

1ST PYChEM Portuguese Young Chemist Meeting



**15-17
October 2008**

**INSTITUTO SUPERIOR TÉCNICO – LISBON
IST Congress Center**



1ST PYCchem

Portuguese Young Chemist Meeting

Lisbon 15th-17th of October 2008



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WELCOME

We are delighted to welcome you to the 1st Portuguese Young Chemists Meeting - 1PYCheM. The 1PYCheM is a joint organization of Grupo de Químicos Jovens (GQJ), Sociedade Portuguesa de Química (SPQ) and Instituto Superior Técnico (IST).

The idea of organizing a meeting for and with young chemist's steamed from a SPQ congress dinner, last October. After one year, several were the adventures and challenges overcome, and today we are proud to bring to you this meeting. We hope that the 1st and forthcoming editions of PYCheM are able to build a dynamic of cooperation and collaboration between the participants, leading to fruitful results.

The meeting will incorporate 4 plenary conferences, 21 oral communications, 18 flash communications and 61 posters, with the participation of more than 120 chemists, arriving not only from Portugal, but also from Romania, Spain, Germany, USA, Belgium, Sweden and France.

We would like to express our sincere gratitude to all of those that have contributed to the organization of 1PYCheM, including the Scientific Commission, the authors (thank you for all the beautiful artwork and excellent science), the IST organizing commission and the SPQ staff.

Last, but not least, our thanks go to our sponsors, supporters whose names are given in the following pages. Without their support, the organization of 1PYCheM would be impossible.

We truly hope that this meeting will be the first of many, and that the Grupo de Químicos Jovens became a reference for activities organized with the contribution of all the young chemists.

We wish you a pleasant meeting and stay at Lisbon

Lisbon, October 2008

Carlos Baleizão

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Organization



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Scientific Programme

Wednesday, 15th October

12h00 – 14h00 Registration

14h00 – 14h30 Opening

Chairman Ricardo Branco

14h30 – 15h20 **PL1** – Stephen Caddick
Synthetic Chemistry: Underpinning Science for Biology and Medicine

15h20 – 15h40 **OC1** – Nuno Maulide
New strategies for the synthesis of cyclic structures: from orthoesters to riches

15h40 – 16h00 **OC2** – Jalmira Mulchande
Balance Between the Chemical Reactivity and Serine Proteases Inhibition of β -Lactams by Changing the C-4 Substituents

16h00 – 16h30 Coffee Break and Poster Session

Chairman Carla Portugal

16h30 – 17h10 **FC1** – Alexandre F. Trindade
Di-rhodium (II) catalysts for arylation of aldehydes

FC2 – Ana Sofia Anselmo
Morphology of Thin-Films of Polyfluorene: Fullerene Blends

FC3 – André Pontes da Costa
New Cp-Functionalized N-Heterocyclic Carbenes and Their Coordination to Iridium and Rhodium*

FC4 – Ana S. Mestre
Activated carbons for adsorption of clofibric acid

FC5 – Andreia Ruivo
Interplay Between Energy and Electron Transfer in the Luminescence Quenching of Eu (III) in Glass by d-Metals

FC6 – Andreia S. Farinha
New Calix[4]pyrrole Dimers: Synthesis and Anion Binding Studies

17h10 – 17h30 **OC3** – Cátia Teixeira
Computational Studies of the Binding Mode Between BMS-378806 and HIV-1 gp120

17h30 – 17h50 **OC4** – M. T. Viciosa
TSDC and DRS: Two Powerful Techniques in Dynamical Characterization of a Large Variety of Materials

Thursday, 16th October

Chairman Nuno Maulide

- 09h00 – 09h50 **PL2** – João Rocha
New Light-Emitting Zeolites and Metal Organic Frameworks
- 09h50 – 10h10 **OC5** – Artur J. Moro
Combining Fluorescence with Intelligent Nanomaterials: the Future of Highly Selective Sensor Devices
- 10h10 – 10h30 **OC6** – Bruno L. Oliveira
Re^{99m}Tc Tricarbonyl Complexes Containing Guanidinium Moieties for Probing iNOS in vivo
- 10h30 – 11h00 Coffee Break and Poster Session

Chairman Leonel Silva

- 11h00 – 11h40 **FC7** – Carolina S. Marques
Application of “Borrowed” P,P-Ligands in Catalytic Asymmetric Synthesis
- FC8** – Konstantin V. Luzyanin
Metal-mediated Transformations of Nitriles and Isocyanides: The Routes to Imines and Heteroatom-Stabilized Carbenes
- FC9** – M. Pessêgo
Reactivity of phenol nucleophiles towards nitroso compounds
- FC10** – Maria Vasconcellos-Dias
Catalytic Studies of Heptacoordinate Mo(II) and W(II) Complexes Supported in a Mesoporous Material
- FC11** – M. Sardo
Surface-Enhanced Raman Scattering of trans-3-Hydroxycinnamic Acid Adsorbed On Silver Nanoparticles
- FC12** – Nuno Basílio
¹H NMR Study on Micellization of Amphiphilic Sulfonatocalix[4]arenes
- 11h40 – 12h00 **OC7** – J. P. M. Nunes
Enzymatic Resolution of a 4,5-Dihydroxylated Cyclopentenone Obtained from an Optimized Rearrangement of a Pyranone
- 12h00 – 12h20 **OC8** – Patrícia M. Reis
High-valent Oxo and Imido Molybdenum and Rhenium Complexes as Catalysts for Reductions
- 12h20 – 12h40 **OC9** – Pedro D. Vaz
Clustering issues in environmentally relevant compounds

12h40 – 13h00 Grupo Químicos Jovens

13h00 – 14h30 Lunch

Chairman Luis Branco

14h30 – 15h20 **PL3** – João Pedro Conde

Top-down nanotechnology: how to sculpt a nano-object

15h20 – 15h40 **OC10** – A. Vidal Pinheiro

Lighting the way: Using light to control enzymatic synthesis of nucleic acids

15h40 – 16h00 **OC11** – Carla M. B. Carvalho

New Nanomagnet-Porphyrin Hybrids for the Photoinactivation of Wastewater Bacteria

16h00 – 16h30 Coffee Break and Poster Session

Chairman Artur Moro

16h30 – 16h50 **OC12** – Rafael Antunes

Innovation: Bringing Great Ideas to Market

16h50 – 17h10 **OC13** – Susana Rocha

Watching Single Enzyme Molecules At Work

17h10 – 17h30 **OC14** – Nuno M. T. Lourenço

Ion Jelly[®] - A tailor-made Material for Electrochemical Applications

17h30 – 17h50 **OC15** – R. Perestrelo

Determination of Volatile Compounds in Wines Using Different Isolation Methodologies

20h00 Congress Dinner

Friday, 17th October

Chairman Nuno Lourenço

09h00 – 09h50 **PL4** – Carlos C. Romão

Coordination Chemistry: Trends and Challenges

09h50 – 10h10 **OC16** – Alexander M. Kirillov

Crystal engineering of multicopper compounds with N,O- and N,P-ligands via self-assembly in aqueous medium: synthesis, structural features and catalysis

10h10 – 10h30 **OC17** – Ana Petronilho

Tautomerization of N-Heterocycles by Iridium (III) complexes

10h30 – 11h00 Coffee Break and Poster Session

- 11h00 – 11h40 **FC13** – Nuno M. M. Moura
Porphyrins in 1,3-Dipolar Cycloadditions with Nitrile Imines
FC14 – Pedro Mateus
New Hexaaza Macrobicyclic Cyclophane for Recognition of Tetrahedral Dianions
FC15 – Rui F. Munhá
Cyclam in early transition metal chemistry: synthesis, reactivity and applications of Zr(IV) complexes
FC16 – Sandra C. Gouveia
Helichrysum devium – An Endemic Medicinal Plant from Madeira Archipelago
FC17 – Tiago Rodrigues
Novel 4(1H)-Pyridonimines as Potential Cytochrome bc₁ Inhibitors in Plasmodium falciparum
FC18 – Tiago Silva
Synthesis of bis-(Indolyl)methanes as Highly Selective Colorimetric and Fluorescent Chemosensors for Cu²⁺ Cations
- 11h40 – 12h00 **OC18** – Sofia M. Bruno
An Investigation of Tetrakis(β-diketonate)europium(III) Complexes with Different Counter Cations
- 12h00 – 12h20 **OC19** – Ricardo J. F. Branco
The chemistry of enzymes: A journey from physics to biology
- 12h20 – 12h40 **OC20** – Mário A. P. Nunes
Immobilization of naringinase in PVA–alginate matrix using an innovative technique
- 12h40 – 13h00 **OC21** – J. Frade
Chemistry & Art: The Primitive Flemish Technique and Determination of Lacquered Objects Origin
- 13h00 – 13h30 Closing
- 14h30 – 16h30 Science Museum Visit

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Portuguese Young Chemist Meeting **1ST PYChem**



Plenary Lectures

Synthetic Chemistry: Underpinning Science for Biology and Medicine

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This lecture will focus on the development of new methods for organic synthesis and the use of such methods for making organic molecules of importance in fundamental biological and with potential clinical applications. Themes will include (a) the importance of fundamental studies in organic synthesis; (b) the importance of diversity in chemical synthesis; (c) methods for developing diverse compound collections; (d) the concepts of forward and reverse chemical genetic approaches for biology; (e) Target synthesis and its relevance for biology and medicine; (f) The dual role of small molecules in fundamental and translational research (g) Protein Chemistry and Drug Delivery; (h) Drug discovery in academia.

New Light-Emitting Zeolites and Metal Organic Frameworks

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*'And God said, Let there be light, and there was light.
And God saw that the light was good.'*

Zeolites are hydrated aluminosilicates with a microporous structure, which have found applications in, among others, gas sorption and separation, catalysis and ion exchange. In the nanotechnology era, although these 'conventional' areas of application of zeolites will remain important, microporous solids will find uses in new fields such as optoelectronics.

In the early nineties of the last century, zeolite-type silicates built up of transition-metals (mostly Ti) heteropolyhedra, were developed [1]. By the turn of the century, the constituent elements of heteropolyhedral silicates were extended to lanthanides (Ln) and, thus, light emitting (photoluminescence) properties became available [1-3]. The work in the field of 'bright zeolites' culminated with the reports of the intriguing chiral system $\text{Na}_3[(\text{Y,Ln})\text{Si}_3\text{O}_9]\cdot 3\text{H}_2\text{O}$, for which it was shown that Eu^{3+} photoluminescence spectroscopy with excitation by unpolarised light in the absence of an external magnetic field is able to identify enantiomeric domains in chiral frameworks [4].

With the turn of the century there was a surge of activity on inorganic-organic hybrid solids known as coordination polymers or metal-organic frameworks (MOFs). These materials are of considerable interest because the combination of inorganic and organic fragments produces a large number of new crystal architectures and allows the design of solids with specific functions. Interesting properties which may lead to industrial applications include those of zeolites and optical and magnetic properties. So far, only 10% or so of MOFs are effectively microporous and exhibit zeolite-type behaviour. In particular, very little work is available on microporous photoluminescent MOFs [5,6]. Recently, we reported a new family of magnetic nanoporous MOFs, whose quantum yields and efficiencies are the highest reported for solid-state Eu^{3+} compounds with organic ligands [7]. An ethanol sensor based on the variation of the fluorescence signal at 619 nm was developed.

In this talk I shall show the kaleidoscopic opportunities to engineer photoluminescent centres offered by lanthanide-based microporous silicates and inorganic-organic hybrid MOFs.

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Top-down nanotechnology: how to sculpt a nano-object

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Nanotechnology aims at the study and application of systems whose properties are controlled at length scales of the order of 1 to 100 nm. At these length scales, systems are expected to show properties that are different from their bulk counterparts.

There are currently two main approaches to reach control of matter at these length scales. The "bottom-up" approach, to which chemists have contributed extensively through the development of nanoparticles, self-assembled monolayers, and supramolecular structures, involves the self-assembling of smaller units into a larger, functional structure. The ultimate example of the power of this approach is the complexity and functionality of living organisms. The "top-down" approach derives from the technology developed to fabricate integrated electronic circuits. In this technology, successive cycles of film deposition, patterning, and etching allow the "sculpting" of objects whose lateral dimensions can now be below 20 nm.

In this talk, the focus will be on the "top-down" approach. The main aspects of this technology will be outlined, with an emphasis on their chemical aspects, and applications will be described, focusing on the fabrication and operation of ultra-miniaturized "labs-on-a-chip" for chemical and biological applications.

Coordination Chemistry: Trends and Challenges

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For many decades after its foundation, coordination chemistry expanded the frontiers of chemical bonding and structural chemistry. Understanding metal ion binding, designing and controlling structural arrangements and their physical and chemical properties were the challenges. The trends were directed to man-made applications like magnetic and superconducting 3D coordination structures as well as petrochemical catalysis which resulted from the taming of the σ and π M-C bond chemistry.

Bioinorganic chemistry was the new trend started in the 1970's which led to the fascinating revelation of metalloenzyme structure and function. The initial challenge here was to discover the actual structure of the active sites in metalloenzymes. Surprisingly, the extraordinary and highly efficient/selective chemistry operated by these metal centers is usually carried out by metal ions coordinated to simple, totally classic ligands but cannot be readily reproduced by similar man-made complexes. Clearly, the proteic structure which surrounds those active centres is key to their unusual performance.

Scientifically, the present long-term challenge of Bioinorganic chemistry is to understand, and control the way in which protein folding and structure affects metal-ion reactivity and conversely, the way in which metal ions control the folding of proteins. While this area of work is merely beginning to be studied, mastering or mimicking many biological reactions became an issue of decisive importance in the context of environmentally sustainable economics. This is particularly relevant for reactions that harvest and convert solar energy, like photo-synthesis, hydrogen production and water oxidation or splitting.

Another consequence of the unveiling of the fascinating role of metals in enzymes was to tease human curiosity as to other possible roles of Metals in Biology. Beginners luck led to some astonishing achievements like Salvarsan (1919) and cisplatin (1965). Although the challenge remains cyclopic many recent advances point towards new directions in the search of therapeutical applications of metal complexes.

This lecture will highlight the important advances and expectations in these fields while trying to put them in a perspective hopefully useful to the PYChemist.

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Oral Communications

New strategies for the synthesis of cyclic structures: from orthoesters to riches

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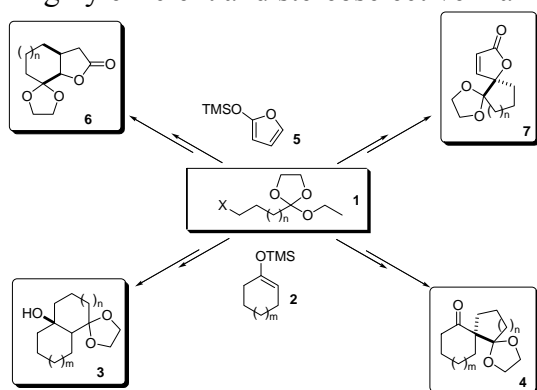
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Though orthoesters have been mostly employed as carboxylic acid protecting groups and acylating agents, their synthetic utility as annelating partners in novel ring forming reactions has been little investigated.^[1]

We have recently been interested in the preparation and use of functionalised orthoesters **1** in annelation reactions (Scheme 1). Preliminary work was aimed at preparation of bicycloalkanols **3** and spirocyclic diketones **4** from cyclic silyl enol ethers **2**, by taking advantage of the unique reactivity profile provided by our ω -halo orthoesters.^[2] More recently, we have shown that the use of the extended silyl enol ether **5** led to a ready access to either bicyclic lactones **6**^[3] or spirobutenolides **7**^[4] at will, in a highly efficient and stereoselective manner.



Scheme 1

The application of this concept to short, efficient and stereocontrolled total syntheses of various natural products have been examined.^[5] As often occurs in organic chemistry, synthetic pitfalls encountered spurred the development of new synthetic methodology^[6,7] and led to the discovery of further applications of the annelating reagents **1**.^[8]

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Balance Between the Chemical Reactivity and Serine Proteases Inhibition of β -Lactams by Changing the C-4 Substituents

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Monocyclic β -lactams are potent inhibitors of elastase, a serine protease implicated in the development of many disorders of the airway [1]. Monobactams **1** (Figure 1) acylate the catalytic serine residue with expulsion of the leaving group, LG, at C-4, in a potential suicide-type inhibition pathway. We evaluated the effect of different oxygen and thiol leaving groups at C-4 on the chemical reactivity and elastase inhibitory potency of **1** [2]. We found that C-4 substituents exerted a purely inductive effect and there is no dependence of the reaction rate on the pK_a of the LG. A good correlation was obtained between the magnitude of the second-order rate constant for the alkaline hydrolysis, k_{OH} , and the second-order rate constant of elastase inactivation. We now report that sulfones at C-4 improve the inhibitory potency, activating the β -lactam carbonyl carbon atom towards nucleophilic attack and leading to an irreversible covalent enzyme-inhibitor adduct with sulfinate departure, as shown by X-ray crystallography and titration of enzymatic activity studies [2].

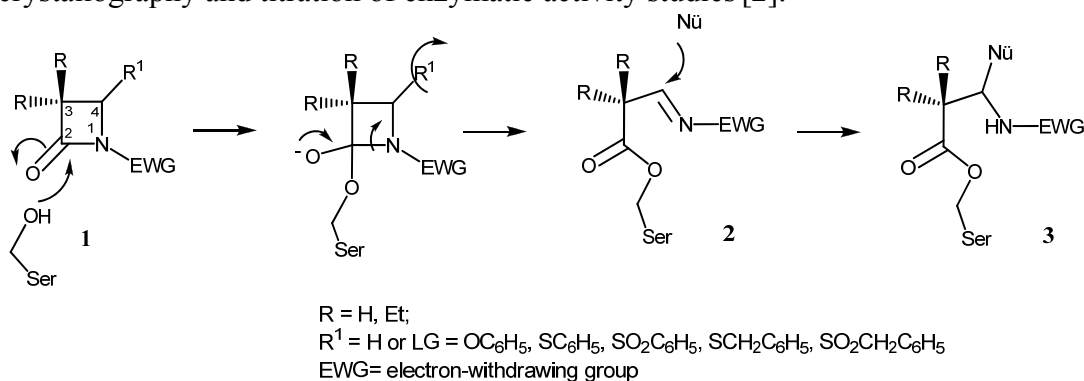


Figure 1 - Serine protease suicide-type inhibition pathway for monobactams **1**.

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Computational Studies of the Binding Mode Between BMS-378806 and HIV-1 gp120.

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Viral penetration of human immunodeficiency virus (HIV-1) into human cells represents the first step of its viral cycle life. This process, involves a molecular recognition of the viral glycoprotein gp120 to the cellular CD4 receptor thus triggering several conformational changes [1]. Therefore, development of compounds, which may inhibit the gp120/CD4 interaction, represents an important avenue of drug therapy.

BMS-378806 is a low-molecular-mass organic compound that targets the viral glycoprotein-gp120 and blocks viral entrance to cells [2]. However, since no experimental structural data is available, the binding mode of BMS-378806 is still not established.

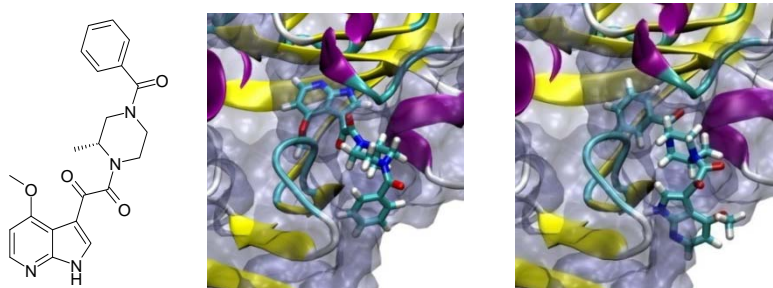


Figure 1: Molecular scheme of BMS-378806 and its two possible binding modes with gp120.

In order to investigate the binding mode of this organic compound, molecular docking calculations were firstly produced. From these results, two possible BMS-378806 conformations, representing head/tail orientations, were selected (figure 1). To discriminate between these two modes of interaction both gp120/BMS-378806 structures were submitted to 3ns of Molecular Dynamics (MD) simulations with explicit solvent.

The persistence of complexes after 3ns indicates that these two binding modes should have a biological role. The free energy of binding for both complexes was obtained by using the MMPBSA method. Also, other structural studies, like H bonding networks, were performed to discriminate between the two binding modes. All of these original results yield new atomic insight into the binding pocket of gp120 and thus allowing us to rationally predict the binding mode between BMS-378806 and gp120.

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TSDC and DRS: Two Powerful Techniques in Dynamical Characterization of a Large Variety of Materials

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It is well known that the macroscopic properties of the materials depend strongly on their chemical structures. Nevertheless, there are other factors that also influence the macroscopic behaviour such as the molecular mobility. To study this dynamic behaviour, the two dielectric related techniques of Thermally Stimulated Depolarization Currents (TSDC) and Dielectric Relaxation Spectroscopy (DRS) are often used, and provide complementary information about dipolar reorientational motional processes. In both cases, the application of an electric field over the sample originates a polarization, and the central parameter to be extracted from the experimental data is the so-called relaxation time.

In the case of TSDC a persistent polarisation is created by cooling down the sample in the presence of a d.c. electric field; the depolarisation current is then measured as the sample recovers the equilibrium state in a constant rate heating ramp. On the other hand, DRS measures the response of the material as a function of the frequency of a sinusoidal field in isothermal conditions. Both techniques combined provide information about molecular motions with characteristic times between 10^{-10} and 10^3 seconds.

In this presentation we describe some selected examples where the information provided by these techniques allowed a characterization of the dynamic behaviour that grounded future applications: crystallization of a low molecular weight compound, thermal polymerization, phase transitions in liquid crystals, interaction with water molecules in a biopolymer, changes in conductivity, glass transition characterisation in supercooled liquids and diversity of the secondary relaxations in the amorphous solid state.

In all those examples, the knowledge of the temperature dependent relaxation time associated with the molecular motions allowed the prediction of the behaviour of the materials in the course of time and, consequently, to enhance the future applications.

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Combining Fluorescence with Intelligent Nanomaterials: the Future of Highly Selective Sensor Devices

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The use of fluorescent dyes as chemical sensors is a widely known approach in the scientific community of today. Their high sensitivity makes them an attractive tool for the investigation of chemical processes and selective analyte sensing. In our research, we combine fluorescent sensing with the technique of Molecular Imprinting [1]. The concept is based on the formation of cavities in a polymer matrix, which are capable of recognising a specific analyte. The synthesis of the material consists on three steps: (i) formation of a pre-organised complex between the analyte and a molecule which possesses a polymerisable moiety i.e. a functional monomer, (ii) the polymerization of this complex in the presence of an excess of cross-linker and (iii) the removal of the analyte, thus creating specific binding sites for that molecule inside the polymer matrix.

Currently, we are focused on the development of fluorescent monomers for nucleotides. These biomolecules play major roles in living organisms, namely energy storage (e.g. Adenosine triphosphate, ATP, and Guanosine triphosphate, GTP) and regulation of metabolic pathways (e.g. cyclic Adenosine monophosphate).

Within this framework, a fluorescent sensor for cAMP based on a styrylpyridinium fluorophore [2] was modified to contain a methacrylate group (m-DMASP). Several MIPs were produced against cAMP using this fluorescent monomer to optimize the binding performance of the resulting polymer. Also within the current research, a new sensor based on a naphthalimide fluorophore for the detection of nucleotides containing pyrophosphates, e.g. ATP and GTP is being developed.

The nanoscale approach to Molecular Imprinting is currently being developed as a part of a Marie Curie Research Training Network (www.nascent.qmul.ac.uk) that integrates 8 academic partners and 3 industrial partners, and will ultimately result on the production of nanodevices capable of selective analyte recognition.

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Re/^{99m}Tc Tricarbonyl Complexes Containing Guanidinium Moieties for Probing iNOS *in vivo*

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Nitric oxide synthase (NOS) catalyzes the oxidation of L-arginine to L-citrulline and NO. Overproduction of NO has been associated to several diseases, including cancer [1]. The visualization of NOS expression *in vivo* using a radiolabeled substrate/inhibitor of NOS could provide insight into a wide variety of pathologies.

Within our research effort to introduce novel radioactive probes for *in vivo* tumor targeting [2], we report herein the synthesis and characterization of Re(I) and ^{99m}Tc(I) tricarbonyl complexes anchored by a pyrazolyl-diamine ligand containing guanidinium moieties for iNOS recognition (**Fig. 1**). The relationship between the structure of the compounds and their affinity to murine iNOS, determined by enzymatic studies, will be presented and discussed. The biological evaluation of the ^{99m}Tc complexes in specific cell lines will also be also presented.

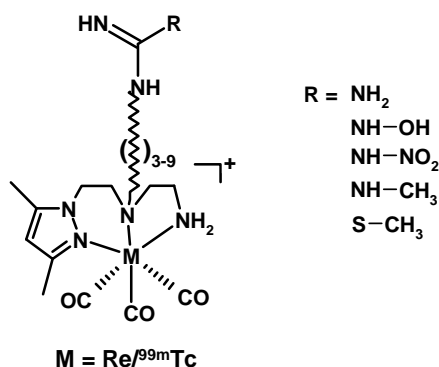


Figure 1. Re/^{99m}Tc Tricarbonyl complexes with guanidinium moieties.

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Enzymatic Resolution of a 4,5-Dihydroxylated Cyclopentenone Obtained from an Optimized Rearrangement of a Pyranone

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Cyclopentanoids are present in the structure of a variety of natural and commercially important biomolecules such as Neocarzinostatin and Kedarcidin chromophores [1], as well as several carbocyclic nucleosides and prostaglandins. Certain enantiomers of *trans*-dihydroxylated cyclopentenones, which are more synthetically challenging than their *cis* counterparts, are of particular interest for the synthesis of selectable target molecules. Early successes by Johnson [2] and Hiramama [3] based on a lengthy step by step approaches were later superseded by Hoffmann's palladium catalysed pyranone rearrangement [4]. Caddick and co-workers studied this rearrangement thoroughly having reported rearrangement without metal catalysis, enzymatic desymmetrizations for the resolution of *trans* enantiomers [5] and synthetical manipulations of the cyclopentenone ring showing its versatility as a building block [6].

Having recognized the value and simplicity of this transformation we have sought to further enhance this rearrangement (Figure 1) by optimizing the effect of solvent, amine base and temperature. We have also studied its enzymatic resolution, hoping to improve the previously reported method [5].

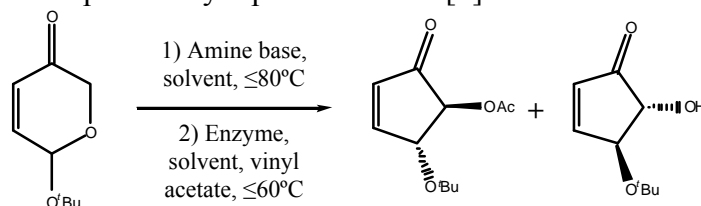


Figure 1. Pyranone rearrangement to *trans*-4,5-dihydroxylated cyclopentenone and enzymatic resolution.

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High-valent Oxo and Imido Molybdenum and Rhenium Complexes as Catalysts for Reductions

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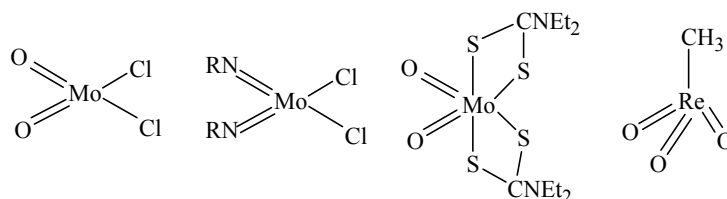
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Recently, we reported that high-valent dioxomolybdenum complexes catalyze the hydrosilylation of carbonyl groups [1]. We have now extended the role of high-valent oxo compounds to reductive processes using hydrogen, a cheaper and more convenient reducing agent than silane [2]. The complexes shown in Scheme 1 catalyze the selective hydrogenation of alkynes to alkenes and the deoxygenation of sulfoxides, pyridine *N*-oxides, nitroarenes and arsenium oxides. DFT calculations have shown that the activation of H₂ by MoO₂Cl₂ and MoO₂(S₂CNEt₂)₂ can take place in a [2+2]-type addition of the H-H bonds to the terminal oxo-multiple bond, followed in the later system by water elimination and formation of a reduced Mo(IV) species. We also report here our latest results on the use of imido Mo(VI) complexes of the type Mo(NR)₂Cl₂(dme) as catalysts in hydrosilylation reactions.



Scheme 1

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Clustering issues in environmentally relevant compounds

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Secondary organic aerosols (SOA) are responsible for a huge amount of carbon in the atmosphere.[1] These aerosols derive from chemical processes – specially oxidative and photochemical – that involve biogenic volatile organic compounds (BVOC), in the atmosphere. The quantity of BVOC in the atmosphere is estimated to be superior to Pg Carbon/year (Gtonnes/year), with isoprene (responsible for an important biosynthetic pathway [2]) being the most abundant (at ca. 50%). These SOA may be observed as a blue haze specially above densely forested areas.[1]

The present work aims to study how BVOC begin the aggregation process that leads to the formation of SOA and to understand the driving forces that govern the aggregation in the microscopic droplets that persist in the atmosphere. BVOC have a plethora of functional groups and hydrogen bonding opportunities. Given that the microscopic droplets may be considered as fluids at a very small scale,[3] it is expected that hydrogen bonding may be responsible, at least partially, for the persistence of aerosols in the atmosphere.

Limonene and carvone (limonene's oxidation product), important terpenoids, were studied using an FT-ICR-MS by electrospray ionization (ESI), MSⁿ / CID (SORI CAD) and high resolution techniques for observing the formation of clusters of such compounds.

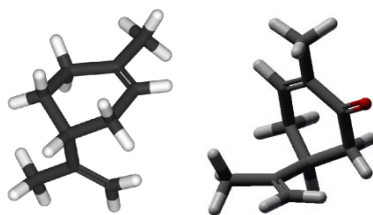


Figure 1. Molecular structures of limonene (left) and carvone (right).

The ESI technique is most adequate due to mild ionization conditions and MSⁿ as well as CID (SORI CAD) and high resolution are most relevant for ion structure elucidation. Results will be discussed considering environmental relevancy.

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Lighting the way: Using light to control enzymatic synthesis of nucleic acids

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Every researcher dreams to control each reaction with a simple glint of light. We have developed a system based on caged-molecules to be used in enzymatic synthesis of nucleic acids, granting full control over the temporal release of substract from their photolabile precursors.

When linked to a photolabile protecting group, the substract has no biological activity.

This activity can be triggered by a pulse of UV or visible light, which releases the photolabile protecting group. This way, the release of the biologically active molecule is controlled with extraordinary temporal precision [1,2].

In order to minimize nucleic acid and protein damage induced by UV radiation, [7-(diethylamino)coumarin-4-yl]methyl was used as a photolabile protecting group to cage ATP molecules. This caging group exhibits high photochemical yield, high absorptivity ($\epsilon_{390\text{nm}} \approx 30.000 \text{ M}^{-1}\text{cm}^{-1}$) and absorption maxima in the visible region ($\lambda_{\text{max}} = 390\text{nm}$) [3]. DEACM-ATP photochemical characterization was determined concerning fluorescence and photocleavage quantum yield. ATP molecules were then replaced by caged analogue in in vitro transcription reactions using ATP as substract. No RNA formation was detected due to efficient blocking by the coumarin moiety. After laser irradiation caged ATP was released with quantitative precision and RNA polymerization was resumed.

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New Nanomagnet-Porphyrin Hybrids for the Photoinactivation of Wastewater Bacteria

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Magnetic nanoparticles have become an important target of investigation in the last decade since new properties and applications, namely in the field of biology and medicine, are discovered every year [1-3]. Considering the application of new insoluble and recoverable materials as antibacterial agents, we decided to develop and investigate new magnetic nanoparticle-porphyrin (NP-Por) hybrids. In this communication we will describe the immobilization of neutral and cationic porphyrins on functionalized magnetic nanoparticles. We will also present a new approach (via cationization) to stabilize suspensions of NP-Por in water (Fig. 1). Finally, the results of antibacterial activity of those hybrids in natural wastewater samples will be discussed. Experimental procedures and characterization data will be also considered.

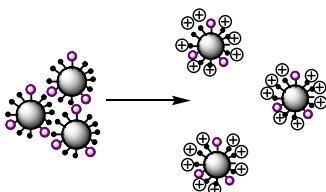


Figure 1. Representation of a NP-Por cluster before and after the cationization process

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Innovation: Bringing Great Ideas to Market

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Europe has been the cradle of modern Chemistry and it's many Scientists, Universities and Industries have done fundamental contributions to the Chemistry we know today. After the World War II, the North Americans took the lead in extracting value from the knowledge developed at the bench. The economical capacity of the USA, in the second half of the 20th century, allowed the creation of some of the most attractive research centers, which, together with the funding activity supported by the government and industry, drained the brains from Europe and Asia.

In the late 90's and beginning of the 21st Century the emerging Asian markets were able to attract back its students, now with PhDs and post-docs or with Western industrial experience. This knowledge allied with the low cost manufacturing has created a major productive driving force that threatens the western model of predominance. With a different mindset, the Chinese and Indian scientists are much more focused on applying the scientific knowledge to the industry, generating value from science. While the European and American Scientist is focused in new discoveries, in pure and fundamental science, the emerging countries are much more interested in how to make money out of chemistry (and other sciences as well).

European science is now gaining a new momentum and the time to learn from others and to regain the importance and brilliance of the past is here. Young Chemists of Europe have a fundamental role and our way of thinking has to follow the new winds. The new strategies for Europe have to involve all players: the Governments, the Industry, the Universities and the Scientists. The Pure and Fundamental Science is what will distinguish us but it will only be viable if it is supported by an objective mindset of how to generate value from it. If a good idea is there, it should not be published in a journal, but patented, it should not be left at the bench stage but matured to be made industrially and generate not only profit but also value enough to support further research.

Watching Single Enzyme Molecules At Work

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Many of the biological processes taking place in cells are mediated by enzymatic reactions occurring in the cell membrane. Understanding interfacial enzymatic catalysis is therefore crucial to the understanding of cellular function. Due to the innate heterogeneity of the system, a full understanding of such interfacial processes is difficult. Single molecule fluorescence spectroscopy is naturally suited to the study of such complex systems as it allows deeper insight into locally inhomogeneous molecular behaviour not otherwise available from ensemble measurements.

We image phospholipase enzymes acting upon bilayers of their natural phospholipid substrate, tracking the diffusion of thousands of individual enzymes while simultaneously visualising local structural changes to the substrate layer (Figure 1). This study comprises several enzyme mutants with different affinities and catalytic activities towards the substrate. Analysis of the trajectories of each enzyme type allows us to successfully correlate the mobility of phospholipase with its catalytic activity. By employing novel, high resolution image reconstruction methods we are also able to visualise ‘hotspots’ of enzyme activity and relate them to local substrate structure.

We believe our methods represent a major advance for the study of biological interfacial systems. While we studied a specific phospholipase, the proposed methods can easily be applied to essentially all kinds of interfacial enzymes as well as other processes occurring at membranes, e.g. active transport, signalling processes and so on.

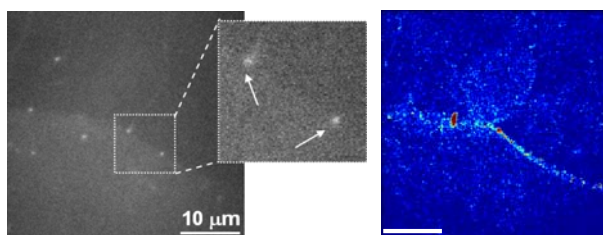


Figure 1 (a) Fluorescence image of labeled enzyme on phospholipid labeled multilayers. Discrimination of single enzymes is possible (indicated by arrows). **(b)** Histogram-based image reconstruction showing the spatial distribution of enzyme molecules on the substrate

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Ion Jelly[®] - A tailor-made Material for Electrochemical Applications

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A common feature to electrochemical devices, such as batteries, capacitors, fuel cells, actuators, photovoltaic cells, electrochromic windows and light emitting cells is the presence of an electrolyte whose properties have a pronounced effect on the device performance. A reasonable conductivity (above 10^{-4} S cm⁻¹), and a large electrochemical window (above 1 V) are some of the criteria that an electrolyte must meet to be suitable for utilization in an electrochemical device. Room-temperature ionic liquids (ILs) fit these requirements [1], with conductivities usually within the range 0.1-14 mS cm⁻¹, and electrochemical windows of 4-5.7 V, respectively [1]. Near nonvolatility, nonflammability and excellent chemical and thermal stability have made ILs an environmentally attractive alternative to conventional organic solvents [2].

Gelatine is a widely available, inexpensive and well studied gelling agent. It is prepared by the thermal denaturation after an acid or alkaline pre-treatment of collagen. Gelatine is a well-known biopolymer for its biocompatibility in several applications.[3]

Here we report a very simple way to obtain a PCM by making use of the ability of ILs to dissolve gelatin. The resulting viscous solution jellifies by cooling below 35 °C, yielding an 'Ion Jelly'[4] that combines conductivity, which is a characteristic of ILs, with the mechanical flexibility of a biopolymer.

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Determination of Volatile Compounds in Wines Using Different Isolation Methodologies

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The characterization of volatile compounds from commercial wines is the most important criteria for the determination of their organoleptic characteristics. More than 800 compounds from different families, like alcohols, esters, fatty acids, carbonyl compounds, terpenes, volatile phenols have been identified, but about 40 of them can be odour-active [1]. The unique wine aroma depends on factors, such as grape variety, growing region, climatic conditions, agricultural practice, winemaking technology, maturation and aging process [2].

The aim of this study was to compare the effectiveness of different extraction methodologies like stir bar sportive extraction in combination with liquid desorption (SBSE-LD), headspace solid-phase microextraction (HS-SPME) and solid-phase extraction (SPE) followed by gas chromatography-mass spectrometry (GC-qMSD) for the analysis and differentiation of volatile compounds from commercial wines produced in Madeira Island, with the main goal of detecting a great number of characteristic volatile and semi-volatile compounds. More than ninety volatile compounds were identified in commercial wines extracts and their percent amounts obtained by each methodology were determined. Qualitative and quantitative differences were observed among the volatile profiles obtained using these methodologies. From the results, SPE methodology extracted more volatile compounds than SBSE and HS-SPME methodologies. Consequently, SBSE is more efficient for the extraction of low-volatile compounds like esters, acetates, fatty acids and terpenes, while SPE achieved the highest percentages of alcohols and volatile phenols. SPME methodology comparatively to SPE, showed a higher affinity for terpenes and acetates; however a lower affinity for volatile phenols. According the results these three methodologies are therefore complementary.

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Crystal engineering of multicopper compounds with N,O- and N,P-ligands via self-assembly in aqueous medium: synthesis, structural features and catalysis

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Recently, we have developed self-assembly synthetic methods in aqueous medium leading to a variety of multicopper complexes and coordination polymers, which show interesting structural, catalytic, magnetic and host-guest features [1–3]. The present contribution summarizes this work with an emphasis on the following topics:

- Multinuclear copper compounds derived from aminopolyalcohols and different auxiliary ligands (benzenepolycarboxylates, amines and inorganic anions) [1];
- Water-soluble copper complexes with dipicolinate [2] or 1,3,5-triaza-7-phosphaadamantane (PTA) [3] ligands;
- Applications of the abovementioned compounds: (i) in host-guest and supramolecular chemistries as H-bonded networks and metal-organic matrixes for the storage of different water clusters, and (ii) as highly efficient bio-inspired catalysts for the mild and green peroxidative oxidation of alkanes (mainly cyclohexane) into derivatives with industrial significance.

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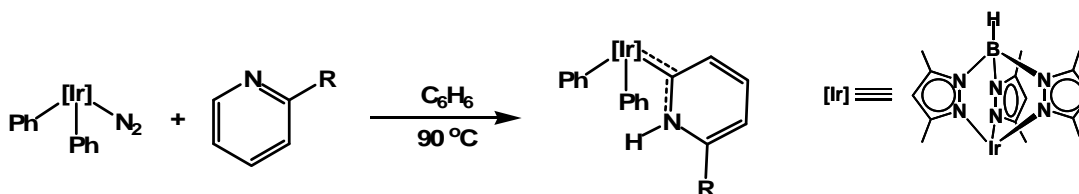
Tautomerization of N-Heterocycles by Iridium (III) complexes

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The tautomerization of six-membered N-heterocycles was not known until very recently. This was attributed to the high energy barrier for the isomerization, despite the additional stability that the metal fragment could provide to the carbene type structure. We recently observed that the iridium (III) complex $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_6\text{H}_5)_2\text{N}_2$ can promote the tautomerization of 2-substituted pyridines, a process dependent on the steric hindrance around the nitrogen atom.



The extension of these studies to the iridium (III) complex, $\text{Tp}^{\text{Mes}}\text{IrN}_2$ has now allowed us to observe that the tautomerization can be extended to pyridine itself and other N-heterocycles without steric hindrance in the nitrogen surroundings.

The reactivity of the NHC carbenes generated by this process was also studied and all the results will be reported in this communication.

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An Investigation of Tetrakis(β -diketonate)europium(III) Complexes with Different Counter Cations

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Recently, it has been recognized that the combination of lanthanides with ionic liquids (ILs) may lead to new types of advanced luminescent materials [1]. For these applications it is desirable to design lanthanide compounds that are either highly soluble in ILs or that are ILs themselves. Tetrakis(β -diketonate) complexes of the type $[C][Ln(diket)_4]$ are promising in this respect [1,2]. By introducing imidazolium, pyridinium or quaternary ammonium cations (C) in the ionic complex, the solubility in the corresponding IL $[C][A]$ (A = anion such as BF_4^- or PF_6^-) can be enhanced.

In this work, tetrakis(naphthoyltrifluoroacetate)europium(III) complexes containing the cations tetrabutylammonium, 1-butyl-3-methylimidazolium ($[C_4mim]^+$), and 1-butyl-3-methylpyridinium, have been prepared and their photoluminescence properties studied. In an attempt to prepare an immobilized analogue of the complex $[C_4mim][Eu(nta)_4]$, a mesoporous silica was derivatized with 1-propyl-3-methylimidazolium groups and used as a support for the $[Eu(nta)_4]^-$ anion.

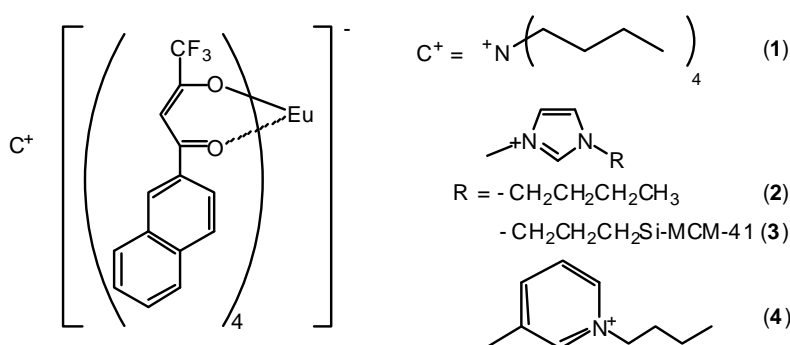


Figure 1. Tetrakis(β -diketonate)europium(III) complexes.

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The chemistry of enzymes: A journey from physics to biology

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The biological function of a protein is ultimately rooted in its physical motions and imprinted in its tridimensional structure. For that reason, proteins evolve in Nature as a delicate balance between flexibility and stability, conserving the essential features required to carry out catalysis efficiently and selectively. The complexity of a protein can be decomposed in three main components: the active site defined normally by few catalytic residues or cofactors which are responsible for the chemistry of a specific reaction; the protein environment which guides the substrate and products on a well-defined potential landscape; the solvent and ions that generate specific microenvironments and singular energetic pathways inside the folded structure of a protein. These features provide a set of ideal conditions for specific substrate binding modes and selective chemical reactions to occur. Theoretically, a suitable protein or biocatalyst could be screened in Nature or at least engineered based on a pre-existent protein scaffold, for any synthetic process.

Two different examples of oxidoreductase enzymes will be presented to demonstrate the fine control of the metallic cofactor on the activation barrier and energy of the catalysis, as well as the role of the protein environment and solvent on the productive binding modes of the substrate. A third example of a non-metalloprotein will be introduced and its structural and chemical properties contrasted with the previous one, based on a quantum mechanical and molecular mechanical approach.

Immobilization of naringinase in PVA–alginate matrix using an innovative technique

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A synthetic polymer, polyvinyl alcohol (PVA), a cheap and non-toxic synthetic polymer to microorganisms, has been used for biocatalysts immobilization [1].

An extracellular naringinase (an enzyme complex consisting of α -L-rhamnosidase and β -D-glucosidase activity) that hydrolyses naringin (a trihydroxy flavonoid) was used for the production of naringenin, glucose and rhamnose. Naringin and its aglicone, naringenin, are healthy compounds with biological and pharmacological activities, such as anti-oxidant, anti-inflammatory and anti-cancer, showing a high potential in the pharmaceutical industry.

Studies regarding immobilization of naringinase on polymer matrices, calcium alginate [2], k-carrageenan [3], and the reusability of the immobilized enzyme have been reported.

A simple and economical technique of enzyme immobilization with PVA is PVA–boric acid method. However there are problems associated with this method such as the agglomeration of PVA gel beads and toxicity of saturated boric acid. Nevertheless, with the addition of sodium alginate, the agglomeration of PVA gel beads can be reduced.

The main focus of this study was to investigate the feasibility of the PVA–boric acid and alginate method and evaluate the PVA–alginate beads in terms of the enzyme activity within the beads, immobilization yield, and at the same time the stability of the PVA–alginate beads. Different sodium alginate concentration was used. The effects of matrix concentration, temperature, agitation, beads size, enzyme load and pH on immobilization efficiency were studied.

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Chemistry & Art: The Primitive Flemish Technique and Determination of Lacquered Objects Origin

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Since 19th century, science has been applied to the field of arts and archaeology, largely contributing to the knowledge and preservation of cultural heritage. The scientific study of works of art may have different objectives such as the identification of the materials that constitute the object and the technique of its execution, the investigation of its state of conservation, its authentication or epoch of production [1].

Though a great sort of materials can be found in works of art, they can be grouped into few classes: oils, resins, gums, proteins, waxes, lacquers, pigments (mainly inorganic salts or oxides) and dyes. The identification of these materials can be made by using the most common analytical techniques. The only limitation is the small size of samples ranging from some millimeters to few micrometers. This restricts the analytical methods employed to those capable of analyzing microsamples. From the available methods, the most frequent techniques applied are: X-ray fluorescence spectrometry for elemental analysis; X-ray diffraction, infrared spectroscopy, and microchemical reactions carried under an optical microscope for the identification of pigments; infrared spectroscopy and chromatographic methods for the determination of organic materials [1, 2].

In this communication we intend to show how chemistry is applied to the field of fine arts presenting two case studies: one about the technique of execution of a set of Primitive Flemish panels from the *Museu de Évora*, and another where the origin of a lacquered shield was determined. In both cases, cross-sections of the samples were prepared and their multilayered structure was visualized. Materials were then identified and, in the case of the shield, lacquer type identification allowed to determine its origin.

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Portuguese Young Chemist Meeting **1ST PYChem**



Flash Communications

Di-rhodium (II) catalysts for arylation of aldehydes

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Di-rhodium(II) complexes are bi-metallic complexes highly popular among the organic chemistry community due to their remarkable efficiency in the generation of metalo-carbenoids from diazo compounds. These complexes exhibit a Rh-Rh bond, two axial ligands, and four bridging ligands which are responsible for controlling the electrophilicity and asymmetry. When compared with the bridging ligands, the two axial ligands form a weaker bond with the electrophilic center (normally solvent molecules) and are thought to play a less important role in catalysis as they are easily displaced.¹ Fürstner et al shown that di-rhodium tetraacetate in presence of in situ generated N-heterocyclic carbenes (NHCs) can participate in aldehyde arylation reactions.²

We prepared complexes of Rh₂(OAc)₄ with one and two NHCs attached on the axial positions were successfully isolated, fully characterized and used as active catalysts in the reaction. These catalysts provided a highly efficient new methodology for the arylation of aryl, alkyl and vinyl aldehydes using arylboronic acids as the aryl transfer agent. The results obtained taken together with theoretical and structural studies performed on this system, have unveiled a new reaction mode for di-rhodium(II) complexes that does not follow a traditional transmetallation pathway.³

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Morphology of Thin-Films of Polyfluorene:Fullerene Blends

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Organic semiconductors have spawn new solutions in optoelectronics, and are doing so as well in photovoltaics (PVs). Even though the energy conversion efficiency of organic solar devices is still considerably lower than that of conventional inorganic PVs and improvement is necessary before commercial applications are possible, they present some other advantages such as high flexibility and low-cost production. These contribute towards broadening the application field and towards turning PVs a more widespread energy resource. One promising candidate is the polymer:fullerene blend solar cell, that has reached an efficiency of 4 – 5% [1]. Efficiency improvements are closely linked to the understanding of the processes involved in the generation, the transport and the collection of charge carriers within the active layer of solar devices, which are directly influenced by the morphology of the layer.

In our research project, morphological issues in thin-films spin-coated from blends of low-bandgap polyfluorenes and fullerene derivatives are being investigated. Film morphology is manipulated through (a) choice of solvent and spin-coating conditions; (b) control of surface energy of the substrate; and (c) use of specifically tailored molecules aimed at promoting vertical versus lateral structures. Characterization of the thin-film topography is performed through Atomic Force Microscopy (AFM), and the in-depth organization of the blend components through dynamic Secondary Ion Mass Spectrometry (dSIMS).

Previous studies have shown self-stratified films of polyfluorene:fullerene blends to form spontaneously under specific conditions, which improved solar cell performance [2, 3]. The mechanisms leading to these results can be rationalized with thermodynamic and kinetic models of nucleation and phase separation [4]. In recent studies an increased tendency for self-stratification was found on a series of films prepared from fullerene blended with polymers that had been especially synthesized with varying fractions of a polar monomer.

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New Cp*-Functionalized N-Heterocyclic Carbenes and Their Coordination to Iridium and Rhodium

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Recently, we have reported the first pentamethylcyclopentadienyl-functionalized N-heterocyclic carbene ligand Cp*-NHC^{Me} and its coordination to Ir. The chiral Ir complex was obtained as a racemic mixture of the two possible enantiomers.[1] Herein, we report new synthetic pathways for Cp*-functionalized-NHCs that allow us to isolate the enantiomerically pure chiral Cp*-NHC^{Ph} ligand and prepare in gram scale the novel pentamethylcyclopentadienyl-ethyl-NHC ligand (**1**). Coordination of these new ligands to Ir and Rh will be discussed.

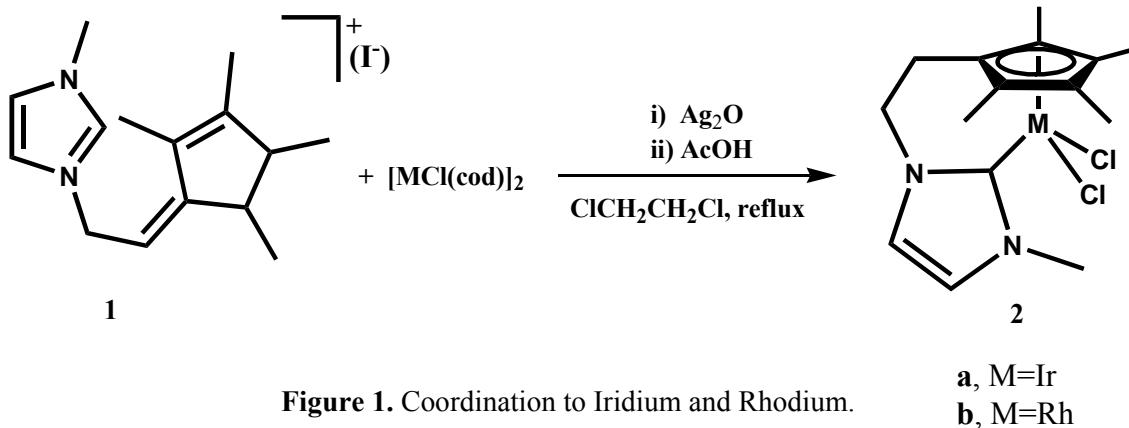


Figure 1. Coordination to Iridium and Rhodium.

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Activated carbons for adsorption of clofibric acid

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Clofibric acid is the active metabolite of the blood lipid regulators clofibrate, etofyllin clofibrate, and etofibrate, being one of the most frequently detected chemicals in environment monitoring of pharmaceuticals [1,2]. It has been found in wastewaters, surface waters, groundwater, and seawater [2]. The first clofibric acid detections were reported in samples from sewage treatment plants in the U.S. in the 1970s [2], and nowadays, this metabolite is regarded as one of the most persistent drug residues with an estimated persistence in the environment of 21 years. Since the contamination of waters with clofibric acid is a reality, it is important to search for effective removal technologies. Ternes et. al. (2002) report that the use of activated carbons filtration associated to ozonation may be an effective technology to remove this metabolite from aqueous media.

The aim of this work was to assess the potentialities of two cork-based activated carbons, prepared following a previously optimized procedure [3], for the removal of clofibric acid from aqueous solutions. For comparison purposes two commercial activated carbons commonly used in water treatment were also assayed. The textural and chemical properties of activated carbon samples and the effects of solution pH and initial clofibric acid concentration in the adsorption process were evaluated. Clofibric acid concentration was determined by HPLC. The kinetic results of clofibric acid adsorption at 30 °C and at pH 2, 3.6 and 5 were studied. Equilibrium isotherms were carried out at pH 3.6. The results highlight the fundamental importance of the solution pH in the adsorption process on all the studied carbons. The highest removals and the fastest adsorption were obtained for pH 2. The equilibrium adsorption isotherms are sigmoidal indicating that, the interaction between the adsorbate and the carbons is unfavorable for low concentrations but favored at higher concentrations.

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Interplay Between Energy and Electron Transfer in the Luminescence Quenching of Eu (III) in Glass by *d*-Metals

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Lanthanide ions such as Eu(III) display an intense luminescence that has been used in many multidisciplinary areas such as Biology, Chemistry and Earth Sciences.¹ In particular, Eu(III) is introduced as a fluorescent impurity in glass, enabling the production of glass materials with the ability of glowing under UV light, with applications in both technological applications and art. For example these materials have been recently exploited in Fine Arts, in order to access new aesthetic possibilities using luminescence in Glass Sculptures. Coloured luminescent glasses offer new possibilities to artists, but the use of *d* metals to colour glasses has the drawback of suppressing the Rare Earths luminescence. A detailed study of the quenching properties of these elements is essential for the future development of these new materials.

In this communication, we present results in inorganic glass constituted by Na₂O-CaO-SiO₂ doped with Eu(III) and using Co(II), Mn(IV), Fe(III), Cu(II) and Cr(III) as fluorescence quenchers. Europium was chosen as a probe rare earth element due to its unique luminescence properties [2-4], with sharp emission lines, with sharp emission lines. This work consist in the study of the interactions between Eu³⁺ and with *d* transition metals, namely the influence of the glass matrix in the Eu³⁺ luminescence, the oxidation state of the *d* transition metals in the glass and the nature of the luminescent quenching, if it is energy or electron transfer nature.

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New Calix[4]pyrrole Dimers:

Synthesis and Anion Binding Studies

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Compounds capable of selective binding and recognition of anionic substrates are of considerable interest due to the importance of such anionic species in areas such as environmental chemistry and biology [1,2]. Among the compounds able to bind anions, recently calixpyrroles have gained a significant attention; compounds of this type are being used as optical sensors for anions [3-5].

In this communication we will describe the synthesis of two new calix[4]pyrrole dimers obtained from the reaction of octamethylcalix[4]pyrrole-2-carbaldehyde (**1**) [3] or 3-(octamethylcalix[4]pyrrol-2-yl)prop-2-enal (**2**) with hydrazine. The abilities of those dimers to bind different anions will be also reported.

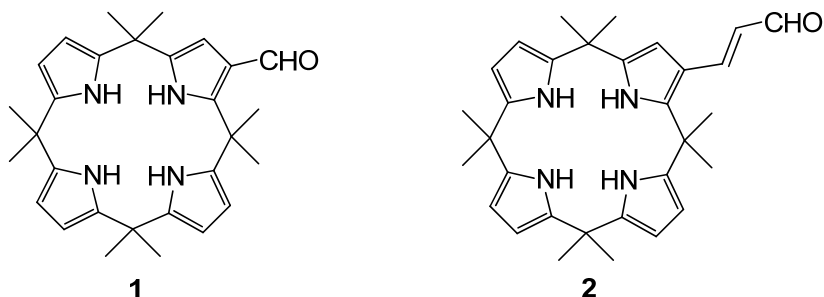


Figure 1. Compounds **1** and **2**.

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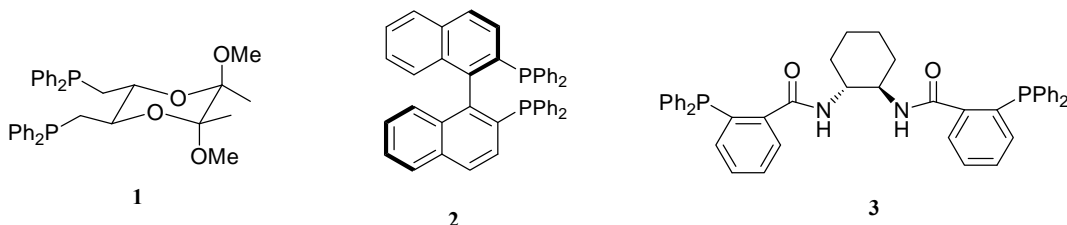
Application of “Borrowed” *P,P*-Ligands in Catalytic Asymmetric Synthesis

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Catalytic asymmetric synthesis is an exceedingly powerful way to access useful enantiomerically pure compounds. Over the last few decades some outstanding endeavours in this field have been achieved using catalysts containing diphosphine ligands for asymmetric hydrogenation of different kinds of unsaturated systems. We have been looking at the application of key diphosphine ligands like Berens ligand **1**^[1,2], (R)-BINAP **2**^[3,4] and (R,R)-DACH-phenyl Trost ligand **3**^[5] with a proven track record in various catalytic reactions like, asymmetric allylic alkylations^[6], hydroborations-oxidations^[7] and hydrosilylations^[7].



In this communication we will discuss highlights from our studies on the employment of these key ligands in the aforementioned catalytic asymmetric reactions.

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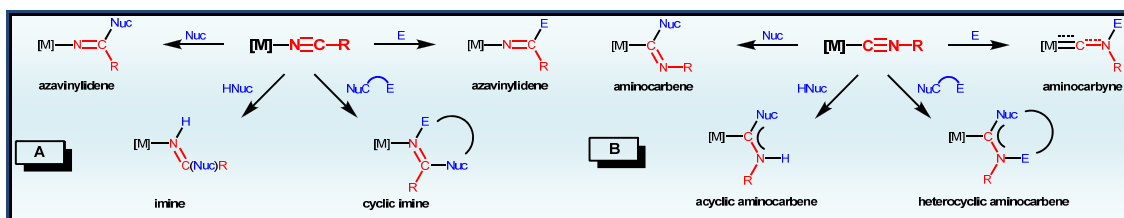
Metal-mediated Transformations of Nitriles and Isocyanides: The Routes to Imines and Heteroatom-Stabilized Carbenes

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Activation upon coordination to a metal center of nitriles and isocyanides (**Scheme 1**) is currently a relevant research direction in Coordination and Organometallic Chemistry [1]. Being isoelectronic with dinitrogen but far more reactive, these species are employed as versatile precursors for the preparation of important products, such as amides, imines, phthalocyanines, 1,3,5-triazapentadienes, iminoisoindolinones, *etc.* [2,3]. For example, transformations of isocyanides allow the stereoselective synthesis of *bis*-amides, heterocycles and peptides *via* multicomponent reactions. Moreover, $RN\equiv C$ species attract attention due to their ability to form *heteroatom-stabilized metallacarbenes*, prominent in organometallic catalysis, *e.g.* for hydrosylation of alkenes and cross-coupling reactions (*e.g.*, Heck, Suzuki, Suzuki–Miyaura, Sonogashira, Kosugi–Migita, and Stille).



Scheme 1. Metal-mediated transformations of nitriles (A) and isocyanides (B).

This report provides a synthetic, structural and mechanistic overview of the recent advances in the field of metal-mediated transformations of organonitriles and isocyanides with a particular emphasis addressed to the activation of the $C\equiv N$ moiety towards the addition of weak protic nucleophiles and dipoles.

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Chemistry & Art: The Primitive Flemish Technique and Determination of Lacquered Objects Origin

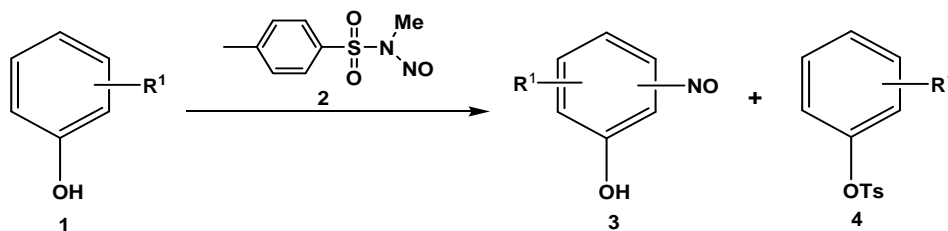
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Phenolic compounds are known to act as natural antioxidants and inhibitors of N-nitroso compound formation, because they usually react with nitrite more rapidly than most amino compounds [1]. Much discussion has been going on whether the reaction occurs directly on the carbon atom [1,2,3] or if the previous formation of an O-nitroso intermediate is involved [4,5]. In order to further enlighten the reaction mechanism, kinetic experiments involving the transnitrosation of a series of substituted phenols **1** by N-Methyl-N-Nitroso-*p*-toluenesulfo-namide **2** (MNTS) were run (Scheme 1). The ambident character of the electrophile leads, in some cases, to occurrence of the phenol *p*-toluenesulfonate **4** along with **3**.

The halogenated phenols studied reacted only very slowly with MNTS. Phenols with methoxy substituents in positions 2, 4 and/or 6 do not react at all as well as 2,6- and 3,5-*t*-Butylphenols. Phenols exhibiting a measurable rate constant and fittable absorbance-time data showed that the reaction is first-order in phenol and base-catalysed. The existence of a linear relationship between *k* and the *pK_a* of the phenolic oxygen atom strongly suggests that reaction occurs exclusively through that atom. Further support to this hypothesis comes from the observation that no reaction occurs between MNTS and anisole under the same conditions.



R^1 = 2-Me-5-*i*-Pr; 2-*i*-Pr-5-Me; 2,6-*t*-Bu; 3,5-*t*-Bu; 2-F; 2-Cl; 4-Cl; 2-Br; 3-Br; 4-Br; 2-OMe; 3-OMe; 4-OMe; 2,3-OMe; 2,6-OMe; 3,5-OMe.

Scheme 1. Nitroso group transfer from N-Nitrosobenzenesulfonamides to substituted phenols.

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Catalytic Studies of Heptacoordinate Mo(II) and W(II) Complexes Supported in a Mesoporous Material

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The immobilization of complexes on solid supports is one of the most important routes for developing novel heterogeneous catalysts. Organometallic complexes can efficiently and selectively catalyze many reactions, ^[1] so that the heterogeneization procedure should preserve these features and add the advantages of heterogeneous catalysts (easy separation of products and recovery of catalysts). $[MX_2(CO)_3(MeCN)_2]$ complexes (M=Mo, W; X=Br, I), were synthesized with selected N-N ligands and subsequently immobilized in a MCM-41 material by reaction with the previously supported analogous silylated ligands. Porous materials (PMO) were prepared in a one-pot synthesis containing the ligands and allowed to react with the complex precursors. The complexes and the new materials were characterized by standard techniques, and their catalytic activity was tested in the epoxidation of olefins and allylic alcohols, in the presence of t-BuOOH as oxidant, in homogeneous and heterogeneous conditions. The effects of metal (Mo and W), ligands, and homogeneous vs. heterogeneous catalysis were analyzed.

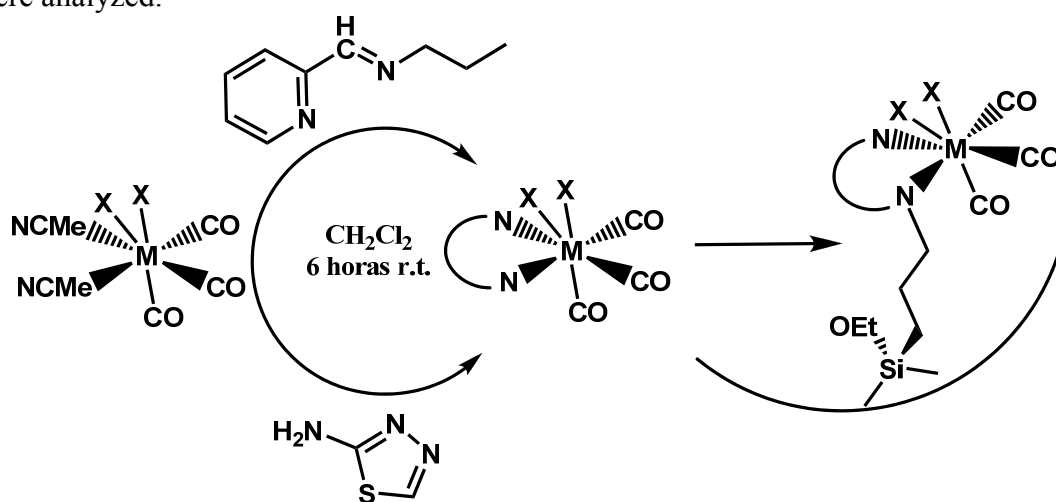


Figure 1: Scheme

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Surface-Enhanced Raman Scattering of *trans*-3-Hydroxycinnamic Acid Adsorbed On Silver Nanoparticles

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SERS has been widely used to study the adsorption of a large group of organic molecules on metal surfaces, mostly because it allows for accurate structural studies of adsorbates at very low concentration. This technique can be used to determine which species are adsorbed, which functional groups are in contact with the surface and even the conformation of the adsorbed molecule. It is rather easy to find SERS of aromatic acids adsorbed on silver surfaces^{1, 2} reported in the literature but it is more difficult to find SERS records of molecules such as alcohols, perhaps because they have little affinity to the metal surface.

In this study, Raman and SERS spectra of *trans*-3-Hydroxycinnamic acid (*t*-3OHCIA) adsorbed on silver colloids at different pH values have been recorded. From the analysis of the SERS it is possible to conclude that this acid is adsorbed as an anion, in good agreement with the pK_a=4.5 found in the literature³.

The contribution of the charge transfer (CT) mechanism to the SERS enhancement (SERS-CT) has been investigated as well. This mechanism involves the resonant transfer of an electron from the metal to the adsorbate and it is found to be quite important in the SERS of aromatic molecules, where it is characterized by the selective enhancement of vibration 8a;v_{ring}. Vibration 8a plays a key role in SERS-CT because this particular vibration connects the equilibrium geometries of both electronic states involved in the resonant process: $G + e \rightarrow E$, namely the ground state of the adsorbed species (G) and that of CT-excited state (E).

It has been found that the resonant CT processes are involved in the SERS records of *t*-3OHCIA, explaining the observed selective enhancement of the 8a mode.

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1H NMR Study on Micellization of Amphiphilic Sulfonatocalix[4]arenes

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In this communication we present the results of the NMR study carried out on the micellization of an amphiphilic sulfonatocalix[4]arene. We obtained diffusion coefficients (D) from the Diffusion Ordered Spectroscopy (DOSY) above and below the critical micellization concentration (cmc). From these values it is possible to determine the cmc, the hydrodynamic radius and the number of aggregation. Usually, rapid exchange occurs between the monomers in the bulk and in the micelles and NMR techniques show averaged signals for the surfactant molecules in their various states. However, from the simple ^1H NMR spectra, for concentrations above the cmc we observed the undergoing exchange equilibrium among the two set of signals corresponding to the monomer and to the micelle. We have further characterized the exchange by complete lineshape analysis and additional experiments such as saturation transfer difference (STD) NMR. The results provided a detailed characterization of the micellization of this special class of surfactants molecules.

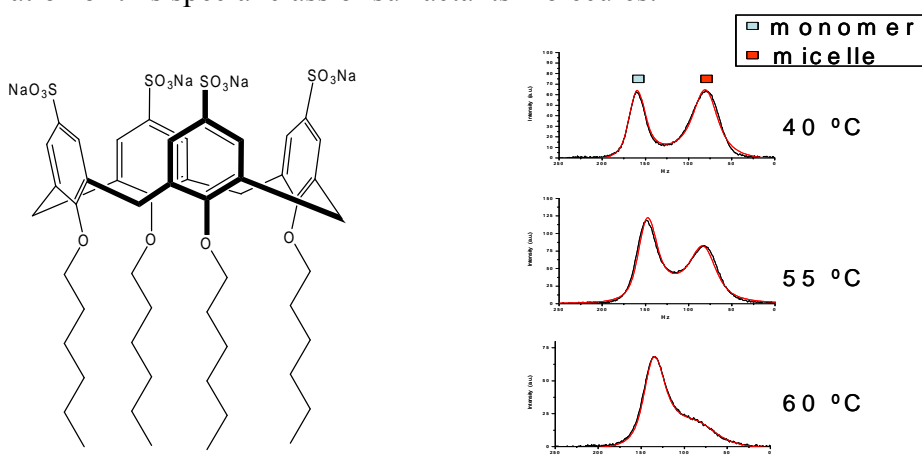


Figure 1. Structure of the amphiphilic calix[4]arene and the exchange phenomenon observed by H NMR between monomer and micelles signals.

Acknowledgements: N.B. acknowledges to the Fundação para a Ciência e Tecnologia(FCT) for a doctoral grant (SFRH/BD/29218/2006).

Porphyrins in 1,3-Dipolar Cycloadditions with Nitrile Imines

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The development of new synthetic methods leading to reduced porphyrins (mainly chlorins and bacteriochlorins) is an area of big interest. This is due to the significant potentialities of this type of compounds as efficient photosensitizers for photodynamic therapy (PDT) [1]. Our group has shown that *meso*-tetraarylporphyrins can participate in 1,3-dipolar cycloaddition reactions with a variety of 1,3-dipoles leading to chlorins, bacteriochlorins and isobacteriochlorins in good yields [2].

Nitrile imines (propargyl-allenyl type 1,3-dipoles) have been extensively used in 1,3-dipolar cycloaddition reactions with alkenes to synthesize pyrazolines and pyrazoles [3]. In this communication we will report our systematic studies concerning the 1,3-dipolar cycloaddition of several nitrile imines to *meso*-tetrakis(pentafluorophenyl)porphyrin with different bases and solvents. Pyrazole-fused chlorins **3** are the main products of such reactions.

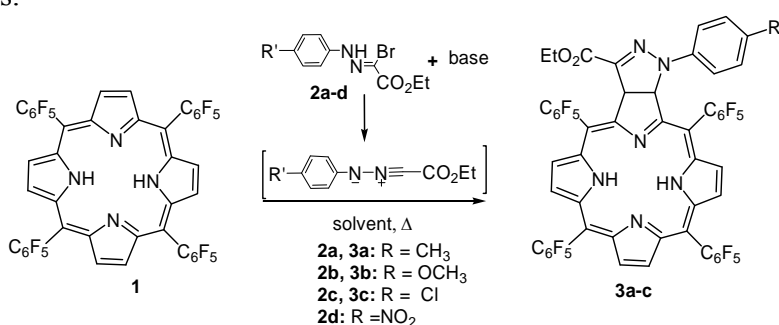


Figure 1 - Synthesis of **1** through a 1,3-dipolar cycloaddition reaction.

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New Hexaaza Macrobicyclic Cyclophane for Recognition of Tetrahedral Dianions

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The selective binding, extraction and separation of anions are pointed out as potential solutions to several environment related problems. Oxoanions in particular, such as nitrate, phosphate, sulfate, chromate, selenate, arsenate and pertechnetate, are relevant targets as the uncontrolled spread of these contaminants poses risks to human health and to the environment. [1,2]

Aiming to contribute to the control of oxoanions, we designed a new hexamine cage (Figure 1) to be used as receptor for their selective binding. This compound was synthesized in good yield by a [2+3] Schiff-base condensation followed by sodium borohydride reduction. The protonation constants of the new receptor, as well as its binding constants with Cl^- , I^- , NO_3^- , AcO^- , ClO_4^- , H_2PO_4^- , SO_4^{2-} , SeO_4^{2-} and $\text{S}_2\text{O}_3^{2-}$, were determined by potentiometry at 298.2 K in MeOH/H₂O and at ionic strength 0.10 mol dm⁻³ in TsOK. These studies revealed the selective binding of dianionic tetrahedral anions by the receptor.

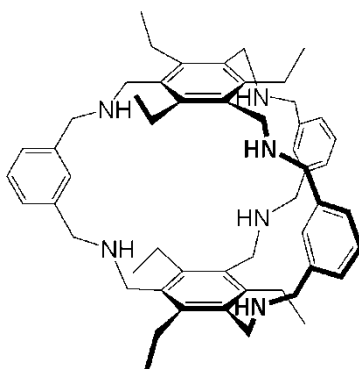


Figure 1. New hexaaza macrobicyclic cyclophane.

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Cyclam in early transition metal chemistry: synthesis, reactivity and applications of Zr(IV) complexes

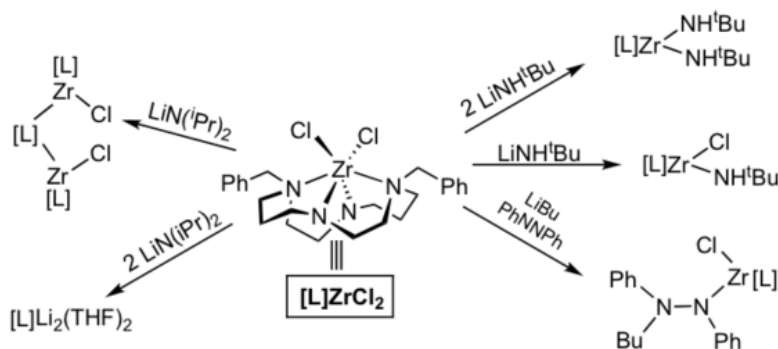
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Modern coordination chemistry can be defined as a series of steps. The first step is to design a ligand with the correct balance of electronic and steric properties; the second step is to develop a synthetic methodology for the preparation of the metal complexes; and thirdly, to study the reactivity and potential applications of the newly prepared compounds. Although cyclam has been thoroughly studied, its early transition metal chemistry remains unexplored and limited to sporadic examples. In our laboratory we have prepared novel zirconium complexes supported by cyclam-based diamido/diamine ligand sets¹. The challenge now lies in studying its reactivity and some examples are outlined in Scheme 1. Reactivity studies with hydrazines and attempts to generate an imido fragment have been object of intense study due to the potential application of these complexes in hydroamination reactions. In addition, the zirconium amido compounds have proved to be excellent catalysts for the polymerization of ϵ -caprolactone, evidencing the versatility and the promising chemistry of this new type of compounds.



Scheme 1

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***Helichrysum devium* – An Endemic Medicinal Plant from Madeira Archipelago**

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Plants of the genus *Helichrysum* belong to the Asteraceae family. In Madeira Archipelago (Portugal) *Helichrysum devium* Johns, endemic sub-specie of *Helichrysum*, is used in traditional folk medicine for treating bronchitis and pharyngitis. Preliminary biological tests such as evaluation of *Artemia salina* toxicity and antimycobacterial activity were performed over raw methanol extracts of the aerial parts. These extracts showed very high activity over *Mycobacterium tuberculosis* (<50 µg/mL).

Subsequently, different morphological parts (flowers and leaves) of *H. devium* were extracted with solvents of increasing polarity (*n*-hexane, chloroform, ethyl acetate and methanol).

The antioxidant activities of these extracts were evaluated using 3 methods: α - α -Diphenyl- β -picrylhydrazyl (DPPH), 2,2'-azinobis (3-ethyl-benzothiazoline-6-sulfonic acid) (ABTS) and ferric reducing power (FRAP). The content of total phenolic compounds was determined by the Folin-Ciocalteu method. The obtained results from these methods are in good agreement with one another and showed a clear distinction between flowers and leaves: while the *n*-hexane extract of flowers exhibits the highest antioxidant activity, (followed by the ethyl acetate, chloroform and methanol extracts, respectively), for leaves, ethyl acetate extract exhibits the highest antioxidant activity, followed by chloroform, *n*-hexane and methanol extracts.

Analysis by HPLC-DPPH on-line method was used for screening the several radical scavenging components in these extracts: when radical scavengers are present, the DPPH radical is reduced to a colourless product. This reduction is observed after an HPLC separation by a visible wavelength detector as a decrease in absorption at 517 nm. All extracts contain several substances with antioxidant activity, some of them tentatively identified as derivatives of quinic acid.

Acknowledgements:

SG thanks FCT for a PhD grant SFRH/BD/24227/2005.

Novel 4(1*H*)-Pyridonimines as Potential Cytochrome *bc*₁ Inhibitors in *Plasmodium falciparum*

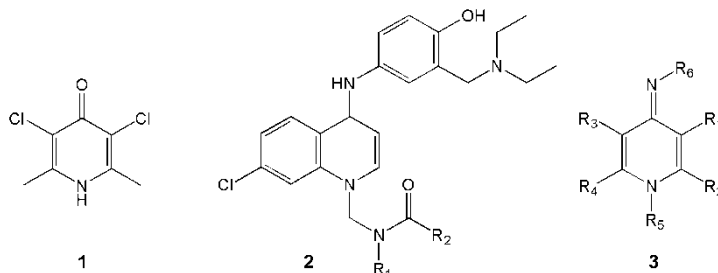
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Malaria is one of the major diseases in the world, killing 1 to 3 million people a year [1]. The emergence of resistant strains of malaria suggests the need to discover both new drug targets and active molecules [2]. Cytochrome *bc*₁, from the mitochondrial electron transport chain, is one attractive and validated drug target, for which few efficient inhibitors are known today [3]. Clodipol, **1**, is a known *bc*₁ complex inhibitor and has been taken as a lead for structural optimization [4].

Recently we described a series of amodiaquine-like derivatives, **2**, which display good antimalarial activity [5] and a similar double bond arrangement to clodipol, **1**. Removal of the fused benzene ring led to the 4(1*H*)-pyridonimine scaffold, **3**. In this work, a series of compounds **3** were subjected to quantum mechanical studies to determine the major structural and electronic features that might be relevant to understand the ligand interaction with cytochrome *bc*₁. A docking study revealed stabilization of the cyt *bc*₁-ligand complex through hydrophobic interactions, but with a new pose within *bc*₁ complex Q₀ site [6]. An outline of the study will be given and the implications of the results discussed.



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Synthesis of *bis*-(Indolyl)methanes as Highly Selective Colorimetric and Fluorescent Chemosensors for Cu²⁺ Cations

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The transition metal Cu²⁺ is the third in abundance, after Fe²⁺ and Zn²⁺, amongst the essential heavy metal ions in all living forms, from bacteria to humans, and it plays a determinant role in several physiological processes. On the other hand, excess in Cu²⁺ concentration in physiological tissues showed severe toxicity which include cellular homeostasis and neurodegenerative diseases, like Alzheimer's disease. There has been a growing interest in the development of heterocyclic compounds as fluorescent and colorimetric chemosensors for the recognition of transition metals, particularly the ones involved in biological processes [1]. Among the chemosensors developed so far, few could be applied in aqueous solutions due to the strong hydration ability of the ions. Also, none of them are based in pyrrolic NH group which is mostly applied for anion detection. In fact the first cation receptor with this functional group was only reported recently [1,2]. Therefore we decided to synthesize new *bis*(indolyl)methanes containing functionalized aryl and thienyl moieties. These heterocycles were prepared in good to excellent yields by reaction of indole with formyl- aryl and thienyl derivatives, in the presence of a base in methanol at room temperature. Functionalized (oligo)thiophenes have been used recently, by us, due to their optical and electronic properties, with various optical applications such as colorimetric and/fluorimetric sensors[3].

The synthesized compounds were studied as cation chemosensors by colorimetric and fluorescence techniques and the results showed that *bis*(indolyl)methanes containing functionalized aryl and thienyl groups could be used as selective fluorescent and colorimetric molecular chemosensors for Cu²⁺ ions, in aqueous/acetonitrile solution.

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Portuguese Young Chemist Meeting **1ST PYChem**



Poster Presentations

Structural and Magnetic Characterization of $[\text{Ni}(\alpha\text{-tpdt})_2]$ Salts With Fe Spin-Crossover Cations.

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The development of multifunctional and switchable materials is one of the current trends in materials science. The molecular building-block approach lead us to prepare combined salts with a paramagnetic anionic complex $[\text{Ni}(\alpha\text{-tpdt})_2]^-$ ($\alpha\text{-tpdt}$ = 2,3-thiophenedithiolate), that proved to be a suitable unit for preparing molecular magnetic materials¹, and mononuclear cationic Fe^{III} with Hqsal ligand derivatives (Hqsal = *N*-(8-quinolyl)salicylaldimine),² which are well known spin-crossover systems.

The synthesis, crystal structure and magnetic properties are presented for the salts $[\text{Fe}(3\text{-X-qsal})_2][\text{Ni}(\alpha\text{-tpdt})_2] \cdot \text{CH}_3\text{CN}$ ($\text{X} = \text{Br}, \text{Cl}$). Using single-crystal X-ray diffraction, the structures were found to be identical, composed of alternated layers of anions and cations along *c*. The anionic layers show the typical arrangement of $[\text{Ni}(\alpha\text{-tpdt})_2]$ salts. The coordinating bond lengths for Fe^{III} are within the expected values for both spin states of $[\text{Fe}(\text{Hqsal})_2]^+$ salts which is in agreement with the magnetic measurements that indicate a spin-crossover transition above 300K.

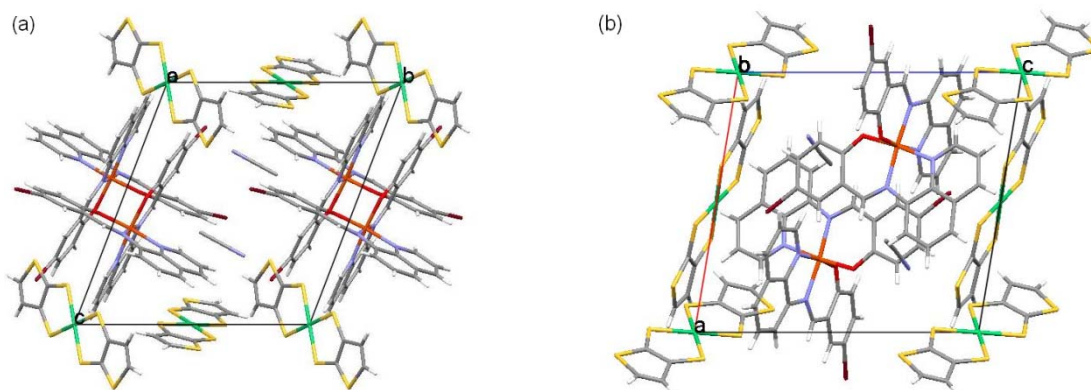


Figure 1. Crystal structure of $[\text{Fe}(3\text{-Br-qsal})_2][\text{Ni}(\alpha\text{-tpdt})_2] \cdot \text{CH}_3\text{CN}$ viewed along *a* (a), and along *c* (b).

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Phenols Glycosylation Promoted by the Zeolite HY

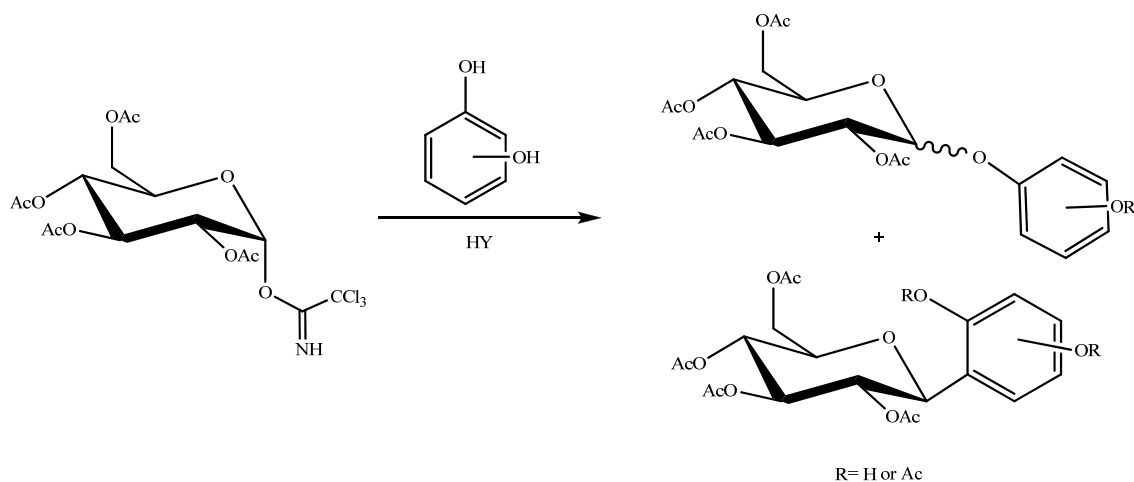
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The main objective of this work consisted in the investigation of new and environmental methodologies for phenols glycosylation. For that purpose zeolite HY was used as promoter of catechol and resorcinol condensation with glucosyl donor 2,3,4,6-tetra-*O*-acetyl- α -D-glucopyranosyl trichloroacetimidate (see Scheme 1). Its synthesis was accomplished by selective anomeric deacetylation of peracetyl glucose with ammonium carbonate in DMF for 20h, followed by the treatment with potassium carbonate and trichloroacetonitrile at room temperature [1].



Scheme 1. Phenols glycosylation using zeolite HY as promoter.

In this work two different methodologies were used. In one of them, the reaction mixture was extracted with ethyl acetate, the zeolite was filtered off, the solvent evaporated and the residue was submitted to column chromatography. In alternative, peracetylation of the reaction mixture prior to the separation of the compounds was accomplished in order to enhance the separation efficiency. The major reaction product was the β -*O*-glucoside, but α -*O*- and β -*C*-glucosyl derivatives were also isolated in lower yield for both aglycones.

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Vinylsulfones as a Michael acceptor scaffold in the design of caspase inhibitors

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Apoptosis, or programmed cell death, is a major process important for development and defense of organisms. The uncontrolled proteolysis can lead either to pathological loss of cells (stroke, neurodegeneration, liver failure) or excessive accumulation of cells (cancer).[1]

At the center of this death process is a family of proteases named caspases or cysteinyl aspartate-specific proteases.[2] In consequence, caspases are recognized as novel therapeutic targets for central nervous diseases in which cell death occurs mainly by an apoptosis mechanism. One type of cysteine proteases inhibitors that has received special attention in the last few years are those based on Michael acceptor scaffold.[3] However there are very few examples of cysteine proteases inhibitors for the clan CD, to which caspases belong to.

Herein, we describe the synthesis of vinylsulfones as Michael acceptor scaffolds and as potential caspase inhibitors (Figure 1). The choice of this scaffold was based on the successful results demonstrated by vinylsulfones for other clans of cysteine proteases.[4]

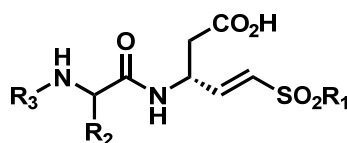


Figure 1 – Vinylsulfones as potential caspase inhibitors

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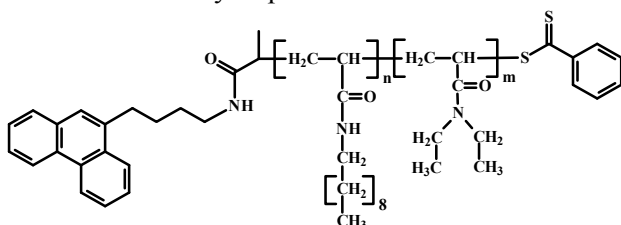
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Micellar Aggregation of Poly(DcA-*b*-DEA) Amphiphilic Copolymers in Water

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Amphiphilic block copolymers of poly(*N*-decylacrylamide-*b*-*N,N*-diethylacrylamide) (p(DcA-*b*-DEA)), with the same pDcA hydrophobic block and pDEA hydrophilic blocks of several lengths were synthesized by RAFT. These copolymers with structure I bear a phenanthrene group at the end of the hydrophobic block.



These copolymers self-assemble in water forming micelles with dimensions that vary with temperature owing to the thermosensitivity of the pDEA block.

The micellar aggregates were characterized by light scattering. The static light scattering allows the

calculation of the molecular weight, M_w , and the second Virial coefficient, A_2 , of the micellar aggregates in water. The aggregation number of the micelles is independent of the length of the hydrophilic block, $N_{agg} = 30$. The second Virial coefficient is also independent of the length of the hydrophobic block. Figure 1 shows the variation with temperature of the hydrodynamic radius of the micelles at several temperatures.

The hydrodynamic radius vary with temperature according to the scaling law: $R_H = R_C + bm^v$ Derived from then star micelles model [1,2]. From the global fit of the experimental curves it was possible to recover the radius of the core, $R_C = 4.3$ nm and the scaling coefficient, a , at several temperatures. The radius of the core from the model compares with that obtained from the FRET measurements between the phenanthrene labeled polymers and anthracene homogeneous dispersed in the core of the micelles. The scaling coefficient decreases with temperature from $v=0.64$ at 7 °C to $v=0.59$ at 25 °C according to the decrease of the quality of water to pDEA with temperature increase.

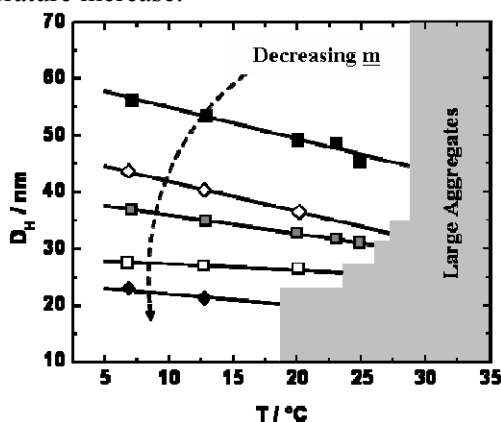


Figure 1. The hydrodynamic radius with temperature

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Partial Oxidation of Methane Over Heterobimetallic Nickel-Lanthanide Oxides

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The partial oxidation of methane (POM) constitutes a proper way to produce syngas ($\text{CO} + \text{H}_2$) and provides a suitable H_2/CO ratio for the methanol and Fischer-Tropsch synthesis. Nickel catalysts supported on ceria [1] and lanthanum oxide [2] has been investigated for partial oxidation of methane to syngas. They were reported to be active catalysts for this reaction. The purpose of this work was to study the performance of binary intermetallic compounds of the type LnNi ($\text{Ln} = \text{Pr}$, Gd and Tm) used as catalytic precursors [3] for partial oxidation of methane from 350°C at 800°C. The results were compared with those of nickel oxide. This study was performed for a high GHSV (8500 $\text{mL}_{\text{CH}_4}/\text{g}_{\text{cat}} \cdot \text{h}$). At 750 °C, the activity expressed as percentage of methane converted is: NiO (22%), PrNi oxide (26%), GdNi oxide (84%), TmNi oxide (80%). The last two are more active than nickel oxide with selectivities to H_2 and CO of 78% and 21% respectively, and H_2/CO ratio of 4.

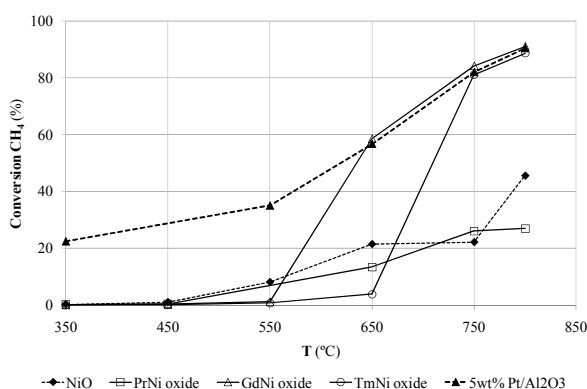


Figure 1. POM over heterobimetallic nickel-lanthanide oxides

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Peptidomimetics by multi-component synthesis

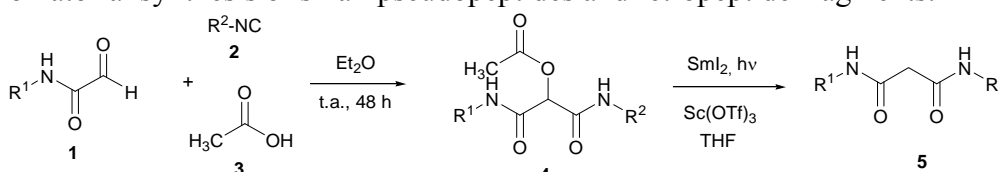
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The synthesis of retro- and retro-inverso peptides, peptide analogues in which one or more peptidic bonds are inverted, was shown to be an effective strategy for the development of peptidomimetic drugs with improved bioavailability and metabolic stability.¹

As a result of our interest in the use of multi-component reactions, we have recently reported a synthesis of hydroxyglycine retropeptidic derivatives through a Passerini condensation² of glyoxylic acid derivatives.³ In an extension of this work, we wish to report here the synthesis of peptidomimetics containing malodiamide as a retropeptidic subrogate of glycine. The Passerini reaction forms acylated tartronamide derivatives (**4**), which are readily transformed into the desired pseudopeptides (**5**) by reductive deacetoxylation with SmI_2 in the presence of UV irradiation and catalytic $\text{Sc}(\text{OTf})_3$ (Scheme 1). The versatility of this procedure, which allows introducing different amino acid residues at both ends of the tartronamide unit, makes it useful for the combinatorial synthesis of small pseudopeptides and retropeptide fragments.



Scheme 1

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Carbohydrates Extraction From Aqueous Solutions Using Ionic Liquids

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Carbohydrates extraction from aqueous solutions have been reported using quaternary ammonium salts and lipophilic boronic acids, which can form reversible covalent complexes with diol groups in carbohydrates [1,2]. Here is described a much simpler method for the extraction where a hydrophobic ionic liquid (**Figure 1**) can extract directly the carbohydrate from an aqueous solution without the need of a surfactant, or a buffer solution in the aqueous phase.

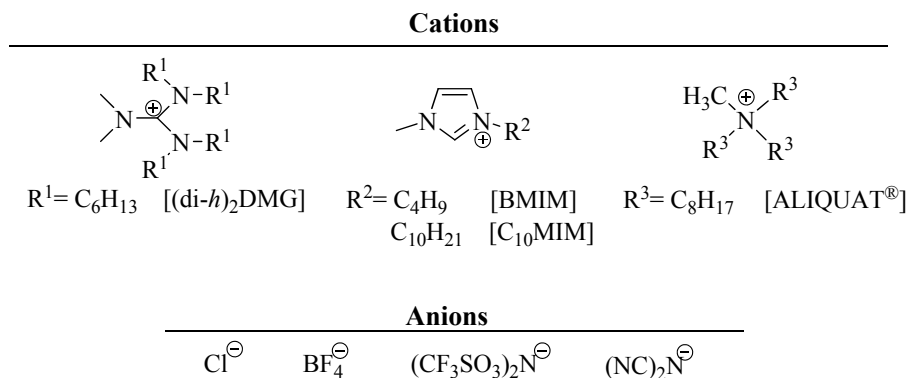


Figure 1 – Ionic Liquids tested for the extraction of carbohydrates from aqueous solution.

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Switchable Molecular Conductors: New Iron III Compounds

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As the world's technology progresses, the need for multifunctional materials increases exponentially. To obtain smaller electronic equipments it is necessary that its components accumulate several distinct functions. In the last years there's been a continuous interest in the development of molecular conducting systems where the electrical conducting properties can be modulated by variations in the spin state of spin cross-over (SCO) units, used as building blocks in the these materials. Powered by this objective we prepared two new Fe III cationic complexes, expected to give rise to salts exhibiting SCO. The chosen ligands present extended π systems (NSal₂-trien and Papa), which are expected to induce strong π - π interactions between the ligands from neighbouring cations, thus leading to a strong cooperativity in the SCO phenomena, in the same way as in [Fe(pap)₂]X.S (X=ClO₄ and PF₆)[1],[2] . A variety of salts with different anions were prepared, and the [Ni(dmit)₂]⁻ based salts were used as precursors to obtain the conducting materials.

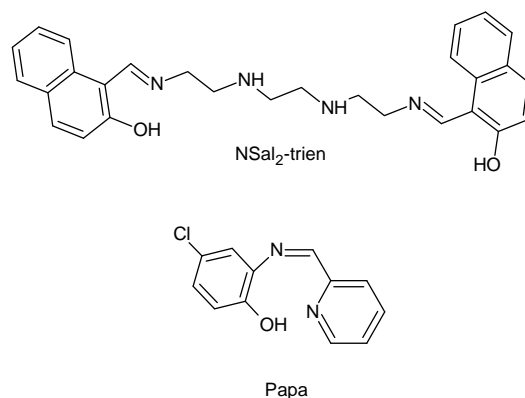


Figure 1: NSal₂-trien and Papa

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Evaluation of total Polyphenolic content and Antioxidant activity from *Helichrysum malaleucum* Rchb. ex Holl

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The increasing market of phytotherapeutic compounds of high added-value, justifies the great number of chemical and pharmacological studies involving traditional medicinal plants.

Madeira Archipelago has several endemic subspecies of *Helichrysum* (*Asteraceae* family) and two of them (*H. Malaleucum* and *H. devium*) are used in traditional folk medicine for the treatment of bronchitis and pharyngitis. The crude methanolic extract of these subspecies were tested against strains of *Mycobacterium tuberculosis* and found to be very active.

For the present work, *H. malaleucum* was harvested in the wild in two geographic locations of the island: Fajã da Nogueira, a mountainous location, and São Vicente, in the north coast.

Aerial parts of *H. malaleucum* were extracted with solvents of increasing polarity (*n*-hexane, chloroform, ethyl acetate and methanol). The total phenolic content and antioxidant activity were evaluated: the total phenolic content was measured by the Folin-Ciocalteau method, and the antioxidant activity was evaluated by FRAP (Ferric reducing power), DPPH (α - α -Diphenyl- β -picrylhydrazyl) and ABTS (2,2'-azinobis(3-ethyl-benzothiazoline-6-sulfonic) methods.

The obtained results from these four methods are in good agreement and show that the methanol extracts exhibit the highest phenolic content and antioxidant activity, followed by *n*-hexane, chloroform and ethyl acetate extracts, in that order.

These preliminary studies are useful to compare properties of plants from the same species but from different subspecies.

Acknowledgements:

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Amino-acids in Clays – towards environmental applications

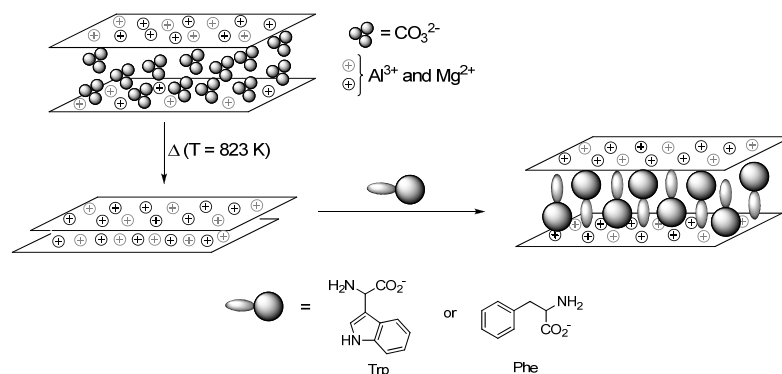
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Layered double hydroxides, available as minerals or from synthesis, and known as anionic clays, are very versatile. Hydrotalcite (HTC) is an anionic clay from this family, based on Mg and Al cations, but a wide range of compositions with general formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2](A^{m-})_{x/m} \cdot nH_2O$ ($M^{2+} = Mg^{2+}, Zn^{2+}, Ni^{2+}$ etc., $M^{3+} = Al^{3+}, Cr^{3+}, Ga^{3+}$ etc) is possible.[1] A rich intercalation chemistry can be obtained not only from the anion exchange process, but also from substitution of the di- and trivalent cations in the layers. In the present work two amino acids, tryptophan and phenylalanine were intercalated inside the interlayer space of the clay. The composite materials were afterwards characterized by FTIR, powder XRD, among other techniques to confirm the successful intercalation of the hosts.



The composite materials were tested as matrices in *Matrix-Assisted Laser Desorption/Ionization* (MALDI) experiments. Results show that unexpectedly the amino acid residue ions are not detected in negative mode. Surprisingly, when working in positive mode ions of the amino acids are readily detected. These results and a mechanism that may be responsible for such findings are discussed. Further work is ongoing towards the use of such composite materials for metal complexation and catalytic usage afterwards.

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Modification Of Glassy Carbon Electrodes With Ion-Exchange Polymers

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The properties and preparation of polymer-coated electrodes has been a subject of relevant interest over the last three decades [1]. The modification of electrodes with ion-exchange polymers for the voltammetric determination of metal cations provides a fast preconcentration of those species, followed by their sensitive detection [1-4].

The study of the adsorption features, structural architectures and molecular incorporation properties of the immobilized polymers on the electrode is of crucial importance for developing electrochemical sensing devices [1,3,5].

In the present work, glassy carbon electrodes were modified with coatings of two polyelectrolytes: the cation-exchanger poly(sodium 4-styrenesulfonate) (PSS) and the anion-exchanger polyallylamine hydrochloride (PAH), followed by mercury deposition to produce modified thin mercury film electrodes (PSS-TMFE or PAH-TMFE).

This study reports the preparation, optimization and characterization of those chemically modified electrodes. Both approaches produced reproducible and stable electrodes, suitable for the fast and direct determination of lead(II) at trace levels ($[Pb] = 6.00 \times 10^{-8}$ M, for an accumulation time of 20 s) in solutions of high ionic strength (0.5 M NaCl). The incorporation features of such films towards lead(II) at trace levels were correlated with the polymer mass loading deposited on the electrode surface, the ionic strength of the polymer casting solution and the morphologic characteristics of the coating, that were assessed by scanning electron microscopy (SEM).

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Enzymatic Resolution and Separation of sec-Alcohols Based on Fatty Esters as Acylating Agents

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The high demand for chiral compounds in enantiomerically pure form, especially in the pharmaceutical industry, is the major driving force for the development of efficient strategies of asymmetric synthesis and racemic mixtures separation.^[1]

In order to achieve such compounds, several efficient and stereoselective strategies have been developed and reported, namely enzymatic resolution.^[2]

The enzymatic resolution of racemic alcohols is a robust methodology and a practical route for the attainment of enantiomerically enriched precursors of pharmaceutical drugs.^[3,4] However, this method presents some limitations in the separation step. While at the laboratory scale the chromatography techniques are feasible on the enantiomers separation (normally one as an alcohol and other as an ester), this techniques are a major problem on large scale.

On course of previously work developed in this laboratory, where ionic liquids and ionic acylating agents were applied,^[5] we present here a more sustainable process for irreversible kinetic resolution of secondary alcohols using fatty esters as acylating agents and solvent, in the presence of CAL B as biocatalyst. The great improvement of this method is the possibility of recycle the enzyme for the recovery of the remaining enantiomer just by enzymatic transesterification, as well as the use of green separation techniques, such as low pressure distillation.

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Characterization of Volatile Biomarkers in Individuals with Oncologic Pathologies by HS-SPME-GC-qMSD

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Nowadays, there is an increase interest on the determination of volatile biomarkers for clinical diagnosis and therapeutical monitorization. Since the early 90's, several groups of investigators described some volatile compounds as markers of metabolic processes and clinical diagnosis from various pathologies, including cancer. The existence of this pathologic state leads to the production of determined volatile organic compounds (VOC's) namely, aldehydes (pentanal, hexanal, octanal, nonanal), alkanes (decane, *n*-undecane) and aromatic hydrocarbons (benzene, xylene, toluene), in biological fluids like blood and urine [1].

Several methods have been employed for the discovery of biomarker patterns of major human diseases, especially for various types of cancer. Current sample preparation is one of the most time consuming aspect in analytical chemistry. The development of solid-phase microextraction (SPME) has experienced significant growth since its introduction as a new approach to sample preparation in the 90's [2].

The purpose of this work was to identify the volatile organic compounds in biological fluids by means of HS-SPME-GC-qMSD (headspace solid phase-microextraction) described in the literature as possible biomarkers of cancer from individuals with oncologic pathologies (oncologic group) and without pathology (control group).

The results obtained showed variability between individuals in both groups (oncologic and control) and multivariate analysis (SPSS 16.0) was also employed to differentiate the referred groups.

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Valorisation of the Essential Oil of *Mentha Pulegium* by chemical modification

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Mentha pulegium L. (pennyroyal) essential oil (EO) is known to be composed of C-3 oxygenated p-menthane compounds, mainly ketones, with little clinal variation. The plant, known in Portugal as “poejo”, is widely used as a culinary herb in the south of the Iberia peninsula. Pennyroyal essential oil should not be used in aromatherapy and even in small doses produces acute liver and lung damage. It is considered to be a toxin and an abortifacient (due to the pulegone content) and, if ingested in large doses, can be fatal.

Accordingly, other applications for this cheap and abundant oil are under investigation and one possibility is the conversion of its constituents into more added value, and non-toxic, substances.

For the present work, the EOs were obtained from dried aerial parts of plants, cultivated the experimental fields of Escola Superior Agrária de Elvas (ESAE) from species collected in the wild in several locations of Alentejo. The composition of the OEs was determined by gas chromatography with FID and with mass spectrometric detection (GC-MS) and found to consist mostly of isomenthone and pulegone.

These ketones have industrial interest since they can be used as a starting material for the manufacture of synthetic menthol and its isomers.^[1,2]

One of our goals was to reduce the major constituents pulegone and menthone of this oil into their correspondent alcohols pulegol and menthol, without previous isolation. Using lithium aluminum hydride (LiAlH₄), the total reduction was achieved in two hours, with 100% selectivity towards the desired alcohols and > 90% recovery of the final products, using a method previously described by our group.^[3]

The chemical reduction was also performed with sodium tetrahydridoborate (NaBH₄) I order to increase enantioselectivity. The characterization of the reaction products was made by GC-MS and 1H and 13C NMR.

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Experimental and Theoretical Study of the Inclusion Complexes of 3-Carboxycoumarin Acid with Cyclodextrins

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The association process of a Host-Guest system, Cyclodextrins (CD) - 3-carboxycoumarin acid (3-CumCOOH) was followed by means of UV-Vis, circular dichroism and steady-state fluorescence spectroscopies in two buffered solutions, pH=1 and pH=10. These methods were chosen in order to get information on stoichiometry, equilibrium constants and geometry of the inclusion complexes[1]. The UV spectra evidence changes in both the maxima and the intensities of the bands allowing for the estimation of the association constant and the stoichiometry of the formed complexes. In the circular dichroism spectra, a positive induced signal was obtained reflecting that the guest penetrates the cavity in such a way that the transition moment of the electronic band is quasi parallel to the host main axis. The experimental data correlate in a satisfactory way with the results of Molecular Mechanics calculations on the optimized geometry of the most stable complex

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Polyurethane Foams For Enhanced Stir Bar Sorptive Extraction

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Stir bar sorptive extraction (SBSE) is a novel sample preparation technique proposed in the 90's [1] suitable to monitor, at trace level, several classes of priority pollutants and is based in the use of polydimethylsiloxane (PDMS), an extracting phase with high affinity for non-polar compounds. Nevertheless, PDMS presents some limitations concerning the enrichment of polar compounds, and therefore, the development of new polymers that can overcome this drawback is of great importance. Several authors have already proposed new strategies but with limited range of applicability, without embracing the robustness and the wide range of applicability demonstrated by PDMS. [2,3] Polyurethane (PU) foams are polymers with a wide variety of applications, which have been described to have a high capacity to retain organic vapors in their open cell structure. [4] They are produced by the reaction of polyisocyanate with polyols and water in the presence of a specific catalyst, thus obtaining a very versatile material and a very attractive polymeric phase for SBSE, as it has been demonstrated by our group. [5]

In this contribution we describe the synthesis of new PUs and propose their application for SBSE. The best synthesized formulation showed high thermal stability between 250 and 300 °C, excellent resistance to extreme pH conditions and to various organic solvents. Triazinic herbicides and their metabolites, steroids and acidic pharmaceuticals, to which SBSE(PDMS) has showed weak affinity, were analyzed by SBSE(PU) followed by liquid desorption (LD) and HPLC-DAD. Remarkable recoveries, suitable detection limits, good linear dynamic ranges and excellent reproducibility were observed. The ability of PU foams to extract the more polar compounds rather than PDMS makes this polymer a very valuable contribution for SBSE, thus enhancing the enrichment at trace level of this type of compounds.

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The Effect of Ethanol on Monomer Release from a Dental Resin Biomaterial

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Hard chair-side reline resins have been used to improve the fit of denture bases, thereby providing better retention and stability for removable dental prostheses. The biomaterial results from a polymerization reaction between the components of a powder and a liquid supplied in commercial packages. The composition of these materials is based on polyethylmethacrylate (PEMA) derivatives in the powder, whereas, the liquid composition varies among materials [1]. During the polymerization reaction of the resins, the conversion of monomer into polymer is not complete and assorted amounts of unreacted monomers remain in the polymerized material [2]. These monomers may diffuse out of the denture and thus into adjacent tissues frequently resulting in irritant and allergic reactions [3]. Among the liquid components of the reline resin Rebase, our focus was on the characterization of the acetoacetoxyethylmethacrylate (AAEM) monomer release in the presence of ethanol, in order to evaluate the chemical stability of the biomaterial towards alcoholic beverages.

We have conducted AAEM release “in vitro” studies with Rebase plates. A set of plates, produced according to the manufacturers’ instructions, was divided into 4 different groups ($n = 12$) and exposed to water and ethanol/water mixtures (20%, 40% and 96% v/v) for a period of 24 hours at 37 °C under continuous stirring. Samples collected at different times of incubation were analyzed using HPLC [4] and the amount of AAEM released from the plates was quantified. Average concentration of AAEM increased more rapidly as ethanol content in the mixture increased, but only plates exposed to ethanol 96% loose their rigid structure. Data were fitted in terms of kinetic characterization of monomer release and results shown a release decline over time.

The observed increase in the leaching of AAEM due to ethanol requires further investigation in order to study the influence of alcoholic consumption in the chemical stability of Rebase dental biomaterial.

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Characterization of Volatiles in Aromatized Vinegars and Cider Produced in Madeira Islands using HS-SPME

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Vinegar is a product that result from alcoholic and subsequent acetic fermentation of any fermentable starting material rich in carbohydrates [1]. This product has good reputation, being appreciated in gastronomy used not only as a condiment, but also as ingredient and as a preservation product for a wide range of foods [2]. Several hundreds of volatile compounds from different chemical families formed during alcoholic and acetic fermentation, maturation and aging processes are responsible for vinegar flavor [3].

The purpose of this study was to characterize different aromatized vinegar samples produced in Madeira Islands, based on the headspace solid-phase microextraction (HS-SPME) methodology combined with GC-qMSD. The performance of six SPME fibres were evaluated and the best efficiency of extraction was obtained using PDMS fibre at 50 °C during an extraction time of 30 min with constant stirring (800 rpm), after saturating the sample with NaCl (30 % w/v). Following the extraction methodology optimization, several aromatized vinegar samples were analyzed with the best working conditions, allowing the identification of about ninety volatile compounds from different biosynthetic pathways like alcohols, ethyl esters, fatty acids, carbonyl compounds and terpenes. Twenty one of these volatiles, namely ethyl acetate, ethanol, 2-methylpropan-1-ol, isoamyl acetate, 3-methylbutan-1-ol, hexyl acetate, ethyl lactate, hexan-1-ol, acetic acid, vitispirane I, vitispirane II, dl-2-ethyl hydroxycaproate, diethyl succinate, 2-phenylethyl acetate, hexanoic acid, (Z)-geranyl acetone, 2-phenylethanol, dodecan-1-ol, octanoic acid, eugenol and 4-ethylphenol were common in all analyzed samples, however, their contribution for aroma profile is different for each sample.

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High Pressure Modulation of *alpha*-L-Rhamnosidase and *beta*-D-Glucosidase Activities Expressed by Naringinase

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High pressure effects on enzymatic reactions were considered able to revolutionize biocatalysis [1] as it can be developed as a powerful tool to modulate both the stability and activity of enzymes or even give some information on protein structure [2].

Both *alpha*-L-rhamnosidase and *beta*-D-glucosidase are found in naringinase enzyme complex, from *Penicillium decumbens*, which are involved in several industrial applications [3]. Naringin hydrolysis towards prunin and naringenin has been studied [4]. Flavonoids, naringin and naringenin may be useful to fight against inflammation and cancer.

Previous studies on the hydrolysis of naringin by naringinase enzyme complex under high pressure, showed an activation volume of $-15.0 \pm 1.8 \text{ mL} \cdot \text{mol}^{-1}$ [4]. In this work we have studied the activation through high pressure of *alpha*-L-rhamnosidase and *beta*-D-glucosidase activities, expressed by naringinase enzyme complex. By this way, specific substrates were used: 4-nitrophenyl-*alpha*-L-rhamnopyranoside and 4-nitrophenyl-*beta*-D-glucopyranoside.

Preliminary high-pressure (0 – 250 MPa) kinetic studies showed distinct pressure-induced naringinase activation according to each substrate hydrolysis. The activation volumes of *alpha*-L-rhamnosidase and *beta*-D-glucosidase, from naringinase enzyme complex, were evaluated.

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Application of in-vitro models for the prediction of the intestinal absorption and metabolism of flavonoids

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In vitro models are becoming more popular for prediction of drug metabolism and bioavailability. These models are more prone to automation and high throughput screening, but also allow reduction of the use of animals in preliminary tests where usually most compounds are discarded. Being less complex systems they are easier to interpret and correlate with *in vivo* observations. Among the *in vitro* systems for the study of drug absorption the most used are the cell model Caco-2 [1] and the artificial model PAMPA [2], but other models are also available.

Flavonoids are a large group of compounds naturally occurring in several plants and fruits, as glycosides or as their aglycones. Their abundance in human diet and their role in the prevention of cancer and cardiovascular diseases has attracted substantial attention [3]. However, despite all the evidence of biological activity, there is limited acceptance of some of these compounds as valuable therapeutic agents which is mostly related to their physical-chemical properties and pre-systemic metabolism, which may significantly affect the therapeutic outcome due to bioavailability issues. Some of these compounds have to be metabolized prior to absorption but this may be hampered due to their low solubility [4]. Solubility issues may usually be tackled by the preparation of suitable formulations containing solubilization aids, however for particularly difficult compounds the preparation of a prodrug may be necessary.

The work here presented refers to the application of *in vitro* models to evaluate the permeability and metabolism of soluble phosphate derivatives of the glycosilated flavonoid diosmin, prepared with the objective of increasing the availability for metabolism by glycosidases produced by intestinal microflora and consequently, increase intestinal absorption. Results are compared with those obtained for the parent compound and other related flavonoids.

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Incorporation of α -Tocopherol in Polymethylmethacrylate Acrylic Bone Cement

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Polymethylmethacrylate acrylic bone cement is a biomaterial widely used in orthopedic interventions to anchor cemented prosthesis to the bone. Inflammation, caused by the release of leachables from the acrylic bone cement, is a major contributor to the aseptic loosening of these implants [1,2].

The aim of this work was to incorporate α -tocopherol into the acrylic bone cement so that the local inflammatory response could be reduced [3]. In order to achieve this, α -tocopherol quantification and thermal stability assays were performed. Additionally, different amounts of α -tocopherol were incorporated into the acrylic bone cement and its mechanical and organoleptical characteristics were analyzed.

A normal phase, isocratic high performance liquid chromatography (HPLC) method was used to quantify α -tocopherol. The analyte was detected at 295 nm by an UV-spectrophotometer [4]. Linearity and repeatability were analyzed and considered acceptable.

The thermal stability assays were performed with two sets of samples, which were exposed to the same experimental conditions ($T = -20^{\circ}\text{C}$, 37°C , 60°C , 100°C ; $t = 30$ min, 60 min, 24 h). When exposed to 100°C for one hour, α -tocopherol degradation was observed. Since the polymerization of the acrylic bone cement only reaches 70°C , α -tocopherol will not be decomposed during the setting of the polymer.

The influence of α -tocopherol on the acrylic bone cement characteristics, both mechanical and organoleptical, was analyzed. It was demonstrated that α -tocopherol negatively affects the mechanical characteristics of the acrylic bone cement and alters its organoleptical characteristics. Every sample prepared did not show the proper characteristics in order to be used in orthopedical interventions.

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Determination of the Combustion Enthalpy of Crystalline Pentachloronitrobenzene by Rotating-Bomb Calorimetry

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The establishment of relations between energetic and structural properties of the compounds is relevant to explain their behavior in terms of reactivity. In our research group, we are involved in the study of polychloronitrobenzenes derivatives. The experimental work reported here represents a contribution to this study.

Pentachloronitrobenzene (Quintozene) is especially important in industry, preventing the formation of slime in residual waters. It is also largely used as a fungicide in gardens and agricultural areas, protecting cotton and grain seeds like potatoes, onions and rice from the growth of fungi. Quintozenes may represent a health hazard, given its extensive use on a multitude of crops which leads to cumulative exposure and potential liver damage.

The standard ($p^\circ = 0.1$ MPa) molar enthalpy of combustion in oxygen of Quintozenes, at the temperature 298.15 K, was measured by rotating-bomb calorimetry from which the standard molar enthalpy of formation, in the crystalline phase was derived.

This work was complemented with the determination of the standard molar enthalpy of sublimation, at the temperature 298.15 K, by other researchers [1,2] using two different methods: Calvet microcalorimetry and Knudsen effusion technique.

The values of the standard enthalpies of formation in the condensed phase and the values of the standard enthalpies of sublimation were combined to derive the standard molar enthalpies of formation in the gaseous phase.

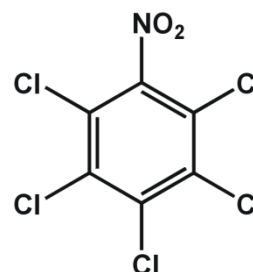


Figure 2 - Chemical Structure of Pentachloronitrobenzene.

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Metalloporphyrins as Catalysts in the Oxidation of Monoterpenes with H₂O₂

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Many compounds with every day applications can be prepared throughout oxidative transformations. The need for mild, catalytic systems to prepare new value-added products is a subject of great importance, centered on the use of benign, safe and cheap oxidants. The development of new alternatives to the current oxidation methodologies is a very important target [1]. The use of H₂O₂ as a cheap, environmentally clean and easy to handle oxidant [2], in association with metalloporphyrins as catalysts, might lead to efficient procedures to perform some essential oxidative reactions [3-6]. It has already been reported that abundant substrates like terpenes [7,8] can be oxidized in the presence of manganese(III) porphyrins as catalysts, using H₂O₂ as oxidant.

We will present the results obtained with Mn(III) and Fe(III) porphyrin complexes, namely Mn(TDCPP)Cl and Fe(TF₃PP)Cl, in the oxidation reactions of some monoterpenes, such as, linalool, linalyl acetate, (R)-(+)-limonene, (-)-carveol and terpinene. The results obtained will be shown.

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Fluorimetric and Circular Dichroism Study of the Interaction Between Atenolol and Albumins

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The interaction of the cardiovascular drug atenolol with two serum albumins, human (HSA) and bovine (BSA), has been studied by means of steady-state fluorescence, synchronous fluorescence and circular dichroism spectroscopies. At pH 7.4, both HSA and BSA produce a quenching of the ligand fluorescence. Treatment of the experimental data allowed for the estimation of the Stern-Volmer quenching constants, binding constants and of the number of protein binding sites. The binding distance and the energy transfer efficiency between ligand and substrates were also determined. The circular dichroism data revealed the conformational changes in the secondary structure of the proteins upon their interaction with atenolol. On the basis of these findings, the nature of the ligand–substrate interactions was revealed. These data contribute to a better understanding of the action mechanism of atenolol in physiological conditions.

Synthesis of Furochromones by [4+1] Cycloaddition of 3-Formylchromone with Isocyanides

Jesús Díaz-Álvarez, Ana G. Neo, Rosa M. Carrillo, Leda Garrido, José Delgado, and Carlos F. Marcos

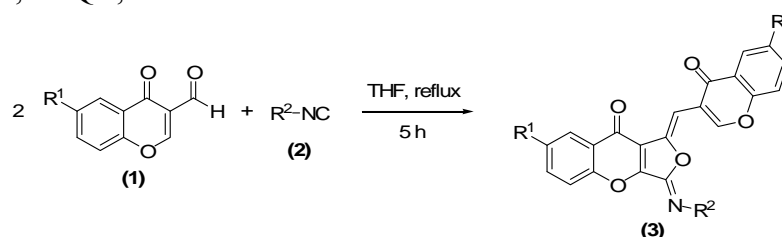
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Benzopyrones constitute an important class of natural products, which includes coumarins, chromones and flavones. Many polycyclic metabolites containing the furochromone system are characterised by possessing distinct biological activities. Examples of natural furochromones are the ergot pigments ergoflavin, ergochrysin A and ergoxanthin; cytotoxic rotenoid amorphispironone.¹ ...

In the last years, the preparation of natural product-like libraries is becoming a major strategy for the discovery of new drugs.² In this context, polycyclic benzopyrones have become an important synthetic target.

We report here a new synthesis of natural product-like chromenylmethylene furochromenones (**3**) by a tandem transformation of formylchromones (**1**) and isocyanides (**2**). The final products (**3**) are obtained through a [4+1] cycloaddition reaction between 3-formylchromone (**1**) and isocyanide (**2**) followed by the addition of a second molecule of formylchromone. The structure and stereochemistry of **3** were unequivocally determined by spectroscopic techniques including HREIMS, ¹H-NMR, COSY, ¹³C-NMR, HSQC, ¹H-¹³C HMBC and NOESY.



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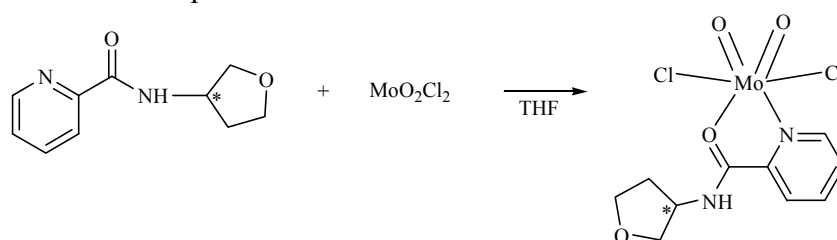
Chiral Molybdenum(VI)-Pyridinamide Complex as Highly Efficient Catalyst for Olefin Epoxidation

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We have been studying the coordination of oxazoline ligands to molybdenum and the use of these novel complexes as catalysts for olefin epoxidation. Some years ago, we reported the preparation of the first chiral molybdenum(VI) complexes of the type *cis*-[MoO₂(N,O)₂] containing anionic chiral bidentate oxazolinylphenolate ligands [1]. The activity trends observed for different catalytic systems studied by us proved that the coordination of a non-labile chiral ligand appeared crucial to induce selectivity in the epoxidation process [2,3]. As a result of these findings, we considered preparing novel tridentate oxazoline ligands of the type *N,ON',O*, in order to prevent metal decoordination under catalytic conditions. While attempting the synthesis of functionalized-oxazoline ligands, an unexpected pyridinamide ligand was obtained and coordinated to molybdenum. Its preparation, molecular structure and catalytic activity in olefin epoxidation will be presented.



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New Materials For Organic Photovoltaic Cells

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Organic Photovoltaic Cells (OPVs) are a new generation of renewable energy sources. In spite of the significant progress made, their efficiency is still significantly lower than that of inorganic cells. Semiconducting polymers exhibit remarkable advantages for photovoltaic applications over conventional inorganic materials, as their properties, such as energy levels and band gaps, can be tuned *via* molecular design, and they combine mechanical flexibility and low density with low-cost processing technologies [1]. The most efficient OPVs combine electron-donor with electron-acceptor components to favour charge separation after photoexcitation.

In this communication, we report on the synthesis and properties of conjugated materials specially designed for OPVs. These materials consist on conjugated blocks, derived from poly(p-phenylene vinylene), with either donor or acceptor character, containing reactive end groups which allow their easy copolymerisation. Our studies aimed at selecting the most efficient donor/acceptor pairs in terms of their ability to generate charge upon photoexcitation, to be used either as mixtures or as copolymers in OPVs. From cyclic voltammetry measurements, UV-Vis absorption and steady state fluorescence spectroscopy studies, we were able to establish several donor/acceptor pairs and select those showing the highest fluorescence quenching, a phenomenon which is indicative of efficient excited state charge transfer.

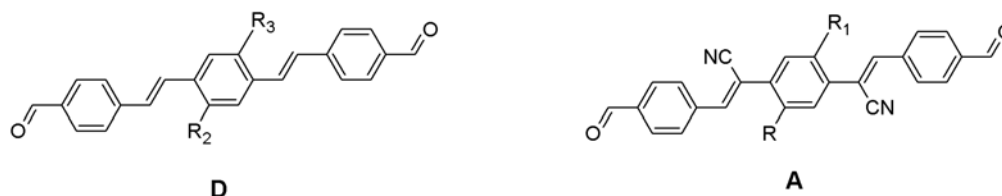


Figure 1. General structure of the donor (D) and acceptor (A) materials synthesised.

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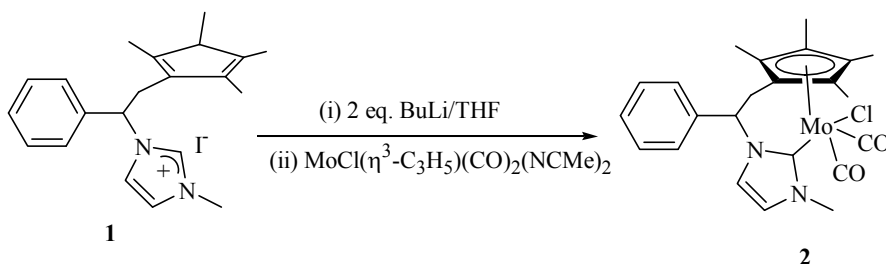
Cp*-Functionalized N-Heterocyclic Carbene Complexes of Molybdenum

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The chemistry of the NHC complexes of Group VI transition metals is not as advanced as that of the late transition metals [1]. Studies of NHC complexes of molybdenum are scarce, and most of them concern to carbonyl molybdenum(0) complexes [2]. In an attempt to extend the NHC chemistry of molybdenum, we have synthesized a Mo(II) complex containing the pentamethylcyclopentadienyl-functionalized N-heterocyclic carbene ligand Cp*-NHC^{Me} (**1**), previously reported by us [3]. We describe here the preparation of the novel molybdenum complex (Cp*-NHC^{Me})Mo(CO)₂Cl (**2**) by reaction of the deprotonated imidazolium **1** and MoCl(η³-C₃H₅)(CO)₂(NCMe)₂. Reactivity studies of **2** toward the catalytic activity in the epoxidation of olefins will be discussed.



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Synthesis, Characterization and Application of Thermoresponsive Polymer Core-Shell Nanoparticles as a Support for DNA Hybridization

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Poly(N-isopropylacrilamide) (PNIPAM) is a thermoresponsive polymer, with a lower critical solution temperature (LCST) in water, of about 31-33°C. These materials have been studied for application in drug controlled release, immunologic tests, concentration and isolation of proteins, DNA, RNA or viruses from biological samples, etc.

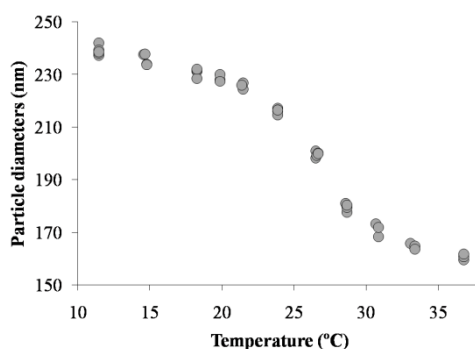


Figure 1. Hydrodynamic diameter of the thermoresponsive core-shell nanoparticles at several temperatures (core diameter: 130 nm)

In this work we present the synthesis by emulsion polymerization, of monodisperse nanoparticles with a glassy core of poly(methylmethacrylate) (PMMA) and a shell of PNIPAM containing positive charges. These core-shell particles are used as a DNA support for DNA in suspension diagnostic tests. First, oligonucleotides (ODN) labeled with an electronic energy donor are adsorbed onto the particles at low temperature. The collapse of the PNIPAM shell above the LCST is used to position the ODN chains in a way that optimizes their recognition by the complementary ODN, labeled with an energy acceptor. The DNA sequence used is associated to the Lieden V Factor, the most common genetic cause of thrombosis. The DNA hybridization is detected by resonance energy transfer (FRET).

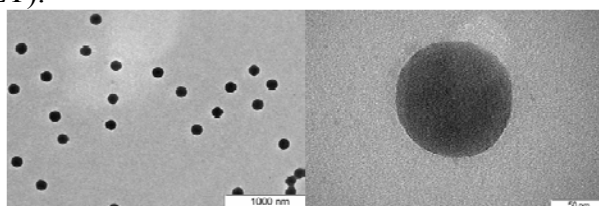


Figure 2. TEM micrography of dried core-shell nanoparticles

Conversion of clofibric acid in water by heterogeneous catalytic oxidation with H₂O₂

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In the last decades human use of pharmaceutical drugs has increased to high level. Pharmaceuticals used by human are not degraded inside the body of the patient completely. High percentages of many pharmaceuticals can be excreted through urine or feces from the body unmetabolized and enter wastewater as biologically active substances. Many drugs are not completely removed during the wastewater treatment and as a result pharmaceuticals have been found in a wide range of environmental samples including surface water, groundwater and drinking water [1]. Clofibric acid (CA) is the bioactive metabolite of drugs such as clofibrate and etofyllineclofibrate, widely used as blood lipid regulators [2]. Advanced oxidation processes (AOP) have been used for the degradation of different organic pollutants (e.g. pharmaceuticals compounds). These processes are characterized by the formation of OH radicals, which ensure high reactivity and low selectivity [3]. In this work, we report the heterogeneous catalytic oxidation of clofibric acid with H₂O₂ over transition metal complex dispersed in the polymeric matrix.

The transition metal complexes of Ni, V, Mn and Co were dispersed in the PDMS matrix according to Neys et al. [4]. The catalytic reactions were carried out in a batch reactor at ambient temperature under magnetic stirrer. The experiments were carried out using aqueous solutions containing 10 mg.L⁻¹ of CA, 1 g of catalyst and 1 mL of hydrogen peroxide. Different reaction parameters, such as, amount of catalysts, H₂O₂ concentration and temperature were optimised.

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SOLCHEMAR: HIGH QUALITY IONIC LIQUIDS

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Solchemar was founded in 2004 as a spin-off of REQUIMTE, FCT/UNL and relies on highly motivated experts committed to the development of high quality Ionic Liquids. In recent years, Ionic Liquids (ILs)^[1], which consist of organic cations and appropriate anions (liquid compounds until 100 °C) have received much attention due to their potential as an alternative recyclable environmentally benign reaction media for chemical processes. They have intrinsically useful properties, such as thermal stability, high ionic conductivity, negligible vapour pressure and a large electrochemical window. ILs can be called as “*designer solvents*” because their physical properties (such as melting point, viscosity, density and hydrophobicity) can be modified according to the nature of the desired application by modification of their cations and anions.

Applications of Ionic Liquids include their use as recyclable media for chemical processes; dissolution of cellulose and other organic or inorganic materials; extraction, separation and clean processes; in fuel or solar cells and more recently in energy, biotechnology, medicine or spatial science.

In Solchemar are available up to 70 ionic liquids based on imidazolium^[2] and guanidinium^[3] cations combined with several inorganic or organic anions. Also several task-specific ionic liquids (TSILs) and a spectroscopic high pure grade have been developed in order to improve the correspondent properties and desired applications.

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Intramolecular C-H Insertion Using NHC-Di-rhodium(II) Complexes: The Influence of Axial Coordination

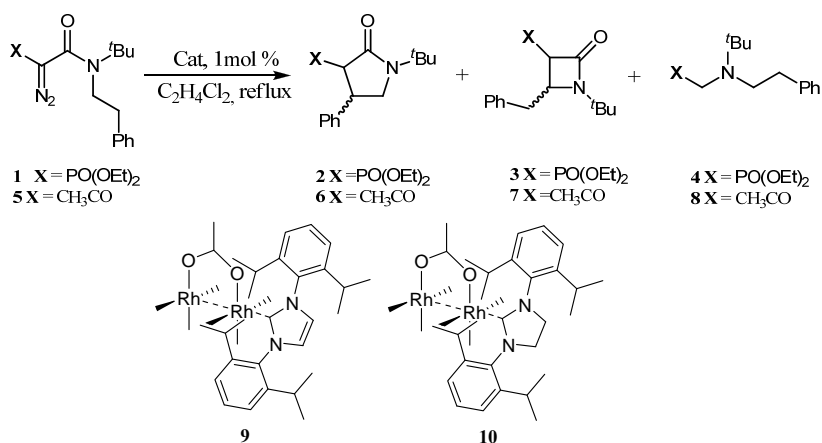
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The di-Rh(II) catalysts are well known for their ability to react with diazo substrates generating metallo-carbenes and then perform C-H insertion reactions. Usually, these catalysts have two labile axial positions where NHC ligands can coordinate and potentially alter the complex reactivity. The first Rh(II)-NHC complex developed was used in the decomposition of diazo substrates though it was not stable in the reaction conditions^[1]. In this work was studied the reactivity of catalysts **9** and **10**^[2] in the intramolecular C-H reactions of α -diazo-acetamides. These catalysts, apart from affording the usual lactams also yielded a new products (**4,8**) which clearly highlighted that the NHC coordination at the di-rhodium(II) axial position can in fact influence the reaction pathway.



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Synthesis and Reactivity Studies of New Cyclam Zirconium(IV) Complexes

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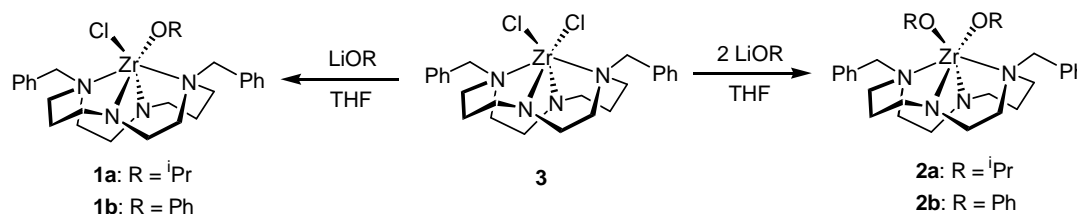
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High-molecular weight poly(ϵ -caprolactone) (PCL) and its copolymers are very promising bioresorbable materials for biomedical application.

Usually the typical polymerization of lactides and lactones is carried out in the presence of tin compounds such stannous octoate, aluminium and transition metal halides, alkoxides or organo-complexes. Unfortunately, the toxicity of tin, aluminium and heavy metal compounds and the impossibility to remove them from the synthesized material hampers the synthesis of biocompatible polyesters making the search for new catalytic systems an interesting topic^[1].

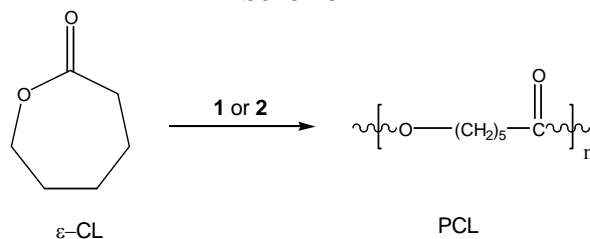
Following our studies on *trans*-N,N'-Bn₂Cyclam based complexes^[2,3], we report now the synthesis of new alkoxide derivatives **1** and **2** (Scheme 1).

Scheme 1



All complexes display high activity as catalysts for ring opening polymerization of cyclic esters leading to the synthesis of PCL (Scheme 2).

Scheme 2



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Constructal Theory and the Chemistry and Biochemistry Design

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Developments on Chemistry, Biochemistry and Engineering provide us better opportunities for quality of life; they have the ability to shape our own modern societies [1-3]. But the shapes of Sciences like Chemistry, Biochemistry, Biophysics and Biology are also subject to the influence from scientific and technological developments, like Constructal Theory [4-5-6-7-8-9], directly and indirectly.

The Constructal Theory deals with the maximization of global performance [2]; the main principle of the Constructal Theory is that every system is destined to remain imperfect [2-9].

The Constructal Law states that “For a flow system to persist in time (to survive) it must evolve in such a way that it provides easier and easier access to the currents that flow through it” [2-9]; the thermodynamic formulation of the Constructal Law that followed it, and the questioning, study and investigation on its connections, applications and extensions [8] makes the deep knowledge on Constructal Theory a crucial advantage for the curriculum design of any Young Chemist.

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Phenols Oxidation with Hydrogen Peroxide Catalyzed by Porphyrin and Chlorin Manganese(III) Complexes

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The demand of efficient catalysts for the selective oxidation of organic molecules has been the target of many studies; some of them have been developed to understand and mimic the *in vivo* activity of cytochrome P450 dependent monooxygenase [1,2]. Several porphyrins have been intensively investigated and, depending on their structures, have shown to be efficient catalysts in the oxidation of terpenes and phenols with hydrogen peroxide under homogeneous conditions [3].

Herein, we report the oxidation of several phenols, some of them of terpene type, with hydrogen peroxide in the presence of the complex **Mn(Chlorin)**. The results will be compared with the ones obtained with the metalloporphyrin **Mn(Porph)** (Figure 1). All reactions were carried out at room temperature in acetonitrile, using aqueous hydrogen peroxide as oxidant and ammonium acetate as the co-catalyst. The influence of catalyst/co-catalyst ratio was also studied and will be discussed.

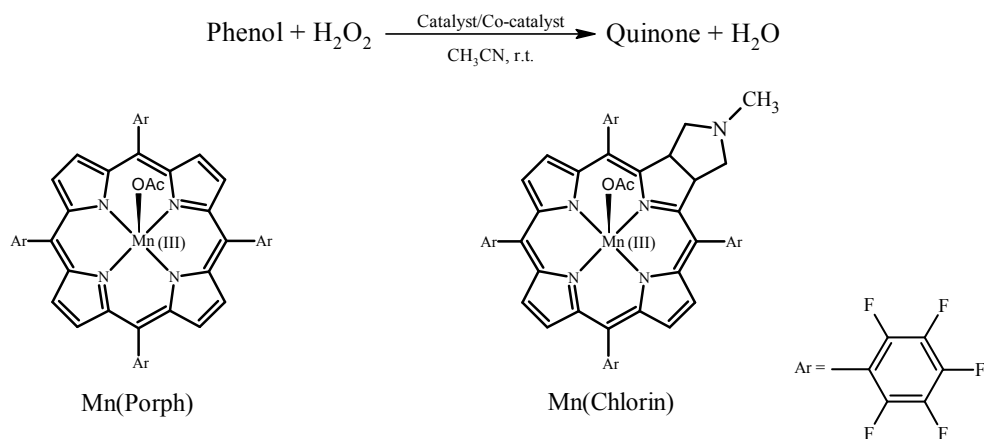


Figura 1: Studied catalysts in this work

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Dye-a-End-Labelled Thermisensitive Block Copolymers Synthesized by Raft Polymerization for FRET Studies

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Thermoresponsive polymers are among the most attractive smart diblock copolymers since changes in temperature are easy to control and appropriate for biological applications either in vitro or in vivo. However, very few fluorescence studies were devoted to study the conformation and dynamics of thermoresponsive block copolymers. Förster resonance energy transfer (FRET) is an appropriate tool to study these properties once the polymers are labelled with fluorescent donors or acceptors.

In this work, we describe the synthesis of block copolymers composed of a hydrophilic block of *N,N*-dimethylacrylamide (DMA) and a thermoresponsive block of *N,N*-diethylacrylamide (DEA) that changes from hydrophilic to hydrophobic when temperature increases above the LCST. These block copolymers are functionalized at the hydrophilic chain-end either by a FRET donor (Rhodamine-B) or acceptor (Malachite Green). Radical Addition-Fragmentation chain Transfer (RAFT) polymerization was chosen since acrylamides can be polymerized with a good control by this technique. In addition, it is possible to use a dye-labelled chain transfer agent (CTA) to obtain directly the α -end-functionalized block copolymers (Figure 1).

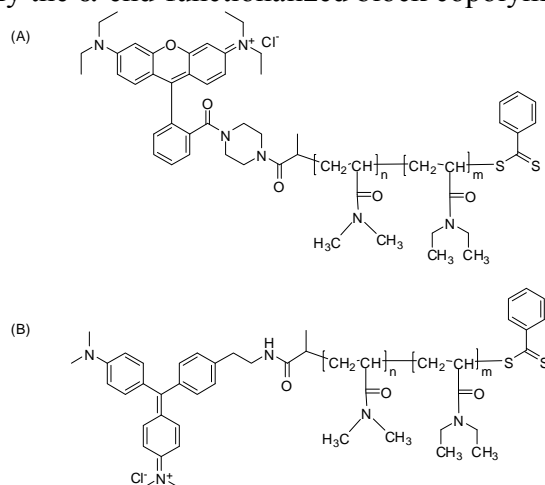


Figure 1. structures of Rhodamine B-labelled (A) and Malachite Green-labelled (B) poly(*N,N*-dimethylacrylamide)-*block*-poly(*N,N*-diethylacrylamide) block copolymers.

Phase stability of anhydrous-hydrate systems in different ambient conditions probed by Raman spectroscopy: a methodology

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Upon review of the pharmaceutical literature, it is clear that it has long been known that pharmaceutical solids can exist in more than one solid-state crystal form [1] which can have significantly different pharmaceutical properties, such as solubility, dissolution and bioavailability [2]. Depending on the environmental conditions (temperature and vapor pressure) it has been reported that approximately one-third of pharmaceutical solids are capable of incorporating water into the crystal lattice to form hydrate [3]. As water may be incorporated in the lattice in several ways, two or more distinct crystalline hydrated forms may be formed. Therefore, the knowledge and ability to monitor the physico-chemical changes of pharmaceutical materials is of utmost relevance for avoiding unwanted transformations. In this work, the structural effects of water activity and diffusion on theophylline (TP) and caffeine (CA), naturally occurring drugs pharmacologically active as central nervous stimulant are assessed through FT-Raman spectroscopy. This technique, that provides an excellent method for probing solid-state hydrogen bonding interactions between molecules, including polymorphs and solvates, is gaining acceptance as a powerful quantitative tool in the pharmacy field [4]. The main purpose of the methodology herein applied is gather information about the underlying structural aspects that give rise to the observed Raman spectral differences. The results show that TP and CA hydration is a single-step process with a half-life time of *ca.* 5 and 12 hours, respectively. In addition, the critical relative humidity for anhydrous TP and CA was found to be at *ca.* 79% and above 81%, respectively.

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Novel Folic Acid Derivatives as Histone Deacetylase and Dihydrofolate Reductase Inhibitors

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Histone deacetylases (HDACs) are a family of enzymes involved in the regulation of gene expression, DNA repair and stress response. These processes are often altered in tumours and HDAC inhibitors have emerged as new targets for cancer therapy with promising results in clinical trials. HDACs are divided into three structural classes depending on sequence identity and domain organization. HDAC8 is included in the Class I of zinc-dependent amidohydrolases with a conserved catalytic core [1].

Folate-dependent enzymes, *e.g.* dihydrofolate reductase (DHFR), are also associated to certain types of cancer and other inflammatory states; they play an important role in the *de novo* biosynthesis of purine nucleotides. The inhibition of DHFR leads to a partial depletion of the intracellular reduced folate pool and to the accumulation of dihydrofolate restricting the synthesis of thymidylate and purine nucleotides, which are essential precursors of DNA synthesis. Folate-based compounds *e.g.* Methotrexate (MTX) are currently used as anticancer and as antibacterial drugs [2].

On these bases we design and synthesized some new bifunctional compounds, namely folic acid derivatives bearing different linear chains as linker to a hydroxamic acid as zinc binder. These compounds were tested on human recombinant HDAC8 and showed a good inhibitory potency against this enzyme. Some docking studies confirmed the favourable features of these compounds and prompted us to further investigate their biological activity, namely the antiproliferativity in cell cultures.

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Mo(II) Complexes Immobilized In Porous Materials And Their Application as Oxidation Catalyst Precursors

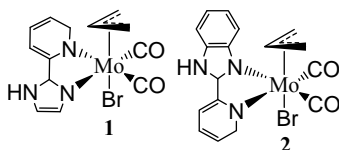
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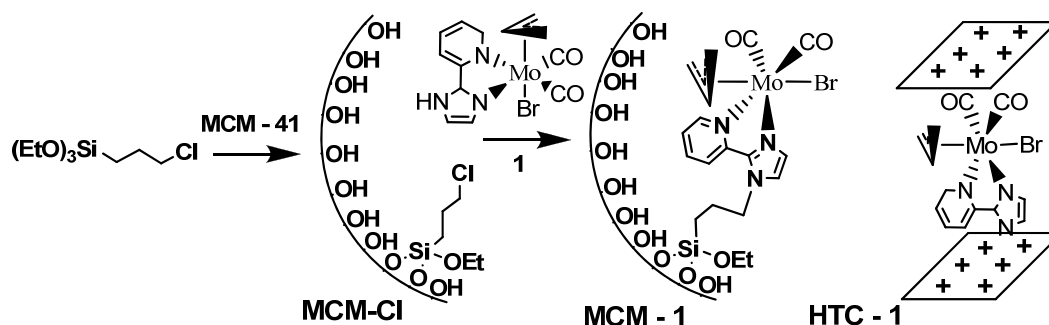
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[Mo(η^3 -C₃H₅)Br(CO)₂(N-N)] complexes (Scheme 1) were prepared from the precursor [Mo(η^3 -C₃H₅)Br(CO)₂(CH₃CN)₂], by reaction with the ligands 2,2'-pyridylimidazole (**L2**), and 2,2'-pyridylbenzimidazole (**L3**).



Scheme 1. Complexes [Mo(η^3 -C₃H₅)Br(CO)₂(N-N)] (**1,2**)

After preparation of MCM-41, the material was functionalized with Cl(CH₂)₃Si(OEt)₃ (MCM-Cl), and the complexes immobilized by reaction of the N-H groups with MCM-Cl, as shown in Scheme 2 (left). Attempts to immobilize the complexes **1** and **2** in HTC clay were performed by deprotonation of the N-H groups, as shown in Scheme 2 (right).



Scheme 2. Synthetic pathways of materials

All the materials were characterized by powder X-ray diffraction, N₂ adsorption analysis, FTIR, and ²⁹Si and ¹³C CPMAS solid state NMR spectroscopy. The materials were tested as catalyst precursors for cyclooctene and styrene epoxidation with TBHP.

Acid Zeolites as Environmental Benign Promoters for Carbohydrate Key Transformations

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Acid zeolites have been recently used for a variety of transformations with the advantage of being solid catalytic eco-friendly materials, known for their activity, selectivity and reusability [1]. Due to their unique intrinsic architecture, zeolites are shape-selective in reactant, transition state and product, many times leading to reaction regioselectivity uncommon in classical procedures.

In our research group these materials have been applied in carbohydrate chemistry as promoters, replacing hazardous reactants, in several key reactions, namely in the formation of protecting groups, such as benzylidene acetals and acetonides using different sugar scaffolds [2a], as well as in the *O*-, *C*- and *S*-glycosylation of several aglycones [2b, 2c], including alcohols, phenols, flavonoids and thiols. An overview of the obtained results will be presented, focusing on the kinetic control, efficiency and stereoselectivity of the reaction and its correlation with the physical and chemical properties of the zeolites.

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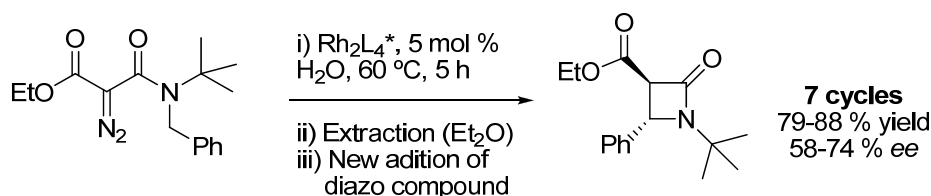
Intramolecular Asymmetric C-H Insertion of α -Diazoacetamides in Water

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The metallocarbenoid asymmetric C-H insertion deriving from α -diazo carbonyl compounds is a powerful tool for the preparation of highly valuable compounds. However, the enantioselective dirhodium-catalyzed intramolecular C-H insertion is still an open issue, particularly for the α -diazo acetamides compounds where the right chiral dirhodium catalyst for each family of α -diazoacetamides still has to be found.[1]

In our previous studies we concluded that the success of intramolecular C-H insertion in water is strongly dependent on the substrate and catalyst solubility.[2] Chiral dirhodium complexes based on carboxylates are known for their ability to catalyze and to induce chirality on intramolecular C-H insertion reactions. Taking advantage of natural products chiral pool and derivatives, the use of water as reaction medium[3] and the known protocol for the formation of new dirhodium(II) complexes by ligands exchange starting from dirhodium(II) tetraacetate[4] we developed a protocol for the *in situ* formation of new catalysts. A novel catalyst for the aqueous intramolecular C-H, based on natural chiral amino acid L-phenyl alanina was developed and further employed in the cyclisation of *N*-(benzyl)-*N*-(tert-butyl)-2-(carboethoxy)-2-diazo-acetamide affording the corresponding β -lactam in good yields and enantioselectivities after 7 cycles as indicated above.



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Antimicrobial Screening of *Plectranthus ecklonii*;

Isolation and Antimicrobial Activity of Sugiol.

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Abietane diterpenes are widely distributed naturally occurring products in the plant kingdom. Due to their wide distribution and interesting biological activities, many studies of isolation and identification of the compounds have been report.[1] Sugiol, an abietane type diterpene, identified from several plants including *Salvia* [2], was isolated from *Plectranthus ecklonii* Benth. for the first time. This metabolite has been described as antiproliferative,[3] anti-inflammatory,[4] and antimicrobial agent. [5-7].The aim of this study was described the phytochemical and the antimicrobial proprieties of acetone extract and chromatographic fractions of *P. ecklonii*, as well the isolation and structure of sugiol.

The antimicrobial activity were performed by disc diffusion method against *Pseudomonas aeruginosa*, *Escherichia coli*, *Staphylococcus aureus*, *Mycobacterium smegmatis* and *Candida albicans*. Fractions PE₂ and PE₅-PE₈ showed antibacterial activity against *S. aureus* and *M. smegmatis* (6 to 9 mm). Bioassay-guided chromatographic fractionation of the antibacterial active PE₂ fraction led to the isolation and identification of sugiol. Minimum Inhibitory Concentration (MIC) value of sugiol was obtained against five methicillin-resistant *Staphylococcus aureus* (MRSA) strains and four vancomycin-resistant *Enterococcus* spp. (VRE) strains by micro dilution method. Sugiol MIC values for MRSA and VRE were 125-250 µg/mL, except for *Enterococcus faecalis* with MIC of 62.5µg/mL. Further studies are being carried on the antimicrobial fractions PE₅-PE₈.

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Synthesis of Painting Pigments White Lead and Red Lead

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Before the 19th century, painters prepared their own materials, especially pigments. The pigments manufacture was made by apprentices that work at the painter workshop. The knowledge about the materials and their manufacture was transmitted verbally or through technical books. Some of these books contained detailed instructions, although others presented only scarce information. On the other hand, some were written by artists and described their own procedures, while others are collections of recipes with different origins done by who do not have knowledge in those matters and we do not know the exact composition of the pigments prepared accordingly to these recipes. So, we are involved in a project aiming to elucidate the composition of some pigments, produced by some of the more unintelligible recipes mentioned in Portuguese treatises, and the importance of the procedure details on the pigments properties. In this context we attempt to prepare white lead (basic lead carbonate) and minium (lead oxide), following the recipes reported by Filipe Nunes' treatise on painting, first published in 1615 [1]. We attempt to establish protocols that can be used in the laboratory and the preliminary results of these syntheses are present here.

The manufacture of the pigments was monitorized by X-ray powder diffraction (XRD) patterns, that were recorded on a Philips PW 1710 diffractometer, using CuK α ($\lambda = 1.5406 \text{ \AA}$) as incident radiation. The morphologic analysis was done by scanning electron microscopy in a JEOL (JSM -6301F) microscope with an electron beam voltage of 15 kV.

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Flavonoid-Matrix Clusters in MALDI-MS

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Matrix-Assisted Laser Desorption/ionization (MALDI) has been extensively used for the mass spectrometric analysis of large, nonvolatile biomolecules, high molecular weight synthetic polymers, fullerene and fullerene derivatives, high molecular weight environmental materials, as well as non-covalent complexes.[1] The application of MALDI to the analysis of small molecules (<500Da) has been hampered because of usually high matrix background signals in the low mass region.

The matrix plays an important role in MALDI, it absorbs the laser light energy causing substrate vaporization and allowing easier analyte ionization.[2]

Matrix-analyte cluster formation is not uncommon in MALDI mass spectrometry. Many of the common matrices show complex ionization behavior yielding protonated, deprotonated and even-electron cluster ions.[3,4] These cluster ions may play an important role in the MALDI ionization process and it is believed that they form the prerequisite for an efficient photoionization.[5] To explore matrix ion formation and its relation with ionization mechanisms, the MALDI spectra of 2,5-DHB one of the most commonly used matrices were investigated in the present study. The formation of DHB cluster ions, mainly DHB-H₂O cluster ions is here reported.

Flavonoids are a class of compounds with biological interest. The MALDI mass spectra of four flavonoids: quercetin, naringenin, luteolin, and myricetin, using 2,5-DHB as matrix were also investigated. These spectra exhibited flavonoid-matrix clusters ions that may contribute to the establishment of the ion formation mechanisms for small molecules under MALDI conditions.

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Characterization of Triacylglycerols in *Annona cherimola* Mill. Seed Oil by NARP-HPLC-APCI-ITD-MS

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Annona cherimola Mill. produced in Madeira island is consumed as fresh fruit and part of the production is exported. The main drawback for cultivars is the low commercial yield, as about half of the production is lost. This means that about 500 tons of annona waste are produced each year. Transforming this residue into a profitable by-product is a challenge to the scientific community of the region. Seeds represent a quarter of the residue's weight and contain about 25% of oil. The characterization of annona's seed oil is essential to evaluate its suitability for the production of biodiesel.

Non-aqueous reversed-phase high-performance liquid chromatography (NARP-HPLC) is the most used technique for the separation of triacylglycerols (TAG). Retention of TAG is related with its total carbon number (CN) and the number of unsaturations present (DB), as it increases with increasing equivalent carbon number ($ECN = CN - 2 DB$)^[1]. Atmospheric pressure chemical ionization (APCI), being one of the mildest ionization techniques available, produces relatively simple mass spectra and the possibility of identifying positional isomers in TAG.^[2] Ion trap mass analysers (ITD-MS) allow subsequent fragmentation and, therefore, can give more information about the fatty acids (FA) present in TAG.

In *Annona cherimola* seed oil, 6 major groups of TAG were separated according to their ECN, which ranged from 40 to 50. MS spectra of most TAG exhibited predominantly $[M+NH_4]^+$, $[M+H]^+$ and $[M+H-RCOO]^+$ ions. MS/MS spectra allowed the elucidation of the structure of the FA as some fragments indicated, for example, the position of the unsaturations. The characterization of TAG can be a good approach for evaluating the oil's suitability for the production of biodiesel.

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Natural weathering of ABS: Effects of the U.V. radiation in chemical, thermal, rheological and mechanical properties

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Acrylonitrile-butadiene-styrene is a styrenic copolymer with wide applications in plastics processing industry due to their excellent combination between cost, mechanical properties and convenient manufacturing conditions.

However, ABS copolymers are known to present susceptibility to oxidative degradation, when exposed to UV radiation in the presence of oxygen, which result in chemical modifications such as crosslinking and scission of the macromolecular chains, colour changes and loss of mechanical properties [1].

Some additives are included in ABS formulations to extend polymer lifetime [2]. Presently, the stabilization is made with empirically foundation and we proposed to develop a stabilization system enhance its performance against UV radiation.

ABS films, obtained by extrusion, were submitted throughout 3 months to natural weathering in Lisbon, in accordance with ASTM Method D 1435, at an angle of 45°, facing south.

The specimens were removed periodically and characterized by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR); yellow index; mechanical, thermal and rheological properties.

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From Discovery to Production in the Pharmaceutical Industry

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During the early development stages of drug discovery, synthetic chemists are required to provide small quantities of the drug. Linear synthetic routes, expensive starting materials and hazardous or costly reagents can be used to synthesise grams of the drug for the early phases of drug development. These synthetic routes are often designed to allow the synthesis of analogues during medicinal chemistry studies. As soon as the drug is selected for development, suddenly very much larger quantities are required for further evaluation. Along with larger quantities of the drug being required their synthesis has also to follow GMP guidelines, so that they can be administered to human subjects.

To ensure the supply of an ever growing demand of the drug, development of an industrial synthesis which is safe, efficient, robust and amenable to scale-up has to be conducted. This synthetic route should also give the best quality at the least cost and environmental impact.

This poster highlights the differences between discovery and industrial synthesis of drugs and the steps involved in the development, process research and scale-up of pharmaceutical drug synthesis.

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Adsorption of Colloids to Lipid Membranes. A Monte Carlo Study

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The adsorption of colloids of varying sizes and charges onto a surface that carries both negative and positive charges, representing a membrane, has been investigated using a simple model employing Monte Carlo simulations. The membrane is made of positive and negative charges (headgroups) that are allowed to move along the membrane, simulating the translational diffusion of the lipids, and are also allowed to protrude into the solution, giving rise to a fluid and soft membrane.

When an uncharged colloid is placed in the vicinity of the membrane, a short-range repulsion between the colloid and the membrane is observed and the membrane will deflect to avoid coming into contact with the colloid. When the colloid is charged, the membrane response is twofold: the headgroups of the membrane move toward the colloid, as if to partly embrace it, and the positive headgroups of the membrane approach the oppositely charged colloid, inducing the demixing of the membrane lipids (polarization). The presence of protrusions enhances the polarization of the membrane. Potential of mean force calculations show that protrusions give rise to a more long-range attractive colloid-membrane potential which has a smaller magnitude at short separations.

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A 1D copper coordination polymer derived from N-ethyldiethanolamine and terephthalic acid: synthesis, structure and catalytic properties

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The design of copper coordination polymers is an intensively growing research field due to the interesting structural and practical characteristics of such materials such as their catalytic and magnetic properties [1], usually different from the related mononuclear species. We have shown that aromatic polycarboxylic acids along with aminopolyalcohols are convenient building blocks in designing copper-organic polymeric materials with varying topologies [1].

As a continuation of these studies, we report herein the self-assembly synthesis of the novel 1D Cu(II) coordination polymer $[\text{Cu}_2(\text{Et-Hdea})_2(\mu\text{-tpa})]_n \cdot 2n\text{H}_2\text{O}$ (**1**), derived from N-ethyldiethanolamine (Et-H₂dea) and terephthalic acid (H₂tpa), used as main chelating ligand and spacer, respectively. Compound **1** (Fig. 1) has been characterized by IR spectroscopy, elemental and single crystal X-ray diffraction analyses.

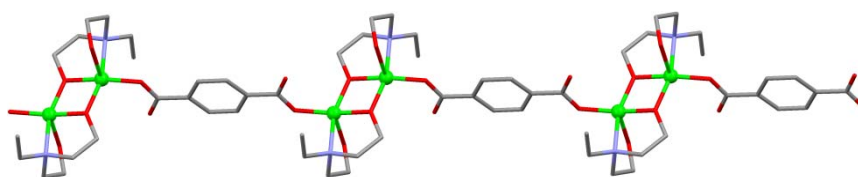


Figure 1. Structural representation of infinite 1D metal-organic chain of **1**.

The obtained compound acts as a catalyst precursor for the mild peroxidative oxidation of cyclohexane, by hydrogen peroxide in acidic MeCN medium, to cyclohexanol and cyclohexanone. An overall molar yield of products up to 20% (based on cyclohexane) has been reached. The effects of various parameters on the catalytic activity have been investigated.

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Evaluation of Environmental Conditions and Pollutants Concentrations in Tagus Estuary, Portugal

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Nowadays, pollution has become one of the major problems concerning estuarine ecosystems through the World. Due to this, many commissions have been created, as the example of OSPAR, an international organization for the protection of the marine environment of the North-East Atlantic which gives the main guidelines for studies and protection of marine ecosystems.

Tagus Estuary, the largest in Portugal and one of the largest in Europe [1], is located near many important metropolitan areas which originate a considerable number of effluent discharges into the estuary causing elevated concentrations of pollutants. For these reasons, Tagus Estuary has a relevant importance in scientific and strategic domains.

The Hydrographic Institute of the Portuguese Navy has a monitoring program in the Tagus Estuary since 1981 through which evaluates the state of environmental conditions and pollution using a sampling web with stations placed in the principal areas of the estuary. The current study focuses the period between September 2004 and September 2007 presenting the results for classics parameters (pH, salinity, dissolved oxygen, total suspended solids) as well as for heavy metals (cadmium, copper, chromium, iron, mercury, nickel, manganese, lead, zinc and arsenic). The sampling stations for the study were chosen considering the proximity to pollutants discharge points and to urban and industrial communities. With the obtained results, a comparison to OSPAR commission guidelines is made considering the tolerance maximum values for living organisms.

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Sulfate Anion Templatation of a Neutral Pseudorotaxane Assembly Using an Indolocarbazole Threading Component

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The use of sulphate as a template in the formation of a neutral pseudorotaxane assembly, between a neutral indolocarbazole thread and an isophthalamide macrocycle [1], was evaluated by means of molecular dynamics simulations and Molecular Mechanics Poisson Boltzman Surface Area (MM-PBSA) calculations, in acetonitrile solution. Results demonstrated sulphate as being vital in the templatation of the assembly, allowing for the simultaneous establishment of hydrogen bonds between the isophthalamide and indolocarbazole N-H binding sites and the sulphate oxygens. The observed binding arrangement further allowed for π - π staggered stacking interactions between the hydroquinone rings and the aromatic indolocarbazole unit. MM-PBSA results clearly indicated the pseudorotaxane assembly to be energetically favoured.

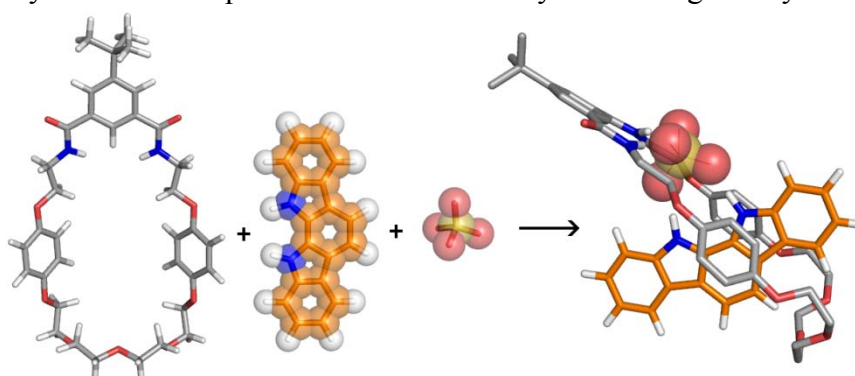


Figure 1. Components (left: isophthalamide macrocycle, indolocarbazole unit and sulphate anion, respectively) involved in the pseudorotaxane formation (right).

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A Spectroscopic Study of Fullerene C₇₀ in Room Temperature Ionic Liquids

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Room temperature ionic liquids (ILs) are usually salts of bulky and asymmetric organic cations. They have unique chemical and physical properties such as negligible vapor pressure, good thermal stability, high ionic conductivity and the ability to dissolve a wide range of substances. One of the driving forces behind research on ionic liquids is their application as “green solvents” in alternative to the conventional volatile and toxic organic solvents, nevertheless they have also been applied in synthesis, catalysis, batteries, and fuel cells [1].

Some work has also focused on the photochemistry and photophysics both *of* ILs and *in* ILs [2]. A very important aspect here is the optical purity of the ILs that are frequently colored even after purification. This color results from impurities that are difficult to remove [3]. Only recently have a few spectroscopic studies been published using ultra-pure ILs [4].

Fullerenes and their potential applications opened a new field of research. The most common fullerenes, C₆₀ and C₇₀, present unique photophysical properties. One of the most interesting, first observed in our group [5], is thermally activated delayed fluorescence (TADF). Outstanding temperature and oxygen sensors based on the TADF of fullerene C₇₀ were recently developed [6].

Encouraged by the particular spectroscopic properties of fullerenes and the advantages of the use of ionic liquids as solvents, we decided to study the spectroscopic properties of fullerene C₇₀ in several ionic liquids. The fluorescence behavior of C₇₀ in imidazolium, aliquat and phosphonium based ILs will be presented and possible applications discussed.

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Novel Mn(III) chlorin as catalyst in epoxidation of alkenes

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Manganese(III) porphyrin complexes have been intensively investigated as catalysts in several oxidation reactions, mimicking the *in vivo* activity of cytochrome P450 enzymes. High catalytic activities have been observed, mainly with catalysts containing electron-withdrawing substituents at the *meso*- and/or β -pyrrolic positions^[1]. Transformation of the macrocycle can bring different catalytic properties; also it can give rise to changes in the selectivity or allow the binding of the porphyrin to other molecules or solid supports. Here we report the synthesis of the new complex **Mn(Chlorin)**, (figure 1), using well established strategies.^[2] The catalytic efficiency of this complex is evaluated and compared with the efficiency of the well-established **Mn(Porph)**^[3] in the epoxidation of cyclooctene, cyclohexene, 1-*H*-indene and styrene using H₂O₂ as oxidant and ammonium acetate as co-catalyst.

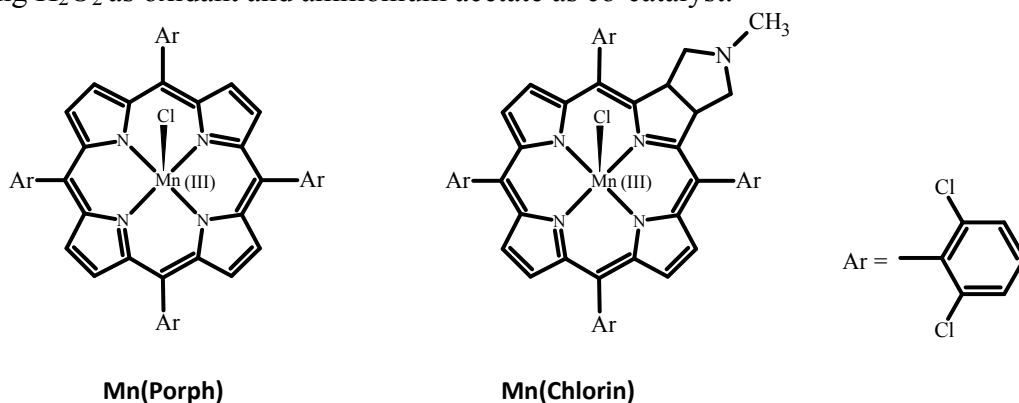


Figure 1 – Studied catalysts

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Electron Transfer And Exciplex Formation In Systems With Sulphur-Containing Electron Donors

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Amines and other nitrogen-containing compounds, due to their electron donor character, can form excited state emissive complexes in systems that comprise an electron acceptor [1,2]. Sulphur-containing heteroaromatic compounds such as phenoxathiin or thianthrene are also well-known for their electron donor character. Starting from these two considerations, we aimed at finding exciplexes in which the electron donor contains sulphur. We studied the emission properties of several D-A pairs in solvents of different polarity. An electron transfer process subsequent to irradiation was observed in binary systems such as phenoxathiin/thianthrene with a coumarin derivative without formation of new excited species. On the other hand, the systems phenoxathiin-thioxanthone and thianthrene-thioxanthone present a new emission band at longer wavelength than the D and A bands in nonpolar solvents, which is quenched in polar ones. In order to explain the exciplex formation, the standard free enthalpy for the electron transfer process was calculated according to the Rehm-Weller equation [3]. The equilibrium constants and the activation barrier for the exciplex formation were determined as well from steady-state emission data at different donor concentrations and at different temperatures, respectively.

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New oxidation routes for the linear PAH's tetracene and pentacene by hydrogen peroxide catalysed by [Mn(TDCPP)Cl]

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Many advantages are brought by the use of adequate catalysts in chemical processes. Greater selectivity in mild conditions is an important achievement for economical and ecological reasons and in some cases new and unexpected routes are obtained. The use of metalloporphyrins as catalysts for oxidation reactions was initially inspired on the activity of the prosthetic group of cytochrome P450, a monooxygenase which mediates oxidations even of inert and apolar xenobiotic substrates, in order to facilitate its excretion from the body [1].

In the last decades some robust and easily obtainable metalloporphyrins have been tested as oxidation catalysts. The [Mn(TDCPP)Cl] showed an inedited capability to promote the oxidation of small polycyclic aromatic hydrocarbons by hydrogen peroxide. [2] This system was tested in the oxidation of linear fused compounds with four and five rings, pentacene and tetracene. New quinones and diepoxides are obtained (Figure 1), which can have photochemical and biological applications.

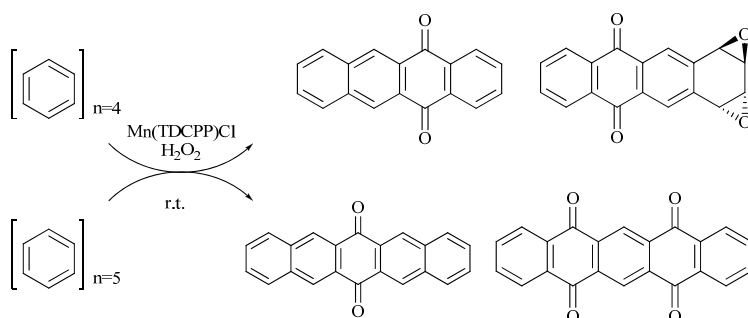


Figure 1. Oxidation of tetracene and pentacene catalysed by a metalloporphyrin.

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Hybrid Core-shell Nanoparticles for Application in Photonic Materials

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In this work, we synthesized core-shell nanoparticles with a silica core and a soft polymer shell for application in photonic materials.

We obtained silica particles by the Stöber method [1] and silica nanoparticles labeled with perylene by a modified Stöber method, using a perylene derivate with two etoxy silane groups.

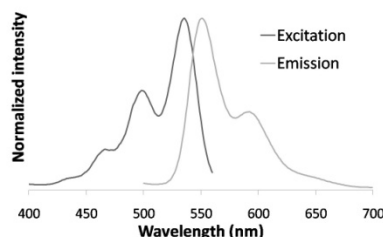


Figure 1. Excitation and emission spectrum of silica nanoparticles with perylene

The nanoparticles were modified with 3-trimethoxysilyl propyl methacrylate (MPS) at the surface and were used as seeds in the emulsion polymerization of a poly(butyl methacrylate) shell.

From aqueous dispersions of clean core-shell particles, with and without perylene, flexible films were prepared with controlled dimensions of the core and intercore distance.

The obtained materials were characterized in terms of dimension, polydispersivity, morphology and optic proprieties, using transmission electron microscopy (TEM), confocal microscopy, steady-state and time-resolved fluorescence.

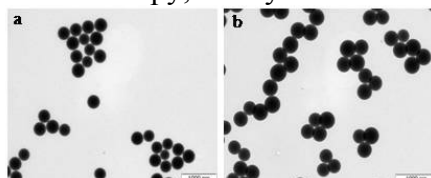


Figure 2. TEM of the silica core (a) and the silica core labeled with perylene (b)

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Determination of the sublimation enthalpy of 1,3,5-trichloronitrobenzene by Knudsen effusion method

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The halogenated aromatic compounds are characterized by their long life, chemical stability and non-biodegradability and across the years have become a serious environmental issue. The polychloronitrobenzenes are frequently used in the synthesis of fungicides and pharmaceuticals. They are also starting materials for the production of azo and sulfur dyes.

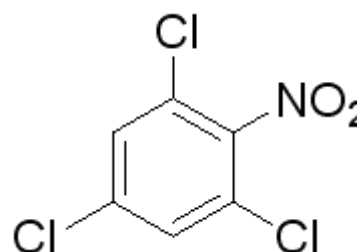


Figure 3 - Chemical Structure

However, these compounds show some levels of toxicity to skin, eyes, blood and immune system.

The present work aims to study the vapor pressures of 1,3,5-trichloronitrobenzene using the Knudsen effusion method. This is an indirect method introduced by M. Knudsen in order to evaluate the heat involved in the phase transition through the measure of vapor pressures in the range of 0.1 and 1 Pa, at several temperatures. Applying the Clausius-Clapeyron equation, it is possible to determine the standard enthalpy of sublimation, at $T = 298.15$ K. In this work the apparatus described by Ribeiro da Silva and Monte [1] was used. The value of the standard enthalpy of sublimation was confirmed by other researchers [2] by a direct method (Calvet microcalorimetry).

This work was complemented by other colleagues [3] by determining the standard enthalpy of formation ($p^\circ = 0.1$ MPa), in the crystalline phase, at $T = 298.15$ K, by means of combustion calorimetry using a rotating-bomb calorimeter.

The combination of the values of the standard enthalpy of formation, in crystalline phase, and of the standard enthalpy of sublimation, allowed the calculation of enthalpy of formation ($p^\circ = 0.1$ MPa), in gaseous phase, at $T = 298.15$ K.

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Molecular Dynamics Study of the Uptake of Aromatic Carboxylate Anions by Polyazamacrocycles

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The development of cationic synthetic receptors capable of recognizing aromatic carboxylate anions is a relevant research area due to the importance of this group of anions as environmental contaminants [1].

The molecular recognition process of selected aromatic carboxylate anions (pyrc⁻, anthc⁻, naphc⁻, iph²⁻ and btc³⁻) by two novel polyaza macrocycles, containing two 1,10-phenanthroline (phen) units ([30]phen₂N₆ and Me₂[34]phen₂N₆), were studied using conventional Molecular Dynamics simulations, in aqueous solution. The results showed that a folded conformation, with the anions inserted between the macrocycle phen units, is adopted, being stabilized by π - π stacking and multiple hydrogen bonding interactions. Theoretical binding free energies were determined and larger binding constants were found for pyrc⁻ and anthc⁻, underlining the importance of the π - π stacking interactions in the molecular recognition process between the protonated receptors and these extended aromatic anions. A comparison between theoretical and experimental results will be presented.

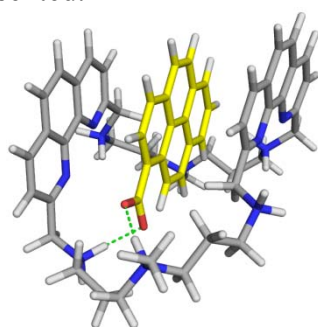


Figure 1. Binding Model obtained by docking of [$\{H_6Me_2[34]phen_2N_6\}(pyrc)\}^{5+}$].

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Temperature Sensor with Fullerene C₇₀ Encapsulated in Polymer Nanoparticles

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Continuous real-time temperature monitoring is needed in areas as diverse as biotechnology, health care, environmental sciences, aerospace industry, nuclear industry, and marine sciences. Temperature optical sensors offer the opportunity for non-contact measurement, essential in some applications. Among the many optical methods used for sensing, fluorescence has attracted special attention because it is highly sensitive, versatile, and can be used even in very strong electromagnetic fields, which are employed, for example, in cancer therapy. Other advantages are the fast response and the spatial resolution that can go from the macroscale (e.g. luminescent paints) down to the nanoscale confocal fluorescence microscopy).

Fullerene C₇₀ has a quantum yield for triplet formation close to one and an intrinsic triplet lifetime in the order of several milliseconds, originating an exceptionally intense thermally activated delayed fluorescence, TADF that can be used as a very sensitive temperature or oxygen sensor.^[1, 2]

We prepared monodisperse polystyrene (PS) nanoparticles with a diameter of 60 nm containing fullerene C₇₀. The encapsulation of fullerene C₇₀ in the PS nanoparticles was achieved by miniemulsion polymerization. The nanostructured material displays a fluorescence intensity and lifetime that is strongly temperature and oxygen dependent, encompassing both the physiologically temperature range and much higher temperatures, or in alternative, very low oxygen concentrations.

Fluorescence emission at 20°C and in the presence of oxygen is very low and independent of the temperature. However, in the absence of oxygen we observe a linear increase of the fluorescence intensity with the temperature, as well as a decrease in the lifetime of delayed fluorescence. The nanoparticles can be used as a non-contact temperature or oxygen sensor in various applications, from industrial high temperature sensing to *in vivo* diagnosis.

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Selective aerobic oxidation of benzyl alcohol to benzaldehyde in water catalyzed by aqua-soluble triethanolamine copper(II) compounds

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The development of selective and mild oxidation processes of benzylic alcohols to the corresponding carbonyl compounds is of significant importance in organic synthesis and chemical industry. The use of air or dioxygen as oxidants provides a clear benefit in view of both environmental and economical concerns. However, clean and mild aerobic oxidations usually require the application of transition metal catalysts combined with nitroxyl radicals such as TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) [1].

In pursuit of our interest on the oxidative catalysis [2,3], herein we report new catalytic systems based on the aqua-soluble multicopper(II) compounds [3], $[\text{Cu}_2(\text{H}_2\text{tea})_2(\text{pma})\text{Na}_2(\text{H}_2\text{O})_4]_n \cdot 10n\text{H}_2\text{O}$ (**1**) and $[\text{O}=\text{Cu}_4(\text{tea})_4(\text{BOH})_4][\text{BF}_4]_2$ (**2**) (H_3tea = triethanolamine), for the mild, selective and clean oxidation of benzyl alcohol into benzaldehyde. This reaction proceeds in aqueous solution at ca. 25–50 °C, with O_2 (1 atm) as oxidant and is mediated by TEMPO. Molar yields of benzaldehyde (based on benzyl alcohol) up to 49 and 74% have been achieved (with >99% selectivity) for catalyst precursors **1** and **2**, respectively. Attempted reactions in the absence of either a copper compound or TEMPO lead only to traces of product (<1%). The effects of oxygen pressure, reaction time, temperature and concentration of K_2CO_3 additive (base) have been studied.

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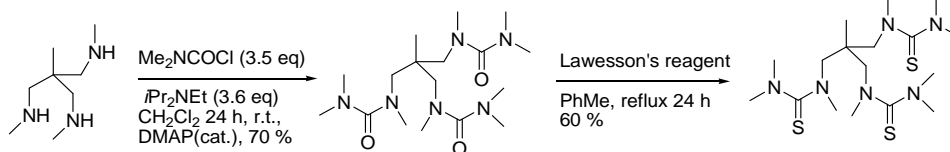
Synthesis of *tris*-Thiourea and its Application as Ligand for Pauson-Khand Reaction

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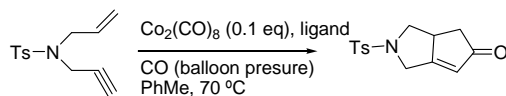
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Tetrasubstituted thioureas have been recently very successfully applied as ligands for various transition metal catalysed organic reactions. Tetramethylthiourea (TMTU) was applied with great success in Pauson-Khand reaction (PKR) with palladium and cobalt catalysts[1,2].

Tris(N,N',N''-dimethylthiocarbamoyl)-1,1,1-tris(methylaminomethyl)ethane ligand – *tris*-thiourea - was prepared from very cheap and commercially available tris-1,1,1-(hydroxymethyl)ethane in five step synthesis and applied as ligand in 1:1 coordination to cobalt in catalytic Pauson-Khand reaction with Co₂(CO)₈ as catalyst.



The *tris*-thiourea vs TMTU was studied as ligand in the PKR on the enyne compound requiring high TMTU loading for good performance under Tang's conditions[2].



The synthesis of the ligand and the catalysis will be discussed[3].

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