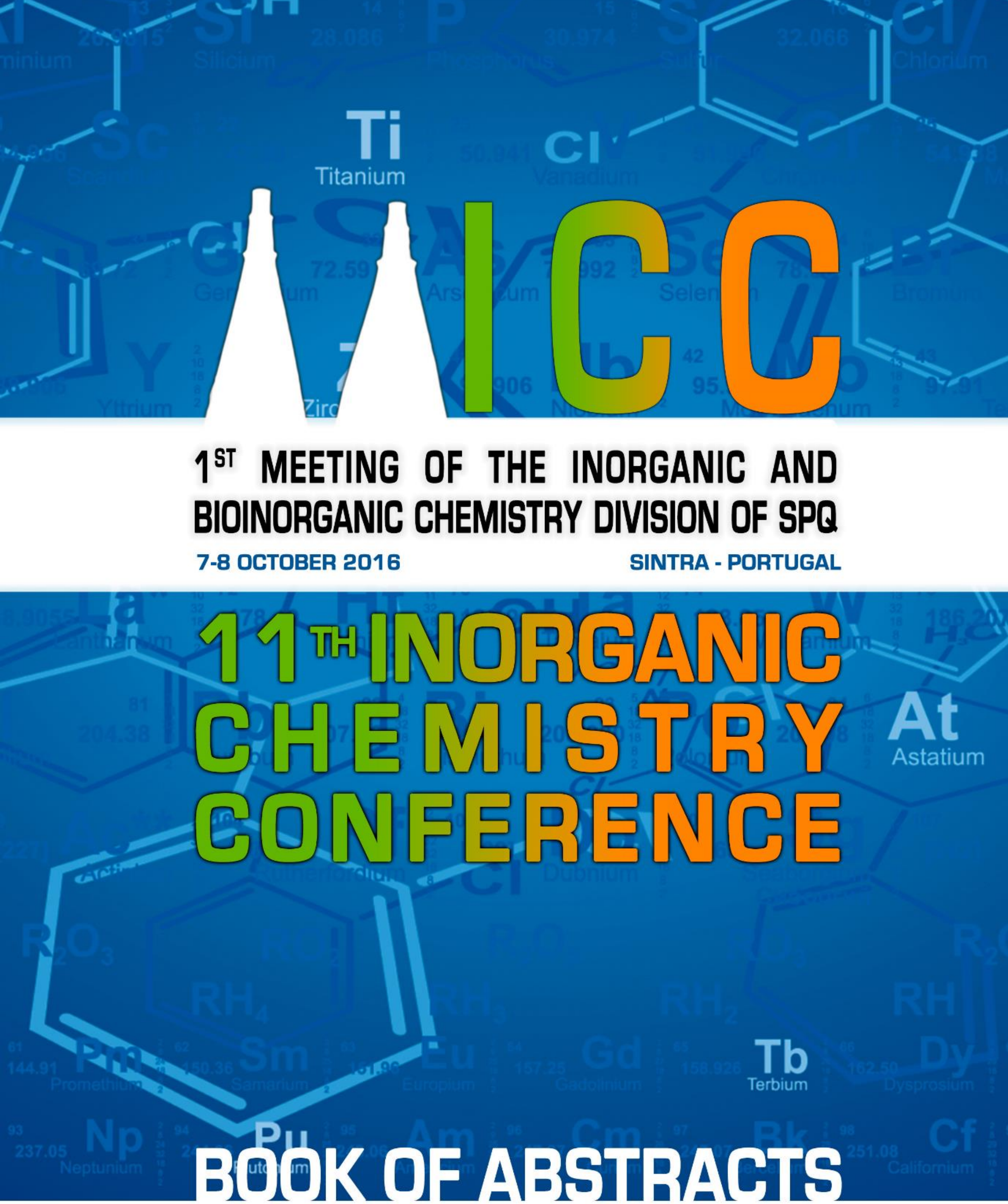

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1ST MEETING OF THE INORGANIC AND BIOINORGANIC CHEMISTRY DIVISION OF SPQ

7-8 OCTOBER 2016
SINTRA - PORTUGAL

11TH INORGANIC CHEMISTRY CONFERENCE

BOOK OF ABSTRACTS

SOCIEDADE PORTUGUESA DE QUÍMICA

11th Inorganic Chemistry Conference

1st Meeting of the Inorganic and Bioinorganic Chemistry Division of SPQ

Book of Abstracts

Sintra, Portugal

7-8 October 2016

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Welcome Message

The Inorganic and Bioinorganic Chemistry Division of the Portuguese Society of Chemistry (SPQ) has the pleasure to present its *11th Inorganic Chemistry Conference***,** taking place in Sintra on 7-8 October 2016. It is also the *1st Meeting of the Inorganic and Bioinorganic Chemistry Division of the Portuguese Society of Chemistry*, to mark the new designation and scope of the Division.

The aim of this biennial Conference of SPQ is to provide a forum to discuss all inorganic and bioinorganic chemistry topics, particularly those on the frontier with other scientific areas. The importance of inorganic chemistry in catalysis, energy, materials, nanotechnology, biology and medicine is immense and current research challenges require active discussions in the inorganic chemistry community.

The scientific programme includes plenary and keynote lectures, as well as oral communications and poster presentations. Young researchers are particularly in evidence by participating and communicating their work.

- The third edition of the *Alberto Romão Dias Prize*, introduced by SPQ in 2009, is presented during the Conference and there is a plenary lecture by the prize recipient António Pires de Matos (IST-UL and FCT-UNL).
- The Conference has the special presence, as plenary lecturer, of Luis Oro (Universidad de Zaragoza), recipient of the *Prémio Luso-Espanhol de Química 2015* (Conferência Lourenço-Madinaveitia), a prize jointly instituted by the SPQ and the Real Sociedad Española de Química.
- Luigi Casella (Università degli studi di Pavia) is presenting the *ChemPubSoc Europe* plenary lecture, highlighting the generous support of the *ChemPubSoc Europe* consortium to the Conference.

On behalf of the Scientific and Organizing Committees of the 11th Inorganic Chemistry Conference and 1st Meeting of the Inorganic and Bioinorganic Chemistry Division of SPQ, welcome.

Joaquim Marçalo

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11th Inorganic Chemistry Conference

1st Meeting of the Inorganic and Bioinorganic Chemistry Division of SPQ

Sintra, 7-8 October 2016

Programme

Friday, October 7th	9:00 – 10:15	**Registration**		
	10:15 – 10:30	**Opening Session**		
	10:30 – 11:15	**Organometallics**	Chairs: *Maria José Calhorda* and *Beatriz Royo*	**Prémio Luso-Espanhol de Química 2015** ***Conferência Lourenço-Madinaveitia*** **PL1 - Luis A. Oro,** *Mechanistic studies on rhodium-N-heterocyclic carbene catalysts*
	11:15 – 11:30			**OC1 - Konstantin V. Luzyanin**, A*cyclic diaminocarbenes as powerful ancillary ligands for emerging catalytic applications*
	11:30 – 11:45			**OC2 - Clara S. B. Gomes,** *Synthesis of* $[Ni(\eta^5\text{-}C_5H_5)(\alpha\text{-diimine})]PF_6$ *complexes and their reactivity towards DEAC. Applications in ethylene polymerisation*
	11:45 – 12:00			**OC3 - Sónia Barroso**, *Reactivity and DFT studies on diamine bis(phenolate) vanadium(III) and –(V) complexes*
	12:00 – 12:30			**KL1 - Ana Isabel Tomaz**, *Tracking antitumor metallodrugs with ruthenium candidates*
	12:30 – 12:45			**OC4 - Dina Maciel**, *A new family of poly(alkylidenamine)s metallodendrimers ruthenium based: synthesis, characterization and cytotoxicity studies*
	12:45 – 13:00			**OC5 - Marta Maroto-Díaz**, *Synthesis, anticancer activity and the reactivity with biomolecules of carbosilane metallodendrimers functionalized with N-donor monodentate or with N,N-chelating ruthenium(II) arene complexes*
	13:00 – 14:30	**Lunch Break**		
	14:30 – 15:15	**Bioinorganic**		**ChemPubSoc Europe Lecture** **PL2 - Luigi Casella**, *What do we know about the redox reactivity of metal ions bound to neuronal peptides*
	15:15 – 17:00	**Poster Session & Coffee Break**		
	17:00 – 17:30	**Bioinorganic**	Chairs: *José J. G. Moura* and *João C. Pessoa*	**KL2 - Nuno S. Cerqueira,** *Theoretical and computational studies devoted to Mo dependent enzymes*
	17:30 – 17:45			**OC6 - Luísa B. Maia**, *Molybdenum-dependent nitric oxide-forming nitrite reductases*
	17:45 – 18:00			**OC7 - Ricardo O. Louro**, *Detailed characterization of multicentre redox enzymes involved in metal respiration pathways*
	18:00 – 18:15			**OC8 - Ana P. Fernandes**, *Interaction studies between periplasmic cytochromes from* Geobacter sulfurreducens *provide insights on the functional role of the nanowire*
	18:15 – 18:30			**OC9 - Ana Petronilho**, *Synthetic methodologies for N-heterocyclic carbenes derived from nucleosides*
	18:30 – 18:45			**OC10 - Pedro Adão**, *Copper(II) complexes derived from N-picolyl, N-carboxymethyl and N-carboxyethyl amino acids as catalysts in asymmetric oxidative coupling of 2-naphthol*
	18:45 – 19:00			**OC11 - Filipe Monteiro-Silva**, *Development of catechol-based rosamine chemosensors with dual fluorescence and paramagnetic response*
	19:00 – 19:15			**OC12 - Manuel Aureliano**, *Isostructural decavanadate and decaniobate decompose into different oligomers: biochemical relevance*
	19:15 – 20:00	**Meeting - Inorganic and Bioinorganic Chemistry Division of SPQ**		
	20:15 – Late	**Conference Dinner**		

Saturday, October 8th	9:00 – 9:45	**Materials**	Chair: *Cristina Freire*	**PL3 - Tito Trindade,** *Water purification using nanomaterials, magnetism and light*
	9:45 – 10:00			**OC13 - Filipa L. Sousa**, *Spontaneous self-assembly of metal-oxide nano-objects*
	10:00 – 10:15			**OC14 - César A. T. Laia**, *Highly luminescent sulfide clusters confined in zeolites*
	10:15 – 10:30			**OC15 - Paulo N. Martinho**, *Transition temperatures and cooperativity in tridentate iron(III) dynamic spin crossover compounds*
	10:30 – 10:45			**OC16 - Sandra Gago**, *Flavylium dyes confined in mesoporous silica materials and in metal organic frameworks*
	10:45 – 11:15	**Coffee Break**		
	11:15 – 11:45	**Materials**	Chair: *A. Jorge Parola*	**KL3 - Carlos Baleizão**, *Silica nanoparticles: a window of opportunities, not just light sand*
	11:45 – 12:00			**OC17 - Ana L. Daniel-da-Silva**, *Boosting the performance of eco-friendly magnetic nanoadsorbents via engineered-surface functionalization*
	12:00 – 12:15			**OC18 - Sara Realista**, *Mononuclear single molecule magnet behavior in a Mn(II) tridentate Schiff-base complex*
	12:15 – 12:30			**OC19 - Helena Nogueira**, *Raman imaging and SERS studies on polyoxometalates and its nanocomposites*
	12:30 – 12:45			**OC20 - Diana M. Fernandes**, *POM@carbon hybrids: preparation, characterization and their electrocatalytic activity for hydrogen evolution reaction*
	12:45 – 13:00			**OC21 - Clara Pereira**, *Energy storage on smart textiles: tailoring supercapacitor performance through carbon/*MFe_2O_4 *nanomaterials*
	13:00 – 14:30	**Lunch Break**		
	14:30 – 15:00	**Miscellaneous**	Chairs: *João Rodrigues* and *Carlos Romão*	**KL4 - John K. Gibson**, *Actinide inorganic chemistry from a gas-phase perspective*
	15:00 – 15:15			**OC22 - Nuno A. G. Bandeira**, *Where are the bonds? Probing into the electronic structure of actinide disulphides of the type* η^2-AnS_2^{2+} *(An = Th, U, Np)*
	15:15 – 15:30			**OC23 - Luís C. Branco**, *Ionic liquids and deep eutectic solvents with metals: more than solvents*
	15:30 – 15:45			**OC24 - Luís G. Alves**, *Metal-cyclam complexes: from chemical to biological applications*
	15:45 – 16:00			**OC25 - Frederico F. Martins**, *Spin crossover tuning: a comprehensive study on the halogen effect*
	16:00 – 16:15			**OC26 - Filipe Teixeira**, *Vanadium-catalyzed epoxidation of allylic alcohols: theoretical models from coupled AIMD/QTAIM studies*
	16:15 – 16:30			**OC27 - Andreia Ruivo**, *Photoluminescent nanocrystals in aluminoborosilicate glasses*
	16:30 – 17:15			**Prémio Alberto Romão Dias 2016** **PL4 - António Pires de Matos,** *How amazing it is to work in Inorganic Chemistry*
	17:15 – 17:30	**Closing Session**		

Plenary Lectures

MECHANISTIC STUDIES ON RHODIUM-N-HETEROCYCLIC CARBENE CATALYSTS

Luis A. Oro

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The catalytic activity of a set of rhodium complexes with N-heterocyclic carbene (NHC) ligands [1] in three specific homogeneous reactions, vinyl selective H/D exchange, alkyne hydrothiolation and alkyne hydrophosphination, has been studied. The high steric hindrance and powerful electron-donor capacity of the bulky NHC´s used, along with ancillary N-donor ligands, seems to be determinant to get selective transformations and to facilitate valuable information about the mechanism of the mentioned reactions.

Rhodium(III)-NHC complexes containing quinolinato or acetonitrile ligands are active and selective catalysts for the H/D exchange of aromatic α-olefins, using CD_3OD as deuterium source. Most of these complexes resulted to be selective in the vinylic-H/D exchange of styrene without the concomitant deuteration of the aromatic region, being able to deuterate the vinylic β-positions with very high selectivity. The proposed mechanism implies an initial H/D exchange, a 1,2 or 2,1 insertion of the coordinated olefin on the Rh-D bond, to give linear or branched alkyl products, followed by rotation and β-elimination. Interestingly, the steric constraints exerted by the bulky IPr NHC ligand (IPr = 1,3-bis(2,6-diisopropyl-phenyl)imidazol-2-carbene) control the rotation of the alkyl intermediate, which in turn determines the selectivity towards H/D exchange at the β-position of aromatic α-olefins.

Rhodium(I) compounds of formula $[Rh(\mu\text{-}X)(IPr)(\eta^2\text{-olefin})]_2$ (X = Cl, OH), $RhCl(IPr)(py)(\eta^2\text{-olefin})$ and $Rh(oq)(IPr)(\eta^2\text{-olefin})$ (py = pyridine, oq = quinolinolate) are very active catalysts for alkyne hydrothiolation under mild conditions, presenting high selectivity towards α-vinyl sulphides. Several intermediates relevant for the catalytic process have been detected. Most of the studied rhodium carbene catalysts have in common a mechanism that proceed via oxidative addition of the S-H bond to rhodium(I) intermediates and successive alkyne insertion into the Rh-S, or Rh-H, bond followed by reductive elimination steps.

The $[Rh(\mu\text{-}Cl)(IPr)(\eta^2\text{-cyclooctene})]_2$ complex has resulted to be an efficient catalyst precursor for the addition of diphenylphosphine to terminal alkynes. Interestingly, this complex is able to catalyze the regioselective double hydrophosphination of a wide range of terminal aromatic or aliphatic alkynes. The distinctive stereoelectronic properties of the NHC ligand prevent the catalyst poisoning by diphosphine coordination thereby allowing for the closing of a productive catalytic cycle. The process is initiated by ligand exchange between diphenylphosphine and cyclooctene and cleavage of the chlorido bridges to give a mononuclear phosphine complex, followed by oxidative addition of the P-H bond to generate a terminal phosphido Rh(III) hydride species.

[1] Oro, L.A. et al.; *Chem. Comm.,* **2016**, *52,* 5554; *Chem. Eur. J.,* **2014,** *20,* 8391**;** *ACS Catalysis* **2013**, *3,* 2910; *Angew. Chem. Int. Ed.,* **2013,** *52,* 211; *J. Am. Chem. Soc.,* **2012,** *134,* 8171; *Angew. Chem. Int. Ed.,* **2011**, *50,* 3938.

WHAT DO WE KNOW ABOUT THE REDOX REACTIVITY OF METAL IONS BOUND TO NEURONAL PEPTIDES

Luigi Casella

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Growing evidence supports the view that disruption of metal homeostasis in the brain is linked to neurodegenerative diseases such as Alzheimer and Parkinson's diseases [1]. Toxic effects of metal ions such as iron and copper may be directly associated with the possibility to promote and stabilize oligomers of neuronal peptides, but in most cases depend on their redox properties and production of reactive oxygen species (ROS). In particular, it can be anticipated that the interaction of these ions with the peptides will influence: (i) the metal redox potential and hence their reactivity towards dioxygen or hydrogen peroxide, which leads to ROS, (ii) the ability to promote metal-mediated oxidation of external substrates present in the environment, and (iii) the post-translational modifications in the endogenous peptides. It is therefore of extreme importance to clarify to which extent the interaction of metal ions with neuronal peptides has pro-oxidant effects.

We are involved in a systematic investigation of the binding and reactivity of copper(II) and ferric heme with peptide fragments of β-amyloid (Aβ), α-synuclein (αS), tau protein ($R_n\tau$), and prion protein (PrP), containing the residues which act as binding sites for the metal ions. The first important exogenous target of the oxidative reactivity of metal-peptide complexes are the catecholamine neurotransmitters, such as dopamine, because of their reactivity and diffusion in the brain. In the case of copper(II), these studies showed that the reactivity markedly depends on the peptide, as Aβ and PrP strongly promote, $R_1\tau$ slightly enhances, and αS depresses the oxidative capacity of the ion [see e.g. 2,3]. However, also the environment affects the reactivity, as the interaction of copper-peptides with membranes changes the redox properties of the ion.

Neuronal toxicity of the heme is particularly relevant under conditions of heavy heme release occurring, e.g. on traumatic brain injury, or when the reactivity is prolonged for long times, e.g. by oxidative stress resulting from neuroinflammation. Indeed, the pseudo-enzymatic activity of heme-peptide complexes is modest under normal conditions [see e.g. 4,5], although binding of the heme can promote the aggregation propensity of the peptide.

Acknowledgements: The Italian MIUR is gratefully acknowledged for funding through a PRIN project (2015T778JW).

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WATER PURIFICATION USING NANOMATERIALS, MAGNETISM AND LIGHT

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Water is the most precious resource to life. The shortage of drinking water in some parts of the world has put on the global agenda the need for renewed efforts to find technological solutions that ensure sustainable water supply for all populations. Nanotechnology has here an important role by providing more efficient processes for the management and use of water resources. An important example concerns the use of nanomaterials for water decontamination processes, whether in natural deposits or in treatment stations in industrial and laboratory units.

This lecture will give an integrated view concerning the application of nanomaterials for water purification. In the past years, several types of nanomaterials have been investigated in our research group and illustrative cases will be briefly discussed. Among these systems, a more detailed discussion will follow for nanomaterials that can be employed in nanotechnologies for water purification assisted by magnetism or light. In particular, two main issues will be addressed: i) the removal of water pollutants such as inorganic mercury by using surface modified magnetic nanoparticles; ii) the photodegradation of organic pollutants using metal sulfide decorated carbon nanostructures, such as graphene oxide. Future developments on the use of functionalized nanomaterials for water remediation will be put on perspective, including the implementation of coadjutant monitoring processes, by emphasizing the challenges ahead concerning the chemistry of inorganic surfaces.

Acknowledgements: Research funded trough the project FCT UTAP-ICDT/CTMNAN/0025/2014 and by the project CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER- 007679 (FCT Ref. UID /CTM /50011/2013), with national funding (FCT/MEC) and also co-funded by FEDER (PT2020 program).

HOW AMUSING IT IS TO WORK IN INORGANIC CHEMISTRY

António Pires de Matos

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I am very honoured and grateful to receive from the Portuguese Chemical Society the Prize Alberto Romão Dias, which is obviously extended to my colleagues from the *ex-Instituto Tecnológico e Nuclear* now part of the *Instituto Superior Técnico,* and also to my colleagues from the Research Unit "Glass and Ceramic for the Arts", whose laboratories are in the *campus de Caparica* of the *Universidade NOVA de Lisboa*. Allow me to stress that Alberto Romão Dias was a very good friend; his humour and kindness will always be present in my memory.

In this communication the work made with the *f* elements, namely with all the lanthanides except promethium and with the actinides thorium, protactinium, uranium, neptunium, plutonium, americium and curium will be reported. A special attention will be given to "Fourier Transform Ion Cyclotron Resonance Mass Spectrometry" in the study of ion molecule reactions of *f* elements.

Another field that will be presented is the research in glass including provenance studies of Portuguese glass, optical properties of glass doped with lanthanides and a new process of making ruby glass using gamma radiation.

Keynote Lectures

TRACKING ANTITUMOR METALLODRUGS WITH RUTHENIUM CANDIDATES

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Cancer is the second largest cause of death in developed countries. Cancer mortality is projected to rise to over 13,1 million people by 2030 as a consequence of world population growth and of a longevity increase. Ruthenium complexes exhibiting a wider spectrum of action and lower toxicity, emerged as effective alternatives to the noxious platinum-based chemotherapeutics approved for clinical use worldwide. In this context, the development of new ruthenium-organic complexes that combine stability, adequate solubility in aqueous media and a spectrum of activity against several types of cancer models is a hot topic in metallodrug research. We are currently screening our new ruthenium-based families exhibiting either piano-stool [1,2,3] or octahedral structures [4] for their chemotherapeutic potential.

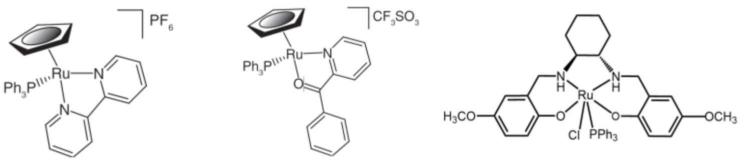

Figure 1: Some examples of new highly active ruthenium complexes with the piano-stool {Ru(II)(η^5-Cp)} scaffold (left and center) or Ru(III)-octahedral structure (on the right).

These compounds exhibit *in vitro* moderate to high cytotoxicity, largely surpassing that of cisplatin in most cases, and are active against cisplatin resistant cell lines. Different aspects of the mode of action of these prospective metallodrugs are addressed, namely the possibility of distribution by the blood due to serum protein binding (human albumin) and how that binding influences the activity of the compounds. The major type of cell death involved, the cellular uptake/sub-cellular distribution of the compounds and ultrastructural alterations brought upon the cell are used to conclude on their possible cellular targets. Differences in their sub-cellular distribution in comparison to cisplatin suggest that the major targets for these ruthenium complexes are possibly located at the membrane and cytosol rather than the nucleus, but their mode of action can differ when the structural differences on the ligands are subtle.

Acknowledgments: This work was financed through the Portuguese Foundation for Science and Technology (*FCT -Fundação para a Ciência e Tecnologia*) in the scope of project UID/QUI/00100/2013 and project IF/01179/2013 within the *Investigator IF2013* Initiative (POPH, Human Potential Operational Program; FSE, European Social Fund).

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THEORETICAL AND COMPUTATIONAL STUDIES DEVOTED TO Mo DEPENDENT ENZYMES

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It is remarkable how nature has been able to construct enzymes that, despite sharing many similarities, have simple but key differences that tune them for completely different functions in living cells. Periplasmic nitrate reductase (Nap) and formate dehydrogenase (Fdh) from the DMSOr family are representative examples of this. Both enzymes share almost identical three-dimensional protein foldings and active sites, in terms of coordination number, geometry and nature of the ligands. The substrates of both enzymes (nitrate and formate) are polyatomic anions that also share similar charge and stereochemistry. In terms of the catalytic mechanism, both enzymes have a common activation mechanism (the sulfur-shift mechanism) that ensures a constant coordination number around the metal ion during the catalytic cycle. In spite of these similarities, they catalyze very different reactions: Nap abstracts an oxygen atom from nitrate releasing nitrite, whereas FdH catalyzes a hydrogen atom transfer from formate and releases carbon dioxide [1].

In this communication, a critical analysis of structure, function, and catalytic mechanism of the molybdenum enzymes periplasmic nitrate reductase (Nap) and formate dehydrogenase (Fdh) is presented. Special attention will be given to the computational results that obtained and were able to predict the sulfur shift mechanisms and other aspects of the catalytic mechanism of these enzymes that later on were validated by experimental means [1, 2, 3, 4].

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SILICA NANOPARTICLES: A WINDOW OF OPPORTUNITIES, NOT JUST LIGHT SAND

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Silica nanoparticles (SiNP) have been extensively used as supports/carriers in catalysis, nanomedicine and imaging, or as fillers in coating applications. Their unique properties such as low toxicity, biocompatibility, versatile surface chemistry, high mechanical strength, tunable morphology/porosity, and large surface area, have leverage the applicability of SiNP in fields with high societal impact.

The characteristics of SiNP can be tuned during the synthesis to obtain a wide range of particle diameters (from a few tens to several hundreds of nm), different porosities (from compact Stöber particles to porous particles) and even different morphologies (spheres or rods). Additionally, it’s possible to incorporate molecules such as catalysts, drugs, or fluorophores by physical entrapment inside the core or covalent attachment to the silica network.

In particular, Mesoporous Silica Nanoparticles (MSNs) have emerged in the last years has exceptional supports/nanocontainers for molecules and polymers, due to the well-defined and controllable particle porous structure, opening a new range of applicability’s not achieved by compact Stöber SiNPs. The most common processes to synthesize MSNs leads to diameters that are usually larger than 100 nm. However, for applications in sensing and/or delivery, especially in organelles inside cells or to pass the blood brain barrier, particle diameters of a few tens of nm are desirable. In the literature, very few works describe MSNs below 100 nm diameter, essentially with a low degree of control over the properties of the obtained MSNs.

The preparation of hybrid MSNs requires the presence of an organic molecule (with terminal trialkoxysilanes in the moiety) during the synthesis, which becomes aligned with the pores, thus impervious to aggregation and self-quenching effects.

In this communication, I will cover the different synthetic aspects involved in the preparation of hybrid SiNPs, with special emphasis on the control of the diameter, morphology and porosity of MSNs. I will also highlight the recent efforts of my group in the development of functional hybrid SiNPs and MSNs, for applications in delivery, imaging, and energy.

Acknowledgements: The author acknowledge the students and young researchers of his group at CQFM/IN, for their dedication and hard work. Financial support from Fundação para a Ciência e a Tecnologia (FCT-Portugal) and COMPETE (FEDER), within projects PTDC/CTM/101627/2008, PTDC/CTM-NAN/2354/2012, RECI/CTM-POL/0342/2012, and UID/NAN/50024/2013.

ACTINIDE INORGANIC CHEMISTRY FROM A GAS-PHASE PERSPECTIVE

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Gas-phase transition metal ion chemistry has been an active area of study for several decades. Attributes of this approach include intrinsic chemistry absent condensed-phase perturbations, elucidation of the inherent stability and reactivity of bonding motifs, and close interaction with computational chemistry to both understand observations and evaluate theory.

Gas-phase ion chemistry of the 5f actinide elements is particularly valuable because of the ability to study scarce and highly radioactive isotopes at the far reaches of the periodic table. The following recent and current pursuits in this field reveal key attributes, including the crucial interplay between experiment and theory.
(1) Evaluation of fundamental redox behavior by synthesis and reactivity of complexes having actinides in extreme high or low oxidation states, such as Np(VII) and Cf(II).
(2) Synthesis and characterization of uranium, neptunium and plutonium complexes with discrete actinide-carbon bonds.
(3) Association reactions of actinide oxides with water to assess bond covalency, a central aspect of contemporary actinide science.

A new research direction is gas-phase ion chemistry of late 5f actinide elements (No, Lr) and 6d transactinide elements (Rf, Db, Sg, etc.). This collaboration between chemical and nuclear sciences will enable the first direct studies of chemical reactivity of these heavy elements. The goal is to expand understanding of the periodic table, including relativistic chemical effects for unexplored 6d transition elements.

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Oral Communications

ACYCLIC DIAMINOCARBENES AS POWERFUL ANCILLARY LIGANDS FOR EMERGING CATALYTIC APPLICATIONS

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Acyclic diaminocarbenes (ADCs) are contemporary ancillary ligands of great significance in catalysis [1,2]. ADCs possess comparable electronic properties to related *N*-heterocyclic carbenes (NHCs) combined with excellent donating abilities. Wider N-C-N bond angles in ADCs, when compared to NHCs, improve the stability of corresponding metal complexes, while rotational freedom of the ADC ligands ensures catalyst core adaptation throughout the catalytic cycle. Metal-ADC complexes can be prepared via several approaches, including nucleophilic addition to metal-isocyanides recognized as the most versatile one. In pursuit of our studies, we assembled a wide range of novel types of metal-ADCs starting from isocyanide precursors (**Figure 1**) [3,4]. Prepared metal-ADC complexes were evaluated as catalysts for various transition metal-catalysed reactions demonstrating outstanding efficiencies [3,4].

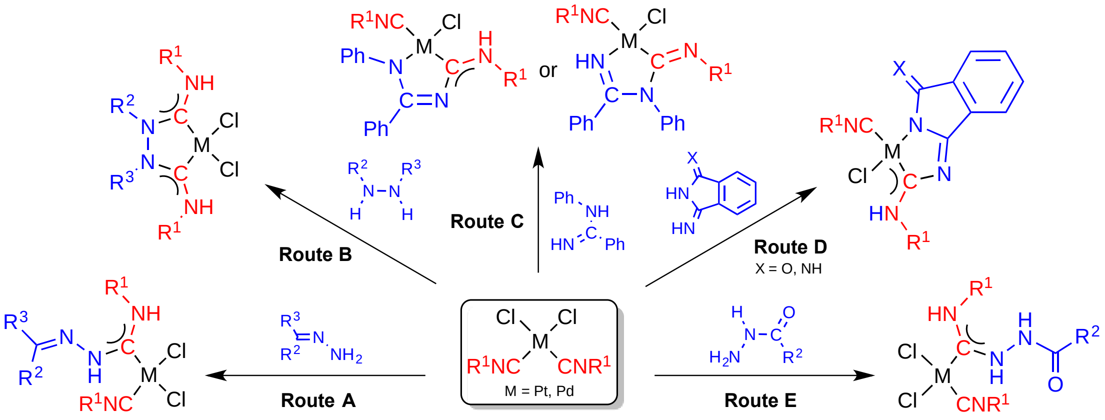

Figure 1: Representative metal-ADCs prepared from isocyanide precursors.

In this report, we systematize recent data on generation and properties of metal-ADC species and draw attention to the advantages that application of ADCs gives to synthetic organometallic chemistry and catalysis.

Acknowledgements: This work was supported by the Fundação para a Ciência e a Tecnologia (Portugal), Russian Fund of Basic Research (grants 14-03-01005 and 15-33-20536), Saint Petersburg State University (Russia), and University of Liverpool (UK).

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SYNTHESIS OF [Ni(η^5-C_5H_5)(α-DIIMINE)]PF_6 COMPLEXES AND THEIR REACTIVITY TOWARDS DEAC. APPLICATIONS IN ETHYLENE POLYMERISATION

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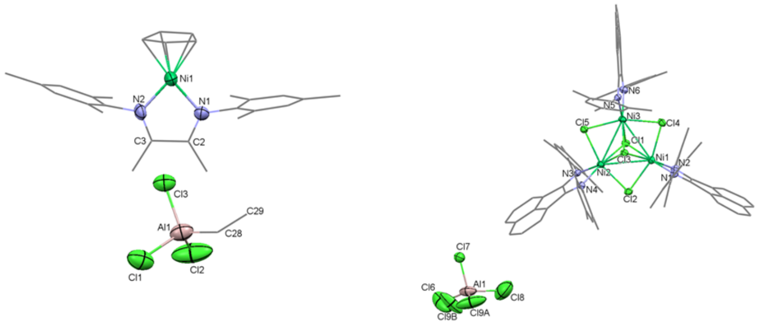
The search for new nickel and palladium based catalysts for the preparation of high molecular weight polyethylenes with controlled branching has been a subject of interest both in academia and industry [1]. In this field the work of Brookhart *et al.*, reporting Ni(II) and Pd(II) catalyst systems bearing bulky α-diimine ligands, was seminal [1a].

We have been interested in complexes of nickel containing either aryl-BIAN or cyclopentadienyl (η-C_5H_5) ligands. Herein, we report the synthesis of the first cationic nickel(II) complexes bearing simultaneously a cyclopentadienyl ring and an α-diimine ligand [2a]. Their reactivity towards diethyl aluminium chloride (DEAC) was investigated leading to the formation of new diamagnetic cationic Ni(II) complexes containing the same cation and an $AlEtCl_3^-$ anion (Figure 1a). When the reaction was performed with complex [Ni(η^5-C_5H_5)(Mes-BIAN)]PF_6, a paramagnetic cationic trinuclear α-diimine Ni cluster, containing five bridging Cl ligands and an $AlCl_4^-$ anion was also obtained (Figure 1b) [2b]. All complexes catalysed efficiently the polymerisation of ethylene, when a supplementary number of equivalents of the cocatalyst DEAC was employed.



(a) (b)

Figure 1: Molecular structures of (a) diamagnetic and (b) paramagnetic Ni complexes containing Al counterions.

Acknowledgements: We thank the Fundação para a Ciência e a Tecnologia, Portugal, for financial support (Projects PTDC/EQU-EQU/110313/2009, UID/QUI/00100/2013 and RECI/QEQ-QIN70189/2012) and for a fellowship to C.S.B.G. (SFRH/BPD/107834/2015).

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REACTIVITY AND DFT STUDIES ON DIAMINE BIS(PHENOLATE) VANADIUM(III) AND –(V) COMPLEXES

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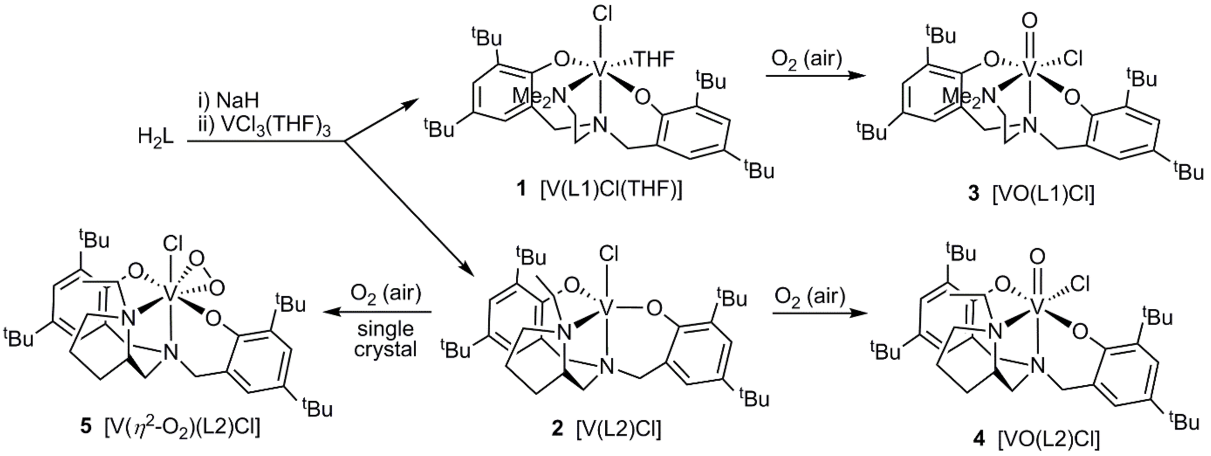
The coordination chemistry of vanadium has received considerable attention in the last decades due to its role in biological and pharmacological processes and its ability to catalyze oxidation and oxo transfer reactions [1]. We have previously reported chiral and achiral vanadium(III) and -(V) complexes supported by tripodal diamine bis(phenolate) ligands and their reactivity in sulfoxidation catalysis with excellent conversions, although no enantioselectivity was achieved [2].

In this work we report new chiral vanadium complexes that revealed interesting reactivity. The oxidation of V(III) complex **1** with air, both in solution and solid state, gives the expected terminal oxido V(V) complex **3** [2] while the exposure of **2** to air gives a mixture of the V(V) complex **4** and decomposition products. Pure **4** could only be obtained by very slow diffusion of air over a solid sample of **2**. The rare non-oxido η^2-peroxovanadium species **5** was obtained by slow diffusion of air into a crystal of **2**. Oxovanadium complexes **3** and **4** are also obtained from the reactions of **1** and **2** with the nitroxyl radical TEMPO. Remarkably, TEMPO-CH$_2$Ph is also obtained as a by-product in the later reactions due to the radical activation of toluene, used as the reaction solvent. The experimental results were complemented with DFT studies.



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A NEW FAMILY OF POLY(ALKYLIDENAMINE)S METALLODENDRIMERS RUTHENIUM BASED: SYNTHESIS, CHARACTERIZATION AND CYTOTOXICITY STUDIES

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Advances in nanotechnology have provided new compounds and drugs in diagnosis and the therapy of cancer and infectious diseases [1]. Dendrimers offer excellent properties and are extensively explored for biomedical applications. They are highly branched and well-defined nanostructures, with good physiological stability and excellent biocompatibility [2,3].

Metallodendrimers combine the advantages of dendrimers (*e.g.*, improved solubility) with the therapeutic properties of metals and metal complexes. The use of metal compounds such as those based on ruthenium presents some advantages when compared with the traditional metallodrugs (*e.g.* cisplatin) [4]. This is attributable to their diverse mode of action, as well as their ability to mimic the behavior of iron, by binding proteins in the plasma [4].

In this study we present the synthesis and characterization by NMR, MS and IR of poly(alkylidenamine)-based dendrimers. Based on our previous experience on the field [5] we prepared dendrimers (generation 0 and 1) with different terminal groups including nitrile, amine, sulfonated and carboxylated terminations. In our approach the nitrile terminal group on the surface of the dendrimers served to grow the dendrimer generation and acted as a bridging group for the complexation of metallodrugs such as $Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2Cl$ and $[RuCl(\eta^6\text{-}p\text{-cymene})]$ derivatives. In the near future, the inhibitory capacity of these metallodendrimers against HIV infection, as well as their anticancer activity will then be evaluated.

Acknowledgments: This research was supported by Fundação para a Ciência e a Tecnologia (FCT) with Portuguese Government funds through the CQM Strategic Project UID/QUI/00674/2013, the NMR Network – (PTNMR-2015) and the Ph. D. Grant SFRH/BD/102123/2014 (D.M). The support of the international network CYTED 214RT0482 in the domain of the HIV infection is highly appreciated.

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SYNTHESIS, ANTICANCER ACTIVITY AND THE REACTIVITY WITH BIOMOLECULES OF CARBOSILANE METALLODENDRIMERS FUNCTIONALIZED WITH N-DONOR MONODENTATE OR WITH N,N-CHELATING RUTHENIUM (II) ARENE COMPLEXES

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Cisplatin remains to be the most metallic complex using in clinical for cancer treatment.[1] However, a number of drawbacks including its limited spectrum activity, acquired resistance and severe side effects. For that it would be desirable to develop carrier platforms that could improve the efficacy and reduce toxicity of cancer treatment by specific delivery of the therapeutic agents to the tumor sites. In this sense, the antitumoral properties of some metallodendrimers based on DAB or PPI scaffolds have been described, including η^6-*p*-cymene-ruthenium (II) systems.[2-4].

A series of new ruthenium (II) arene organometallic carbosilane dendrimers (first and second generation) and their corresponding non-dendritic mononuclear derivatives were prepared. We have demonstrated the potential of new carbosilane-based ruthenium dendrimers as anticancer agents. These metallodendrimers are active against a number of cisplatin resistant cell lines in the low micromolar range while showing a dendritic effect (enhancement of the activity when compared to their mononuclear counterparts). The interaction of selected metallodendrimers described here with DNA is weak. These facts point to a mode of action of these ruthenium derivatives different from that of cisplatin. First generation dendrimers show relevant inhibitory properties on Cathepsin-B (a protease that has been proposed as possible therapeutic target for the control of tumor progression) with having an IC_{50} in the range of the antimetastatic agents RAPTA-C and RAPTA-T.

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MOLYBDENUM-DEPENDENT NITRIC OXIDE-FORMING NITRITE REDUCTASES

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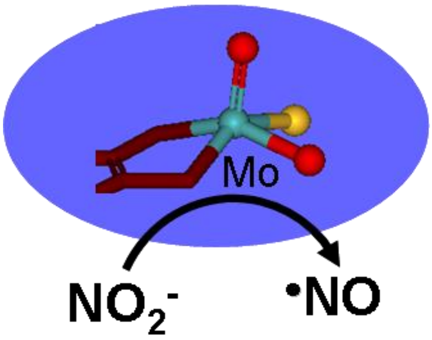
Nitric oxide radical (NO) is a signalling molecule involved in several physiological processes, in both prokaryotes and eukaryotes, and nitrite is being recognised as a NO source particularly relevant to cell signalling and survival under challenging conditions. The "non-respiratory" nitrite reduction to NO is carried out by "non-dedicated" nitrite reductases, making use of metalloproteins present in cells to carry out other functions, such as several molybdenum-containing enzymes - a new class of molybdenum-dependent NO-forming nitrite reductases [1,2].

The molybdoenzymes xanthine oxidase/dehydrogenase (XO/XD) and aldehyde oxidase (AO) are two of the most promising mammalian nitrite reductases and in this work we undertook a comprehensive kinetic characterisation of their NO synthase activity [3,4]. A unified molecular mechanism of this surprising reaction is proposed to explain the simultaneous oxygen atom insertion and abstraction by the enzymes molybdenum centre [5].



Acknowledgements: This work was supported by the Unidade de Ciências Biomoleculares Aplicadas-UCIBIO which is financed by national funds from FCT/MEC (UID/Multi/04378/2013) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER-007728). LBM thanks Fundacão para a Ciência e a Tecnologia, MEC, for a fellowship grant (SFRH/BPD/111404/2015, which is financed by national funds and co-financed by FSE).

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DETAILED CHARACTERIZATION OF MULTICENTRE REDOX ENZYMES INVOLVED IN METAL RESPIRATION PATHWAYS

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Multiheme cytochromes are recognized key players in numerous anaerobic metabolic processes, some of which can be traced to very ancient activities such as photoferrotrophism and dissimilatory metal or sulfate reduction. Some of these metabolic capabilities are nowadays being co-opted for the development of microbial electrochemical technologies that rely on the role of multiheme cytochromes for connecting the microbial metabolism to solid conducting surfaces.

The structure of cytochromes with up to 16 hemes per polypeptide chain has been reported and decaheme cytochromes appear to be very common [1,2]. The detailed functional characterization of such complex proteins is compounded by the fact that most spectroscopic techniques do not provide sufficient discrimination of the individual hemes.

NMR spectroscopy is a very powerful tool to study these proteins since it can provide the necessary discrimination of the individual hemes even while the protein is poised at different degrees of oxidation. This allows for the detailed characterization of their microscopic redox properties [3-5] and for characterizing protein-protein or protein-ligand interactions that are usually transient and weak [fonseca 2013, Paquete 2014b].

The elucidation of the organization of electron transfer networks of metal metabolizing bacteria and the characterization of the molecular mechanisms performed by multiheme cytochromes using NMR spectroscopy will be presented. together with insights into novel strategies for extending the capabilities of NMR spectroscopy to more complex cytochromes.

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INTERACTION STUDIES BETWEEN PERIPLASMIC CYTOCHROMES FROM *GEOBACTER SULFURREDUCENS* PROVIDE INSIGHTS ON THE FUNCTIONAL ROLE OF THE NANOWIRE DODECAHEME CYTOCHROME GSU1996

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Geobacter bacteria usually prevail among other microorganisms in soils and sediments where Fe(III) reduction has a central role [1]. This reduction is achieved by extracellular electron transfer, where the electrons are exported from the interior of the cell to the surrounding environment. This ability makes these organisms a potential target for bioelectrochemical systems applied to bioremediation of contaminated environments, energy generation and many other potential applications [1].

The electron transfer chain of *Geobacter sulfurreducens* (*Gs*) comprises several *c*-type cytochromes, although the exact redox partners are still unknown. Redox protein complexes show weak affinity and short lifetime, which makes them difficult to identify. Nuclear Magnetic Resonance (NMR) spectroscopy methodologies have been useful to probe such partners and allow the identification of interacting partners and determination of its associated parameters, but can also be used to locate the specific docking sites and structural modifications upon formation of such transient complexes. In the present work, a combination of NMR techniques allowed the identification of an interaction between GSU1996 and PpcA, two periplasmic *c*-type cytochromes that were proposed to be involved in extracellular electron transfer in *Gs* [2–4]. This work also allowed the location of the docking site between these putative redox partners. Identification of interacting partners represents a crucial step not only to understand the extracellular electron transfer pathways in *Gs*, but also to improve the practical implementation of bioelectrochemical devices using this organism.

Acknowledgements: This work was supported by grants SFRH/BD/86439/2012 (to APF), SFRH/BPD/96952/2013 (to CMP), PTDC/BBB-BQB/3554/2014 (to CAS) and UID/Multi/04378/2013 (to UCIBIO-REQUIMTE) from Fundação para a Ciência e a Tecnologia, Portugal. The NMR spectrometers are part of the National NMR Facility, supported by Fundação para a Ciência e a Tecnologia (RECI/BBB-BQB/0230/2012).

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SYNTHETIC METHODOLOGIES FOR N-HETEROCYCLIC CARBENES DERIVED FROM NUCLEOSIDES

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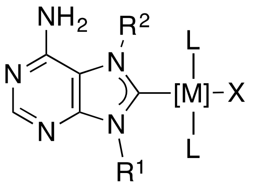
Alkylation of DNA nucleobases to form DNA adducts, resulting from endogenous or exogenous sources is a crucial modification of the genome involved in regulating many cellular processes, from epigenetics to the formation of carcinogenic mutations.[1] Once formed, DNA adducts derived from methylation are formally N-heterocyclic carbene precursors and readily undergo exchange with deuterium[2].
DNA adducts can easily form stable carbenes upon proton loss, an in fact NHCs are proposed as intermediates in a variety of processes leading to mutagenic lesions. [3] Their role is nevertheless poorly understood.



R^1= ribose, desoxyribose
R^2= H, Me

Figure 1. Nucleoside based NHC derived from guanine

Our group has developed methodologies for the formation of NHCs derived from nucleobases and nucleosides, by means of oxidative addition from the corresponding halogenated precursors. These complexes were evaluated for they behavior in physiological media and will be discussed in this communication.

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COPPER(II) COMPLEXES DERIVED FROM N-PICOLYL, N-CARBOXYMETHYL AND N-CARBOXYETHYL AMINO ACIDS AS CATALYSTS IN ASYMMETRIC OXIDATIVE COUPLING OF 2-NAPHTHOL

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The catalytic oxidative coupling of phenols is a direct method for the synthesis valuable biaryls such as nigerone and other perylenequinones.[1] We recently reported several water-soluble Cu^{II}-[N-picolyl(amino acid)] complexes capable of catalysing the oxidative coupling of 2-naphthol to BINOL (1,1'-Bi-2-naftol) under mild conditions, using O_2 as oxidant.[2] Despite the promising results, the system requires the presence of a mild base and of an inorganic additive such a KI for optimal performance. Nevertheless, quinone formation was still prevalent. To address these issues, we prepared simpler Cu^{II} complexes derived from N-carboxymethyl and N-carboxyethyl amino acids, which have shown to be more active, selective and enantioselective than the previous system. While no basic additive is required, KI appears to be a necessary additive for activity of the catalytic system. We are confident that these simple amino acid derived Cu^{II} catalysts are a valuable addition to the development of mild and effective synthetic procedures for biphenols such as BINOL.

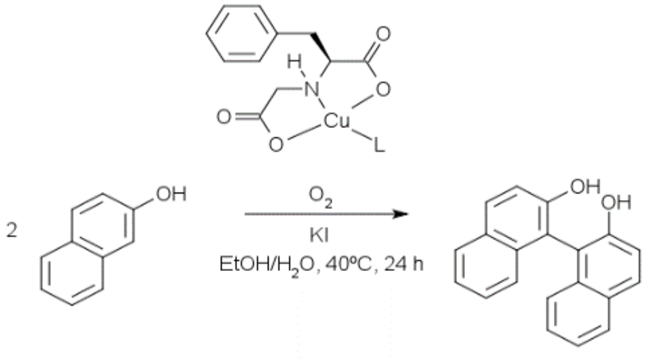

Figure 1: Aerobic oxidative coupling of 2-naphthol catalysed by Cu^{II}-[N-carboxymethyl(amino acid)] complexes

Acknowledgements: We thank the Fundação para a Ciência e a Tecnologia for financial support (UID/QUI/00100/2013, REM2013, RNNMR, RECI/QEQ-QIN/0189/2012, RECI/QEQ-MED/0330/2012, PTDC/QUI-QUI/119561/2010, grants SFRH/BPD/73941/2010, SFRH/BPD/79778/2011, PD/BD/106078/2015 and BL/CQE-2014-001).

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DEVELOPMENT OF CATECHOL-BASED ROSAMINE CHEMOSENSORS WITH DUAL FLUORESCENCE AND PARAMAGNETIC RESPONSE

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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. Such type of ligands have found interesting applications in medicinal chemistry as iron(III) probes in biological samples, exhibiting high affinity and selectivity provided by the catechol unit[1] and also as pH sensors, in combination with other pH-responsive groups.[2] Our results show that the behavior of rosamines is environment-dependent. In particular, the rosamine carrying the 3,4-dihydroxybenzene ligand showed unique characteristics towards specific analytes, including primary amines, metal ions and pH, changing the fluorescence intensity and/or the emission wavelength. In addition, by interacting with primary amines, changes in the EPR signal are observed, thus validating the response of the chemosensor.

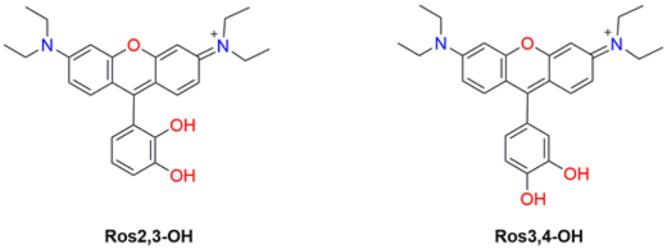

Figure 1: Catechol-based rosamines – Ros2,3-OH and Ros3,4-OH.

Acknowledgements: This work is financed by the ERDF – European Regional Development Fund through the Operational Programme for Competitiveness and Internationalisation - COMPETE 2020 Programme and by National Funds through the FCT (Fundação para a Ciência e a Tecnologia / Portuguese Foundation for Science and Technology) within project «POCI-01-0145-FEDER-006961» and Spanish Funds (project CTQ2012-3161). This work was also supported by FCT, European Union, QREN, FEDER and COMPETE, projects M-ERA-NET/0005/2014, NORTE-07-0162-FEDER-000048, NORTE-07-0124-FEDER-000066/67, UID/QUI/50006/2013 (LAQV/REQUIMTE) and UID/Multi/04378/2013 (UCIBIO/REQUIMTE). A.L. and C.Q. also thank FCT their grants (SFRH/BPD/85793/2012 and SFRH/BD/79702/2011, respectively).

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ISOSTRUCTURAL DECAVANADATE AND DECANIOBATE DECOMPOSE INTO DIFFERENT OLIGOMERS: BIOCHEMICAL RELEVANCE

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The decaniobate ion, (Nb_{10}=$[Nb_{10}O_{28}]^{6-}$) being isoelectronic and isostructural with the decavanadate ion (V_{10}=$[V_{10}O_{28}]^{6-}$), has been useful in advancing the understanding of V_{10} toxicology and pharmacological activities. In the present study, the solution chemistry of Nb_{10} and V_{10} between pH 4 and 12 is studied by Raman spectroscopy (Fig. 1). Solutions of V_{10} and Nb_{10} are both kinetically stable at basic pH conditions for at least two weeks, at moderate temperatures. Whereas the Raman spectra of V_{10} shows that this vanadate species remains detectable until pH 8.59, the Nb_{10} species is detected in solution up to pH 10.80. It is suggested that, under alkaline conditions, V_{10} dissociates into smaller tetrahedral vanadate oligomers such as V_2 and V_4, whereas Nb_{10} dissociates into Nb_6 [1]. These findings have relevant biochemical consequences and the toxicology activities and pharmacological applications of vanadate and niobate polyoxometalates are discussed.

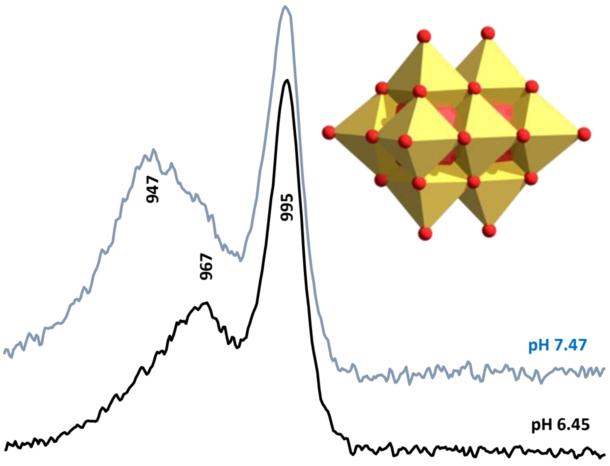

Figure 1: Decavanadate (995 and 967 cm^{-1}) decomposes into V_4 oligomers (947 cm^{-1}) at neutral and alkaline pH.

Acknowledgements: MA, LAEBC and MPMM thank to national funds through FCT - Foundation for Science and Technology (UID/Multi/04326/2013 and UID/Multi/00070/2013).

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SPONTANEOUS SELF-ASSEMBLY OF METAL-OXIDE NANO-OBJECTS

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In the last decades chemists, trying to mimic the biologically inspired processes, have developed synthetic design strategies that are based upon the concepts of self-assembly. Polyoxometalate chemistry provides different means of exploiting the advantages of self-assembly to synthesize a variety of nano-sized entities, which are based on the linking of transferable building blocks under "one-pot" reaction conditions.[1] Aqueous solutions of molybdates – in particular in acidic medium and under reducing conditions – offer a unique library where an enormous variety of species showing different extent of connectivity can be formed by linking together metal-oxide building blocks. Examples include: the $\{Mo_{36}\}$ and $\{Mo_{57}M_6\}$ type clusters, the big-spheres of the type $\{Mo_{132}\}$ and $\{Mo_{72}M_{30}\}$, the big-wheel of the type $\{Mo_{154}\}$ and the largest structurally well characterized cluster $\{Mo_{368}\}$ with the shape of a lemon.[1-3] These nano-objects allow specific reactions at well-defined positions and show reversible interactions with their environment, while keeping their overall basic shape/structural skeleton intact.

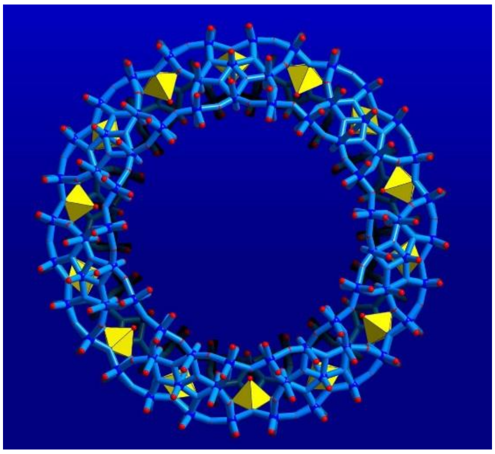

Figure 1: Structure of the nanosized Mo_{154}-type wheel

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HIGHLY LUMINESCENT SULFIDE CLUSTERS CONFINED IN ZEOLITES

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Zeolites offer a unique template in which small atom clusters may be confined, giving rise to unique and enhanced luminescence properties.[1] This communication incorporates sulphur clusters in sodalite type zeolites with very stable luminescence. An extensive characterization of the synthesis and photoluminescence properties of sulphide cluster-based zeolitic materials with the general formula $Na_8[SiAlO_4]_6S_xCl_{2-2x}$ is here presented. The employed experimental conditions yielded highly luminescent S-zeolites composed of a mixture of sodalite and nepheline crystalline phases in variable proportions. An emission band at 650 nm for low sulphur concentration is observed, fully consistent with S_2^- clusters as light emitting centres. For higher sulphur concentrations a conversion to other light emitting centres at 780 nm is observed, attributed to polysulfide clusters (tentatively S_4^{2-} species). Rather large photoluminescence external quantum efficiencies (EQE's) are observed for x=0.2 (53%), but with increasing sulphur a quenching is observed. Time-resolved experiments allow the elucidation of the photoluminescence quenching mechanism, in which S_2^- excited-state is suppressed in the vicinity of polysulfide clusters. Optimal EQE values were obtained when the formation of polysulfide clusters and nepheline crystalline phase is avoided. Additionally, these composites display a remarkable temperature stability up to 450 °C. Giving the high EQE values, large Stokes shifts, and temperature stability, the materials presented in this report can find applications in light down-conversion for photovoltaic cells or as luminescent phosphors in lightning devices.

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TRANSITION TEMPERATURES AND COOPERATIVITY IN TRIDENTATE IRON(III) DYNAMIC SPIN CROSSOVER COMPOUNDS

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The phenomenon of spin crossover (SCO) observed for d^4-d^7 first row transition metal ions is normally accompanied by drastic changes in the magnetic, optical and structural properties of molecules and materials,[1] making them very attractive for potential applications in data storage, molecular switching, molecular sensing and other molecular electronic devices.[2] Molecules exhibiting SCO may also present polymorphism which can affect dramatically their magnetic profile and their function.[3] Here we discuss polymorphism in tridentate Schiff-base Fe(III) complexes with salEen (salEen = *N*-ethyl-*N*-(2-aminoethyl)salicylaldiminate) derived ligands. We have found that the temperature of both synthesis and crystallization highly influences the magnetic profile and transition temperatures for their perchlorate and tetrafluoroborate salts.[4] Interesting is that very small changes in the packing of the compounds result in either abrupt spin transitions or exotic spin crossovers with stepped transition and hysteresis (Figure 1).

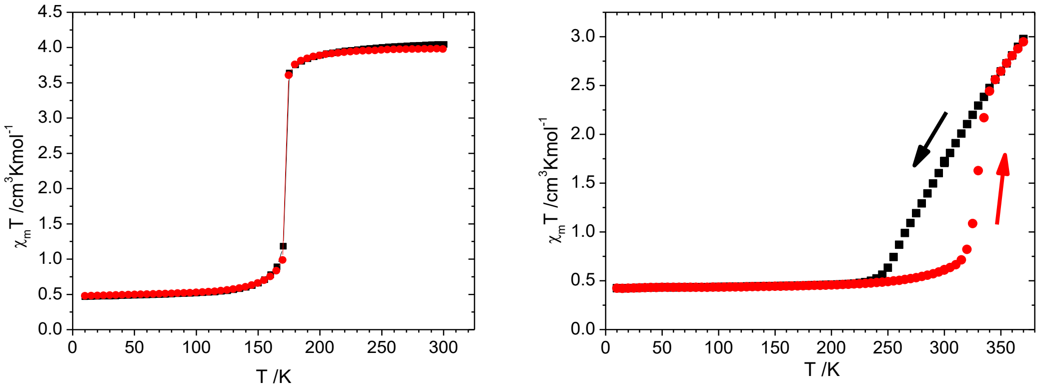

Figure 1: Magnetic profiles of two Fe(III) polymorphs.

Acknowledgements: The authors thank Fundação para a Ciência e a Tecnologia for financial support UID/MULTI/00612/2013 and PTDC/QEQ-QIN/3414/2014. PNM thanks FCT for financial support (SFRH/BPD/73345/2010).

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FLAVYLIUM DYES CONFINED IN MESOPOROUS SILICA MATERIALS AND IN METAL ORGANIC FRAMEWORKS

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Flavylium compounds belong to an important family of molecules that comprises anthocyanins, anthocyanidins and deoxyanthocyanins, whose basic structure is the 2-phenyl-1-benzopyrylium (flavylium) cation. These dyes are responsible for the bright colours of flowers, fruits and leaves and found applications in the food and cosmetic industries, as models for optical memories and even as light absorbers in solar cells aiming at a greener solar energy conversion [1].

Different substituted flavylium salts were immobilized on MCM-41 and SBA-15 by covalent attachment (Figure 1A). The materials were characterized by several solid state characterization techniques that confirm the successful covalent bonding of the flavylium moieties with loadings in the range 11-17% (w/w) [2]. MOF-5, a member of Metal Organic Frameworks (MOFs) family, known as microporous material with a high surface area and large pore volume, consists of Zn_4O units connected by linear 1,4-benzenedicarboxylate to form a cubic framework [3]. This material was synthetized and used for adsorption of 4′-7-dihydroxyflavylium by immersion in several aqueous solutions at different pH values. Curiously, independently of the pH, the quinoidal base is the species preferentially adsorbed (Figure 1B).

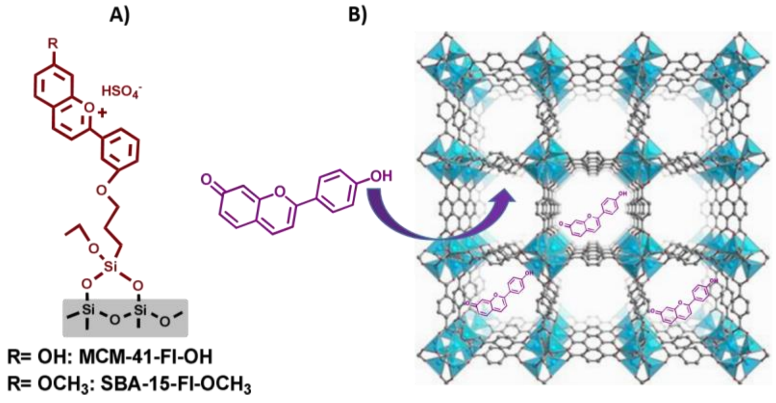

Figure 1: A) Hybrid mesoporous materials based on MCM-41 and SBA-15. B) Adsorption of quinoidal base of 4′-7-dihydroxyflavylium by MOF-5.

Acknowledgements: This work was supported by LAQV which is financed by national funds from FCT/MEC (UID/QUI/50006/2013) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER – 007265).

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BOOSTING THE PERFORMANCE OF ECO-FRIENDLY MAGNETIC NANOADSORBENTS VIA ENGINEERED-SURFACE FUNCTIONALIZATION

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Water pollution either by inorganic or organic contaminants is a matter of concern because of their adverse impact on environment and human health. Among available sorbents, magnetic nanomaterials are very attractive because besides bearing a large surface area favorable for adsorption processes, possess magnetic features that allows the easy magnetically assisted separation of the adsorbents from the treated water. Although a number of magnetic materials have been explored as adsorbents, further research is needed to develop more effective nanomaterials for application in water treatment, namely through the optimization of the functionalization of nanomaterials surface for maximizing contaminant removal and reuse [1].

Herein, we will report the preparation of magnetic nanosorbents with the polysaccharide κ-carrageenan, which is extracted from red seaweeds, anchored to the magnetic core using three distinct surface functionalization strategies [2-4]: (i) non-covalent biopolymer immobilization and covalent attachment of the biopolymer via (ii) post-synthesis surface modification and (iii) one-step hybrid shell formation. The adsorption behavior of the magnetic nanoadsorbents was evaluated in distinct conditions of contact time and pollutant concentration in the uptake of the dye methylene blue (MB) used as a model pollutant. The stability of the prepared sorbents in suspension medium and their capability for regeneration and reuse was also investigated. Overall the one-step method for the surface modification of magnetic nanoparticles led to magnetic nanoadsorbents that exhibited very high adsorption capacity over consecutive adsorption/desorption cycles, which demonstrates the reusability potential and robustness of these hybrid sorbents. The exceptional performance of these materials could be ascribed to surfaces enriched with ester sulphate groups due to extensive grafting of κ-carrageenan over the siliceous domains by using a new surface modification method.

Acknowledgements: This 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. A.L. Daniel-da-Silva acknowledges FCT for the IF-2014 FCT Investigator Programme.

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MONONUCLEAR SINGLE MOLECULE MAGNET BEHAVIOR IN A Mn(II) TRIDENTATE SCHIFF-BASE COMPLEX

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Single ion magnets (SIMs) are a class of materials with potential application as high-density magnetic memories and quantum-computing devices in spintronic field.[1] The size of the barrier of the reversal magnetization (U_{eff}) is the determining factor to the suitability of a single ion magnet to be applied in data storage devices. Efforts aiming at maximizing the anisotropy by an appropriate ligand field have been made to achieve high barriers.[2] Octahedral complexes of the Mn(III) d^4 metal ion display a Jahn-Teller (JT) distortion. This feature turns Mn(III) into an promising ion to study its magnetic properties, namely spin crossover[3] and single ion magnet[2]. We report the synthesis of Mn(III) Schiff base cationic complexes (Figure 1) using different counter anions. SQUID magnetometry showed that all compounds are in the high-spin state with one pair of bond lengths (Mn-Namine) considerably longer than the others (Figure 1). AC susceptibility measurements carried out using a MagLab2000 system showed that one of the new compounds displays single ion magnet behaviour, thus making it a good candidate for further investigation and possible application in data storage.

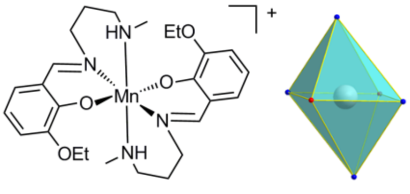

Figure 1: Mn(III) cation

Acknowledgements: The authors thank Fundação para a Ciência e Tecnologia for financial support UID/MULTI/00612/2013 and PTDC/QEQ-QIN/3414/2014. PNM and SR thanks FCT for financial support (SFRH/BPD/73345/2010 and PD/BD/52368/2013)

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RAMAN IMAGING AND SERS STUDIES ON POLYOXOMETALATES AND ITS NANOCOMPOSITES

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The current developments of techniques such as Raman imaging, through high resolution Raman mapping with short measurement times, have brought a new look on composites and its applications. Using Raman imaging, composite particles can now be evaluated from its Raman signal over a specific surface area with spatial resolution within the sub-micrometer range. Such an image can show either the chemical heterogeneity or a specific response such as SERS (surface-enhanced Raman scattering) activity [1] or a labeling process [2] (Figure 1).

SERS also brings new insights in the studies on the molybdenum blue polyoxometalates such as the hedgehog-shaped {Mo_{368}} cluster in which the high number of delocalized electrons allows the measurement of the SERS spectrum [3].

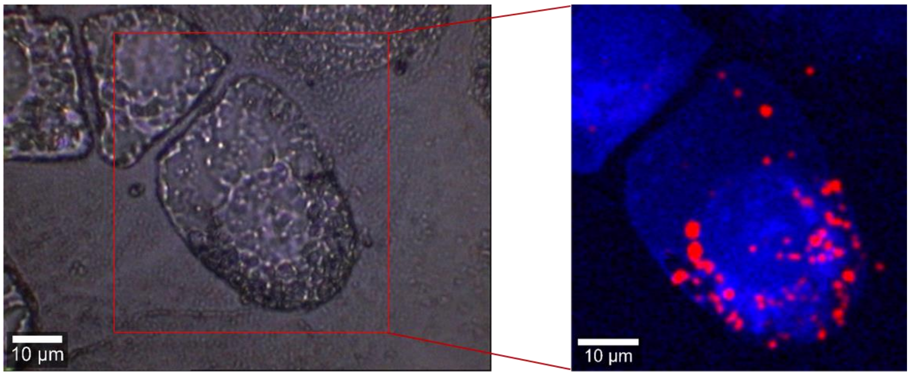

Figure 1: Bio-labeling of human bladder cancer cells using lanthanopolyoxotungstate/silica nanocomposites: optical image (left) and Raman imaging of the selected area (right).

Acknowledgements: Thanks are due to Fundação para a Ciência e a Tecnologia (FCT, Portugal), CICECO - Aveiro Institute of Materials and COST CM1203 action for funding.

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POM@CARBON HYBRIDS: PREPARATION, CHARACTERIZATION AND THEIR ELECTROCATALYTIC ACTIVITY FOR HYDROGEN EVOLUTION REACTION

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Hydrogen (H_2), as a renewable and environment-friendly energy, has triggered broad attention to replace the fossil fuels because of the increasingly serious energy crisis and environmental contamination [1]. Producing H_2 from electrocatalytic splitting of water by the hydrogen-evolution reaction (HER) has become a research focus because of the high efficiency of energy conversion [2]. Pt group metals are the state-of-the-art catalysts to generate H_2 with high current density at low overpotential (η) in acidic media. However, the scarcity, high costs, and the instability of Pt limits the widespread application for the HER [3]. Recently, non-noble electrocatalysts have been widely studied showing promising results but much work remains necessary to decrease the overpotentials required to drive efficiently the HER [4,5].

Our strategy to achieve this goal was to prepare a new electrocatalyst combining carbon materials and a polyoxometalate (POM). POMs are a unique class of materials with different properties and application depending on their versatile structures. One of the more important is their good proton and electron reservoir abilities. The novel nanocomposite was fully characterized by several solid state techniques which confirmed its successful preparation. More importantly, modified electrodes showed promising results towards HER in acidic solution with an overpotential of 58 mV at 10 mA cm^{-2}.

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ENERGY STORAGE ON SMART TEXTILES: TAILORING SUPERCAPACITOR PERFORMANCE THROUGH CARBON/MFe$_2$O$_4$ NANOMATERIALS

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The escalating growth of the market of Smart and Functional Textiles has been creating new opportunities for the development of garments with innovative functionalities. The recent advances on portable and wearable electronics boosted the development of new energy storage devices. In particular, the integration of flexible supercapacitors in textiles has been a major milestone to power smart phones, sensors, flexible displays, among others [1].

Carbon-based nanomaterials and transition metal oxide nanoparticles emerged as promising building blocks for the design of smart textile-based supercapacitors (SCs), while preserving the comfort, weightlessness and flexibility of the fabric [1,2].

In this work novel flexible textile-based SCs for energy storage were produced (Figure 1) using composite electrode materials combining carbon black (CB) with metal ferrite nanoparticles (MFe$_2$O$_4$, M(II) = *d*-block transition metal) [2]. To achieve that goal, cotton substrates were coated with CB and MFe$_2$O$_4$ nanoparticles followed by the assembly of the resulting textile electrodes and electrolyte in a multi-layered configuration. The influence of the type/composition of the electrodes on the performance of the resulting SC fabrics was evaluated by solid-state cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge/discharge tests.

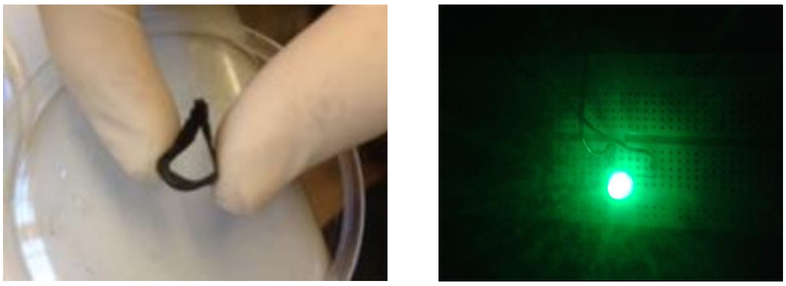

Figure 1: Flexible cotton-based SC prototype and LED powered by the cotton fabric SC [2].

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WHERE ARE THE BONDS? PROBING INTO THE ELECTRONIC STRUCTURE OF ACTINIDE DISULPHIDES OF THE TYPE η^2-ANS$_2^{2+}$ (An = Th, U, Np)

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The recent discovery[1] that dicationic uranium disulphide possesses a triangular geometry as opposed to the well-known linear dioxide (UO_2^{2+}) congener poses the question of whether this trend is maintained with the immediate neighbour of uranium in the periodic series namely neptunium (see Figure 1). The characterisation of these high energy species is mostly performed through mass spectrometry which does not itself provide sufficient structural information, so that reliance on computational tools is paramount to discern the electronic and geometric factors at play.

I shall present my recent findings on the nature of the chemical bond in these fascinating structures and attempt to provide some clues as to the preference for the triangular binding mode in thorium, uranium and neptunium disulphides. To this aim we performed full numerical optimisations of the three η^2-AnS$_2^{2+}$ (An=Th,U,Np) at the CASPT2 level of the ground state root in several spin multiplicities and an effective bond order analysis.

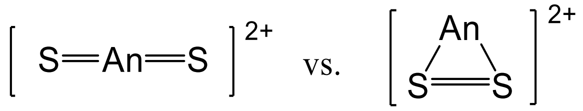

Figure 1: Linear versus triangular actinide di-sulphides.

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IONIC LIQUIDS AND DEEP EUTECTIC SOLVENTS WITH METALS: MORE THAN SOLVENTS

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Ionic liquids (ILs) and more recently deep eutectic solvents (DES) as sustainable media for several applications have been reported [1]. The application and interaction of ILs or DES and metals have been described in particular for dissolution of metal catalysts, preparation and stabilization of metal nanoparticles as well as efficient metal extraction and deposition processes [2].

In last years, we have reported the use of ILs as suitable solvents for metal catalytic reactions [3] (e.g. dihydroxylation of olefins in the presence of osmium catalyst) and nanocatalysis [4] (e.g. hydrogenation of CO_2 to methane in the presence of ruthenium nanoparticles). Recently, our group developed ILs and DES incorporating metals in the cationic or anionic structure as advanced materials for future applications [5-7]. Herein, we describe recent examples of ILs or DES based metals:

a) Vanadium and Molybdenum based ILs for application as electrochromic materials and oxidative catalysts
b) Iron and Manganese based ILs for application as magnetic materials
c) Transition Metal complexes based ILs for application as responsive materials
d) Lanthanides based ILs for application as luminescent materials
e) DES and Transition Metals for application as sustainable and efficient combination for application in catalysis and electrochemistry

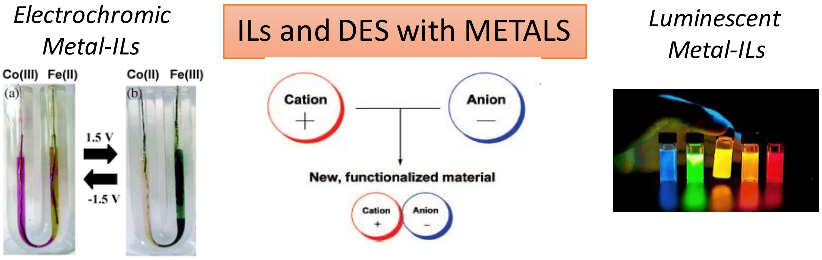

Figure 1: Novel Ionic Liquids and Deep Eutectic Solvents incorporating metals for application as advanced materials

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METAL-CYCLAM COMPLEXES: FROM CHEMICAL TO BIOLOGICAL APPLICATIONS

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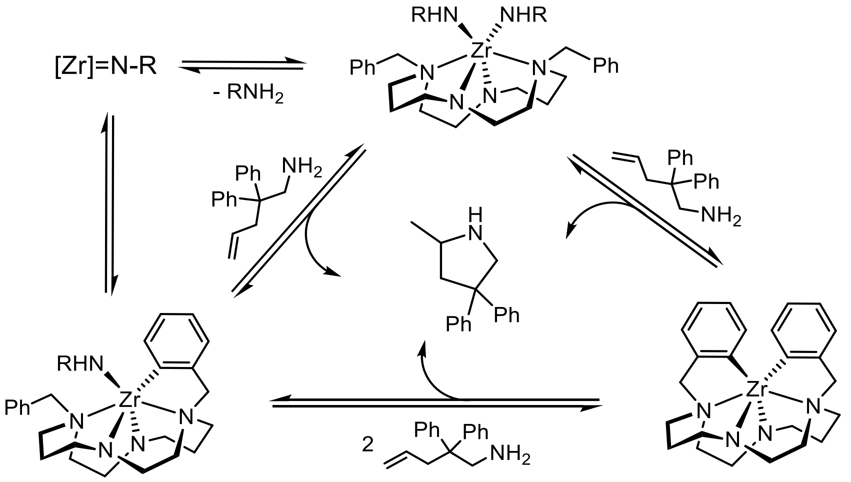
Cyclam based zirconium complexes are the unique macrocyclic-based hydroamination catalysts reported to date [1]. The intramolecular hydroamination of aminoalkenes involves a cooperative metal-ligand mechanism (Scheme 1). Through this process it was possible to obtain several azarings that are the scaffold of natural occurring molecules.



Scheme 1

Several applications of copper complexes based on cyclams can be found in the literature [2]. New Cu(II) complexes supported by *trans*-disubstituted cyclam derivatives were found to promote 1,3-dipolar cycloadditions converting aryl boronic acids into aryl 1,2,3-triazoles [3]. Complexes of the type $[(H_2Bn_2Cyclam)Cu](CH_3COO)_2$ were tested as antifungal agents revealing biological activity against *Candida* species.

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SPIN CROSSOVER TUNING: A COMPREHENSIVE STUDY ON THE HALOGEN EFFECT

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Technological advances have been pushing the limits of chemistry for the last few years towards creating more efficient and multifunctional molecules and materials. A phenomenon that shows great promise in molecular electronics is spin crossover (SCO).[1] This switching between two spin states can be harnessed to develop materials with a wide range of possible applications such as memory or sensing nano-devices.[2] Halogen derivatized SCO molecules are of great interest as they can interact with neighboring molecules through either halogen or hydrogen bonds and additionally they can be modified through substitution or coupling reactions conferring additional properties and high versatility to the SCO molecules.[3,4]

Here we report the synthesis and characterization of halogen (F, Cl, Br, I) derivatized SCO compounds with an Fe(III) metallic center coordinated to tridentate (N2O) Schiff-base ligands. We have found that all compounds exhibit SCO with profiles ranging from gradual to abrupt with hysteresis (shown in Fig.1 for Br). The halogen influence on these properties will be addressed also by DFT calculations.

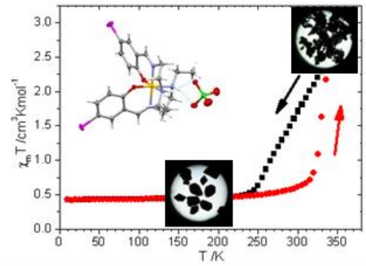

Figure 1: Sample magnetic profile, X-ray structure and optical microscopy images for a SCO compound.

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VANADIUM-CATALYZED EPOXIDATION OF ALLYLIC ALCOHOLS: THEORETICAL MODELS FROM COUPLED AIMD/QTAIM STUDIES

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The vanadium-catalysed epoxidation of geraniol and other allylic alcohols plays an important role in the synthesis of medicines and fragrances for the pharmaceutical, perfume and food industries[1]. The complexity of this process is partly due to the presence of multiple active species in the reaction medium[2]. In this study, a set of elementary epoxidation reactions were studied using Born-Oppenheimer Ab Initio Molecular Dynamics (AIMD). Samples along the trajectories were taken and further studied using Bader's Quantum Theory of Atoms in Molecules (QTAIM). The results show that the activation barrier is mostly due to the movement of the substrate towards the active complex, whereas the bond-breaking and bond-formation processes occur after the Transition State in a nearly synchronized manner. Proton-transfer phenomena (when occurring) is either synchronized or delayed with respect to the formation of the epoxide ring. Moreover, analysis of the trajectories, activation energies and QTAIM characteristics of the system allowed the characterization of the driving forces leading to the regiosselectivity of the vanadium-catalysed epoxidation of geraniol.

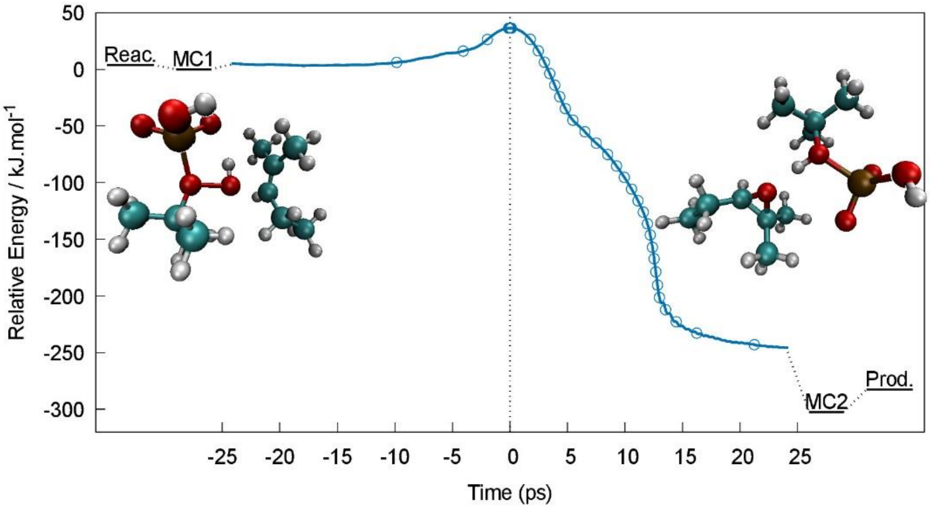

Figure 1: Energy profile of the epoxidation step of 2-methyl-2-pentene with $VO_2(OH)(TBHP)$. Points along the profile represent samples taken for QTAIM analysis. The molecular momplexes preceding (MC1) and following (MC2) the Transition State (occurring at 0 ps) are also depicted.

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PHOTOLUMINESCENT NANOCRYSTALS IN ALUMINOBOROSILICATE GLASSES

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UV-visible down conversion is technologically very important with applications in lighting and Luminescence Solar Concentrators for photovoltaic cells. Luminescent stable materials can be particularly valuable to produce down converters. From previous research blue photoluminescent glasses when irradiated by UV-light, were developed by forming lead bromide nanocrystals.[1] In this study, other halogens were used giving rise to stable and non-expensive aluminoborosilicate glasses with several photoluminescence colours, by doping the glass matrix with Pb(II) and sodium halides. While glasses with NaF and NaCl exhibit almost no luminescence, glasses doped with NaBr and NaI display, at room temperature, a broad emission band at 435 nm and 530 nm, respectively.

The observed room-temperature photoluminescence is attributed to nanocrystals whose presence is revealed by transmission electron microscopy. The crystalline nature of the particles is also revealed by anisotropy measurements for Br and I doped samples which present an anisotropy of 0.19 and 0.2, respectively.

Time-resolved luminescence measurements show a mixed-order kinetics system, with second-order recombination of self-trapped electron centers and a first-order nonradiative rate constant connected with pathways due to nanometric confinement of self-trapped centers. The optical characterization show several variations with the halogens in the absorption and emission spectra and in the photoluminescent decays, suggesting a charge-transfer from the halide to Pb (II), probably linked to the existence of abovementioned self-trapped centers.

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Poster Communications

METAL-ORGANIC STRUCTURES AND THE ACTIVATION OF CO$_2$

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Currently hydrocarbon fuels are the most important source of energy because of their ready availability, stability, and high energy density. The increasing atmospheric concentration of CO$_2$ has been predicted by models which suggest dramatic and irreversible changes if actions are not taken urgently. It is now well established that CO$_2$ may be sequestered and stored as liquid CO$_2$ or solid carbonate but both solutions are energetically demanding and financially costly [1]. Recently reports of reaction of pressurised CO$_2$ with epoxides to form polycarbonates [2] or cyclic carbonates [3] have attracted both academic and industrial interest, but generally, the recycling of CO2 to produce high value products via low-cost catalysts has not been exploited. Nelson's cryptands [4] are an example of a dynamic structure with useful applications, which demonstrated the ability to capture and convert CO$_2$ to carbonate and methyl carbonate following its coordination to encapsulated metal ions. Here we describe how CO$_2$ was fixed by derivatised dinuclear Cu(II), Ni(II), Zn(II) and Co(II) cryptates (Figure 1) where the phenyl ring was modified (R = H, Br, NO$_2$) to control CO$_2$ reactivity and engineer these metal-organic structures into supramolecular assemblies.

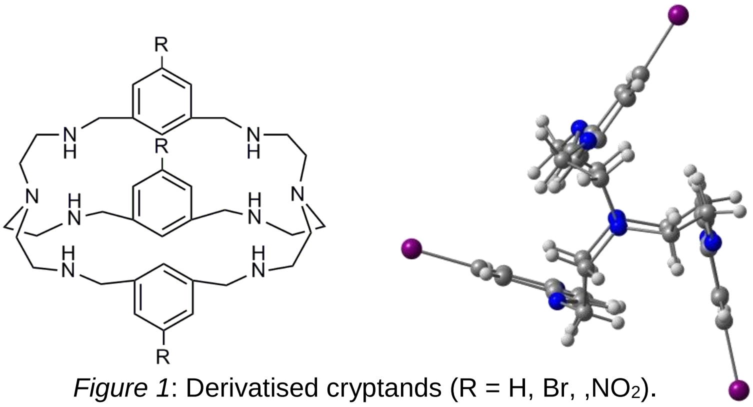

Figure 1: Derivatised cryptands (R = H, Br, ,NO$_2$).

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SURFACE FUNCTIONALIZED FERRITE NANOPARTICLES FOR SORPTION OF NON-ESSENTIAL TRACE ELEMENTS FROM WATERS

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Currently, humans demand from the Earth's ecosystems more than is sustainable. With the discharge of effluent into waterways and the beginning of industrialization, the volume of dumped debris in waters has increased, surpassing the self-cleaning capacity and purification of rivers and oceans. Thus, water reservoirs with quality for human consumption are being depleted due to increased population and contamination of diverse origin. Non-essential trace elements in aquatic environments cause problems because of its toxicity and non-degradation [1]. Exposure of an aquatic living being to water contaminated by non-essential elements may cause its sorption by the body, occurring bioaccumulation and biological amplification along the food chain. Therefore, there is a need to find innovative solutions that assure the quality of water supplies. In recent years, magnetic nanoparticles (NPs) have been investigated as sorbents for quantification and uptake of non-essential trace elements from waters. Our own interest in this field led us to report dithiocarbamate functionalized Fe_3O_4 NPs as highly effective for the uptake of Hg(II) from water by using magnetic separation techniques.[2]

The research communicated here concerns the application of this strategy to other ferrites such as $MnFe_2O_4$ and $CoFe_2O_4$ NPs. These NPs have been synthesized and subsequently coated, via a one-step process, with amorphous silica enriched in dithiocarbamate moieties. The magnetic NPs were then characterized using various techniques and evaluated for their sorption characteristics of non-essential trace elements present in water. Hence, the removal process using such magnetic NPs was investigated for As(III), Pb(II) and Hg(II), as water contaminant species. Additionally, an economic and alternative method for quantification of Hg(II) in powdered sorbents will be also reported. The kinetics of the removal experiments was evaluated using three kinetic sorption models and it was found that the Elovich model provides the best fitting to the experimental data. Finally, the use of functionalized $MnFe_2O_4$ and $CoFe_2O_4$ NPs as compared to the application of the Fe_3O_4 analogues will be discussed, by considering diverse criteria such as cost, sorption capacity and magnetic behavior.

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BIOCHEMICAL CHARACTERIZATION OF CYTOCHROME c_{552} AND THE ELECTRON TRANSFER SUBUNIT OF NITRIC OXIDE REDUCTASE FROM *MARINOBACTER HYDROCARBONOCLASTICUS*

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Nitric Oxide Reductase (NOR) is able to catalyze the reduction of NO to N_2O in the denitrification pathway. It is present in a variety of organisms belonging to different taxonomic groups and isolated from different environments. The enzyme isolated from the marine halophilic bacterium *Marinobacter* (*M.*) *hydrocarbonoclasticus* comprises two subunits (NOR-B and NOR-C) harboring an electron transfer *c*-type heme (on the NOR-C subunit), and a catalytic site consisting of a *b*-type heme, and a b_3-type heme linked via an oxo-bridge to a non-heme Fe atom on the NOR-B subunit. Cytochrome c_{552} is proposed to be the physiologic electron transfer partner [1], but that the interaction interface is still not known.

The present study describes the heterologous expression, purification and biochemical characterization of a hydrophilic deletion mutant of NOR-C (lacking the N-terminal membrane-anchoring α-helix) and cytochrome c_{552} from *M. hydrocarbonoclasticus*. The expressed cytochrome c_{552} exhibits the classic UV-visible and NMR characteristics of a low-spin *c*-type heme protein. A pH shift towards more alkaline values changes the spin-state to a high-spin form, which is reversed lowering the pH to more acidic values, followed by both UV-Vis and NMR spectroscopies, and as observed in other *c*-type cytochromes [2]. An NMR protein-protein titration experiment reveals that a transient interaction with the soluble subunit of NOR, with a K_D value of 1.2 µM, in agreement with the formation of a short-lived electron transfer complex.

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MONONUCLEAR URANIUM SINGLE-MOLECULE MAGNETS: HOW TO SWITCH ON SMM BEHAVIOUR

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Single-molecule magnets (SMMs) are molecules that are characterised by their ability to remain magnetised, for a certain time, in the absence of a magnetic field [1]. The process is related to an intrinsic molecular magnetic anisotropy and to an energy barrier (U_{eff}) between opposite directions of the magnetic moment. Given that one molecule could be seen as one bit, SMMs could have application in ultrahigh-density data storage devices and quantum computing.

The last two decades have witnessed an increasing development of this field, boosted by the identification of SMM behaviour in mononuclear lanthanide-based compounds [2]. However, SMM behaviour is far from being well understood, particularly the parameters that govern the quantum tunnelling effect that shortcuts the energy barrier. In this context, uranium-based compounds emerge as promising candidates to study the SMM phenomenon due to their stronger spin-orbit coupling, larger magnetic anisotropy and enhanced exchange interactions [2].

Following our previous work in this field [3], we report here the dynamic magnetic properties of some mononuclear uranium complexes anchored on a trisamidotriazacyclononane ligand [4]. All compounds were studied by AC and DC magnetisation measurements, under different temperatures, frequencies and magnetic fields. The results obtained can be understood in the light of an effective electrostatic model based on the crystal-field theory and the full single-ion Hamiltonian. These studies clearly demonstrated the influence of the coordination environment in the SMM behaviour and revealed a new strategy to design SMM compounds with non-Kramers ions by using radical ligands.

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SYNTHESES, STRUCTURAL INVESTIGATIONS AND LANGMUIR-BLODGETT THIN FILMS OF SPIRO-BINO-SPIRO TRIMERIC PHOSPHAZENES CONSIST OF N_2O_2 DONOR TYPE SYMMETRIC TETRADENTATE LIGANDS

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Cyclophosphazenes refer to a significant family of heterocyclic compounds with an inorganic skeleton that includes the repeating unit $[NPX_2]_n$ (n=3-40; X=halogens, different inorganic, organic and organometallic groups) [1 and 2]. The hexachlorocyclotriphosphazene (cyclic trimer, $N_3P_3Cl_6$) is the well-known starting compound for the substituted-trimeric phosphazene derivatives [3 and 4]. In this study, the partly substituted spiro-bino-spiro (sbs) phosphazene was obtained from the reaction of trimer with the symmetric N_2O_2 donor type tetradentate bulky ligand. All the Cl atoms of this compound are substituted with pyrrolidine, morpholine and 1,4-dioxa-8-azaspiro[4,5]decane (DASD) groups to give fully substituted phosphazenes (Figure 1). The structures of all the phosphazenes were evaluated using FTIR, MS, ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectral data. The crystal structure of octapyrrolidino sbs-phosphazene was determined using X-ray crystallography. In addition, the ultrathin and highly ordered Langmuir-Blodgett (LB) film of this compound was also fabricated. The LB thin films of the phosphazene derivative is the first example in the literature. The structural characterization of the LB film was achieved using GAIR and HATR techniques.

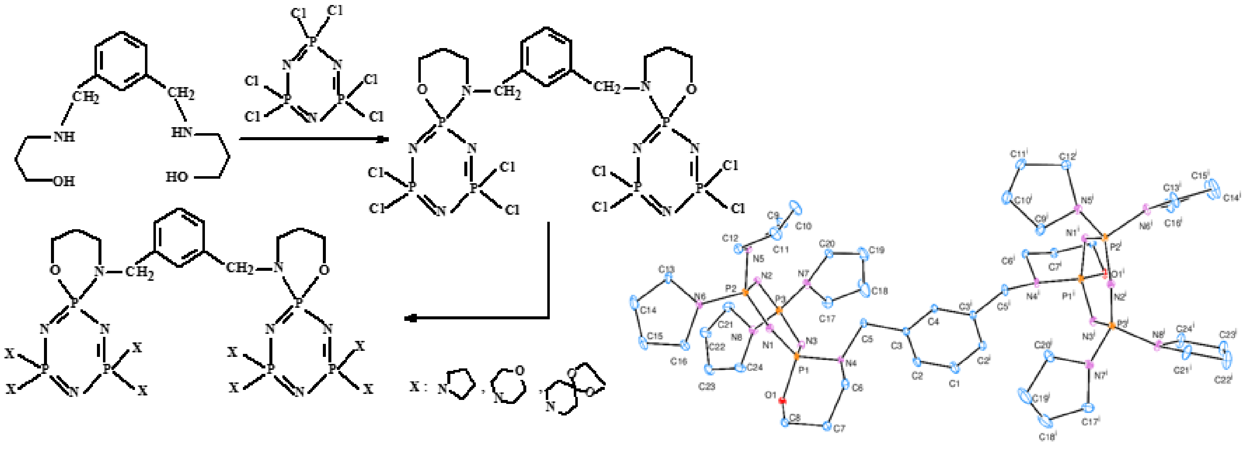

Figure 1. The reaction pathway for the sbs-trimeric phosphazene derivatives.

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NOVEL RUTHENIUM(II) THIOSEMICARBAZONE COMPLEXES AS ANTICANCER METALLODRUG CANDIDATES

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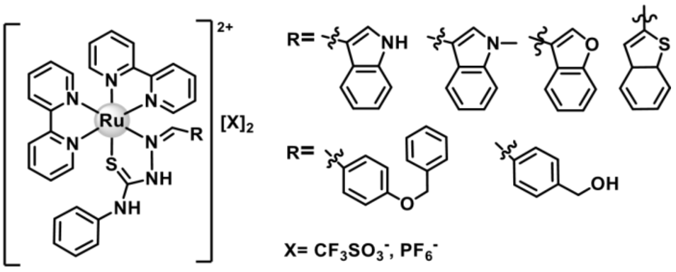
Cancer is the second largest cause of death in developed countries. Two in every five people born today will be diagnosed with cancer at some time during their life, and one of them will effectively perish from that condition [1]. Ruthenium complexes are a recognized effective alternative to cisplatin and other platinum complexes, typically offering a wider spectrum of activity and the potential to overcome tumour platinum-resistance, as well as different mechanisms of action and a lower toxicity in general [2]. In the search for metal-based agents, octahedral ruthenium polypyridyl complexes containing *N*,*N*-chelating ligands, such as 2,2'-bipyridine (bpy), have shown an interesting profile, being their anticancer activity modulated, to some extent, by the additional organic ligand, especially if it exhibits biological activity on its own. Thiosemicarbazones (TSCs) have often been reported to possess a broad range of biological activity, such as antimicrobial, antifungal and antitumor properties [3], and can be used as the bidentate ligand [4]. In this work new aromatic TSCs and novel Ru(II) complexes of the type $[\mathrm{Ru}(NN)_2(\mathrm{TSC})][\mathrm{X}]_2$ (*NN*=2,2'-bipyridine; X=$\mathrm{PF_6^-}$, $\mathrm{CF_3SO_3^-}$) were synthetized and fully characterized by several techniques. Their anticancer activity was evaluated *in vitro* against ovarian adenocarcinoma and triple-negative breast human cancer cells. We present herein our first results on these new highly promising agents.



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THE UNEXPECTED CONVERSION OF A 4-MEMBERED CYCLOPHOSPHAZANE RING TO A 6-MEMBERED CYCLOMONOPHOSPHAZENE RING

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Recently, new types of cyclophosphazenes having very active P-halogen bonds were synthesised from the de-protonation reaction of aminocyclotriphosphazene derivatives contain a P-NHR group in the side chain [1-3]. Investigation of the nucleophilic substitution reactions of these new cyclophosphazene structures is a new area for phosphorus-nitrogen chemistry.

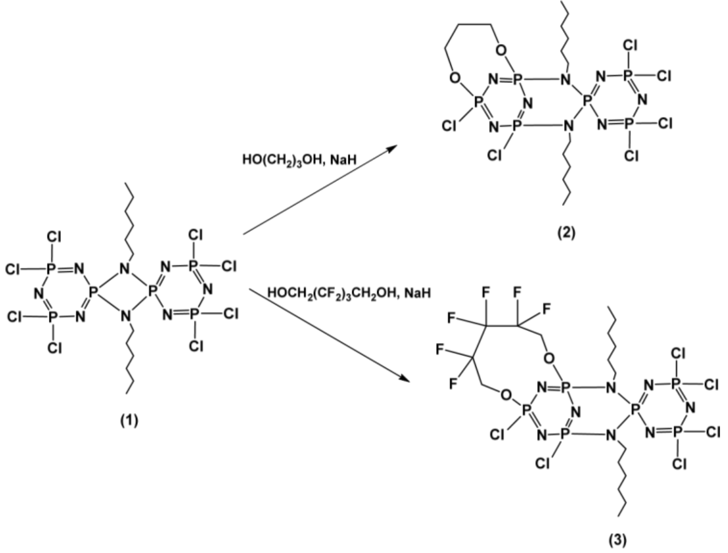

Figure 1: Synthesis of compounds **2** and **3**.

In this study, nucleophilic substitution reactions of the *N*(*R*),*N*(*R*)-*spiro* bridge octachlorobiscyclotriphosphazene, $N_3P_3Cl_4[N(CH_2)_5CH_3]_2N_3P_3Cl_4$ (**1**) with sodium salts of alcohols (1,3-propanediol and 2,2,3,3,4,4-hexafluoro-1,5-pentanediol) give the ansa products (**2** and **3**) via an unexpected rearrangement [4]. These products were characterized by elemental analysis, mass spectrometry, ^{1}H and ^{31}P NMR spectroscopy. The molecular structures of compound **3** were also established by Xray crystallography [4].

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NEW APPROACH FOR SYNTHESIZING NANOSTRUCTURED INTERMETALLIC COMPOUNDS CONTAINING *f* BLOCK ELEMENTS

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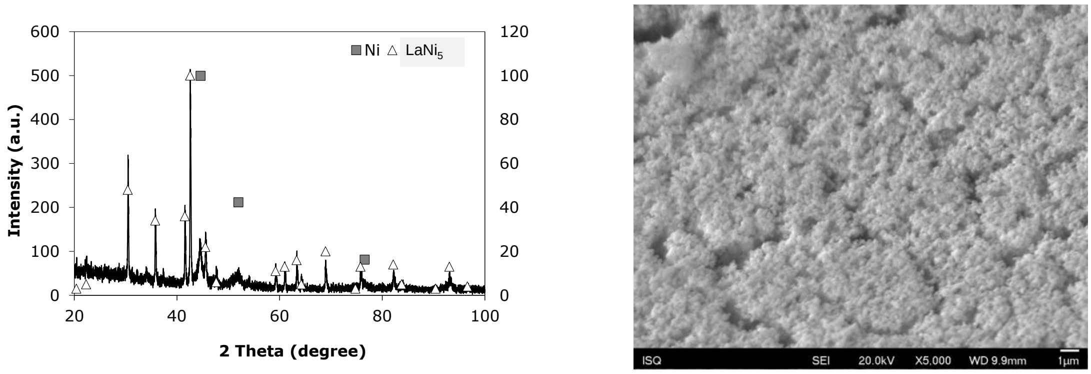
Intermetallic compounds (IC) have a well-defined crystal structure and chemical formula. IC applications are mainly linked to their magnetic properties and ability to reversibly absorb hydrogen [1]. Electrospinning is a technique that has been originally developed to produce ultra-fine polymer fibers [2, 3]. This route enables low cost production of nanometer scale fibers with tunable surface properties. Such fibers have extremely high surface area, very high porosity, high permeability, low basic weight, ability to retain electrostatic charges, among others properties [4].

The purpose of this work was to apply electrospinning for the preparation of IC nanofibers/nanoparticles containing *f* block elements. Moreover, the expected high surface area could bring benefits to the catalytic properties of these materials, which will be the aim of future studies. IC nanoparticles containing *f* block elements such as LaNi$_5$, SmCo$_5$, and DyFe$_3$ were successfully produced by this technique. To our knowledge, this is the first time that such results are reported using electrospinning as preparation technique. Fig. 1 shows the XRD patterns and SEM image of LaNi$_5$ IC nanoparticles. Preliminary catalytic results suggested they are good catalysts for the selective hydrogenation of isoprene (2 methyl-1,3-butadiene) with selectivity > 70% to obtain 2-methy-2-butene + 2methyl-1-butene, compounds with industrial value (precursors for TAME production).



(A) (B)

Figure 1: LaNi$_5$ nanoparticles characterization (A) XRD pattern, (B) SEM image.

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STRUCTURAL AND ELECTRONIC EFFECTS IN THE ARCHITECTURES OF [Mo(η^3-C_3H_5)(CO)$_2$X(LL')] COMPLEXES

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The allylic complexes [Mo(η^3-C_3H_5)(CO)$_2$X(LL')] were reported in the 1960s,[1,2] and can be described as pseudo-octahedral, assuming that the centroid of the allyl group corresponds to one ligand. A search in the Cambridge Crystallographic Data Base [3] has shown that two main isomers, equatorial and axial, are usually observed. They are depicted in Figure 1 for [Mo(η^3-C_3H_5)(CO)$_2$Br(phen)] (phen = 1,10-phenanthroline) in a scheme and a 3-D representation. The experimentally determined structure (single crystal X-ray diffraction) is the equatorial one. In both isomers the facial arrangement of the two carbonyl and the allyl centroid is observed, the exo conformation of the allyl being also preferred. This complex is fluxional in solution. Both isomers are detected, as well as the exo conformer of the equatorial isomer.

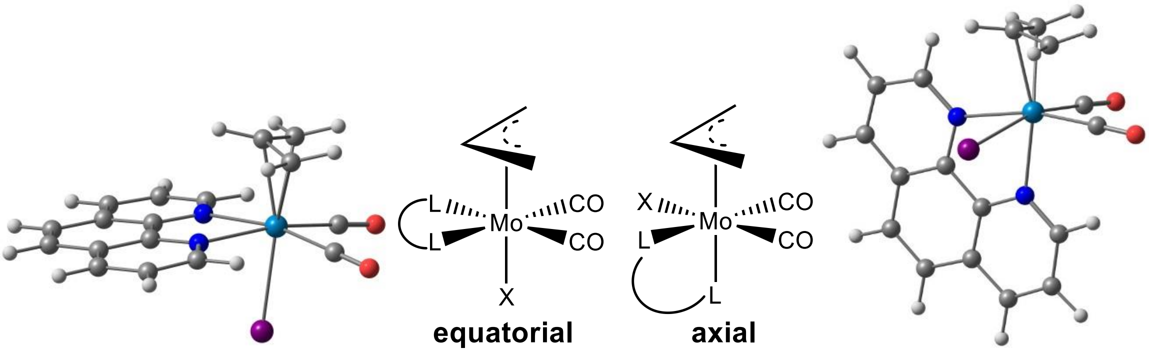

Figure 1. Two isomers of [Mo(η^3-C_3H_5)(CO)$_2$Br(phen)].

In this work, we analyze the structural preferences of this family of formally seven-coordinate Mo(II). An energy decomposition analysis was performed on the α-diimine derivatives using DFT calculations (ADF program) in order to rationalize the role of steric and electronic effects

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SYNTHESIS OF LOW GENERATION METALLODENDRIMERS AS AN ANTICANCER PRODRUG

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Cancer is a public disease worldwide, that cause a million deaths and new cases each year [1, 2]. Several strategies to fight this disease have been explored, but the use of powerful agents such *cisplatin* have demonstrated some limitations in cancer therapy [1, 3]. Thus, to attenuate the side effects, the need to create innovative and effective anti-cancer agents has led to the design and development of metal-based drugs using nanocarriers, like dendrimers [1, 4-6].

To improve the toxicities and increase the efficacy of *cisplatin* as an anticancer drug, anionic poly(amidoamine) (PAMAM) dendrimer generation 0.5 and 1.5 were used by us as a platform to transport this metallodrug inside the cells.

Our preliminary results show that *cisplatin* was coordinated to the anionic PAMAM dendrimers. In the ^{1}H-NMR spectra of the prepared compounds, it is mainly visible a new signal around 4.4 ppm related to the presence of the NH_3 groups of *cisplatin*, and the shift of the carboxylate and carboxyl groups in ^{13}C-NMR. The FTIR spectrum also indicates a dual band between 3200-3400 cm^{-1} related to the NH stretching groups of *cisplatin*.

Currently, studies on different types of cancer cell lines are being performed with the aim of evaluating the efficacy on the use of our approach regarding resistance to chemotherapy and toxicity of the prepared metallodendrimers.

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ACTIVATION OF SULFUR DIOXIDE BY GAS-PHASE URANYL(V) COMPLEXES

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It has previously been demonstrated that addition of molecular oxygen to gas-phase $U^{V}O_2^+$ results in oxidation to $U^{VI}O_2(O_2)^+$, which comprises a superoxo O_2^- ligand [1]. Several gas-phase anionic uranyl(V) complexes $[U^{V}O_2X_2]^-$ (including X = CH_3CO_2) were produced by electrospray ionization (ESI) and reacted with O_2 in a quadrupole ion trap (QIT) mass spectrometer to form uranyl(VI) superoxo complexes, $[U^{V}O_2X_2(O_2)]^-$ [2]. We surmised that a molecule with an electron affinity (EA) higher than that of O_2 (EA = 0.4 eV [3]), such as NO_2 (EA = 2.3 eV [3]), should also oxidize uranium(V) complexes. In fact, it was found that NO_2 associates with $[U^{V}O_2(CH_3CO_2)_2]^-$ to yield $[U^{VI}O_2(CH_3CO_2)_2(NO_2)]^-$ in which oxidation of U^{V} to U^{VI} is achieved by the reduction of NO_2 to NO_2^- [4]. SO_2 has an EA = 1.1 eV [3] intermediate between O_2 and NO_2 and therefore is a good candidate to be tested in reactions with uranyl(V) complexes. Previously, the $[U^{V}O_2(CH_3SO_2)(SO_2)]^-$ complex was prepared by collision induced dissociation (CID) of $[U^{V}O_2(CH_3SO_2)_2]^-$ in a QIT via C-S bond cleavage and CH_3 elimination; the SO_2 ligand can be considered as an SO_2^- anion [5].

Uranyl(V) acetate anionic complexes were produced by ESI and allowed to react with O_2 and SO_2 in a QIT mass spectrometer leading to uranium(VI) complexes (eqn. 1-2). The exchange reaction of SO_2 by O_2 was observed (eqn. 3) but the reverse reaction does not occur.

$$[U^{V}O_2(CH_3CO_2)_2]^- + O_2 \rightarrow [U^{VI}O_2(CH_3CO_2)_2(O_2)]^- \tag{1}$$

$$[U^{V}O_2(CH_3CO_2)_2]^- + SO_2 \rightarrow [U^{VI}O_2(CH_3CO_2)_2(SO_2)]^- \tag{2}$$

$$[U^{VI}O_2(CH_3CO_2)_2(SO_2)]^- + O_2 \rightarrow [U^{VI}O_2(CH_3CO_2)_2(O_2)]^- + SO_2 \tag{3}$$

We have demonstrated that neutral SO_2 can be activated by uranyl(V) complexes and be reduced to SO_2^-.

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Ag(I) CAMPHOR COMPLEXES: CYTOTOXIC AND ANTIBACTERIAL PROPERTIES

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Camphor derivatives of the imine type (L_A, L_B, L_C, Figure 1) bind to silver nitrate affording mono and polynuclear Ag(I) complexes including complexes of the polymer type.

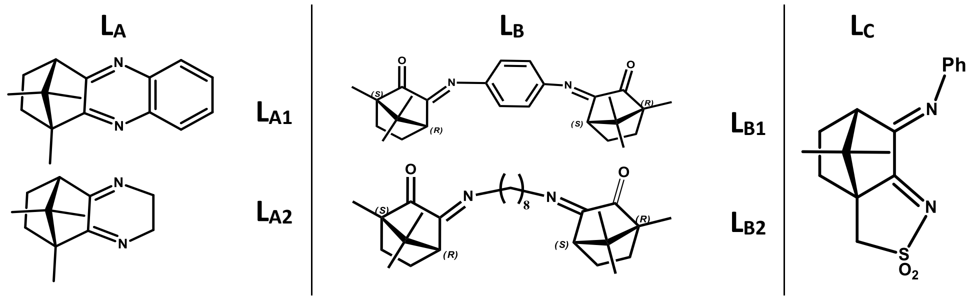

Figure 1: Camphor derivatives used as ligands

The biological properties of complexes $[Ag(NO_3)(L)]$ were assessed for antimicrobial properties showing that they have moderate to very high antibacterial activity against Gram-negative and Gram-positive strains. The sulphonylimine camphor imine complex $[Ag(NO_3)(L_C)]$ additionally displays anti-proliferative activity which is one order of magnitude higher than *cisplatin* (Table 1).

Table 1 – Antibacterial (MIC) and anti-proliferative (IC_{50}) for Ag(I) camphor imine complexes

	MIC values (μg mL^{-1}) [1]				IC_{50} (μM)	
COMPLEX	*S. aureus Newman*	*P. aeruginosa 477*	*B. contaminans IST408*	*E. coli ATCC 25922*	A2780	A2780cisR
$Ag(NO_3)(L_C)$	259	138	127	123	0.76 ± 0.29	0.51 ± 0.10
$Ag(NO_3)(L_{A1})$	118	68	97	98		
$Ag(NO_3)(L_{A2})$	95	39	81	49		
$Ag(NO_3)(L_{B1})$	73	19	36	20		
$Ag(NO_3)(L_{B2})$	119	105	96	98		

Acknowledgements: Financial support by FCT-Fundação para a Ciência e Tecnologia (UID/QUI/00100/2013, UID/Multi/04349/2013, RECI/QEQ-MED/0330/2012 and RECI/QEQ-QIN/0189/2012) and the NMR Network (IST-UTL Node) for facilities.

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DECORATED NANOPARTICLES FOR MAGNETIC HYPERTHERMIA

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Heat dissipation by magnetic materials when exposed to alternating magnetic fields, known as magnetic hyperthermia, is an emergent and promising technique, which has been explored as a therapy for cancer treatment in combination with radiation- and/or chemo-therapy, and also for other applications in nanomedicine. It has been predicted that the best nanoheaters should be obtained by tailoring the magnetic properties of core-shell materials.[1] In fact, the combination of different magnetic phases in core-shell nanoparticles (NP) has already shown to provide unique magnetic characteristics enhancing the hyperthermia performance. [2]

In this work, a different route to synthesize NP composed of a hard and a soft magnetic material is presented. The first nanoparticles (named as core) were prepared by an established procedure in gelatinous medium[3]. The second magnetic material was precipitated afterwards, in the presence of the core NP, and a rotating system was used to facilitate the homogeneous coverage. Different combinations of materials (among Fe_3O_4, $CoFe_2O_4$ and $MnFe_2O_4$) were used to prepare these *decorated* NP. Their structure and morphology were evaluated by XRD, SEM and TEM. The magnetic characterization was investigated by SQUID magnetometry and ^{57}Fe Mössbauer spectroscopy. Induction heating measurements under an AC magnetic field were performed in optimized non-adiabatic conditions[4]. The results show a clear enhancement of the specific loss power values for some *decorated* NP (depending on composition) when compared with the individual phases.

Cytotoxicity and uptake assays of the NP were performed on human breast (MDA-MB-231) and colon (Caco-2) cancer cell lines. The kinetics uptake of these NP incubated with cancer cells indicate that the composition and ratio of the materials affect their cellular uptake, with MDA-MB 231 internalizing more NP than Caco-2 cells. All samples are nontoxic to both cancer cells for concentrations below 1.8 mg mL^{-1}.

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ELECTROCHEMICAL CHARACTERIZATION OF THE INTERACTION BETWEEN NITRIC OXIDE REDUCTASE AND REDOX PARTNER

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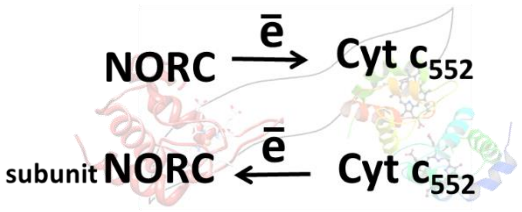
Nitric Oxide Reductase (NOR) is an enzyme that takes part in the denitrification pathway, catalyzing the reduction of NO to N_2O. The enzyme isolated from the marine halophilic bacterium *Marinobacter hydrocarbonoclasticus* comprises two subunits (NORB and NORC) harboring an electron transfer *c*-type heme (on the NORC subunit), and a catalytic site consisting of a b_3-type heme linked to a non-heme Fe atom and a b-type heme (on the NORB subunit). Cytochrome c_{552} (Cyt c_{552}) is proposed to be its physiologic electron transfer partner [1], although the interface and mechanism of interaction are still not clear. The comparison of NOR and its soluble domain subunit NORC behavior/interaction with Cyt c_{552} should benefit the understanding of the nature of the interaction and the electron transfer mechanisms operating between these proteins. In the present work, NORC, the electron-transfer subunit soluble fragment of the NOR was cloned, heterologously produced, purified and biochemically and electrochemically characterized. The redox behavior was compared with the native NOR [2,3]. The interaction of NORC with Cyt c_{552} was also evaluated by cyclic voltammetry.



Acknowledgements: This work was supported by the Unidade de Ciências Biomoleculares Aplicadas-UCIBIO, which is financed by national funds from FCT/MEC (UID/Multi/04378/2013) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER-007728). The authors also acknowledge FCT/MEC for funding of project "Denitrification – How to handle NO and N2O", ref PTDC/BBB-BQB/0129/2014, and post-doctoral fellowships SFRH/BPD/91288/2012 and SFRH/BPD/0293/2011, to S.R and R.M.A, respectively.

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LAYERED LANTHANIDE HYDROXIDES: A MAGNETIC STUDY

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Layered Lanthanide Hydroxide (LLnH) with composition $Ln_8(OH)_{20}Cl_4\cdot nH_2O$ (Ln = Nd, Sm-Tm and Y, Fig. 1) were originally prepared by Sasaki and co-workers.[1] These ionic lamellar materials are structurally composed of positively charged layers and charge balancing anions in the interlayers, which gives them compositional flexibility to target a specific application.[2]

Although the initial studies were mainly focused on their optical properties, more recently the magnetic characterization of the layered dysprosium hydroxide material $Dy_8(OH)_{20}Cl_4\cdot 6H_2O$ (LDyH) by our group revealed the existence of slow magnetic relaxation, a behaviour characteristic of single-molecule magnets (SMM).[3]

In order to understand the influence of the Dy–Dy interactions in this behaviour, two different samples were prepared: one with LDyH diluted in the diamagnetic yttrium analogous matrix (LYH:0.04Dy) and the other intercalated with 2,6-naphthalene dicarboxylate anions (LDyH-2,6-NDC). The results obtained support the idea that this slow relaxation probably arises mainly from single ion effects, with the Dy–Dy interactions, although non-negligible, playing a secondary role.[4]

These stimulating results encouraged us to pursuit the study with other lanthanide ions, namely terbium, holmium and erbium. Similarly to the previous results with the dysprosium analogue it was expected that 3D ferromagnetic interactions to be dominant in undiluted LTbH, LErH and LHoH, while for LYH:xLn with the Ln cations diluted within the diamagnetic LYH matrix an improved SMM character is observed. The most remarkable feature is attributed to the difference between the lanthanide ions themselves, being the slow relaxation more evident in the diluted erbium analogue.[5]

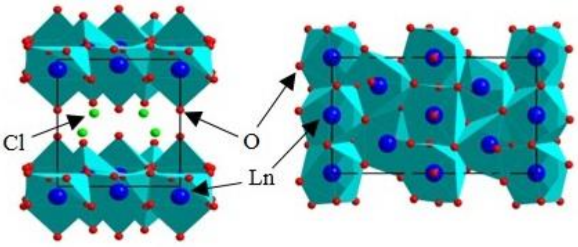

Figure 1 - The $Ln_8(OH)_{20}Cl_4\cdot nH_2O$ unit cell viewed along the *a* axis (right) and *c* axis (left).

With the purpose of understanding which contributes to this different results this study will be supported by theoretical calculations of crystal field splitting of the lanthanide levels in different crystallographic sites which also intends to put separately into evidence the single ion and the 3D Ln-Ln interaction effects.

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SYNTHESIS OF IRON(II) AND COBALT(II) COMPLEXES STABILIZED BY 5-ARYL-2-IMINOPYRROLYL LIGANDS AND THEIR APPLICATION IN CATALYTIC HYDROBORATION

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Catalytic hydrofunctionalization has a high impact in organic synthesis, therefore being a key provider of added value compounds [1]. In particular, hydroboration is a good source of organoboron entities, often used in cross-coupling or oxidation reactions [1]. As in most carbon-based functionalization reactions, hydroboration is commonly catalyzed by the expensive and relatively toxic platinum group elements [2]. As such, it is important to develop cheap, abundant and harmless mediators of these reactions, for the sake of global sustainability. However, this matter remains relatively unexplored [3].

In this work, a family of iron(II) and cobalt(II) complexes of 5-aryl-2-iminopyrrolyl ligands (N^N$^-$) of the type [M(N^N)(Py)Cl] (M = Fe (**1a**-**c**), Co (**2a**-**c**)) is reported and its characterization described. The reaction of styrene with pinacolborane (**HBPin**) in the presence of 1 mol% of **1a**-**c** and **2a**-**c**, activated by $KHBEt_3$, yielded the respective mixture of organoboranes (**A-MK**, **MK**) (Fig. 1). Enhanced selectivity in the Markovnikov product (**MK**) is observed when the steric bulk of the N^N$^-$ ligand is increased. In fact, complex **1c** yielded the **MK** product almost exclusively. Complex **2a**, on the other hand, always gave rise to pure anti-Markovnikov products when different terminal α-olefins were used.

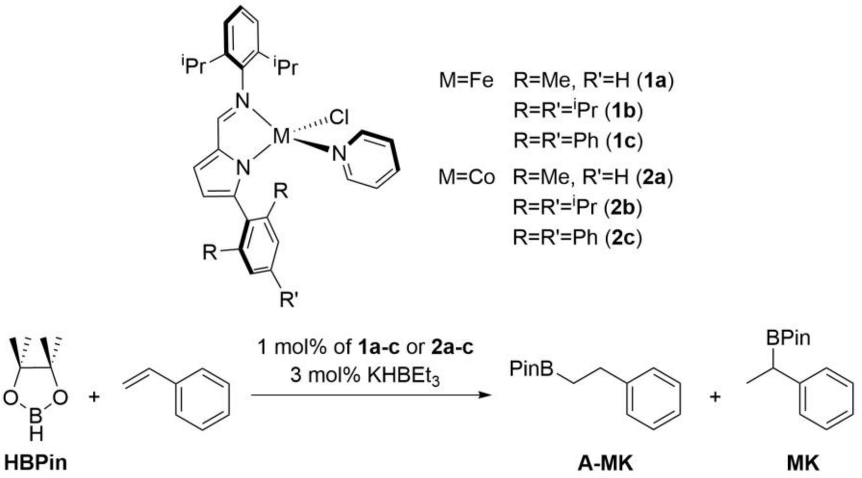

Figure 1: Complexes **1a-c** and **2a-c** and the catalytic hydroboration reaction.

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Pd-CATALYZED AMINOCARBONYLATION REACTIONS UNDER MICROWAVE IRRADIATION USING ALTERNATIVE SOURCES OF CARBON MONOXIDE

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Carbonylation reaction is a very effective and sustainable catalytic process to promote the one-pot synthesis of amides and heterocyclic compounds, starting from halogenated or triflate aromatic hydrocarbons. Microwave promoted catalytic carbonylation reactions is considered a valuable alternative to the classical methods, especially regarding selectivity, atom economy and energy-saving which is in line with the demand for more sustainable industrial processes. [1] Nevertheless the use of gaseous CO combined with the need for high-pressure reaction conditions is considered a drawback for many industrial processes. More recently, different methodologies have been developed to overcome the handling of gaseous CO, such as the use of metal carbonyls as CO *in situ* sources. [2]

Herein, we present the microwave assisted Pd-catalyzed aminocarbonylation of aryl-heterocycles using $Mo(CO)_6$ as CO source, as a sustainable approach for the synthesis of structurally diverse carboxamides using amines as N-nucleophiles, namely allylamine.

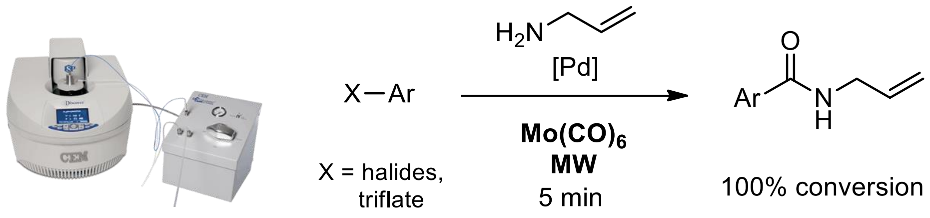

Figure 1: Pd-catalyzed aminocarbonylation of aryl heterocycles under microwave irradiation

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METAL SULFIDE NANOCRYSTALS AS PHOTOCATALYSTS IN THE DEGRADATION OF ORGANIC DYES

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There is an urgent need to develop technologies that guarantee safe and sustainable water supplies. Advanced oxidation processes (AOPs) have emerged as economically and ecologically safe options that might contribute to solve pollution problems. In particular, photocatalysis stands out as an environmentally friendly AOP for the degradation of organic pollutants into H_2O, CO_2 and other innocuous species. These processes are based on the generation of highly reactive species such as hydroxyl radicals which can easily combine with pollutants molecules resulting in their oxidative degradation.[1,2] Narrow band gap semiconductors, such as certain metal sulfides (e.g. CuS and Ag_2S), have been investigated as photocatalysts with strong absorption in the visible that might extend to the near IR spectral region.[3] These metal sulfides can efficiently harvest photons in the visible spectral region and can be prepared as nanosized particles showing quantum-size effects, hence showing optical properties distinct from those of the bulk analogues.[4] Since their discovery, graphene has emerged as a remarkable scaffold for the development of multifunctional hybrid photocatalysts. Graphene exhibits remarkable properties such as very high surface area (~2630 m^2/g), excellent mechanical strength, high electron mobility, high conductivity for electron capture and transport, and can be produced on a large scale at low cost. Here we report recent research aiming at developing graphene-based photocatalysts for the degradation of organic dye pollutants. In particular, the photocatalytic efficiency and stability of graphene oxide flakes decorated with $Cu_{2-x}S$ or Ag_2S will be presented and discussed. Several approaches have been investigated including the use of hydrogen peroxide as an environmentally friendly co-catalyst. Although the experiments presented here involved the photodegradation of organic dyes, the results obtained will be also discussed by considering the future use of the photocatalysts in the degradation of emergent pollutants, such as pharmaceutical products.

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NEW WATER SOLUBLE Ir(III)-NHC COMPLEXES FOR WASTE VALORIZATION

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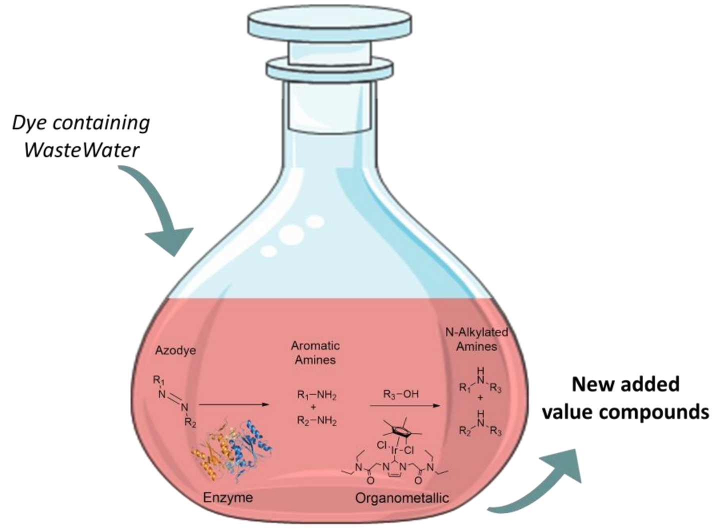
Dyeing processes produce a large amount of wastewater rich in azo (-N=N-) dyes, which represents an environmental hazard. Degradation of azo dyes has been accomplished using an enzyme extracted from *Pseudomonas putida* (PpAzoR) [1]. From this enzymatic degradation aromatic amines are formed, which are important building blocks in several chemical processes. These amines can be valorized through chemical modifications like N-alkylation of amines with alcohols. Our aim is to develop a compatible organometallic complex to perform cooperative catalysis with the enzymatic system in order to valorize waste.

N-alkylation of amines with alcohols has already been performed by several iridium based complexes but only few in water [2]. The development of water soluble metalcatalysts allows more sustainable chemical processes. Water solubility can be accomplished through the use of appropriate ligands like N-Heterocyclic Carbenes (NHCs) [3]. These are very versatile ligands and the metal-NHC bond is highly stable to hydrolysis, which is an attractive feature in coordination chemistry and catalysis.

We report herein preliminary results of new water-soluble Cp*Ir(NHC)Cl_2 complexes in N-alkylation of amines with alcohols.



Scheme 1: Cooperative Catalysis

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MAGNETIC HYBRID NANOSORBENTS FOR HERBICIDE UPTAKE FROM WATER

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Due to over growth of population and intensive industrialization, several natural water resources have been in risk of contamination by the presence of emerging chemical pollutants (ECPs)[1,2]. In some cases, ECPs have been detected in significant quantities in drinking water sources requiring innovative approaches for their elimination[2]. Among such ECPs, there are chemical compounds used as herbicides that have raised serious concerns due to their negative impact to the human health[3].

Herein, the synthesis of magnetic nanosorbents of hybrid nature, i.e. composed of biopolymer shells and iron oxide cores, will be reported. These hybrid nanosorbents were then investigated in the removal of herbicides from water via magnetic separation (Fig.1). The adsorption behavior of the magnetic nanosorbents was assessed by using distinct conditions, namely for variable contact times and using distinct herbicide concentrations. The stability and uptake efficiency of the prepared materials will be discussed in order to inquire about the robustness of these systems and their ability for regeneration.

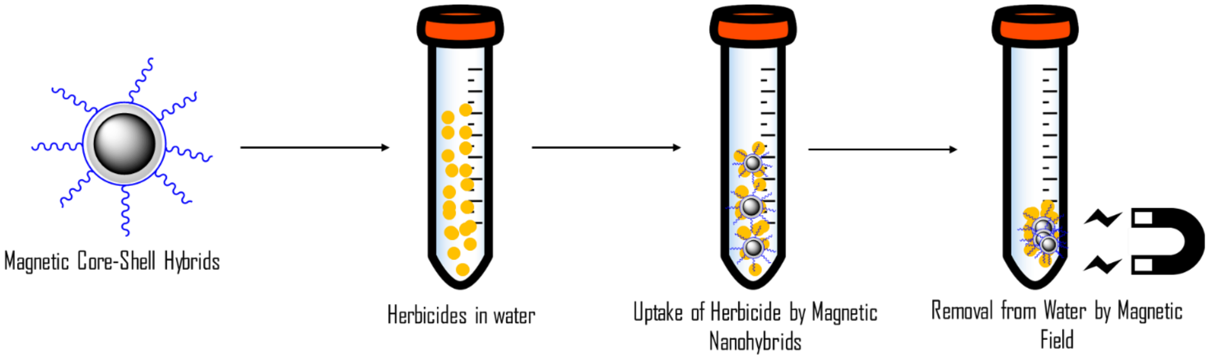

Figure 1: Scheme illustrating the use of magnetic nanosorbents for herbicide uptake from water.

Acknowledgements: This 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. A.L. Daniel-da-Silva acknowledges FCT for the IF-2014 FCT Investigator Programme.

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BIOFOULING PREVENTION: A NEW ECO-FRIENDLY STRATEGY FOR BIOCIDES IMMOBILIZATION IN POLYMERIC MATRICES

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The spontaneous colonization of surfaces in contact with water by aquatic organisms forms the so-called Biofouling. It constitutes a global problem in water management systems for several industrial activities, with serious environmental and economic penalty's [1]. In this work, non-releasing biocidal systems were developed by providing new functional biocides (e.g. Econea-NCO) [2], capable of being tethered in polymeric coatings. No damage on biocides structures was identified from FTIR and RMN spectra analysis after their functionalization. Bioactivity assessment of biocides, in particular of Econea-NCO, evidenced bioactivity against *E. faecalis*, *S. aureus* and *C. albicans* microorganisms, thus suggesting that the bioactive function of its non-modified counterpart was not significantly affected after the functionalization process. Minimal inhibitory concentrations (MIC) were also determined. Validation of biocides immobilization was performed in silicone based coating, further tested in terms of antifouling performance in simulated (aquarium) and real field conditions (Atlantic seawater). To date, coated prototypes immersed in seawater for 66 weeks (more than a year) in static conditions remain relative clean. This novel approach is here presented as an attractive alternative to the conventional toxic-releasing strategies.

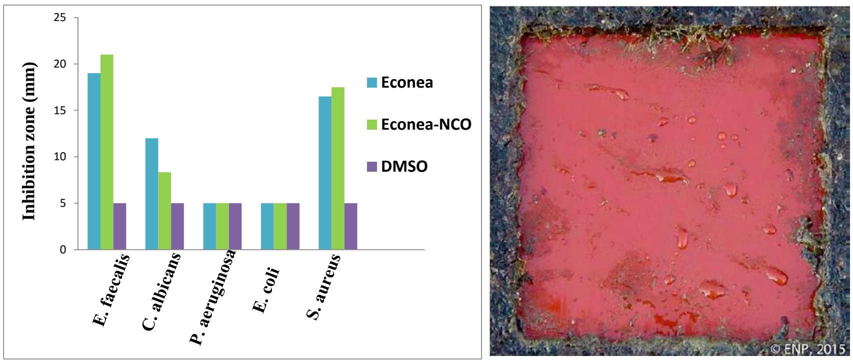

Figure 1: Bioactivity of Econea biocides by a well diffusion method) (left); and (right) representative antifouling effect on a coated prototype with a silicone marine based coating containing immobilized Econea (0.56 wt.%) after 66 weeks immersed in Atlantic seawater (Photo gently provided by ENP, SA)

Acknowledgements: O. Ferreira is grateful for the financial support from the ECOFOULESS project (PROMAR,OF/6923/2014/DPA/DRAPALG). E. R. Silva acknowledges Fundação para a Ciência e a Tecnologia (FCT) for the Post-Doc fellowship SFRH/BPD/88135/2012. The authors also thank the support of FCT (Pest UID/MULTI/00612/2013), HEMPEL A/S and ENP for the work collaboration.

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IMINOPYRROLYL NICKEL(II) CATALYSTS FOR THE PRODUCTION OF HYPERBRANCHED POLYETHYLENE

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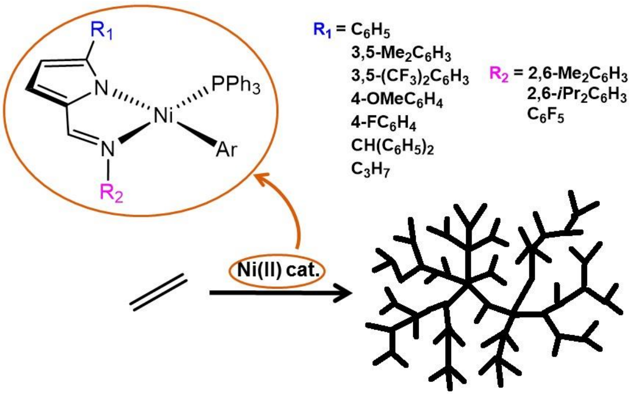
Advances in the olefin polymerisation field relates not only to the catalysts but also to the polyolefin materials obtained thereof, in order to achieve innovative characteristics to be used for several applications. In particular, there has been interest in obtaining dendritic polymers due to their distinctive spherical architecture, which confers important features such as low viscosity, good solubility and high surface of reactive sites or functionalities [1]. Nevertheless, the branching is generally introduced by non-commercial monomers, requiring multistep synthesis and limiting the scale and scope of applications. Therefore, it is important to develop catalytic processes that use simple and commercially available monomers such as ethylene [2,3]. Hyperbranched polymers are within the dendritic category and are characterised by an irregular branched topology that can mimic the regular dendrimers with the advantage of being easily synthesised. Guan *et al.* have demonstrated that, in the presence of the Brookhart's type palladium-diimine catalysts, it is possible to control the resulting PE microstructure from linear to hyperbranched by modifying the ethylene pressure admission [4]. This is due to the intrinsic chain-walking mechanism, an important feature of this type of late-transition metal catalysts, of their nickel analogues, and also of some similar systems [5]. We have been developing a family of nickel(II) complexes with 2-iminopyrrolyl ligands to be used as aluminiumfree catalysts in the polymerisation of ethylene. Several tests were performed, in the presence or absence of [Ni(COD)$_2$] and at different pressures and temperatures. The PE products obtained were characterised by ^{1}H and ^{13}C NMR spectroscopy and GPC/SEC chromatography, presenting the highest branching degree so far reported (160-170/1000C).



Acknowledgements: Authors thank the Fundação para a Ciência e a Tecnologia, Portugal, for financial support (Projects UID/QUI/00100/2013 and RECI/QEQ-QIN70189/2012) and for fellowships to C.A.F. (SFRH/BPD/112340/2015) and P.S.L. (SFRH/BD/88639/2012).

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ENCAPSULATION OF RUTHENIUM ON MAGNETICALLY-RECOVERABLE CHITOSAN-BASED NANOPARTICLES THROUGH A NOVEL ONE-STEP WET IMPREGNATION METHOD

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Recently, magnetic hybrid metal nanomaterials have drawn great attention due to their superior physicochemical properties, allowing applications in catalysis, biology, as well as in optical and electronic devices.[1,2] Ruthenium nanoparticles (Ru NPs) are one of the most versatile catalysts in many catalytic studies, including the hydrogenation of several substituted aromatic nitro compounds.[3] In this study, a novel ruthenium-supported magnetically-separable chitosan-based nanomaterial (Mn@CS@Ru) was prepared via one-step wet impregnation technique based on ionic gelation using sodium tripolyphosphate (TPP) as a cross-linking agent. Ionic gelation of chitosan acted as a supporting matrix to promote the embedment of $MnFe_2O_4$ and Ru NPs. The as-prepared Mn@CS@Ru was characterized by Fourier transform infrared spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, scanning electronic microscopy, transmission electronic microscopy, vibrating sample magnetometry, and dynamic light scattering. The catalytic activity of the Mn@CS@Ru nanomaterial was evaluated in the reduction of 4-nitrophenol in the presence of sodium borohydride as reducing agent at room temperature. The high loading of active Ru-supported NPs (1.4%) lead to a remarkable catalytic performance, with 98% of substrate conversion in a very short reaction time (45 s). Furthermore, the nanocatalyst was easily recovered by magnetic separation after catalytic reaction and could be reused for at least 10 cycles without significant loss of activity, confirming its superior stability.

Acknowledgements: Support for this work was provided by Fundação para a Ciência e a Tecnologia (FCT)/MEC and FEDER under Program PT2020 (project UID/QUI/50006/2013). AF Peixoto acknowledges financial support from FCT for a postdoctoral grant (SFRH/BPD/72126/2010). We would also like to extend our appreciation towards Erasmus Mundus Action 2: “INTERWEAVE” project for giving an opportunity for the research collaboration between University of Porto and Universiti Kebangsaan Malaysia.

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TWO PHOTON ABSORPTION PROPERTIES OF TRANSITION METAL COMPLEXES OF TETRAARYLAZADIPYRROMETHENE COMPOUNDS

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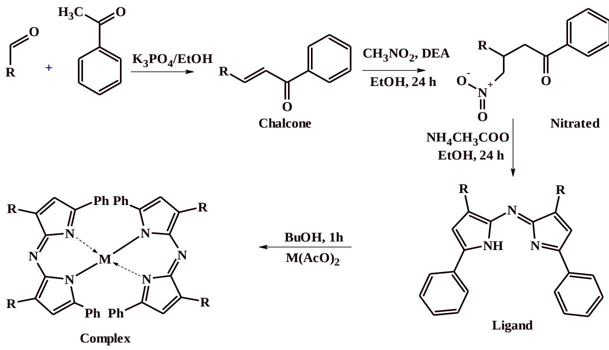
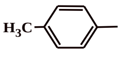
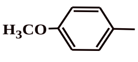
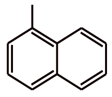
Materials with enhanced two photon absorption (TPA) properties have attracted attention due to their wide range of potential applications including TPA imaging microscopy[1], optical data storage, and photodynamic therapy[2].



R	Chalcone	Nitrated	Ligand	Metal	Complex
	1a	2a	L^1	Co^{2+}	**$Co(L^1)_2$**
				Ni^{2+}	**$Ni(L^1)_2$**
				Cu^{2+}	**$Cu(L^1)_2$**
				Zn^{2+}	**$Zn(L^1)_2$**
	2a	2b	L^2	Co^{2+}	**$Co(L^2)_2$**
				Ni^{2+}	**$Ni(L^2)_2$**
				Cu^{2+}	**$Cu(L^2)_2$**
				Zn^{2+}	**$Zn(L^2)_2$**
	3a	3b	L^3	Co^{2+}	**$Co(L^3)_2$**
				Ni^{2+}	**$Ni(L^3)_2$**
				Cu^{2+}	**$Cu(L^3)_2$**
				Zn^{2+}	**$Zn(L^3)_2$**

Scheme 1 Synthetic routes to the tetraphenylazadipyrromethene metal complexes.

New tetraarylazadipyrromethene metal complexes with four coordinate metals (Co(II), Ni(II), Cu(II) and Zn(II)) and three moieties (4-methylphenyl, 4-methoxyphenyl and 1-naphthyl) were designed and synthesized targeting applications with two photon absorption. The effects of metals and substituents on the charge transfer mechanism and two photon absorption properties of tetraarylazadipyrromethene compounds were investigated by ultrafast pump–probe spectroscopy and open aperture Z-scan experiments. Ultrafast transient absorption spectra provide evidence of an efficient photoinduced intramolecular charge transfer between the ligand and metals which are independent of filled or unfilled d orbitals of metals. Due to the charge transfer mechanism, metal complexes of tetraarylazadipyrromethene compounds exhibit two photon absorption properties in the femtosecond regime at 800 nm wavelength. The greatest two photon absorption cross section value were measured as 2690 GM for $Zn(L^2)_2$ and 2374 GM for $Co(L^3)_2$ complexes.

Acknowledgements: We acknowledge financial support by the Scientific and Technical Research Council of Turkey (TUBITAK) (No. 214Z192).

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SYNTHESIS AND CHARACTERIZATION OF NEW DOUBLE ARMED BENZO-15-CROWN-5 LIGANDS AND ALKALI METAL COMPLEXES

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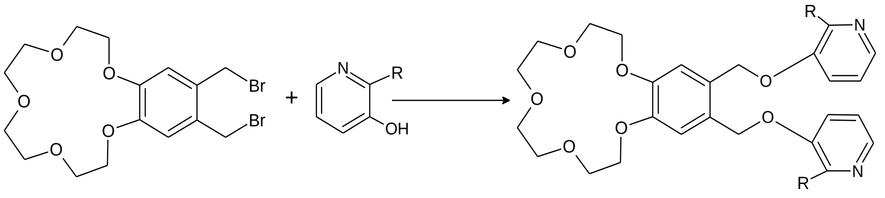
Crown ethers have attracted great interest in the last four decades, not only from the synthetic and selectivity alkaline and alkaline earth metal cation complexation properties point of view, but also with respect to their unusual structural characteristics [1,2]. The combination of pyridine derivatives with a crown ether group results in the formation of the ditopic receptor. The 15-crown-5 group can bind with alkaline and alkaline earth metal cations, whereas the pyridine group binds transition and heavy metal ions.



R	Comp.
H	**1**
Cl	**2**
Br	**3**

(**1-3**)

(**1a-3a**) (**1b-3b**)

Figure 1: Synthesized ligands (**1-3**), sodium (**1a-3a**) and potassium complexes (**1b-3b**)

In this study, new double armed benzo-15-crown-5 ligands and complexes containing pyridine substituted groups were prepared (Figure 1). Compounds (**1-3**) were synthesized after the reaction of 4’,5’-bis(bromethyl)benzo-15-crown-5 with 3-hydroxypyridine, 2-chloro-3-hydroxypyridine or 2-bromo-3-hydroxypyridine. Sodium and potassium complexes (**1a-3a and 1b-3b**) of crown ether form crystalline 1:1 (Na^+:ligand and K^+:ligand), respectively. All solid crown ether ligands and complexes were described and their mass, IR, ^{1}H- and ^{3}C-NMR spectral data were reported.

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REACTIVITY STUDIES ON SALEN- AND SALAN-TYPE TITANIUM(IV) COMPLEXES

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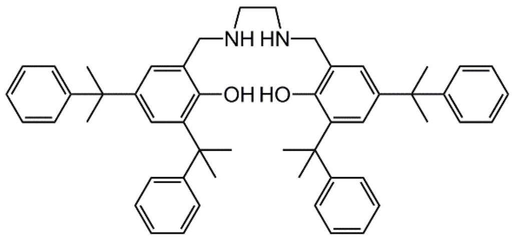
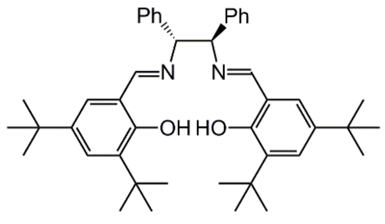
Titanium complexes bearing [ONNO]-type of ligands have received considerable attention in the last decade due to their cytotoxic and catalytic properties [1]. In previous studies we have explored these properties with tripodal diamine bis(phenolate) titanium complexes [2]. Here we report new titanium complexes supported by salan- and salen-type ligands (H_2L1 and H_2L2) and their different reactivity.

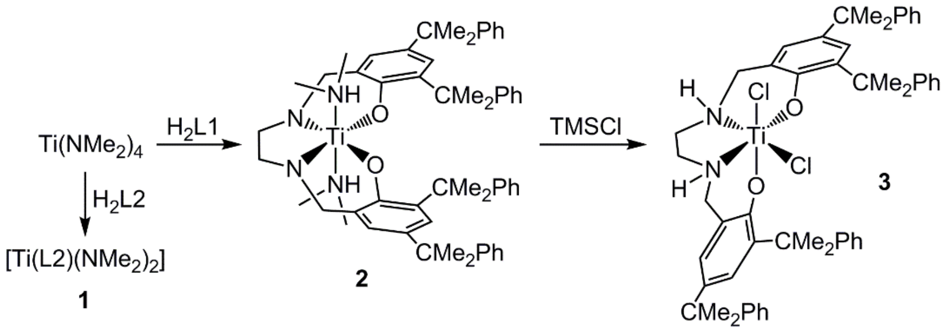


H_2L1



H_2L2

The reactions of H_2L1 and H_2L2 with one equiv. of $Ti(NMe_2)_4$ give the respective titanium complexes **1** and **2**. The formation of **2** reveals a non-innocent behaviour of the salan ligand that converts in a tetra-anionic diamido bis(phenolate) ligand by intramolecular exchange of a proton to the dimethylamido ligands. The reaction of **2** with TMSCl results in the formation of **3** displaying an unexpected rearrangement in the coordination mode of the ligand.



Acknowledgements: The authors thank the FCT for funding (SFRH/BD/114399/2016, SFRH/BD/87679/2012, SFRH/BPD/86815/2012, SFRH/BPD/7394/2010 and UID/QUI/00100/2013).

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NOVEL TACRINE-HYDROXYPHENYLBENZIMIDAZOLE HYBRIDS AS POTENTIAL DRUG CANDIDATES FOR ALZHEIMER´S DISEASE

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Alzheimer's disease (AD) is an age-related neurodegenerative disorder with multifactorial origin and no cure so far, hence the development of adequate therapy is extremely important. The main pathological hallmarks of AD brains are the acetylcholine deficit associated to memory loss, the formation of extracellular amyloid plaques (due to aggregates of β-amyloid (Aβ) fibrils), increased oxidative stress and disruption of metal homeostasis (implicated in the formation of Aβ aggregates or of ROS) [1,2]. Focusing on these AD factors, several compounds have been developed with multitarget ability in order to attain polypharmacological efficiency [3,4]. Herein, we present the design and evaluation of a series of tacrine(TAC)-hydroxyphenylbenzimidazole derivatives which contain an acetylcholinesterase (AChE) inhibitory moiety (TAC) and a hydroxyphenylbenzimidazole group to assure antioxidant, metal chelating ability and potential inhibitory capacity for Aβ aggregation. The size of the linker between the two main moieties was defined through molecular modeling studies, in order to guarantee bimodal interaction within the active site of AChE. The synthesized compounds were assayed in terms of metal (Cu, Zn) chelating ability, antioxidant activity as well as AChE inhibitory capacities. These compounds seem to be able to fulfill important AD targets, therefore being promising as potential anti-AD drugs.

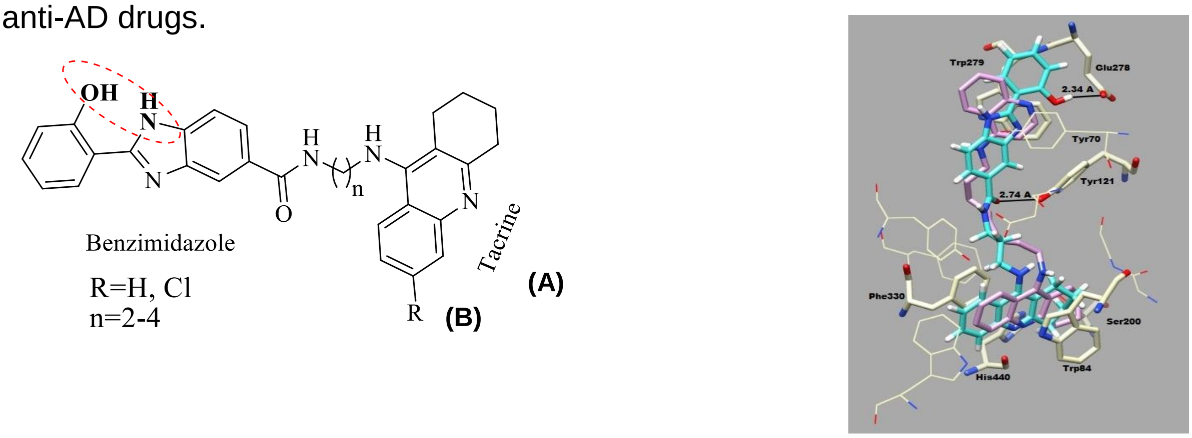

Figure 1: (A) General structure of TAC-hydroxyphenylbenzimidazole hybrids; (B) Molecular docking of a hybrid (n=3, Cyan) with TcAChE and superimposition with original ligand (PDB entry 10DC, Pink).

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2-(*N*-ALKYLIMINO)PYRROLYL BORON COMPLEXES: SYNTHESIS, STRUCTURE, AND LUMINESCENT PROPERTIES

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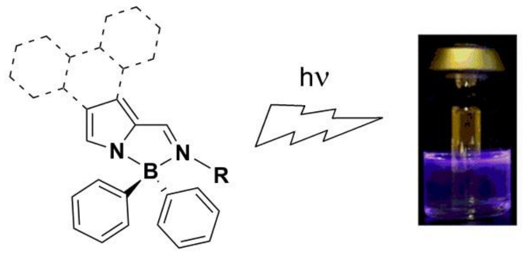
The 2-iminopyrrolyl ligands are a class of monoanionic bidentate chelating ligands that have proved to be versatile spectator ligands in catalytic species. We have been involved in the synthesis of a variety of coordination compounds using 2-iminopyrrolyl ligands. In particular, we prepared a family of boron organometallic complexes containing differently substituted *N*-aryl groups, which showed very interesting luminescent properties [1]. Moreover, we also synthesised some bridged binuclear boron compounds that enabled the fluorescence tuning from blue to yellow [2]. These findings induced us to prepare new boron complexes containing 2-(*N*alkylimino)pyrrolyl derived ligands.

Herein, we report the synthesis of a series of boron emitters by reacting aliphatic 2-iminopyrrole or 2-iminophenanthro[9,10-*c*]pyrrole derived chelating ligand precursors with triphenylboron, in toluene. All the new compounds were isolated and characterised by elemental analysis, multinuclear NMR and single-crystal XRD studies. The photophysical properties of these complexes are studied, both in solution and films, exhibiting good quantum yields. In addition, the DFT and TDDFT studies and the fabrication of OLED devices based on these compounds are also presented.



R = Me, *i*-Pr, *t*-Bu, *n*-oct, Cy and adamantyl

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support (Projects UID/QUI/00100/2013, UID/MULTI/00612/2013, UID/EEA/50008/2013 and RECI/QEQ-QIN70189/2012) and for fellowships to P.K., C.S.B.G., B.F., and D.V.V. (SFRH/BPD/89167/2012, SFRH/BPD/107834/2015, SFRH/BD/80122/2011, and SFRH/BD/81017/2011, respectively).

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SYNTHESIS AND CHARACTERISATION OF GRAPHENE DOPED WITH NITROGEN AND SULPHUR HETEROATOMS

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Graphene is a two-dimensional sheet of carbon atoms in a hexagonal configuration with atoms bonded by sp^2 bonds [1], which is considered to be the brick to other carbon materials. Since it was experimentally discovered, fundamental studies and applications about graphene have sprung up. Doping graphene with heteroatoms can effectively tune its electronic structure and other intrinsic properties. Such doped materials have unique properties, and can improve the efficiency and chemical stability of graphene-supported nanocatalysts. In particular, nanophotocatalysts combining graphene flakes with semiconductor nanoparticles are promising candidates for emerging pollutants treatment.

Herein, liquid-phase exfoliation of graphite to produce graphene flakes (GFs) was used. Parent graphite was dispersed in organic solvents, followed by sonication and centrifugation.

The exfoliation was monitored by UV-Vis spectroscopy. The resulting GF were doped with nitrogen and sulphur heteroatoms by ball milling. Sulphur and sulphur-containing different triazoles were used as doping agents. Figure 1 shows the potential structure of N,S-doped GF. The parent graphite, GF and N,S-doped GF were characterized by FTIR spectroscopy, XPS, TEM and XRD. The results confirmed the presence of few-layered graphene and successful incorporation of the heteroatoms.

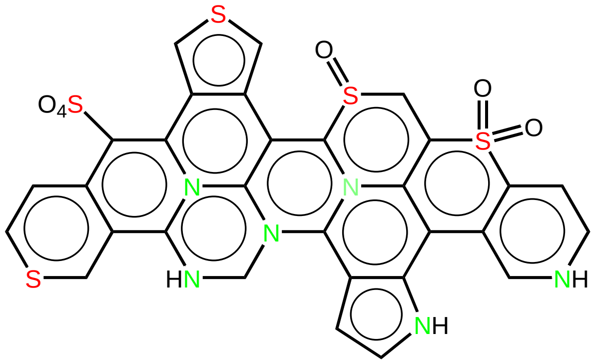

Figure 1: Schematic structure of N,S-doped GFs.

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FORMATION ENTHALPIES OF Na, K, Rb AND Cs SALTS WITH 1,2-ETHANEDIOL AND 1,4-BUTANEDIOL

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In this communication we report the study of the direct reactions of alkaline metals, Na, K, Rb and Cs with 1,2-ethanediol and 1,4-butanediol. For the Na and K metals it was also performed the reaction of metals with 1,2-ethanediol in ammoniacal media. In these cases both synthesis lead to identical final compounds. The energetics of the synthesized compounds was studied and the corresponding enthalpies of formation determined by reaction-solution calorimetry. The results address the importance of a second reactive function in the alcohol and the importance it can assume in the energetic of the alkaline salts. The enthalpies of formation were compared with literature existing values for several alkoxides [1-3], phenoxides [4], cyclopentadienyls [5] and thiolates [6]. Those comparisons show that, despite the fact of having a second chemical function, those alkoxides behave exactly as expected for a simple function alkoxide (Figure 1).

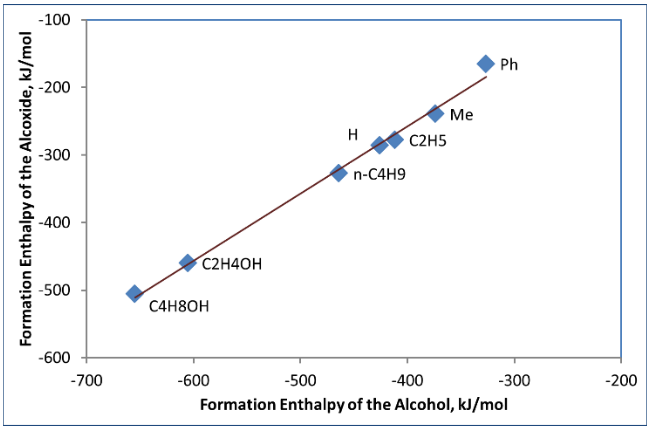

Figure 1: Formation Enthalpies of the Alkoxides vs. Formation Enthalpies of the Alcohols. The fitting line had a unitary slope and a correlation of 0.9933.

Acknowledgements: This work was partially supported by Fundação para a Ciência e a Tecnologia, Portugal (Project PTDC/QUI/65507/2006).

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DESIGN OF A WATER SOLUBLE FLUORESCENT 3-HYDROXY-4-PYRIDINONE LIGAND ACTIVE AT PHYSIOLOGICAL pH VALUES

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In the present work we report the structure and the spectroscopic characterization of a new fluorescent 3-hydroxy-4-pyridinone ligand D-3,4-HPO. The analysis of the variation of the absorption spectrum with pH allowed the determination of four pK_a values (pK_{a1}=3.50, pK_{a2}=4.50, pK_{a3}=9.60, pK_{a4}=10.20) and establishment of the corresponding distribution diagram. The study of the fluorescence properties of the ligand show that in the pH range between 4 and 9 the fluorescence intensity is constant and has its maximum value thus allowing its further use at physiological pH values. The interaction of the ligand with copper(II) was accessed by fluorescence spectroscopy in MOPS buffer and the results show that the presence of copper(II) quenches the fluorescence of the ligand in ca 94% at a ligand: metal ratio of 2:1. The latter result is consistent with the formation of a copper(II) complex with the bidentate ligand, as confirmed by the EPR spectroscopy.

More recently other metals were tested and the results are also reported.

Figure 1: New water soluble fluorescent ligand active at physiological pH values.

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LUMINESCENT Au(I) ORGANOMETALLIC SYSTEMS: HYDROGELS, RODS AND VESICLES

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Metallogels are a subject of study in the last few years.[1] The reason for the growth of interest stems from the availability and the diversity of metal-ligand coordination that could readily induce or control the self-assembly process of the gel formation and thereby influence the gel properties, as a difference with what occurs in organic gels. Organometallic Au(I) complexes present the additional advantage to use both classical supramolecular interactions (*e.g.* π-π stacking or hydrogen bonding) together with the establishment of Au(I)···Au(I) bonds (aurophilic interactions), which are particularly strong. Furthermore, these complexes exhibit interesting emissive properties that usually are modulated by the presence of the aurophilic interactions.

We have reported on the formation of luminescent Au(I) hydrogels based on water soluble organometallic alkynyl complexes where aurophilic intermolecular interactions are involved on the gelation process.[2-5] Slight modifications on the chemical structure can induce significant changes on the supramolecular assemblies leading to hydrogels, rods or vesicles.

A detailed analysis of the thermodynamic and photophysical parameters that modulate and are modulated, respectively, by the gel formation has been performed and the results are supported by theoretical data.

The mononuclear[2,3] and polynucleal gold(I) supramolecular assemblies that are formed in water can be reorganized by the presence of particular molecules. In particular the assemblies containing charged residues or coordinating moyeties are sensitive to the presence of anions and cations and the changes in morphology impact the spectroscopic features opening an unexplored potential of these assemblies for sensing.

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HYBRID NANOSTRUCTURES COMPOSED OF CARBON AND METAL SULFIDES

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Semiconductor nanocrystals have been extensively explored due to their unique size dependent optical and electronic properties, which are of interest in a number of applications including sensors, solar cells, catalysts and optoelectronic devices [1]. Graphene based materials have also attracted great interdisciplinary importance due to their structure-dependent physical and chemical properties [2].

The implementation of technologies combining these two types of materials opens new routes for the development of innovative materials. However, there are few synthetic routes that result in morphological uniform hybrid materials comprising both components, which in some cases can be related to lack of knowledge about surface chemical effects on the synthesis itself.

Following previous work on the use of single-molecule precursors [3,4] for surface modification of several materials, we present here our efforts to develop decorated carbon nanostructures with metal sulfide nanophases. In particular, the in situ growth of Ag_2S or CdS nanocrystals, in the presence of GO flakes dispersed in ethanol, will be reported and discussed by also considering previous research using other types of substrates.

Several reaction parameters have been investigated in order to optimize the experimental conditions for obtaining morphological uniform hybrid nanomaterials. The hybrid nanostructures were characterized for their morphological features using SEM and TEM. Additionally, Raman spectroscopic methods have been applied to monitor the surface nature of GO obtained from the exfoliation of graphite, due to their potential impact on the nucleation and growth of the metal sulfide nanophases onto the GO surfaces.

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MICROWAVE ASSISTED HYDROGEN TRANSFER REDUCTION OF KETONES WITH Fe-NHC BIFUNCTIONAL CATALYSTS

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The selective reduction of carbonyl functionalities is an important and useful reaction in organic synthesis. Catalytic transfer hydrogenation process is an attractive alternative to direct hydrogenation procedure for the reduction of ketones to alcohols, since offers selective reduction avoiding the use of eventually hazardous H_2 gas, and using hydrogen donors readily available and easy to handle [1]. Usually, hydrogen transfer processes are catalysed by noble metals such as Pd, Pt, Ir, Ru, and Rh. However, these metals have limited availability, are very expensive and toxic. The use of iron, an earth-abundant, cheap and non-toxic metal, as catalyst for the reduction of organic functionalities is highly desirable. Our group has been involved during the last few years in the development of well-defined iron metal complexes for reduction reactions [2]. Herein, we describe the synthesis of a new family of iron complexes with N-heterocyclic carbenes (NHCs) bearing an OH functionality (Scheme 1), and their application in the catalytic transfer hydrogenation of ketones using microwave heating. Under these conditions, an interesting improvement on reaction time and amount of base needed in the process was obtained.

Scheme 1: Fe-NHC catalysts in hydrogen transfer of ketones

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DESIGN OF CATIONIC CARBOSILANE DENTRITIC SYSTEMS AS NEW ANTI-NEURODEGENERATIVE AGENTS

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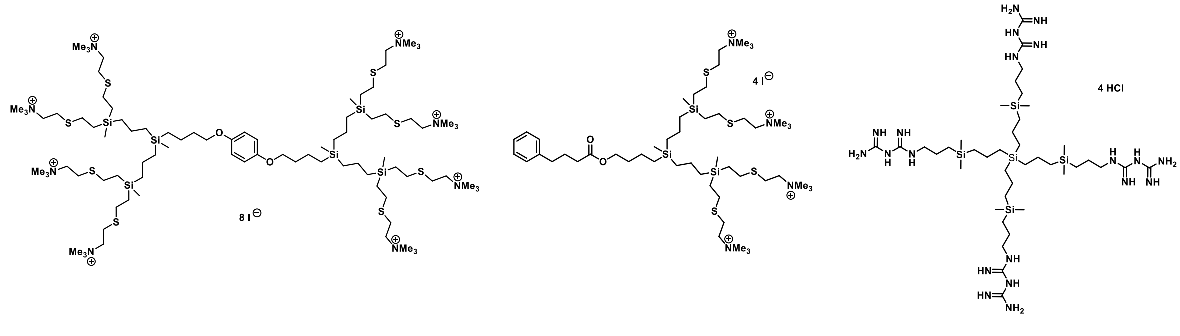
Neurodegenerative disease occurs as a result of changes in the native conformation of proteins, followed by accumulation of these misfolded amyloidogenic proteins in the central nervous system, which in turn causes progressive neurological impairment and neuronal dysfunction. This is the molecular basis of the most devastating neurodegenerative diseases known to date such as Alzheimer's disease (AD), Parkinson's disease (PD), Huntington's disease (HD), and amyotrophic lateral sclerosis (ALS) [1].

Search for the agents preventing fibrillation of proteins in neurodegenerative diseases has also involved dendritic structures. Dendrimers are macromolecules suitable for different biomedical applications due to their specific structure and large amount of functional groups [2]. It has been shown to affect the aggregation of amyloid peptids making them promising anti-neurodegenerative agents.

In our researcher group, we are developing new carbosilane systems by different synthetic approaches. Use carbosilane dendrimers makes possible to use low generations in contrast with other types of dendrimers (PAMAM, PPI) and high biocompatibility is obtained as a result. We have synthetized different topologies of carbosilane structures, with diverse therapeutic group on the surface or focal point (ammonium groups, biguanides, isobutiric acid derivates) in order to study their ability as new anti-neurodegenerative agents.



Bow-tie dendrimer **Dendron** **Sferic dendrimer**

Figure 1. Different topologies of carbosilane dendrimers.

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SYNTHETIC APPROACHES FOR NEUTRAL AND CATIONIC PENTABENZYLCYCLOPENTADIENYL MAGNESIUM COMPLEXES AS CATALYSTS FOR THE ACTIVATION OF POLAR SUBSTRATES

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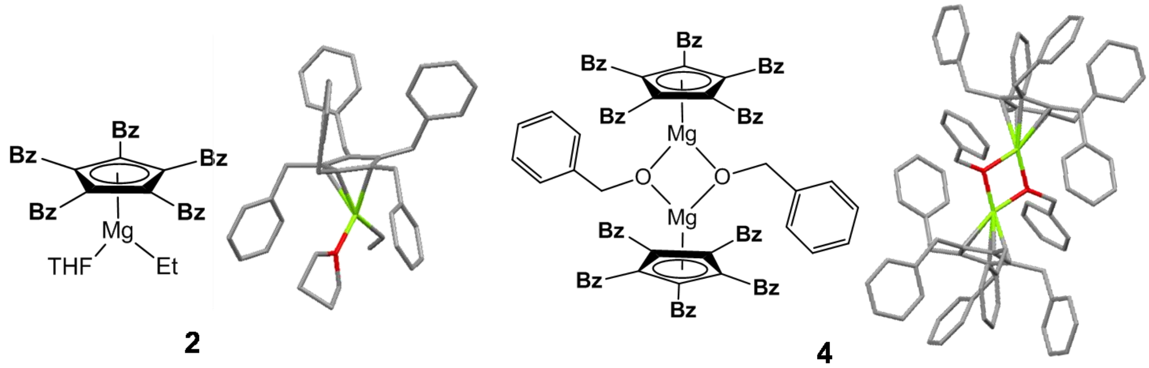
Activation of polar substrates, in particular oxygen-based fragments, is extremely important in synthetic transformations. Commercial high-value products may be obtained from catalytic ring-opening reactions involving epoxides, ethers or cyclic esters (lactones) by using neutral and cationic organometallic systems with strong Lewis acid metals [1]. Zinc and magnesium divalent species are in the lead of the catalysts that promote such transformations. The interest in magnesium complexes has been growing over the last years with the development of ligands containing N- and O- donor atoms [2]. Nevertheless, substituted cyclopentadienyl frameworks as supporting ligands for magnesium compounds have not been frequently explored. Herein, we present the syntheses of new neutral magnesium complexes supported by one pentabenzylcyclopentadienyl (Cp^{Bz}) ligand, $[Cp^{Bz}MgR(THF)_n]_m$ (n = 1, m= 1, R = Me (**1**), Et (**2**); n = 1, m = 2, R = Br (**3**), n = 0, m = 2, R = OCH_2Ph (**4**))). Magnesocene $[Cp^{Bz}{}_2Mg]$ (**5**) was also prepared. All compounds were fully characterised by NMR spectroscopy and X-ray diffraction. Attempts to generate cationic species afforded very reactive and unstable compounds that could be identified and assigned by 2D NMR (DOSY, HOESY) and DFT calculations supported these results. In particular, **1** and **2** react with $B(C_6F_5)_3$ and carry out fast group exchanges between Mg and B atoms to generate cationic species possessing $[B(C_6F_5)_4]^-$ as counterion.



2

4

Figure 1: Schematic representations of magnesium complexes **2** (left) and **4** (right)

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia (FCT) for financial support (SFRH/BD/87679/2012 and UID/QUI/00100/2013).

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METAL SUBSTITUTED RUBREDOXIN: MODELLING STUDY

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Nature uses proteins as scaffolds for building in metal cofactors, in order to control biological processes. Chemists have learned how to adapt naturally occurring scaffolds as catalysts for new performances.

Rubredoxin (Rd) is a small (~52 aa) non-heme iron electron transfer protein containing an distorted tetrahedral $Fe(CysS)_4$ site, stabilizing Fe^{II} or Fe^{III} formal oxidation states, surrounded by a pair of iron-ligating (CysS)xx(CysS) loops and have extraordinary resistance to denature and metal release.[1] A wide range of metal substituted derivatives have been studied in order to elucidate the structural and electronic properties of metal sites and they proof to be useful as model systems. Among these, Ni-Rd is a simple model of Ni-hydrogenases,[2] and recently Mo-Rd, presented expanded coordination spheres of the type $\{Mo(CysS)_4(O)X\}$, X=thiol and showed to be models for oxygen atom transfer processes carried out by mononuclear molybdenum enzymes, like arsenite oxidase.[3]

Here we discussed two cases: **i)** In the Mo substituted Rds, with a catalytic site such as $\{Mo(Cys)_4(O)X\}$ unit, X was exchanged by several potential exogenous ligand in order to tune the redox potential. A wide range of substrate activities was explored (nitrate, formate, drug metabolism). A wealth of information may be extracted on the ligand effect at Mo/W-site of native enzymes. **ii)** Copper substituted Rds (Cu-Rd) and the redox processes involving Cu^{II}-Rd and Cu^{I}-Rd pairs are complex.[4] Mononuclear Cu^{II}-thiolate centres are fascinating to chemist due to their intense, Cu^{II}-thiolate electronic absorption features, that reflect the covalency of the copper-thiolate bond, which make major contributions to reactivity in proteins such as red, blue, green cupredoxins.[5] We probe the electronic transfer process between the Cu^{II}-Rd center and proximal amino acid residues, such as, Tyr, Trp and Cys. Two irreversible peak at E_{pa}= -0.12 V and E_{pc} = -0.66 V with large separation (ΔEp = 0.54 V) indicates that the geometry of Cu-site suffers rearrangement during the redox process. When Cu^{I}-Rd is oxidized to Cu^{II}-Rd, intrinsic Trp fluorescence intensity is highly quenched, indicating electron communicates between Trp and the Cu-center. The UV/vis spectra (detected under anoxic in dark and light conditions) indicate that Cys residues cannot reduce the Cu^{II}-site, but the reduction step takes place mainly photochemically and Tyr and Trp residues are involved in the process.

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REDOX EVENTS IN BIS(PHENOLATE) CYCLAM URANIUM CHEMISTRY: URANIUM-LIGAND MULTIPLE BOND FORMATION

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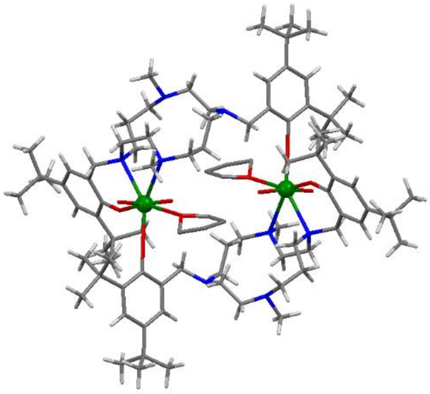
Low valent uranium complexes capable of performing reduction reactions are important for accessing high uranium oxidation states and in establishing the usefulness of these complexes for organic transformations and for the activation of small molecules [1]. Moreover, these reactions often lead to the formation of uranium-ligand multiple bonds [2], in which the metal varies in oxidation state from +4 to +6. One of the interests in these actinide species arises from the need for a better understanding of the unique bonding in uranyl ion $\{O{=}U{=}O\}^{2+}$, with its apparent chemical inertness, and its technological relevance to the nuclear fuel cycle and the environment.

We recently demonstrated that the enhanced reactivity of a new U(III) complex, $[U(\kappa^6\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\})I]$, as reductant allowed to synthesize and structurally characterize a series of new uranium species in different oxidation states anchored on a dianionic bis(phenolate) cyclam ligand [3], including the unprecedented neutral monobridged nitride U(IV) complex, $[U(\kappa^4\text{-}\{^{tBu2}ArO)_2Me_2\text{-cyclam}\})(N_3)(\mu\text{-}N)U(\kappa^5\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\})]$. Furthermore, the reactive nature of the U(III) complex and the hemilabile behavior of the macrocycle core allowed to cleave the N=N bond of azobenzene and form the *trans*-bis(imido) U(VI) complex $[U(\kappa^4\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}(=NPh)_2]$, comprising an analogue of the uranyl ion. In an effort to synthesize uranium-oxo compounds anchored on the bis(phenolate) cyclam ligand, reactions of the complexes $[U^{III}(\kappa^6\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\})I]$ and $[U^{IV}I(\kappa^6\text{-}\{(^{tBu2}ArO)_2Me\text{-cyclam}\})]I$ with oxygen-atom-transfer reagents (e.g. pyridine-*N*-oxide, $NaNO_2$) were tested. These recent results will be presented in this communication, including the dimeric uranyl complex $[(UO_2)_2(\mu\text{-}\{(^{tBu2}ArO)_2Me\text{-cyclam})_2(thf)]_2$ (Figure) obtained from oxidation of the U(IV) compound with $NaNO_2$.



Acknowledgments: LM thanks the Fundação para a Ciência e a Tecnologia (FCT) for financial support (grant SFRH/BPD/101840/2014). This work has also been financed by FCT under the projects UID/Multi/04349/2013 and RECI/QEQ-QIN/0189/2012.

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PINCER PNP COMPLEXES OF M(III) EARLY METALS (M = Y, Ti, V)

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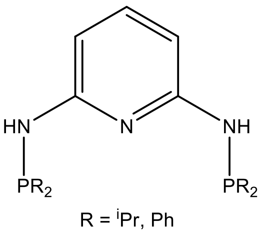
Pincer ligands are tridentate species that bind to three coplanar coordination sites of transition metals, mostly in a meridional configuration. The general form EXE may be used to describe this type of chelating ligands, where X is the central, anchoring donor and E are two flanking Lewis donors. A wide range of pincer ligands, such as PCP, SCS, NCN and PNP, has been reported in the literature and pincer complexes of a large variety of medium to late transition metals have been described and employed in various stoichiometric and catalytic processes [1].



In this presentation we describe the syntheses of the first (^{R}PNP)M(III) (R = ^{i}Pr, Ph) complexes of yttrium, titanium and vanadium. The solid-state structures of (^{Ph}PNP)$TiCl_3$ and (^{iPr}PNP)VCl_3, determined by single-crystal X-ray diffraction, are presented. Reactions of (^{Ph}PNP)VCl_3 with oxidizing agents as well as chloride exchange reactions will be discussed.

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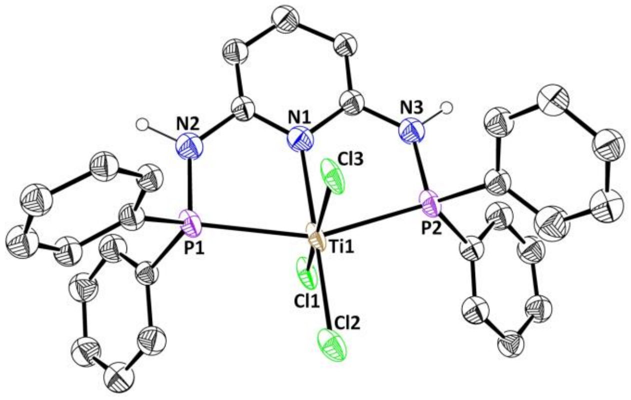

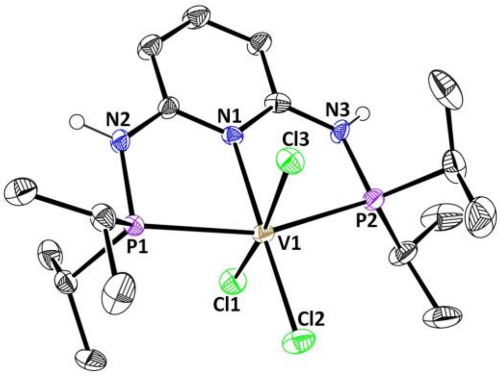

Acknowledgements: The authors thank the FCT for funding (SFRH/BPD/86815/2012 and UID/QUI/00100/2013).

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COPPER(II) COMPLEXES OF ARYLHYDRAZONE OF ETHYL 2-CYANOACETATE: *E*/*Z* ISOMERIZATION; DNA, BSA BINDING AND CYTOTOXIC PROPERTIES; CATALYSTS FOR ALCOHOL OXIDATION

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Arylhydrazones of active methylene compounds (AHAMCs) are versatile ligands in the synthesis and design of coordination compounds [1]. Their ability to undergo reversible *E/Z* isomerism can influence the AHAMCs metal complexes behaviour in their physical and paharmacological proprieties and even in catalytic reactions [2,3].

A series of water soluble copper(II) complexes, $Cu_2(X)_2(\mu\text{-}HL)_2$, X = CH_3OH (**1**) or $(CH_3)_2NCHO$ (**2**), and $[Cu(en)_2HL]\cdot CH_3OH\cdot H_2O$ (**3**) (Figure 1) were prepared by reaction of Cu^{II} nitrate hydrate with the new (*E/Z*)-4-(2-(1-cyano-2-ethoxy-2-oxoethylidene)hydrazinyl)-3-hydroxybenzoic acid (H_3L), in the presence (for **3**) or absence (for **1** and **2**) of ethylenediamine (en), and characterized by conventional analyses. It is shown that cooperative $E,Z \rightarrow E$ isomerization of H_3L, induced by coordination and ionic interactions, occurs upon interaction with the Cu^{II} centre in presence of en. The interaction of calf thymus DNA (CT DNA) and bovine serum albumin (BSA protein) and *in vitro* anti-proliferative studies in cancer cell lines with complexes **1-3** has been investigated by absorption and fluorescence titration methods. Complexes **1-3** act as active catalysts for the solvent-free microwave (MW) assisted selective oxidation of alcohol substrates. Reaction parameters were optimized and also additives influence and chemoselectivity were studied.

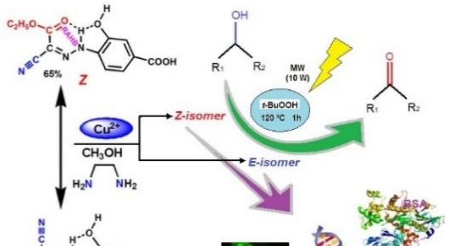

Figure 1: *E/Z* isomerization of H_3L^1 in the synthesis of Cu^{II} complexes **1−3** and their applications.

Acknowledgements: This work has been partially supported by the Foundation for Science and Technology (FCT), Portugal (UID/QUI/00100/2013). N.M.R.M is thankful to FCT for his CatSus PhD fellowship (SFRH/BD/52371/2013). The authors acknowledge the Portuguese NMR Network (IST-UTL Centre) for access to the NMR facility, and the IST Node of the Portuguese Network of mass-spectrometry for the ESI-MS measurements.

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THE 19TH CENTURY STAINED GLASS PANELS FROM PALÁCIO NACIONAL DA AJUDA: STUDY OF THE COBALT BLUE ENAMEL DETERIORATION AND ASSESSMENT OF CLEANING PERFORMANCE BY IONIC LIQUIDS

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One of the main conservation issues found in stained glass is the formation of white hard corrosion crusts on top of glass enamels, more specifically in cobalt blue ones. These crusts, mainly composed by calcium sulphates, are damaging the blue enamel, leading to its detachment from the surface where it as applied. The conventional solvents normally used in these situations, are ineffective and may be damaging for the glass substrate and painting materials. In order to solve this degradation issue a new class of materials is being was studied extensively - the ionic liquids (ILs). The selected and synthetized IL was the luminescent trihexyltetradecilphosphonium 1-anilino-naphtalene 8-sulfonate ([$P_{6,6,6,14}$][ANS]), its fluorescence is the most attractive advantage of this ionic liquid as it enables to control its removal after the cleaning process. This said, the aim of this paper is to assess the performance of [$P_{6,6,6,14}$][ANS] for the removal of calcium sulphates and study its interaction with the blue glass enamel surface. Four cobalt blue enamel historical recipes were selected and produced for painting on glass substrates. On this, an artificial layer of calcium sulphate was applied and the ionic liquid was used to remove this salt. The results of the salt removal as well as the interaction between the ionic liquid and the glass enamel surface were access by optical microscopy techniques (optical microscopy and SEM), infrared spectroscopy and UV-Vis (FTIR-ATR, µ-Raman and FORS), colorimetry measurements and 3D perfilometry images.

The analytical results showed the [$P_{6,6,6,14}$][ANS] effectiveness in dissolving the corrosion crusts, however, it was verified that it may cause alterations in the enamels surface.

ULTRASONIC METAL WELDING – THE CHEMISTRY BEHIND THE PROCESS

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Ultrasonic metal welding was discovered around 1950 and is now widely used on the industry in applications that involve softer and high conductivity alloys or metals like copper or aluminum. [1,2] In this process the metals are joined by the application of high frequency vibrations, under moderate pressure, in which the vibrations are applied parallel to the interface between the parts. The high frequency relative motion between the parts forms a solid-state weld through progressive shearing and plastic deformation over the surface asperities that disperses oxides and contaminants and brings an increasing area of pure metal contact between adjacent surfaces.[3] The problems of oxides, high thermal conductivity, high electrical conductivity, intermetallic and brittle alloys are not significant in the ultrasonic welding since the ultrasonic equipment should be capable of monitoring energy and controlling the critical welding variables.[4] However, on automotive industry, for applications that involve the ultrasonic welding of cables it has been seen that depending on the insulation material of cables the metal bonding is not always stronger as it should be. To understand the chemistry on the surface of ultrasonically welded metals a study, involving Energy Dispersive X-ray spectrometer (EDX) analysis, was conduct to identify what is causing the negative effect (figure 1).

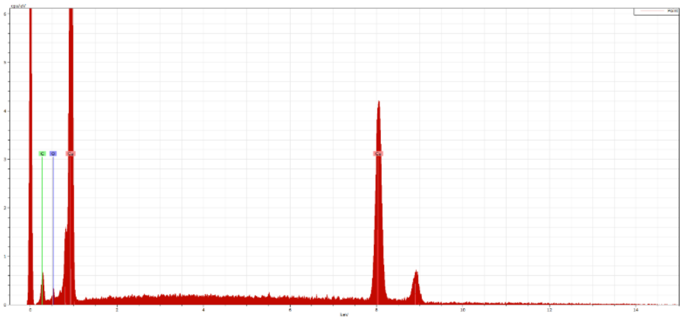

Figure 1: EDX Spectrum of cable with CuSn copper alloy

Acknowledgements: We would like to thank to SCANSCI and Institute Ricardo Jorge that allow us to use the TM3030Plus Microscope to analyze our samples. Thanks also to Fernando Nóbrega from SCANSCI that organized all the means to accomplish with the tests.

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3-HYDROXY-4-PYRIDINONE FUNCTIONALIZED WITH HYDROPHILIC ETHOXYLATED CHAINS AND THEIR METAL ION COMPLEXES

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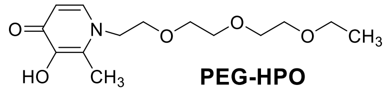
Metal ions are crucial for supporting all forms of life and alterations in their cellular homeostasis are finely related to many disorders thus implying the need of regulation of their concentration. Our group has long been interested in the design of 3-hydroxy-4-pyridinone (3,4-HPO) and their complexes with M(II) and M(III) metal ions for several applications. In the sequence of our research, the improvement of water solubility of the ligands, by developing more hydrophilic chelators, remains crucial. As oligo(ethylene glycol)s (OEGs) have been refereed as molecules with high hydrophilicity [1], these fragments have been considered for the design of novel 3,4-HPOs.

The first pegylated highly water soluble 3,4-HPO functionalized with a hydrophilic ethylene glycol chain (PEG-HPO) designed by our group (Fig.1) and its respective iron(III) complex were recently reported [2]. In the synthetic approach for the production of the ligand, the amino-terminated OGE reacts with the protected pyrone where the oxygen atom of the ring was substituted by the nitrogen of the anime group of the chain, yielding the protected 3,4-HPO. Subsequently, the protecting group was removed under hydrogen atmosphere in the presence of Pd/C (10%) and HCl, to obtain the dihydrochloride salt of PEG-HPO. The improved hydrophilicity of both the PEGylated 3,4-HPO ligand and its iron(III) complex were fully investigated in an analytical application for determination of iron in waters. The new ligand provided better sensitivity and a lower LOD for iron determination than that obtained for *N*-alkyl-3,4HPO. New ligands and their respective M(II) and M(III) complexes are currently being synthesized and characterized.



PEG-HPO

Figure 1: Formula of 3,4HPO functionalized with a hydrophilic PEG chain (PEG-HPO).

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 NORTE-07-0162-FEDER-000048 UID/Multi/04378/2013. T. Moniz thanks FCT for her PhD grant (SFRH/BD/79874/2011).

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LAYERED EUROPIUM HYDROXIDE SYSTEMS FOR PHOSPHOROUS SENSING AND REMEDIATION

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A Layered Lanthanide Hydroxide (LLH) material based on europium (LEuH, $Eu_8(OH)_{20}Cl_4\cdot 6H_2O$) was intercalated with 2,6-naphtalene dicarboxilate (NDC) yielding a material presenting both direct UV fluorescence of NDC, as well as the bright red luminescence characteristic of Eu^{3+} through energy transfer from NDC. Consequently, the material behaves as a dual-channel sensor towards anions which displays the ability to intercalate anions within the LLH matrix, displacing the NDC. The sensor was tested with several anions (phosphate, citrate, sulphate, pyrophosphate, acetate, oxalate, tetraborate and sulphonyl anions) and the changes in NDC (λ_{em} = 380 nm) and europium (λ_{em} = 615 nm) emission intensities upon excitation of NDC (λ_{ex} = 357 nm) were used to discriminate between the different anions. Phosphate was found to have the highest degree of intercalation, yielding a160% fold increase on the fluorescence intensity of NDC, and simultaneous decrease in emission of europium due to the reduction of the overall energy transfer efficiency. Intercalation of phosphate was further confirmed with Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES). Taking advantage of LEuH selectivity towards phosphate, its applicability in phosphorus remediation was studied presenting high sequestration capacity followed by controlled release of phosphate in three consecutive cycles. These results highlight the significant potential of LLHs as new scavenging agents for inorganic phosphate.

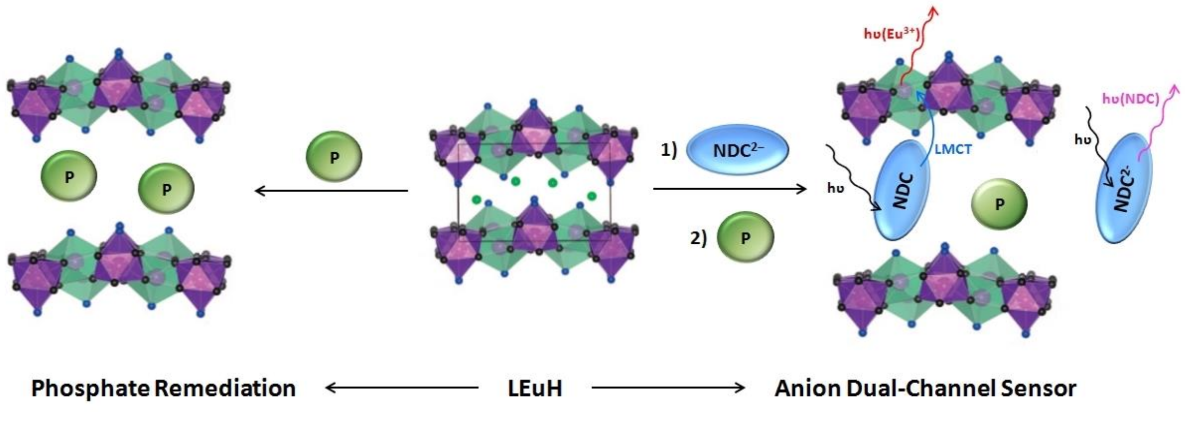

Figure 1: Schematic representation of the dual-channel sensor mechanism (→) and the sequestration mechanism of the remediation process (←).

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POLYPHENOLIC CARBOSILANE DENDRIMERS AS PROSTATE ANTICANCER AGENTS

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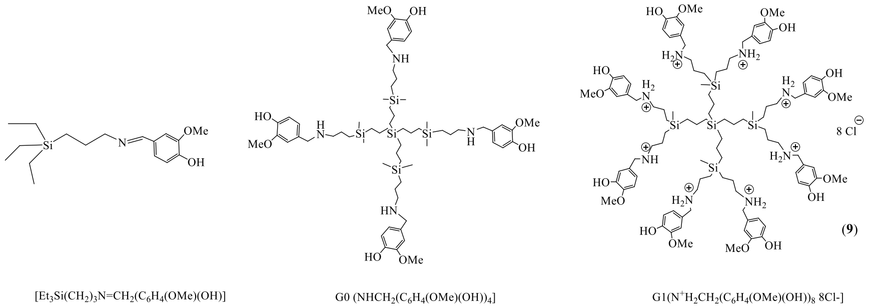
Prostate cancer is one of the most commonly diagnosed cancer. It is also the second leading cause of cancer-related death in men, making it one of the largest public health concerns today. Also, oxidative stress has been associated with prostate cancer development and progression due to an increase of reactive oxygen species (ROS).[1] Many natural, such as vanillin, polyphenols have emerged as very promising anticancer bioactive compounds.[2]

We have carry out the synthesis and characterization of new spherical carbosilane dendrimers with vanillin on the surface in order to combine the unique antioxidant an anticancer properties of polyphenols and the precisely designed structure of the dendrimers,[3] with the aim to evaluate them as a new class of potential antioxidant and anticancer agents and to see the effect of the multivalence of dendrimers on these activities. The antioxidant capacity was determined by DPPH and ABTS assays and the results showing their antioxidant power as free-radical scavengers. In addition, all dendrimers synthetized have better antioxidant efficacies than vanillin. The anticancer activity has been studied against two cancer cell lines, HeLa cervical and PC3 (PC-3) human prostate cancer by MTT assays, Also, proliferation, cell cycle, adhesion and migration in human prostate tumor cells have been studied. The dates showing a general trend that indicates that the polyphenolic dendrimers of zero and first generation are in general more cytotoxic than their analogous monopolyphenolic counterparts in both cancer cell lines.



(9)

$[Et_3Si(CH_2)_3N{=}CH_2(C_6H_4(OMe)(OH)]$ G0 $(NHCH_2(C_6H_4(OMe)(OH))_4]$ G1$(N^+H_2CH_2(C_6H_4(OMe)(OH))_8$ 8Cl-]

Figure 1. Proposed structures for dendrimers

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NEW BIS(THIOSEMICARBAZONATO) Cu(II) COMPLEXES BEARING CYCLIC AMINES FOR CANCER THERANOSTICS

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Aiming to explore alternative mechanisms of cellular uptake and cytotoxicity, we have studied a new family of copper(II) complexes (**CuL^1-CuL^4**) with bis(thiosemicarbazone) (BTSC) ligands containing pendant protonable cyclic amines (morpholine and piperidine). Herein, we report on the synthesis and characterization of these new complexes, as well as on their biological performance (cytotoxic activity, cellular uptake, protein and DNA binding properties), in comparison with the parental Cu^{II}ATSM, a radiopharmaceutical used for the PET imaging of hypoxia [1].

The new compounds have been characterized by a range of analytical techniques including ESI-MS, IR spectroscopy, cyclic voltammetry, reverse-phase HPLC and, in some cases, X-ray spectroscopy. *In vitro* cytotoxicity studies revealed that the copper complexes are cytotoxic, unlike the corresponding ligands, with a similar potency to that of CuATSM. Unlike CuATSM, the new complexes were able to circumvent cisplatin resistance.

In vitro studies in cancer cell lines with **^{64}CuL^1–^{64}CuL^4** showed a remarkably augmented cellular uptake compared with ^{64}CuATSM. The enhanced cellular uptake together with the citotoxicity of **^{64}CuL^1-^{64}CuL^4** indicates that this new family of Cu^{II}BTSC complexes have potential to act as strong radiotoxic agents against tumoral cells and deserve to be further evaluated in the design of metallodrugs for cancer theranostics.

Acknowledgements: The authors would like to acknowledge FCT for financial support through PTDC/QUI-QUI/114139/2009 and EXCL/QEQ-MED/0233/2012 research grants, postdoctoral fellowships SFRH/BPD/29564/2006 to S. Gama and SFRH/BPD/80758/2011 to E. Palma, and grants Ciência 2008 to G. Morais and FCT Investigator to F. Mendes and I. Correia).

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FLUORESCENT MATERIALS FROM ENCAPSULATED FLAVYLIA

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Flavylium compounds constitute an important family of dyes that comprise natural anthocyanins, responsible for most of the flowers' and fruits' reds and blues. Wherever water is present they undergo several reactions originating a chemical reaction network.[1] The mole fraction distribution of species in this network can be controlled by several stimuli, such as light and pH, that led these compounds to be exploited as pH-coupled photochromic systems.[2] Several efforts have been carried out to transfer these molecular networks to matrices in order to develop new pigments as well as new photochromic and luminescent materials.

In this work, the encapsulation of flavylium cations into zeolites is described. Direct encapsulation by difusion as well as ship-in-a-bottle syntheses were used to obtain coloured and highly fluorescent materials using five different flavylium salts. The synthesis, structural and spectroscopic characterization of these materials will be presented; one of the materials showed up as a relative humidity sensor.

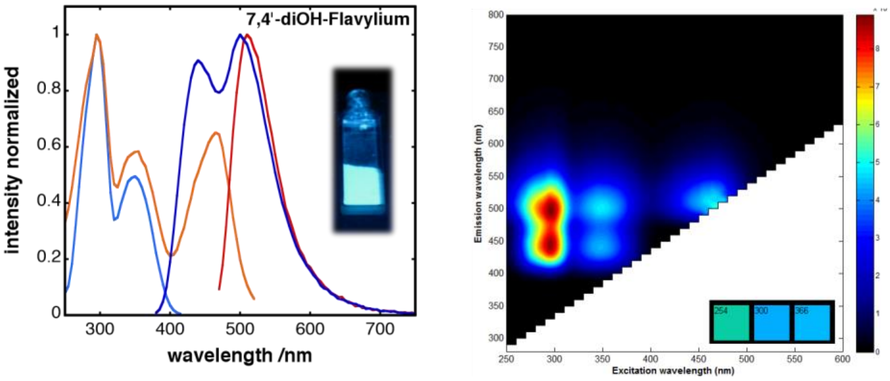

Figure 1: Emission and excitation spectra of 4',7-dihydroxyflavylium encapsulated in faujasite (left) and 2D fluorescence map (right). There are several species contributing to the emission spectra indicating the presence of energy transfer processes.

Acknowledgements: EC (project NMP4-SL2012-310651) and Portuguese FCT-MCTES (project UID/QUI/50006/2013) co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER – 007265) are acknowledged for financial support.

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HETEROBIMETALLIC Pt(II)/M(I) (M = Re, ^{99m}Tc) COMPLEXES WITH DUAL ANTICANCER PROPERTIES

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In this communication, we report on the development of new metal-based “hybrid” anticancer agents with imaging, chemotherapeutic and photosensitizing properties. For this purpose, a new heterobimetallic complex (**Pt-LQ-Re**) was prepared by linking a non-conventional *trans*-chlorido Pt(II) complex to a photoactive Re tricarbonyl unit (**LQ-Re**). Importantly, it could be demonstrated that the Re tricarbonyl unit in **Pt-LQ-Re** can be replaced by the radionuclide ^{99m}Tc to allow *in vivo* imaging. Planar scintigraphic images of mice injected with **Pt-LQ-Tc** clearly showed that the radioactive compound is uptaked by the excretory system organs, namely liver and kidneys, without significant retention in other tissues.

Furthermore, we report on the photophysical properties of the new complexes and on their biological evaluation, in the dark and upon light irradiation, which comprised the study of their DNA interaction, cellular localization and uptake, and cytotoxic activity.

All in all, the strategy of conjugating a chemotherapeutic compound with a PDT photosensitizer endows the newly synthesized complexes with an intrinsic cytotoxic activity in the dark, driven by the non-classical platinum core, and a selective activity upon light irradiation. Most importantly, the possibility of integrating a SPECT imaging radiometal in the structure of these new heterobimetallic complexes might allow for the *in vivo* and non-invasive visualization of their tumor accumulation, a crucial issue to predict the therapeutic outcome.

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A EUROPIUM TETRAKIS(β-DIKETONATE) RTIL WITH THERMOCHROMISM DUE TO THE β-DIKETONATE LIGAND AND THE COUNTERION

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An intrinsic photoluminescent ionic liquid based on europium(III) tetrakis(β-diketonate) complex with a tetraalkylphosphonium as counterion was synthesized (Figure 1). This Room Temperature Ionic Liquid (RTIL) showed thermochromism characterized to the naked eye by a light yellow liquid at 25ºC and a strong red colored compound close to 80ºC, moving to purple at higher temperatures near 100ºC. It has a quantum yield (ϕ) of 34% and revealed unique photophysical properties exhibiting an unprecedented case of thermally activated charge transfer processes.

Absorption and emission spectra showed that heating does not affect europium photophysical properties.

The thermal stability of this transformation is highlighted by its reversibility, turning this one example of an optical thermometer sensitive to higher temperatures.

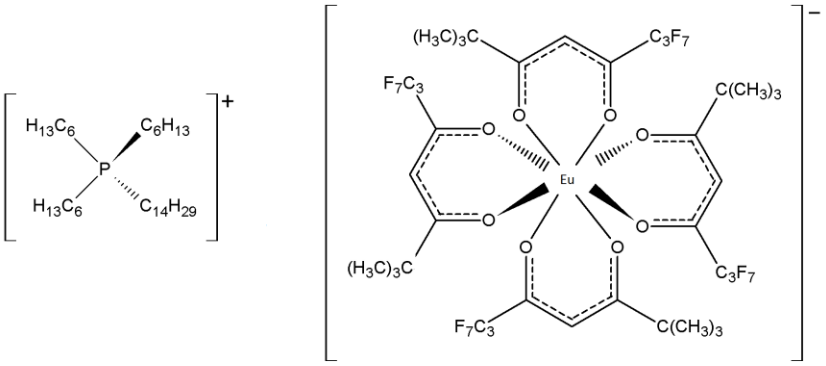

Figure 1: [$P_{6,6,6,14}$][Eu(FOD)$_4$] ionic liquid. P6,6,6,14 is trihexyltetradecylphosphonium and FOD is 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione

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HYBRID CONJUGATES OF Fe_3O_4@SiO_2 NANOPARTICLES AND CORROLE FOR PDT

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Photodynamic Therapy (PDT) is a cancer treatment that has been extensively studied and used, due to its proved efficiency in fighting several tumors, namely of the skin and esophageal. This method involves three main agents: light, a photosensitizer, and oxygen. Briefly, after light irradiation the photosensitizing agent generates reactive oxygen species, such as singlet oxygen – which causes oxidative damage, leading to the death of cancer cells [1]. Tetrapyrrolic macrocycles have been top choices to be used as photosensitizers due to their intrinsic photochemical properties. The use of corroles (tetrapyrrolic macrocycles) as photosensitizers, have also been evaluated with promising results [2]. The combination of corroles with magnetic nanoparticles opens the way to explore new functionalities in PDT. For instance, the magnetic guiding of such photosensitizer hybrids to cancer cell targets, might enhance locally the photodynamic effect, or the possibility to use complementary therapeutic strategies such as hyperthermia [3]. In this communication, we report the synthesis and characterization of spherical and cubic hybrid conjugates composed of corrole molecules and Fe_3O_4@SiO_2 nanoparticles. The functionalized nanoparticles were obtained by chemical grafting of the Ga(III) complex of 5,10,15-tris(pentafluorophenyl)corrole onto the surfaces of previously prepared colloidal Fe_3O_4@SiO_2 nanoparticles. Finally, the optical and morphological properties of the new materials will be presented and the results will be discussed in the context of their application as photosensitizers in PDT.

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pH-TUNABLE FLUORESCENCE AND PHOTOCHROMIC PROPERTIES OF FLAVYLIUM-BASED MCM-41 PIGMENTS

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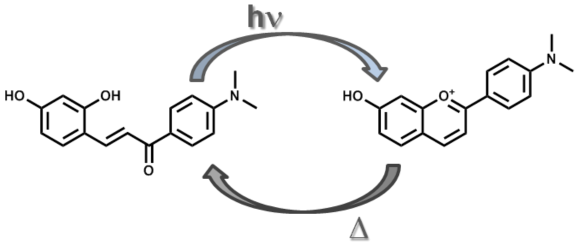
The pH driven chemical reaction network of flavylium compounds exhibits a diversity of differently coloured compounds. The presence of photoisomerizable chalcones allowed to exploit these comounds as photochromic systems. Transfer of this solution photochromism to the solid state through immobilization of the systems in organized matrices is an undergoing project with the aim of developing photochromic and luminescent materials. Since the chalcone/flavylium photochromism is known to be enhanced in CTAB micelles, flavylium species were incorporated in CTAB micelles and a sol-gel process followed for the formation of MCM-41 silica particles, avoiding the calcination step in order to keep the micellar phase inside the pores.

Five pigments were synthesized employing five different flavylium salts, with dye contents of < 1%. The materials show pH dependent reflectance spectra according to the known chemistry of flavylium cations, i.e., flavylium and chalcone are present at acidic and neutral pH values while at basic pH values deprotonated chalcones are present. Photochromism was studied at slightly acidic pH values where strong colour contrasts were observed. The chalcone – flavylium conversion is observed with fast response to light, reaching the colored state in a few minutes, while the thermal dark recovery occurs in the hours time scale.



Several photochromic cycles were run with a slight degradation observed for amino-substituted flavylium cations. The fluorescence quantum yields were measured at acidic pH values where only the flavylium form is present and at basic pH values where only deprotonated trans-chalcones are formed. The quantum yields of the flavylium-based materials vary between 10 – 40 % while those of the chalcones range in 20 – 45%.

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INTERACTION OF $VO(ACAC)_2$ WITH SERUM PROTEINS

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For the prospective therapeutic use of metal complexes the understanding of their transport and delivery to cells is a crucial issue. Strong evidence has been given indicating that most of the vanadium in the serum is bound to transferrin (hTF) at the Fe-binding sites [1]. Some of us reported [2] the geometry optimization calculations, based on the known X-ray diffraction structure of the N-lobe of hTF, of the binding of $V^{IV}O^{2+}$ at the Fe-binding site of the N-lobe of hTF.

It was demonstrated that when vanadium is administered in the form of a complex, *e.g.* $V^{IV}O(carrier)_n$, where carrier is an organic compound acting as a bidentate or tridentate ligand, two types of $V^{IV}O$-carrier-hTF binding have been proposed: one with V^{IV} at the Fe-binding site, the other at surface imidazole or carboxylate groups [3]. The binding of a $V^{IV}O(carrier)_n$ species to surface His or Asp is possible and was recently confirmed by a x-ray diffraction study with lysozyme [4].

$V^{IV}O(acac)_2$ has been shown to have insulin-enhancing properties and potential as anticancer agent [5]. It was reported to bind neither to hTF nor to albumin (HSA), [3] or to bind only to HSA [5].

In this work we demonstrate that $V^{IV}O(acac)_2$ binds to hTF, and that at least up to three V-centers may be bound to it, two of them more tightly. The techniques used for the studies are circular dichroism, EPR and fluorescence spectroscopy, as well as mass spectrometry and DFT calculations. Elution through size-exclusion columns and determinations of the V content by ICP in the protein fractions were also done to estimate the number of V-centers bound to hTF or HSA. No indication of relevant binding of $V^{IV}O(acac)_2$ complexes to HSA was obtained. A comparison and discussion of the results obtained by fluorescence spectroscopy and other techniques is also done.

The IC_{50} value (66 μM) was the concentration of $V^{IV}O(acac)_2$ selected to carry out intracellular distribution studies. Data on the uptake of $V^{IV}O(acac)_2$ by A2780 ovarian cells after 24 h of incubation is reported and discussed.

Acknowledgements: The authors thank Fundação para a Ciência e Tecnologia (FCT) and PEst-OE/QUI/UI0100/2013 for financial support.

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SERS-ACTIVE MAGNETIC NANOSORBENTS FOR DETECTION OF ANTIBIOTICS IN WATER

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The resistance of some pathogenic microorganisms to conventional antibiotics became an essential issue for public health and there is interest in the elimination of these pharmaceutics from aquatic ecosystems[1]. The inefficiency of conventional water treatment processes for the elimination of such compounds has encouraged interest in developing new materials for water purification. Our interest in this field, prompted us to develop colloidal nanosorbents for the removal of water contaminants via magnetic separation[2]. The upgrade of such sorbents for simultaneous use in water purification and contaminant detection is a challenging task but of great practical interest.

The research described here approaches that objective through the development of SERS-active magnetic sorbents, as innovative platforms for the magnetic removal and also the Raman detection of antibiotics dissolved in water. Therefore, surface modified magnetite nanoparticles decorated with plasmonic nanoparticles (Au, Ag) were investigated as magnetic sorbents for the uptake of antibiotics from water. Taking advantage of the plasmonic properties of the metal nanoparticles located at the surfaces of the sorbents, Raman spectroscopic studies (SERS) were carried out aiming at the optical detection of vestigial amounts of antibiotics (e.g. penicillin G). Additionally, microscopic methods, including Raman confocal microscopy, have been employed to characterize the SERS substrates and the detection process. These results will be discussed from a perspective of using these nanomaterials for laboratorial monitoring and in water treatment units.

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NEW IRON CATALYSTS FOR ENVIRONMENTALLY FRIENDLY OXIDATION REACTIONS

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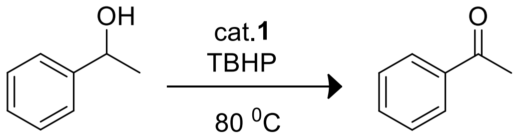
The low price, high abundance, and non-toxicity of iron, along with the great popularity of N-heterocyclic carbene (NHC) ligands in catalysis have motivated the growing interest in developing the chemistry of Fe-NHC.[1] Our group has contributed to this area of research with the development of piano-stool iron(II)-NHC complexes, and their application as efficient catalysts for the reduction of functional groups through hydrosilylation and hydrogen transfer processes.[2]

Herein, we describe the synthesis and characterisation of iron complexes containing the “Fe-bis-NHC” fragment combined with the ancillary ligands 2,2-bipyridine (bipy) and 1,10-phenanthroline (phen), and their reactivity towards oxidation processes. The complex Fe(bis-NHC)(bipy)I_2 (**1**) resulted to be an effective catalyst for the oxidation of 1-phenylethanol to acetophenone, with *tert*-butylhydroperoxide (TBHP) under neat conditions at 80 °C, Figure 1. The scope of the reaction and the influence of different solventes in the performance of the catalyst will be discussed. Crystallisation of **1** by slow diffusion of Et_2O into MeCN solutions afforded single crystals of [Fe(bis-NHC)(bpy)$_2$]I_2; its structure has been determined by X-ray diffraction studies.



[Fe(bis-NHC)(bipy)I_2]
1

Figure 1: Oxidation of alcohols in neat conditions with TBHP using the iron catalyst Fe(bis-NHC)(bipy)I_2.

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FLUORESCENT LIGANDS DERIVED OF 5-AMINOISOPHTHALIC ACID FOR THE DETECTION OF METALS IONS AND GASES

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Nowadays there is a constant demand for new ligands to develop functional Coordination Polymers (CPs), in order to improve their applicability in different areas like sensing and adsorption/separation of gases, optics and catalysis.[1] Our group has been developing CPs based on 5-aminoisophthalic acid (H_2Aip, Figure 1 a). One of our research goals is the synthesis of fluorescent building blocks for the synthesis of CPs and according to this we have been preparing compounds containing rhodamine and naphthalimide as fluorophores and H_2Aip as a functional ligand (Figures 1b, 1c). In the case of rhodamine derivatives to different bonds between the fluorophore and the ligand have been used (Figure 1 b). These building blocks were fully characterized and are being applied in the detection, in solution, of transition metal ions, including Zn(II), Cu(II) and Fe(III) and in the preparation of new CPs. According to the results obtained the development of optic fiber devices will be considered as well as their potential application in the detection of gases.[2]

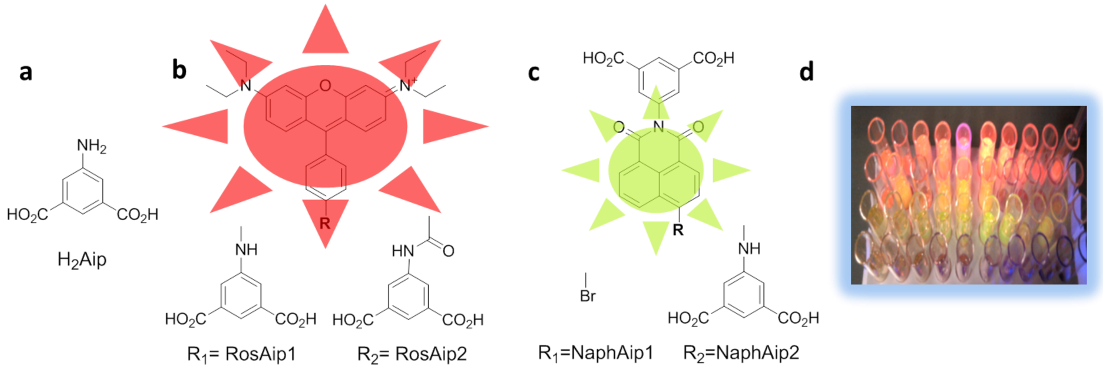

Figure 1. Structures of: a) 5-aminoisophthalic acid (H_2Aip), b) rhodamine derivatives based on H_2Aip and c) naphthalimide derivatives based on H_2Aip; d) chromatographic purification of one of the esterified rosamine compounds (RosAip1).

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HETERODINUCLEAR Ni(II) AND Cu(II) SCHIFF-BASE COMPLEXES

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The versatility of salen-type (salen = *N*,*N* – bis(salicylidene)ethylenediamine) complexes has been shown, among others, in their extensive applications in electrochemistry owing to their electrochromic[1], sensor[2] and catalytic[3] properties. Within our interest in engineering materials with synergic properties arising from different catalytic centres, we synthesised two new asymmetric heterodinuclear monomers (Ni-Cu **1**, Cu-Ni **2**). They were used to obtain new electropolymeric films (**Poly1, Poly2**) and evaluate their performance towards oxygen reduction reaction (ORR). They were compared with the homodinuclear analogous complexes (Ni-Ni **3**, Cu-Cu **4**) and their electropolymers (**Poly3, Poly4**). The heterodimetallic complexes of Ni(II) and Cu(II) were prepared via our *in situ* template method[4]. Their characterization was made by FTIR spectroscopy, elemental analyses and HR-mass spectrometry. Modified electrodes were prepared by electrochemical polymerisation of the monomers on both Pt and glassy carbon electrodes in tetrabutylammonium hexafluorophosphate. The redox behaviour of these polymers was characterised by cyclic voltammetry and the study of the morphologic properties performed by atomic force microscopy (AFM). In order to assess the electrocatalytic activity for the ORR, heterogeneous catalytic studies were made in phosphate solutions (pH=7).

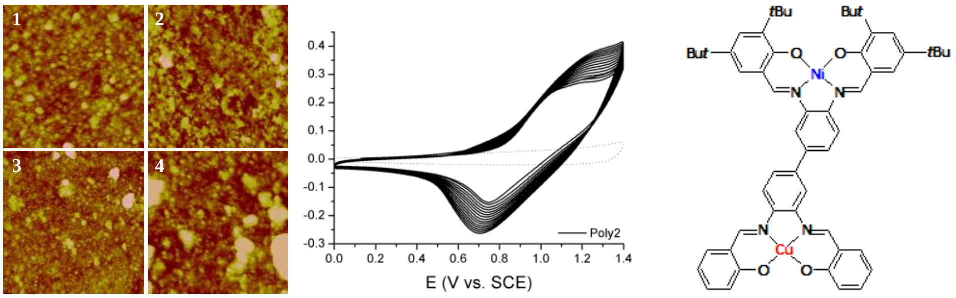

Figure 1. AFM images (2 µm x 2 µm with Z = 60 nm) of **Poly1** (1), **Poly2** (2), **Poly3** (3) and **Poly4** (4) films formed under potentiodynamic mode at 200 mV s^{-1}(left) and cyclic voltammogram of the potentiodynamic growth of **Poly2** film on GCE from 1 mM dichloromethane solution of the monomer. Schematic representation of the heterodinuclear monomer **2** (right).

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p-SUBSTITUTED 2-(*N*-ARYLIMINO)PYRROLYL BORON COMPLEXES – THE HEAVY ATOM EFFECT IN PHOTOLUMINESCENCE PROPERTIES

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The tetracoordinate mononuclear boron compounds containing *N,N*-chromophores revealed good results when applied as emitters in light-emitting diodes (LEDs) [1]. The 2-iminopyrrolyl ligand scaffold allow multiple changes (steric and electronic), which makes it useful for a large number of applications, for example in the synthesis of coordination and organometallic compounds with photoluminescent properties [2]. In fact, the 2-(*N*-arylformimino)pyrrolyl diphenylboron chromophore has been employed in recent studies, their emission colour tunability being highly dependent on the structure of the 2-iminopyrrolyl moiety [3].

In view of the great advantages exhibited by TADF emitters in the efficiency of OLED devices, and of the internal heavy atom effect in promoting intersystem crossing leading to triplet state formation, we report in this communication the synthesis of new *p*-halogen substituted 2-iminopyrrolyl boron complexes by reaction of different 2(*N*-*p*-halogen-phenylimino)pyrrole ligand precursors with triphenylboron (Fig. 1). The molecular features of the complexes obtained and their highly luminescent properties, obtained from their photophysical characterisation, are herein discussed.

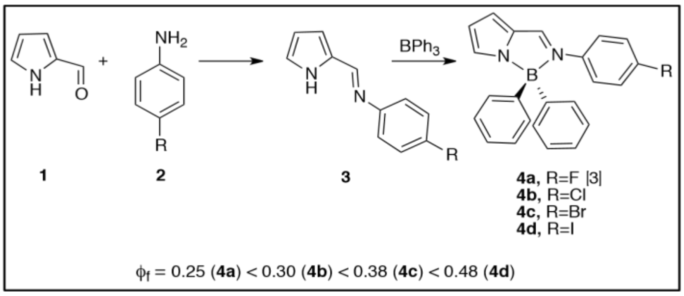

Figure 1: Synthesis of 2-iminopyrrolyl-BPh_2 complexes **4a-d** and their quantum yields relationships.

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SYNTHESIS AND EVALUATION OF A MAGNETIC HYBRID PHOSPHINE MATERIAL *VIA* HYDROFORMYLATION REACTION CATALYTIC EVALUATION

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Olefin hydroformylation is a widely used process, both in large scale and on fine chemistry, being the catalyst reutilization one of the main objectives. In recent years, development of immobilized catalysts on solid supports that enable their recovery and reuse, when applied in catalytic hydroformylation of aromatic and aliphatic olefins, have boosted the field of heterogeneous catalysis [1]. The use of magnetic nanoparticles (MNP) as supports for homogeneous ligands represent one of the most promising systems for heterogeneous catalysis due to its easy recovering with an external magnet [2,3].

Herein we present the synthesis and characterization of a new hybrid material bearing a triphenylphosphine derivative covalently anchored. Furthermore its catalytic activity and reutilization in the hydroformylation of olefins reaction will be presented and discussed.

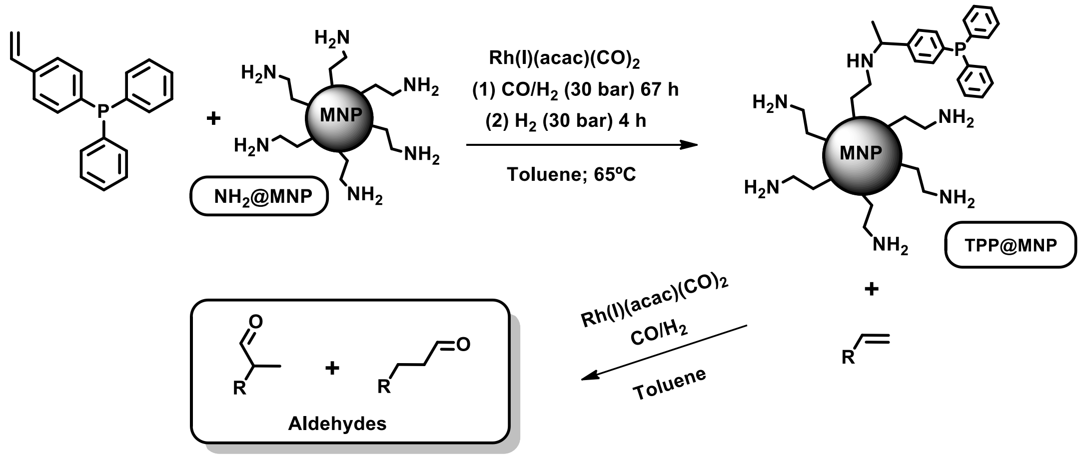

Figure 1: Synthesis of phosphine magnetic nanomaterial used in this work.

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CHITOSAN-SILICA HYBRID NANOADSORBENTS FOR THE UPTAKE OF PHARMACEUTICALS FROM WATER

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Pharmaceutical products have been frequently found in surface waters, since wastewater treatment plants lack efficient treatment procedures to remove them [1]. To overcome this problem alternative treatment methods are needed. Compared to other methods, adsorption is an attractive process in view of its simplicity of implementation and low cost.

Nanoparticles (NP), owing to small size and high surface to volume ratio are very interesting sorbents. In addition, magnetic nanoparticles (MNP) can be easily isolated in the presence of a magnetic external field, which is convenient for magnetically assisted removal of pollutants from water. Furthermore, enhanced adsorption and selectivity of the NP toward target pollutants can be achieved by surface functionalization with biopolymers. In the present study, novel biosorbents comprising magnetite (Fe_3O_4) and non magnetic nanoparticles were both coated with chitosan hybrid siliceous shells and tested for the uptake of three distinct pharmaceutics from water: diclofenac (DCF), tetracycline (TET) and metoprolol (MTP).

The method of synthesis comprised the modification of chitosan with an alkoxysilane containing isocyanate groups and the hydrolysis of a mixture of the resulting precursor with TEOS. [2] For the synthesis of magnetic nanosorbents the same procedure was used in the presence of Fe_3O_4 particles. The materials were characterized using electron microscopy (TEM/SEM), infra-red spectroscopy, elemental analysis and zeta potential measurements. Adsorption experiments with non-magnetic sorbents were performed at different pH and variable initial concentrations of each compound. The non magnetic hybrid prepared have shown higher affinity for DCF even though the differences were not very significative.

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MODULATION OF THE ENERGY TRANSDUCTION PROPERTIES WITHIN A FAMILY OF TRIHEME CYTOCHROMES FROM *GEOBACTER SULFURREDUCENS*

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A family of triheme cytochromes from *Geobacter sulfurreducens* plays an important role in extracellular electron transfer [1]. In addition to their role in electron transfer pathways, two members of this family (PpcA and PpcD) were also found to be able to couple e^-/H^+ transfer through the redox-Bohr effect observed in the physiological pH range, a feature not observed for cytochromes PpcB and PpcE [2]. As part of understanding the molecular control of the redox-Bohr effect in this family of cytochromes, which is highly homologous both in amino acid sequence and structures, it was observed that residue 6 is a conserved leucine in PcpA and PpcD, whereas in the other two characterized members (PpcB and PpcE) the equivalent residue is a phenylalanine. To determine the role of this residue located close to the redox-Bohr center, we replaced Leu6 in PpcA with Phe and determined the redox properties of the mutant, as well as its solution structure in the fully reduced state. In contrast with the native, the mutant PpcAL6F is not able to couple e^-/H^+ pathway. We carried out the reverse mutation in PpcB and PpcE (*i.e.*, replace Phe^6 in these two proteins by leucine) and show that the mutant proteins showed an increased redox-Bohr effect. The results clearly establish the role of residue 6 in the control of the redox-Bohr effect in this family of cytochromes, a feature that can enable rational design of *G. sulfurreducens* strains carrying mutant cytochromes with optimal redox-Bohr effect as suitable for various biotechnological applications.

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BIOCHEMICAL ASSESSMENT OF THE ENZYMATIC SUPEROXIDE ANION PRODUCTION BY CYTOCHROME b_5 REDUCTASE

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Primary cultures of cerebellar granular neurons are adequate as *in vitro* models to study cellular conditions that promote cell death of glutamatergic neurons. Most of the cellular insults, that induce cell death in these neurons, are associated to an increase of oxygen and nitrogen reactive species that trigger the event (or are mediator components), before activation of the non-return check point associated to proteases activation [1,2]. Using an apoptotic model that mimics the lack of synaptic transmission, we have found the existence of an oxidative stress bust associated to the plasma membrane of neurons in apoptosis, being the superoxide anion radical one major component [2,3]. Superoxide anion production was concomitant to clustering and overexpression of cytochrome b_5 reductase (Cb_5R) in the neural plasma membrane lipid rafts from rats [4,5]. In this work, we assess the formation of superoxide anion by overexpressed soluble human Cb_5R, using different methodologies, supporting that this flavoprotein is a novel source of superoxide anion [6]. Also, we critically address the difficulties involved in the measurement of superoxide anion formation under these conditions.

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MOLYBDENUM COMPLEXES AS CATALYSTS IN EPOXIDATION AND SULFOXIDATION REACTIONS

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New molybdenum complexes from the family [MoBr(η^3-C_3H_5)(CO)$_2$(L)] were synthesised by reaction of the precursor [MoBr(η^3-C_3H_5)(CO)$_2$(CH_3CN)$_2$] with a family of bidentate ligands derived from 2,2'-dipyridylamine, as shown in Figure 1. All new compounds prepared were characterized by FTIR, NMR of ^{1}H e ^{13}C as well as elemental analysis.

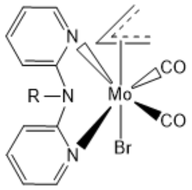

Figure 1: Molybdenum complexes from 2,2'-ddipyridylamine derivatives.

All complexes were tested as homogeneous pre-catalysts in the oxidation of olefins and sulfides, such as cis-cyclooctene, styrene, cis-3-hexen-1-ol, trans-2-hexen-1-ol, geraniol, methylphenylsulfide and diphenylsulfide, using hydrogen peroxide, tert-butyl hydroperoxide or cumene hydroperoxide as the oxidant. These studies were carried out in order to determine the influence of the length of the alkyl chains of the ligands on the complexes catalytic activity.

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IMPLICATIONS FOR IRON BINDING OF HUMAN HOLO-TRANSFERRIN GLYCATION.

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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 that 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, a detailed study of holo-Tf glycation is described, trying to verify its implications for iron binding and the origin of NTBI in DM. human holo-Tf was incubated with increased concentration of glucose under pseudo-physiological conditions, and the occurred modifications were identified by hyphenated liquid chromatography – mass spectrometry (LC-MS). Tf saturation was monitored spectrophotometrically in the course of the reaction.

A total of 19 lysine residues were found to be susceptible to undergo glycation in holo-Tf, with lysines 103, 312 and 380 presenting the highest reactivity. This result compares with the 12 lysines found to undergo glycation in apo-Tf [3]. Only the modification of 4 residues was found to be common in the two protein isoforms. Iron release was found to be mild, but together with the reduction of iron-binding capacity resulting from apo-Tf glycation, may be a fundamental contributor to the occurrence of NTBI.

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BIOPOLYMER-SILICA HYBRID PARTICLES PREPARED BY A NON-EMULSION METHOD FOR ENVIRONMENTAL APPLICATIONS

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Silica based hybrid materials merge the properties of organic and inorganic components to provide improved properties such as better mechanical properties and higher thermal decomposition temperatures. The development of silica hybrid materials derived of polysaccharides has experienced remarkable growth due to attractive properties of polysaccharides such as biocompatibility, biodegradability, low cost and availability.This research aimed to develop novel organic-inorganic hybrid nanomaterials derived from polysaccharides extracted from renewal resources. The method developed allows preparing biopolymer-silica hybrids in the form of uniform spherical particles with submicrometer size, without using surfactants. Herein, we report a non-emulsion method for preparing biopolymer-silica hybrid particles from a number of polysaccharides. The biopolymer was reacted with the alkoxysilane 3-isocyanatopropyltriethoxysilane (ICPTES) and the resulting compound was mixed with a silica precursor (tetraethyl orthosilicate, TEOS) to yield uniform spherical hybrid particles via a sol-gel method (Figure 1) [1]. This method also allows to coat magnetic nanoparticles with a thin shell with hybrid composition comprising a biopolymer covalently bonded to the silica network, imparting new properties to hybrid materials [2]. The resulting materials were extensively characterized using electron microscopy (TEM, SEM), solid state NMR, FTIR spectroscopy and elemental analysis. Results on the application of these materials as nano-adsorbents for the efficient removal of emerging chemical pollutants from water will be also presented.

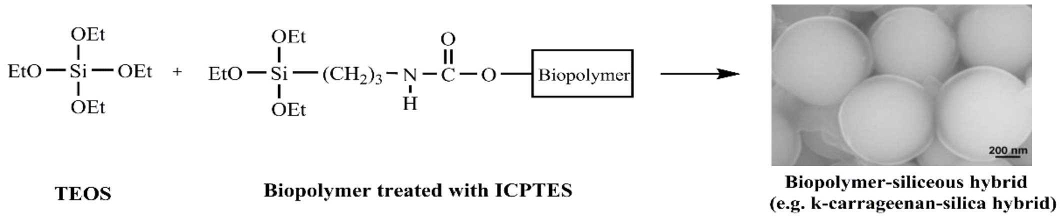

Figure 1: Scheme of the reactions involved in the synthesis of biopolymer-siliceous hybrid particles.

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IRON-(AMINO ACID) COMPLEXES IN OXIDATIVE CATALYSIS

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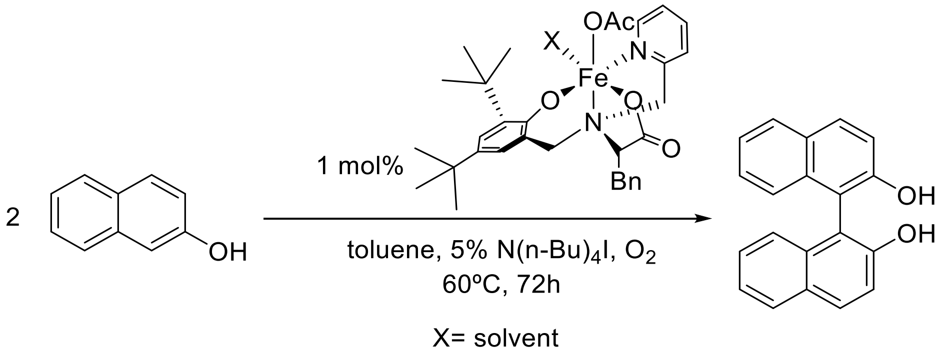
The importance of carbon-carbon bond forming reactions is well known for the preparation of relevant fine chemicals such as active pharmaceutical ingredients, dyes, fragrances, pesticides and polymers. The development of efficient transition metal catalysts for sustainable C-C bond forming reactions, in order to reduce the negative environmental impact of many processes in the fine chemicals industry, has gained relevance in the last years. The subject of our study is the synthesis and application of iron amino-acid-based complexes as catalysts for C-C coupling reactions, using environmentally-friendly conditions. Herein we describe the synthesis of novel iron (III) complexes derived from chiral amino acid-based ligands and their application as homogeneous catalysts for the asymmetric oxidative coupling of 2-naphthol [1, 2] (***Figure 1***). The results obtained show that these structurally simple iron complexes can be used as catalysts in the development of mild and environmentally-friendly procedures for the oxidative coupling of 2-naphthol.



yield: 46%
e.e: 19%

Figure 1: General procedure for the oxidative coupling of 2-naphthol mediated by Fe-(amino acid) complexes.

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SYNTHESES, STRUCTURAL CHARACTERIZATIONS, ANTIMICROBIAL ACTIVITIES AND DNA INTERACTIONS OF *cis*- AND *trans*-DISPIROCYCLIC FERROCENYLPHOSPHAZENES

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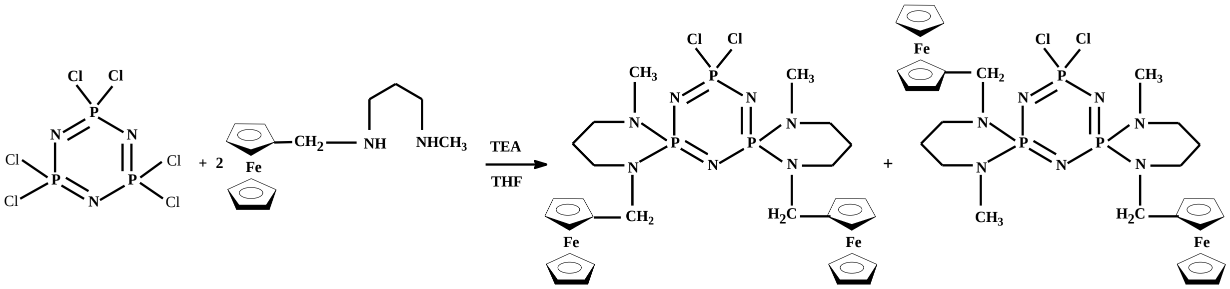
Cyclophosphazenes containing $(NPX_2)_n$ (n = 3 and 4) repeat unit sequentially are important starting materials for inorganic heterocyclic ring systems and polymers [1-3]. The condensation reaction of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, with N-methyl-N-monoferrocenyl-1,3-propanediamine, $FcCH_2NH(CH_2)_3NHCH_3$, produced mainly new *cis*- (**1**) and *trans*- (**2**) dispirocyclic ferrocenylphosphazenes (Scheme 1). The FTIR, ^1H, ^{13}C and ^{31}P NMR techniques were used for the characterization of these compounds. In addition, the crystal structures of **1** and **2** were determined using X-ray crystallography. The dispirocyclic ferrocenylphosphazenes (**1** and **2**) were screened for antimicrobial activity against G(+) and G(-) bacteria and fungi. Moreover, the interactions between the compounds and pBR322 plasmid DNA were investigated.



*Scheme 1***:** Syntheses route of *cis*- (1) and *trans*- (2) dispirocyclic ferrocenylphosphazenes

Acknowledgements: The authors acknowledge Scientific and Technological Research Application and Research Center, Sinop University, Turkey, for the use of the Bruker D8 QUEST diffractometer.

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SYNTHESIS AND CHARACTERIZATION OF NEW POLYPHOSPHAZENES AS CATHODE MATERIALS

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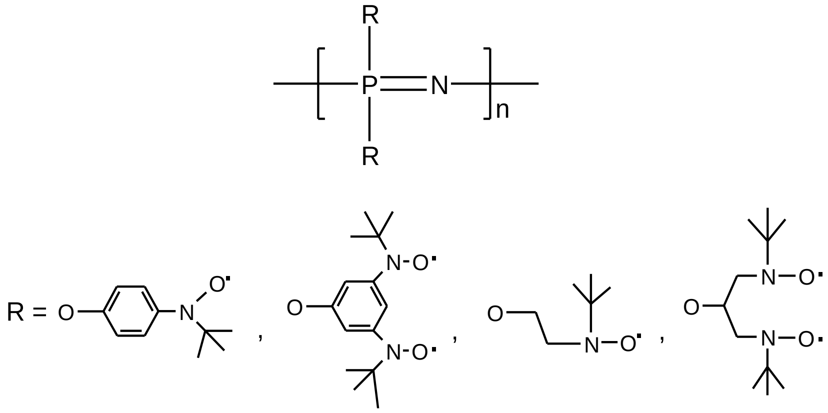
The development of lithium-ion batteries has been currently very prominent and active area in fundamental research because of their widely used as a power source in portable electronic devices and electric vehicles [1]. Li-ion batteries have also high energy and power density, however during high current charging or discharging, mass transfer limitations and other factors increase the cell temperature and thus the energy density and cycle life of the battery is decreased [2]. One of the challenges to overcome this problem can be the development of suitable cathode materials. Redox-active stable radical polymers which are a class of cathode materials of rechargeable lithium-ion batteries are alternative to inorganic metal oxide cathodes. Because, the radical-polymer cathode lithium ion battery energy density can be increased by increasing the number of the radical on per monomer unit [3].

In this study, it was synthesized and characterized of new polyphosphazenes carrying nitrogen-oxide radical groups (**1**-**4**) and investigated of their potential usage in rechargeable lithium-ion battery cathode active material (Fig. 1).



(**1**) (**2**) (**3**) (**4**)

Figure 1: Synthesized Radical Polymers (**1**-**4**)

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SELF-ASSEMBLY OF MULTIFUNCTIONAL IRON(III) MAGNETIC SWITCHES

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Spin crossover (SCO) complexes have long been considered as promising candidates for the next generation of data storage devices [1,2]. SCO candidate compounds can be found among a limited group of $3d^4$–$3d^7$ transition metal ions, the most common being Fe(II), Fe(III) and Co(II). Fe(III), $3d^5$, with its redox stability, is a good candidate for fabrication of SCO materials, an area towards which research has been moving [3]. We recently synthesised a mononuclear Fe(III) compound displaying a wide hysteresis window centred at room temperature [4]. We also found that this compound undergoes a phase transition coupled with the thermosalient effect resulting in crystal fragmentation with no loss of both SCO and hysteresis. Here we present the synthesis and characterisation of the $[Fe(SalEen)_2]^+$ derivative and its self-assembly into nanowires using template-free fabrication techniques. Variable temperature Raman and AFM are used to investigate both the SCO and the thermosalient effect of the new materials, Figure 1.

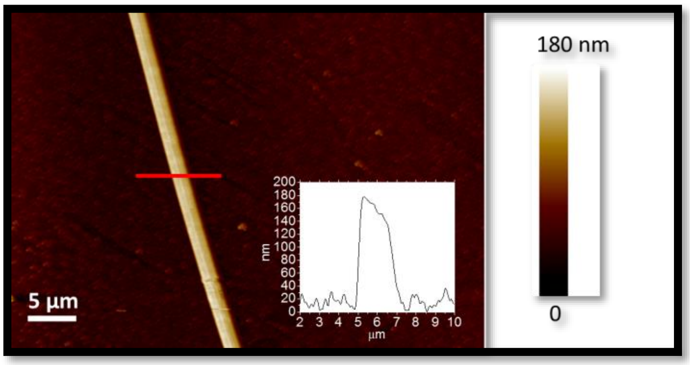

Figure 1: Magnetic profiles of two Fe(III) polymorphs.

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NEW IRON(III) SPIN CROSSVER COMPOUND WITH SYMMETRY BREAKING SPIN-STATE TRANSITION AND ORDERED INTERMEDIATE STATE

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The spin crossover (SCO) phenomenon can be found in a variety of $3d^4-3d^7$ transition metal complexes and has been extensively studied in past decades [1,2]. In these complexes, the spin state of the transition metal can be reversibly switched between the low-spin (LS) and high-spin (HS) states by the application of an external perturbation (such as temperature, pressure, magnetic field, light irradiation). The bistability between the HS and LS states is quite promising for the application as molecular memories and switches, as it is associated with changes in the physical properties (crystal structure, magnetism, color, etc.) and its progress can be monitored using a variety of techniques [1−3]. Here, we report the first example of a two-step SCO mononuclear FeIII complex, [Fe(nsal$_2$trien)]SCN, with structural symmetry breaking in the intermediate phase (with the doubling of the unit cell) and a “re-entrant” behavior as the LS crystal structure is isostructural to the one in the HS phase. The hexadentate nsal$_2$trien ligand (see Figure 1) was obtained by condensation of triethylenetetramine with 2-hydroxy-1-naphthaldehyde.

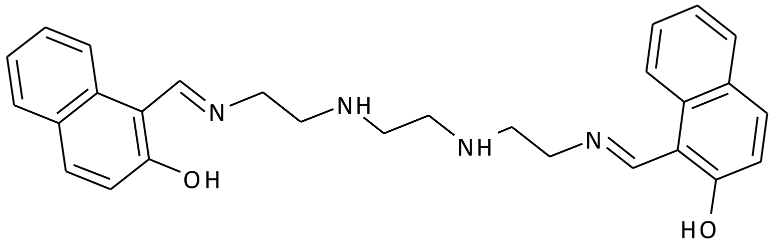

Figure 1: nsal$_2$trienH$_2$.

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THE SYNTHESIS OF SELECTIVE MERCURY(II) ION FLUORESCENCE SENSORS BASED ON PHOSPHAZENE CORE

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Metal ions play a significant role in a wide range of chemical reactions, including biological metabolisms as well as many other processes. Among various trace elements in environmental and biological systems, concentration levels of mercury(II) ions which shows highly toxic effect even very low amounts in living organisms, are mg/L, µg/L in this media and because of complexity of this media analysis of the mercury(II) ion is difficult [1]. In recent years, using optical methods for chemical analysis are getting important in sensor area. Especially, research, investment and active researchers about fluorescence signal for chemical detection is getting increase. In environmental monitoring, clinical investigations and control of industrial processes, optical sensors have been great interest [2].

In this study, the design, synthesis and investigation of properties of new compounds which can be used as selective and sensitive fluorescence sensor for mercury(II) ions were planned (fig. 1). The novel compounds were fully characterized by the standard spectroscopic techniques such as ^{1}H, ^{13}C and ^{31}P NMR, mass spectrometry (MALDI-TOF). The chemosensor behaviors of this pyrene substituted cyclic phosphazene compounds against to mercury(II) ions was determined by UV and fluorescence spectrophotometry.

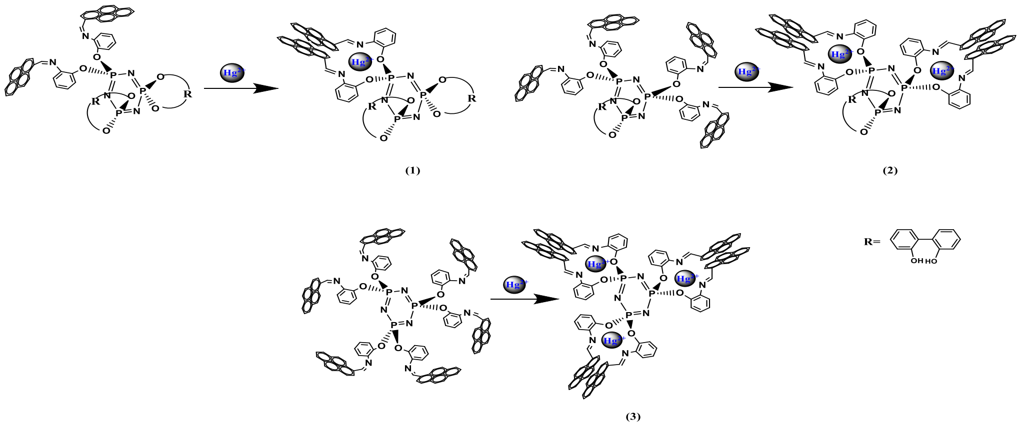

Figure 1: The structure of the pyrene substituted cyclic phosphazene chemosensors.

Acknowledgements: This work was supported by the Scientific and Technological Research Council of Turkey (TUBITAK), Project Number 214Z069.

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[2] Xu, J.; Dou, S.; Liu, H.; Dai, L., *Nano Energy*, **2013**, *2*, 439-442.

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Friday, October 7th

9:00		**Registration**
9:15		
9:30		
9:45		
10:00		
10:15		**Opening session**
10:30	**Organometallics**	**Plenary** *Luis A. Oro* **Prémio Luso-Espanhol**
10:45		
11:00		
11:15		*Konstantin V. Luzyanin*
11:30		*Clara S. B. Gomes*
11:45		*Sónia Barroso*
12:00		**Keynote** *Ana Isabel Tomaz*
12:15		
12:30		*Dina Maciel*
12:45		*Marta Maroto-Díaz*
13:00		**Lunch break**
13:15		
13:30		
13:45		
14:00		
14:15		
14:30	**Bioinor.**	**Plenary** **ChemPubSoc Europe** *Luigi Casella*
14:45		
15:00		
15:15		**Poster session** **&** **Coffee break**
15:30		
15:45		
16:00		
16:15		
16:30		
16:45		
17:00	**Bioinorganic**	**Keynote** *Nuno S. Cerqueira*
17:15		
17:30		*Luísa B. Maia*
17:45		*Ricardo O. Louro*
18:00		*Ana P. Fernandes*
18:15		*Ana Petronilho*
18:30		*Pedro Adão*
18:45		*Filipe Monteiro-Silva*
19:00		*Manuel Aureliano*
19:15		**Meeting** **Inorganic and Bioinorganic** **Chemistry Division of SPQ**
19:30		
19:45		
20:00		
20:15		**Conference dinner**
Late		

Saturday, October 8th

Materials	**Plenary** *Tito Trindade*	9:00
		9:15
		9:30
	Filipa L. Sousa	9:45
	César A. T. Laia	10:00
	Paulo N. Martinho	10:15
	Sandra Gago	10:30
	Coffee break	10:45
		11:00
Materials	**Keynote** *Carlos Baleizão*	11:15
		11:30
	Ana L. Daniel-da-Silva	11:45
	Sara Realista	12:00
	Helena Nogueira	12:15
	Diana M. Fernandes	12:30
	Clara Pereira	12:45
	Lunch break	13:00
		13:15
		13:30
		13:45
		14:00
		14:15
Miscellaneous	**Keynote** *John K. Gibson*	14:30
		14:45
	Nuno A. G. Bandeira	15:00
	Luís C. Branco	15:15
	Luís G. Alves	15:30
	Frederico F. Martins	15:45
	Filipe Teixeira	16:00
	Andreia Ruivo	16:15
	Plenary *António Pires de Matos* **Prémio A. Romão Dias**	16:30
		16:45
		17:00
	Closing session	17:15