process to the lanthanide emitting center within the material.

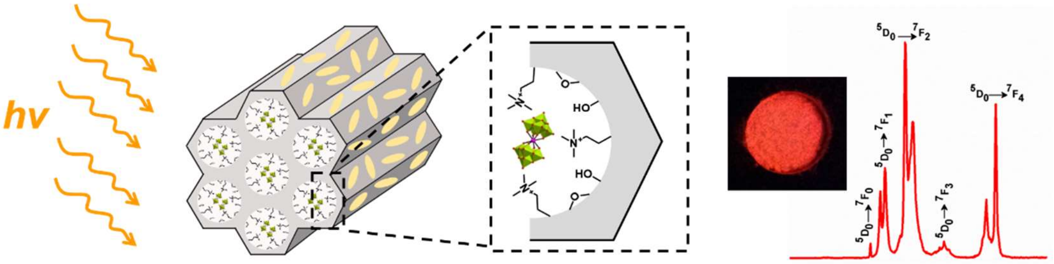

Figure 1: Representation of EuPOM-incorporated on a bifunctional periodic mesoporous organosilica and corresponding emission spectrum.

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P6*

TERNARY IRON AND RUTHENIUM COMPLEXES FOR CANCER THERAPY: CYTOTOXICITY AND DNA INTERACTION

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Complexes of metal ions other than platinum can lead to metallodrugs of lower toxicity and broader spectrum of action than platinum-based compounds. Systemic toxicity can be lowered upon incorporation of endogenous metal ions into the complexes, since the human body is more prepared to deal with these metals. This inspired us to develop a group of iron(III) complexes of tripodal aminophenolate ligands bearing aromatic heterocyclic co-ligands. Complexes of tripodal aminophenolates have been studied as analogues of mononuclear non-heme iron centers present in a variety of proteins. The introduction of bidentate *o*-phenanthroline derivatives as co-ligands may enforce their biological activity as anti-tumour agents. Overall, the complexes exhibit cytotoxic activity against several human cancer cell lines with IC_{50} values at a clinically relevant concentration (<<100 μM). Cells treated with the complexes display morphological features typical of apoptosis (Fig. 1). Distinct conformational changes observed in DNA incubated with the iron complexes is imposed by different co-ligands.

Additionally, since ruthenium-based complexes also emerged as alternatives to platinum drugs due to their milder toxicity and ability to target metastasis, some even reaching clinical trials, ruthenium(III) complexes bearing the tripodal aminophenolate ligand and monodentate co-ligands were also synthesized and tested. These complexes display cytotoxic activity against several human cancer cell lines and good selectivity for cancer *vs.* normal cells.

Hence, these preliminary studies show promising anticancer activity and potential for further studies.

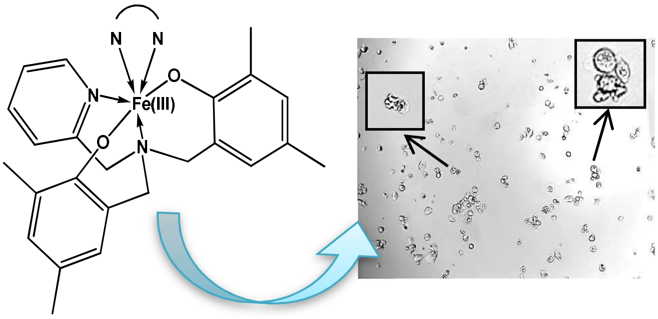

Figure 1

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P7

GREEN DESULFURIZATION SYSTEMS USING A PEROXOPHOSPHOMOLYBDATE AS CATALYST

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Some sulfur compounds present in liquid fuels are very difficult to remove during the refining processes causing some environmental concerns about the possible emissions of SO_x prevenient from the combustion of fuels. To minimize the environmental problems associated with these exhaust gases, a considerable number of countries around the world imposed restricted regulations for sulfur content in fuels (<10 ppm S).[1] The development of efficient desulfurization technologies is a necessary requirement. The oxidative desulfurization (ODS) method, which combines oxidation with extraction steps, has shown good results when applied with model and real liquid fuels.[2,3] The oxidation step is generally performed using an environmentally friendly oxidant (H_2O_2) and a catalyst. Transition metal-oxo species with W(VI) and Mo(VI) metal centers have been extensively applied as catalysts of oxygen atom transfer reactions, being a well-known example the Venturello compounds. However, in ODS their application is still scarce.[4]

In the present work, efficient desulfurization of model and real diesels were achieved, using a suitable peroxophosphomolybdate $TBA_3[PO_4(MoO(O_2)_2)_4]$ as catalyst under "green" conditions (low O_{xidant}/S_{ulfur} ratios and no extraction organic solvents used). The peroxophosphomolybdate showed a high recyclable catalytic capacity for ten consecutive cycles without a significant loss of activity.

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P8

THE POTENCIAL ROLE OF SOIL APPLICATION OF A *TRIS*(3-HYDROXY-4-PYRIDINONATE) IRON (III) COMPLEX IN IRON DEFICIENCY CHLOROSIS TREATMENT

Elsa Rodrigues[1,2], Sofia Ferreira[3], Andreia Leite[4], Tânia Moniz[4], Maria Rangel[3], Marta W. Vasconcelos[2], Susana M. P. Carvalho[1], Carla S. Santos[2]

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Iron (Fe) Deficiency Chlorosis (IDC) is a serious environmental problem affecting the growth of several crops in the world, mainly in alkaline soils. The application of synthetic Fe chelates is one of the most common measures to avoid IDC. This nutritional disorder is characterized by a significant decrease in leaf chlorophyll content and in yield and crop quality. This is due to the fact that in high pH soils there is a limited Fe bioavailability, due to the low solubility of Fe hydroxides and the consequent impairment Fe uptake. Here, we tested the capacity of a *tris*(3-hydroxy-4-pyridinonate) Fe(III) complex, [Fe(mpp)$_3$], in comparison with FeEDDHA, to amend IDC in soybean (*Glycine max*) plants grown under alkaline soil conditions. Seeds were firstly primed using a solution of each Fe chelate and, thereafter, two methods of application were applied to the plants: irrigation and foliar spraying. Plants treated with the Fe chelates showed a better performance when compared with controls. Plant emergence when treated with [Fe(mpp)$_3$] by irrigation was two days longer than in FeEDDHA treated plants. However, chlorophyll concentration (SPAD values) at the end of the assay was 20% higher on [Fe(mpp)$_3$] treated plants than on FeEDDHA treated plants. When treated by foliar spraying, [Fe(mpp)$_3$] plants did not differ from the FeEDDHA treated plants on the number days till emergence and, SPAD values were 21% higher for [Fe(mpp)$_3$] treated plants. Further work is in progress in order to evaluate biomass production and mineral distribution on the different treatments. These preliminary results show the great potential held by [Fe(mpp)$_3$] in IDC treatment in an agricultural context.

Acknowledgements: This work was supported by National Funds from FCT – Fundação para a Ciência e Tecnologia through project PTDC/AGR-PRO/3515/2014.

We would also like to thank the scientific collaboration under the FCT project UID/Multi/50016/2013 and UID/QUI/50006/2013-POCI/01/0145/FEDER/007265.

P9

EFFICIENT TITANIUM-POLYOXOMETALATE SUPPORTED BY SBA-15-TM AS CATALYSTS AND ITS PERFORMANCE IN OXIDATIVE DESULFURIZATION

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A titanium-polyoxometalate with a μ-hydroxo dimeric structure $[(PW_{11}O_{39}Ti)_2OH]^{7-}$($(PW_{11}Ti)_2OH$) was used efficiently for the desulfurization of a model diesel containing a mixture of various refractory sulfur compounds present in real fuels. The catalytic performance of the μ-hydroxo dimeric compound was compared in its homogeneous ($(PW_{11}Ti)_2OH$) and heterogeneous forms ($(PW_{11}Ti)_2OH$@TM-SBA-15, Figure 1). An optimization study was performed using both catalysts to obtain high catalytic efficiency, sustainability and cost-effectiveness of the system. Different optimized conditions were found using the homogeneous and heterogeneous catalysts. Lower amounts of solvent extraction (MeCN, 175 μL), catalyst (0.5 μmol of active center) and oxidant (50 μL) were used to produce sulfur-free model diesel after 2 h at 70 °C, using the heterogeneous catalyst. On the other hand, complete desulfurization was achieved with homogeneous catalyst after only 40 min, although higher amounts of MeCN (750 μL), catalyst (1.5 μmol) and oxidant (75 μL) were used. Both systems combined liquid–liquid extraction and catalytic oxidation, and presented a high capacity to be reused/recycled for consecutive desulfurization cycles.

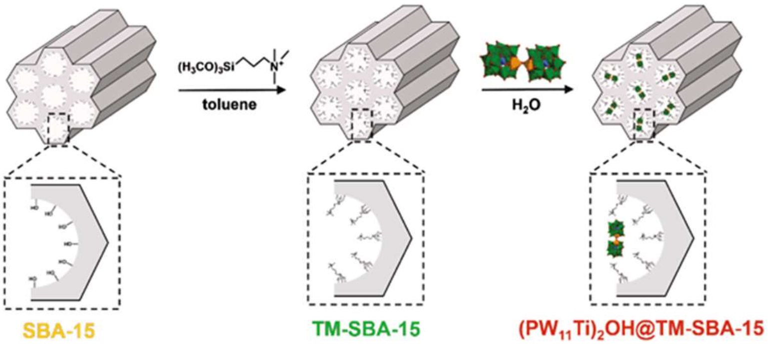

Figure 1: Representative pathway of trimethylammonium-functionalized SBA-15 support (TM-SBA-15) and the corresponding $(PW_{11}Ti)_2OH$@TM-SBA-15 composite.

Acknowledgements: This work was partly funded through the national projects REQUIMTE-LAQV [FCT (Fundação para a Ciência e a Tecnologia) Ref. UID/QUI/50006/2013] and by FEDER (Fundo Europeu de Desenvolvimento Regional) under the PT2020 Partnership Agreement. The FCT and the European Union are acknowledged for the post-graduation Grants SFRH/BD/95571/2013 (to SOR) and SFRH/BPD/73191/2010 (to CMG) co-funded by Ministério da Ciência, Tecnologia e Ensino Superior (MCTES) and the European Social Fund through the program POPH of QREN. The authors also acknowledge the research group of Dr. Isabel Gonçalves from CICECO Laboratory, University of Aveiro, Portugal.

P10

MoS_2 NANOMATERIALS AS HETEROGENEOUS CATALYST IN NITROARENE REDUCTION

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The reduction of aromatic nitro compounds to the respective amines (anilines) are catalytic reactions of extreme importance in organic synthesis, especialy in the production of pharmaceuticals. Heterogeneous catalysts demonstrate several advantages over homegeneous systems, such as easy recovery and recycling of the catalysts. Naturaly, due to their high surface area, easy separation and reusability a variety of materials ranging from metal nanoparticles to bulk materials [1] are being researched as heterogeneous catalysts. A crucial issue for the general application of catalysts for nitro reduction is selectivity. In this respect, adding surface modifiers, tailoring the metal particle size, or modifying the support, can all improve the chemoselectivity of heterogeneous catalysts. Recently, Corma and co-workers demonstrated that Au-based catalysts show high selectivity for the reduction of nitro arenes.[2,3] Nevertheless, the limited availability of precious metals makes it desirable to search for alternatives that are more economical and sustainable.

The main goal with this type of catalysts is to work under room temperature, atmospheric pressure and, ideally, in water moiety since with typical hydrogenation the conditions are very extreme, expensive and not very selective.

In recent years nanoparticles emerged as catalysts and there has been an increasing research in the synthesis of inorganic nanoparticles (NPs) due to their low density, high surface area, good permeation and distinct optical properties compared to bulk materials. These materials improved performance for applications in many fields.

With this in mind, in this work we synthesized MoS_2 [4] nanoparticles with the aim of reducing a nitroarene group to an arylamine compound under mild conditions; sodium borohydride under room temperature and atmosferic conditions was used as source of hydrogen, instead of high-pressure hydrogen gas and high temperature. The solvothermal method was used for the synthesis of MoS_2 NPs. Catalytic reactions were monitored through UV/Vis spectroscopy and yields were determined with GC-MS.

The MoS_2 NPs were efficient and showed to be very active and chemoselective in the product of anilines. The reducing agent was always in excess but borohydride concentration also played an important role in the efficiency of the system.

Acknowledgements
Fundação para a Ciência e Tecnologia (FCT), POCI and FEDER Portugal projects EXPL/QEQ-QIN/1137/2013 and PEst–OE/QUI/UI0612/2013, were acknowledged for financial support

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P11

BIFUNCTIONAL PORPHYRIN-BASED NANO-METAL-ORGANIC FRAMEWORKS: CATALYTIC AND CHEMOSENSING STUDIES

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MOFs constitute nowadays an outstanding class of crystalline materials [1]. These materials are prepared from metal ions, or cluster nodes, and organic linkers and because to the endless number of potential combinations between these units, it is easy to imagine the large structural diversity which can be attained. In this regard, the use of porphyrins as linkers in the construction of MOFs has shown great promise in recent years [2]. This is mainly attributed to two key driving forces: on the one hand, Pors have intrinsically remarkable properties; on the other hand, their pivotal role in Nature in diverse biological functions is also well-known [3]. In recent years, our research group has been focused on the development of new MOFs based on linkers bearing phosphonic acid groups coordinated to lanthanide cations [4]. Herein, we describe our most recent efforts to extend our research to porphyrins in order to prepare novel materials with a wide array of capabilities such as catalysis and Chemosensing properties (Figure 1) [5].

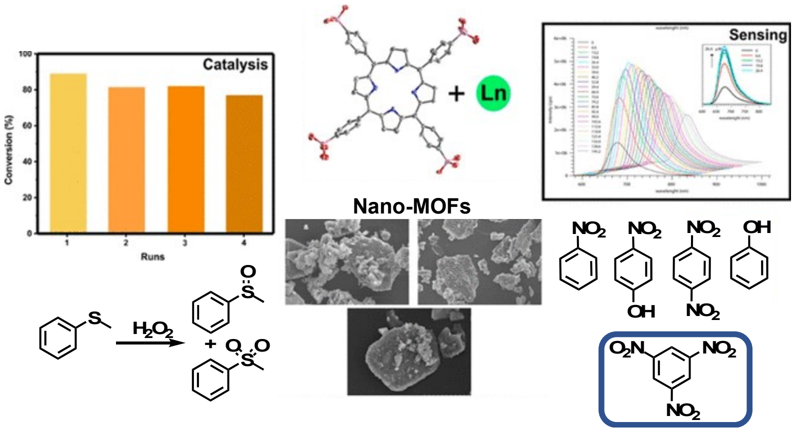

Figure 1: Bifunctional Porphyrin-based Nano-Metal-Organic Frameworks

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P12*

DESIGN OF NEW BIO-MOFS AS MULTIDELIVERY SYSTEMS FOR OSTEOPOROSIS TREATMENT

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Metal-Organic Frameworks (MOFs) are a class of hybrid materials that present the remarkable ability to combine properties of different organic linkers and metallic centres in a coordination-based network. Depending on the components and their functionalities, it is possible to obtain materials with specific characteristics, for further applications in the most diverse areas.

The present work focuses particularly on the development of new bio-MOF materials for the treatment of osteoporosis. The network is designed to combine both (i) the anti-osteoporotic properties of a well-known bisphosphonate drug – alendronate (used as organic linker); with (ii) the beneficial effects of calcium and/or magnesium (used as metallic centres). The preparation of the MOFs is described, along with an extensive characterisation, with resource to Powder X-Ray Diffraction (PXRD), Nuclear Magnetic Resonance (NMR), Fourier Transform Infra-red Spectroscopy (FTIR), Thermogravimetry (TGA) and Scanning Electron Microscopy (SEM). In the end, two new materials are identified, along with others previously reported. Their complete physico-chemical characterisation, as described, is a vital first step towards the application of these new bio-MOFs in osteoporosis therapy.

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P13*

MAGNETIC BIO-HYBRID NANOCARRIERS FOR pH-RESPONSIVE RELEASE OF DOXORUBICIN

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Doxorubicin is one of the most widely used anti-cancer drugs, but side effects and lack of selectivity create a demand for alternative drug delivery systems that favor drug release in target tumour sites. [1] In this work, a biopolymer-based hybrid magnetic nanomaterial was tested as a pH-dependent doxorubicin delivery carrier. Magnetic iron oxide nanosized cores enveloped in siliceous shells of κ-carrageenan (Fe_3O_4@SiκCRG, Figure 1) were synthetized via a two-step process comprising the synthesis of the magnetic core and subsequent encapsulation in silanized carrageenan. [2] The nanoparticles are easily manipulated under a magnetic gradient and their surface is enriched in an organic polymer of renewable origin. Two forms of this nanomaterial were tested, with 50 and 10 nm sized spheroidal cores. The pH responsiveness of the nanomaterials was assessed in phosphate buffers at blood (pH 7.4) and tumour microenvironment (pH 4.2-5) pH levels. The nanomaterials exhibit a high loading capacity (>100 µg DOX/mg NP) for doxorubicin, but the smallest nanoparticles showed the most favorable drug release profile: a high drug release (>80%) at acidic pH and a low release (<30%) at neutral pH, a performance comparable to the most promising reported systems. [3] The results show clear potential for the hybrid nanomaterial as an alternative drug carrier for magnetic-guided delivery of doxorubicin.

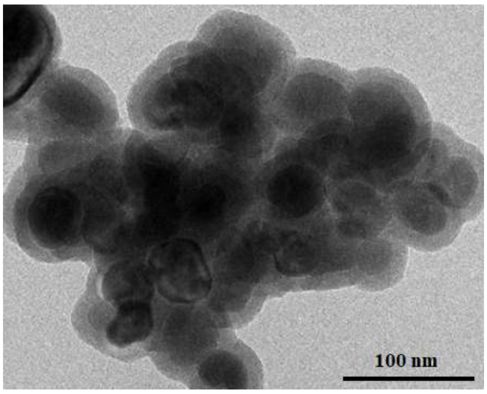

Figure 1: Transmission electron microscopy image of the Fe_3O_4@SiκCRG nanoparticles.

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P14

THE *f*-ELEMENTS IN THE GAS PHASE – INORGANIC CHEMISTRY CHALLENGES AT THE BOTTOM OF THE PERIODIC TABLE

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The *f*-elements are roughly 1/4 of the Periodic Table. They have unique electronic structures and chemical properties that highlight the most important rules of atomic structure and bonding. The lanthanides (4*f*) are essential in high-tech gear, while the actinides (5*f*) are crucial in all stages of the nuclear fuel cycle and particularly as high-level radioactive waste.

In condensed phases, the dense environments of solvent or lattice have important effects on chemical processes. Conversely, in gas-phase ion-chemistry studies, the physical and chemical properties of ionic species can be studied in the absence of perturbations and the relationships between electronic structure, reactivity and energetics can be probed directly. These studies typically rely on mass-spectrometry techniques, in a close interplay with computational studies.

For some years, we have been using FTICR and QIT mass spectrometry to examine the gas-phase ion chemistry of the lanthanides from La to Lu (except Pm) and the actinides from Th to Cm [1]. We have revealed new species, determined thermodynamic properties of neutral and ionic molecules, and, in the case of the actinides, probed the role of 5*f* electrons in bonding and the issue of covalence.

We will present some examples from current studies that comprise: the reactivity of uranium oxide anionic clusters with methanol, including kinetics and mechanistic studies; the hydrolysis of lanthanide oxide nitrate anions to probe high oxidation states in the 4f series, namely the access to uncommon Pr(V); and the activation of small hydrocarbons by lanthanide, thorium and uranium oxide anions that involve radical oxygens.

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P15*

ANTITUMOR AGENT–PORPHYRIN CONJUGATES FOR TARGETED PHOTODYNAMIC THERAPY

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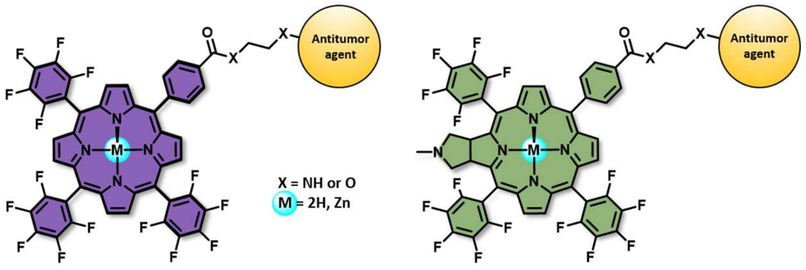
Photodynamic therapy (PDT) is a form of photo-chemotherapy approved for cancer treatment that combines visible light, molecular oxygen and a photosensitizer (PS) to achieve an efficient therapeutic effect [1]. The success of PDT depends strongly on the ability of the PS to accumulate selectively in tumor tissues and to generate singlet oxygen.

In order to obtain highly efficient photosensitizers with optimized properties for PDT, a series of porphyrin–metallodrug conjugates, where the metallodrug fragment is the well-known cisplatin, a new-generation platinum [2] a ruthenium complex [3], are being studied. Herein, we describe our latest results on the conjugation of a porphyrin and a chlorin (7,8-dihydroporphyrin) with enzyme inhibitors and cytotoxic ruthenacarborane complexes, through bio-cleavable ester or stable amide bonds (Figure 1). Photophysical properties, *i.e.*, fluorescence quantum yield and absorption extinction coefficients, of these new conjugates will also be discussed.



porphyrin (λ_{max} = 420 nm) chlorin (λ_{max} = 650 nm)

Figure 1: Antitumor agent–porphyrin and –chlorin conjugates.

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P16

URANIUM(III) COMPLEXES SUPPORTED BY HYDROBIS(MERCAPTOIMIDAZOLYL)BORATES: SYNTHESIS AND OXIDATION CHEMISTRY

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The oxidation of a metal center is a well-suited reaction to study the influence of the supporting ligand on reactivity. Since trivalent uranium has a high reducing power, its complexes are extremely reactive with oxidizing substrates. Studies of U(III) redox chemistry and small molecule activation have been reported using diverse U(III)-ligand systems leading to unprecedented transformations and structures [1].

Hydrobis(mercaptoimidazolyl)borate ligands are mono-anionic soft chelates, analogues to the [N_2]-donor hydrobis(pyrazolyl)borate ligands, that provide [S_2]-donor ligands. Previous results obtained by us demonstrated that the bis(mercaptoimidazolyl)borate ligands $[H(R)B(tim^{Me})_2]^-$ are able to stabilize the cationic uranium(III) complexes [U{κ^3-*H,S,S′*-H(R)B(tim^{Me})$_2$}$_2$(thf)$_3$][BPh$_4$] (R = H, Ph) [2]. Revisiting our studies with these [S_2]-donor chelators, we will report here the synthesis and characterization of the neutral U(III) complexes [U{κ^3-*H,S,S′*-H(R)B(tim^{Me})$_2$}$_2$I(thf)$_2$] (R = H (**1**), Ph (**2**)) and the use of **2** as an U(III) precursor in electron-transfer reactions to access new tetravalent and hexavalent uranium complexes supported by soft bis(azolyl)borate ligands (Fig. 1), including the first homoleptic κ^3- H,S,S′ -based f-element complexes [3].

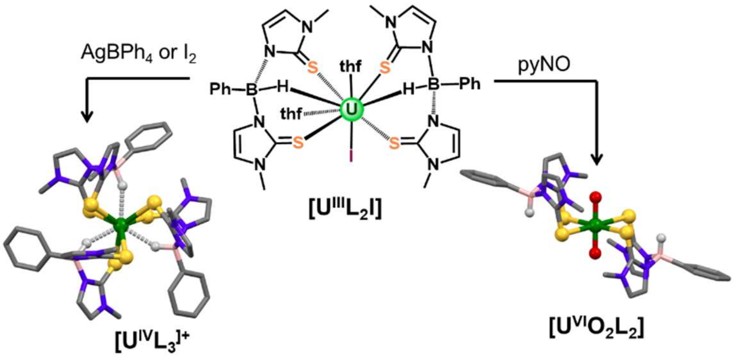

Figure 1: Reactions of complex 2 with oxidizing substrates.

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P17*

LAYERED MOF-BASED MATERIALS PREPARED IN IONIC LIQUIDS: OXIDATIVE CATALYSIS ACTIVITY

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Metal-Organic Frameworks (MOFs) are crystalline materials that consist of metal centres connected by organic molecules, known as ligands or linkers, usually obtained by conventional hydro/solvothermal methods. This type of materials possesses remarkably interesting applications in gas storage, catalysis and electronic chemistry, among others. Ionic Liquids (ILs) have been applied as reaction media, structural templates or charge-compensating groups, thus contributing greatly to the formation of new materials with unique structural properties. Tuning the structural properties of ILs and then transmitting these effects to the construction of MOFs, is an important strategy for achieving novel functional MOF materials.[1]

In the present work, Cobalt and Zinc MOF materials have been prepared by the reaction of 1,4-benzenedicarboxylic acid (H_2BDC) with respective metal salts in different 1-alkyl-3-methylimidazolium halides (chloride, bromide and iodide), acting as ionic medium instead of the traditional hydro-solvothermal one. The MOFs structures were determined by single-crystal X-ray diffraction as layered metal–organic frameworks and further characterization was performed by Powder X-ray diffraction, FT-IR and TGA techniques. Furthermore, the materials were evaluated as potential sustainable heterogeneous catalysts for the oxidation of olefins.[2]

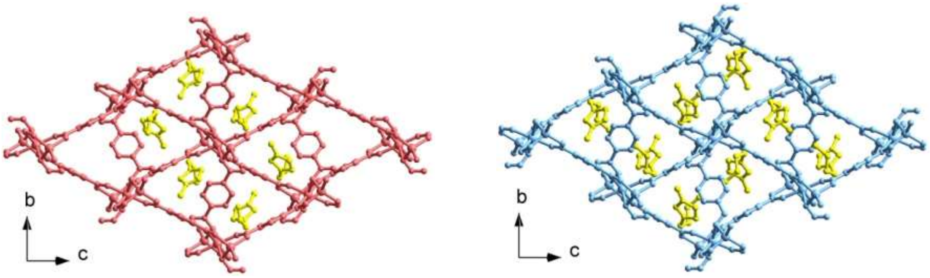

Figure 1: Structural representation of Cobalt layered MOFs obtained in related ILs: 1-propyl-3-methylimidazolium bromide (left) and 1-propyl-3-methylimidazolium bromide (right)

Acknowledgements: the work was co-financed by UE, FEDER – Fundo Europeu de Desenvolvimento Regional and COMPETE 2020 – POCI (POCI-01-0145-FEDER-007265) through PT 2020 and by national funds through the FCT/MCTES – Fundação para a Ciência e a Tecnologia/Ministério da Ciência, Tecnologia e Ensino Superior for the research centre REQUIMTE-LAQV (UID/QUI/50006/2013); additional thanks to the FCT/MCTES for the PhD fellowship SFRH/BD/95574/2013 (to ADSB) and the post-doctoral grant SFRH/BPD/111899/2015 (to LCS).

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P18*

CAFFEINE BASED NICKEL(II) N-HETEROCYCLIC CARBENES: SYNTHESIS AND CATALYTIC APPLICATIONS

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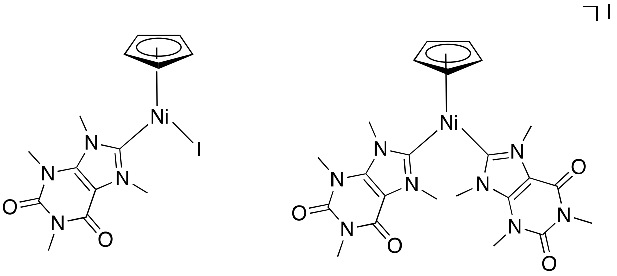
Xanthines (3,7-dihydropurine-2,6-diones)) are purine derivatives widely found in nature, and of which caffeine and theobromine are well known representatives[1]. Xanthines can easily form N-heterocyclic carbenes, and caffeine derivatives stabilized by gold and palladium have been reported [2]. Less explored is their role as ligands for transition metal catalysts, where their electronic properties and similarity to nucleobases can be further utilized. Following earlier reports of the reactivity of nickelocene for the synthesis of N-heterocyclic carbene complexes, we have evaluated this methodology for synthesis of methylated caffeine derivatives. Two nickel(II) N-heterocyclic carbene (NHC) complexes have been synthesized by direct metalation of the corresponding methylated caffeine with nickelocene, NiCp2. The compounds were characterized by mass spectrometry and NMR. The monocarbene compound **1** is formed initially, but in the presence of unreacted caffeine, converts rapidly to biscarbene complex **2**.



1

2

Figure 1: Nickel NHC complexes **1** and **2**.

Kinetic studies indicate that compound **1** is an intermediate in the formation of compound **2**, in line with observations reported for analogous triazolium salts [3b]. The compounds **1** and **2** were evaluated as catalysts for Suzuki−Miyaura cross-coupling of aryl iodides and phenylboronic acid, and these results will be reported in this communication.

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P19*

A HIGHLY ACTIVE N-HETEROCYCLIC CARBENE MN(I) COMPLEX FOR SELECTIVE ELECTROCATALYTIC CO_2 REDUCTION TO CO

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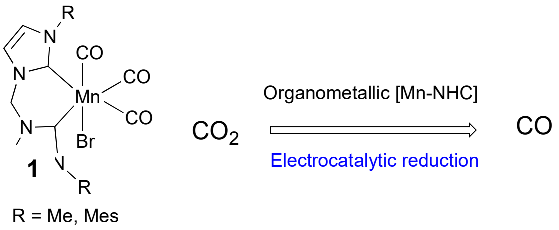
Utilisation of CO_2 as cheap and abundant C1 raw material is a promising strategy to mitigate global warming. In this context, development of catalysts capable to activate CO_2 for the formation of chemicals is a topic of increasing interest. In particular, the use of cheap, earth-abundant and non-toxic metals such as Mn as catalysts would have a significant impact.[1] Herein, we present our results on electrocatalytic studies for the reduction of CO_2 performed with Mn-NHC complexes of general type $[MnBr(bis\text{-}NHC)(CO)_3]$ (1). Experimental data showed that complex 1 efficiently and selectively converted CO_2 into CO in anhydrous aprotic organic solvents. Complementary FTIR-SEC measurements and computational data suggest that the strongly nucleophilic character of the Mn atom is likely responsible for the positive ligand effect on catalysis.[2]



Scheme 1: Electrocatalytic reduction of CO_2 to CO with Mn-NHC.

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P20*

Detection of C-reactive protein using functionalized gold nanoparticles

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C-reactive protein (CRP) is the most well-known biomarker of inflammation in cardiovascular diseases, being used for standard clinical practice. Gold nanoparticles (Au NPs) have been used for CRP detection due to their facility to conjugate with biomolecules and exceptional electrical and optical properties. Current assays for CRP detection involve the preparation of complex materials using antibodies and frequently require costly equipment for detection that leads to expensive assays [1]. In the present work, two novel strategies for the functionalization of Au NPs aiming CRP detection were investigated: the covalent attachment of cytidine 5'- diphosphocholine (CDP) onto the NPs surface (Au_NPs@MUDA@CDP) and the simple modification with an aptamer (Au_NPs@ssDNA), (figure 1). were prepared, characterized and tested against CRP.

Au NPs with distinct size were synthesized through Turkevich and seed-growth method. After synthesis and surface modification the materials were characterized using UV-vis and FTIR spectroscopy, zeta potential and DLS measurements and transmission electron microscopy (TEM). Au NPs@ssDNA and Au NPs@MUDA@CDP were tested against CRP, using solutions of known concentration (10-100 nM). The detection of CRP was monitored using UV-vis spectroscopy. The increase of aggregation ratio between absorbance at 620 nm and the absorbance of LSPR band (A_{620}/A_{LSPR}) was monitored along time and, indicated that CRP was detected using functionalized Au NPs. For the systems Au NPs@MUDA@CDP and Au NPs@ssDNA it was possible to find a linear correlation between the ratio A_{620}/A_{LSPR} and the CRP concentration, within the concentration range 20 - 50 nM (R^2=0.9425) and, 20 - 45 nM (R^2=0.9382), respectively.

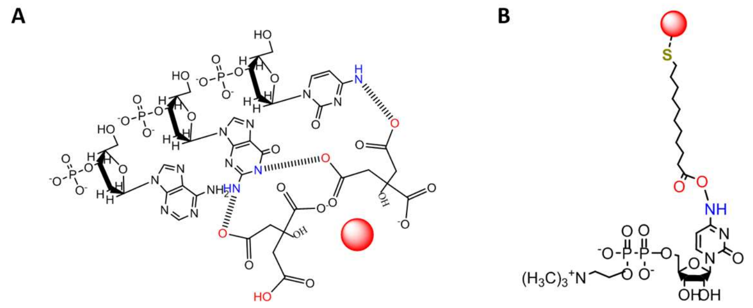

Figure 1: Schematic illustration of A) Au NPs@ssDNA e B) Au NPs@MUDA@CDP.

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P21*

Design of functionalized materials for application in analytical methods for determination of Fe(III)

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Iron is an essential element for living organisms although it is required that its concentration lies within a particular range to avoid toxicity. Therefore, it is important to monitor iron levels. The quantification of iron is often carried out by inductively coupled plasma mass spectrometry and absorption spectroscopy that use highly toxic species such as thiocyanate and 1,10-phenantroline [1]. Thus, the development of new materials and methods that can provide a faster detection, *in situ* analysis and that do not use toxic reagents is still necessary. The design of functionalized matrices with chelating units with high affinity and selectivity for specific Fe(III) is being considered as an innovative method for the quantification of several metal ions.

The main objective of this project is the design and synthesis of functionalized materials for quantification of Fe(III). Epoxy-activated sepharose-6B was used as solid matrix where three ligands were coupled, to conclude which of the ligands provides a maximization of sepharose functionalization and a greater retention capacity of iron. Two ligands belonged to 3-hydroxy-4-pyridinone class, a bidentate ligand (3,4-HPO-NH) [2] and a hexadentate ligand (tris-3,4 -HPO-NH) and one ligand from the family of catechols, the dopamine.

The sepharose column functionalized with tris-3,4-HPO-NH showed a low percentage of matrix functionalization, so assays with this ligand were not pursued. From the other two functionalized matrices, the sepharose functionalized with the 3,4-HPO-NH ligand proved to be the most promising material for iron quantification.

In conclusion, new functionalized materials can represent an effective alternative to toxic analytical reagents in several detection methods and may contribute to enlarge the fields of application.

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P22

SYNTHESIS AND EVALUATION OF FLUORESCENCE PROPERTIES OF A EUROPIUM-FUNCTIONALIZED MOF

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A metal-organic framework (MOF) is a porous crystalline structure, in general, with a high surface area which potentiates its application in catalysis, ion exchange, and many other technological areas. For example, luminescent MOFs with stable porosity have attracted enormous interest in the field of light-emitting sensors [1,2].

The zirconium MOF [UiO-66(Zr)-$(COOH)_2$] was prepared in water using conventional heating and attempts to prepare the material using other methods, such as microwave- assisted synthesis (MWAS) were performed. The material was dispersed in water and mixed with $EuCl_3 \cdot 6H_2O$ salt using the same type of heating to obtain Eu@MOF. The purpose of this work is to prepare a material with good luminescence properties that could be used as a fluorescence sensor [3].

The structures were confirmed by powder X-ray diffraction (PXRD). The Eu@MOF material was also characterized by FTIR (Fourier-transform infrared spectroscopy), SEM (Scanning Electron Microscopy) and its fluorescence quantum yield was determined.

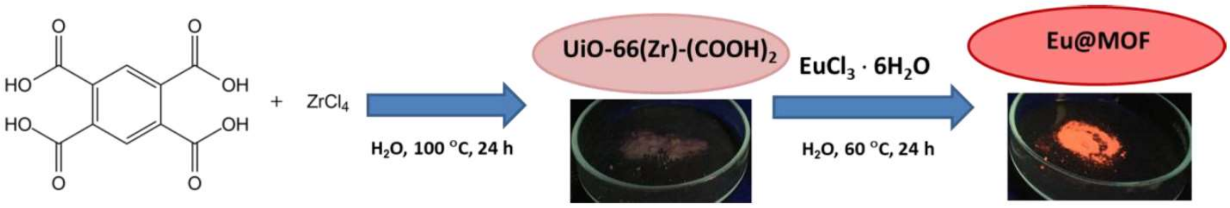

Figure 1: Synthetic pathway for the preparation of UiO-66(Zr)-$(COOH)_2$ and Eu@MOF (materials irradiated with UV light).

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P23*

EVALUATION OF THE ANTIBACTERIAL ACTIVITY AGAINST GRAM-POSITIVE AND GRAM-NEGATIVE STRAINS OF *BIS*(3-HYDROXY-4-PYRIDINONATO) COPPER(II) COMPLEXES

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Antibiotic-resistant bacteria are globally spread and are jeopardizing the effective treatment of many infections. In this context, screening new compounds for antibacterial activities may pave the way to find novel and alternative scaffolds to combat multidrug-resistant bacteria.

This work describes the synthesis of several copper (II) complexes with 3-hydroxy-4-pyrones and pyridinone ligands and assessment of their antibacterial activity against Gram-positive and Gram-negative strains, including references strains and multidrug-resistant isolates. Potential synergies between $Cu(L1)_2$ (Figure 1), which showed to have the best antibacterial activity, and antibiotics where explored against methicillin-resistant *Staphylococcus aureus* (MRSA) and vancomycin-resistant *Enterococcus faecalis* (VRE).

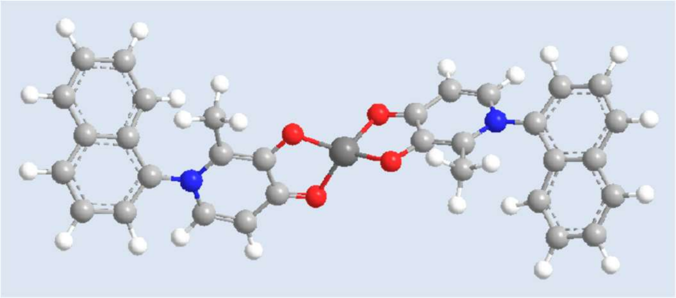

Figure 1: Chemical structure of complex $Cu(L1)_2$

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P24*

EFFICIENT GRAPHENE-BASED ELECTROCATALYSTS FOR EMERGING POLLUTANTS DETERMINATION

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Taking advantage of the electroactivity of some drugs and biomolecules, the application of electrochemical sensors for biological analysis has been growing rapidly, mainly due to the simplicity, accuracy, precision, low cost and rapidity of the electrochemical techniques [1]. In order to develop electrochemical sensors with higher selectivity and sensitivity, the chemical modification of electrode surfaces has been a major focus of research. Graphene, in particular, emerged as a "superstar" material in the last years. Its properties, such as fast electron transportation, high thermal conductivity, excellent mechanical strength and high surface area, suggest its ability to detect analyte molecules and to promote a fast electron transfer between the electrode and the analyte, which make it a promising electrocatalyst [1-3].

This work reports the preparation of novel graphene-based nanomaterials based on nitrogen and sulphur doping through a mechanochemical synthesis followed by carbonization under nitrogen atmosphere. Then, the pristine and doped graphene were modified with Co_3O_4 and Mn_3O_4 nanoparticles. All prepared nanomaterials were fully characterized by FTIR, XPS, Raman and XRD. Finally, we explored their application as electrocatalysts towards the detection of different emerging pollutants.

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P25*

Co/Al hydrotalcite with Au_{NP} for environmental catalytic applications.

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Layered double hydroxides (LDH) are known materials whose structure consists of layers of inorganic hydroxides of mixed metal cations. The most important feature of these materials is its ability to anion exchange. In particular, hydrotalcite (HT) compounds form, at present, a large class of inorganic materials, extensively studied as catalysts, precursors and catalyst supports, anionic exchangers, sorbents, additives among other[1].

Following our previous work[2], the main objective of this work was the preparation of inorganic nano-hosts based on HT intercalated catalytically active species.. To accomplish this, an $HT_{Co/Al}$ (containing Co and Al with 2:1 ratio) was synthesized. After being anion exchanged to intercalate methionine (met) as ligand in the material, gold nanoparticles (Au_{NP}) were introduced. X-ray powder diffraction (DRX), FTIR, TEM, SEM, UV-Vis, and TGA were employed to assess the structure, morphology and further properties of the synthesized materials.

The catalytic mineralization of organic dye molecules[2], RhB and Rh6G, in the presence of $NaBH_4$ using $HT_{Co/Al}$-CO_3 and $HT_{Co/Al}$-met-Au_{NP} as catalysts. After the completion of the reaction, the initial pink colored RhB and orange Rh6G solutions became colorless. Catalysts were tested for robustness, being reused to assess their capability in consecutive tests.

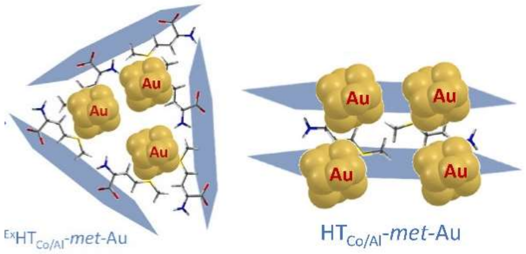

Figure 1: Structure of the $HT_{Co/Al}$-met-Au_{NP} materials in exfoliated (left) bulk (right) forms.

Acknowledgements: The authors thank FCT, POCI and FEDER (PEst-OE/QUI/UI0612/2013) for financial support.

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P26*

MICROFLUIDIC PAPER-BASED ANALYTICAL DEVICE FOR THE DETERMINATION OF SALIVARY CALCIUM

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The determination of salivary calcium concentration may anticipate potential problems or help to improve target therapies [1,2]. In fact, the concentration of calcium in saliva can be a symptom of cystic fibrosis or medication abuse. The concentration of calcium in saliva depends mainly on the pH and the salivary flow rate. A fast, non-evasive, disposable, on-the-moment test device available to be used in a routine consultation would facilitate the overall diagnostic.

Microfluidic paper-based analytical devices (μPADs) have several benefits which make them ideally suited to conduct on-location analyte determinations. While many of the current monitoring techniques require specialised skills, laborious laboratory processes, or/and expensive equipment, μPADs provide an avenue for very quickly and cheaply attain an analytical result. These μPADs are composed of a hydrophilic zone, consisting of paper, and a hydrophobic zone that delimits them. The paper cellulose fibers enable liquids transportation by capillarity.

In this work, a novel approach was used to the design the hydrophilic/hydrophobic areas. The developed μPAD was employed to determine the salivary calcium concentration as an economical and in-loco alternative. The method was based on the reaction between calcium and o-cresolphthalein complexone, generating a coloured complex, quantified through pixel readings [3]. The consumption of both reagents and sample is rather low, about 10 μL. This feature, along with the intrinsic portability of the μPADs, enabled to obtain a device suitable for regular monitoring at routine consultation to be used by unskilled operators.

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P27

LAMELLAR COORDINATION POLYMER WITH A REMARKABLE CATALYTIC ACTIVITY

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Metal-Organic Frameworks (MOFs) and Coordination Polymers (CPs) have already proven to be efficient alternatives in a myriad of applications. The versatility of these materials, allied to their structural design and stability led MOFs and CPs to be tested in different areas, with uses as catalysts, sensors, conductors and extensively utilised as gas sorbents.[1] In this work we report a new positively charged lamellar coordination polymer is reported. $[Gd(H_4nmp)(H_2O)_2]Cl\cdot 2H_2O$ (**1**) is obtained in a typical one-pot approach using water as a "green" solvent and by forcing the inclusion of additional acid sites by employing HCl in the synthesis. Compound **1** performs as a heterogeneous, versatile acid catalyst, with outstanding activity in four different organic reactions. For all reaction systems, very high conversions were reached (92-97%) in only 15-30 min, under mild conditions (35 ºC, atmospheric pressure). Allied to these catalytic results, the material also exhibits interesting protonic conductivity values of 1.23×10^{-5} Scm^{-1} at 98% RH at 40 ºC.[2]

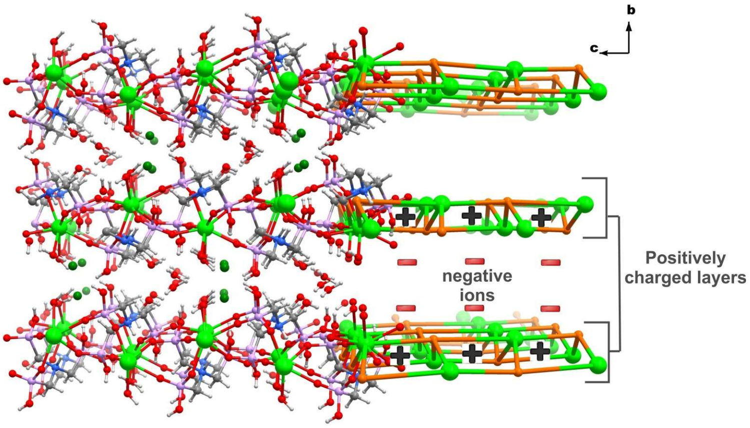

Figure 1: Schematic representation of the crystal packing of $[Gd(H_4nmp)(H_2O)_2]Cl\cdot 2H_2O$ (**1**).

We thank FCT, the European Union, QREN, FEDER through *Programa Operacional Factores de Competitividade* (COMPETE), and CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID/CTM/50011/2013), financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. We also thank FCT for funding the R&D project FCOMP-01-0124-FEDER-041282 (Ref. FCT EXPL/CTM-NAN/0013/2013). FCT is also acknowledged for the grants Nos. SFRH/BD/84231/2012 and SFRH/BD/46601/2008 (to RFM and PS, respectively), and Nos. SFRH/BPD/89068/2012 and SFRH/BPD/96665/2013 (to MMA and PB, respectively), and the Development grant No. IF/01174/2013 (to FF).

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P28

STRUCTURE, ELECTROCHEMISTRY AND ANTICANCER ACTIVITY OF NOVEL THIOSEMICARBAZONE COMPLEXES OF RUTHENIUM(II)

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Cancer is the second global killer condition worldwide [1]. In the search for metal-based agents for cancer therapy, ruthenium complexes have attracted significant attention due to their unique and versatile biochemical properties. Ru complexes have emerged as a promising alternative to the conventional platinum-based chemotherapeutics since they present in general lower toxicity, different mechanisms of action and the capacity to surmount tumor platinum-resistance [2]. Thiosemicarbazones (TSC) have been described to possess a wide biological activity such as antimicrobial, antifungal and antitumoral properties [3]. In this context, a new set of complexes bearing a common TSC as bidentate ligand and different Ru(II) fragments (Ru-cyclopentadienyl, Ru-polypyridyl, Ru-phosphane), was prepared and fully characterized. We present herein our first studies on some of these systems. The TSC ligand adopts a different coordination mode accordingly to which Ru(II) fragment is bound to, and compounds' biological properties are significantly altered.

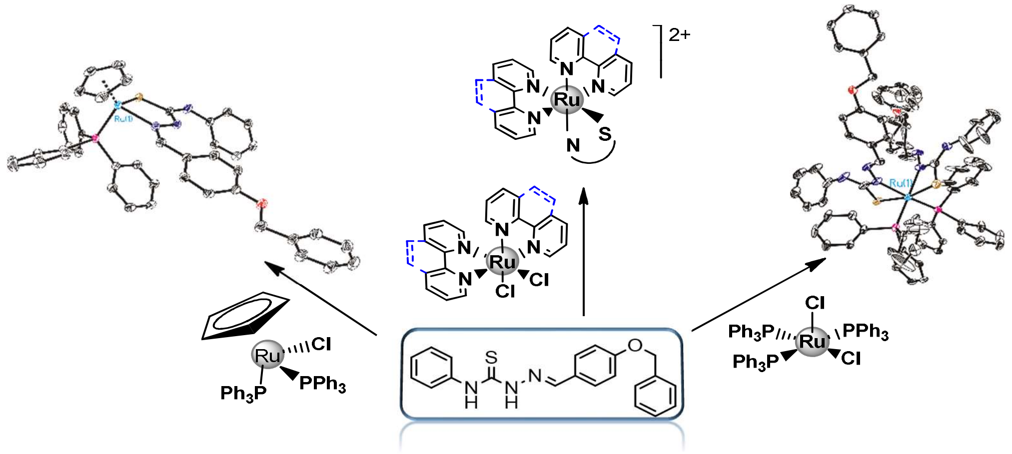

Figure 1: Some ruthenium(II) complexes presented in this work.

Acknowledgements: The Portuguese Foundation for Science and Technology (FCT), through projects UID/QUI/00100/2013, UID/Multi/04378/2013, IF/01302/2013 and IF/01179/2013 (POPH, Human Potential Operational Program; FSE, European Social Fund).

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P29*

MICROWAVE ENHANCED SYNTHESIS OF AZIDE SUBSTITUTED PORPHYRINS

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The development of new therapeutic options for fighting various tumours has emerged from the lack of selectivity in cancer treatment. Photodynamic therapy (PDT) is a form of photochemotherapy that requires the use of three important elements: a photosensitizer (PS), which should accumulate specifically in the targeted tissue, visible light and oxygen. Side effects of current PSs and their sub-optimal selectivity are major driving forces for the design of new structures selective for specific neoplastic conditions [1]. Various examples of combining PSs to peptide and proteins, using copper-catalyzed azide-alkyne cycloaddition (CuAAC), have been described as a promising approach for enhancing the selectivity and efficacy of PDT [2].

Here we describe an efficient and more sustainable approach, by using microwave heating, to obtain azide-substituted porphyrins (Figure 1) to be combined with peptides *via* a CuAAC (Huisgen [3+2] cycloaddition) [3]. The microwave-assisted protocols and the photophysical properties of the obtained porphyrins will be presented and discussed.

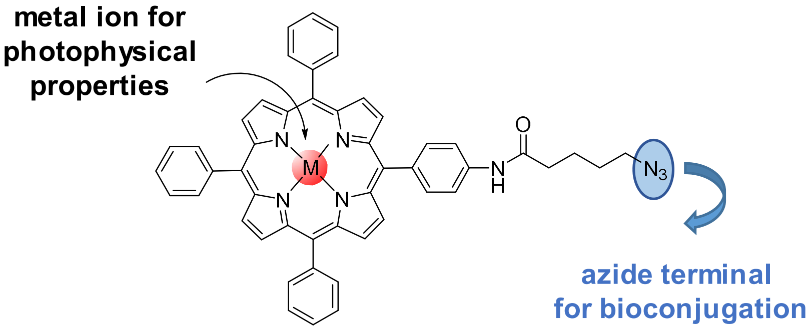

Figure 1: Structure of azide substituted porphyrins

Acknowledgements: The work was financed by European Union, FEDER (Fundo Europeu de Desenvolvimento Regional) through PT2020 and by national funds through the FCT (Fundação para a Ciência e a Tecnologia), QREN, and COMPETE, NORTE-07-0162-FEDER-000048, UID/QUI/50006/2013 (LAQV/REQUIMTE).

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P30*

NEW GENERATION OF ENERGY STORAGE DEVICES: CARBON-BASED MICROSUPERCAPACITORS

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In the Era of the Internet of Things, the portability and miniaturization of electronic devices are current hot topics, which have stimulated the development of micro-size devices, such as energy storage technologies [1]. Microbatteries have been used for energy storage in portable devices but present several limitations, such as short lifetime and limited power density, which difficult their integration. Therefore, microbatteries limitations increased the interest on the development of microsupercapacitors (μ-SCs). μ-SCs have been pointed out as an interesting solution due to their long cycle life, high power density and fast charging [1–3]. Carbon-based nanomaterials are promising electrode materials for μ-SCs due to their high specific surface area, good conductivity, mechanical stability and high operating temperature range [3].

This work reports on the fabrication of a flexible all-solid-state μ-SC based on nanostructured carbon electrodes coated on PET substrates. The μ-SC was produced by lithography with the carbon-based electrodes separated by a solid-gel electrolyte (Figure 1). The topology and structural characterization was performed by scanning electron microscopy, energy dispersive spectroscopy and X-ray diffraction. The electrochemical performance was evaluated by cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy. The all-solid-state μ-SC showed excellent performance, with a volumetric specific capacitance of 6.65 F cm^{-3} and a working voltage of ~2 V. This resulted in an energy density of 3.70 mWh cm^{-3} and a power density of 1.49 W cm^{-3}.

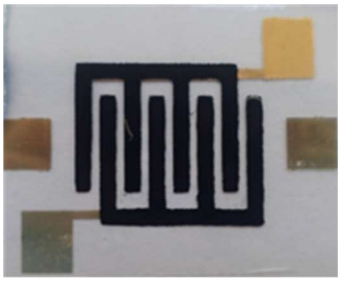

Figure 1: Photography of the produced μ-SC based on carbon nanomaterials.

Acknowledgements: This work was funded by FCT/MEC and FEDER under Program PT2020 (UID/QUI/50006/2013-POCI/01/0145/FEDER/007265). R.S.C. and C.P. thank FCT for MSc. grant and FCT Investigator contract (IF/01080/2015), respectively.

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P31*

THE INFLUENCE OF POLYOXOMETALATE STRUCTURES IN OXIDATIVE CATALYTIC SYSTEMS: ACTIVATION STRATEGIES

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Transition-metal oxygen anion clusters referred as polyoxometalates (POMs) are constituted by early transition metal cations (W, Mo, V, Nb, Ta and Ti) and oxide anions. The unique properties of POMs make them of fundamental and practical interest. POMs have single physical and chemical properties, e.g., strong Brönsted acidity, strong oxidizing agents, an unmatched range of molecular structures, efficient adsorbents, green catalysts, and redox activity. Their properties as green catalysts are due mainly to their sustainable synthesis procedures and also their compatibility with some environmentally friendly oxidants, such as H_2O_2.[1] Other advantages of POMs are their high solubility and stability in ionic liquids (ILs) media.[1,2] POMs have demonstrated to be active catalysts for oxidative desulfurization processes (ODS).[1-2] The most used POMs in ODS processes are mainly Keggin $[XM_{12}O_{40}]^{n-}$, Lindqvist $[M_5O_{19}]^{p-}$ and Anderson-type $[M_7O_{24}]^{q-}$ (M = W, Mo and V). The research line of our group has been focused on the application of Keggin-type POMs in ODS processes to treat model and real diesels.[1-3] An effort has been made to immobilize these active POMs in different solid supports to form robust recyclable catalysts. In the present work, POMs with different structures (Keggin-type and sandwich-type), were immobilized in an IL phase (POMs@IL), and in MOFs structures (POMs@MOFs) and mesoporous silica supports (POMs@SBA-15). A correlation between catalytic performance, structure and immobilization strategy was investigated.

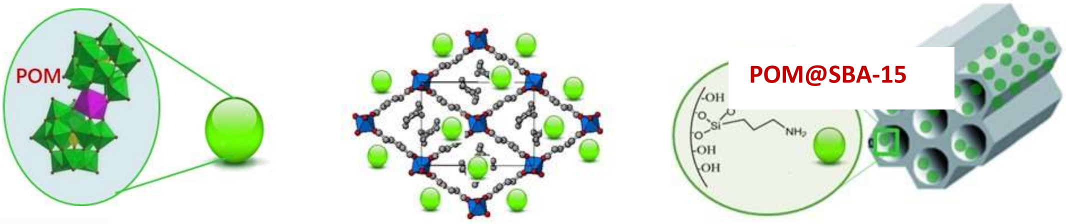

Figure 1: Representation of POM structure and composites: POM@MOF and POM@SBA-15.

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P32

MICRO-STRUCTURAL CHARACTERIZATION OF ULTRASONICALLY WELDED WIRES

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Ultrasonic metal welding is applied when metal pieces are joined by application of pressure and high frequency vibrations to them, causing dynamic shear stresses high enough for plastic deformation bond the pieces at solid state[1]. Soft materials, like copper or aluminum and their alloys are the most easily welded structural metals by this method. Since no electrical current actually passes through the material being welded, the heat of the weld is not high enough to affect the mechanical properties of the welded sample. Ultrasonic welding process has some limitations as thickness, but for the wires used in this, this limitation may not be an issue[1,2].

The purpose of this study is to understand the materials characteristics involved in the ultrasonic welding of copper or aluminum splices used in automotive industry. The study was mainly focused on the microstructural, chemical and surface characterization of wires to be used in manufacturing of automotive harnesses. Identification of failure analysis of the ultrasonic welded splices and finally microstructural characterization of impact of insulation materials used on wires[3,4]. Materials investigation was performed using analytical instrumentation and techniques, which include optical microscopy, scanning electron microscopy and X-ray energy dispersive spectroscopy[4]. Data analysis provided information on texture, chemistry and surface conditions of the wires and the root cause of ultrasonic welding failure, as well as on the microstructure of the polymers used on the insulation of wires.

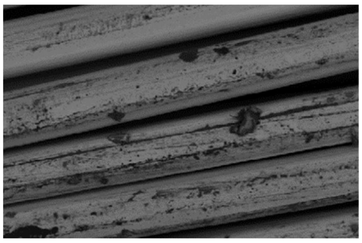

Figure 1: SEM analysis of copper wires

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P33*

MULTI-ELEMENTAL CHARACTERIZATION AND DIFFERENTIATION OF PORTUGUESE WINES ACCORDING TO THEIR PROTECTED GEOGRAPHIC INDICATIONS

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Portugal produces unique wines at special and demarcated regions, whose quality is increasingly recognized worldwide. In consequence, the uniqueness of each demarcated region demands the development of methods that can ensure their quality and authenticity. Since mineral composition of wines reflects the mineral composition of the “bedrock”, the multi-elemental analysis of wines may be a valuable tool to ascertain its authenticity and geographic origin.

With this postulate in mind, 70 red and white wine samples, from 9 different Portuguese Protected Geographical Indications (PGI) were analyzed for a wide panel of elements (53) by Flame Atomic Absorption Spectroscopy (FAAS) - for Na, K, Ca and Mg determination - and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) - for trace element determination.

The analytical procedures used were those recommended by the Organisation of Vine and Wine (OIV) and, since the OIV methods were only validated for 14 elements, the study includes the validation of the analytical methods for a wider panel of elements, which was achieved for an additional set of 37 elements for the wine matrix. The study also includes the characterization of Portuguese wines according to their elemental composition.

The multi-elemental analysis of the samples showed that the concentration of several elements was significantly different among wines and regions and that, despite none of those elements could be labelled as significant for daily nutrient intake, Portuguese wines seem to have an excellent quality since Pb and Cd were well below the established limits in all the analyzed wines.

Discriminant analysis was used to find the elements with greater discriminant power to distinguish among regions and, despite being a preliminary work performed on a limited set of samples, it was possible to verify that the concentration of certain elements is discriminant among PGI regions.

Acknowledgements: This work received financial support from the European Union (FEDER funds POCI/01/0145/FEDER/007265) and National Funds (FCT/MEC, Fundação para a Ciência e Tecnologia and Ministério da Educação e Ciência) under the Partnership Agreement PT2020 UID/QUI/50006/2013.

P34*

IMPROVEMENT OF THE SYNTHESIS OF 3-HYDROXY-4-PYRIDINONE CHELATORS: A COMPARATIVE STUDY USING CONVENTIONAL, MICROWAVE AND OHMIC HEATING

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In the past decade our group has worked on the design and synthesis of chelators and metal chelates for biomedical, environmental and agriculture applications. In the context of agriculture applications, the Fe-chelate [Fe(mpp)$_3$] proved to be a strong candidate as a new iron fertilizer to correct Iron Deficiency Chlorosis [1]. The improvement to the synthetic protocol of the ligand and its Fe-chelate is a necessary requirement for its future use in large scale.

Herein we describe our last results involving the synthesis of the Hmpp chelator, and its corresponding FeL$_3$ complex, by means of sustainable chemistry procedures. The synthetic protocols can be considerably improved in what concerns heating methods and we propose to optimize the procedures using conventional, microwave and ohmic heating [2, 3] which will significantly reduce heating times and enhance reaction yields.

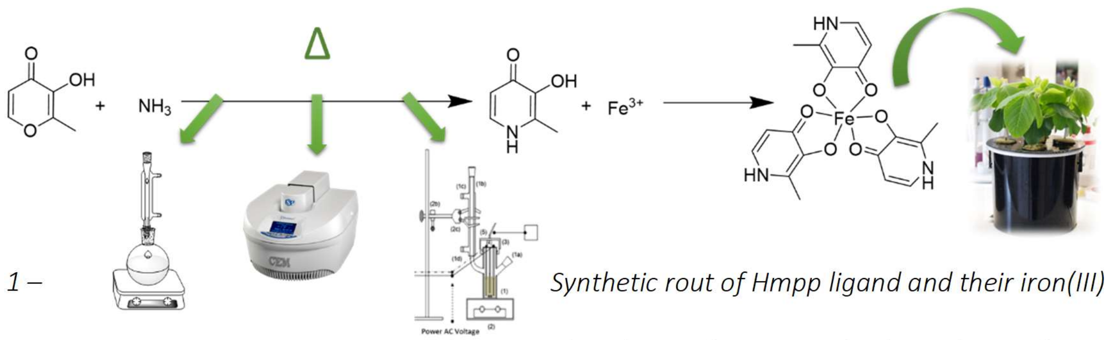

Figure 1 – Synthetic rout of Hmpp ligand and their iron(III) complex.

Acknowledgements: UID/QUI/50006/2013-POCI/01/0145/FEDER/007265; PTDC/AGRPRO/3515/2014-POCI-01-0145-FEDER-016599.

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P35*

THE POTENTIAL ROLE OF THREE *TRIS* (3-HYDROXY-4-PYRIDINONATE) IRON(III) COMPLEXES ON IRON DEFICIENCY CHLOROSIS PREVENTION

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Iron (Fe) is an essential nutrient for plants and legumes are major sources of Fe in human and animal diets. However, the absorption of Fe by plant roots is compromised when grown in alkaline soils, which correspond to 30% of the world's arable land. As a consequence, plants suffer from Fe deficiency chlorosis (IDC), characterized by chlorosis, yield losses, and lower concentrations of Fe in edible plant parts. Soil application of synthetic Fe(III) chelates remains one of the most common measures to correct IDC.

We compared the potential of three *tris*(3-hydroxy-4-pyridinonate) Fe(III) complexes [Fe(mpp)$_3$], [Fe(dmpp)$_3$] and [Fe(etpp)$_3$], to amend IDC in hydroponically grown soybean (*Glycine max*) plants.

The application of all Fe complexes improved plants condition when compared to those grown with no added Fe treatment. Moreover, plants treated with [Fe(mpp)$_3$] exhibited the best overall results. Plants treated with [Fe(mpp)$_3$] presented: (a) higher chlorophyll content, with 18% and 13% significantly higher SPAD values when compared to [Fe(dmpp)$_3$] and [Fe(etpp)$_3$] respectively; (b) higher biomass development, with 16% and 6% greater shoot and root dry weight in [Fe(mpp)$_3$], when compared to [Fe(dmpp)$_3$] and [Fe(etpp)$_3$] treated plants; and (c) higher Fe accumulation, with 6% and 11% greater total Fe content when compared to [Fe(dmpp)$_3$] and [Fe(etpp)$_3$].

Stress condition of plants was further evaluated by measuring root reductase activity at the end of the assay. Plants treated with [Fe(etpp)$_3$], showed the highest reductase activity levels, whilst those treated with [Fe(mpp)$_3$] and [Fe(dmpp)$_3$] exhibit lower values. This result was confirmed by the gene expression analysis of the *FRO2*-like gene.

Acknowledgements: This work was supported by National Funds from FCT – Fundação para a Ciência e Tecnologia through project PTDC/AGR-PRO/3515/2014.

We would also like to thank the scientific collaboration under the FCT project UID/QUI/50006/2013-POCI/01/0145/FEDER/007265 and UID/Multi/50016/2013.

P36

DESIGN OF A NEW FLUORESCENT CARBOXYROSAMINE LABELLED 3-HYDROXY-4-PYRIDINONE IRON(III) CHELATOR WITH POTENTIAL ANTIBACTERIAL ACTIVITY

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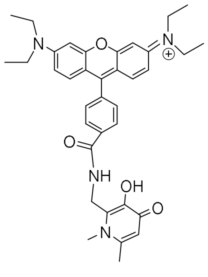
The restricted number of antibiotics to treat infections caused by common multidrug resistant bacteria demands a continuous search for new molecules with antibacterial activity. Bacterial iron deprivation seems to represent a promising alternative strategy [1]. Our group has demonstrated that iron chelators based on 3-hydroxy-4-pyridinone (3,4-HPO) units conjugated with a xanthene framework can limit the access of iron to bacteria and have a significant inhibitory effect on bacterial growth [2, 3]. Our previous results demonstrated that chelation of iron is a determinant but not sufficient property for antibacterial activity. Also, results have shown that the inhibitory effect is dependent on the molecular framework of the fluorophore and is correlated with the affinity of the molecules to lipidic phases and membranes [4]. In order to find the most promising structure, parent chelators have been designed in which different functional structural groups were considered. In the present work we report the synthesis and characterization of a new fluorescent 3,4-HPO iron chelator functionalized with a carboxyrosamine fluorophore (MRB20, Fig.1). *In vitro* studies for evaluation of its potential antibacterial action were performed in parallel.



MRB20

Figure 1: Formulae and numbering of the new chelator MRB20.

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P37

ZINC(II), COPPER(II), NICKEL(II) AND COBALTO(II/III) MIXED LIGAND COMPLEXES AS MULTI-PURPOSE METALLODRUGS

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Coordination compounds of almost all transition metal elements in what concerns biosciences are getting more and more importance because of their roles either in biochemical, pharmacological or medicinal chemistry. Their different stereo-electronic properties, due to their coordination characteristics, kinetic behavior or oxidation state, all metal-centre dependent, afford them a wide/versatile spectra of applications.

Few metal compounds have attracted so much amount of research as the metallodrug *cis*-Pt [1], the most brilliant star in this field of anti-carcinogenicity apart from Ru or Gd (this involved in MRI diagnostic medicine). However, the associated *cis*-Pt drawbacks, or the incapacity of promising compounds to succeed final clinical approval [2], with scarce exceptions, prompted research community to look for other metal compounds, such as with zinc, copper or cobalt, all invaluable in living systems.

On the other hand, non-steroidal anti-inflammatory drugs, NSAIDs, are common anti-inflammatory, analgesic and antipyretic agents also exhibiting anti-tumorigenic activity. Complexes with NSAIDs provide advantages over these drugs themselves, as they can display a wider range of biological activities than original NSAIDs. The combination of two or more active parts into the same molecule can generate a multipurpose-therapeutic agent, through the synergic action of the metal residue once the coordination compound has dissociated inside the biological tissue [3].

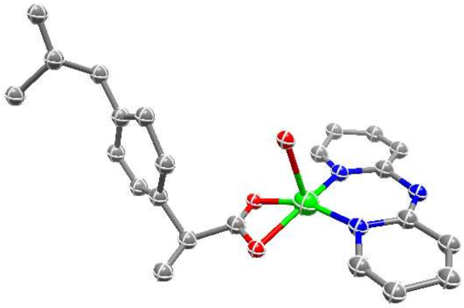

Figure 1: Crystal structure of a Cu(II)/ibuprofen/2,2'-bipyridylammine complex

Here our results on the synthesis and characterization of new Zn(II), Cu(II), Ni(II) and Co(II/III) complexes coordinated with NSAIDs are presented (Fig.1). New compounds have been prepared by standard procedures and characterized by EA, UV-vis and IR spectroscopies, TGA and single crystal X-ray analysis.

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