XIII Encontro Nacional de Química-Física
II Simpósio de Química Computacional

Faro
Portugal

4 - 6 junho 2018

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Boas Vindas

Preâmbulo

A área de Química-Física é um vasto campo de investigação, na interface da Química e da Física, que procura explicar e prever os fenómenos envolvendo as diversas formas da matéria. Os progressos da investigação nesta área têm sido significativos, sendo atualmente esta disciplina um suporte fundamental para outras áreas do conhecimento, tais como o ambiente, as ciências da vida, a astronomia, os materiais, a energia, etc..

Para este progresso muito contribuiu o desenvolvimento da Química Computacional, disciplina que tem tirado partido da enorme capacidade dos computadores para o estudo de sistemas cada vez mais complexos. O aumento da precisão dos cálculos de estrutura eletrónica com aplicação ao estudo de sistemas de grande dimensão, o desenvolvimento da modelação molecular que permite visualizar o desenrolar dos processos químicos e, ainda, a generalização de novos algoritmos de cálculo numérico baseados em inteligência artificial, fizeram da Química Computacional uma parceira indispensável da Química-Física.

O XIII Encontro Nacional de Química-Física que decorrerá em Faro de 4 a 6 de junho, conjuntamente com o II Simpósio de Química Computacional, constituirá uma oportunidade para nos encontrarmos, aprendermos uns com os outros e estabelecermos colaborações, contribuindo, assim, para fortalecer o desenvolvimento desta tão importante área do conhecimento em Portugal.

O Presidente da Divisão de Química-Física da Sociedade Portuguesa de Química

João Brandão

Universidade do Algarve

Rede sem fios

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A cidade de Faro

Faro é uma cidade milenar a (re)descobrir. De origem pré-romana, conhecida como Ossónoba, era um dos mais importantes centros urbanos do sul da península. A sul, o território é delimitado por um cordão dunar com 19 km de comprimento, o qual é interrompido por ligações entre o mar e a Ria Formosa, formando 3 ilhas. As ilhas, visitáveis de barco embora 1 tenha acesso viário, são lugares de excelência para disfrutar de dias muito agradáveis em contacto com a natureza e com a Ria Formosa, usufruindo de passeios de barco, de bicicleta ou a pé para observação das aves na Ria. A gastronomia local, dependente dos alimentos colhidos na Ria Formosa e as praias de areia branca e águas amenas, galardoadas com a bandeira azul, nalguns sítios habitadas apenas por aves migratórias, são entre outros, aspetos a descobrir nas ilhas da Ria Formosa e que potenciam a oferta ao nível do turismo de natureza. Faro é rico em património natural e cultural e convida-o à sua descoberta[1].

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[1] Texto e fotografia retirados do site http://www.cm-faro.pt/menu/469/turismo.aspx

Programa

Horas	dia 4/06/2018, segunda-feira
09:30-11:00	Receção
11:00-11:30	Abertura
11:30-13:00	OC1: Maria José Calhorda
	CO1: Luís Viegas
	CO2: Luís P Silva
13:00-14:30	Almoço
14:30-16:00	OC2: Maria DMC Ribeiro da Silva
	CO3: Nuno FM Branco
	CO4: Rui Afonso
16:00-17:00	Apresentação dos pósteres / Pausa para café
17:00-18:30	OC3: A Jorge Parola
	CO5: César Mogo
	CO6: Sandra CC Nunes
18:30-19:30	Reuniões da DQF e do GQC

Horas	dia 5/06/2018, terça-feira
09:30-11:00	OC4: Alberto Martin-Molina
	CO7: Alan FY Matsushita
	CO8: João AP Coutinho
11:00-11:30	Pósteres / Pausa para café
11:30-13:25	OC5: António JEG Candeias
	CO9: Fernando JAL Cruz
	CO10: Pedro MP Fernandes
	CO11: Mirtha AO Lourenço
13:25-15:00	Almoço
15:00-19:30	Actividade
19:30	Jantar

Horas	dia 6/06/2018, quarta-feira
09:30-11:00	OC6: M Ermelinda S Eusébio
	CO12: Mário T Rosado
	CO13: Diogo EP Pinto
11:00-11:30	Pósteres / Pausa para café
11:30-13:00	OC7: Daniel JVA dos Santos
	CO14: German Pérez-Sánchez
	CO15: Nicolas Schaeffer
13:00-14:30	Almoço/Encerramento

OC	Oral Convidada	35+5 min
CO	Comunicação Oral	20+5 min

Apresentações Orais

OC1

THE EFFECT OF SUBSTITUENTS ON THE PHOTOPHYSICAL PROPERTIES OF IMINOPYRROLYL BORON COMPLEXES: A DFT STUDY

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Luminescent organoboron compounds have been receiving considerable attention owing to their potential applications in organic light emitting devices (OLEDs). The iminopyrrolyl ligand [1-5] has been used in the synthesis of mono-, bi- and trinuclear organoboron complexes. The possibility of introducing substituents in different positions has allowed the tuning of the emission properties, such as the range of wave lengths. DFT and TDDFT studies [2] have been performed in order to understand the role of steric and electronic substituent effects in emission, as well as the nature of transitions. The geometries of the ground state and the first singlet excited state have been determined and compared, and the planarity of the iminopyrrolyl ligand appears to play a relevant role. The modifications of the complexes include: i) substituents in the iminopyrrolyl phenyl group with varying steric and electronic properties, ii) substitution of this phenyl group by alkyls, iii) increasing the number of boron atoms to two and three by means of a variety of spacers, iv) increasing the extension of the π-system, v) substituents on the pyrrolyl group.

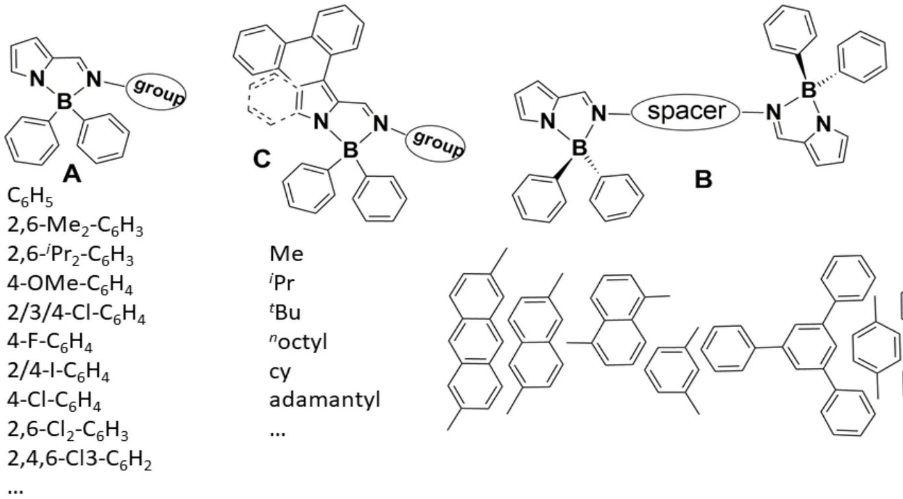

Figure 1: Examples of iminopyrrolyl boron complexes

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OC2

RECENT DEVELOPMENTS ON THE THERMOCHEMISTRY OF HETEROCYCLIC MOLECULES

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In our Research Group, the thermodynamic study of different classes of organic compounds has been involving many researchers whose contributions are relevant to evaluate the reactivity of the molecules. One of our main goals has been to provide reliable values for the standard molar enthalpy of formation in the gas-phase, a reference on the establishment of molecular energetic and structural synergies, as well as an essential thermodynamic parameter to assess the energy associated to a chemical reaction or other transformations in which the compounds are involved, allowing also to derive other related thermodynamic properties.

In this context, we will present some work developed with heterocyclic compounds (mainly five and six membered rings) with oxygen, sulphur or nitrogen heteroatoms. Some examples focusing 1,3-azole derivatives, with one oxygen, sulphur or nitrogen heteroatom in position 1 of the pentagonal ring, and a nitrogen atom in position 3 relatively to that heteroatom, will be described [1,2]. Complementary, an analysis on the properties of heterocycles with one or two benzene rings fused to a five or six membered ring, containing oxygen or sulphur as heteroatoms, will be performed [3,4].

The experimental data are essentially determined from calorimetric measurements, although other sources, in particular vapour pressures measured by the Knudsen effusion studies, are used to get extensive thermochemical information. The results available from computational approaches are used to support the development of strategies allowing the establishment of reliable prediction schemes of the corresponding properties for other species structurally related.

Acknowledgements: Thanks are due to Fundação para a Ciência e a Tecnologia (FCT) of Portugal, Project UID/QUI/UI0081/2013, and FEDER, Projects POCI-01-0145-FEDER-006980 and NORTE-01-0145-FEDER-000028.

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OC3

PHOTOCHROMIC SUPRAMOLECULAR SYSTEMS BASED ON 2-HYDROXYCHALCONES

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The development of systems able to exist in different states whose interconversion can be controlled by different stimuli (light, ions, electrons) may contribute to the appearance of molecular-level devices and materials with new functionalities. Over the last few years, we have worked in systems mainly based on *trans*-2-hydroxychalcones.[1] These photoisomerizable compounds originate in aqueous solution intricate pH-dependent chemical reaction networks involving several species. Among these species, flavylium cations are strongly coloured compounds that have been allowing to explore these chemical networks as pH–coupled photochromic systems.[1]

As aromatic cations, flavylia are electron poor guests able to intercalate into neutral or negatively charged electron rich cavities such as those of molecular clips [2] and cucurbiturils [3]. This allows the use of supramolecular interactions to further control the conversion between different states of the system through functional host-guest complexes with potential applications in drug-delivery, molecular switches, molecular machines, supramolecular polymers, etc. Recent examples of these multistate systems exploited as photochromic,[4] pH-driven self-sorting,[5] and pH-gated photoresponsive pseudorotaxanes with ring translocation [6] (see Fig. 1) will be shown.

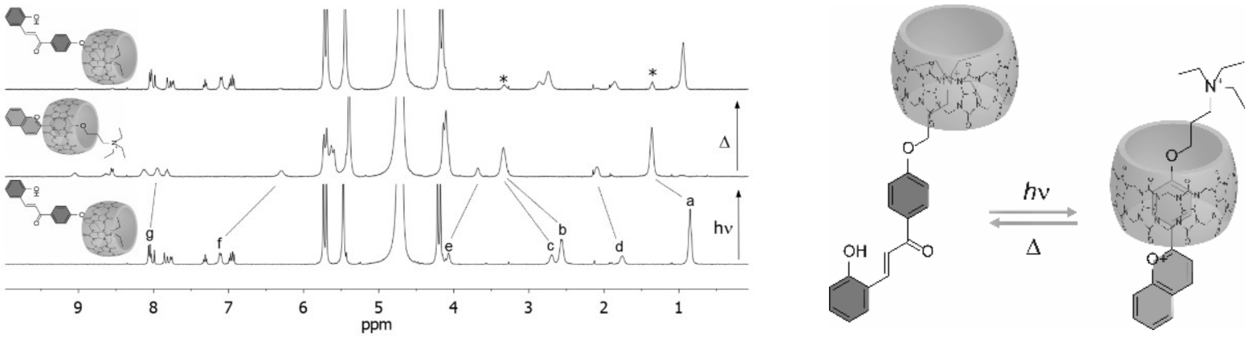

Figure 1: Reversible displacement of the cucurbit[7]uril (CB7) host after photoinduced interconversion (irradiation at 365 nm) of the chalcone:CB7 into the flavyvlium:CB7 complexes and thermal (at 60 °C) back reaction, as followed by ^{1}H NMR in D_2O (0.4 mM, pD = 4.96 (acetate buffer 10 mM) in the presence of 1 equivalent of CB7.

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OC4

MONTE CARLO SIMULATION OF NANOGELS

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In the last decades, micro- and nanogels have attracted considerable attention due to their versatility and high sensitivity to external stimuli. The availability of this system to control the response is considered to be highly advantageous for their future use in the biomedical field, taking into account their enhanced efficacy and ability to carry and release drugs to the targeted tissue.

In this lecture, we present explicit coarse-grained Monte Carlo simulations of nanogels with the help of the bead-spring model of polyelectrolyte and a solvent-mediated hydrophobic interaction potential that captures the swelling behavior of real microgels. First simulations of temperature-sensitive charged nanogels in salt free solutions are presented, in which monovalent and divalent counterions have been considered. Charge profiles inside and outside the nanogel have been computed from simulations, revealing an attractive finding for the use of these nanoparticles as potential drug carriers: When charged nanogels collapse, they can sometimes form a hollow sphere, with the charged beads concentrated on the inner and outer surfaces, and some counterions enclosed in the inner space [1]. Then, simulations of charged nanogels in the presence of 1:1 and 1:3 electrolytes are studied. In particular, two temperature-sensitive charged nanogels have been performed. The presence of salt can often have influence on the thermal response of nanogels, such as the shift of the transition temperature of slightly ionized polyelectrolyte networks. In addition, the surface electrostatic potential obtained from simulations displays a rich behavior when temperature varies, which is conditioned by the interplay between size and charge [2].

Once single nanogels are studied, the second part of the lecture is focused on the interaction between nanogels. Initially, two neutral nanogels with different number of monomers per chain have been simulated. The corresponding effective interaction potentials have been calculated as a function of the distance between their respective centers of mass. These results have been also used to analyze the functional form of the soft-sphere and Hertz potentials [3]. Finally, our simulations have been applied to determine direct forces between charged nanogels. Our results reveal that the electrostatic interactions between charged nanogels are not governed by the net charge of the nanogel, which includes not only the charge of the polymer network but also the charge of ions inside [4].

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OC5

The 12 Labours of HERCULES – bridging Science with Art

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Created in 2009, the HERCULES Laboratory (HERança CULtural, Estudos e Salvaguarda / Cultural Heritage Studies and Safeguard) is a research infrastructure devoted to the study and valorization of cultural heritage, focusing on the integration of chemical, biological and material sciences methodologies and tools in interdisciplinary approaches. HERCULES Lab is based in Évora, a UNESCO World Heritage town, and is supported by both a strong analytic infrastructure. The Lab is currently comprised by a team of 27 PhD researchers from different areas of knowledge, namely chemistry, biochemistry, geology, geochemistry, materials science, conservation science, conservation-restoration and archaeology/archaeometry enabling a truly interdisciplinary approach and scrolling through multiple paths at the level of research, teaching, protection, dissemination and enjoyment of cultural heritage.

In this communication I will present some of HERCULES Lab projects and will focus on two main areas, Heritage Research and novel materials and tools for Cultural Heritage.

Regarding Heritage Research, I will make an overview of our activity presenting some of our projects on artistic, archaeological and built heritage with particular emphasis on multi-analytical and interdisciplinary research and integrated conservation restoration projects and novel approaches, including diagnosis and monitoring, in-situ analysis and imaging, and microanalysis.

The rest of the communication will be devoted to the presentation of some of the solutions being developed at HERCULES Lab (Evora, Portugal), following recent trends on international research, for the improvement and development of novel "green" materials and tools for Conservation, including novel green biocides, bio-probes for in-situ identification of biodeteriogenic microorganisms and digital technologies.

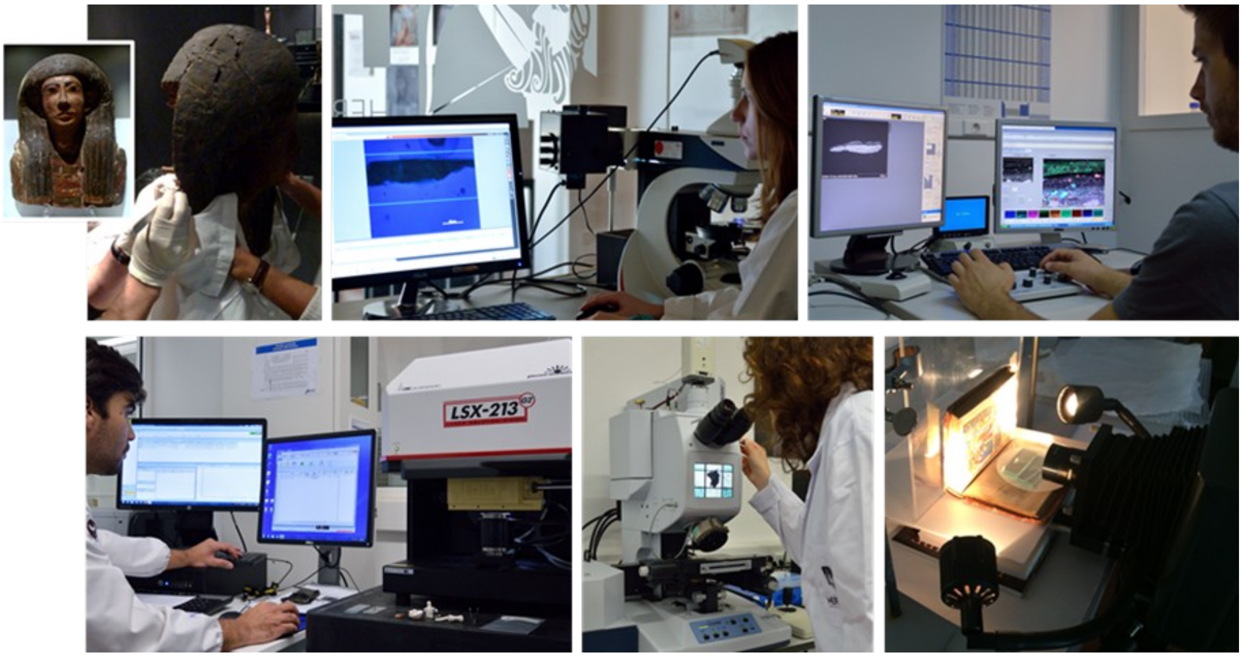

Figure 1: snapshots of HERCULES labours

OC6

PHARMACEUTICAL CO-CRYSTALS
OPPORTUNITIES AND CHALLENGES

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The first choice of the pharmaceutical industry to deliver an active pharmaceutical ingredient, API, is the use of solid dosage forms for oral administration. The solid structure of the API may be critical, as different solid forms display unique physicochemical properties which may impact, for instance, on the API bioavailability, stability and processability. Therefore, the investigation of API solid forms that ensure improved drug performance represents a continuous challenge.

Co-crystals, "crystalline single phase materials, made up of two or more different molecules and/or ionic compounds, in a stoichiometric ratio, which are not solvates nor simple salts"[1], have emerged recently as a promising alternative to traditional API solid forms, polymorphs, solvates and salts. Polymorphs, quite often, display only subtle differences in physicochemical properties and solvates may raise concerns related to thermal stability, for instance. Salt formation needs the presence of ionisable groups in the API (no necessary in co-crystals), with the approved counterions being limited in number. Pharmaceutical co-crystals are made up of the API and one or more co-formers, usually linked together by hydrogen bonded supramolecular heterosynthons. A library of potential co-formers is accessible, including generally recognized as safe substances and other APIs[2].

Co-crystals of a specific API may, *a priori*, be designed from a rational selection of suitable co-formers based on crystal engineering approaches. Design and co-former selection are just the first challenging stages along the pathway of the development of pharmaceutical co-crystals that also includes discovery, synthesis, characterization, evaluation.

In this communication, opportunities and challenges in pharmaceutical co-crystal investigation are discussed and illustrated with examples from our research work on the solid sate of selected APIs [2,3].

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OC7

TARGETING MDR IN CANCER: COMPUTATIONAL STUDIES TO UNDERSTAND OLD PROBLEMS

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At least 11 transporters of the ABC family play roles in human diseases (from Cystic fibrosis or diabetes to intra-hepatic cholestasis), while others are directly linked to multidrug resistance (MDR). MDR to chemotherapy regimens can be achieved by selecting phenotypes that over-express ABC transporters. Over-expression of P-glycoprotein (P-gp/ABCB1), multidrug resistance-associated protein 1 (MRP1/ABCC1) and breast cancer resistance protein (BCRP/ABCG2) were found to be markers of overall poor chemotherapy response and prognosis in various cancers.

We have been developing a research line to discover the main physicochemical features responsible for P-gp modulation through new pharmacophore/QSAR [1] with better classification capability and with the appearance in 2009 of the murine P-gp structure, this information was used in long molecular dynamics runs (up to the microsecond) to study the dynamics of the transporter, how drug efflux occurs and how drug adsorption may affect P-gp activity. The characterization of three drug binding sites in the promiscuous drug-binding pocket (DBP) was achieved by matching experimental information with extensive docking results to unravel elusive drug/P-gp recognition, interactions and modulation mechanisms. A computational classification scheme was proposed to organize molecules in different class types (modulators, substrates, non-substrates). The access of drugs to the drug-binding pocket through a hypothesized gate was also studied by calculating the potential of mean force for the efflux process [2].

Unfortunately, all P-gp modulators entering phase III clinical trials failed by showing a dramatic increase in cellular toxicity (tariquidar) or reduced in vivo effectiveness (zosuquidar, laniquidar). Thus, the problem resides elsewhere, namely in the polyspecificity of the DBP were these molecules interact. All these findings including our latest study of BCRP will be reviewed, discussed and linked with very recent findings as new emerging strategy to overcome the problems found in clinical trials [3].

ACKNOWLEDGEMENTS
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CO1

REACTIVITY OF HYDROFLUOROPOLYETHERS TOWARDS OH: A COST-EFFECTIVE IMPLEMENTATION OF MULTICONFORMER TRANSITION STATE THEORY

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The adverse environmental impact of CFC release into the atmosphere [1,2] has led to an international effort to replace them with acceptable alternatives. The Montreal Protocol led to the phase out of CFCs in industrialized countries because of their elevated ozone depletion and global warming potentials (ODP and GWP). Development of environmentally friendly replacements with lower tropospheric lifetimes (reaction with OH) became urgent, with HCFCs, HFCs and PFCs being selected as first- and second-generation replacements. However, non-zero ODP (HCFCs) and high GWP was still an issue with these compounds, with the latter two classes targeted by the Kyoto Protocol because of their high GWP. The design and development of useful alternatives continued, with hydrofluoropolyethers (HFPEs) appearing as promising third-generation replacements because of their zero ODP and even lower GWP.

Here, we will provide a detailed insight behind the computational strategies used in predicting the reactivity of different HFPEs towards the OH radical. Having a general formula of $R-(OCF_2CF_2)_p(OCF_2)_q-OR$ ($R = CF_2H$, CH_3, CH_2CH_3, $CH_2CH_2CH_3$, $CH(CH_3)_2$), we have calculated nine rate constants: all five possible cases for p0q1, p1q0 ($R = CF_2H$, CH_3), p0q2 (CH_3) and p2q0 (CH_3). In the absence of any reported theoretical results, the quality of our cost-effective approach [3] (with M08-HX/aug-pcseg-2//M08-HX/pcseg-1 DFT calculations and using Eckart tunneling) based on multiconformer transition state theory (MC-TST) [4] will be assessed by comparison with four experimental rate constants [5,6]. Our investigations yield rate constants averaging a factor of ≈ 0.7 (k_{MC-TST}/k_{exp}) of experimental data.

The good agreement with experimental results provides a valid framework for present and future calculations, where this cost-effective approach will prove essential in our objective of unveiling the theoretical details of the unestablished atmospheric chemistry of HFPEs, particularly the effect of different R groups and chain lengths (increasing pq values) on the reactivity. Hopefully, the gained theoretical knowledge will serve as an important tool in the design and development of new greener CFC alternatives.

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CO2

INSIGHT INTO THE PHOTOEXCITATION-FREE PRODUCTION OF EXCITED STATES BY DIOXETANONES FROM TD-DFT AND MULTIREFERENCE CALCULATIONS

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Chemiluminescence consists on the emission of light as the result of a chemical reaction [1]. It does not require photoexcitation, and so, there is no autofluorescence arising from the background signal. The lack of photoexcitation also eliminates the problems associated with light-penetration into biological tissues (except in emission). Thus, chemiluminescent systems have allowed the real-time and noninvasive imaging of target molecules/processes *in vivo*.

In chemiluminescence, the production of excited states is generally caused by the generation and subsequent thermolysis of energy-rich dioxetanone intermediates (Figure 1) [2-4]. However, little is known regarding the mechanism of chemiexcitation. Herein, a theoretical approach using reliable and up-to-date TD-DFT and multireference methodology was used to address this problem. Our calculations demonstrated that efficient chemiexcitation is the result of the reacting molecules having access to a long and biradicalar region of the PES where S_0 and S_1 are degenerate. The use of the activation strain model revealed that this region can be accessed due to increased interaction between the keto and CO_2 moieties of the dioxetanone, which extends the biradical region by preventing the rupture of the peroxide ring. Increased interaction derives from attractive electrostatic interactions between moieties of dioxetanone.

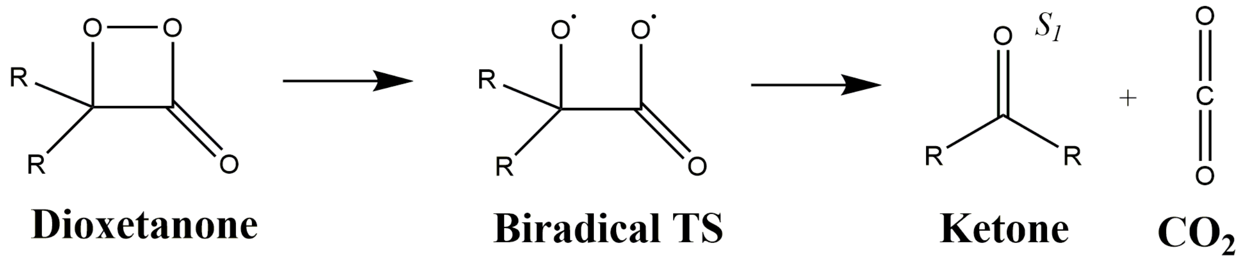

Figure 1: Reaction mechanism of thermolysis of dioxetanones.

ACKNOWLEDGMENT
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CO3

STUDY OF SOLID-LIQUID PHASE DIAGRAMS OF FAME AND ALKANES BY DIFFERENTIAL SCANNING CALORIMETRY

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The availability of energy is essential for the humanity and nowadays a key factor of progress and sustainability. The use and availability of energy at relatively low cost and abundance, are dependent of alternative sources and types of energy. Biodiesel is an important alternative to mineral sources of energy, but some challenges should be overcome in order to optimize their production, usability, sustainability and to decrease their environmental impact.

The study of low temperature behavior, as the study of the effect of the composition in the crystallization on Blends of diesel with Biodiesel.
In this work was explored different mixtures with molar fractions between 0 and 1 to create solid-liquid phase diagrams of alkanes, namely hexadecane, octadecane and eicosane, with methyl esters as methyl stearate and methyl palmitate, to understand the crystallization behavior of the main compounds in Biodiesel with an alkane present in the Diesel fuel

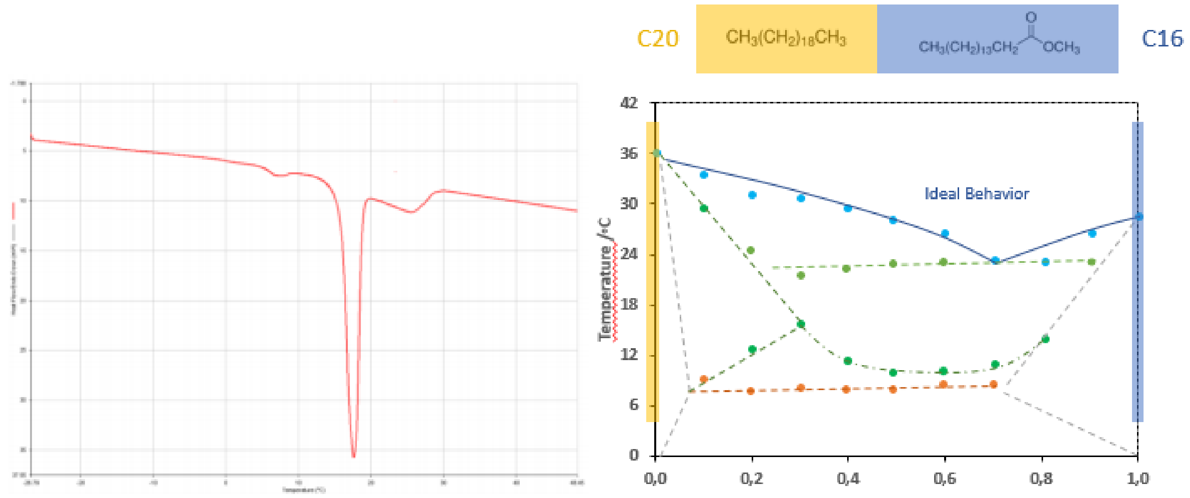

Fig.1. DSC of a mixture of 30 % (mol/mol) of methyl stearate and 70 % (mol/mol) of hexadecane and a typical phase diagram of methyl palmitate and Eicosane

Acknowledgments

This work was financially supported by Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal, European Social Fund (ESF) for the projecto CIQUP, University of Porto (Projects: PEst-UID/QUI/00081/2013, FCUP-CIQ-UP-NORTE-07-0124-FEDER-000065), the project CICECO-Aveiro Institute of Materials (Ref. FCT UID /CTM /50011/2013 and FEDER under the PT2020 Partnership Agreement.) and Galp Energia. N.F.M.B. thanks FCT and Galp Energia for the PhD Research Grant: PD/BDE/113540/2015. A.I.M.C.L.F thanks FCT for the Post-Doc: SFRH/BPD/84891/2012.

CO4

HOW CO_2 BINDS THE SURFACE OF AMINE-FUNCTIONALIZED MESOPOROUS SILICAS: AN ATOMISTIC PICTURE FROM A COMBINED NMR AND DFT STRATEGY.

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Amine-functionalized silicas have emerged as one of the most interesting materials for post-combustion CO_2 capture. Despite extensive research, the nature of the chemisorbed species, formed upon CO_2 reaction with surface amines, remains a highly debated, unresolved issue.

Herein, experimental NMR measurements and theoretical DFT calculations are employed to determine the identity and structure of CO_2-amine adducts formed in silicas functionalized with tertiary amines. DFT structure optimization trials were conducted, with the M06-2X functional and the 6-31G(d) basis set, using clusters of several CO_2-amine adducts supported on silica. Nuclear magnetic shieldings (σ) were determined using the gauge-independent atomic orbital approach and then converted to chemical shifts (δ_{calc}) using a reference compound. δ_{calc} values were then compared with the experimental chemical shifts (δ_{exp}) of different CO_2-sorbed amine-functionalized mesoporous silica samples. This comparison allows unambiguous assignment of the various CO_2 species (Figure 1) present in the samples.

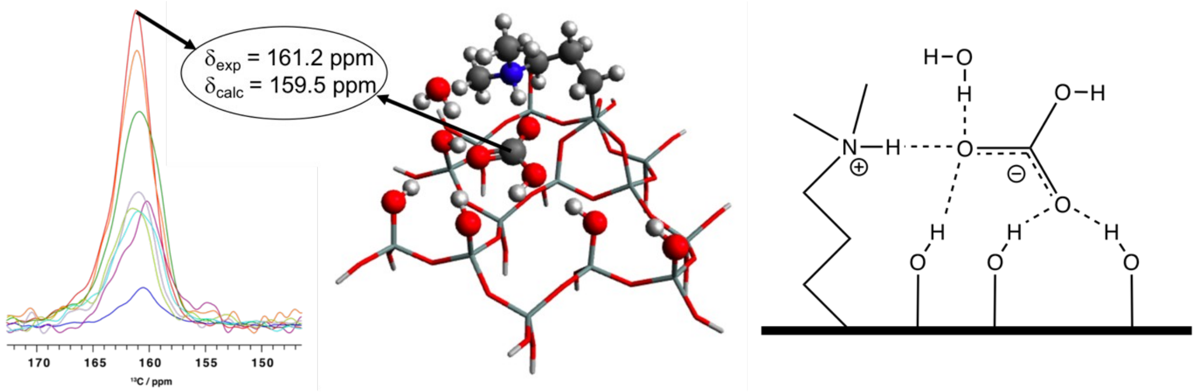

Figure 1: Left: ^{13}C NMR spectrum of CO_2-sorbed amine-functionalized SBA-15 mesoporous silica. Center: 3D representation of the DFT-optimized ammonium bicarbonate structure. Right: 2D representation of the ammonium bicarbonate structure.

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CO5

STUDYING PRESSURE DEPENDENCE OF THE TERMOLECULAR REACTION $\mathbf{H + O_2 + M \longrightarrow HO_2 + M}$

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Potential Energy Surfaces (PES) are used to study the rate of elementary reactions and their dynamics, being useful to compute state to state rate constants. Unfortunately in a complex reactive system, many elementary reactions are normally involved and the overall study becomes difficult. The usual approach to study such system is to make use of all the system's available rate constants and build a system of master equations. This procedure is based in the assumption that reactants are in thermal equilibrium. But studies seem to indicate that the number of non-reactive collisions can be small and the energy distribution of the intermediate species may be far from the Boltzmann distribution. MreaDy program (Multi-process Reactions Dynamics), aims to reproduce complex mechanisms, such as the hydrogen combustion, using accurate PES. This is accomplished by defining a global Potential Energy Surface (gPES) for the process in question, integrating various PESs, each one of them representing an elementary reaction that is expected to play a role in the chemical process, and performing reactive classical dynamic calculations on it[1]. MReaDy was modified in order to study the pressure dependence of the reaction $H+O_2+M \longrightarrow HO_2+M$. This reaction is one of the main sources of uncertainty when modelling hydrogen combustion chemistry, and being a termolecular reaction, it cannot be studied using normal classical trajectory programs. We start with hydrogen atoms and oxygen molecules, forming by collision excited HO2* radicals. We can count how many of the excited HO2* radicals are stabilised by collisions at 1500, 2000, and 2500 K and pressures of 10, 20, 30 and 50 atm., and we calculate the formation rate of stable HO2 radicals. We present preliminary results for this process showing a clear increase of the rate constant with pressure. We are also able to study the rate constants of the different reactions present in the system.

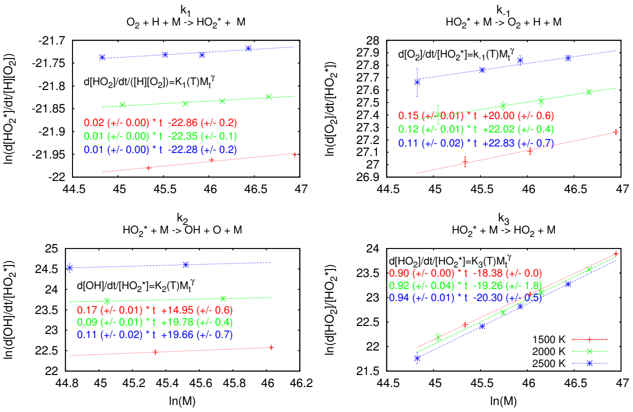

Figure 1: Obtained reaction rate constants for the reactions present the system.

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CO6

BEYOND CHARGE DENSITY: WHAT DICTATES POLYELECTROLYTE ADSORPTION UPON MULTICOMPONENT RESPONSIVE SURFACES?

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Adsorption of polyions onto charged surfaces has long been recognized as a phenomenon of paramount importance in biological and technological applications. This work examines polyelectrolyte adsorption, driven by electrostatics, for model systems where the adsorbing polyanion is, generally, more densely charged than the surface.
Adsorption was inspected by computational simulation in surfaces possessing the same surface charge density but different compositions (number of positive and negative charges, and crowders), and different charge densities.

An intuitive model relating polyelectrolyte adsorption with the imposed features of the polarizable surfaces is proposed, based on Monte Carlo simulations using a coarse-grained approach. It was found that for a constant surface charge density, the number of charged groups in the surface determines the adsorption patterns. Adsorption increases with the number of attractive charges in the surface until reaching a maximum, decreasing thereafter due to the presence of polyanion like-charged particles. Additionally, the presence crowding agents decreases adsorption. These findings were summarized using a descriptive function which allows to simultaneously describe a wide range of adsorption regimes and also accounts for specific non-monotonic trends. It can be used to efficiently predict and manipulate the interaction between charged macromolecules and different substrates.

ACKNOWLEDGEMENTS
The Coimbra Chemistry Centre is supported by the Fundação para a Ciência e a Tecnologia (FCT), Portuguese Agency for Scientific Research, through the Projects PEst-OE/QUI/UI0313/2014 and POCI-01-0145-FEDER-007630.
SCCN and TFGGC acknowledge FCT for Post-Doctoral SFRH/BPD/71683/2010 and PhD SFRH/BD/95459/2013 grants, respectively.

CO7

EFFECT OF Eu(III) AND Tb(III) CHLORIDE ON THE GELIFICATION BEHAVIOR OF POLY(SODIUM ACRYLATE)

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Supramolecular gels are an important class of soft materials: they are basically formed by solvent molecules inside in a 3D network structure and can be considered from soft and weak to hard and tough, depending on the respective mechanical properties [1]. The gelation process can be accomplished in different ways using, for example, the interaction between a charged polymer and a metal ion [2]. In this work, the interaction between poly(acrylic acid) sodium salt (PSA) and the trivalent ion (Eu^{3+} and Tb^{3+}), to form luminescent gels, has been studied. For that, a phase diagram (Fig. 1) for polymer-ion mixture was constructed showing that for high molar ratios Ln^{3+}/PSA different phase transitions occur. We have focused our work in the region where the formation of weak and strong gels is occurring. The phase transitions have been assessed by rheological and luminescence measurements. From rheological measurements, we have found that the mechanical strength of gels increases by increasing the concentration of PSA, since the elastic module (G′) increases when the concentration of PSA increases. A similar trend is found in yield stress values, from which the gel begins to behave as a liquid. Thus, the higher the concentration of PSA the higher is the yield stress. The frequency sweeps shows that Ln^{3+}/PSA gels and weak gels exhibit a rheological solid-type behavior, with a storage module (G′) predominating over loss modulus (G′′) in the studied frequency. The formation of the gel phase can also be followed by fluorescence spectroscopy. It can be observed that the emission of fluorescence increases by increasing the molar ratio Ln^{3+}/PSA. Such behavior may be explained by the binding of Ln^{3+} to deprotonated PSA and a decrease in the number of coordinated water molecules. However, the formation of gel phase is reversible and dependent on the Ln^{3+} concentration. In fact, by increasing the molar ratio values above a certain critical point, disaggregation of the gel structure occurs, mainly due to electrostatic repulsions between ions Ln^{3+} and Ln^{3+}/PSA aggregates; this is supported by the decrease in the emission of fluorescence of Ln^{3+} mixed solutions. The effect of Ln^{3+} in the PSA gel formation mechanism is complemented with the analysis of FTIR, SEM and EDS mapping data.

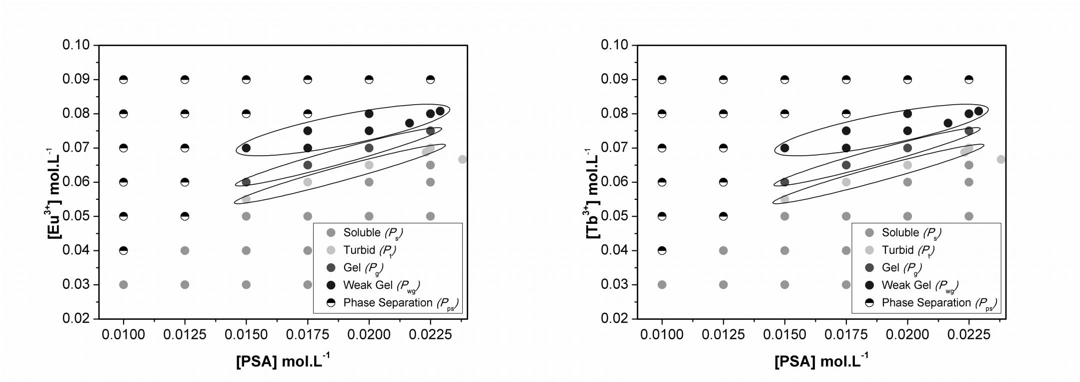

Figure 1: Phase diagram of Eu(III)/PSA and Tb(III)/PSA mixed system.

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CO8

THERMOREVERSIBLE AQUEOUS BIPHASIC SYSTEMS BASED ON HYDROPHILIC ZWITTERIONS

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The ability to induce reversible phase transitions between aqueous homogeneous solutions and biphasic liquid-liquid systems, at pre-defined and suitable operating conditions, appear as an interesting alternative in the design of separation and purification processes since several processing steps can be combined into a single operation. Here is shown for the first time that aqueous biphasic systems (ABS) composed of hydrophilic ZIs combined with aqueous solutions of salts or polymers, have their reversible behaviour triggered by small changes in temperature. Unlike classical liquid-liquid systems, ZI-based ABS allow to work in a wide range of temperatures and compositions which can be tailored to fit the requirements of a given separation process. Opposite trends in temperature, from an upper critical solution temperature (UCST)-type to a lower critical solution temperature (LCST)-type behaviour were observed with the change of ZIs alkyl chains length, suggesting that, depending on the structure of ZI, different types of interactions are occurring in ZI-based ABS. Finally, the potential application of these thermoreversible systems as novel separation platforms was evaluated.[1, 2]

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CO9

EQUILIBRIUM AND TRANSPORT DISTRIBUTIONS OF DNA IN HYDROPHILIC NANOTUBES

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Enhanced sampling techniques spanning a sub-μs timescale reveal that, in the presence of an electric field acting upon single-walled carbon nanotubes (SWCNTs), complete encapsulation of a Dickerson B-DNA dodecamer [1] occurs with fast kinetics (≤ 4.3 ns) and is thermodynamically spontaneous, as demonstrated by a 40 kJ/mol decrease in the system's Gibbs free-energy [2]. Encapsulation is driven by strong electrostatic attractions between the nucleic acid and the solid, which in the early stages of confinement accounts for at least 80 % of the total interaction energy. The encapsulated DNA end-to-end length is similar to that of the canonical B-form (*ca.* 3.8 nm) in the two solid topologies under consideration, (51, 0) and (40, 0); however, consecutive free-energy minima occur in the thermodynamical landscapes, located within the endohedral volume, and corresponding to a 0.25 – 0.5 nm deviation away from the canonical form (Fig. 1). Very interestingly, and contrary to what happens with the (40, 0) hydrophobic analogue, the existence of an electric field on the walls induces biomolecular confinement. Furthermore, and by contrast with the larger (51,0) topology, the ϕ_2 phase space spans a broader range now including non-stable (transient) DNA forms with highly compressed double-strand lengths ($\phi_2 < 3$ nm); these observations are corroborated by independent atomically detailed techniques.

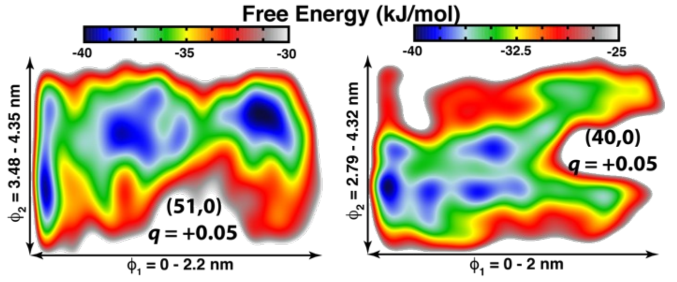

Figure 1: Fee-energy maps of DNA@SWCNT. ϕ_1 is the distance between centres of mass of DNA and the SWCNT, projected along the nanopore's main axis (z), and ϕ_2 corresponds to the DNA end-to-end length. Low-lying free-energy valleys, evidenced as dark blue regions, are distributed along the nanopore internal volume, $\phi_1 < 2$ nm, and linked amongst themselves via a thermodynamical highway with a free-energy penalty ≤ 5 kJ/mol.

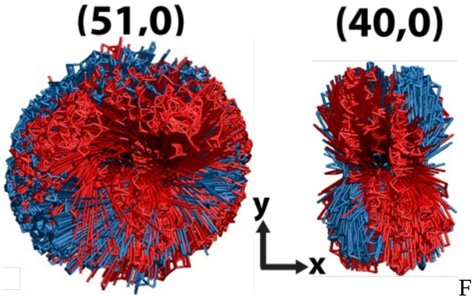

Figure 2: Ensemble space of single-strand individual axes for confined DNA. Each strand individual axis runs from a terminal Phosphorus atom to the last one located on the same strand, thus each strand axis is represented by a different colour: strand A (blue) and strand B (red). Carbon nanotubes are parallel aligned along the z-axis with diameters D(51,0) = 4 nm and D(40,0) = 3 nm.

The effects exerted by the confining solid upon the nucleic acid exhibit a marked dependence on nanopore diameter, and this is attributed to entropic reasons arising from free-volume considerations. Nonetheless, DNA maintains translational mobility inside the nanotube and is able to translocate within a cylindrical volume comprised between termini, according to a (x, y, z) anisotropic self-diffusion mechanism that also involves molecular translation caused by a self-rotation of the double-strand axis; instantaneous velocities are similar for both topologies ($v^{max} \approx 27$ m/s), and short time Fickian self-diffusivities reveal that electrostatic attraction between the walls and DNA induces a slowing down of molecular diffusion in hydrophilic nanotubes as compared to pristine solids [3]. The nanoscopic picture obtained for the single-strand individual axes *ensembles* (Fig. 2) indicate that the biomolecule favours positioning in close contact with the nanopore walls in the (51,0) topology, in contrast with what is observed for the (40,0) nanotube where the DNA's c.o.m. is preferentially located along the pore central axis, $\langle x, y\rangle \approx (0,0)$.

Precise physiological conditions (310 K, [NaCl]=134 mM) allow the extrapolation of results to *in vivo* systems and constitute a novel and thorough contribution to nanotube technology in the areas of nucleic acid encapsulation/delivery and personalized therapeutics.

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CO10

STRUTURAL DETERMINANTS IN THE HUMAN NATIVE 20S PROTEASOME INHIBITION: A MOLECULAR DYNAMICS STUDY

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The Ubiquitin Proteasome Pathway (UPP) plays a pivotal role in intracellular protein degradation and turnover in eukaryotic cells [1]. Therefore, modulation of the UPP emerged as a rational therapeutic approach in cancer, neurodegenerative diseases (Alzheimer, Parkinson), inflammatory pathologies (arthritis, psoriasis, asthma, colitis), organ transplant, infective diseases (malaria), among others [2].

During the last two decades academia and pharmaceutical industry made huge efforts to develop natural and synthetic proteasome inhibitors (PI). In 2003 FDA approved the pioneering dipeptidyl boronic acid derivative PI bortezomib for the treatment of refractory multiple myeloma (MM) and subsequently frontline therapy for MM. However, despite the enormous potential of PI, their use is still limited to certain types of blood cancer and shows severe side effects, dose limiting toxicity, peripheral neuropathy, limited activity in solid tumour and innate or acquired drug resistance [3].

In this work, we have used Molecular Dynamics (MD) simulations to perform the first conformational and structural characterization of the human native 20S proteasome structure [4]. We focused our analysis on the three catalytic subunits well known for their proteolytic activity (β1, β2 and β5) and we further extended our study to additional MD simulations of three different point mutations in the β5 catalytic subunit, with recognized importance in PI's resistance: Ala49Thr, Ala50Val and Cys52Phe. Hopefully, our studies will be able to shed the light on the structural key determinants that regulate the observed PI's resistance in the different mutations, and ultimately use the acquired knowledge in the development of new alternative and efficient proteasome inhibitors.

ACKNOWLEDGMENTS
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CO11

FLUE GAS ADSORPTION ON PERIODIC MESOPOROUS PHENYLENE-SILICA: A DFT APPROACH

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Periodic mesoporous organosilicas (PMOs) were suggested as potential adsorbents for CO_2/CH_4 separation because of their large affinities towards CO_2 and low interaction with CH_4.[1-4]

Herewith, we present a comprehensive computational study on the binding properties of flue gas species ─ the diatomic CO, H_2, N_2, O_2 and NO molecules, the triatomic CO_2, H_2O, H_2S and SO_2 species and the tetratomic SO_3 and NH_3 gases ─ with the pore walls of periodic mesoporous phenylene-silica (Ph-PMO) for understanding the possible impact of other gaseous species in the CO_2/CH_4 separation.

The calculations considered three exchange-correlation functionals (PBE, PBE-D2 and M06-2X) based on the density functional theory. The walls of the periodic mesoporous phenylene-silica were modelled within the cluster model approach. The calculated data demonstrate that the presence of H_2O, SO_2, NH_3, H_2S and SO_3 is a significant threat to CO_2 capture in Ph-PMO and suggest that the Ph-PMO material would present high selectivity for CO_2 over CH_4, CO, H_2 or N_2 adsorption. The adsorption behavior of flue gas constituents in Ph-PMO can be directly related to the dipolar moment and proton affinity of the gaseous molecules.

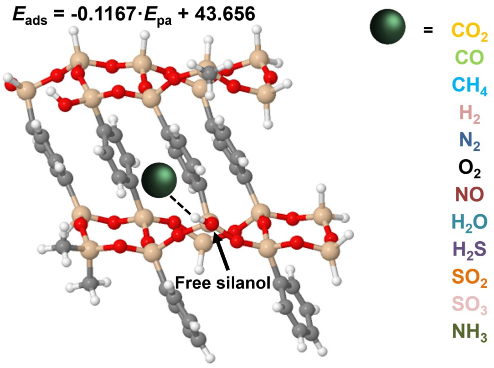

Figure 1: Preferential interaction of flue gas molecules with the free silanol of Ph-PMO.

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CO12

APPLICATION OF COMPUTATIONAL METHODS TO THE STUDY OF CO-CRYSTAL FORMATION

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The synthesis of co-crystals, in which different chemical compounds are part of the same unique crystalline structure, is an important task of current crystal engineering. They have interesting applications in the pharmaceutics and materials industries. Co-crystal formation requires the aggregation of the different molecules as a synthon that can be stabilized by various intermolecular forces, such as hydrogen bonding. The intermolecular interaction between different compounds have to be preferential relative to the aggregation of identical molecules in each pure crystal, provided that the kinetics are favorable.

In this communication, we present some examples of application of computational chemistry methods (post-Hartree-Fock and DFT) to the rationalization of the co-crystal formation processes, often complementary to experimental methods like X-ray diffraction. These will include the energetic evaluation of isodesmic reactions of heterodimer vs. homodimer formation, the analysis of the molecular electrostatic potential mapped on the molecular Hirshfeld surfaces, or the calculation of intermolecular energies in crystals and analysis of the crystalline energy frameworks.

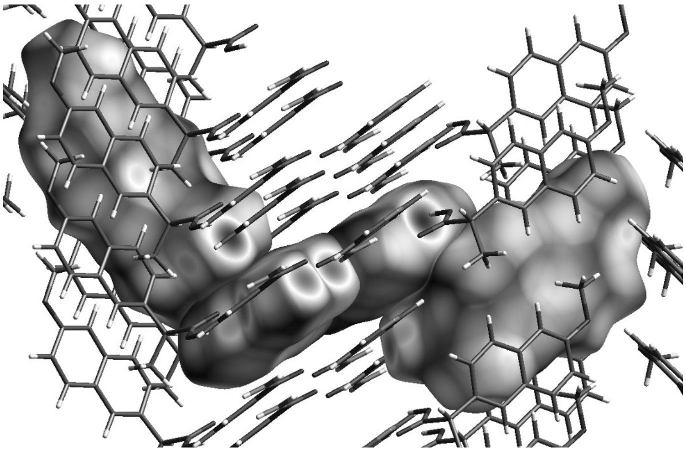

Figure 1: Molecular Hirshfeld surfaces in the naproxen-isonicotinamide co-crystal.

CO13

KINETICS OF THE ADSORPTION OF DNA-COATED COLLOIDAL PARTICLES ON MOBILE PATCHES

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Colloidal particles trapped at oil-water interfaces interact through long-range capillary forces resulting from the deformation of the interface. As a result, kinetically trapped structures are obtained, which hinders the formation of the thermodynamic phases. A protocol was recently proposed to avoid such strong particle-particle interactions and obtain a fully ergodic quasi-2D colloidal dynamics [1]. The idea is to adsorb DNA-coated colloidal particles on complementary functionalized oil droplets. Here, we combine numerical simulations and analytic calculations to shed light on the experimental results and to describe how the coverage of the oil droplet should depend on the thermostat temperature, bulk concentration of colloidal particles, and degree of functionalization of the oil droplet [2]. We also explore the use of a binary mixture of particles and show how the competition between particle sizes affects the dynamics.

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CO14

COARSE-GRAIN MOLECULAR DYNAMICS SIMULATIONS OF IONIC LIQUID ACIDIC AQUEOUS BIPHASIC SYSTEMS FOR THE EXTRACTION COBALT

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Ionic liquids (ILs) have been shown as a good alternative to hazardous volatile organic solvents in extraction processes [1]. Concretely, the ionic nature of ILs can be exploited to capture metal complexes. However, ILs present high viscosity, hence poor transport properties, which reduces their applicability in industrial procedures. This problem can be overpassed upon the mixing of ILs with acidic solutions to yield the so-called acidic aqueous biphasic systems (AcABS). An AcABS is that based on the tributyltetradecylphosphonium chloride (P44414Cl) IL and on the aqueous hydrochloric acid solution, which was already proposed as a good alternative for metal extraction [2]. The metal extraction procedure puts into contact the P44414Cl IL with an aqueous solution with the target metal atoms well solvated in water and the HCl acidic solution. The AcABS system is heated afterwards above the cloud point to induce a phase separation. It is obtained a P44414Cl rich phase and the acid leaches the metal atoms by forming metal-chloride complexes which are adsorbed in the P44414Cl rich phase. A microscopic understanding of the process is lacking since it was not possible to characterize the P44414Cl mesophase with available experimental techniques (e.g. X-Ray or TEM).

It has been previously shown that coarse-grain (CG) molecular dynamics (MD) simulations can be used to understand the complex self-assembly of amphiphilic molecules and their co-operative interactions with other compounds [3]. Herewith, we present the development of a CG MD formalism based on a multiscale approach (from density functional theory to all-atom MD to CG MD) and its validation against the experimental results of the average micelle aggregation number of dilute P44414Cl in aqueous solution below the critical micelle concentration. The entire phase behavior was mapped upon extensive CG MD simulations at different P44414Cl concentrations in water.

The validated model was then employed to analyze in detail the extraction of cobalt using the P44414Cl/HCl/water AcABS for the first time.

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CO15

IONIC-LIQUID-BASED ACIDIC AQUEOUS BIPHASIC SYSTEMS: A PROMISING ALTERNATIVE IN CRITICAL METALS EXTRACTION

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For over a decade, ionic liquids (ILs) have been considered as promising solvent alternatives to volatile organic compounds (VOC). In the field of metal ions extraction, ILs are currently used at a laboratory scale as extracting media for various metals with excellent results. Nevertheless, industrial application of such ILs is limited by (i) the range of available hydrophobic ILs, most being based on fluorinated anions such as bis(trifluoromethanesulfonyl)imide ($[NTf_2]^-$), or on ILs incorporating long alkyl chains, (ii) the viscosity of ILs and (iii) production costs significantly higher than those of classical extracting systems currently in operation.

IL-based acidic aqueous biphasic systems (AcABS) represent a promising alternative to solvent extraction process for the recovery of critical metals in which the substitution of the inorganic salt by an acid allows for the 'one pot' approach to the leaching and separation of metals.[1] However, a more fundamental understanding of AcABS formation remains wanting. In this work, the formation mechanisms of AcABS are elucidated through a comparison with traditional ABS. A large screening of AcABS formation with a wide range of ILs identifies the charge shielding of the cation as the primary structural driver for the applicability of an IL in AcABS. Through a systematic study of tributyltetradecylphosphonium chloride ($[P_{44414}]Cl$) with various chloride salts and acids, we observed the first significant deviations to the cationic Hofmeister series reported for IL-based ABS.[2] Furthermore, the weaker than expected salting-out ability of H_3O^+ compared to Na^+ is attributed to the greater interaction of H_3O_+ with the $[P_{44414}]^+$ micelle surface. Finally, the remarkable thermomorphic properties of $[P_{44414}]Cl$ based systems are investigated with a significant increase in the biphasic region induced by the increase in the temperature from 298 K to 323 K. These finding allows for the extension of AcABS to new acidic systems and highlights their versatility and tuneability.

The ability to manipulate the formation of a biphasic system from a monophasic one and vice-versa simply by changing the temperature avoids the kinetic limitations related to the mass transfer between two-immiscible systems and extends the applicability of the reported AcABS to less acidic leachate solutions. In addition, the partition and separation of critical metals is studied across a range of conditions and compared to those in traditional ABS and ABS-AcABS mixtures. Finally, as AcABS occurs in aqueous solutions, this allows for direct recovery of metals using precipitation or electrodeposition thereby avoiding the required stripping steps of liquid-liquid extraction processes. Taking advantage of this feature, we report a closed-loop process for the the AcABS separation of cobalt and manganese from other metals present in waste NiMH batteries and the direct electrodeposition of cobalt from the IL-rich phase.

ACKNOWLEDGEMENTS

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Pósteres

P01

THE VOLATILITY AND THE THERMODYNAMIC STABILITY OF THE THREE AMINOPHENOLS

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Aminophenols and their derivatives are of increasing commercial importance in chemical and dye industries. They are versatile intermediates and are employed in the synthesis of virtually every class of stain and dye [1]. The vapor pressures of *ortho* and *para* aminophenols were determined using the Knudsen mass-loss effusion method [2] in the temperature intervals T = (321.1 to 343.3) K and T = (337.2 to 359.2) K, respectively. The sublimation vapor pressures of *meta*-aminophenol were measured using the referred to above technique, between (323.2 and 345.2) K, and a static method, based on capacitance diaphragm manometers [3], between (354.5 and 391.8) K. The latter technique was also used to measure the liquid vapor pressures of this isomer over the temperature range T = (370.0 to 423.3) K. The experimental results enabled the determination of the standard (p^{o} = 0.1 MPa) molar enthalpies, entropies and Gibbs energies of sublimation, at T = 298.15 K, of the three isomers, and of vaporization of the *meta* isomer. The temperatures and molar enthalpies of fusion of these compounds were determined using differential scanning calorimetry. The thermodynamic stability of the three aminophenols was evaluated taking into account the standard Gibbs energies of formation in the crystalline and gaseous phases, that were calculated considering the enthalpy of formation in the crystalline phase, reported in the literature [4], the gas-phase absolute entropies, determined using quantum chemical calculations, and the experimental properties of sublimation mentioned to above.

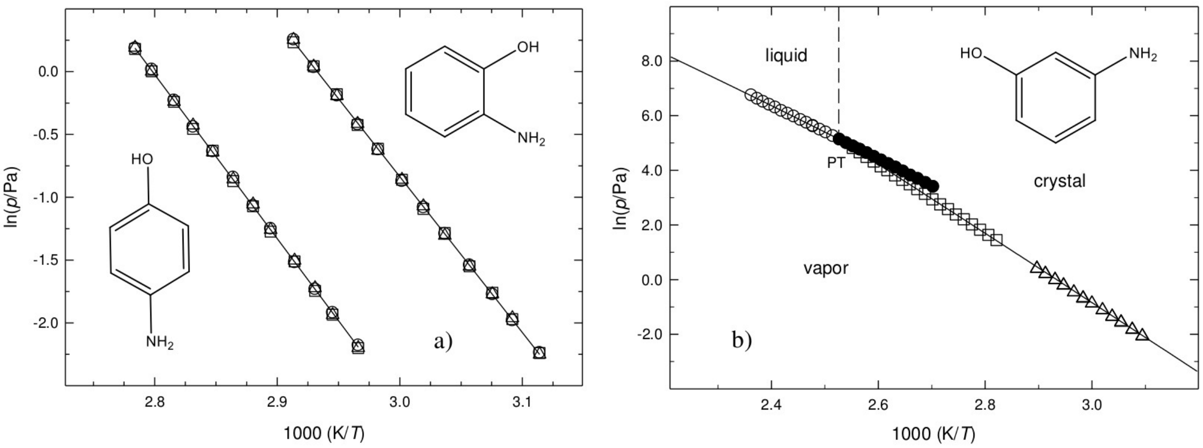

Figure 1: a) Plots of vapor pressure against reciprocal temperature for ortho and para aminophenols. b) Phase diagram of m-aminophenol: open circle, liquid vapor pressures; closed circle, supercooled liquid vapor pressures; square, crystalline static vapor pressures; triangle, crystalline effusion vapor pressures.

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Thanks are due to FCT, Project UID/QUI/00081/2013 and to FEDER (COMPETE 2020), Projects POCI-01-0145-FEDER-006980 and NORTE-01-0145-FEDER-000028. A.R.R.P.A. thanks FCT and the European Social Fund for the award of the postdoctoral fellowship (SFRH/BPD/97046/2013).

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P02

FIRST VOLATILITY STUDY OF 1-ALKYL-3-METHYLIMIDAZOLIUM TRIS(PENTAFLUOROETHYL)TRIFLUOROPHOSPHATE IONIC LIQUIDS

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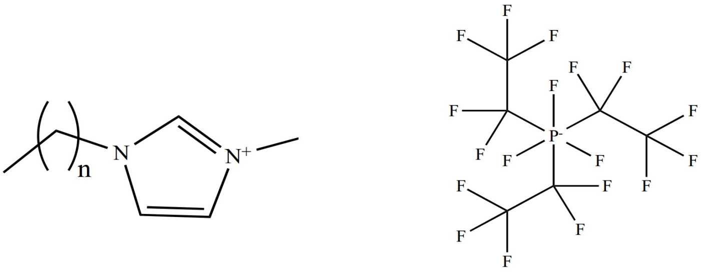
Some ionic liquids (ILs) can be considered as nanostructurated fluids in which the ion pairs arrange themselves into polar and nonpolar domains. It is the interplay of these two domains/interactions that eventually leads to the formation of medium-range nano-scale domains, as well as their dual character, which will affect significantly the physico-chemical properties of ionic liquids.



$[C_nC_1Im]$ $[PAF]^-$

Figure 1: Structures of Ionic Liquids used in this work, (n = 2,4,6).

To date no accurate vaporization studies have been performed for 1-alkyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate series, $[C_nC_1Im][PAF]$, (n = 2,4,6), figure 1. Herein, the vapor pressure at several temperatures for $[C_nC_1Im][PAF]$, (n = 2,4,6), was measured by a Knudsen effusion method combined with a quartz crystal microbalance [1]. The experimental vapor pressure data were fitted to the integrated form of the Clausius-Clayperon equation and the standard ($p^o = 10^5$ Pa) molar enthalpies and entropies of vaporization were derived.

The derived thermodynamic properties of vaporization of the $[C_nC_1Im][PAF]$, (n = 2,4,6), are analyzed together with the results obtained previously for the Imidazolium [CnC1im]$[NTf_2]$ [2] and Pyridinium series [CnPy]$[NTf_2]$ [3], in order to evaluate the effect of the different anions and of the alkyl side chains of the cation, as well as, to get additional insights concerning the nanostructuration of ionic liquids.

ACKNOWLEDGMENTS

Thanks are due to Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal, and to FEDER for the financial support to Centro de Investigação em Quíimica, University of Porto (CIQUP) through the project Pest-C/QUI/UI0081/2013 and the SAM project Norte-01-0145-FEDER-000028. AIMC Lobo Ferreira acknowledges the financial support from Fundação para a Ciência e Tecnologia (FCT) for her PhD Research Grant SFRH/BPD/84891/2012.

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P03

THERMODYNAMIC STUDIES ON IMINODIBENZYL

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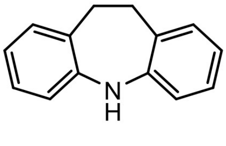
Iminodibenzyl (10,11-Dihydro-5H-dibenzo[b,f]azepine) is a heteropolycyclic compound presenting two benzene rings fused to a central azepane ring (Figure 1). Its derivatives have significant importance in several scientific areas, but its greatest role is in pharmacology, being used as analgesic, antidepressant and antipsychotic agent. Nevertheless, in the literature there is a hiatus on the thermochemical data of this dibenzoazepine and of the corresponding derivatives. The current study addresses an energetic study regarding iminodibenzyl, based on both experimental and computational research studies.

The experimental techniques used were the Knudsen mass-loss effusion method and static bomb combustion calorimetry technique aiming, respectively, the determination of the enthalpy of sublimation and of the massic energy of combustion of iminodibenzyl. These quantities were used to derive its enthalpy of formation in crystal and gas phases, at T=298.15 K.

The computational study performed with the composite G3(MP2)//B3LYP approach, based on the Gaussian-N theory, enabled the optimization of the structure, calculation of its vibrational frequencies and energy at 0 K, as well as its absolute enthalpy at 298.15 K. This parameter was combined with the calculated absolute enthalpies of the compounds involved in selected working reactions, allowing to derive the gas-phase standard molar enthalpy of formation of iminodibenzyl, at 298.15 K.

The experimental and computational enthalpies of formation will be discussed and compared with related heteropolycyclic compounds, providing the possibility of evaluating effects in the enthalpies of formation associated with changes in the ring size [1,2] in the class of these key molecules.

Figure 1: Molecular structure of iminodibenzyl.



ACKNOWLEDGEMENTS
This work was developed within the scope of the projects UID/QUI/0081/2013, POCI-01-0145-FEDER-006980, and NORTE-01-0145-FEDER-000028 (Sustained Advanced Materials, SAM), awarded to CIQUP, financed by Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal, and co-financed in the framework of Operational Programme for Competitiveness and Internationalisation, COMPETE, with community funds (FEDER) and national funds of MEC. VLSF thanks FCT, European Social Fund (ESF), and national funds of MEC for the award of the post-doctoral grant SFRH/BPD/78552/2011, and also to SAM project for the present post-doctoral grant.

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P04

ENERGETIC CHARACTERIZATION OF INDANONE DERIVATIVES INVOLVED IN BIOMASS DEGRADATION PROCESSES

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The indanone derivatives have special relevance for their applications, in particular because they are key intermediates on the synthesis of new products. The importance of this class of compounds has led to an increasing interest in their extraction from biomass. The thermodynamic characterization of these compounds, namely the knowledge of the respective thermophysical and thermochemical properties [1,2], is essential in which concern the evaluation of their reactivity. In this context, this work reports an experimental and computational thermochemical study of 5,6-methoxy-1-indanone (Figure 1).

The study of 5,6-dimethoxy-1-indanone has been developed using calorimetric techniques and a computational methodology. The enthalpies of combustion and of sublimation of this compound were determined from, respectively, static bomb combustion calorimetry and high temperature Calvet microcalorimetry. From these experimental data, the gas-phase standard molar enthalpy of formation was derived. Additionally, the gas-phase standard molar enthalpy of formation of the compound studied was obtained from high level ab initio calculations, at the G3(MP2)//B3LYP level of theory. The computational approach of this indanone derivative allowed to establish the respective molecular structure, coexisting four stable conformations for 5,6-dimethoxy-1-indanone. Furthermore, the energetic effects associated with the presence of one or two methoxy groups in the indanone structure were evaluated. These enthalpic increments were compared with the homologous substitutions in the benzene and naphthalene molecules.

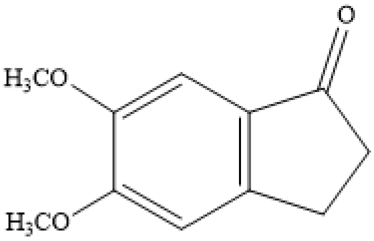

Figure 1: Structural formula of 5,6-dimethoxy-1-indanone.

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Thanks are due to Fundação para a Ciência e a Tecnologia (FCT) of Portugal, Project UID/QUI/UI0081/2013, and FEDER, Projects POCI-01-0145-FEDER-006980 and NORTE-01-0145-FEDER-000028.

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P05

ENERGÉTICA DE ALGUNS ANTIOXIDANTES: ESTUDO TERMOQUÍMICO EXPERIMENTAL E COMPUTACIONAL

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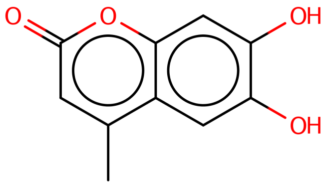
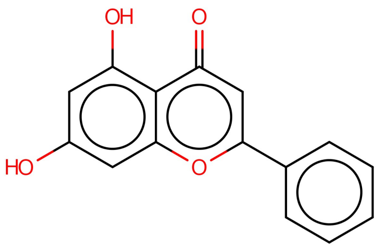
A capacidade antioxidante dos derivados da cumarina e da flavona decorre das propriedades dos seus grupos hidroxilo, em particular da energética da ligação O-H. A caracterização adequada da energética desta ligação química exige em simultâneo a descrição adequada das moléculas intervenientes e também dos respetivos radicais. O estudo destes últimos, no âmbito da química quântica, levanta frequentemente problemas adicionais.





Neste trabalho estudaram-se experimentalmente alguns derivados da cumarina e da flavona, nomeadamente 7-hidroxi-4-metilcumarina (4-Methylumbelliferone), 3-hidroxiflavona e 5,7-dihydroxyflavone (chrysin), recorrendo a técnicas de calorimetria de combustão e microcalorimetria Calvet, com vista à sua caracterização termoquímica. Adicionalmente, utilizaram-se métodos quânticos rigorosos para estudar a energética destes sistemas, bem como da 6-hidroxi-4-metilcumarina, 6,7-dihydroxy-4-methylcoumarin (4-Methylesculetin), cujo estudo experimental não foi possível realizar. Estudou-se também, neste contexto, a energética dos radicais resultantes da quebra homolítica de ligações O-H nos sistemas moleculares anteriores, com vista à determinação das correspondentes energias de dissociação, que são fundamentais na interpretação das respetivas capacidades antioxidantes.

A excelente concordância entre resultados experimentais e computacionais, suportam o alargamento do estudo aos restantes compostos não estudados experimentalmente, permitindo realizar o estudo alargado da energia de dissociação das ligações O-H e sua correlação com as correspondentes capacidades antioxidantes.

P06

ESTUDO TERMOQUÍMICO DO INDOLE-R-METANOL E INDOLE-R-ETANOL (R = 2;3)

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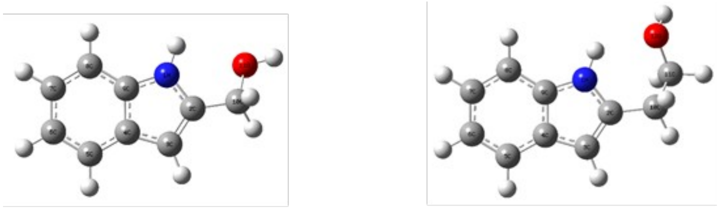
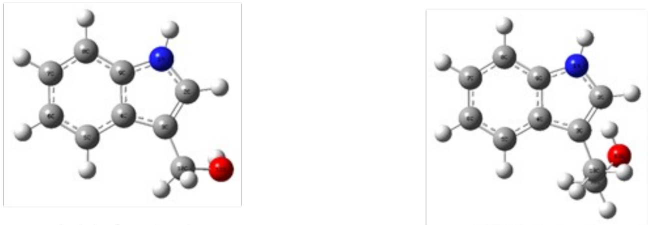
Moléculas contendo o núcleo indole apresentam diversas propriedades biológicas, tais como atividades anti tumoral e anti-inflamatória, sendo usadas como compostos chave na planificação e síntese de novas drogas visando um maior potencial terapêutico. Assim, torna-se imperativo o conhecimento das suas propriedades termodinâmicas assim como a sua relação com a estrutura. Este trabalho focou o estudo termoquímico para a determinação da entalpia de formação dos seguintes compostos: indole-2- e indole-3-metanol, indole-2- e indole-3-etanol. Experimentalmente, determinou-se a entalpia de formação em fase cristalina, (calorimetria de combustão) e a entalpia de sublimação (microcalorimetria Calvet), para o indole-3-etanol. Os parâmetros obtidos permitiram derivar o valor da entalpia de formação para o indole-3-etanol, no estado gasoso. A excelente concordância destas medições com as estimativas computacionais obtidas, usando o método de cálculo, G3(MP2), suportam o alargamento deste estudo à estimativa desta propriedade para os restantes compostos não estudados experimentalmente, permitindo ainda estabelecer as suas estruturas moleculares e determinar os seus parâmetros estruturais. Os resultados obtidos são interpretados em termos de contribuições estruturais.



Indole-2-metanol

Indole-2-etanol



Indole-3-metanol

Indole-3-etanol

Figura 1: Geometrias otimizadas do indole-2-metanol, indole-2-etanol, indole-3-metanol e indole-3-etanol.

P07

THERMODYNAMIC PROPERTIES OF PHASE TRANSITIONS AND PHOTOLUMINESCENCE PROPERTIES OF 2,5-DIPHENYL AND 2,5-DI(1-NAPHTHYL) DERIVATIVES OF 1,3,4-OXADIAZOLE

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Organic semiconductors have been receiving a great deal of attention from the scientific community due to their wide range of applications in modern electronic devices such as organic light-emitting diodes (OLED), organic photovoltaic cells (OPVs) and organic field-effect transistors (OFETs). This new generation of devices is more efficient, less expensive to produce and have less negative impact on the environment [1].

In the present work, we explored the relative volatilities, thermodynamic properties of phase transition and photophysical properties of a couple of 1,3,4-oxadiazole derivatives used as chromophores for light emitting devices and fluorescent dyes [2-4]: 2,5-diphenyl and 2,5-di(1-naphthyl)-1,3,4-oxadiazole. The sublimation vapour pressures of these compounds were measured experimentally by means of a Knudsen effusion apparatus, and the respective thermodynamic properties (standard molar enthalpy, entropy and Gibbs energy) of sublimation were determined from the vapour pressure dependence with the temperature. The enthalpies and temperatures of fusion were determined using differential scanning calorimetry. In addition, fluorescence spectroscopic measurements were executed to determine the quantum yield and the photoluminescence (PL) properties, in solution and in solid phase.

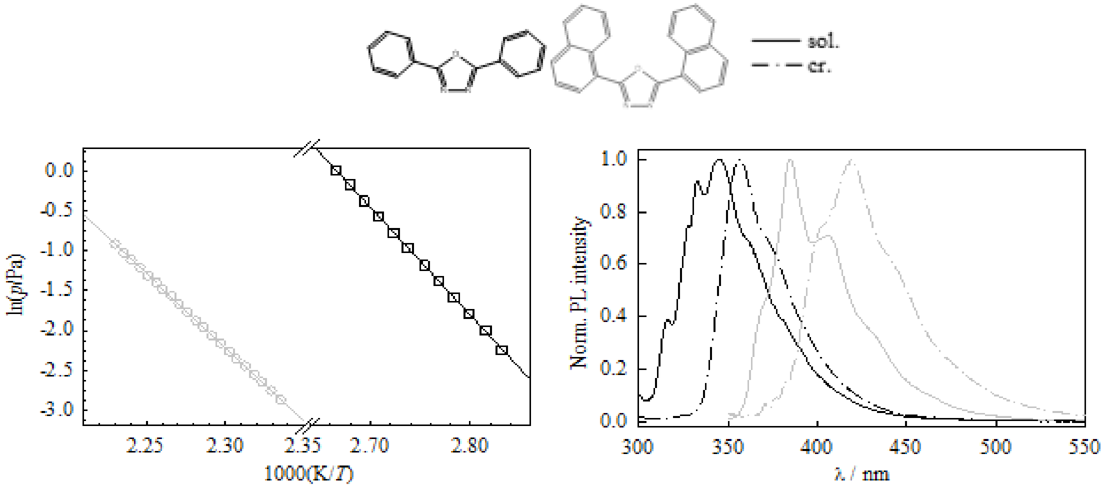

Figure 1.
Vapour pressures and fluorescence spectroscopic results of the two compounds studied.

ACKNOWLEDGMENTS

Thanks are due to Fundação para a Ciência e Tecnologia (FCT) for the financial support to Project UID/QUI/0081/2013 and to FEDER (COMPETE 2020) for the financial support to Projects POCI-01-0145-FEDER-006980 and NORTE-01-0145-FEDER-000028, that supports a research grant to J.A.S.A.O.

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P08

THERMODYNAMIC STUDY OF THE THREE NITROBENZAMIDE ISOMERS

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Benzamide derivatives show diverse biological and pharmacological activities like antimicrobial, anti-inflammatory, analgesic, cardiovascular and anticancer [1]. Nitrobenzamides, in particular, found application in the photochemical cleavage of DNA and in the treatment of neurodegenerative disorders being also used as inhibitors of cytokines and anti-arrhythmic agents [2]. The sublimation vapor pressures of the three isomers of nitrobenzamide were measured at different temperatures using the Knudsen mass-loss effusion technique [3]: *ortho*-nitrobenzamide between (373.1 and 395.2) K, *meta*-nitrobenzamide between (367.2 and 389.2) K, and *para*-nitrobenzamide between (379.1 and 401.2) K. From the temperature dependence of the vapor pressure of the crystalline compounds, the standard ($p^o = 10^5$ Pa) molar enthalpies and Gibbs energies of sublimation, at chosen reference temperatures, were derived. The standard Gibbs energies of formation in crystalline and gaseous phases were determined and used to differentiate the thermodynamic stability of the three isomers. The values of this thermodynamic property were determined considering the reported enthalpies of formation in the crystalline phase [2], the gas phase absolute entropies, calculated using quantum chemical calculations, and the values of vapor pressures and enthalpies of sublimation, determined in the present work. Moreover, differential scanning calorimetry analysis enabled the determination of the temperature and molar enthalpies of fusion of the three compounds. The enthalpies of the intermolecular hydrogen bonds N−H···O in the crystalline phase of the compounds studied were discussed. The contributions of nitro and amide substituents to the sublimation properties of nitrobenzamides were evaluated as well as the eventual interactions between these groups in *ortho*, *meta* and *para* positions.

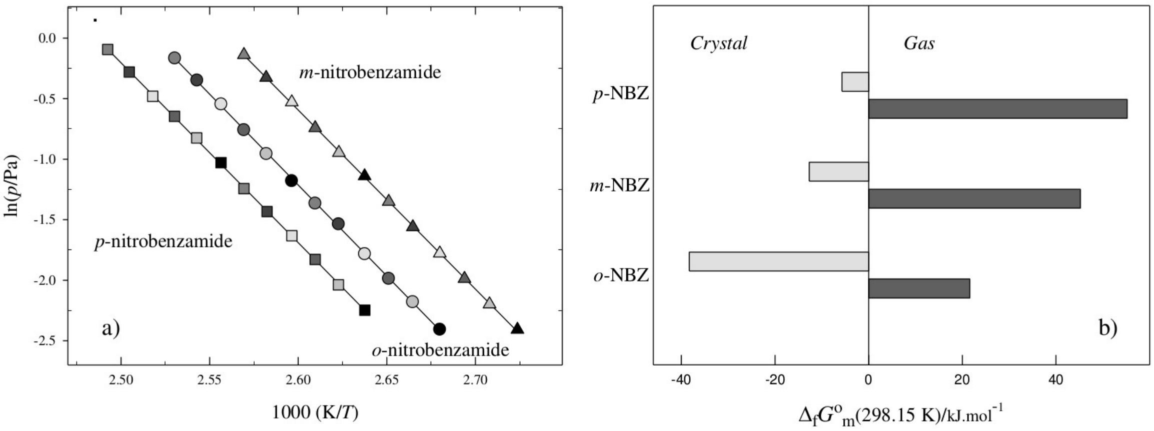

Figure 1: a) Plots of vapor pressures against reciprocal temperature for the nitrobenzamide isomers. b) Standard molar Gibbs energies of formation in the crystalline and gaseous phases of the three nitrobenzamides studied.

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Thanks are due to FCT, Project UID/QUI/00081/2013 and to FEDER (COMPETE 2020), Projects POCI-01-0145-FEDER-006980 and NORTE-01-0145-FEDER-000028, that supports a research grant to B.D.A. Pinheiro. A.R.R.P.A. thanks FCT and the European Social Fund for the award of the postdoctoral fellowship (SFRH/BPD/97046/2013).

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P09

VAPOR PRESSURE MEASUREMENT OF AMINO ACIDS BY KNUDSEN EFFUSION

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The principle of operation, concepts and recent developments of the Knudsen effusion methodology for the vapour pressure measurement of amino acids and other low volatile liquids and solids will be presented as schematically represented in fig.1.

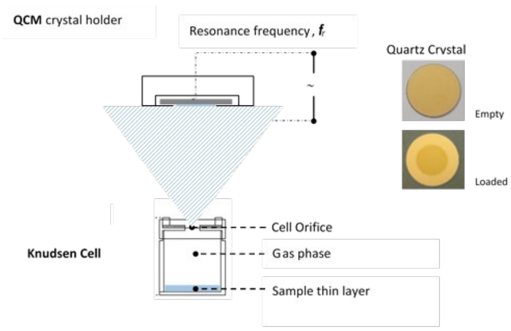

Figure 1: Schematic description of the Knudsen effusion apparatus with QCM detection.

Preliminary results obtained for the vapor pressure measurement of a series of simple amino acids, namely: glycine, L-alanine, L-phenylalanine, L-proline, L-leucine, L-methionine and L-isoleucine, will be presented and discussed.

ACKNOWLEDGEMENTS
We want to thank Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal, and European Social Fund (ESF) for their financial support to CIQUP, University of Porto (Projects: PEst-C/QUI/UI0081/2011, FCUP-CIQ-UP-NORTE-07-0124-FEDER-000065).

P10

POLYMORPHISM OF PINANEDIOL, A PLASTIC CRYSTAL FORMER

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Plastic crystal formation is recognized as been frequent in molecules of approximately globular shape. This special case of solid-solid transition is characterized by loss of orientational order retaining positional order in the crystal. The entropy and enthalpy variations of this transition to a mesophase are much greater than the fusion entropy and enthalpy.

Pinanediol is a chiral cyclic monoterpenoid with an approximately globular structure. Despite having intermolecular hydrogen bonds in the solid sate, the pure enantiomers are plastic crystal formers. This communication presents a study of the polymorphism of the pure enantiomer and racemic pinanediol using several experimental techniques; Differential Scanning Calorimetry, variable temperature FT-IR, Polarized Light Thermal Microscopy, Single Crystal X-ray Diffraction, variable temperature Powder X-ray Diffraction. The samples were prepared using sublimation, melt crystallization and grinding.

A complex polymorphic behavior was observed for the pure enantiomer. Besides the formation of the mesophase, three anisotropic crystalline phases were identified. The formation of a plastic crystal mesophase was investigated for the racemic mixture.

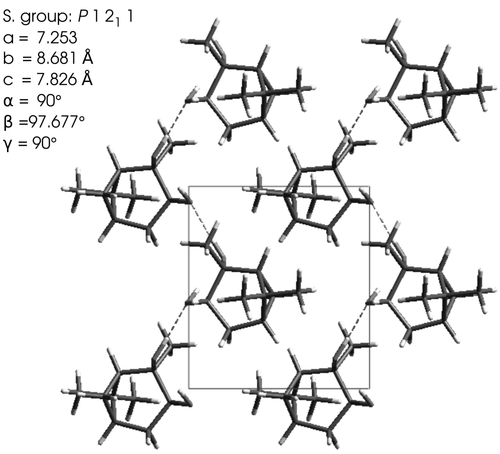

Figure 1: Crystalline structure of one of the polymorphs of (−)-pinanediol.

P11

TOWARDS A COMPREHENSIVE AND ACCURATE ESTIMATION METHOD FOR BIODIESEL HEAT OF COMBUSTION

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There is a growing interest on the use of biodiesel (see e.g. [1]), a mixture of Fatty-Acid Methyl Esters (FAME) obtained from diverse renewable sources such as food-crops (1st generation), non-food crops (2nd gen) or specially engineered energy crops such as algae (3rd gen). Having such diverse origins, biodiesel fuels can present very different compositions.

The heat of combustion (or the high-heating value, HHV) characterizes the energy content and is therefore an important property of a fuel, especially for biodiesels if they are to replace petroleum fuels. Indeed, HHV is one of the most influential parameters that affect the specific fuel consumption, brake thermal efficiency and NOx emissions of an engine.

There are several methods to predict the HHF of biodiesels, the most accurate being based on their FAME composition and using the HHV of each individual FAME. However, reliable data on FAMEs HHV are still lacking, particularly for 3rd generation biodiesels which include some more “unusual” FAMEs. Methods to directly estimate HHV of FAMEs are also scarce and of limited accuracy [2], [3]. On the other and, group additivity methods such as Benson’s have been widely used with great success to estimate heats of formation for many classes of organic compounds. Bridging heats of combustion with heats of formation is trivial but, to the best of our knowledge, except for the references cited in this paragraph this bridge remains mostly uncrossed.

In this work, we developed a computer program to calculate FAME HHVs from their heats of formation obtained with Benson’s method, as extended by Domalski and Hearing to liquid and solid phases [4]. On the other hand, we used computational chemistry methods to address special cases of FAMEs for which experimental data is either unavailable or having conspicuously large uncertainties. Our computational strategy is based on the application of explicitly correlated methods (viz. CCSD(T)-F12). Due to a faster convergence with the basis set size, data near the complete basis set limit for CCSD(T) can be obtained with a more modest and far more manageable double-zeta basis set. Accurate thermochemical data can thus be obtained for fairly large molecules. The largest molecules demanded the use of local methods instead (viz. LCCSD(T)). These allow a linear scaling of the computational cost with the system size, and are therefore particularly suited to study of the FAME molecules. Finally, we intend to use the obtained dataset to test and eventually reparameterize higher order (and therefore potentially more accurate) additivity methods such as the extended Laidler bond additivity (ELBA) method [5].

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P12

TERMOCHEMISTRY OF TWO 2-METHYLNAPHTHOXAZOLES

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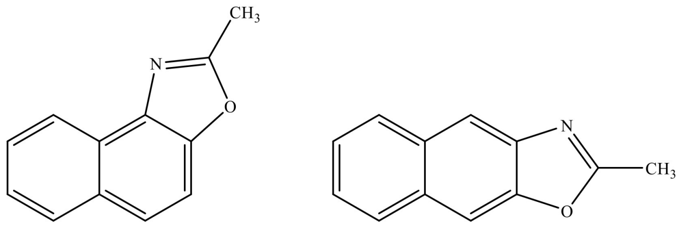
In the context of our interest on thermodynamic properties of heterocyclic compounds presenting a benzene ring fused to a five-membered ring with nitrogen and oxygen/sulphur as heteroatoms, we have been involved in a systematic study to investigate the relationships between structure, energy, and reactivity of several 1,3-benzazoles [1-3]. Recently, studies on some heterocycles with a naphthalene moiety fused to a pentagonal ring containing nitrogen and oxygen heteroatoms have been performed and are reported in the present work. Reliable characterization of their energetic parameters is relevant since it provides the necessary support to properly understand their chemical behaviour.

The present work reports experimental and computational thermochemical results for two 2-methylnaphthoxazoles (figure 1). The standard molar enthalpies of formation, in condensed phase, at T = 298.15 K, of the compounds were derived from their standard molar energies of combustion, at T = 298.15 K, measured by static bomb combustion calorimetry. Their standard molar enthalpies of sublimation/vaporization, at T = 298.15 K, were measured directly, using high temperature Calvet-drop microcalorimetry. Additionally, using high level ab initio calculations, the gas-phase standard molar enthalpies of formation of these compounds were obtained. A discussion on the results obtained will be presented.



(1) (2)

Figure 1: Structural formula of 2-methylnaphtho[1,2-d]oxazole (1) and2-methylnaphtho[2,3-d]oxazole (2).

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P13

THERMOCHEMICAL STUDY OF *N*-CYANOMORPHOLINE

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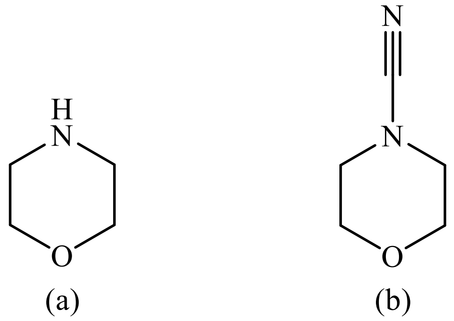
The morpholine has a hexagonal saturated structure with two heteroatoms (oxygen and nitrogen in positions 1 and 4), which gives it a high flexibility with the consequent formation of several conformers. A significant number of morpholine derivatives have relevant applications in the industry, namely as corrosion inhibitors and optical brighteners, as well as in the pharmaceutical area (analgesics, local anaesthetic, and antibiotic agents).

In this work, experimental and computational studies were performed to evaluate and understand the energetic effect inherent to the substitution of the hydrogen of the amino group of in morpholine scaffold by the cyano substituent, according the molecular structure depicted in figure 1. This communication reports the standard internal energy of combustion and the standard enthalpy of vaporization of the morpholine derivative obtained, respectively, from combustion calorimetry and Calvet microcalorimetry measurements. These data were used to derive the standard enthalpies of formation *N*-cyanomorpholine derivatives, in the liquid and gaseous phases, at T=298.15 K. Additionally, computational calculations were performed, using the G3(MP2)//B3LYP composite method.

The structural changes and the inherent energetic effects, associated with the substitution of the hydrogen of the amino group by the cyano substituent will be analysed. [1].



(a) (b)

Figure 1. Structural formulae for morpholine (a) and *N*-cyanomorpholine (b).

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P14

THERMODYNAMICS OF SOLVATION OF ALCOHOLS IN IONIC LIQUIDS

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In this work, results regarding the solution/solvation of alcohols in ionic liquids (ILs) will be presented, gathering the main achievements of our recent work. Enthalpies of solution at infinite dilution of different alcohols in ILs, obtained by Isothermal Titration Calorimetry (ITC), and the derived enthalpies of Solvation will be reported.

Alcohols were selected as solutes in order to explore both the ability of the alcohol hydroxyl group to interact with the IL by dispersive or H-bonds interactions and the ability of the alcohols alkyl chain to interact with the non-polar moieties of the IL, acting as molecular probes of the ILs solvation characteristics.

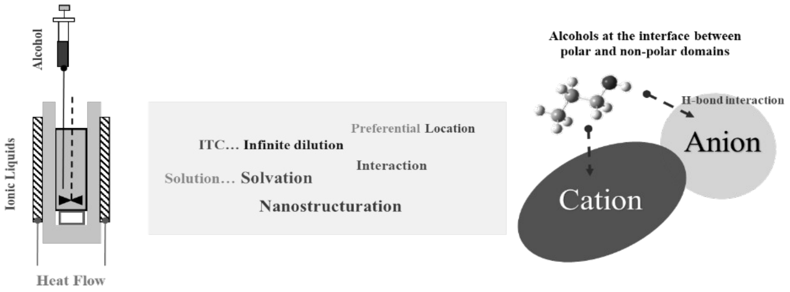

Figure 1: Schematic picture of the methodology and main conclusions.

The results we have obtained for the solvation of small alcohols (propanol, butanol and pentanol) in ILs with different alkyl chain length [1] will be presented along with ongoing results concerning the solvation of alcohols of higher molecular weight in the same ILs. The results reflect the effect of both the alkyl chain length of alcohol and ILs cation, highlighting the nanostructuration of Ionic Liquids and suggesting the preferential location of the alcohols at the interface between polar and non-polar domains of the ILs. The enthalpies of solvation of propanol in ILs with different cations and anions [2], recently published, allow a comprehensive analysis of the anion and cation effect and show evidence for alcohol-anion H-bond interaction. Finally the enthalpies of solvation of alcohols of a different acidity (fluorinated alcohols) will also be presented, strengthening the analysis of the alcohol-anion interaction by H-bond.

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Thanks are due to Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal, and to FEDER for the financial support to Centro de Investigação em Química, University of Porto (CIQUP) through the project Pest-C/QUI/UI0081/2013 and the SAM project Norte-01-0145-FEDER-000028. Inês C. M. Vaz acknowledges the financial support from Fundação para a Ciência e Tecnologia (FCT) for her PhD Research Grant PD/BD/114575/2016.

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P15

TYPE-FENTON BIMETALLIC CATALYSTS FOR DEGRADATION OF DYES IN AQUEOS SOLUTIONS

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Dyes are growing to be a problematic class of pollutants to the environment. The disposal of dyes in water resources has bad aesthetic and health effects, since most of them are carcinogenic and mutagenic [1,2]. It is important to remove them from the environment. Effective and economic treatment by advanced oxidation processes (AOPs) has been attracted great and continuous interest for the degradation of these pollutants [3]. The heterogeneous Fenton-like processes have been paid great attention for its low cost, high efficient and mild conditions among these AOPs processes (20-50°C and atmospheric pressure) [3,4]. Recently, several iron- and copper- based heterogeneous Fenton catalysts have been investigated to be efficient catalytic systems [4]. In this work, zeolite NaY was used as support for Fe, Cu and Mn for preparing type-Fenton catalysts. The type-Fenton catalysts, mono and bimetallic, were prepared by ion exchange method and the catalysts were tested in degradation of textile dyes in a batch reactor using H_2O_2 at different temperatures and atmospheric pressure. It was observed that iron type-Fenton catalysts are active for the degradation, but when the reaction is performed with bimetallic type-Fenton catalysts the degradation becomes faster.

ACKNOWLEDGEMENTS
This work has been developed under the scope of the projects: BioTecNorte (operation NORTE-01-0145-FEDER-000004), PTDC/AAGTEC/5269/2014, and Centre of Chemistry (UID/QUI/00686/2013 and UID/QUI/0686/2016).

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P16

ADSORPTION OF TEXTILES DYES BY MOROCCO CLAY

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The discharge of textile dyes into effluents is an environmental problem due their consequences for quality of water. These compounds are usually toxic to aquatic life and they have a negatively impact to the food chain, because they are carcinogenic and mutagenic [1-3]. In order to reduce their contamination in water, adsorbents based in porous materials are very attractive. Clays are low-cost materials with very good retention capacity of pollutants from water [1,4]. This study aims to study the potential of a natural clay from the Fez region (Morocco) as an inexpensive and readily adsorbent for removing textile dyes from effluents. For the characterization of the clay, several physicochemical methods have been applied: N_2 adsorption (BET surface), Scanning electron microscopy, Fourier Transform Infrared Spectroscopy (FTIR), pH_{pzc}, X-ray diffraction (XRD) and titration. The clay was tested for removing different textile dyes from aqueous solution at room temperature. The parameters as, the initial dye concentration, the contact time, the adsorbent dose and the pH of the solution, were carried out in a batch system for the verification of optimal operating conditions. The data indicated that the adsorption process is fast and spontaneous reaction that proceeds kinetically according to a pseudo-second-order model. The clay adsorption capacity for the textile dyes was verified by adsorption isotherms and the experimental data are adapted to Langmuir and Freundlich models. The results suggest that the natural clay from the Fez region (Morocco) could be employed as a low-cost material for the removal of textile dyes from aqueous solutions.

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P17

DIFLUNISAL CO-CRYSTALS: AN OPPORTUNITY TO DEVELOP IMPROVED FORMULATIONS OF EXISTING DRUGS

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For a pharmaceutical company it is crucial to adopt a research and development strategy aiming at both the design of successful drugs and the resolution of bioavailability issues. Along with the extensive testing of new active pharmaceutical ingredients, APIs, the development of improved formulations of existing drugs plays a fundamental role [1]. Crystal engineering of pharmaceutical solids, co-crystallization included, is a promising approach in this context [1]. Our research group has been investigating co-crystals of diflunisal, a nonsteroidal anti-inflammatory drug, class II of the Biopharmaceutical Classification System, with potential to be incorporated in new pharmaceutical formulations, with improved diflunisal oral bioavailability [2].

In this work, results are presented of the investigation of co-crystal formation between diflunisal and two pharmaceutically acceptable co-formers, Fig.1: *L*-proline, an essential amino acid for collagen synthesis, and isoniazid, an antibiotic used for the treatment of tuberculosis. Co-crystal screening was carried out by mechanochemistry and crystallization from solutions. The solid outcomes were investigated by differential scanning calorimetry, polarized light thermomicroscopy, infrared spectroscopy, single-crystal X-ray diffraction and powder X-ray diffraction.

Two new co-crystals were discovered: diflunisal : *L*-proline (1:1), with potential utility as anti-inflammatory API and in amino acid supplementation; diflunisal-isoniazid co-crystal (1:1), a potential dual therapeutic co-crystal, with tuberculostatic and anti-inflammatory activity. It should be noted that one of the side effects in the treatment of tuberculosis is the development of joint pain.

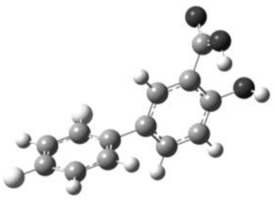	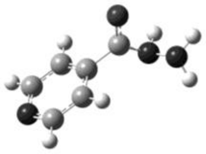	
Diflunisal: 2′,4′-Difluoro-4-hydroxy-[1,1′-biphenyl]-3-carboxylic acid	Isoniazid: 4-Pyridinecarboxylic acid hydrazide	*L*-proline: (*S*)-Pyrrolidine-2-carboxylic acid

Figure 1: Molecular structures of diflunisal and two pharmaceutically acceptable co-formers, isoniazid and *L*-proline.

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P18

MICRORHEOLOGY OF NOVEL CELLULOSE STABILIZED OIL-IN-WATER EMULSIONS

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Diffusion wave spectroscopy (DWS) is a powerful optical technique suitable to investigate turbid samples in a nondestructive and reproducible way, providing information on the static and dynamic properties of the system. This includes the relative displacement of emulsion droplets over time and changes in the viscoelastic properties (Figure 1). Here, novel and promising cellulose-based oil-in-water (O/W) emulsions were prepared and studied, for the first time, by DWS. Cellulose plays the role of a novel eco-friendly emulsifying agent. The hydrolysis time of cellulose was observed to affect the average size of the emulsion droplets and their stability; the longer the hydrolysis time, the more dispersed and stable the emulsions were found to be. Additionally, a good complementarity between the microrheology (DWS) and macrorheology (mechanical rheometer) data was found. Our work suggests that DWS is a highly attractive method to investigate the stability, aging and microrheology properties of cellulose-based emulsions, providing valuable insights on their microstructure. This technique is thus highly appealing for the characterization and design of novel emulsion formulations.

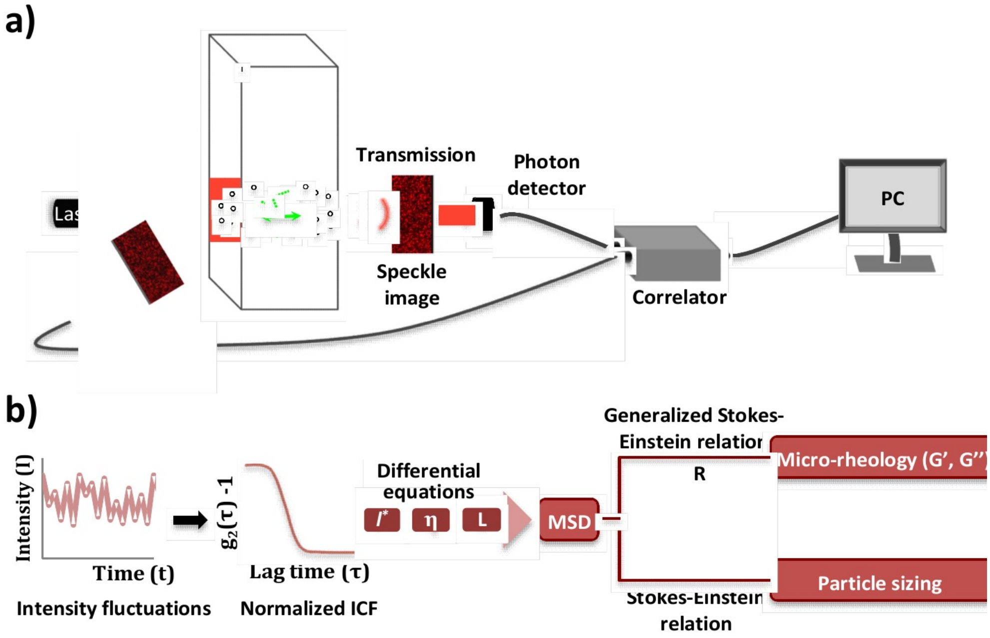

Figure 1: Schematic representation of a DWS setup (a) and the principles of DWS-based microrheology and particle sizing (b).

P18

PYRROLE-2-CARBOXYLIC ACID: A CONFORMATIONAL SWITCH

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The two most stable conformers (**I** and **II**) of pyrrole-2-carboxylic acid (PCA) were trapped in N_2 cryogenic matrix (Figure 1). The two forms differ from each other by a 180º rotation of the carboxylic group relatively to the ring. In respect to the OH group orientation, both forms adopted a cis form, with the dihedral (O=C−O−H) angle equal to 0º, as it is in general the case for small carboxylic acids[1,2]. A new, higher energy conformer of PCA (**III**) was produced, *in situ*, by narrowband near-infrared excitation of the $2\nu_{OH(I)}$ overtone (6953 cm^{-1}) of form **I** (Figure 1). The new form (**III**) differs from the most stable one by a 180º rotation of the OH group around the C−O bond. Form **III** could be reversibly transformed back into form **I**. This reverse transformation was induced by narrowband NIR irradiation at $\lambda = 2\nu_{OH(III)} = 6956$ cm^{-1}. The compound was also irradiated with UV light (λ= 270 nm), yielding photodecomposition to pyrrole and carbon dioxide molecules. Quantum chemistry calculations were used to support the interpretation of experimental data, with the jobs being carried out at the MP2/aug-cc-pVDZ and B3LYP/aug-cc-pVDZ levels of theory.

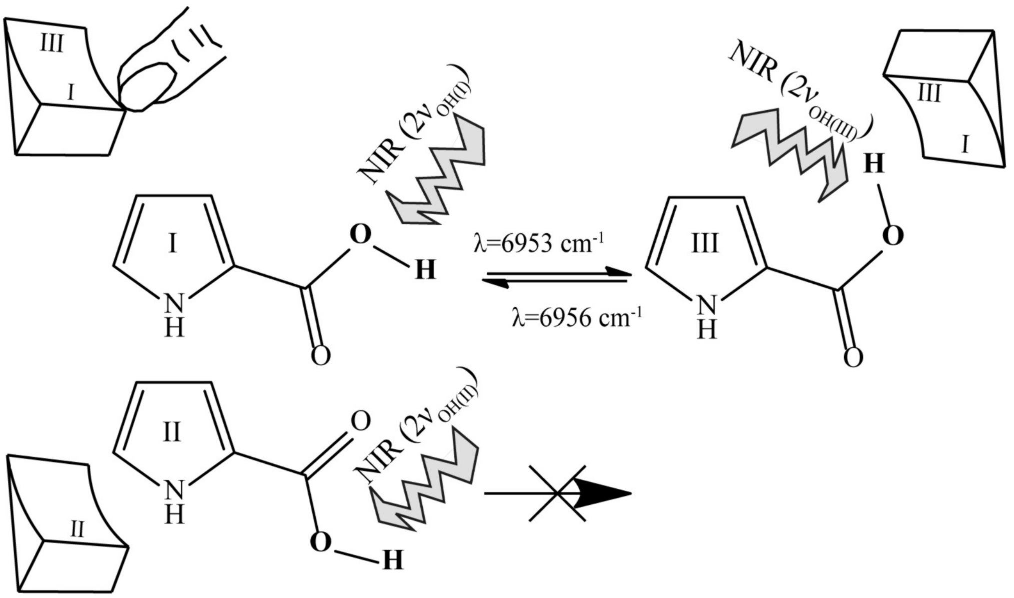

Figure 1: Conformational interconversions of matrix-isolated PCA induced by narrowband tunable near-infrared irradiations.

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P20

DFT STUDY OF ADSORPTION OF ANTIBIOTIC SULFAMETHOXAZOLE BY VERMICULITE

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Contamination of water resources with pharmaceuticals has been one of the top concerns of environmental sciences in the latest years [1, 2]. Antibiotics in particular have been gathering considerable attention and are amongst the most serious worries due to the development of antibiotic resistant bacteria as result of prolonged exposure [2, 3]. Sulfamethoxazole (SMX), a broad-spectrum biostatic sulfanilamide, is among the most worrisome which has led it to be included in some priority pollutants lists [1, 4]. Taking into account the widespread use of sulfonamides and their potential environmental effects, it is important to develop new technologies for removing SMX and similar compounds from points of wastewater discharge. In fact, most conventional wastewater treatment plants are inefficient for the removal of most organic micro-pollutants such as SMX as they were only designed for removing bulk pollutants. Several advanced technologies have been evaluated as options to treat these contaminants, e.g. advanced oxidative processes or membrane filtration, but despite the sometimes high removal efficiencies attained, these technologies are usually too expensive to be considered as viable solutions on a large scale. Adsorption, alone or as part of a more complex water or wastewater treatment process, has been seen as an affordable solution for the removal of many organic micro-pollutants [5], but finding efficient and inexpensive adsorbents is crucial for the success of this alternative. In this work we present a theoretical study on the adsorption properties of a clay material, vermiculite, which has been assessed, in lab studies, to be highly efficient in the adsorption of SMX from water. Therefore, in order to gain a deeper insight into the characteristics that favor the removal of this antibiotic by vermiculite, quantum chemical theoretical calculations were performed using DFT methods on a periodic slab model of the vermiculite surface.

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P21

ASSESSING THE AFFINITY BETWEEN POLYMERS AND PESTICIDES BY MOLECULAR DYNAMICS SIMULATIONS

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The use of pesticides in agriculture is known to have environmental impacts, namely it contributes to the contamination of soils and water. Because of this, the endeavor towards the sustainability of farmer production requires novel strategies to capture pesticides from water and soils.

In this work, we have carried out molecular dynamics simulations to assess the affinity of pesticides to three types of polymers; the GROMACS program [1] has been employed in all MD calculations. We studied three types of polymers (polypropylene, polyacrylic acid and chitosan), while four phytopharmaceuticals (cymoxanil, glufosinate-amonium, imidacloprid and mancozeb) were employed as pesticides. Polymer chains of 3, 5 and 7 monomers have been selected for polypropylene and polyacrylic acid (and 3 monomers for chitosan). In the case of polyacrylic acid and chitosan, we have considered both protonated and deprotonated species. The structure of the polymers and phytopharmaceuticals are shown in Figure 1.

The main results from the present work show that chitosan (both protonated and deprotonated) is the polymer that establishes the strongest interactions with the pesticides. Such interactions are mainly due to the formation of hydrogen bonds. In turn, protonated polyacrylic acid can also establish hydrogen bonds with cymoxanil, glufosinate-amonium and imidacloprid, but it is not effective for mancozeb. In addition, deprotonated polyacrylic acid is totally non-effective in establishing interactions with all pesticides. Although not forming hydrogen bonds, polypropylene is able to attract the cymoxanil and the imidacloroprid pesticides. For both, polypropylene and protonated polyacrylic acid, the interactions tend to be stronger as the polymer chain increases.

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P22

Unraveling the dynamic interplay between the local structure and properties of layered double hydroxides by computer simulation

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Layered double hydroxides (LDHs) are a class of so-called smart materials. They can store functional molecules under the anionic form in the interlayer, compensating the positive charge of the mixed metal hydroxide layers. After an external trigger associated with the presence of other anionic species in solution, the more labile intercalated molecules can be released to the surroundings, while the species that triggered the release are retrieved in the LDH structure.

This mechanism allows LDHs to entrap desired species in the anionic form and to respond to different electrolyte conditions, such as concentration and pH (Figure 1). Depending on the application, they can also make available intercalated molecules in solution to subsequently perform their function. As a result, these materials have found an important role in drug delivery, catalysis, water purification and, in particular, corrosion protection.

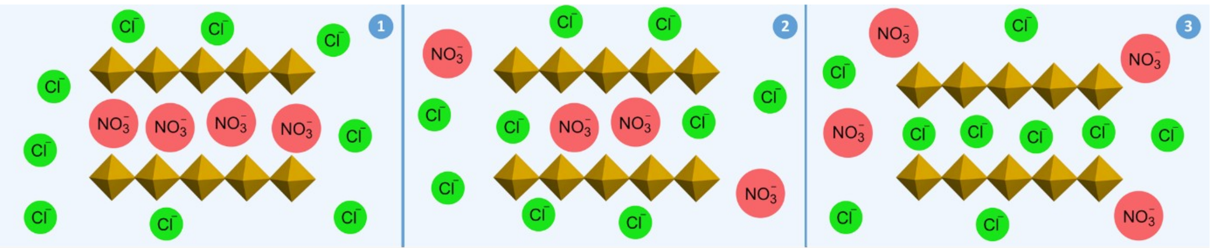

Figure 1: Scheme with the release of nitrate and intercalation of chloride in the LDH interlayer structure. Green/red circles and yellow polyhedra represent, chloride/nitrate anions and the LDH metal hydroxide layers, respectively.

We will present results from electronic density functional theory (DFT) and classical molecular dynamics (MD) simulations used to obtain molecular insights into the arrangement, energetics and dynamics of the anions in the interlayer.

ACKNOWLEDGMENTS
This work was financed by PTDC/QEQ-QFI/4719/2014 [Project 3599 - Promover a Produção Científica e Desenvolvimento Tecnológico e a Constituição de Redes Temáticas (3599-PPCDT) and FEDER funds through COMPETE 2020, Programa Operacional Competitividade e Internacionalização (POCI)] and European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 645662. JT and JRBG are also thankful to FCT for Program IF.

P23

APPLICATION OF EVOLUTIONARY ALGORITHMS TO SOLVE DIFFICULT PROBLEMS IN PHYSICAL CHEMISTRY: GEOMETRY OPTIMIZATION AND FITTING

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Evolutionary algorithms (EAs) are state-of-the-art methods, especially devoted to solve difficult optimization problems. The EAs fall in the class of bio-inspired algorithms, in the sense they employ principles usually associated to the evolution of living beings. Thus, each individual that belongs to the possible set of solutions of a given problem (i.e., the population) may be subjected to crossover and mutation (i.e., the genetic operators). In particular, the EAs developed by our group [1-3] follow a steady-state strategy, where the number of individuals is kept constant during the optimization process and, in each generation, new solutions resulting from the application of genetic operators have to compete with their "parents" to enter in the population. The whole process is repeated for several generations, which leads, in principle, to an effective exploration of the searching space.

In this poster, we overview the main applications of EAs carried out in our group for more than 10 years. Special attention is given to data fitting [3-5] and cluster geometry optimization [1, 6-12]. Concerning the former, we have developed the user-friendly GAFit program [5] (available from https://apps.uc.pt/mypage/faculty/qtmarque/en/software), which has shown to be very useful for fitting potential energy surfaces [4]. In turn, we have developed two codes with EAs for the optimization of structures of either atomic or molecular clusters that were successful in their application to several systems, including microsolvation of ions [7, 8, 11], colloids [9, 10] and materials [12].

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P24

DFT MECHANISTIC STUDIES OF YTTRIUM CATALYZED INTRAMOLECULAR HYDROAMINATION OF AMINOALKENES

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Hydroamination reaction is the addition of N-H bonds across C-C multiple bonds, being an atom economical method for the efficient formation of N-C bonds. Intramolecular hydroamination of aminoalkenes has been studied with lanthanide and early transition metal catalysts [1]. The catalytic activity of cyclam based Zr complexes have been previously reported by us [2]. In this communication we present the most recent studies on cyclam based Y complexes.

Li[Y($^{3,5\text{-tBu2}}$Bn$_2$Cyclam](THF) is a highly active catalyst for the intramolecular hydroamination of 2,2-diphenyl-pent-4-enylamine, forming 2-methyl-4,4-diphenylpyrrolidine, therefore the mechanism of the catalytic cycle was studied by DFT methods using a simplified model, as depicted in Figure 1, proceeding *via* intramolecular cyclization assisted by protonation/deprotonation of the benzyl sidearms on the cyclam. Calculations were preformed using PBE0/SDD,6-311++G**//PBE0/SDD,6-21G** as model chemistry.

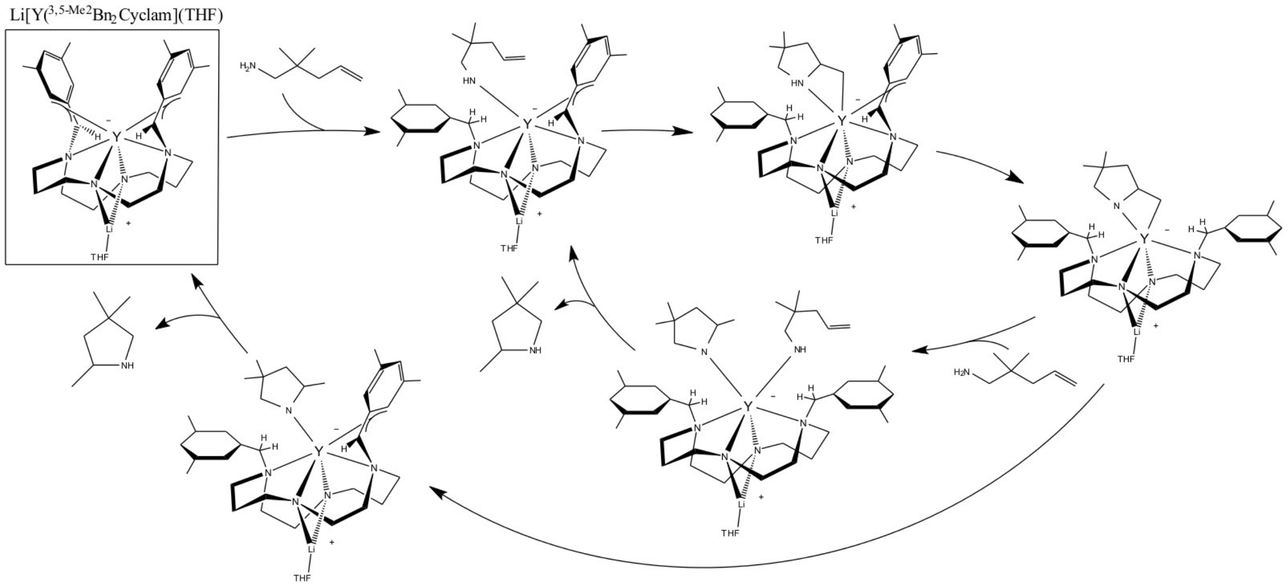

Figure 1

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P25

SIMULATION OF HYDROGEN COMBUSTION CONFINED WITHIN CARBON NANOTUBES

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The present project aims to study the effect of carbon nanotubes(CNT) in the combustion of molecular hydrogen. The confinement of reagents in nanoscale media has been subject of recent experimental[1] and theoretical[2] studies. The confinement of molecules in CNTs has shown to have considerable effect on increasing their reactivity at low temperatures. This was justified by orientation effects of the confined reactants and to the increase of the collision probability due to reflection on the nanotube walls. The stabilization of the HO2 radical by wall collision is an important effect to study in this process being a chain termination step that prevents the explosion of the mixture. Recently, we have developed an innovative method to model complex systems[3]. The MReaDy program, builds a global Potential Energy Surface (gPES), defined by integrating diverse PESs, each one of them representing an elementary reaction that is expected to play a role in the chemical process. The program MReaDy, which has shown to accurately model the gas phase combustion of a mixture of hydrogen and oxygen, will be adapted to study the same reaction confined in a CNT at different conditions of nanotube diameter, gas pressure and temperature. To accomplish this, we will introduce in MReady a full potential for the CNT, including carbon-carbon vibrations and intermolecular forces between the carbon atoms and the reactant molecules. Studing the dynamics, this project aims to study and optimize the conditions for the hydrogen combustion at low temperatures, without flame formation, being the energy released in this process collected as vibration energy of the carbon nanotubes and kinetic energy of the products.

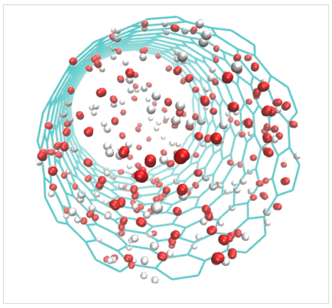

Figure 1: The project aims to study Hydrogen combustion constrained by CNTs.

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P26

VOLUME AND SUBSTITUENT EFFECTS IN MOLECULAR RECOGNITION: A STEP FORWARD IN MODULATING SOFT SUPRAMOLECULAR NANOSTRUCTURES BY FREE ENERGY CALCULATIONS

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Host-guest interactions have been extensively explored for developing supramolecular smart materials to improve solubilization, transportation and targeting of therapeutic agents. A fundamental aspect to be understood is the precise manner in which the guest molecule binds to its host. This includes the effect of the available volume in the host cavity, the nature and size of the guest substituents, the role of solvation, and rationales for the conformational and thermodynamic characterization, both experimentally accessible. Within the latter, free energy calculations provide the most direct connection between experimental and computational investigation.[2] Robust and accurate Molecular Dynamics (MD) based methods, including a novel automated umbrella-sampling procedure[2] and the "flexible molecule" approximation for the calculation of binding constants, allow providing new information that are contrasted to collected experimental observations. Accurate predictions are now available from MD, including the effect of varying the guest substituents and the cavity volume, with direct transposition for the modulation of properties in supramolecular structures based on these complexes. The estimated stability of inclusion complexes between beta- and gamma-cyclodextrins and the model guests, is highly affected by the fit and orientation of the guest into the cavity, the size and nature of the guest moieties and by dessolvation effects. As best models, the interactions among beta- and gamma-cyclodextrins and naphthalene and adamantane derivatives, and also epoxide-containging guests, are selected. The association constants of beta-CD-based complexes are continuously increasing as the size of the guest increases, while those of gamma-CD show higher stability with decreasing degree of substitution. The pattern of substitution has a significant effect on the strength of the interactions: the substitution on the basic guest structure alters the type of the interactions, and a series of different findings prove that this change is the basis in the stability of different cyclodextrin-based complexes.

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H2O2 (A,3A) POTENTIAL ENERGY SURFACE

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The reactions of an oxygen atom in its ground (3P) and first excited (1D) states, resulting from the incidence of solar radiation on stratospheric ozone (Hartley band), with a water molecule play an important role on the modelling of atmospheric chemistry and ozone depletion cycle [1].
These reactions and their reverse reactions, the reaction between two hydroxyl radicals, are relevant for the chemistry of combustion processes [2]. The triplet state of H2O2 assumes special relevance on the studies the combustion reactions of O2 and H2. In this work, we describe a new potential energy surface (PES) for the first excited triplet state of the hydrogen peroxide, H2O2 (a,3A). This new H2O2 PES aim to accurately reproduce all the different dissociation channels in accordance to the Wigner-Witmer rules, namely, O(3P) + H2O, OH + OH, O2 (3Π) + H2 and H + HO2. We have computed a large amount of ab initio energies using the MOLPRO 2009.1 set of programs [4].
The open-shell coupled cluster theories (RCCSD) was used with perturbative triples corrections (RCCSD(T)) as defined by R. J. Bartlett et al. [5]. In our calculations, the geometry is optimized using aug-cc-pVXZ (X=T,Q) basis sets and extrapolated to basis set limit using results from five zeta basis set (aug-cc-pV5Z) with RCCSD-F12 level calculation. They also account for the electrostatic dipole-dipole interaction between two OH (2Π) fragments.
Using the PES for the different reaction fragments, the H2O PES [6] and the HO2 PES[7], and the ab initio points computed extrapolated to basis set limit, we are able to build a PES for the lowest triplet state of H2O2. We present the characterization of transition structures on the H2O2 lowest triplet state.

Dynamical studies of the O(3P)+H2O and OH(2Π)+OH(2Π) reactions on this new PES are the next step of this work.

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LONG RANGE THEORETICAL STUDY

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The lithium chemistry has received a great attention in recent years due to the importance that LiH molecules and its ionic variants can have in the primordial universe[1,2]. The reaction LiH + H → Li + H_2 is considered to contribute to LiH depletion, while the hydrogen-exchange reaction LiH + H → LiH + H leads to the retention of LiH in this process.

In this work we report our recent studies on the long-range interactions between the reactants of those reactions. For the LiHH system, the main contribution for the long-range interactions is the dispersion interaction. To modeling the dispersion interaction, the parallel and perpendicular values of the polarizabilities, α, for the diatomics (H-H and Li-H) have been calculated and fitted (see figure 1).

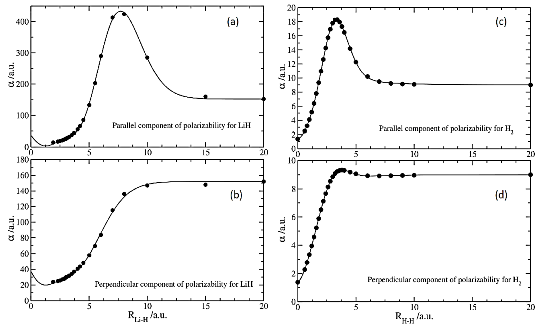

Figure 1: Parallel and perpendicular components of polarizabilities, α, for LiH ((a) and (b)) and H2 ((c) and (d)). Solid lines are the functional form fit to the ab initio calculations (solid dots).

The dispersion interaction coefficients C_6 have been computed as C_8 and C_{10} have been semiempirically estimated from C_6 using a universal correlation. The total dispersion interaction was obtained as a function of C_n and inter-atomic distances[3]. The dynamical correlation energy has been obtained for the interaction H-LiH and Li-HH (see figure 2).

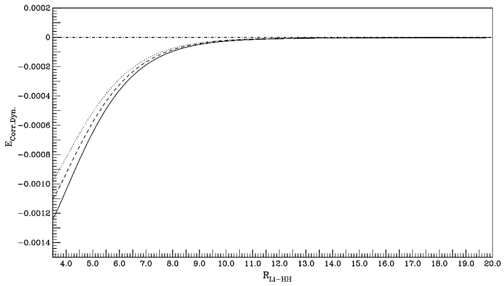

Figure 2: Total dynamical correlation energy for the interaction Li-HH at 0º, 45º and 90º.

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CHEMISTRY EVOLUTION IN INTERSTELLAR SPACE

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The chemistry of the interstellar space is very rich and poorly understood. A large variety of chemical compounds has been observed in star and planet forming regions. They have also been detected in comets and meteorites as a reminiscence of our Solar System formation. The study of their formation in rude environments, where UV and X-ray photons irradiate cold dilute gases and ice-coated dust grains and radicals are profusely produced, need the development of new theoretical approaches.

With this work we intend to develop a new method to obtain trustful data on the chemistry of the interstellar space. A recent and innovative method to model complex systems [1] will be modified and applied to study the evolution of this dilute molecular system, where intermolecular collisions are scarce and thermal equilibrium is not reached. In such conditions, where a product of one reaction reaches another reactant before achieving thermal equilibrium by non-reactive collisions, the use of thermal rate constants for the elementary reactions involved is meaningless.

This work is integrated in the European Cooperation in Science and Technology actions: Our Astro-Chemical History, COST CM1401, and Molecules in Motion (MOLIM), COST CM1405.

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Apontamentos