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
# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Committees</td>
<td>iv</td>
</tr>
<tr>
<td>Welcome Message</td>
<td>vi</td>
</tr>
<tr>
<td>Sponsors</td>
<td>vii</td>
</tr>
<tr>
<td>Programme</td>
<td>v</td>
</tr>
<tr>
<td>Plenary Lectures</td>
<td>1</td>
</tr>
<tr>
<td>Keynote Lectures</td>
<td>7</td>
</tr>
<tr>
<td>Oral Communications</td>
<td>13</td>
</tr>
<tr>
<td>Poster Communications</td>
<td>43</td>
</tr>
<tr>
<td>Author Index</td>
<td>115</td>
</tr>
<tr>
<td>Participants List</td>
<td>123</td>
</tr>
</tbody>
</table>
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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
Sponsors
### Programme

#### Friday, October 7th

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
</tr>
</thead>
<tbody>
<tr>
<td>9:00 – 10:15</td>
<td>Registration</td>
</tr>
<tr>
<td>10:15 – 10:30</td>
<td>Opening Session</td>
</tr>
<tr>
<td>11:15 – 11:30</td>
<td>OC1 - Konstantin V. Luzyanin, Acyclic diaminocarbenes as powerful ancillary ligands for emerging catalytic applications</td>
</tr>
<tr>
<td>11:30 – 11:45</td>
<td>OC2 - Clara S. B. Gomes, Synthesis of [Ni(η⁵-C₅H₅)(α-dimine)]PF₆ complexes and their reactivity towards DEAC, Applications in ethylene polymerisation</td>
</tr>
<tr>
<td>11:45 – 12:00</td>
<td>OC3 - Sónia Barroso, Reactivity and DFT studies on diamine bis(phenolate) vanadium(III) and –(V) complexes</td>
</tr>
<tr>
<td>12:00 – 12:30</td>
<td>KL1 - Ana Isabel Tomaz, Tracking antitumor metallodrugs with ruthenium candidates</td>
</tr>
<tr>
<td>12:30 – 12:45</td>
<td>OC4 - Dina Maciel, A new family of poly(alkylidenamine)s metallodendrimers ruthenium based: synthesis, characterization and cytotoxicity studies</td>
</tr>
<tr>
<td>12:45 – 13:00</td>
<td>OC5 - Marta Maroto-Diaz, 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</td>
</tr>
<tr>
<td>13:00 – 14:30</td>
<td>Lunch Break</td>
</tr>
<tr>
<td>14:30 – 15:15</td>
<td>ChemPubSoc Europe Lecture: PL2 - Luigi Casella, What do we know about the redox reactivity of metal ions bound to neuronal peptides</td>
</tr>
<tr>
<td>15:15 – 17:00</td>
<td>Poster Session &amp; Coffee Break: KL2 - Nuno S. Cerqueira, Theoretical and computational studies devoted to Mo dependent enzymes</td>
</tr>
<tr>
<td>17:00 – 17:30</td>
<td>OC6 - Luisa B. Maia, Molybdenum-dependent nitric oxide-forming nitrite reductases</td>
</tr>
<tr>
<td>17:30 – 17:45</td>
<td>OC7 - Ricardo O. Louro, Detailed characterization of multicentre redox enzymes involved in metal respiration pathways</td>
</tr>
<tr>
<td>17:45 – 18:00</td>
<td>OC8 - Ana P. Fernandes, Interaction studies between periplasmic cytochromes from Geobacter sulfurreducens provide insights on the functional role of the nanowire</td>
</tr>
<tr>
<td>18:00 – 18:15</td>
<td>OC9 - Ana Petronilho, Synthetic methodologies for N-heterocyclic carbene derived from nucleosides</td>
</tr>
<tr>
<td>18:15 – 18:30</td>
<td>OC10 - Pedro Adão, Copper(II) complexes derived from N-picoly1, N-carboxymethyl and N-carboxyethyl amino acids as catalysts in asymmetric oxidative coupling of 2-naphthol</td>
</tr>
<tr>
<td>18:30 – 18:45</td>
<td>OC11 - Filipe Monteiro-Silva, Development of catechol-based rosamine chemosensors with dual fluorescence and paramagnetic response</td>
</tr>
<tr>
<td>18:45 – 19:00</td>
<td>OC12 - Manuel Aureliano, Isostructural decavanadate and decaniobate decompose into different oligomers: biochemical relevance</td>
</tr>
<tr>
<td>19:00 – 19:15</td>
<td>Meeting - Inorganic and Bioinorganic Chemistry Division of SPQ</td>
</tr>
<tr>
<td>19:15 – 20:00</td>
<td>Conference Dinner</td>
</tr>
<tr>
<td>20:15 – Late</td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>Session</td>
</tr>
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</tr>
<tr>
<td>9:00 – 9:45</td>
<td>Materials</td>
</tr>
<tr>
<td>9:45 – 10:00</td>
<td>OC13</td>
</tr>
<tr>
<td>10:00 – 10:15</td>
<td>OC14</td>
</tr>
<tr>
<td>10:15 – 10:30</td>
<td>OC15</td>
</tr>
<tr>
<td>10:30 – 10:45</td>
<td>OC16</td>
</tr>
<tr>
<td>10:45 – 11:15</td>
<td>Coffee Break</td>
</tr>
<tr>
<td>11:15 – 11:45</td>
<td>KL3</td>
</tr>
<tr>
<td>11:45 – 12:00</td>
<td>OC17</td>
</tr>
<tr>
<td>12:00 – 12:15</td>
<td>OC18</td>
</tr>
<tr>
<td>12:15 – 12:30</td>
<td>OC19</td>
</tr>
<tr>
<td>12:30 – 12:45</td>
<td>OC20</td>
</tr>
<tr>
<td>12:45 – 13:00</td>
<td>OC21</td>
</tr>
<tr>
<td>13:00 – 14:30</td>
<td>Lunch Break</td>
</tr>
<tr>
<td>14:30 – 15:00</td>
<td>KL4</td>
</tr>
<tr>
<td>15:00 – 15:15</td>
<td>OC22</td>
</tr>
<tr>
<td>15:15 – 15:30</td>
<td>OC23</td>
</tr>
<tr>
<td>15:30 – 15:45</td>
<td>OC24</td>
</tr>
<tr>
<td>15:45 – 16:00</td>
<td>OC25</td>
</tr>
<tr>
<td>16:00 – 16:15</td>
<td>OC26</td>
</tr>
<tr>
<td>16:15 – 16:30</td>
<td>OC27</td>
</tr>
<tr>
<td>16:30 – 17:15</td>
<td>Prémio Alberto Romão Dias 2016</td>
</tr>
<tr>
<td>17:15 – 17:30</td>
<td>Closing Session</td>
</tr>
</tbody>
</table>
Plenary Lectures
MECHANISTIC STUDIES ON RHODIUM-N-HETEROCYCLIC CARBENE CATALYSTS

Luis A. Oro

Department of Inorganic Chemistry, University of Zaragoza,
Pedro Cerbuna 12, 50009-Zaragoza, Spain
oro@unizar.es

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$_3$OD 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(μ-X)(IPr)(η$^2$-olefin)]$_2$ (X = Cl, OH), RhCl(IPr)(py)(η$^2$-olefin) and Rh(oq)(IPr)(η$^2$-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(μ-Cl)(IPr)(η$^2$-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.

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

Luigi Casella

Dipartimento di Chimica, Università di Pavia, Via Taramelli 12, Italy
luigi.casella@unipv.it

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 (Rnτ), 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, Rnτ 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).

WATER PURIFICATION USING NANOMATERIALS, MAGNETISM AND LIGHT

Tito Trindade

Departamento de Química-CICECO, Universidade de Aveiro, Aveiro, Portugal
tito@ua.pt

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

Grupo de Química dos Elementos-f, Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, 2695-066 Bobadela LRS, Portugal

Centro de Investigação “Vidro e Cerâmica para as Artes”, VICARTE, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa e Faculdade de Belas Artes, Universidade de Lisboa, 2829-516 Caparica, Portugal

apmatos@fct.unl.pt

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
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.

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 metallo-drugs 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).

THEORETICAL AND COMPUTATIONAL STUDIES DEVOTED TO 
Mo DEPENDENT ENZYMES

Nuno M. F. Sousa A. Cerqueira

UCIBO-REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, 
Universidade do Porto, 4169-007 Porto, Portugal

nscerque@fc.up.pt

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].

SILICA NANO PARTICLES: A WINDOW OF OPPORTUNITIES, NOT JUST LIGHT SAND

Carlos Baleizão

CQFM - Centro de Química-Física Molecular and IN – Institute of Nanoscience and Nanotechnology, Instituto Superior Técnico, Universidade de Lisboa, Portugal

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 as 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

John K. Gibson

Lawrence Berkeley National Laboratory, Berkeley, California, USA
jkgibson@lbl.gov

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.

Acknowledgement: Research supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Heavy Element Chemistry Program under Contract DE-AC02-05CH11231.
Oral Communications
ACYLIC DIAMINOCARBENES AS POWERFUL ANCILLARY LIGANDS FOR EMERGING CATALYTIC APPLICATIONS

Konstantin V. Luzyanin

Department of Chemistry, University of Liverpool, Crown Street, Liverpool L69 7ZD, United Kingdom
Saint Petersburg State University, 7/9 Universitetskaya Nab., Saint Petersburg 199034, Russian Federation
konstantin.luzyanin@liverpool.ac.uk

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).

SYNTHESIS OF [Ni(η⁵-C₅H₅)(α-DIIMINE)]PF₆ COMPLEXES AND THEIR REACTIVITY TOWARDS DEAC. APPLICATIONS IN ETHYLENE POLYMERISATION

Clara S. B. Gomes¹, Alejandro F. G. Ribeiro¹, M. Teresa Duarte¹, Pedro T. Gomes¹, Artur Bento¹, M. Rosário Ribeiro¹, Anabela C. Fernandes¹ and Sofia I. Pascu²

¹ Centro de Química Estrutural, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal; ² Chemistry Department, University of Bath, Claverton Down, Bath, UK claragomes@tecnico.ulisboa.pt

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 (η⁵-C₅H₅) 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 AlEtCl₃ anion (Figure 1a). When the reaction was performed with complex [Ni(η⁵-C₅H₅)(Mes-BIAN)]PF₆, a paramagnetic cationic trinuclear α-diimine Ni cluster, containing five bridging Cl ligands and an AlCl₄⁻ 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.

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

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

Sónia Barroso¹, Pedro Adão¹, Maria José Calhorda² and Ana M. Martins¹

¹ Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
² Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, Ed. C8, 1749-016 Lisboa, Portugal
soniabarroso@tecnico.ulisboa.pt

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 η²-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 nitroxy radical TEMPO. Remarkably, TEMPO-CH₂Ph 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

Dina Maciel¹, Mª de los Ángeles Muñoz-Fernández², Helena Tomás¹ and João Rodrigues¹

¹ CQM-Centro de Química da Madeira, MMRG, Universidade da Madeira, Campus Universitário da Penteada, 9020-105 Funchal, Portugal
² Laboratorio de Inmunobiología Molecular, Hospital General Gregorio Marañón, Madrid, Spain
dmaciel@uma.pt

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].

Metallo-dendrimers 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(alkylidenediamine)-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(η⁵-C₅H₅)(PPh₃)₂Cl and [RuCl(η⁶-p-cymene)] derivatives. In the near future, the inhibitory capacity of these metallo-dendrimers against HIV infection, as well as their anticancer activity will then be evaluated.

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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

Marta Maroto-Díaz¹,², Benelita T. Elie³,⁴, Pilar Gómez-Sal¹, Jorge Pérez-Serrano⁵, Rafael Gómez¹,², María Contel³,⁴ and F. Javier de la Mata¹,²

¹ Dpto. de Q. Orgánica y Q. Inorgánica, Universidad de Alcalá, Campus Universitario, Alcalá de Henares, Spain
² Networking Research Center on Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN), Spain
³ Dept. of Chemistry, Brooklyn College and The Graduate Center, CUNY, Brooklyn, New York 11210, USA
⁴ Biology PhD Program, The Graduate Center, CUNY, 365 Fifth Avenue, New York, NY 10016, USA
⁵ Dpto. de Biomedicina y Biotecnología, Universidad de Alcalá, Campus Universitario, Alcalá de Henares, Spain
marta.maroto@uah.es

Cisplatin remains to be the most metallic complex used 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 metallo-dendrimers based on DAB or PPI scaffolds have been described, including η⁶-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 metallo-dendrimers 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 metallo-dendrimers 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 IC⁵₀ in the range of the antimetastatic agents RAPTA-C and RAPTA-T.

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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 molybdenoenzymes 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].

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DETAILED CHARACTERIZATION OF MULTICENTRE REDOX ENZYMES INVOLVED IN METAL RESPIRATION PATHWAYS

Catarina M. Paquete, Ivo H. Saraiva and Ricardo O. Louro

ITQB-NOVA, Av da República (EAN), 2780-157 Oeiras, Portugal
louro@itqb.unl.pt

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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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.

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SYNTHETIC METHODOLOGIES FOR N-HETEROCYCLIC CARBENES DERIVED FROM NUCLEOSIDES

A. Petronilho, Inês Leitão and Nadésda Traskina

Instituto de Tecnologia Química e Biológica, Estação Agronómica Nacional, Oeiras, Portugal
ana.petronilho@itqb.unl.pt

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. Once formed, DNA adducts derived from methylation are formally N-heterocyclic carbene precursors and readily undergo exchange with deuterium. 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.

Their role is nevertheless poorly understood.

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 their behavior in physiological media and will be discussed in this communication.

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

Pedro Adão, Sónia Barroso, Carlos M. Teixeira, M. Fernanda N. N. Carvalho, Maxim L. Kuznetsov and João Costa Pessoa

Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
pedro.m.adao@tecnico.ulisboa.pt

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 CuII-[N-picoly(amino acid)] complexes capable of catalysing the oxidative coupling of 2-naphthol to BINOL (1,1′-Bi-2-naftol) under mild conditions, using O2 as oxidant.[2] Despite the promising results, the system requires the presence of a mild base and of an inorganic additive such as KI for optimal performance. Nevertheless, quinone formation was still prevalent. To address these issues, we prepared simpler CuII 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 CuII 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 CuII-[N-carboxymethyl(amino acid)] complexes


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 and also as pH sensors, in combination with other pH-responsive groups. 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.

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ISOSTRUCTURAL DECAVANADATE AND DECANIOBATE DECOMPOSE INTO DIFFERENT OLIGOMERS: BIOCHEMICAL RELEVANCE

M. Aureliano¹, C. André Ohlin², M. O. Vieira³, M. P. M. Marques³,⁴, W. H. Casey⁵ and L. A. E. Batista de Carvalho³

¹ FCT and CCmar, University of Algarve, 8005-139 Faro, Portugal
² School of Chemistry, Monash University, Clayton, Vic 3800, Australia
³ Unidade de I&D Química-Física Molecular, Department of Chemistry, University of Coimbra, Portugal
⁴ Department of Life Sciences, University of Coimbra, 3004-535 Coimbra, Portugal
⁵ Department of Chemistry, University of California, Davis, California 95616, USA

maalves@ualg.pt

The decaniobate ion, (Nb₁₀=[Nb₁₀O₂₈]⁶⁻) being isoelectronic and isostructural with the decavanadate ion (V₁₀=[V₁₀O₂₈]⁶⁻), has been useful in advancing the understanding of V₁₀ toxicology and pharmacological activities. In the present study, the solution chemistry of Nb₁₀ and V₁₀ between pH 4 and 12 is studied by Raman spectroscopy (Fig. 1). Solutions of V₁₀ and Nb₁₀ are both kinetically stable at basic pH conditions for at least two weeks, at moderate temperatures. Whereas the Raman spectra of V₁₀ shows that this vanadate species remains detectable until pH 8.59, the Nb₁₀ species is detected in solution up to pH 10.80. It is suggested that, under alkaline conditions, V₁₀ dissociates into smaller tetrahedral vanadate oligomers such as V₂ and V₄, whereas Nb₁₀ dissociates into Nb₆ [1]. These findings have relevant biochemical consequences and the toxicology activities and pharmacological applications of vanadate and niobate polyoxometalates are discussed.

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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 \{\text{Mo}_{36}\} and \{\text{Mo}_{57}\text{M}_6\} type clusters, the big-spheres of the type \{\text{Mo}_{132}\} and \{\text{Mo}_{72}\text{M}_{30}\}, the big-wheel of the type \{\text{Mo}_{154}\} and the largest structurally well characterized cluster \{\text{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.

\[\text{Figure 1: Structure of the nanosized Mo}_{154}\text{-type wheel}\]

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HIGLY LUMINESCENT SULFIDE CLUSTERS
CONFINED IN ZEOLITES

A. Ruivo¹,², E. Coutino-Gonzalez³, M. Santos¹, W. Baekelant³, E. Fron³, M. B. J. Roelfaers⁴, F. Pina¹, J. Hofkens³ and C. A. T. Laia¹

¹ LAQV-REQUIMTE, Faculty of Science and Technology, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal
² Research Unit VICARTE, Faculty of Science and Technology, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal
³ Division of Molecular Imaging and Photonics, Department of Chemistry, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium
⁴ Centre for Surface Chemistry and Catalysis, Department of Microbial and Molecular Systems, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium
catt@fct.unl.pt

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 Na₈[SiAlO₄]₆SₓCl₂-2ₓ 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 S₂⁻ 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 S₄⁻² 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 S₂⁻ 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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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-aminomethyl)salicyldidate) 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).
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 Zn₄O 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](image_url)

**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.

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

Ana L. Daniel-da-Silva and Tito Trindade

CICECO-Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
ana.luisa@ua.pt

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.

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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. 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. 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 and single ion magnet. 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.

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RAMAN IMAGING AND SERS STUDIES ON POLYOXOMETALATES AND ITS NANOCOMPOSITES

Sara Fateixa, Filipe Lemos, Tito Trindade and Helena Nogueira

CICECO and Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
helenanogueira@ua.pt

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 \( \text{Mo}_{368} \) cluster in which the high number of delocalized electrons allows the measurement of the SERS spectrum [3].

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

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

Diana M. Fernandes¹, Ali Haider², Ulrich Kortz² and Cristina Freire¹

¹ REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal
² Jacobs University, Department of Life Sciences and Chemistry, P.O. Box 750 561, 28725 Bremen, Germany
diana.fernandes@fc.up.pt

Hydrogen (H₂), 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 H₂ 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 H₂ 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

Clara Pereira$^1$, José Valente$^{1,2}$, Rui S. Costa$^{1,2}$ and André M. Pereira$^2$

$^1$REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal

$^2$IFIMUP-IN, Departamento de Física e Astronomia, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal

ciera.pereira@fc.up.pt

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 $\eta^2$-ANS$_2$^{2+} (An = Th, U, Np)

Nuno A. G. Bandeira

Institute of Chemical Research of Catalonia (ICIQ) - Avda. Països Catalans, 16- 43007 Tarragona, Spain.
Centro de Química Estrutural - Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.
Centro de Química e Bioquímica - Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal.
nuno.bandeira@fc.ul.pt

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 $\eta^2$-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.

$$\left[ \begin{array}{c} \text{S} \equiv \text{An} \equiv \text{S} \end{array} \right]^{2+} \text{ vs. } \left[ \begin{array}{c} \text{An} \\ \text{S} \equiv \text{S} \end{array} \right]^{2+}$$

Figure 1: Linear versus triangular actinide di-sulphides.

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


LAQV-REQUIMTE, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
l.branco@fct.unl.pt

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

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.

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 [(H2Bn2Cyclam)Cu](CH3COO)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

F. F. Martins¹, A. I. Vicente¹, L. P. Ferreira²³, M. D. Carvalho¹, V. H. N. Rodrigues³, M. J. Calhorda¹ and P. N. Martinho¹

¹Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal
²BiolISI, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal
³Departament of Physics, University of Coimbra, 3004-516 Coimbra, Portugal

pnmartinho@ciencias.ulisboa.pt

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 nanodevices.[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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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.

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PHOTOLUMINESCENT NANOCRYSTALS IN ALUMINOBOROSILICATE GLASSES

Andreia Ruivo\textsuperscript{1,2}, Marta Ferro\textsuperscript{3}, Suzana M. Andrade\textsuperscript{4}, João Rocha\textsuperscript{3}, Fernando Pina\textsuperscript{1} and César A.T. Laia\textsuperscript{1}

\textsuperscript{1} LAQV-REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
\textsuperscript{2} Research Unit VICARTE, Glass and Ceramic for the Arts, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
\textsuperscript{3} CICECO, Department of Chemistry, Universidade de Aveiro 3810-193 Aveiro, Portugal
\textsuperscript{4} Centro de Química Estrutural, Complexo 1, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal

a.ruivo@campus.fct.unl.pt

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
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 CO$_2$ 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

Joana C. Almeida, Daniela S. Tavares, Ana Luísa Daniel-da-Silva, Eduarda Pereira and Tito Trindade

Department of Chemistry, CICECO and CESAM, University of Aveiro, 3810-193 Aveiro, Portugal
joana.cruz.almeida@ua.pt

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$_3$O$_4$ 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$_2$O$_4$ and CoFe$_2$O$_4$ 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$_2$O$_4$ and CoFe$_2$O$_4$ NPs as compared to the application of the Fe$_3$O$_4$ 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\textsubscript{552} AND THE ELECTRON TRANSFER SUBUNIT OF NITRIC OXIDE REDUCTASE FROM MARINOBACTER HYDROCARBONOCLASTICUS

Susana Ramos, Rui M. Almeida, Cristina M. Cordas, José J. G. Moura, Sofia R. Pauleta and Isabel Moura

UCIBIO, REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia da Universidade NOVA de Lisboa, Campus de Caparica, 2829-516 Caparica
srg.ramos@fct.unl.pt

Nitric Oxide Reductase (NOR) is able to catalyze the reduction of NO to N\textsubscript{2}O 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\textsubscript{3}-type heme linked via an oxo-bridge to a non-heme Fe atom on the NOR-B subunit. Cytochrome c\textsubscript{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\textsubscript{552} from *M. hydrocarbonoclasticus*. The expressed cytochrome c\textsubscript{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\textsubscript{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

Maria A. Antunes¹, Joana T. Coutinho¹, Isabel C. Santos¹, Joaquim Marçalo¹, Laura C. J. Pereira¹, Manuel Almeida¹, José J. Baldovi², Eugenio Coronado² and Alejandro Gaita-Ariño²

¹Centro de Ciências e Tecnologias Nucleares (C2TN), Instituto Superior Técnico, Universidade de Lisboa, E.N. 10 km 139,7, 2695-066 Bobadela LRS, Portugal
²Instituto de Ciencia Molecular (ICMol), Universitat de València, C/Catedrático José Beltrán 2, E-46980 Paterna, Spain
ma.antunes@ctn.tecnico.ulisboa.pt

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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SYNTHESSES, STRUCTURAL INVESTIGATIONS AND LANGMUIR-BLODGETT THIN FILMS OF SPIRO-BINO-SPIRO TRIMERIC PHOSPHAZENES CONSIST OF N₂O₂ DONOR TYPE SYMMETRIC TETRADENTATE LIGANDS

Nuran Asmafiliz¹, Zeynel Kılıç¹, Mehmet Civan² and Tuncer Hökelek²

¹ Department of Chemistry, Ankara University, 06100 Ankara, Turkey
² Department of Physics, Hacettepe University, 06800 Ankara, Turkey
gurun@science.ankara.edu.tr

Cyclophosphazenes refer to a significant family of heterocyclic compounds with an inorganic skeleton that includes the repeating unit [NPX₂]ₙ (n=3-40; X=halogens, different inorganic, organic and organometallic groups) [1 and 2]. The hexachlorocyclotriphosphazene (cyclic trimer, N₃P₃Cl₆) 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 N₂O₂ 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, ¹H, ¹³C{¹H} and ³¹P{¹H} 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.

NOVEL RUTHENIUM(II) THIOSEMICARBAZONE COMPLEXES AS ANTICANCER METALLODRUG CANDIDATES

Ana Sofia Assis\(^1,2\), Ana Cristina Poeta\(^1,2\), Ricardo Teixeira\(^1\), Andreia Valente\(^1\), Fernanda Marques\(^3\), M. Paula Robalo\(^4\), Susana Santos\(^2\), Ana Isabel Tomaz\(^1\) and M. Helena Garcia\(^1\)

\(^1\) Centro de Química Estrutural, Faculdade de Ciências (CQE-FC), Universidade de Lisboa, Campo Grande, 1749-016, Lisboa, Portugal
\(^2\) Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal
\(^3\) Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, Estrada Nacional 10, 2695-066 Bobadela, Portugal
\(^4\) Centro de Química Estrutural, Instituto Superior Técnico (CQE-IST), Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

asassis@fc.ul.pt

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 \([\text{Ru}(\text{N}N)\text{X}]_2\) (\(\text{N}N=2,2'\text{-bipyridine}; \text{X}=\text{PF}_6^-, \text{CF}_3\text{SO}_3^-\)) were synthetized and fully characterized by several techniques. Their anticancer activity was evaluated \textit{in vitro} against ovarian adenocarcinoma and triple-negative breast human cancer cells. We present herein our first results on these new highly promising agents.


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

Serap Beşli¹, Ceylan Mutlu Balci¹, Hakan Cantürk¹, Semih Doğan¹, Fatma Yüksel¹ and Christopher W. Allen²

¹ Department of Chemistry, Gebze Technical University, 41400 Gebze-Kocaeli, Turkey
² Department of Chemistry, University of Vermont, Burlington, Vermont 05405-0125, USA
besli@gtu.edu.tr

Recently, new types of cyclophosphazenes having very active P-halogen bonds were synthesised from the de-protonation reaction of aminocyclotriphosphazene derivatives containing 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.

In this study, nucleophilic substitution reactions of the N(R),N(R)-spiro bridge octachlorobiscyclotriphosphazene, N₂P₂Cl₄[N(CH₂)₅CH₃]₂N₃P₃Cl₄ (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, ¹H and ³¹P NMR spectroscopy. The molecular structures of compound 3 were also established by Xray crystallography [4].

NEW APPROACH FOR SYNTHESIZING NANOSTRUCTURED INTERMETALLIC COMPOUNDS CONTAINING f BLOCK ELEMENTS

Ana C. Ferreira, Joaquim B. Branco, João Paulo Leal and T. Almeida Gasche

C²TN, IST-UL, Campus Tecnológico e Nuclear, Estrada Nacional 10, ao km 139,7, 2695-066 Bobadela LRS, Portugal
jbranco@ctn.tecnico.ulisboa.pt

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 LaNi₅, SmCo₅ and DyFe₃ 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 LaNi₅ 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).

Figure 1: LaNi₅ nanoparticles characterization (A) XRD pattern, (B) SEM image.

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STRUCTURAL AND ELECTRONIC EFFECTS IN THE ARCHITECTURES OF [Mo(η³-C₃H₅)(CO)₂X(LL’)] COMPLEXES

Maria José Calhorda and Paulo J. Costa

Centro de Química e Bioquímica, DQB, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal
mjc@fc.ul.pt

The allylic complexes [Mo(η³-C₃H₅)(CO)₂X(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(η³-C₃H₅)(CO)₂Br(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.

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.

Acknowledgements: The authors thank FCT for Financial support (UID/MULTI/00612/2013). PJC acknowledges FCT for the "Investigador FCT" Program (IF/00069/2014).

SYNTHESIS OF LOW GENERATION METALLODENDRIMERS AS AN ANTICANCER PRODRUG

Cláudia S. Camacho, Helena Tomás and João Rodrigues

CQM- Centro de Química da Madeira, MMRG, Universidade da Madeira, Campus da Penteada, 9000-390 Funchal, Portugal
ccamacho@uma.pt

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 as 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 metalloendrimers.

Acknowledgments: This research was supported by Fundação para a Ciência e a Tecnologia (FCT) with Portuguese Government funds through the CQM Strategic Project PEst-OE/QUI/UI0674/2013 and the NMR Network – (PTNMR-2015). CC acknowledge a research grant from Núcleo Regional da Liga Portuguesa Contra o Cancro. We recognize the continuous support of our work by VidaMar Resorts Madeira.

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

José M. Carretas1, Adelaide Cruz1, Phuong D. Dau2, John K. Gibson2 and Joaquim Marçalo1

1Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, 2695-066 Bobadela LRS, Portugal
2Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
carretas@ctn.tecnico.ulisboa.pt

It has previously been demonstrated that addition of molecular oxygen to gas-phase U(V)O2+ results in oxidation to U(VI)O2(O2)+, which comprises a superoxo O2− ligand [1]. Several gas-phase anionic uranyl(V) complexes [U(V)O2X2]− (including X = CH3CO2) were produced by electrospray ionization (ESI) and reacted with O2 in a quadrupole ion trap (QIT) mass spectrometer to form uranyl(VI) superoxo complexes, [U(VI)O2X2(O2)]− [2]. We surmised that a molecule with an electron affinity (EA) higher than that of O2 (EA = 0.4 eV [3]), such as NO2 (EA = 2.3 eV [3]), should also oxidize uranium(V) complexes. In fact, it was found that NO2 associates with [U(V)O2(CH3CO2)2]− to yield [U(VI)O2(CH3CO2)2(NO2)]− in which oxidation of U(V) to U(VI) is achieved by the reduction of NO2 to NO2− [4]. SO2 has an EA = 1.1 eV [3] intermediate between O2 and NO2 and therefore is a good candidate to be tested in reactions with uranyl(V) complexes. Previously, the [U(V)O2(CH3SO2)2]− complex was prepared by collision induced dissociation (CID) of [U(V)O2(CH3SO2)2]− in a QIT via C-S bond cleavage and CH3 elimination; the SO2 ligand can be considered as an SO2− anion [5].

Uranyl(V) acetate anionic complexes were produced by ESI and allowed to react with O2 and SO2 in a QIT mass spectrometer leading to uranium(VI) complexes (eqn. 1-2). The exchange reaction of SO2 by O2 was observed (eqn. 3) but the reverse reaction does not occur.

\[
[U(V)O_2(CH_3CO_2)_2]^− + O_2 \rightarrow [U(VI)O_2(CH_3CO_2)_2(O_2)]^− \quad (1)
\]

\[
[U(V)O_2(CH_3CO_2)_2]^− + SO_2 \rightarrow [U(VI)O_2(CH_3CO_2)_2(SO_2)]^− \quad (2)
\]

\[
[U(VI)O_2(CH_3CO_2)_2(SO_2)]^− + O_2 \rightarrow [U(VI)O_2(CH_3CO_2)_2(O_2)]^− + SO_2 \quad (3)
\]

We have demonstrated that neutral SO2 can be activated by uranyl(V) complexes and be reduced to SO2−.

Acknowledgments: The work of JMC and JM was supported by the Fundação para a Ciência e a Tecnologia through RNEM-Portuguese Mass Spectrometry Network and project UID/Multi/04349/2013. The work of PDD and JKG was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Heavy Element Chemistry, at LBNL under Contract No. DE-AC02-05CH11231.

**Ag(I) CAMPHOR COMPLEXES: CYTOTOXIC AND ANTIBACTERIAL PROPERTIES**

João M. S. Cardoso¹, Jorge H. Leitão³, Fernanda Marques², Soraia I. Guerreiro³ and M. Fernanda N. N. Carvalho¹

¹Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1049-001 Lisboa, Portugal
²Centro de Ciências e Tecnologias Nucleares (C²TN), Instituto Superior Técnico, Universidade de Lisboa, Estrada Nacional 10 (km 139,7), 2695-066 Bobadela LRS, Portugal
³iBB - Institute for Bioengineering and Biosciences and Department of Bioengineering, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais1049-001, Lisboa, Portugal

fcarvalho@ist.utl.pt

Camphor derivatives of the imine type (Lₐ, Lₐ₁, Lₐ₂, 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](image)

The biological properties of complexes [Ag(NO₃)(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(NO₃)(Lₐ)] additionally displays anti-proliferative activity which is one order of magnitude higher than cisplatin (Table 1).

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>S. aureus Newman</th>
<th>P. aeruginosa 477</th>
<th>B. contaminans IST408</th>
<th>E. coli ATCC 25922</th>
<th>A2780</th>
<th>A2780 cisR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(NO₃)(Lₐ)</td>
<td>259</td>
<td>138</td>
<td>127</td>
<td>123</td>
<td>0.76 ± 0.29</td>
<td>0.51 ± 0.10</td>
</tr>
<tr>
<td>Ag(NO₃)(Lₐ₁)</td>
<td>118</td>
<td>68</td>
<td>97</td>
<td>98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag(NO₃)(Lₐ₂)</td>
<td>95</td>
<td>39</td>
<td>81</td>
<td>49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag(NO₃)(Lₐ₂)</td>
<td>73</td>
<td>19</td>
<td>36</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag(NO₃)(Lₐ₂)</td>
<td>119</td>
<td>105</td>
<td>96</td>
<td>98</td>
<td></td>
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</tr>
</tbody>
</table>

**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.

DECORATED NANO Particles FOR MAGNETIC HYPERTHERMIA

L. P. Ferreira\textsuperscript{1,2}, M. M. Cruz\textsuperscript{1}, S. G. Mendo\textsuperscript{3}, A. F. Alves\textsuperscript{3}, S. Reis\textsuperscript{4}, S. Costa Lima\textsuperscript{4}, M. Godinho\textsuperscript{1} and M. D. Carvalho\textsuperscript{3}

\textsuperscript{1} BioISI, Biosystems and Integrative Sciences Institute, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa
\textsuperscript{2} Department of Physics, University of Coimbra, 3004-516 Coimbra
\textsuperscript{3} CQB, Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa
\textsuperscript{4} UCIBIO/ Requimte, Department of Chemical Sciences, Faculdade de Farmácia, Universidade do Porto, R. Jorge Viterbo Ferreira, 228, 4050-313 Porto

mdcarvalho@ciencias.ulisboa.pt

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.\textsuperscript{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.\textsuperscript{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\textsuperscript{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\textsubscript{3}O\textsubscript{4}, CoFe\textsubscript{2}O\textsubscript{4} and MnFe\textsubscript{2}O\textsubscript{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\textsuperscript{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\textsuperscript{-1}.


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

Cristina M. Cordas#, Susana Ramos#, Rui M. Almeida, José J. G. Moura, Sofia R. Pauleta and Isabel Moura

UCIBIO, REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

#These two authors contributed equally to this work.
cristina.cordas@fct.unl.pt

Nitric Oxide Reductase (NOR) is an enzyme that takes part in the denitrification pathway, catalyzing the reduction of NO to N2O. 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 b3-type heme linked to a non-heme Fe atom and a b-type heme (on the NORB subunit). Cytochrome c552 (Cyt c552) 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 c552 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 c552 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.

Layered Lanthanide Hydroxide (LLnH) with composition Ln$_8$(OH)$_{20}$Cl$_4\cdot$nH$_2$O (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$6H$_2$O (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 pursue 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]

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.

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

Tiago F. C. Cruz and Pedro T. Gomes

Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa,
Av. Rovisco Pais, 1, Lisboa, Portugal
carpteirocruz@gmail.com

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 KHBEt₃, 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.](image)

**Acknowledgements:** We thank the Fundação para a Ciência e a Tecnologia for financial support (Projects UID/QUI/00100/2013, RECI/QEQ-QIN70189/2012) and for a fellowship to T.F.C.C. (PD/BD/52372/2013).

Poster Communications  PC17

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

Liliana Damas¹, Marta Piñeiro¹, Beatriz Royo² and Mariette M. Pereira¹

¹ CQC, Department of Chemistry, University of Coimbra, Rua Larga, 3004-535 Coimbra
² Instituto de Tecnologia Química e Biológica António Xavier, ITQB, Av. da República, 2780-157 Oeiras, Portugal

lilianadamas90@gmail.com

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](image_url)

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

**Acknowledgements**: The authors thank Fundação para a Ciência e a Tecnologia (FCT) for the financial support to Coimbra Chemistry Centre (PEst-OE/QUI/UI0313/2014) and to the UC-NMR facility. L. Damas acknowledges financial support from FCT (PD/BD/106020/2014 CATSUS PhD Program).

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$_2$O, 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$_2$S), 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$_2$S 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

Ana Fernandes, Lígia O. Martins and Beatriz Royo

Instituto de Tecnologia Química e Biológica/António Xavier-UNL, Oeiras, Lisboa, Portugal
ana.fernandes@itqb.unl.pt

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 metal catalysts 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)Cl₂ complexes in N-alkylation of amines with alcohols.

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MAGNETIC HYBRID NANOSORBENTS FOR HERBICIDE UPTAKE FROM WATER

Tiago Fernandes, Sofia F. Soares, Tito Trindade and Ana L. Daniel-da-Silva

CICECO-Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
jffernandes@ua.pt

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.

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

O. Ferreira¹, P. Rijo², M. J. Calhorda³, J. C. M. Bordado¹ and E. R. Silva¹, ³

¹ Centro de Recursos Naturais e Ambiente, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal
² Research Center in Biosciences and Health Technologies – CBIOS, Universidade Lusófona de Humanidades e Tecnologias, 1749-024 Lisboa, Portugal
³ Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal

olga.ferreira@tecnico.ulisboa.pt

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)

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

Cláudia A. Figueira¹, Patrícia S. Lopes¹, Francisco Lemos² and Pedro T. Gomes¹

¹ Centro de Química Estrutural, ² CERENA, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1, 1049-001, Lisboa, Portugal
claudia.figueira@tecnico.ulisboa.pt

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 ¹H and ¹³C NMR spectroscopy and GPC/SEC chromatography, presenting the highest branching degree so far reported (160-170/1000C).

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

Kin Hong Liew¹,², Mariana Rocha¹, Clara Pereira¹, Ana L. Pires², André M. Pereira², Mohd Ambar Yarmo³, Joon Ching Juan⁴, Rahimi M. Yusop³, Andreia F. Peixoto¹ and Cristina Freire¹

¹ REQUIMTE-LAQV, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal
² IFIMUP-IN, Department of Physics and Astronomy, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal
³ School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM, Bangi, Selangor Darul Ehsan, Malaysia
⁴ Nanotechnology & Catalysis Research Centre (NANOCAT), University of Malaya, 50603 Kuala Lumpur, Malaysia
acfreire@fc.up.pt

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 MnFe₂O₄ 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.

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TWO PHOTON ABSORPTION PROPERTIES OF TRANSITION METAL COMPLEXES OF TETRAARYLAZADIPYROMETHENE COMPOUNDS

M. Hayvali¹, E. Akhüseyin², O. Türkmen¹, B. Küçüköz², H. Yılmaz¹, A. Karatay², G. Sevinç¹ and H. G. Yağlıoğlu²

¹Department of Chemistry, Faculty of Science, Ankara University, 06100 Beşevler, Ankara, Turkey
²Department of Engineering Physics, Faculty of Engineering, Ankara University, 06100 Beşevler, Ankara, Turkey
hayvali@science.ankara.edu.tr

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

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(L²)₂ and 2374 GM for Co(L³)₂ complexes.

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

Serhat Koçoğlu$^{1,2}$ and Zeliha Hayvalı$^1$

$^1$Department of Chemistry, Ankara University, Faculty of Science, 06100, Ankara, Turkey
$^2$Bozok University, Science and Technology Application and Research Center, Yozgat, Turkey
zhayvali@science.ankara.edu.tr

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.

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.

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$_2$L1 and H$_2$L2) and their different reactivity.

The reactions of H$_2$L1 and H$_2$L2 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.

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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).

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

Paramasivam Krishnamoorthy¹, Bruno Ferreira¹, Clara S. B. Gomes¹, Diogo Vila-Viçosa⁴, Ana Charas², Jorge Morgado²-³, Maria José Calhorda⁴, António L. Maçanita¹ and Pedro T. Gomes¹

¹ Centro de Química Estrutural; ² Instituto de Telecomunicações; ³ Dept. of Bioengineering, Instituto Superior Técnico, Univ. Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal ⁴ Centro de Química e Bioquímica, DQB, Fac. Ciências, Univ. Lisboa, Campo Grande, Ed. C8, 1749-016 Lisboa, Portugal

krishnachemist@gmail.com

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-(Nalkylimino)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.

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SYNTHESIS AND CHARACTERISATION OF GRAPHENE DOPED WITH NITROGEN AND SULPHUR HETEROATOMS

Iwona Kuźniarska-Biernacka¹, Renata Matos¹, Catarina Alves¹, Mariana Araújo¹, João H. Belo², João P. Araujo², Clara Pereira¹ and Cristina Freire¹

¹ REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal
² IFIMUP-IN, Departamento de Física e Astronomia, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal
iwonakb@fc.up.pt

Graphene is a two-dimensional sheet of carbon atoms in a hexagonal configuration with atoms bonded by sp² 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.

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

Lígia M. C. Silva¹, Pedro G. Rosado¹, Joaquim B. Branco¹, M. A. Antunes¹ and João P. Leal¹,²

¹Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, 2695-066 Bobadela, Portugal
²Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal
jpleal@ctn.tecnico.ulisboa.pt

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-butaneol. 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.](image)

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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 pKₐ values (pKₐ₁=3.50, pKₐ₂=4.50, pKₐ₃=9.60, pKₐ₄=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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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 polynucleate 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 moieties 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

Joana L. Lopes, Ana C. Estrada and Tito Trindade

Department of Chemistry - CICECO Aveiro Institute of Materials,
University of Aveiro, 3810-193 Aveiro, Portugal
jllopes@ua.pt

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$_2$S 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

Rita Lopes¹, Carolina Vinagreiro², Marta Pineiro², Mariette M. Pereira² and Beatriz Royo¹

¹ Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Av. da República, EAN, 2780-157 Oeiras, Portugal
² Departamento de Química, Universidade de Coimbra, Rua Larga, 3004-535 Coimbra
riopes@itqb.unl.pt

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 H₂ 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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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 peptides 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.

![Figure 1. Different topologies of carbosilane dendrimers.](image)

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

Filipe Madeira, M. João Ferreira, Luís F. Veiros and Ana M. Martins

Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal
filipe.madeira@tecnico.ulisboa.pt

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 (CpBz) ligand, [CpBzMgR(THF)n]m (n = 1, m = 1, R = Me (1), Et (2); n = 1, m = 2, R = Br (3), n = 0, m = 2, R = OCH2Ph (4)). Magnesocene [CpBz2Mg] (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(C6F5)3 and carry out fast group exchanges between Mg and B atoms to generate cationic species possessing [B(C6F5)4] as counterion.

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

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METAL SUBSTITUTED RUBREDOXIN: MODELLING STUDY

Biplab K Maiti, Luisa B. Maia, Artur Moro, João C. Lima, Cristina Cordas, Isabel Moura and José J. G. Moura

UCIBIO, REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
b.maiti@fct.unl.pt

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 Fe⁰ or Fe³⁺ 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 Cu⁰-Rd and Cu¹-Rd pairs are complex.[4] Mononuclear Cu⁰-thiolate centres are fascinating to chemist due to their intense, Cu⁰-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 Cu⁰-Rd center and proximal amino acid residues, such as, Tyr, Trp and Cys. Two irreversible peak at Epån = -0.12 V and Epcc = -0.66 V with large separation (ΔEp = 0.54 V) indicates that the geometry of Cu-site suffers rearrangement during the redox process. When Cu¹-Rd is oxidized to Cu²⁻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 Cu²⁻site, but the reduction step takes place mainly photochemically and Tyr and Trp residues are involved in the process.

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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 \( \text{U(III)} \) complex, \([\text{U(\kappa^6-\{tBu_2ArO\}_2Me_2-cyclam})I]\), 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 \( \text{U(IV)} \) complex, \([\text{U(\kappa^4-\{tBu_2ArO\}_2Me_2-cyclam})\text{(N}_3\text{(\mu-N)}\text{U(\kappa^5-\{tBu_2ArO\}_2Me_2-cyclam})]\). Furthermore, the reactive nature of the \( \text{U(III)} \) complex and the hemilabile behavior of the macrocycle core allowed to cleave the \( \text{N=N} \) bond of azobenzene and form the \( \text{trans-bis(imido) U(VI)} \) complex \([\text{U(\kappa^4-\{tBu_2ArO\}_2Me_2-cyclam})(=\text{NPh})_2]\), 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 \([\text{U(III)}(\kappa^6-\{tBu_2ArO\}_2Me_2-cyclam})\]) and \([\text{U(IV)}(\kappa^6-\{tBu_2ArO\}_2Me-cyclam})\]) with oxygen-atom-transfer reagents (e.g. pyridine-N-oxide, \( \text{NaNO}_2 \)) were tested. These recent results will be presented in this communication, including the dimeric uranyl complex \([\{\text{UO}_2\}_2(\mu-\{tBu_2ArO\}_2\text{Me-cyclam})_2(\text{thf})\}_2\) (Figure) obtained from oxidation of the \( \text{U(IV)} \) compound with \( \text{NaNO}_2 \).

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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 (RPNP)M(III) (R = iPr, Ph) complexes of yttrium, titanium and vanadium. The solid-state structures of (PhPNP)TiCl$_3$ and (iPrPNP)VCl$_3$, determined by single-crystal X-ray diffraction, are presented. Reactions of (PhPNP)VCl$_3$ with oxidizing agents as well as chloride exchange reactions will be discussed.

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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**

Nuno M. R. Martins¹, Sellamuthu Anbu¹, Kamran T. Mahmudov¹,², Luisa M. D. R. S. Martins¹,³, M. Fátima C. Guedes da Silva¹ and Armando J. L. Pombeiro¹

¹Centro de Química Estrutural, IST, Universidade de Lisboa, 1049–001 Lisboa, Portugal
²Department of Chemistry, Baku State University, Az 1148 Baku, Azerbaijan
³Chemical Engineering Department, ISEL, 1959-007 Lisboa, Portugal
nunommartins@tecnico.ulisboa.pt

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 pharmacological proprieties and even in catalytic reactions [2,3].

A series of water soluble copper(II) complexes, 

\[ \text{Cu}_2(X)(\mu-\text{HL})_2, \ X = \text{CH}_3\text{OH (1)} \text{ or } (\text{CH}_3)_2\text{NCHO (2)}, \text{ and [Cu(en)(\mu-\text{HL})-}\text{CH}_3\text{OH-H}_2\text{O (3)} \] (Figure 1) were prepared by reaction of Cu¹¹ nitrate hydrate with the new (E/Z)-4-(2-(1-cyano-2-ethoxy-2-oxoethylidene)hydrazinyl)-3-hydroxybenzoic acid (H₃L), in the presence (for 3) or absence (for 1 and 2) of ethylenediamine (en), and characterized by conventional analyses. It is shown that cooperative \( E,Z \to E \) isomerization of H₃L, induced by coordination and ionic interactions, occurs upon interaction with the Cu¹¹ 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 H₃L¹ in the synthesis of Cu¹¹ complexes 1–3 and their applications.

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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

Sara Martins¹, Andreia Machado², César Laia³ and Marcia Vilarigues¹,²

¹ Department of Conservation and Restoration, Faculty of Science and Technology, Universidade NOVA de Lisboa, Portugal
² Research Unit VICARTE – Glass and Ceramics for the Arts, Faculty of Science and Technology, NOVA University of Lisbon, Portugal
³ LAQV-REQUIMTE, Faculty of Science and Technology, Universidade NOVA de Lisboa, Portugal
sp.martins@campus.fct.unl.pt

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 studied extensively - the ionic liquids (ILs). The selected and synthetized IL was the luminescent trihexyltetradecilphosphonium 1-anilino-naphtalene 8-sulfonate ([P₆,₆,₆,1₄][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 [P₆,₆,₆,1₄][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 profilometry images.

The analytical results showed the [P₆,₆,₆,1₄][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

Sandra Matos and Fernando Veloso

Delphi, Polo Tecnológico de Lisboa, Lt. 4 Estrada do Paço do Lumiar, 1600-545 Lisboa, Portugal
sandra.matos@delphi.com; fernando.veloso@delphi.com

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

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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.

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

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A Layered Lanthanide Hydroxide (LLH) material based on europium (LEuH, \( \text{Eu}_8\text{(OH)}_{20}\text{Cl}_4\cdot6\text{H}_2\text{O} \)) 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 \( \text{Eu}^{3+} \) 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 (\( \lambda_{\text{em}} = 380 \) nm) and europium (\( \lambda_{\text{em}} = 615 \) nm) emission intensities upon excitation of NDC (\( \lambda_{\text{ex}} = 357 \) nm) were used to discriminate between the different anions. Phosphate was found to have the highest degree of intercalation, yielding a 160% 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 (\( \rightarrow \)) and the sequestration mechanism of the remediation process (\( \leftarrow \)).

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POLYPHENOLIC CARBOSILANE DENDRIMERS AS PROSTATE ANTIcANCER AGENTS

Gabriel Mencia¹, Natalia Sanz¹, Laura Muñoz², Marta Maroto¹, Rafael Gomez¹, Paula Ortega¹, Mª José Carmena² and Fco. Javier de la Mata¹

¹ Departamento de Química Orgánica y Química Inorgánica. Universidad de Alcalá, Campus Universitario, E-28871 Alcalá de Henares (Spain) - Networking Research Center on Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN), Spain
² Departamento de Biología de Sistemas. Universidad de Alcalá, Campus Universitario, E-28871 Alcalá de Henares, Spain

paula.ortega@uah.es

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 and 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.

Figure 1. Proposed structures for dendrimers

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

Elisa Palma¹,², Filipa Mendes¹, Goreti Ribeiro Morais¹,³, Inês Rodrigues¹, Isabel Cordeiro Santos¹, Maria Paula C. Campello¹, Paula Raposinho¹, Isabel Correia², Sofia Gama¹,⁴, Dulce Belo¹, Vitor Alves⁵, Antero J. Abrunhosa⁵, Isabel Santos¹ and António Paulo¹

¹ Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, Estrada Nacional 10 (km 139,7), 2695-066 Bobadela LRS, Portugal
² Centro Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1049-001 Lisboa, Portugal
³ Current address: Institute of Cancer Therapeutics, School of Life Sciences, University of Bradford, Bradford, UK
⁴ Current address: Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena, Germany
⁵ Instituto de Ciências Nucleares Aplicadas à Saúde, Universidade de Coimbra, Coimbra, Portugal
elisa@ctn.tecnico.ulisboa.pt

Aiming to explore alternative mechanisms of cellular uptake and cytotoxicity, we have studied a new family of copper(II) complexes (CuL¹–CuL⁴) 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 Cu⁰ATSM, 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 Cu⁰ATSM. Unlike Cu⁰ATSM, the new complexes were able to circumvent cisplatin resistance.

In vitro studies in cancer cell lines with ⁶⁴CuL¹–⁶⁴CuL⁴ showed a remarkably augmented cellular uptake compared with ⁶⁴CuATSM. The enhanced cellular uptake together with the citotoxicity of ⁶⁴CuL¹,⁶⁴CuL⁴ indicates that this new family of Cu⁰BTSC 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.

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FLUORESCENT MATERIALS FROM ENCAPSULATED FLAVYLIA

A. Jorge Parola¹, Sandra Gago¹, César A. T. Laia¹, Fernando Pina¹, Bjorn Dieu² and Eduardo Coutiño²

¹ Dep. Química, FCT, Universidade NOVA de Lisboa, LAQV-RQEUIMTE, Campus de Caparica, 2829-516 Caparica, Portugal
² KU Leuven, Leuven Chem&Tech: Molecular Imaging and Photonics (MIP), Celestijnenlaan 200F post box 2404, 3001 Leuven, Belgium

ajp@fct.unl.pt

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 diffusion 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.

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

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

Leticia Quental¹, Paula Raposinho¹, Filipa Mendes¹, Isabel Santos¹, Carmen Navarro-Ranninger², Amparo Alvarez-Valdes², Huaiyi Huang³,⁴, Hui Chao⁴, Riccardo Rubbiani³, Gilles Gasser³, Adoración G. Quiroga² and António Paulo¹

¹ Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, Estrada Nacional 10, 2695-066 Bobadela LRS, Portugal
² Departamento de Química Inorgánica, Universidad Autonoma de Madrid, ES-28049 Madrid, Spain
³ Department of Chemistry, University of Zurich, CH-8057 Zurich, Switzerland
⁴ School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou, 510275, China
apaulo@ctn.tecnico.ulisboa.pt

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 uptaken 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

J. P. Leal², B. Monteiro², H. Cruz¹, M. Outis¹, F. Fernandes¹,³, C. A. T. Laia¹ and C. C. L. Pereira¹

¹ REQUIMTE, Faculdade de Ciências e Tecnologia, 2829-516 Caparica, Portugal
² Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, E.N. 10 (km 139,7), 2695-066 Bobadela LRS, Portugal
³ Centro de Química-Física Molecular and Institute of Nanoscience and Nanotechnology, Instituto Superior Técnico, University of Lisbon, Lisbon, Portugal
ccl.pereira@fct.unl.pt

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 25°C and a strong red colored compound close to 80°C, moving to purple at higher temperatures near 100°C. It has a quantum yield ($\phi$) 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: [P₆,₆,₆,₁₄][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](image)

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HYBRID CONJUGATES OF Fe₃O₄@SiO₂ NANOPARTICLES AND CORROLE FOR PDT

Rute A. Pereira¹, Joana F. B. Barata¹,² and Tito Trindade¹

¹ Department of Chemistry & CICECO – Aveiro Institute of Materials, University of Aveiro, Aveiro, Portugal
² Department of Chemistry & QOPNA, University of Aveiro, Aveiro, Portugal
rule.pereira@ua.pt

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 Fe₃O₄@SiO₂ 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 Fe₃O₄@SiO₂ 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**

Márcia Pessêgo, Sandra Gago, Fernando Pina, César A. T. Laia and A. Jorge Parola

LAQV@REQUINTE, Departamento de Química, FCT – Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal  
m.pessego@fct.unl.pt

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 compounds 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

João Costa Pessoa¹, Isabel Correia¹, Ielyzaveta Chorna¹, Maxim Kuznetsov¹ and Fernanda Marques²

¹ Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Portugal  
² Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, Portugal  
joao.pessoa@ist.utl.pt

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 V⁴⁺O₂⁻ 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. V⁴⁺O(carrier)ₙ, where carrier is an organic compound acting as a bidentate or tridentate ligand, two types of V⁴⁺O-carrier-hTF binding have been proposed: one with V⁴⁺ at the Fe-binding site, the other at surface imidazole or carboxylate groups [3]. The binding of a V⁴⁺O(carrier)ₙ species to surface His or Asp is possible and was recently confirmed by a x-ray diffraction study with lysozyme [4]. V⁴⁺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 V⁴⁺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 V⁴⁺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 IC₅₀ value (66 μM) was the concentration of V⁴⁺O(acac)₂ selected to carry out intracellular distribution studies. Data on the uptake of V⁴⁺O(acac)₂ by A2780 ovarian cells after 24 h of incubation is reported and discussed.

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SERS-ACTIVE MAGNETIC NANOSORBENTS FOR DETECTION OF ANTIBIOTICS IN WATER

Paula C. Pinheiro and Tito Trindade

Department of Chemistry, CICECO-Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro
pcpinheiro@ua.pt

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

Mara F. Pinto¹, Bernardo de P. Cardoso¹, Sónia Barroso², Ana M. Martins² and Beatriz Royo¹

¹Instituto de Tecnologia Química e Biológica António Xavier, ITQB, Av. da República EAN, 2780-157 Oeiras, Portugal
²Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
mara.pinto@itqb.unl.pt

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)I₂ (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 solvents in the performance of the catalyst will be discussed. Crystallisation of 1 by slow diffusion of Et₂O into MeCN solutions afforded single crystals of [Fe(bis-NHC)(bpy)₂]I₂; its structure has been determined by X-ray diffraction studies.

![Figure 1: Oxidation of alcohols in neat conditions with TBHP using the iron catalyst Fe(bis-NHC)(bipy)I₂.](image)

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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.\textsuperscript{1} Our group has been developing CPs based on 5-aminoisophthalic acid (H\textsubscript{2}Aip, 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\textsubscript{2}Aip 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.\textsuperscript{2}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Structures of: a) 5-aminoisophthalic acid (H\textsubscript{2}Aip), b) rhodamine derivatives based on H\textsubscript{2}Aip and c) naphthalimide derivatives based on H\textsubscript{2}Aip; d) chromatographic purification of one of the esterified rosamine compounds (RosAip1).}
\end{figure}

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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**

Ana I. Rodrigues, Paramasivam Krishnamoorthy, Bruno Ferreira, Clara S. B. Gomes, António Maçanita and Pedro T. Gomes

Centro de Química Estrutural, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
anapalharodrigues@tecnico.ulisboa.pt

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<sub>2</sub> complexes 4a-d and their quantum yields relationships.](image)

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

Fábio M. S. Rodrigues¹, César A. Henriques¹, Sónia A. C. Carabineiro², José L. Figueiredo², Marta Pineiro¹ and Mariette M. Pereira¹

¹CQC, Department of Chemistry, University of Coimbra, Rua Larga, 3004-535 Coimbra, Portugal
²LCM - Laboratory of Catalysis and Materials, Associate Laboratory LSRE/LCM, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal
fmsrodrigues.qui@gmail.com

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

Margarida I. Rodrigues, Sofia F. Soares, Tito Trindade and Ana L. Daniel-da-Silva

CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
mpenedorodrigues@ua.pt

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 (Fe₃O₄) 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 Fe₃O₄ 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

Joana M. Dantas¹, Telma Simões¹, Leonor Morgado¹, Clara Caciones¹, Ana P. Fernandes¹, Marta A. Silva¹, Marta Bruix², P. Raj Pokkuluri³ and Carlos A. Salgueiro¹

¹ UCIBIO-Requimte, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, Caparica, Portugal
² Departamento de Química Física Biológica, Instituto de Química Física Rocasolano, CSIC, Madrid, Spain
³ Biosciences Division, Argonne National Laboratory, Lemont, Illinois 60439, USA
csalgueiro@fct.unl.pt

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 Phe⁶ 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 b5 REDUCTASE

Alejandro K. Samhan-Arias¹, Luísa B. Maia¹, Carlos Gutiérrez-Merino² and José J. G. Moura¹

¹ UCIBIO, REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
² Department of Biochemistry and Molecular Biology, Faculty of Sciences, University of Extremadura, 06006, Badajoz, Spain
alejandro.samhan@fct.unl.pt

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 b5 reductase (Cb5R) 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 Cb5R, 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

Marta S. Saraiva and Maria José Calhorda

Centro de Química e Bioquímica, Faculty of Science, University of Lisbon, 1749-016 Lisboa, Portugal
mssaraiva@fc.ul.pt

New molybdenum complexes from the family [MoBr(η3-C3H5)(CO)2(L)] were synthesised by reaction of the precursor [MoBr(η3-C3H5)(CO)2(CH3CN)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 1H and 13C as well as elemental analysis.

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.

André M. N. Silva¹, Maria M. F. P. M. de Castro², Ângela D. A. Oliveira², Natércia J. Brás¹, João Coimbra¹, Pedro A. Fernandes¹, Maria J. Ramos¹ and Maria Rangel³

¹ REQUIMTE-UCIBIO, Dep. Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre, s/n, 4169-007 Porto, Portugal
² Dep. Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre, s/n, 4169-007 Porto, Portugal
³ REQUIMTE-UCIBIO, Instituto de Ciências Biomédicas Abel Salazar, University of Porto, Rua de Jorge Viterbo Ferreira n228, 4050-313 Porto, Portugal
andre.silva@fc.up.pt

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

Sofia F. Soares, Tania R. Simões, Maria António, Tito Trindade and Ana L. Daniel-da-Silva

CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
soliatsoares@ua.pt

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-isocyanatopropyltrimethoxysilane (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.

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 (project PTDC/CTMNAN/120668/2010) 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.

IRON-(AMINO ACID) COMPLEXES IN OXIDATIVE CATALYSIS

C. Teixeira¹, P. Adão¹, J. Pessoa¹ and B. Royo²

¹Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001, Lisboa, Portugal
²Instituto de Tecnologia Química e Biológica da Universidade Nova de Lisboa, Avenida da República, Campus da Estação Agronómica Nacional, 2780-157 Oeiras, Portugal
carlosbrandaot@tecnico.ulisboa.pt

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.

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

Yasemin Tümer¹, Nuran Asmafiliz², Zeynel Kılıç², Tuncer Hökelek³ and Leyla Açık⁴

¹ Department of Chemistry, Karabük University, 78050 Karabük, Turkey
² Department of Chemistry, Ankara University, 06100 Ankara, Turkey
³ Department of Physics, Hacettepe University, 06800 Ankara, Turkey
⁴ Department of Biology, Gazi University, 06500 Ankara, Turkey
yasemintumer@karabuk.edu.tr

Cyclophosphazenes containing (NPX₂)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, N₃P₃Cl₆, with N-methyl-N-monoferrocenyl-1,3-propanediamine, FcCH₂NH(CH₂)₃NHCH₃, produced mainly new cis- (1) and trans- (2) dispiro cyclic ferrocenylphosphazenes (Scheme 1). The FTIR, ¹H, ¹³C and ³¹P 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 dispiro cyclic 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) dispiro cyclic ferrocenylphosphazenes

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SYNTHESIS AND CHARACTERIZATION OF NEW POLYPHOSPHAZENES AS CATHODE MATERIALS

Aylin Uslu, Serkan Yeşilot, Ferda Hacivelioğlu, Gürkan Sayan, Sedat Küçükęköylü and Rezan Demir Çakan

Gebze Technical University, Faculty of Science, Department of Chemistry, 41400, Gebze/Kocaeli, Turkey
aylin@gtu.edu.tr

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).

\[
\begin{align*}
\text{R} & = \text{O}, \text{O}, \text{O}, \text{O} \\
\text{N} & = \text{N} \\
\text{O} & = \text{O} \\
\text{N} & = \text{N} \\
\text{O} & = \text{O} \\
\text{R} & = \text{O}, \text{O}, \text{O}, \text{O}
\end{align*}
\]

Figure 1: Synthesized Radical Polymers (1-4)

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SELF-ASSEMBLY OF MULTIFUNCTIONAL IRON(III) MAGNETIC SWITCHES

A. I. Vicente¹, A. Joseph¹, S. P. Shannon², L. P. Ferreira³⁴, M. D. Carvalho¹, V. H. N. Rodrigues⁴, M. E. Minas da Piedade¹, G. Redmond², M. J. Calhorda¹ and P. N. Martinho¹.

¹ Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal
² School of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland
³ BioISI, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal
⁴ Department of Physics, University of Coimbra, 3004-516 Coimbra, Portugal

pn martinho@ciencias.ulisboa.pt

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 3d⁴–3d⁷ transition metal ions, the most common being Fe(II), Fe(III) and Co(II). Fe(III), 3d⁵, 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 CROSSOVER COMPOUND WITH SYMMETRY BREAKING SPIN-STATE TRANSITION AND ORDERED INTERMEDIATE STATE

Bruno J. C. Vieira, Laura C. J. Pereira, Vasco da Gama, Isabel C. Santos, Joana T. Coutinho and João C. Waerenborgh

Centro de Ciências e Tecnologias Nucleares (C2TN), Instituto Superior Técnico, Universidade de Lisboa, E.N. 10 ao km 139.7, 2695-066 Bobadela Loures, Portugal
brunovieira@ctn.tecnico.ulisboa.pt

The spin crossover (SCO) phenomenon can be found in a variety of 3d⁴−3d⁷ 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-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-trien ligand (see Figure 1) was obtained by condensation of triethylenetetramine with 2-hydroxy-1-naphthaldehyde.

Figure 1: nsal\textsubscript{2}trien\textsubscript{H\textsubscript{2}}.

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

Serkan Yeşilot, Süreyya Oğuz Tümay, Tutku Yolaçan, Hüsnüye Ardıç Alidaği and Mahmut Durmuş

Gebze Technical University, Faculty of Science, Department of Chemistry, 41400, Gebze/Kocaeli, Turkey
yesil@gtu.edu.tr

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.

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Author index

Abrunhosa, A. J. PC46
Açık, L. PC66
Adão, P. OC3, OC10, PC65
Aguilár, G. G. OC11
Aguiló, E. PC32
Akhüseyin, E. PC24
Alidaği, H. A. PC70
Allen, C. W. PC7
Almeida, Janaina C. PC1
Almeida, Joana C. PC2
Almeida, M. PC65
Almeida, R. M. PC13
Alvarez-Valdes, A. PC29
Alves, A. F. OC24, PC26, PC39
Alves, C. PC29
Alves, L. G. PC46
Alves, V. PC40
Anbu, S. OC27
Andrade, S. M. PC64
António, M. PC4, PC30
Antunes, M. A. PC29
Araújo, J. P. PC29
Araújo, M. PC5, PC66
Asmafiliz, N. PC6
Assis, A. S. OC12
Aureliano, M. OC14
Baekelant, W. PC7
Balci, C. M. PC4
Baldoví, J. J. KL3
Baleizão, C. OC22
Bandeira, N. A. G. PC50
Barata, J. F. B. OC3, OC10, OC18, PC1, PC26, PC54
Barroso, S. OC12
Batista de Carvalho, L. A. E. PC46
Belo, D. PC4
Belo, J. H. PC29
Bento, A. OC2
Besti, S. PC7
Bordado, J. C. M. PC21
Branco, J. B. PC8, PC30
Branco, L. C. OC23
Brás, N. J. PC63
Bruix, M. PC60
Caciones, C. PC60
Çakan, R. D. PC67
Calhorda, M. J. OC3, OC15, OC18, OC25, PC1, PC9, PC21, PC28, PC56, PC62, PC68
Camacho, C. S. PC10
Campello, M. P. C. PC46
Cantürk, H. PC7
Carabineiro, S. A. C. PC58
Cardoso, B. de P. PC54, PC56
Cardoso, J. M. S. PC12
Carmena, M. J. PC45
Carretas, J. M.
Carvalho, M. D.
Carvalho, M. F. N. N.
Casella, L.
Casey, W. H.
Cerqueira, N. S.
Chao, H.
Charas, A.
Chaves, S.
Chorna, I.
Civan, M.
Coimbra, J.
Contel, M.
Cordas, C. M.
Cordeiro, M. N. D. S.
Coronado, E.
Correia, I.
Costa, P. J.
Costa, R. S.
Coutinho, C.
Coutinho, J. T.
Coutiño, E.
Coutino-Gonzalez, E.
Cruz, A.
Cruz, H.
Cruz, M. M.
Cruz, T. F. C.
Cunha-Silva, L.
Damas, L.
Daniel-da-Silva, A. L.
Dantas, J. M.
Dau, P. D.
de Castro, B.
de Castro, M. M. F. P. M.
de la Mata, F. J.
Dieu, B.
Diogo, H. P.
Doğan, S.
Duarte, M. T.
Durmuş, M.
Elie, B. T.
Estrada, A. C.
Fateixa, S.
Fernandes, A.
Fernandes, A. C.
Fernandes, A. P.
Fernandes, D. M.
Fernandes, F.
Fernandes, P. A.
Fernandes, T.
Ferreira, A. C.
Ferreira, B.
Ferreira, L. P.
Ferreira, M. J.
Ferreira, O.
Ferro, M.
Figueira, C. A.
Rubbiani, R.  PC48
Ruivo, A.  OC14, OC27
Ruivo, R.  PC39
Salgueiro, C. A.  OC8, PC60
Samhan-Arias, A. K.  PC61
Santos, G.  OC18
Santos, I.  PC46, PC48
Santos, I. C.  PC4, PC38, PC46, PC69
Santos, M.  OC14
Santos, M. A.  PC27
Santos, S.  PC6
Sanz, N.  PC45
Saraiva, I. H.  OC7
Saraiva, M. S.  PC62
Sayan, G.  PC67
Sevinç, G.  PC24
Shannon, S. P.  PC68
Silva, A. M. G.  OC11, PC31, PC55
Silva, A. M. N.  PC43, PC63
Silva, E. R.  PC21
Silva, L. M. C.  PC30
Silva, M. A.  PC60
Simões, T.  PC60
Simões, T. R.  PC64
Soares, S. F.  PC20, PC59, PC64
Sousa, F. L.  OC13
Tavares, D. S.  PC2
Teixeira, C. M.  OC10, PC65
Teixeira, F.  OC26
Teixeira, R.  PC6
Tomás, H.  OC4, PC10
Tomaz, A. I.  KL1, PC6
Torroba, T.  OC11
Traskina, N.  OC9
Trindade, T.  PL3, OC17, OC19, PC2, PC18, PC20, PC33, PC50, PC53, PC59, PC64
Tümay, S. O.  PC70
Tümer, Y.  PC66
Türkmen, O.  PC24
Uslu, A.  PC67
Valente, A.  PC6
Valente, J.  OC21
Veir, L. F.  OC24, PC36
Veloso, F.  PC42
Viana, A. S.  PC56
Vicente, A. I.  OC15, OC25, PC68
Vieira, B. J. C.  PC69
Vieira, M. O.  OC12
Vilariques, M.  PC41
Vila-Viçosa, D.  PC28
Vinagreiro, C.  PC34
Waerenborgh, J. C.  PC69
Yagüez, H. G.  PC24
Yarmo, M. A.  PC23
Yeşilot, S.  PC67, PC70
Yılmaz, H.  PC24
Yolaçan, T.  PC70
Yüksel, F.

Yusop, R. M.

PC7

PC23
## Participants List

<table>
<thead>
<tr>
<th></th>
<th>Name</th>
<th>Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Laura Abreu</td>
<td>Universidade da Madeira</td>
</tr>
<tr>
<td></td>
<td>Pedro Adão</td>
<td>IST - Universidade de Lisboa</td>
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<td>Janaina C. Almeida</td>
<td>FC - Universidade de Lisboa</td>
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<td>Joana C. Almeida</td>
<td>Universidade de Aveiro</td>
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<td></td>
<td>Rui M. Almeida</td>
<td>FCT - Universidade Nova de Lisboa</td>
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<td></td>
<td>Luís G. Alves</td>
<td>IST - Universidade de Lisboa</td>
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<td>Maria Augusta Antunes</td>
<td>IST - Universidade de Lisboa</td>
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<td></td>
<td>Nuran Asmafiliz</td>
<td>Ankara University, Turkey</td>
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<td>Ana Sofia Assis</td>
<td>FC - Universidade de Lisboa</td>
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<td></td>
<td>Manuel Aureliano</td>
<td>Universidade do Algarve</td>
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<td>Teresa Avilés</td>
<td>FCT - Universidade Nova de Lisboa</td>
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<td>B</td>
<td>Carlos Baleizão</td>
<td>IST - Universidade de Lisboa</td>
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<td></td>
<td>Nuno A. G. Bandeira</td>
<td>ICIQ – Tarragona, Spain</td>
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<tr>
<td></td>
<td>Sónia Barroso</td>
<td>IST - Universidade de Lisboa</td>
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<td></td>
<td>Mohamed A. Bensegueni</td>
<td>Université Frères Mentouri Constantine, Algeria</td>
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<tr>
<td></td>
<td>Serap Besli</td>
<td>Gebze Technical University, Turkey</td>
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<td></td>
<td>Joaquim B. Branco</td>
<td>IST - Universidade de Lisboa</td>
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<td></td>
<td>Luís C. Branco</td>
<td>FCT - Universidade Nova de Lisboa</td>
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<td>C</td>
<td>Maria José Calhorda</td>
<td>FC - Universidade de Lisboa</td>
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<td>Cláudia S. Camacho</td>
<td>Universidade da Madeira</td>
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<td>José M. Carretas</td>
<td>IST - Universidade de Lisboa</td>
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<td>M. Fernanda N. N. Carvalho</td>
<td>IST - Universidade de Lisboa</td>
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<td>Maria de Deus Carvalho</td>
<td>FC - Universidade de Lisboa</td>
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<tr>
<td></td>
<td>Luigi Casella</td>
<td>Università degli studi di Pavia, Italy</td>
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<td>Baltazar de Castro</td>
<td>FC - Universidade do Porto</td>
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<td>M. Margarida Castro</td>
<td>FCT - Universidade de Coimbra</td>
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<td>Nuno S. Cerqueira</td>
<td>FC - Universidade do Porto</td>
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<td>Cristina M. Cordas</td>
<td>FCT - Universidade Nova de Lisboa</td>
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<td>Joana T. Coutinho</td>
<td>IST - Universidade de Lisboa</td>
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<td>Adelaide Cruz</td>
<td>IST - Universidade de Lisboa</td>
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<td>Tiago F. C. Cruz</td>
<td>IST - Universidade de Lisboa</td>
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<td>D</td>
<td>Liliana Damas</td>
<td>FCT - Universidade de Coimbra</td>
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<tr>
<td></td>
<td>Ana L. Daniel-da-Silva</td>
<td>Universidade de Aveiro</td>
</tr>
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<td>M. Teresa Duarte</td>
<td>IST - Universidade de Lisboa</td>
</tr>
<tr>
<td>E</td>
<td>Ana C. Estrada</td>
<td>Universidade de Aveiro</td>
</tr>
<tr>
<td>F</td>
<td>Ana Fernandes</td>
<td>ITQB - Universidade Nova de Lisboa</td>
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<td>Ana P. Fernandes</td>
<td>FCT - Universidade Nova de Lisboa</td>
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<td>Diana M. Fernandes</td>
<td>FC - Universidade do Porto</td>
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<td>Tiago Fernandes</td>
<td>Universidade de Aveiro</td>
</tr>
<tr>
<td></td>
<td>Ana C. Ferreira</td>
<td>IST - Universidade de Lisboa</td>
</tr>
</tbody>
</table>
Olga Ferreira  
Cláudia A. Figueira  
Cristina Freire  
Akogor Ukpor Friday  
Olga Ferreira  
Cláudia A. Figueira  
Cristina Freire  
Akogor Ukpor Friday  
Sandra Gago  
Carlos F. G. C. Geraldes  
John K. Gibson  
Dietmar Glindemann  
Marion Glindemann  
Clara S. B. Gomes  
Pedro T. Gomes  
Sandra Gago  
Carlos F. G. C. Geraldes  
John K. Gibson  
Dietmar Glindemann  
Marion Glindemann  
Clara S. B. Gomes  
Pedro T. Gomes  
Mustafa Hayvali  
Zeliha Hayvali  
Joana Hipólito  
Asha Hiremathad  
Mustafa Hayvali  
Zeliha Hayvali  
Joana Hipólito  
Asha Hiremathad  
Paramasivam Krishnamoorthy  
Iwona Kuzniarska-Biernacka  
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César A. T. Laia  
João Paulo Leal  
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Joaquim Marçalo  
Leonor Maria  
Marta Maroto-Díaz  
Maria Paula Marques  
Paulo N. Martinho  
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Rui Martins  
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Rui Martins  
Sara Martins  
Belkhiria Marwa
Sandra Matos Delphi - Lisboa
Tânia Moniz FC - Universidade do Porto
Bernardo Monteiro IST - Universidade de Lisboa
Filipe Monteiro-Silva FC - Universidade do Porto
Isabel Moura FCT - Universidade Nova de Lisboa
José J. G. Moura FCT - Universidade Nova de Lisboa

Helena Nogueira Universidade de Aveiro

Luís A. Oro Universidad de Zaragoza, Spain
Paula Ortega Universidad de Alcalá, Spain

Elisa Palma IST - Universidade de Lisboa
A. Jorge Parola FCT - Universidade Nova de Lisboa
António Paulo IST - Universidade de Lisboa
Clara Pereira FC - Universidade do Porto
Cláudia C. L. Pereira FCT - Universidade Nova de Lisboa
Laura C. J. Pereira IST - Universidade de Lisboa
Mariette M. Pereira FCT - Universidade de Coimbra
Rute A. Pereira Universidade de Aveiro
Márcia Pessêgo FCT - Universidade Nova de Lisboa
João Costa Pessoa IST - Universidade de Lisboa
Ana Petronilho ITQB - Universidade Nova de Lisboa
Marta Piñeiro FCT - Universidade de Coimbra
Paula C. Pinheiro Universidade de Aveiro
Mara F. Pinto ITQB - Universidade Nova de Lisboa
António Pires de Matos IST - U. Lisboa/FCT - U. Nova de Lisboa

Carla P. A. Queirós FC - Universidade do Porto

Priscila C. Ramgi FC - Universidade de Lisboa
Maria Rangel ICBAS - Universidade do Porto
Sara Realista FC - Universidade de Lisboa
Ana I. Rodrigues IST - Universidade de Lisboa
Fábio M. S. Rodrigues FCT - Universidade de Coimbra
João Rodrigues Universidade da Madeira
Margarida I. Rodrigues Universidade de Aveiro
Carlos C. Romão ITQB - Universidade Nova de Lisboa
Beatriz Royo ITQB - Universidade Nova de Lisboa
Andreia Ruivo FCT - Universidade Nova de Lisboa

Carlos A. Salgueiro FCT - Universidade Nova de Lisboa
Alejandro K. Samhan-Arias FCT - Universidade Nova de Lisboa
Marta S. Saraiva FC - Universidade de Lisboa
André Seco FCT - Universidade Nova de Lisboa
André M. N. Silva FC - Universidade do Porto
Elisabete R. Silva FC - Universidade de Lisboa
Sofia F. Soares Universidade de Aveiro

125
<table>
<thead>
<tr>
<th>Name</th>
<th>Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filipa L. Sousa</td>
<td>Universidade de Aveiro</td>
</tr>
<tr>
<td>Carlos M. Teixeira</td>
<td>IST - Universidade de Lisboa</td>
</tr>
<tr>
<td>Filipe Teixeira</td>
<td>FC - Universidade do Porto</td>
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<td>Ana Isabel Tomaz</td>
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<tr>
<td>Tito Trindade</td>
<td>Universidade de Aveiro</td>
</tr>
<tr>
<td>Yasemin Tümer</td>
<td>Karabük University, Turkey</td>
</tr>
<tr>
<td>Aylin Uslu</td>
<td>Gebze Technical University, Turkey</td>
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<td>Ana I. Vicente</td>
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<td>Bruno J. C. Vieira</td>
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<tr>
<td>Serkan Yesilót</td>
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<tr>
<td>Time</td>
<td>Friday, October 7th</td>
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<tr>
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<td>Ana Petronilho</td>
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<tr>
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