1-3 July 2015 COIMBRA PORTUGAL

XXIV ENCONTRO NACIONAL da Sociedade Portuguesa de Química

LIVRO DE RESUMOS
BOOK OF ABSTRACTS

SOCIEDADE PORTUGUESA DE QUÍMICA

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Caros Conferencistas, Colegas e Amigos,

A Sociedade Portuguesa de Química (SPQ) e a sua Delegação de Coimbra, em colaboração com a Universidade de Coimbra, têm o prazer de convidá-los a participar no XXIV Encontro Nacional da Sociedade de Portuguesa de Química (XXIV ENSPQ). Este Encontro pretende ser uma oportunidade única para os investigadores e professores de química, com interesses pluridisciplinares, poderem apresentar as suas mais recentes descobertas, inovações e formas alternativas de "*pensar sobre a química*" como um rumo ao desenvolvimento de uma sociedade mais sustentável.

Incentivando a participação de cientistas com interesses nas diversas áreas da química, pretendemos estabelecer uma plataforma entre jovens cientistas, investigadores, professores e industriais, que fortaleça a troca de ideias e o estabelecimento de novas colaborações, promover o desenvolvimento de áreas com forte impacto na construção de uma sociedade mais sustentável. Salientamos a química como ciência central no âmbito das energias alternativas, novos materiais, novos processos para remediação ambiental e desenvolvimento de fármacos envolvendo processos de síntese baseados nos princípios da “química verde”.

O Encontro, cujo tema principal é "Química para um Desenvolvimento Sustentável", inclui Lições Plenárias (PL) apresentadas por cientistas nacionais e internacionais de mérito reconhecido, Comunicações Convidadas (IL), Comunicações Orais (OC) e Comunicações em Poster (P). Para repensar o futuro da química nas Escolas e na Sociedade, terá lugar um debate entre orgãos oficiais, directores dos Departamentos de Química do País, representantes da indústria química nacional e professores do ensino secundário. Ocorrerão ainda em paralelo cursos temáticos e uma apresentação feita pela Comissão de Coordenação e Desenvolvimento Regional do Centro (CCDRC) acerca de programas de financiamento para a investigação nos próximos cinco anos. Destacamos ainda a realização do VI DEDQ, com sessões dedicadas aos professores de química do ensino básico e secundário, ação creditada com 0,6 créditos (15h) mediante processo de validação de assiduidade e avaliação, e acreditada pelo Conselho Científico-Pedagógico da Formação Contínua.

A Organização do XXIV ENSPQ pretende ir para além da química, proporcionando a todos os participantes a possibilidade de assistir ao “Tempo de Encontro(s)”, dedicado à cultura e história da emblemática cidade de Coimbra e da sua Universidade – Património Unesco da Humanidade desde 2013. Convidamo-los a todos a integrar as comemorações do 725º Aniversário da Universidade de Coimbra, assistindo ao espetáculo de multimédia **Videomapping “725 anos UC”**.

É, para nós, um prazer recebê-los em Coimbra e desejar-lhes uma participação ativa e estimulante.

Em nome da Comissão Organizadora do XXIV ENSPQ

Mariette Pereira e Marta Piñeiro

Dear Attendants, Colleagues and Friends,

The Portuguese Society of Chemistry (SPQ) and its Coimbra Delegation are delighted to invite all of you to participate in the XXIV National Meeting of the Portuguese Society of Chemistry (XXIV ENSPQ). This meeting intends to provide a unique opportunity for chemists with multidisciplinary interests to show their findings and innovations on alternative ways of “*thinking about chemistry*” toward the development of a more sustainable society.

By encouraging the participation of scientific researchers working in all chemistry areas, we intend to provide a platform for young scientists, chemical engineers, universities and industrial researchers to exchange their ideas, to establish new collaborations and to support the improvement of emerging areas. We intend to highlight the role of Chemistry as a central science for the improvement of new processes for environment remediation, alternative energies, new materials and development of drugs using chemical processes based on the main principles of “green chemistry”.

The Meeting, whose main theme is “*Chemistry for a Sustainable Development*”, will include Plenary Lectures (PL) presented by recognized national and international scientists, Invited Lectures (IL), Oral communications (OC) and Poster communications (P). To rethink the future of chemistry in schools and society, there will be a debate between official entities, directors of the chemical departments of Portuguese Universities, representatives of the national chemical industry and secondary school teachers. Other thematic courses will also occur and a presentation by Coordination and Regional Development Commission (CCDRC) about funding programs for research over the next five years. We highlight the realization of the VI DEDQ with sessions devoted to the chemistry of basic and secondary school teachers, action credited with 0.6 credits (15h) by means of attendance and assessment validation process, and accredited by the Scientific and Pedagogical Council of Continuous Training.

The Organization of the XXIV ENSPQ plan to go beyond chemistry, providing all participants the opportunity to attend "Tempo de Encontro(s)", dedicated to the culture and history of the emblematic city of Coimbra and its University - UNESCO World Heritage since 2013, and we invite you to join the celebrations of the 725º anniversary of the Coimbra University, watching the multimedia show **Videomapping "725 years UC "**.

We are pleased to welcome you to Coimbra and wish you an active and stimulating participation.

On behalf of the XXIV ENSPQ Organizing Committee

Mariette Pereira and Marta Piñeiro

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LOCAL DO ENCONTRO

A Universidade de Coimbra (UC) foi fundada em 1290, um século após a fundação de Portugal, estando entre as Universidades mais antigas do Mundo.

A UC é uma referência indiscutível do ensino superior e da investigação em Portugal, devido à formação académica de elevada qualidade fornecida pelas suas oito faculdades, e também devido aos avanços alcançados pela investigação pura e aplicada em diversas áreas do conhecimento.

O prestígio da UC é hoje demonstrado pela posição que ocupa no ranking internacional de universidades e centros de pesquisa. Esta Universidade é, não só um verdadeiro ícone da cultura Portuguesa no mundo, como seguidora de uma política de melhoria constante em vários campos, que lhe permitem afirmar a alta qualidade da pesquisa e do ensino, bem como o desempenho de um papel ativo no desenvolvimento da indústria em Portugal, e em atividades envolvendo um conhecimento intensivo, em parceria com diversas organizações multinacionais e internacionais pioneiras.

Com os seus edifícios monumentais e históricos (património mundial da UNESCO desde 2013), a Universidade de Coimbra atrai visitantes de todo o mundo, tornando a cidade um importante destino turístico. Entre os locais mais visitados, encontram-se o Pátio das Escolas, a Biblioteca Joanina (biblioteca de estilo barroco construída entre 1717 e 1728, contendo livros dos séculos XVI a XVIII), a Sala dos Capelos, a Capela da Universidade e o Jardim Botânico, que convidamos a visitar.

As tradicionais celebrações académicas são adotadas pela cidade como suas: a "Latada" (ou receção ao caloiro) no início do ano letivo, e a "Queima das Fitas" em Maio, são parte das comemorações de Coimbra, que trazem milhares de visitantes em cada ano. Finalmente, o Fado de Coimbra é também um símbolo cultural inegável da cidade. Este Fado, estreitamente ligado às tradições académicas da Universidade, é uma canção melancólica cantada por antigos e atuais alunos, envergando o traje académico, e acompanhados pela viola portuguesa.

A comissão organizadora agradece a colaboração da Reitoria da UC na realização deste Encontro. Esperamos que a hospitalidade oferecida pela nossa Universidade faça a vossa estadia em Coimbra uma experiência especialmente agradáve

MEETING VENUE

The University of Coimbra (UC) is among the world's oldest Universities, having been founded in 1290, one century after the foundation of Portugal.

The UC is an indisputable reference in higher education and research in Portugal, due to high quality academic training provided by its eight Faculties and to the advances achieved in pure and applied research in various areas of knowledge.

The prestige of UC is nowadays demonstrated by the position it holds in the international rankings of universities and research centres. This University is not only a true icon of Portuguese culture in the world, but it also pursues a policy of constant improvement in various fields, which allow it to assert the high quality of research and teaching, as well as playing an active role in the development of business and industry, and in activities involving intensive knowledge in Portugal, in connection with pioneer multinational and international organisations.

With its monumental buildings and history (UNESCO world's heritage), the University of Coimbra attracts visitors from around the world, making the city an important touristic destination. Among the most visited places, are *Pátio das Escolas* (The Schools' Courtyard). *Biblioteca Joanina* (Joanine Library, a baroque-style library built between 1717 and 1728, housing books from the 16th to the 18th centuries), *Sala dos Capelos* (The Grand Hall), the University Chapel and the Botanical Garden.

The traditional students' celebrations are adopted by the city as their own: the "*Latada*" (or *freshman* reception) in the beginning of the academic year and the "*Queima das Fitas*" in May, are part of Coimbra celebrations, which bring thousands of visitors every year. Finally, the Fado of Coimbra (Portuguese traditional song) is also an undeniable cultural symbol of the city. This Fado, closely linked to the academic traditions of the University, is a melancholic song performed by present and former students, wearing the academic outfit and accompanied with the Portuguese classical guitar.

XXIV SPQ 2015

Wednesday, 1st July			Thursday, 2nd July			Friday, 3rd July		
HOUR	SESSION	ROOM	HOUR	SESSION	ROOM	HOUR	SESSION	ROOM
			09:00	Plenary Lecture	Main (**PL2**)	09:00	Plenary Lecture	Main (**PL3**)
			09:15			09:15		
			09:30			09:30		
			09:45			09:45		
			10:00	Invited Lecture	Main (**IL4**)	10:00	Invited Lectures	Main (**CCDRC pres.**)
			10:15			10:15		
			10:30	Coffee Break/ Posters		10:30		Main (**IL10**)
			10:45			10:45		
			11:00	Invited Lectures and Oral Comms	Main (**O16-O19, IL5**) (**CAS pres.**)	11:00	Coffee Break	
			11:15			11:15	Oral Comms	Main (**O30-O32**)
			11:30		Chem (**QLabo pres.**) (**IL8, O23-O25**)	11:30		Chem (**O37-O42**)
			11:45			11:45		
12:00	Registration and Opening Session	Main	12:00		Phys (**IL9, O26-O29**)	12:00	Invited Lecture Main **Prémio Vicente de Seabra** (**IL11**)	
12:15			12:15			12:15		
12:30			12:30	LUNCH		12:30	LUNCH	
12:45			12:45			12:45		
13:00			13:00			13:00		
13:15			13:15			13:15		
13:30			13:30			13:30		
13:45			13:45			13:45		
14:00			14:00			14:00		
14:15			14:15			14:15		
14:30	Plenary Lecture Main (**Prémio Ferreira da Silva**) (**PL1**)		14:30	**Discussion** “Is Chemistry sustainable in Portugal?”	Main	14:30	Plenary Lecture	Main (**PL4**)
14:45			14:45			14:45		
15:00			15:00			15:00		
15:15			15:15			15:15		
15:30	Coffee Break/ Posters		15:30			15:30	Coffee Break	
15:45			15:45	Coffee Break/ Posters		15:45	Invited Lectures and Oral Comms	Main (**IL12, O33*-O36**)
16:00	Oral Comms	Main (**IL1, O1-O5**)	16:00			16:00		
16:15			16:15	Invited Lectures	Main (**IL6, IL7**)	16:15		Chem (**O43-O48**)
16:30			16:30			16:30		
16:45		Chem (**IL2, O6-O10**)	16:45			16:45		Phys (**IL13, O49-O52**)
17:00			17:00			17:00		
17:15		Phys (**IL3, O11-O15**)	17:15	Oral Comms	Main (**O20-O22**)	17:15	Closing Ceremony	Main
17:30			17:30			17:30		
17:45	Social Event		17:45			17:45		
20:00	Welcome Reception		20:00	Meeting Dinner		18:00		

Main – Main Auditorium; **Chem** – Chemistry Auditorium; **Phys** – Physics Auditorium

***3 Julho**-15h45 **ENEQUI** prize presentation Main auditorium

2 Julho-11h **QLabo** presentation Chem auditorium

2 Julho-12h **CAS SciFinder** presentation Main auditorium

3 Julho-10h “Sustentabilidade na UC” **Helena Freitas (Vice-Reitora UC); CCDRC (Jorge Brandão)** “PT2020” Main auditorium

Divisão de Ensino e Divulgação da Química – SPQ – VI DEDQ

Quarta-feira, 1 Julho			Quinta-feira, 2 Julho			Sexta-feira, 3 Julho		
HOUR	SESSION	ROOM	HOUR	SESSION	ROOM	HOUR	SESSION	ROOM
			09:00	Lição Convidada	C13-Chem (**IL14**)	09:00	Lição Convidada **A V Olimpíadas**	C13-Chem
			09:15			09:15		
			09:30			09:30		
			09:45			09:45		
			10:00	**PechaKucha**		10:00	Comunicações Orais	C13-Chem (**O56-O59**)
			10:15			10:15		
			10:30	Café e Posters		10:30		
			10:45			10:45		
			11:00	**Workshop** “Química (mais) verde nas escolas”	Lab Chem	11:00	Café	
			11:15			11:15	**Workshop** “Integração simbiótica da química laboratorial”	Lab Chem
			11:30			11:30		
			11:45			11:45		
12:00	Registo e Sessão de Abertura	Main	12:00			12:00		
12:15			12:15			12:15		
12:30			12:30	ALMOÇO		12:30		
12:45			12:45			12:45		
13:00			13:00			13:00	ALMOÇO	
13:15			13:15			13:15		
13:30			13:30			13:30		
13:45			13:45			13:45		
14:00			14:00			14:00		
14:15			14:15			14:15		
14:30	Plenary Lecture Main (**Prémio Ferreira da Silva**) (**PL1**)		14:30	**Debate** “É a Química sustentável em Portugal?”	Main	14:30	Lição Plenária	Main (**PL4**)
14:45			14:45			14:45		
15:00			15:00			15:00		
15:15			15:15			15:15		
15:30	Café e Posters		15:30			15:30	Café	
15:45			15:45	Café e Posters		15:45	Feira da Ciência	2Andar Chem
16:00	**Debate** “Ensino da Química e da Física”	C13-Chem	16:00			16:00		
16:15			16:15	Lição Convidada	Main (**IL6**)	16:15		
16:30	**Workshop** “Química e Música”		16:30			16:30	**Debate** “Física e Química: diálogos (im)possíveis”	C13-Chem
16:45			16:45	Lição Convidada	C13-Chem (**IL15, O53-O55**)	16:45		
17:00			17:00			17:00		
17:15			17:15	Comunicações Orais		17:15	Encerramento	Main
17:30			17:30			17:30		
17:45	Social event		17:45			17:45		
18:00	Receção de Boas Vindas		18:00	Jantar do Congresso		18:00		

Main – Auditório UC; **C13-Chem** – Dpto. Química

Comunicações Científicas/Scientific Contributions

(Clique no Título para obter o Resumo correspondente)
(Click on the Title for corresponding Abstract)

PLENARY LECTURES ABSTRACTS

LIÇÕES PLENÁRIAS (RESUMOS)

PL-01 MATERIAIS DE CARBONO EM CATÁLISE: O PAPEL DA QUÍMICA SUPERFICIAL

José Luís Figueiredo

Laboratório Associado LSRE-LCM, Faculdade de Engenharia, Universidade do Porto

A química superficial dos materiais de carbono é determinante para as suas aplicações, particularmente em catálise. Uma vez que estes materiais apresentam geralmente uma estrutura grafítica, os átomos de carbono insaturados nas extremidades das camadas grafénicas ou em defeitos dos planos basais podem reagir facilmente com oxigénio, água ou outros compostos, originando diferentes tipos de grupos funcionais.

A natureza e a concentração dos grupos funcionais na superfície dos materiais de carbono podem ser modificadas por meio de tratamentos químicos ou térmicos, ou durante a própria síntese do material. Podem incorporar-se grupos oxigenados por meio de agentes oxidantes, tanto em fase líquida como gasosa. Materiais com grupos azotados podem ser obtidos por carbonização de precursores contendo azoto, ou por meio de tratamentos subsequentes, enquanto a funcionalização com grupos ácido sulfónico se consegue geralmente por tratamento com ácido sulfúrico. Tratamentos térmicos controlados permitem afinar a química superficial, removendo selectivamente grupos indesejados, servindo também para preparar amostras com diferentes concentrações dos grupos pretendidos. A dessorção térmica programada (TPD) e a espectroscopia de fotoelectrões de raios-X (XPS) são os métodos mais adequados para a análise quantitativa dos grupos funcionais na superfície dos materiais de carbono.

Estes grupos podem ser usados para ancorar complexos metálicos (heterogeneização de catalisadores moleculares) ou precursores das fases activas (preparação de catalisadores suportados); alternativamente, podem funcionar como centros activos em catálise, ou podem servir para modificar (promover ou inibir) a actividade/selectividade do catalisador. Em particular, materiais de carbono isentos de fases metálicas têm vindo a demonstrar excelente desempenho como catalisadores, tanto em processos de oxidação/redução como em catálise ácido-base.

Serão apresentados exemplos relevantes, realçando o papel da química superficial em cada caso.

Serp P.; Figueiredo, J.L. (Ed.). *Carbon Materials for Catalysis*. John Wiley, Hoboken, NJ, **2009**.
Figueiredo, J.L.; Pereira MFR, *Catal. Today*, **2010**, *150*, 2-7.
Figueiredo, J.L. *J. Mater. Chem. A*, **2013**, *1*, 9351-9364.
Figueiredo JL, Pereira MFR, Freitas MMA, Órfão JJM, *Carbon*, **1999**; 37: 1379-1389.

PL-02 NON-NOBLE METAL CATALYSIS FOR MAKING PRECIOUS MOLECULES

Matthias Beller

Leibniz-Institut für Katalyse an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany
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Despite numerous important methodological advancements in all areas of chemistry, still most organic synthesis as well as the industrial production of chemicals can be improved. Currently, more than 80% of all products of the chemical industry are made via catalysis. In this regard, the development of new and more efficient catalysts constitutes a key factor for achieving a sustainable production of all kinds of chemicals today and in the future. Here, several major challenges will be presented in the talk; e.g. the selective reduction of amides to bio-relevant amines. Furthermore, it will be shown that recently developed molecular-defined as well as nano-structured cobalt and iron catalysts enable us to perform catalytic hydrogenation processes of esters and nitro derivatives with high yields and unprecedented selectivity. Specific examples which demonstrate the potential of catalytic processes with bio-relevant metal complexes compared to more traditional catalytic reactions will include apart from hydrogenations also dehydrogenations for the synthesis of heterocycles. In the future, also for industrial processes improved economics based on the presented novel catalysts might be expected.

[1]Das, S.; Wendt, B.; Möller, K.; Junge, K.; Beller, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 1662.
[2] Westerhaus, F.; Jagadeesh, R.; Wienhöfer, G.; Pohl, M.-M.; Radnik, J.; Surkus, A.-E.; Junge, K.; Junge, H.; Beller, M. *Nature Chem.* **2013**, *5*, 607-612.
[3] Nielsen, M.; Alberico, E.; Baumann, W.; Drexler, H.-J.; Junge, H.; Gladiali, S.; Beller, M. *Nature* **2013**, *494*, 85-89.
[4] Fleischer, S.; Zhou, S.; Junge, K.; Beller, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 5120-5124.
[5] Boddien, A.; Mellmann, D.; Gärtner, F.; Jackstell, R.; Junge, H.; Dyson, P. J.; Laurenczy, G.; Ludwig, R.; Beller, M. *Science* **2011**, *333*, 1733-1736.

PL-03 THE NANOTECHNOLOGY OF GOLD

Mathias Brust

University of Liverpool, UK

The overarching theme of this conference is “Chemistry for Sustainability”, and I believe that Nanotechnology is a reasonable activity in view of this goal, even though I am not an expert in Sustainability. In fact, I work with gold, which as an element is extremely rare and hence its sustainability is regulated chiefly by its price, which would make larger scale applications prohibitively expensive. While Nanotechnology can contribute to a more sustainable economy, for example, by developing new catalysts that save resources of raw materials, solvents, water, and energy, or, more pertinently, cost effective and robust systems to convert solar energy, it will not offer a unified grand solution to the problems we are facing, which are only in part scientific or technological. In order to gain an immediate understanding of the dimension of the sustainability problem, it is enough to compare the time scale needed by nature to create solar energy reserves in the form of fossil fuels, with that we have needed to consume them almost completely. Interestingly, devastating climatic effects are expected to kick in even before these resources have been fully exploited, while humankind continues to demonstrate inability to counteract these global trends. With all this in mind, I will talk about the curious story of gold, which has become one of the most important elements in nanotechnology, while otherwise there are virtually no technological uses of it, except in dentistry. The reasons for its popularity as a nanomaterial are two-fold. Primarily, it is one of very few materials that remain relatively stable under ambient conditions even at near molecular dimensions so that small things can be made of gold and remain metallic and stable for a long time. On the other hand, even gold becomes somewhat reactive as a small particle, and there are currently very interesting rapidly growing developments of its uses as a catalysts, which will probably soon make up about 50% of all gold nanotechnology. After a general introduction of the preparation, properties and applications of gold nanoparticles, I will focus on our own work related to basic questions of fundamental interest but also to applications in medicine, in both diagnostics (imaging) and therapy, and I will conclude with very recent research from our laboratory that demonstrates that certain gold nanoparticles can act as ion channels or pores in biological membranes.

PL-04 SOME LIKE IT HOT

Prof. Dr. Klaus Roth

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The plant genus *Capsicum*, ranging from bell peppers to chili peppers, bestows upon us a set of condiments now beloved the world over, and which allow one to “jazz up” dishes not only visually, but also with respect to taste. *Capsicum* offers us many chemical surprises. The brilliant red color of ripe fruits is based on the “*paprika ketones*,” a dye that only *Capsicum* can produce. The extraordinary pungency, which many humans enjoy so much, is due to capsaicin and dihydrocapsaicin, both also exclusively synthesized by *Capsicum*. We will try to explore the scientific background behind this sensation, which fades only gradually.

When a bowl of *chili con carne* is described as “tasting good” because the level of spiciness (or “hotness”) is just right, strictly speaking this is incorrect, because we are actually only able to “taste” sweet, bitter, sour, salty, and umami. Hot/spicy isn’t on the list! But why not? The reason for a strict differentiation here has to do with neuronal processing. Information about taste (flavor) is acquired through special sensory cells in the tongue, the responses of which are passed to the brain by way of three cranial nerves, *Nervus facialis*, *N. glossopharyngealis*, and *N. vagus*. Messages related to spiciness and temperature come through a different cranial nerve, the *Nervus trigeminus*.

After knowing *capsicums*’s unique and outstanding chemical achievements and the chemical basis of a gradually fading “*tongue on fire*”, you will enjoy more qualified and relaxed any hot food. This is just another proof that chemistry not only can be exciting but also taste good. Bom apetite!

INVITED LECTURES

ABSTRACTS

LIÇÕES CONVIDADAS
(RESUMOS)

IL-01 ONE-POT SYNTHESIS OF USEFUL BIO-PRODUCTS VIA CATALYTIC CONVERSION OF CARBOHYDRATE BIOMASS-DERIVED PLATFORM CHEMICALS

Anabela A. Valente

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Concerns about global warming, depletion of fossil fuels and energy safety have led to increasing interest in producing transportation fuels and consumer products from renewable sources. The use of fairly widespread lignocellulosic biomass has been proposed as part of the solution to replace some petroleum derived products. The main components of lignocellulosic biomass are carbohydrates. Amongst the important platform chemicals derived from carbohydrates are 5-(hydroxymethyl)furfural (HMF) and furfural (FUR). Increasing the market penetration of these furanic compounds and broadening their application profiles can be beneficial for the bio-based economy. In this respect, it is important to develop efficient conversion strategies for the valorisation of FUR and HMF. HMF, FUR and the derived furfuryl alcohol (FA) can be converted to bio-products such as furanic ethers and levulinate esters, with applications in the biofuels sector, etc. These reaction systems are complex, involving various chemical transformations. As the number of synthesis steps increases, the global processes tend to become increasingly demanding in terms of time and resources. One-pot synthesis strategies using multifunctional catalysts may allow process intensification. However, it is challenging to control different chemical reactions in one operation. For this purpose, we seek to understand the reaction pathways occurring under the reaction conditions, and the influence of material properties on the reaction networks.

Acknowledgements: Valuable contributions from all colleagues indicated in the references are greatly acknowledged. We thank: FCT, EU for grants SFRH/BPD/79910/2011, SFRH/BPD/89068/2012, SFRH/BPD/73540/2010; BP Amoco Chemical Company for P.V.W.'s grant; FEDER through COMPETE, national funds through FCT/MEC within CICECO-FCOMP-01-0124-FEDER-037271 (PEst-C/CTM/LA0011/2013), CICECO-Aveiro Institute of Materials (FCT-UID/CTM/50011/2013), under PT2020 Partnership Agreement.

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IL-02 STORING SUNLIGHT INTO ELECTROCHEMICAL ENERGY: THE NEW WORLD OF SOLAR CHARGE REDOX FLOW BATTERIES

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Energy from renewable sources is often hardly dispatchable – the availability and demand times do not match; to bridge this gap storage is essential. In 2010, the European Commission, in its pursue for energy sustainability, released the nearly zero-energy buildings (NEZB) European directive (Directive 2010/31/EU), which states that "member states shall ensure that by 31 December 2020 all new buildings are nearly zero-energy buildings; and after 31 December 2018, new buildings occupied and owned by public authorities are nearly zero-energy buildings […]" [1].

Photoelectrochemical (PEC) cells for water splitting are an emerging and promising technology for transforming solar radiation directly into storable hydrogen energy. However, despite much progresses, the efficiency of stand-alone water splitting devices remains low and the development of an unbiased system is elusive. The use of PEC cells for converting solar into electrochemical energy in a redox flow battery arrangement is a disruptive approach that allows local and efficient storage of solar energy. A PEC panel installed in a residential building would be able to harvest thermal and solar energies with very high overall energy efficiency. On the other hand, the redox flow battery can be charged simultaneously by PV and PEC panels taking advantage e.g. of the aesthetic features of the emerging perovskite solar cells [2] for covering facades and the less aesthetic PEC cells for covering the roof.

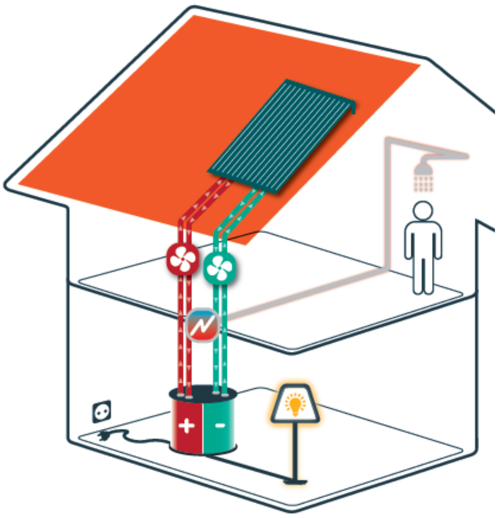

Figure 1: Conceptual idea: PEC cell on the roof for direct solar charging a redox flow battery coupled with a thermal system.

The concept and promising results on charging vanadium redox pairs with a PEC cell will be presented. It will be described a protected photoelectrode of cadmium sulfide charging an all vanadium redox flow battery with a standard potential difference of 0.6 V ($V^{3+}|V^{2+}||V^{3+}|VO^{2+}$).

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IL-03 SOLID PHASE EXTRACTION IN FLOW ANALYSIS PLATFORMS

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The analysis of complex matrices like food and environmental samples pose a number of challenges in terms of selectivity, limit of detection and even analyte speciation. In this scenario, novel methods are demanded that might provide analyte enrichment and minimisation of interferences. Additionally, a focus on devising greener chemistries and minimisation of sample and reagents consumption is also envisaged.

The use of solid phase extraction (SPE) to reach the above-mentioned objectives has gained increased importance due to some advantageous features like avoiding the use of organic solvents. However, its operation in the usual batch manual way may lead to some lack of reproducibility, being the quality of results usually dependent on the operator skill.

One way to overcome these difficulties is the implementation of SPE in flow analysis systems. Different approaches have been described, either using the solid material in the reusable mode, in packed columns, or in a renewable and disposable mode, using the so-called bead injection approach. The first one allows saving solid sorbent but is often prone to saturation, contamination, and overpressure build-up. The renewable mode overcomes these limitations and allows to carry out chemistries and detection on the solid material itself, namely in the so-called solid phase spectrometry mode. When coupled to miniaturized detectors, the overall analytical process may be configured in portable systems.

In this paper, some alternative flow configurations for this purpose are presented and discussed in terms of applicability, selectivity, sensitivity, and reagent consumption. Some selected applications developed in our group to tackle different challenges in food and environmental analysis are presented.

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IL-04 IRON AND NICKEL COMPLEXES WITH N-HETEROCYCLIC CARBENES

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A key scientific challenge of the 21st century in metal-mediated catalysis is the search for catalysts based on Earth-abundant metals. The limited availability of noble metals (Pd, Pt, Rh, Ir), and their high price and toxicity make it more desirable to search for more economical and environmentally friendly alternatives. In our research group, we are interested in developing the chemistry of first-row transition metals with N-heterocyclic carbenes (NHC), and exploring their use as catalysts in a variety of catalytic reactions. In recent years, we have disclosed the efficient catalytic activity of half-sandwich iron and nickel NHC complexes in the reduction of carbonyl groups, by hydrosilylation and hydrogen transfer reactions, and in the reduction of sulfoxides [1-3]. Here, we present our latest results on the use of iron and nickel NHC complexes as catalysts for the reduction of nitroarenes [4] and for the dehydrogenative coupling of alcohols and thiols with silanes [5,6].

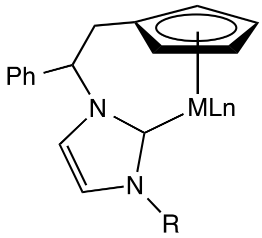

Figure 1: Half-sandwich iron and nickel NHC complexes.

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IL-05 THE FIFTY SHADES OF GREEN

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In the last decade, sustainable methodologies become an imperative of modern organic synthesis. New innovative solutions using alternative solvents or solventless reactions, and employing greener energy inputs such as microwaves, sonication, mechanochemical mixing, and high-speed ball milling are overviewed [1]. The latest developments in the emerging field of catalyst-free *in-water* and *on-water* reactions are also highlighted [2]. Finally, a special focus is given on novel materials synthesised using supercritical CO_2, with relevant applications in sensors and nanomedicine [3,4].

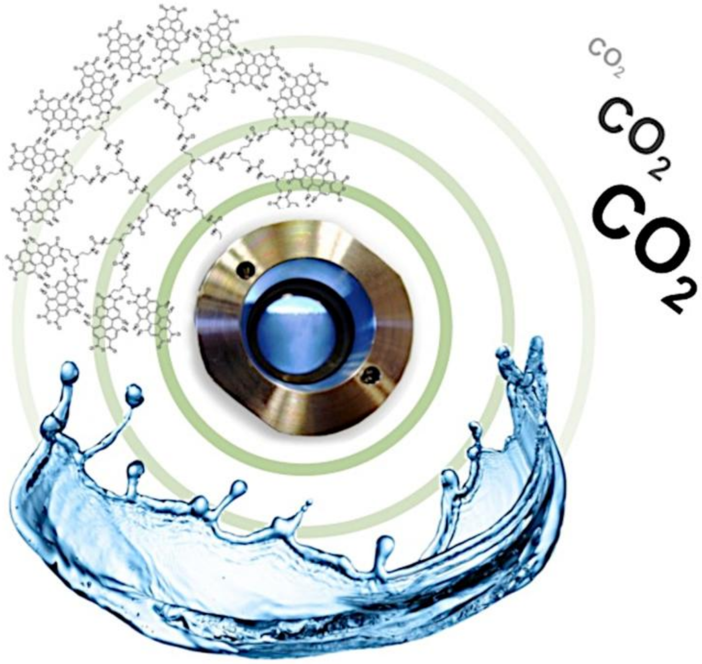

Figure 1: Alternative solvents, solvent-free chemistry, ultrasound-assisted synthesis and mechanochemistry are new tools for the modern synthetic chemist.

Acknowledgements: Fundação para a Ciência e a Tecnologia (FC&T Lisbon) is acknowledged thought projects PTDC/CTM/099452/2008 and EXPL/CTM-ENE/1502/2013.

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IL-06 A LUZ NA HISTÓRIA DA CIÊNCIA

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O estudo da luz foi um dos mais ricos e fecundos capítulos na história da ciência.
Nesta apresentação mostraremos como em torno deste assunto se desenvolveram ideias radicalmente originais, problemas novos, e concepções arrojadas, que influenciaram muitas outras disciplinas científicas.

IL-07 THE CONCEPT OF CHEMICAL METAMORPHOSIS

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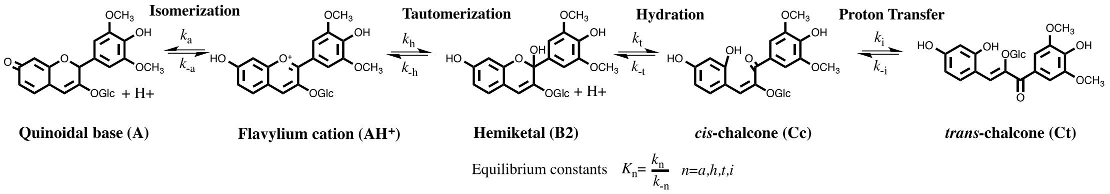
Complexity is the study of the phenomena emerging from a collection of interacting objects. While in supramolecular chemistry the complexity is achieved through a bottom up approach, there is another alternative to obtain complexity: one molecule, the generator molecule, gives one other and this one another and successively, giving rise to a multistate of different molecules exhibiting different properties. The complexity is achieved at the bottom. We coined this approach metamorphosis.[1] Anthocyanins and related compounds are a good example of this concept, Scheme 1.



Scheme 1: The multistate of flavylium derivatives

Some examples of the flavylium multistate properties will be given. In particular those regarding photochemistry; i) emptying and loading cavities by light inputs;[2,3] ii) Addressing *cis*-*trans* Isomerization and ring opening-closure by two different light inputs.[4]

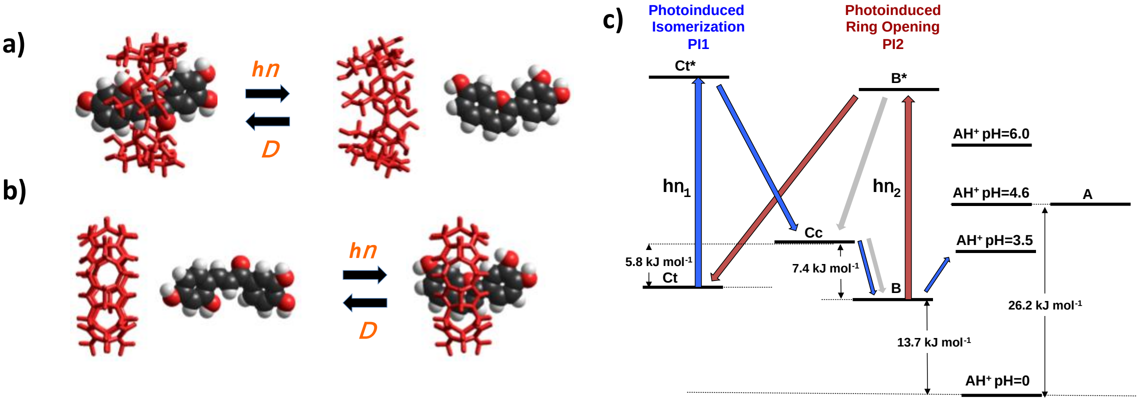


Figure 1. a) emptying the cyclodextrin cavity upon the reaction of *trans*-chalcone to give flavylium cation; b) loading the cucurbituril cavity upon the same reaction; c) dual photochromic system; photoinduced isomerization and ring opening with different lights.

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IL-08 PHARMACEUTICALS IN THE ENVIRONMENT: SOURCES, FATE AND FUTURE CHALLENGES

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Pharmaceuticals play an important role in assuring populations' health. However their use is not exempt from negative effects whose importance has been recognized recently. Indeed, every day tons of these compounds are loaded in the sewage systems and reach wastewater treatment plants (WWTPs). The removal efficiency of pharmaceuticals in WWTPs have been studied and a very wide range of values is observed, from compounds which pass these plants almost intact and others presenting a removal efficiency close to 100% [1]. Their incomplete removal makes that there is a continuous discharge of pharmaceuticals into the environment. Pharmaceuticals have been detected (at ng L^{-1} and µg L^{-1} levels) in a wide variety of water samples, such as effluents (from medical care units, landfills, and municipal sewage), seawater, drinking water, and surface- and groundwater [2, 3]; but also in soils and sediments (from µg kg^{-1} to mg kg^{-1}) [4]. Based on this, and to preserve water and soil quality, it is imperative to develop remediation techniques to study the degradation and removal of these contaminants [5].

Advances in analytical technology have been a key factor for the detection of pharmaceuticals, their metabolites, and transformation products in environmental matrices at very low concentrations (e.g. in the ng L^{-1} range) with the high degree of certainty given by the use of liquid chromatography coupled to tandem mass spectrometry (LC–MS/MS) [6]. Sample preparation is also a very important step in order to improve detection sensitivity and eliminate matrix effects. Solid phase extraction (SPE) is still the most commonly used extraction technique for liquid samples and QuEChERS methods are a new approach for soils and sediments.

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IL-09 HOMEOSTASIS OF FREE CHOLESTEROL IN THE BLOOD – KINETIC PARAMETERS AND MODELING OF ITS PASSIVE TRANSPORT

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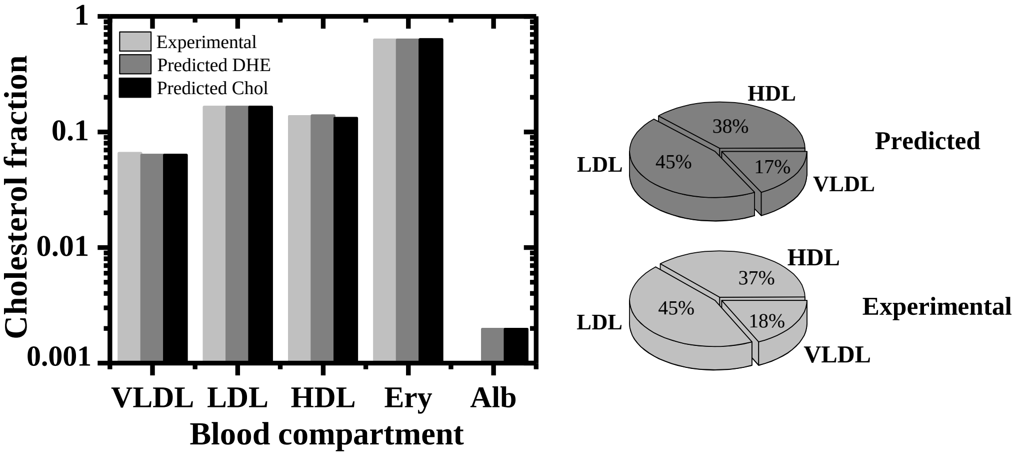
The rate of non-catalyzed transfer of cholesterol among lipoproteins and cells in the blood is of fundamental importance as a baseline to assess the role of active transport mechanisms but remains unknown. Here we address this gap by characterizing the association of the cholesterol analogue ergosta-5,7,9(11),22-tetraen-3β-ol (DHE) with the lipoproteins, VLDL, LDL, HDL_2 and HDL_3. Combining these results with data for the association of DHE with liposomes, we elaborated a kinetic model for the non-catalyzed exchange of free cholesterol among blood compartments. The computational results are in good agreement with experimental values. The small deviations are explained by the non-equilibrium distribution of unesterified cholesterol in vivo, due to esterification and entry of new unesterified cholesterol, and eventual effects introduced by incubations at low temperatures.

The kinetic profile of the homeostasis of unesterified cholesterol in the blood predicted by the model developed in this work [1] is in good agreement with the observations in vivo highlighting the importance of passive processes.



Steady state distribution of unesterified cholesterol in the various blood compartments

Acknowledgements: This work was supported by FCT, Portuguese Ministry for Higher Education and Scientific Research, through the POCTI program. LMBBE and HLAF acknowledge support from FCT through grants SFRH/BD/6746/2001 and SFRH/BD/65375/2009.

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IL-10 TECHNOLOGY PLATFORM FOR SUSTAINABLE CHEMISTRY: AN OPPORTUNITY TO INNOVATE AND COLLABORATE

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European Technology Platforms were created more than 10 years ago, as public-private collaborative forums. They are industry driven structures with the participation of all the R&D&I agents, being one of their main objectives the development of a medium to long term vision Research and Innovation agendas in concrete technological areas. One of this European Technology Platforms was on Sustainable Chemistry: SusChem.

Shortly after, given the importance and influence, Technology Platforms started to appear in the different Member States. In 2005, one year later SusChem was launched, SusChem-Spain was created, with the objective of promoting research and innovation in the field of Sustainable Chemistry and Industrial Biotechnology.

Chemical Industry is present in a big number of economic sectors; Innovations in Sustainable Chemistry can contribute to a solution to most of the grand societal challenges; Both European (H2020) and National (and even regional) Research, Development and Innovation Plans are focused on Societal Challenges. SusChem is actually working on how from our 4 technology pillars (Advanced Materials, Reaction & Process Design, Industrial Biotech and Chemical Valorization) Chemistry can provide solutions to these challenges.

IL-11 DESIGN OF ROBUST AND MULTIFUNCTIONAL METAL-ORGANIC FRAMEWORKS

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The endless combination of metal centers and organic ligands renders the field of Metal-Organic Frameworks (MOFs) an extremely rich playground for the design of new functional materials. The symbiotic co-existence of organic and inorganic components in these compounds embody the final products with unusual properties, which may, for example, ally photoluminescence with catalysis and even thermal robustness for more advanced technological applications.
Our research group has focused over the last decade on the development of functional MOFs based on rare-earth cations and polyphosphonate organic ligands, many of which designed and prepared in our laboratories. This communication summarizes our efforts towards the synthesis, structural elucidation and striking photophysical and catalytic properties of novel one- (1D), two- (2D) and three-dimensional (3D) materials prepared using various organic linkers: for example, tripodal nitrilotris(methylenephosphonic acid) (H_6nmp) and (benzene-1,3,5-triyltris(methylene))triphosphonic acid (H_6bmt), and the bipodal 1,4-phenylenebis(methylene)diphosphonic acid (H_4pmd). A number of interesting systems have been prepared: $[La_2(H_3nmp)_2(H_2O)_4]\cdot 4.5H_2O$ and $[Ln(H_4bmt)(H_5bmt)(H_2O)_2]\cdot 3H_2O$ (systems 1 and 2: 1D), $[Ln_2(H_3bmt)_2(H_2O)_2]\cdot H_2O$ (system 3: 3D), and $[Ln(Hpmd)(H_2O)]$ (system 4: 3D) (please note: Ln stands for a rare-earth cation) [1-4]. Systems 1 and 2 are outstanding heterogeneous catalysts in the methanolysis of styrene oxide or the acetalization of benzaldehyde at nearly ambient temperature, even outperforming the well-known nano-sized HKUST-1 MOF material. System 3 exhibits unusual photoluminescent properties: the Tb-containing material has an absolute emission quantum yield of *ca.* 46%; for the Eu-containing compound this value is easily increased from *ca.* 15% to 54% by removing under vacuum all water molecules in the material, this being only possible to the observed typical zeolitic behaviour. System 4 can be prepared in large quantitites as either micro- or nano-sized crystals, with the latter exhibiting a remarkable high heterogeneous catalytic activity.

Acknowledgements: I wish to give a personal and heartfelt “thank you” to all the collaborators and students involved in the research in my group over the past years. All contributed immensely with work and discussions to the great body of results. Fundação para a Ciência e a Tecnologia (FCT, Portugal; EXPL/CTM-NAN/0013/2013 - FCOMP-01-0124-FEDER-041282 and past projects), the European Union, QREN, FEDER, COMPETE and Laboratório Associado CICECO (UID/CTM/50011/2013) are also gratefully acknowledged for funding this research and dissemination of the results.

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IL-12 PIEZOPHOTONIC MATERIALS: FROM THE LAB BENCH TO THE MARKET

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Piezophotonic materials are capable of the fast and efficient conversion of the energy in a laser pulse into a high frequency broadband pressure impulse transient. Thermoelastic expansion has been considered an inefficient method to convert light into pressure, but the proper consideration of material properties and thickness, chromophore ultrafast non-radiative decay processes and constraining boundaries, yields materials with conversion efficiencies higher than 8%. The process of development of new piezophotonic materials [1] guided by the fundamental theoretical understanding of the thermoelastic processes involved and by the ability to develop adequate chromophores and substrates for light-to-pressure transduction will be presented.
Pressure waves with 1 MPa amplitude and center frequencies of 100 MHz generated by laser pulses in conjugation with piezophotonic materials can permeabilize biological barriers, such as the skin or cellular membranes, with a reversibility that allows skin to recover its protective function and cells to remain viable.[2,3] Proof-of-concept with efficient intradermal delivery by piezoporation of local anesthetics, large molecules employed in photodynamic therapy, hyaluronic acid, large proteins, [4] and also cell transfection will be presented.

We will follow the piezoporation technology journey from the laboratory benches to its availability to the public: from the development of the first prototypes of a medical device to the certified products with distinctive design; from *in vitro* experiments to trials on human volunteers, passing animal tests and human safety tests; and the intellectual property strategy. Pros and cons of technology-based entrepreneurship will be discussed.

The contribution of piezophotonic molecules and materials for launching of a new generation of medical devices for active permeation and also for applications in diagnostics, therapeutics and imaging will be further discussed.

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IL-13 AN AUTOMATED METHOD TO FIND TRANSITION STATES USING CHEMICAL DYNAMICS SIMULATIONS

Emilio Martínez-Núñez

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A procedure to automatically find the transition states (TSs) of a molecular system (MS) is presented in this talk [1]. The method has two components: high-energy chemical dynamics simulations (CDS), and an algorithm that analyzes the geometries along the trajectories to find reactive pathways.
Two levels of electronic structure calculations are involved: a low level (LL) is used to integrate the trajectories and also to optimize the TSs, and a higher level (HL) is used to re-optimize the structures. The method has been tested in several MSs: formaldehyde, formic acid (FA), vinyl cyanide (VC), and propenal using MOPAC2012 and Gaussian09 to run the LL and HL calculations, respectively.

Both the efficacy and efficiency of the method are very good, with around 15 TS structures optimized every 10 trajectories, which gives a total of 7, 12, 83 and 276 TSs for formaldehyde, FA, VC, and propenal respectively. The use of CDS makes it a powerful tool to unveil possible nonstatistical behavior of the system under study. Figure 1 shows an example of the number of TSs found for propenal as a function of the number of trajectories.

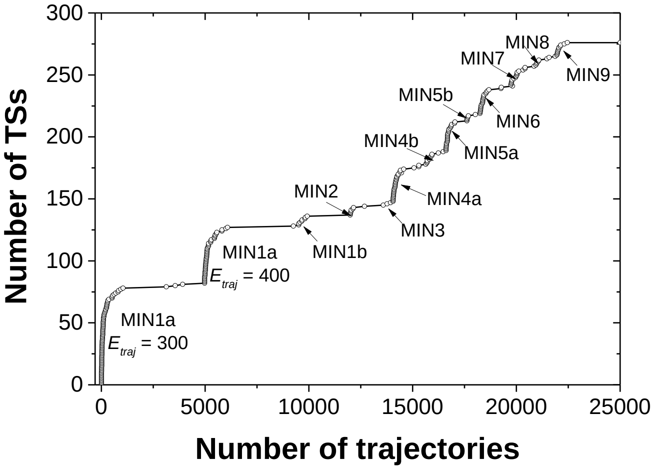

Figure 1: Number of transition state structures found for propenal as a function of the number of trajectories employed in the TSSCDS method. Only the TSs optimized at the HL are depicted in the figure.

Acknowledgements: The author thanks “Centro de Computación de Galicia (CESGA)” for the use of their facilities

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IL-14 UM 'PORTFOLIO' DE ACTIVIDADES DE PROMOÇÃO E DIVULGAÇÃO DA QUÍMICA

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In the last 15 years, the Department of Chemistry and the CICECO – Aveiro Institute of Materials (University of Aveiro) have been carrying out several activities concerning the citizen’s scientific culture – usually described as “Public awareness of science” (PAwS) or “public understanding of science” (PUS), more recently “Science with and for Society”, or simply “reaching out/science outreach”.

As a result, we have now a portfolio of activities of diverse nature, which includes students’ contests at national level (Chemistry Olympiads) [1], chemistry demonstration shows (e.g., Química por Tabela 2.0) [2], national broadcast programs [3,4], multimedia resources [3,5], and wide-audience science cafés and debates (e.g., Havíamos de Falar Disso) [6], among others.

This portfolio of activities is the starting point for a discussion around the meaning and importance of scientific culture in society, the role assigned to those who have the knowledge, the (good) reasons for engagement in these rewarding activities, and also to provide a few clues for success.

Figure – Logotypes from some representative activities

[1] Olimpíadas de Química / Chemistry Olympiads, Paulo Ribeiro-Claro (Coord. 2001-2012), http://olimpiadas.chemistry.pt/

[2] Química por Tabela / Chemistry by the Table, Paulo Ribeiro-Claro and Brian Goodfellow, http://www.ua.pt/fabrica/PageText.aspx?id=7316

[3] A Química das Coisas / The Chemistry of Things, Paulo Ribeiro-Claro (Coord.), www.aquimicadascoisas.org/

[4] Moléculas Sensacionais / Sensational Molecules, Paulo Ribeiro-Claro e Catarina Lázaro, http://www.ciceco.ua.pt/moleculassensacionais

[5] Lugar ao Sal / Salt Science, Maria Clara Magalhães (Coord.), http://sal.spq.pt/

[6] Havíamos de Falar Disso / We would talk about it, Paulo Ribeiro-Claro, João Rocha e Nuno Camarneiro (Coord.), http://www.ciceco.ua.pt/haviamosdefalardisso/

IL-15 HISTÓRIA DA QUÍMICA E ARTE: DIÁLOGO EDUCATIVO COM O RETRATO DE NOVA QUÍMICA

Fátima Paixão

Instituto Politécnico de Castelo Branco & Centro de Investigação Didática e Tecnologia na Formação de Formadores, Universidade de Aveiro, Portugal

Entre aspetos da relevância da química, está o seu forte contributo para a integração de sabres e, como tal, se impõe a sua abordagem educativa numa perspetiva de cultura científica identificada com ciência motivadora, tanto para futuros químicos como para não químicos. Além da utilidade que pode advir da compreensão e aplicação prática de leis, teorias, princípios e conceitos (aspetos técnicos, interpretativos e preditivos…) é indispensável compreender partes da história da ciência e os contextos nos quais ela foi construída e como foi moldada por forças de toda a ordem (social, económica, política, estética…). Assim, tomamos a ideia de que aprender química exige também aprender sobre química e encetar diálogos muitas vezes improváveis, como o que se pode estabelecer entre esta ciência e objetos da arte.

O objetivo do diálogo que queremos estabelecer, não é tanto do ponto de vista da estética associada à química (esse seria outro) mas do que o retrato realista de "Lavoisier e sua esposa", pintado em vida do casal, e muito representado nos livros escolares, em geral com mera função ilustrativa, pode ensinar de química e sobre química e transformar a monótona temática da conservação da massa num desafio de integrar a construção da nova química no seu contexto multifacetado e ensinar a compreender o sentido das transformações químicas de uma forma cientificamente mais útil e socialmente mais relevante.

ORAL COMMUNICATION ABSTRACTS

COMUNICAÇÕES ORAIS

(RESUMOS)

OC-01 ENHANCED CATALYTIC BEHAVIOUR OF HIERARCHICAL SAPO-11 SYNTHESISED UNDER MICROWAVE RADIATION

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Microwave (MW) radiation was used to prepare small sized SAPO-11 materials with secondary mesoporosity, which is particularly relevant in *n*-decane hydroisomerization reaction that is supposed to occur at the surface of the crystals (pore mouths). The materials were prepared using the following gel composition ($1.0Al_2O_3$: $1.0P_2O_5$: $0.4SiO_2$: 1.5DPA: $50H_2O$) at 170 ºC [1], but under different experimental MW conditions. The MW samples are referred to as S-x-y where x, y are the heating rate (min), reaction time (min), respectively. The samples were characterized by XRD, N_2 sorption, SEM, ^{27}Al, ^{31}P and ^{29}Si MAS-NMR and pyridine adsorption followed by IR spectroscopy. The metal function was introduced by mechanic mixture with Pt/Al_2O_3 to obtain Pt/SAPO-11 with 0.5 wt.% metal loading. The samples were tested in the hydroisomerization of *n*-decane.

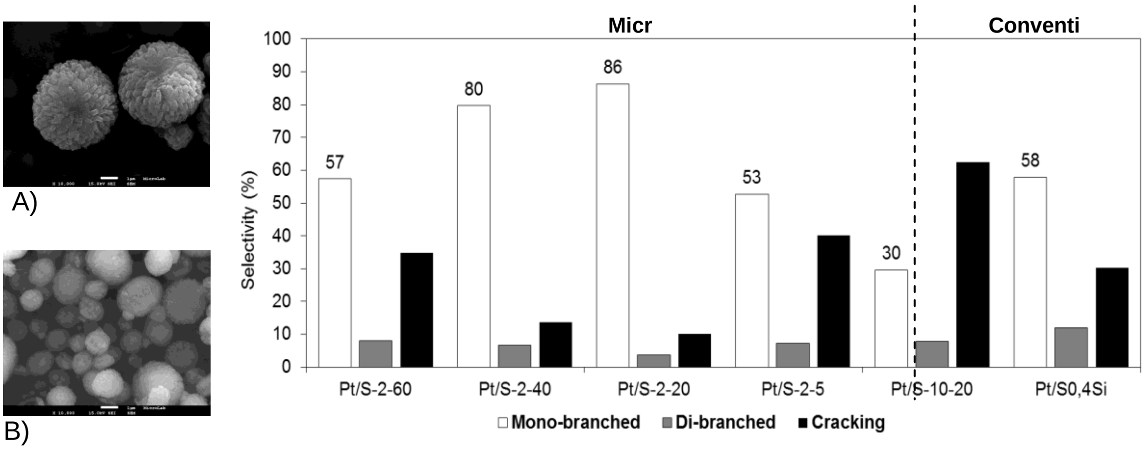

Figure 1. SEM of conventional S0.4Si (A) and hierarchical S-2-20 (B) samples, Selectivity of mono- ,di-branched isomers and cracking products for *n*-decane 10% of conversion at 330°C, for SAPO-11 samples (0.4g), with 0.5 wt% Pt, and $H_2/n\text{-}C_{10}=3$ (C).

All the SAPO-11 (AEL structure) samples are pure and well crystalline. The samples synthesized with MW present higher external surface area and mesoporous volume, when compared with S0,4Si sample, denoting that the mesoporosity is generated as a result of agglomeration of small particles (Figure 1 A and B) The catalytic results (Figure 1 C) show higher selectivity for the desired mono-branched isomers and reduced cracking products, especially for S-2-40 and S-2-20 samples. These results clearly demonstrate that the use of MW radiation is an effective tool to design catalysts for isodewaxing of long chain *n*-alkanes.

Acknowledgements: The authors thank Portuguese FCT for financial supports (SFRH/BD/73234/2010 and SFRH/BPD/91397/2012).

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OC-02 OXIDOVANADIUM COMPLEXES ANCHORED ON CARBON MATERIALS FOR OXIDATION REACTIONS

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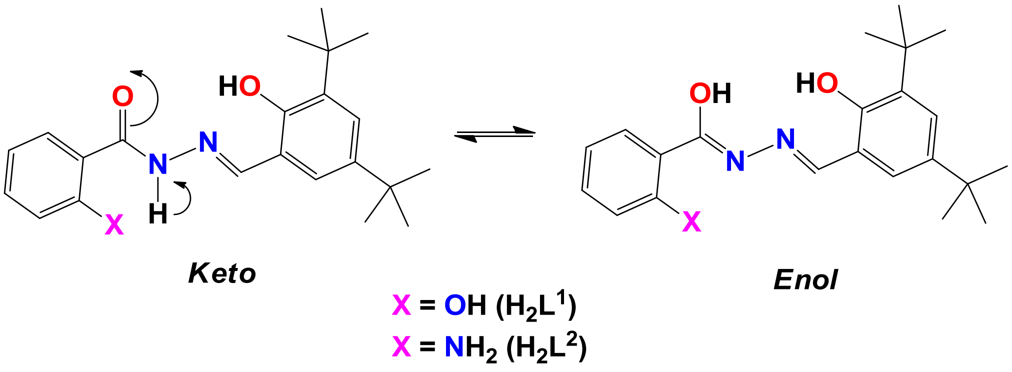
Oxidovanadium complexes are good candidates as catalysts for oxidation of alkanes [1] and aerobic oxidation of secondary alcohols [2], with good yields and high selectivities. Oxidovanadium (V) compounds with the aroylhydrazone Schiff bases (3,5-di-tert-butyl-2-hydroxybenzylidene)-2-hydroxybenzohydrazide (H_2L^1) and (3,5-di-tert-butyl-2-hydroxybenzylidene)-2-aminobenzohydrazide (H_2L^2) (Scheme 1) were synthesized and characterized: $[VOL^1(OEt)]$ (**1**), $[Et_3NH]^+[VO_2L^1]^-$ (**2**), $[VOL^2(OEt)]$ (**3**), $[Et_3NH]^+[VO_2L^2]^-$ (**4**), $[VOL^1(\mu\text{-}O)VOL^1]$ (**5**) and $[VOL^2(\mu\text{-}O)VOL^2]$ (**6**). Complexes **1**-**6** were heterogenised on carbon materials, namely activated carbon (AC), carbon xerogel (CX), carbon nanotubes (CNT) and nanodiamonds (ND), with different surface treatments [3].

The catalytic activity of **1**-**6** was tested, both in homogeneous and heterogeneous conditions, in *i*) the peroxidative oxidation of cyclohexane to cyclohexanol and cyclohexanone by H_2O_2 in acetonitrile, and *ii*) the microwave-assisted solvent-free peroxidative oxidation of 1-phenylethanol by *t*-BuOOH. In general, supported compounds exhibit higher catalytic activity than the corresponding homogeneous analogues, while maintaining the selectivity (no traces of by-products were detected), also allowing reuse up to 9 consecutive cycles with preserved activity.



Scheme 1

Acknowledgements: Fundação para a Ciência e a Tecnologia (FCT) I and projects UID/QUI/00100/2013, QREN, ON2 and FEDER (Project NORTE-07-0124-FEDER-0000015) and Investigador FCT research grants (for SACC and MS). The LA LSRE/ LCM is supported by FCT and FEDER through project UID/EQU/50020/2013.

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OC-03 SUSTAINABLE SELECTIVE CATALYTIC OXIDATION OF ALKANES

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The main oxidised products of cyclohexane are of great industrial significance. A large amount of cyclohexanol and cyclohexanone is produced worldwide, mostly to be used as precursors to the manufacture of added-value products, such as Nylon-6 and Nylon-6,6 [1,2]. Industrially, the reaction is performed using a cobalt(II) naphthenate catalyst at 160◦C and 15 bar, yielding 4% conversion into oxidised products with 80% selectivity towards cyclohexanol and cyclohexanone [2,3]. The development of economical heterogeneous catalysts based on first row transition metal complexes that work under mild and sustainable reaction conditions in the activation of C H bonds is very important. Transition-metal complexes of the first row (V(IV), Mn(III), Fe(III) Co(III) and Cu(II)) with biomimetic Schiff base ligands with N_2O_2 coordination sphere, as well as an N_4 (Fe(II)) were screened as homogeneous catalysts in the room-temperature oxidation of cyclohexane using environmentally benign reagents: hydrogen peroxide (30 wt%) as the oxygen source and acetonitrile as the solvent. Addition of nitric acid promoted the oxidation reaction [4]. Cyclohexanone and cyclohexanol were the main products of the oxidation of cyclohexane, obtained when the following complexes were used as homogeneous catalysts in only 1 mol% based on the substrate: VO(IV), Fe(III) and Cu(II) complexes with the N_2O_2 Schiff base, new Fe(II) complex with the Schiff base with N_4 coordination sphere and commercial [$VO(acac)_2$] with O_4 coordination sphere [4]. Cyclooctane and *n*-hexane could also be oxidised to the corresponding ketones and alcohols with higher turnover numbers than cyclohexane by the Fe(III) complex with N_2O_2 Schiff base ligand [4]. Commercially available iron(II) and iron(III) acetylacetonate acted as well as homogeneous catalysts in the oxidation of cyclohexane and *n*-hexane [5]. Therefore they were immobilised onto amine functionalised economical and environmentally acceptable solid porous supports: hexagonal mesoporous silica and activated carbon. They were active as heterogeneous catalysts in the oxidation of cyclohexane and *n*-hexane at room temperature with hydrogen peroxide, giving the respective alcohols and ketones. They could also be recycled at least two times without loss of catalytic activity in the oxidation of cyclohexane [5].

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OC-04 ADSORPTION OF ANTHOCYANINS AND PHENOLIC ACIDS IN CLAYS

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Anthocyanins from natural extracts have been finding increasing use as food colorants in replacement of synthetic pigments following reports of their beneficial health effects. The stability of anthocyanins towards chemical and physical factors has been the limiting effect of their use in food products.

For the present work, we use extracts of *Myrica faya* berries, a rich source of cyanidin-3-glucoside (C3G) [1], and evaluated the adsorption of several compounds on a natural clay from Porto Santo, Madeira (Portugal), which was well characterized in previous studies [2].

Phenolic acids, such as chlorogenic, ferulic, caffeic, sinapic and p-coumaric acids were evaluated individually by measuring concentration before and after adsorption using HPLC-DAD. The same procedure was applied to *Myrica faya* extracts using standard C3G.

Results show that the clay is able to adsorb over 75% of the anthocyanins from the aqueous solution but does not remove them from methanol solutions. The adsorption rate from the methanol solutions of phenolic acids ranged 5.7 – 29.9%.

Degradation studies revealed a low result for anthocyanins (2.4%), while phenolic acids presented a degradation range between 1.3 and 10.2%. Desorption of anthocyanins was negligible over a wide range of pH and materials kept their color after several months.

Acknowledgements: *This work was supported by FCT - Fundação para a Ciência e a Tecnologia, through projects PTDC/CTM-CER/1121295/2010 and PEst-OE/QUI/UI0674/2014.*

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OC-05 A STRATEGY FOR IMPROVING ENZYME'S STABILITY VIA IMMOBILIZATION OVER MULTI-WALLED CARBON NANOTUBES

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Due to their exceptional mechanical, electrical and chemical properties, carbon nanotubes (CNT) have been used in the nanotechnology field to create new nanostructures. Consequently, there is an increasing interest in understanding and controlling the interactions of this nanomaterial with biological molecules, such as enzymes. In this context, peroxidases have been immobilized on CNT for various potential applications, such as sensing, drug delivery and biocatalysis. However, there are but a few studies about the influence of the nanoscale environment on the function of these enzymes.

In this work multi-walled carbon nanotubes (MWCNTs) with different surface chemistry were used as supports for enzymes (laccase and peroxidase) immobilization by adsorption with the aim at developing highly stable biocatalysts (Fig. 1) [1, 2]. The effect of MWCNTs surface functionalization, through oxidation followed by the selective removal of oxygen-containing surface groups (such as carboxylic acids, phenols, anhydrides, lactones and quinones) at different temperatures, on the immobilization efficiency, catalytic activity, and thermal and operational stability of peroxidase was assessed.

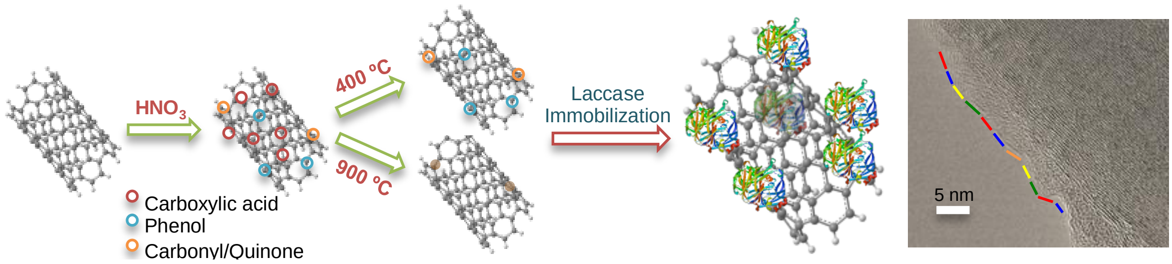

Figure 1: Laccase immobilization over surface modified MWCNTs [2].

Acknowledgements: This work was co-financed by FCT/MEC and FEDER under Programme PT2020 (Project UID/EQU/50020/2013), by QREN, ON2 and FEDER through Project NORTE-07-0124-FEDER-000015 (CGS). APMT acknowledge the financial support (Programa Ciência 2008) from FCT.

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OC-06 PREDICTING VOLATILITY PROPERTIES OF HALOBENZENES FROM THE VOLUME AND ELECTRON AFFINITY OF HALOGEN ATOMS

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Halogenated organic compounds are ubiquitous contaminants in the environment, being their physico-chemical properties strongly influenced by the halogen substituents. Halobenzenes form a class of compounds with a huge number of members – ca. 1500 different halobenzenes may exist theoretically. For a reliable prediction of the fate and transport of these pollutants in the environment, consistent data of vapour pressures and enthalpies of vaporization are needed.

This study presents a simple method for accurate predictions of these two properties, at 298.15 K, for any of these compounds, from mono to hexa halobenzenes, based on the volume and electron affinity of the halogen atoms.

Application of predictive equations to halogenated substituted benzenes and some polycyclic aromatic species was tested with success.

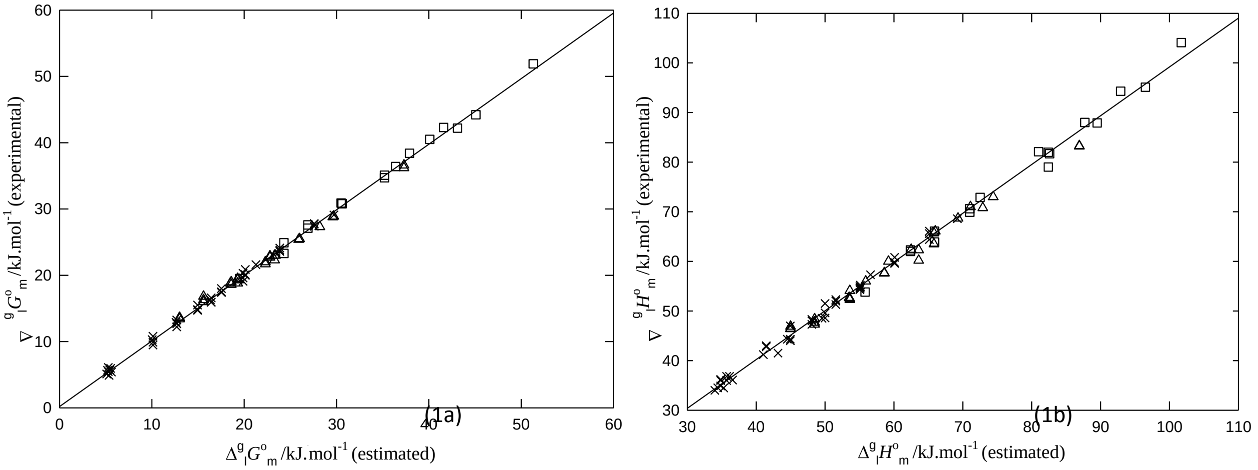

Figure 1 Correlation between experimental and estimated values of standard Gibbs energy (1a) and enthalpy (1b) of vaporization of halogenated benzenes and polycyclic aromatic species

Acknowledgements: Thanks are due to projects (PEst-C/QUI/UI0081/2013) and QREN (FCUP-CIQ-UP-NORTE-07-0124-FEDER-000065). Thanks are also due to FCT and ESF for the award of the postdoctoral fellowship (SFRH/BPD/97046/2013) of A.R.R.P.A., and to Prof. Alexandre L. Magalhães for helpful discussions.

OC-07 COMPUTATIONAL STUDY OF STRUCTURE AND RAMAN SPECTRA OF FLUOROMETHANE TYPE I HYDRATE

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Clathrate hydrates (or gas hydrates) are non-stoichiometric inclusion solids where water molecules form a crystalline regular network through hydrogen bonding, leaving cage structures that enclathrate small guest molecules such as CO_2 or CH_4, arranged into periodic lattices, at low temperatures or moderately high pressures [1]. Gas hydrates have attracted large research efforts from different scientific and technological communities due to the number of processes and applications where they are involved [2], as for instance their potential to capture and retain molecules implied in the atmospheric greenhouse effect [3].
One of the most important families of greenhouse effect gases are chlorocarbons, which have been extensively used in the past as industrial refrigerants. Nowadays, those compounds are being substituted by hydrofluorocarbons. In spite of their comparatively reduced capabilities to deplete the ozone layer, fluoromethane represents an important environmental threat due to its atmospheric half-life of 3.7 years and a global warming potential computed for 100 years of 150 points, compared to 21 points for methane in the same scale. Type I gas hydrate is one of the alternatives for fluoromethane capture and storage, and for this reason it represents a subject of increasing interest.
In this work, fluoromethane type I hydrate has been studied by means of electronic Density Functional Theory (DFT) and the Quantum Theory of Atoms in Molecules (QTAIM). Both types of cells included in its structure were modelled as flexible cages, either empty or containing one CH_3F guest molecule, with single occupancy. Calculation of Raman spectra was made, taking special care of considering anharmonic corrections to analyze Fermi resonance. In addition, isotopic substitution on the water network allows to isolate and to identify the main characteristic bands to confirm the formation of the hydrate, and its main structural characteristics. Use of experimental bibliographic spectra validates our model to perform further calculations, and the presented results suggest that the hydrate guest occupancy might be calculated from the comparison of experimental and predicted Raman spectra.

Acknowledgements: Authors would like to acknowledge Centro de Supercomputación de Galicia (CESGA) for the computational resources, and also project FIS2012-33621 from the spanish Ministerio de Economía y Competitividad (MINECO), co-funded by EU-FEDER funds.

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OC-08 NEAR-INFRARED INDUCED GENERATION OF HIGHER-ENERGY CONFORMERS AND SPONTANEOUS PROTON TUNNELING IN CARBOXYLIC ACIDS ISOLATED IN CRYOGENIC MATRICES

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For the conformational equilibria occurring at ambient temperatures, the species with energies higher by more than 10 kJ/mol with respect to the most stable forms, have very small populations and are difficult to be experimentally observed. In the matrix isolation technique, the vapors of molecules of interest (guest molecules) are trapped in rigid host materials (usually solidified noble gases at 5-15 K). If the barriers for conformational relaxation are high enough, not only the most stable structure, but also the higher-energy conformers may be trapped and stabilized in low-temperature matrices.

Using tunable narrow-band (fwhm < 1 cm^{-1}) near-infrared light, it is possible to excite *in situ*, in a very selective way, only molecules adopting a particular conformation. A conformational conversion induced by such excitation can lead to depopulation of one of the conformers and to its transformation into another structure. The idea consists in exciting, with near-infrared light, a particular vibration and hence providing a studied molecule with energy that is higher than the torsional barrier for the conformational conversion. Usually it concerns excitation of an overtone of OH stretching vibration. In the course of vibrational energy redistribution to the torsional coordinate, a new conformer may be formed [1].

This contribution will cover some experimental results obtained over the past few years through collaboration between the Coimbra and Warsaw laboratories. The obtained results provide a new insight into the conformational behavior of several matrix isolated carboxylic acids [2-4]. The state-of-the-art experimental methods were applied in these studies. For the studied carboxylic acids, new, previously unknown higher-energy conformers were generated and spectroscopically characterized.

In several cases, a spontaneous conversion of the photogenerated higher-energy conformers into the most stable forms of the studied compounds was also observed. These processes, occurring in matrices *via* proton tunneling, will be also addressed.

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OC-09 PERMANENT MEMORY EFFECT OF PDLC FILMS: A NEW MEMORY DEVICE

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BACKGROUND: Polymer dispersed liquid crystal (PDLC) films have a range of application varying from switchable windows to new optical memory devices. They switch from an opaque state, when liquid crystal molecules are randomly dispersed, to a transparent state, when liquid crystal molecules are aligned, simply by applying a small voltage. On some PDLC films, the transparent state is retained even when the voltage is switched off; this is called permanent memory effect (PME). This process is totally reversible, returning to the initial opaque state either through heating or applying a higher frequency electric field when using a two frequency liquid crystal.
RESULTS: On this work, the impact on the electro-optical response of PDLC films as a result of adding an additive was studied. This performance is affected by several factors being the most important the anchorage force. This anchorage force is modified with the addition of an additive such as TX-100. As a result, it was verified that the addition of TX-100, increased the PME up to 98,7% and decreased the voltage required to achieve 90% of maximum transmittance to 2 V/µm.
CONCLUSIONS: The addition of a surfactant, as TX-100 in this case, was shown to be valuable method to control the PME in PDLC systems in particular those prepared by PIPS from the oligomer polyethylene glycol dimethacrylate and the monomer triethylene glycol dimethacrylate in mixture with the nematic LC E7 .This new advance on liquid crystal field also allows to develop a new memory device based on a write-read-erase cycle.

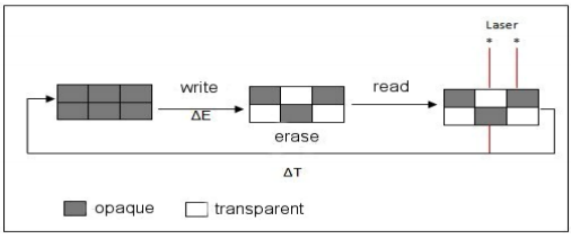

Figure 1: Representative scheme of digital writing using 6 PDLC units

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OC-10 ELECTROKINETIC SOIL REMEDIATION - AN EFFICIENCY STUDY FOR CADMIUM REMOVAL

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The growing of the industrial activity, together with the inadequate elimination of the wastes generated by our society and/or the uncontrolled deposits of them, brings contamination, by both heavy metals (mainly Cr, Cu, Pb and Ni) and/or organic pollutants (specially chlorinated compounds) among others [1], in the neighboring soils. Heavy metals, which are not biodegradable, can pass to the water-bearing and later to the living beings causing several diseases (skin, lung, digestive, cancer, etc)

This work presents the use of the electrokinetic remediation method for soils affected by contaminated deposits, as a method to eliminate such heavy metals [2-4]. In particular, it is focused on the cadmium removing which is frequently present in utilities. In the past, many researchers have been devoted to the use of electrokinetic remediation to remove different pollutant substances. Nevertheless, in most of the cases the objective was the feasibility of the remediation method itself but not the understanding of the physicochemical fundaments of the technique. This work goes towards the establishment and optimization of an electrokinetic cell and optimization of the different experimental parameters (pH, electrical field applied and electrolysis time, soil characteristics, use of adsorbent materials) used as base for modeling this electrochemical process.

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OC-11 METHOD DEVELOPMENT AND VALIDATION FOR SIMULTANEOUS DETERMINATION OF MAJOR, TRACE AND RARE EARTH ELEMENTS IN SEDIMENTS BY ICP-OES AND ICP-MS

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Sediment chemical composition is recurrently used to assess the environmental status of marine ecosystems [1]. Furthermore, interest on rare earth elements in sediments increased due to the use of these elements in various industrial products. Simple and adequate sediment digestion methodologies prior to element content quantifications are crucial for the environmental interpretation. Presently, there is no accepted method for simultaneous digestion and quantification of major, trace and rare earth elements in marine sediments.

The aim of this work was therefore to develop and validate a new digestion procedure, using closed-vessel microwave acid digestion approach followed by plate heating for simultaneous determination of Al, Ca, Fe, K, Mg, Na (major elements), Cr, Cu, Li, Ni, Pb, Sr, V, Zn, As, Be, Co, Mn, Ni, U, Zn, Mo, Sb (trace elements) and La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu (rare earth elements), using inductively coupled plasma-optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS). Both equipments were used due their inherit advantages, such as the simultaneous multi-elementar analysis and the trueness of results at trace and ultra-trace levels [2].

Modifications to the method proposed by EPA-3052 were tested, varying the acid mixture, microwave temperature and pressure. A complete digestion of marine sediments was achieved and the developed method was validated. The validation process included the study of method performance characteristics such as selectivity, linearity, limits of detection and quantification, trueness, recoveries, precision and parallel testing. Both the precision and trueness of the digestion procedure were below 20%, verified using a certificated reference material (CRM – MESS 3). The developed method revealed to be efficient and rapid. The application to marine sediments allowed quantifying all the mentioned elements with recoveries between 80 and 120 %. This presentation will elucidate about the key aspects regarding the method development and validation work.

Acknowledgements: The authors thank Fundação para a Ciência e a Tecnologia (FCT), FSE and POPH for funding (UID/AMB/50017/2013). The authors also thank Laboratório Central de Análises supported with funds from the University of Aveiro.

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OC-12 ESTIMATION OF MERCURY METHYLATION RATES IN SEDIMENTS FROM TWO PORTUGUESE ESTUARIES USING MERCURY STABLE ISOTOPES

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Neurotoxic methylmercury (MMHg) is formed from inorganic divalent mercury (Hg^{II}). Many procedures have been developed to measure the concentration of MMHg from different sample matrices, and the use of isotope enriched mercury species now provides opportunities to determine its formation and degradation rates.

In this study, solutions containing stable isotope tracers of $^{199}Hg^{2+}$ and $CH_3{}^{201}Hg^+$ were spiked into salt-marsh plants colonized and non-colonized sediments cores collected in Tagus and Guadiana estuaries. $^{200}HgCl_2$ and $CH_3{}^{202}HgCl$ were added as internal standard for the respective analyses. Ambient concentrations of THg and MMHg were determined by measuring ^{202}Hg and $CH_3{}^{200}Hg$ in the same samples during the respective THg and MMHg analysis. Rates of methylation and demethylation were measured simultaneously in sediments to directly monitor and compare the concurrent processes of mercury methylation and methylmercury demethylation.

The formation of $CH_3{}^{199}Hg^+$ and the decrease in $CH_3{}^{201}Hg^+$ were measured simultaneously in time series experiments using gas chromatographic separation and isotope-specific detection by inductively coupled plasma mass spectrometry. Specific rate constants for the two processes were calculated and compared to concentrations of the ambient, standing pool of methylmercury in the same sample.

The rate of methylation for the inorganic mercury tracer $^{199}Hg^{2+}$ led to concentrations of $CH_3{}^{199}Hg^+$, which were high compared to the ambient ratio of Hg^{2+} to MMHg, indicating that the added tracer Hg^{2+} is more readily available for methylation than the ambient Hg^{2+}. The degradation of tracer and ambient methylmercury proceeded at a similar rate, showing no significant differences between added tracer and ambient methylmercury.

The paper will discuss site-specific differences controlling the rates of methylation and demethylation at the two locations. Special emphasis will be paid to the effect of marsh vegetation on mercury species transformation by comparing data from non-colonized locations with those from locations colonized with mature *Spartina maritima* plants.

OC-13 ESPECTROFOTOMETRIA – REFRATOMETRIA NO IPQ

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Os Laboratórios de Espectrofotometria e Refratometria do Instituto Português da Qualidade (IPQ) têm atividades de calibração, certificação e operações de controlo metrológico, cumprindo com a missão do Departamento de Metrologia do IPQ de assegurar o rigor e a rastreabilidade das medições no território nacional, através dos padrões de medida necessários à indústria e à sociedade portuguesa [1].

O Laboratório Espectrofotometria proporciona serviços de calibração baseado sobre um espectrofotómetro Lambda 950 da Perkin Elmer e um espectrofotómetro Cary 5E da Varian assim como padrões de fatores de transmissão e de comprimento de onda, calibrados no Laboratório Primário de Espectrofotometria do NPL. Estes espectrofotómetros, com duplo feixe e duplo monocromador, possuem sistemas de iluminação e de deteção que permitem analisar em várias ordens de grandeza de densidade ótica no intervalo [200 nm; 3300 nm] [2].

O Laboratório de Refratometria, além da calibração de refratómetros de soluções líquidas e de certificação e preparação de soluções padrão de fração mássica em açúcares, até 85,00 cg/g, ou de fração volúmica potencial em etanol, até 75,00 cL/L, efetua ensaios de aprovação de modelo e de primeira verificação do controlo metrológico dos refratómetros utilizados para determinação do título alcoométrico volúmico potencial dos mostos de uvas. [3].

Os Laboratórios aplicam a definição da calibração do Vocabulário Internacional de Metrologia [4], seguindo a metodologia do *Guide to the Expression of Uncertainty in Measurement* [5] com um modelo linear da função de calibração em intervalos adequados da mensuranda. São dados exemplos com folhas de cálculo desta prática para obtençao de resultados de medição em laboratórios.

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OC-14 DEVELOPMENT AND VALIDATION OF A SIMPLE SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF METHYLDOPA IN BOTH BULK AND MARKETED DOSAGE FORMULATIONS

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Methyldopa (MTD), chemically known as α-methyl-3,4-dihydroxyphenylalanine, is a catechol derivative (catecholamine) widely used as an antihypertensive agent. MTD is a centrally acting α_2-adrenoreceptor agonist, which reduces sympathetic tone and produces a fall in blood pressure [1].

A simple, precise, sensitive, rapid, specific and economical spectrophotometric method was developed to determine MTD content in bulk and pharmaceutical dosage formulations. The proposed method was based on the formation of a colored product from the nitrosation reaction of MTD with sodium nitrite in an acid medium. The resultant nitroso derivative species reacts further with sodium hydroxide and is converted it into a more stable compound. This yellow nitrosation product exhibited an absorption maximum at 430 nm.

Aliquots of reference substance stock solution ranging from 6.37 to 82.81 μg ml^{-1} MTD were transferred to a series of 5.0 ml volumetric flasks. To each flask, 1.0 ml of hydrochloric acid (1.6 x 10^{-2} mol l^{-1}) and 1.0 mL of sodium nitrite (0.6 mol l^{-1}) were added and kept aside for five min; then 1.0 ml of sodium hydroxide (5.0 x 10^{-2} mol l^{-1}) was added to the solution. After five minutes, the volume was then made up with deionized water. The absorbance was measured at 430 nm against the corresponding reagent blank. Calibration graphs were prepared by plotting absorbance against drug concentration. These graphs or the corresponding linear least squares equations were used to convert absorbance into MTD concentration, for any given analyzed sample.

Beer's Law was obeyed in a concentration range of 6.37 to 82.81 μg ml^{-1} MTD with an excellent coefficient of determination (R^2 = 0.9998). No interference was observed from common excipients in formulations. The results showed the method to be simple, accurate and readily applied for the determination of methyldopa in pure form and in pharmaceutical preparations. The analytical results obtained for these products using the proposed method are in agreement with those of the Brazilian Pharmacopoeia procedure at a 95% confidence level.

Acknowledgements: We would like to thank FAPEMA, CNPq and INCUBEM/PROEX/UFMA Foundations (Brazil) for financial support.

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OC-15 ARSENIC IN SOILS – NEW PARADIGMS, NEW CHALLENGES!

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Soils considered contaminated can be a source of hazardous elements to the living beings. Demographic pressure and human activities can increase the amount of those elements in soils. In the last decades has been given special attention to arsenic, as massive poisoning of human beings, by contaminated food and water, is occurring in some regions of the Earth as Bangladesh, China or India.

The effect of any chemical element in the living beings only exists if interactions occur between the chemical element and the organism. In soils, microorganisms and plants have mechanisms for mobilization/immobilization of chemical elements, but these processes are dependent on the soil solid phases composition, and the soil physical and chemical properties as temperature, pH, moisture or redox potential. However, plants interact with soils in different ways depending on the plant species, the element and the soil composition and properties. Depending on the hazardous elements concentrations in plants, their impact in the food chain is possible.

The research on arsenic immobilization in the environment continues to give a strong emphasis on the use of solid phases containing arsenic(V), iron(III), calcium and/or magnesium (considered as environment friendly) that have been shown not be suitable both for long lasting and environmentally safe concentrations purposes [1]. Elements, originating less soluble solid phases, must be considered when thinking about the immobilization of arsenic in the environment even if they are considered less environmentally friendly. If a chemical element is the component of a solid with very low solubility, in an environment that will not allow its mobilization, what will be the meaning of the soil elemental total concentration as a measure of environmental impact? The experimental conditions necessary to determine the soils elemental total concentrations are far from the actual activity of the living beings in their interaction with soils. The soil available fraction intends to be a more accurate measurement of the actual impact of the soils composition in the surrounding environment [2]. Which challenges brings the change from the soil elemental total concentration to the soil elemental available fraction as a measure of environmental impact?

In this presentation will be analyzed some of the challenges that this change of paradigm brings to the analysis of soils and by extension to the sediments. The present concept of environmentally friendly chemical elements will also be revisited in the frame of the new approaches to the environmental issues. Which have been the impacts, in the environment, of avoiding the use of the considered hazardous chemical elements? New approaches to the environmental issues are needed.

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OC-16 CATALYTIC AMINOCARBONYLATION: A SUSTAINABLE APPROACH FOR THE SYNTHESIS OF AMIDE DERIVATIVES

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Amides constitute one of the most important functional groups in contemporary chemistry, since they can be found in numerous natural compounds and are among the most prolific moieties in modern pharmaceutical products.[1] Despite their importance, the majority of amide bond syntheses require stoichiometric amounts of coupling reagents, making them generally expensive and wasteful procedures. In this regard, Pd-catalyzed carbonylation emerged as a sustainable one-step alternative for the synthesis of amide derivatives.[2]

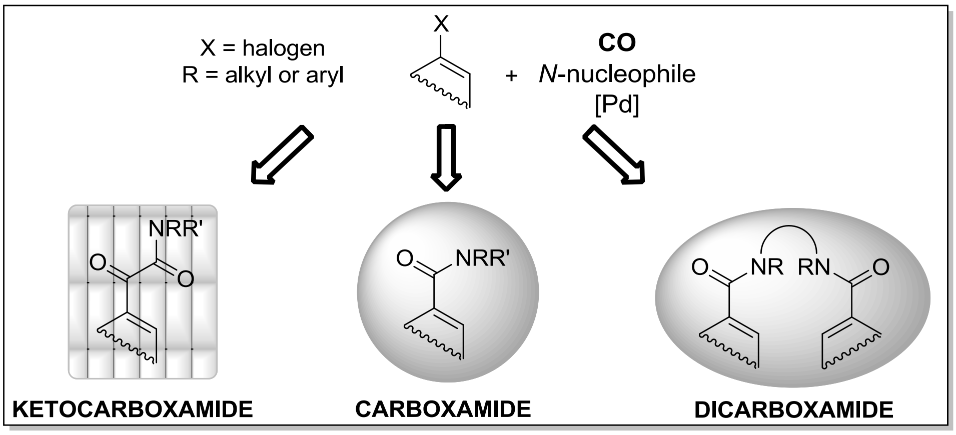

Figure 1: Different types of aminocarbonylation products.

In this communication, we present our recent achievements on the application of Pd-catalyzed aminocarbonylation of aryl and alkenyl halides (Figure 1) as a versatile synthetic tool to prepare different families of carboxamides,[3] ketoamides[4] and dicarboxamides[5] with biological relevance, structurally diverse as steroid, alkaloid and phthalocyanine derivatives.

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OC-17 COMPOSING MATERIALS: A PHOTOCATALYST SYMPHONY

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Solar to chemical energy conversion is the key process by which the biosphere works the energy cycle. The uses of solar energy are manifold in what concerns chemical and engineering applications. From photochemical water treatment to photogeneration of molecular hydrogen and oxygen (H_2 and O_2) from water splitting, passing through photocatalytic synthesis of fine and specialty chemicals, a portfolio of promising technologies and processes is available. In the past years, various inorganic and organic systems, consisting of single or multiphase materials, have been developed as performance photocatalysts for many technological applications. However, the base knowledge on the subject is still very limited. A good example is the degradation of emerging pollutants: a 10-year search on the photocatalytic decomposition of pharmaceuticals like tetracycline (and metabolites), shows no more that a few hundred papers (Figure 1).

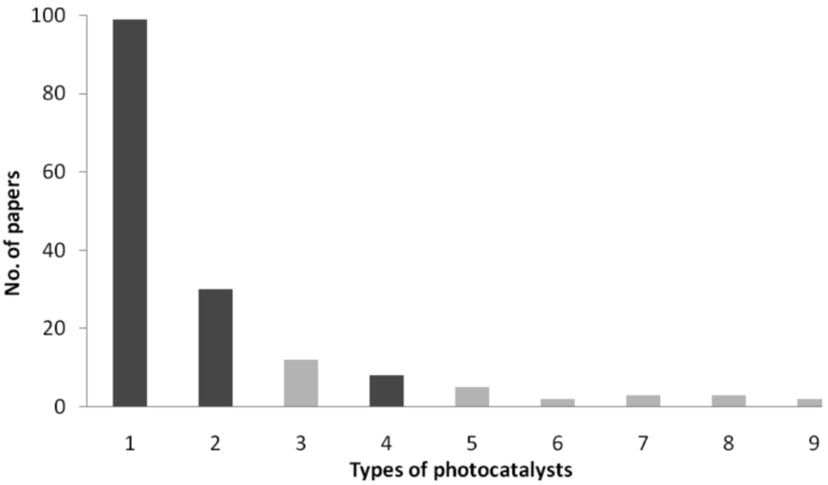

Figure 1: Number of publications (2004-2013) concerning photocatalytic degradation of tetracycline pharmaceuticals with different available photocatalysts: **1. TiO_2, 2. metal and non-metal doped TiO_2,** 3. photo-Fenton catalyst, **4. ZnO**, 5. SiO_2, 6. mixed metal oxides, 7. Titanate nanofibers, 8. graphene-TiO_2 composites, 9. TiO_2/fly-ash.

In this communication we will pass on review our recent breakthroughs in the development of composite photocatalysts and reaction engineering systems, for solar and artificial light applications in environment, energy and synthesis.

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OC-18 PHOTOLUMINESCENT LANTHANIDE-POLYPHOSPHONATE MOFs AS HETEROGENEOUS CATALYSTS

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Metal-Organic Frameworks (MOFs) are organic-inorganic hybrid materials that owing their intrinsic properties (*e.g.*, porosity, catalysis and luminescence) have found potentiality to be applied in gas storage and separation processes, sequestration of CO_2, capture of hazardous chemical species, drug delivery, heterogeneous catalysis, as optical sensors, among others [1].

The self-assembly between (benzene-1,3,5-triyltris(methylene))triphosphonic acid (H_6bmt) and lanthanide chloride salts led to the preparation of two families of lanthanide-based MOFs: i) 3D $[Ln_2(H_3bmt)_2(H_2O)_2]\cdot H_2O$ [where Ln^{3+} = La^{3+} (**1**), Ce^{3+} (**2**), Pr^{3+} (**3**), Nd^{3+} (**4**), $(La_{0.95}Eu_{0.05})^{3+}$ (**5**) and $(La_{0.95}Tb_{0.05})^{3+}$ (**6**)] under hydrothermal conditions (180 ºC for 3 days) or microwave irradiation (5 minutes above 150 ºC); and ii) 1D $[Ln(H_4bmt)(H_5bmt)(H_2O)_2]\cdot 3H_2O$ [where Ln^{3+} = La^{3+} (**7**), $(La_{0.95}Eu_{0.05})^{3+}$ (**8**) and $(La_{0.95}Tb_{0.05})^{3+}$ (**9**)] under microwave irradiation (40 ºC for 5 minutes). The catalytic performances of **1** and **7** were investigated in the methanolysis of styrene oxide (PhEtO; Figure 1), with **7** exhibiting an outstanding activity converting 100% of PhEtO at 55 ºC for only 30 min. The photoluminescent properties of **5** and its dehydrated form (**5-dehyd**) were also studied.

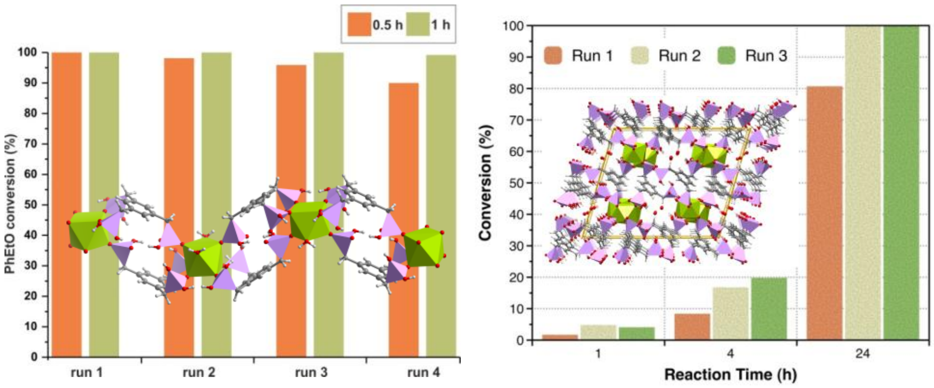

Figure 1: Catalytic performance of MOFs **1** and **7** in the methanolysis of PhEtO.

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OC-19 APPLIED ORGANIC MATERIALS AS FUNTIONAL IONIC LIQUIDS

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The development of applied organic materials as functional ionic liquids that can combine one or more properties is relevant for academic and industrial applications [1]. In this context, we have prepared different multi-responsive ionic liquids based on photochromic (*light effect*); electrochromic (*electrical potential effect*); luminescent (*UV light effect*) and magnetic (*magnetic field effect*) scaffolds. Firstly, two intrinsically photochromic and magneto-electrochromic based on azobenzene and EDTA metal complexes were prepared and characterized respectively [2,3]. Then, novel electrochromic ionic liquids based on symmetric and non-symmetric disubstituted alkyl- and oxo-bipyridinium cations combined with iodide or bromide, bis(trifluoromethanesulfonyl)imide [NTf_2] and docusate [AOT] as anions have been prepared[4]. The most promising electrochromic bipyridinium ILs have been tested in efficient liquid and solid state electrochromic devices using an adequate electrolyte. The type of electrochromic based IL and selected counter-ions influence; their reversibility and stability performances[5,6]. Also, intrinsically luminescent and magnetic ionic liquids incorporating organic fluorescent moieties as well as paramagnetic metal complexes (e.g. transition metals and lanthanides) have been developed[6,7]. The selection of paramagnetic ion and biocompatible counter-ions can be relevant in order to investigate their potential for selective separation processes as well as biological or medical applications.

Figure 1: *Examples of Applied Organic Materials based on Functional Ionic Liquids*

Finally, novel tribological and energetic ionic liquids based on task-specific salts and high-rich nitrogen cation and anion scaffolds such as guanidinium; alkylimidazolium; triazolium and tetrazolium as well as dicyanamide, tricyanomethane, thiocyanate, tetracyanoborate and azide have been developed [8].

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OC-20 PHOTORHEOLOGICAL SYSTEMS BASED ON 2-HYDROXYCHALCONES, CINNAMIC ACIDS AND COUMARINES

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Photoresponsive materials are subject of longstanding fundamental and practical interest. In particular, fluids whose rheological properties, such as viscosity, can be controlled by light are of interest for a variety of applications.[1] We have recently integrated photochromic 2-hydroxychalcone units as an addressable functionality to achieve the reversible control of the organization process that induces sol-to-gel transitions [2] or the photocollapsing of pNIPAM particles.[3]

Recently, we have engaged into the synthesis of photoresponsive ionic liquids based on the photochemical reactions of coumarins and cinnamic acids. Irradiation of these materials leads to significant changes in melting points and viscosity. For cinnamic acid derivatives, Figure 2, irradiation leads to *trans-cis* photoisomerization (NMR) with significant reduction of melting temperatures (DSC) of the ionic liquids due to the destruction of an intricate network of supramolecular interactions (X-ray crystallography). Physical and chemical transformations are completely reversible upon irradiation at lower wavelengths of ionic liquid solutions in acetonitrile.[4] In the case of coumarin-based ionic liquids, irradiation leads to an increase in viscosity (rheological measurements). The commonly observed photodimerization reaction of coumarins is not responsible for this outcome as suggested by NMR and by the fact that the reaction quantum yield is concentration independent over 4 orders of magnitude. Apparently, there is an opening of the lactone ring with formation of carboxylic acids which will promote a higher extent of hydrogen bonding and an increase in viscosity. A review of all these results will be presented.

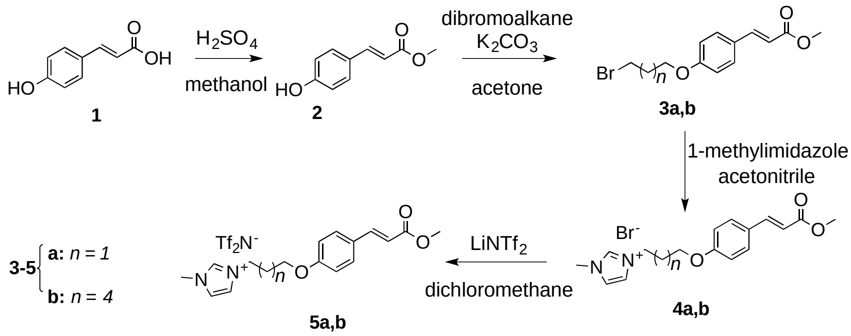

Figure 2. Synthetic pathway for the preparation of cinnamate ionic liquids.

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OC-21 POTENTIATION OF PRO-OXIDANT AND ANTIOXIDANT EFFECTS IN PHOTODYNAMIC THERAPY

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Reactive oxygen species (ROS), notably superoxide ($O_2^{\bullet-}$), hydrogen peroxide (H_2O_2) and hydroxyl radical ($OH^{\bullet}$), can damage a variety of biomolecules. Interestingly, compared with their normal counterparts, many types of cancer cells have increased levels of ROS [1]. The hypothesis that tumor cells could be more vulnerable to additional production of ROS was explored by several therapeutic approaches including photodynamic therapy (PDT) [2].

The local oxidative stress produced by PDT is antagonized in cells by three major antioxidant mechanisms: superoxide dismutase (SOD), catalase and glutathione system. Small molecules such as vitamin E and vitamin C (ascorbate) complement the control of ROS by the antioxidant enzymes.

This work reports the combination of F_2BMet (or LUZ11) [3] PDT with the pro- or antioxidant effect of ascorbate, and with the inhibitors of antioxidant defenses in A549 (human lung adenocarcinoma) and CT26 (mouse colon adenocarcinoma) cells.

The PDT efficacy is potentiated by the inhibition of Mn-SOD in cells with lower SOD levels, such as A549 cells. The addition of ascorbate further potentiates phototoxicity in A549 cells, presumably by electron transfer to the radical cation of the photosensitizer and consequent increase in the turnover of radicals. CT26 cells have a higher SOD activity level and are less sensitive to Type I processes. The phototoxicity towards CT26 cells seems to be mostly mediated through singlet oxygen. This contribution to the understanding of the cellular responses to oxidative stress offers guidance to improve the outcome of PDT in combination with other therapies.

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OC-22 CHARACTERIZATION OF THE EXCITED STATES OF 7-HYDROXY-4-METHYL-8-NITROCOUMARIN

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Coumarins are, and in particular the 7-hydroxycoumarins (the umbeliferones), naturally occurring compounds with applications in pesticides, sensors, laser dyes, photosensitizers, etc. [1, 2]

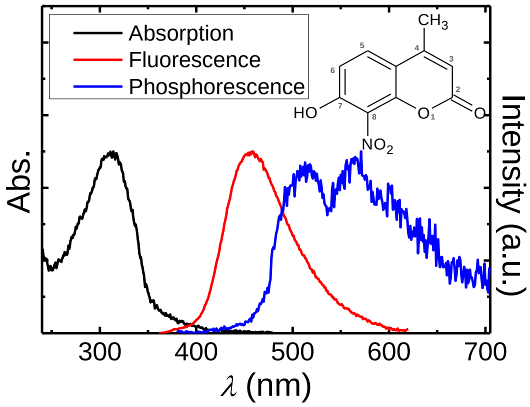

Figure 1: (A) Structure and (B) electronic spectra of 7H4M8NC in water (pH~2.1) [phosphorescence emission in a mixture of ether: ethanol: ammonia (10:9:1)].

A comprehensive investigation of the coumarin 7-hydroxy-4-methyl-8-nitrocoumarin (7H4M8NC) has been undertaken aiming to understand the effect of the addition of the nitro group in the photophysical properties of 4-methylumbeliferone (4MU). The study includes the photophysical characterization (steady state and time-resolved fluorescence and/or phosphorescence) in water as a function of pH and of the water fraction in dioxane:water mixtures as in other (basic, neutral and acid) media. As with other 4MUs [2,3], the ground and excited state present different species depending on the solvent media. From the overall study pK_a and pK_a^* values were determined and a kinetic scheme was proposed (with the determination of all rate constants) aiming to rationalize the photophysical behaviour of 7H4M8NC.

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OC-23 EUGENOL MICROENCAPSULATED USING SIMPLEX-CENTROID MIXTURE DESING

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Eugenol is a phenolic compound present naturally into different essential oils or in plants extracts, including cinnamon, basil, nutmeg, and clove. It is known for its antioxidant properties [1] and activity against different microorganisms, like *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeuroginosa*, *Salmonella typhy* [2]. However, its volatility, hydrophobic nature and instability in presence of oxygen, humidity and heat, must be overcome when using eugenol in certain food systems. Microencapsulation in biocompatibles materials is a promising alternative to allow its use in numerous food products and the efficiency of microencapsulation is a key parameter to be determined. The objective of this work was to evaluate the encapsulation efficiency of eugenol according to varying proportions of encapsulating agents by mixture design. Microparticles were obtained by spray-drying of dispersion using carrageenan and proteins (whey protein with low lactose content, rice bran protein and bovine serum albumin) as encapsulating agent and Tween-80 as surfactant. Concentrations of eugenol, carrageenan and Tween-80 were fixed in all experiments, and the proteins concentration varied according to simplex-centroid mixture design. Were studied each one of the proteins isolated, and its binary and ternary interactions. Eugenol recovery (defined as the amount of eugenol present in the microcapsules after the spray-drying process) and encapsulation efficiency (eugenol effectively encapsulated in the capsules) were calculated by UHPLC with UV-Vis detector at 280 nm. The variation of protein mixture has significant influence on the values of recovered eugenol and encapsulation efficiency. Formulations with rice bran protein and of albumin, applied alone, presented greater values of eugenol recovery (104.5 and 86.5%wt, respectively), demonstrating that these proteins allow to obtain stable dispersions during spray-drying, minimizing the loss of eugenol during the process. The interaction of rice bran protein and albumin allowed greater value of encapsulation efficiency. The encapsulation efficiency results for the ternary interaction formulations were less than 18%wt. Results demonstrated that the eugenol can be efficiently encapsulated using the spray-drying process when albumin and rice bran protein were combined, with efficiency encapsulations up to 79,3%wt the conditions studied.

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OC-24 MULTIELEMENT COMPOSITION OF SKINS, SEEDS AND BERRIES OF GRAPES AND ITS RELATIONSHIP TO SPECIFIC SOIL TYPE

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Trace elements are generally defined by biological and biochemical research as elements that are present in very low concentrations in the organism (usually below 0.01%) and should be defined as elements not identified as essential for living beings [1]. Among those elements, micronutrients (e.g. Zn, Mn, B, Cu) are sometimes also referred to and classified as trace elements. Elements are taken up by the roots of plants and passed on to the grapes, which means that wine multielemental composition is strongly influenced by the solubility of inorganic compounds of the soil [2]. It has been shown that individual vineyard areas have unique isotopic and/or trace-element “signatures” that permit to identify the provenance of a specific wine [3]. Inductively coupled plasma mass spectrometry (ICP-MS) has been widely used in the determination of trace elements composition and quantification. In this work, samples of berries, skins and seeds from grapes of two different vineyards from distinct Wine Regions of Portugal (*Quinta dos Carvalhais* – Dão Wine Region and *Herdade do Peso* – Alentejo Wine Region), whose different soils had been previously characterized, were collected and their multielement composition determined by ICP-MS, after suitable pretreatment of the samples by high-pressure microwave digestion. The objective of this work is to determine if there is a relation between specific soil type and respective trace elements composition and pin-point with consistency the organoleptic characteristics these elements can convey to the wine.This knowledge will lead to a more accurate and sustainable vineyard management by improving efficiency in resource usage and defining tailor-made strategies for the production of wines with expected characteristics, minimising risks, costs and targeting particular markets as well as consumer’s preferences.

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OC-25 ARGON-ENRICHED ATMOSPHERES PRESERVE THE OVERALL QUALITY OF BUCKLER SORREL DURING COLD STORAGE

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Nowadays, consumers are looking for healthy, convenient and more sustainable foods with different organoleptic properties of those daily consumed. Wild edible plants can contribute to this demand, since they are important inputs of health-promoting compounds and considered as added-value foods for commercialization [1]. A good example is buckler sorrel (*Rumex induratus* Boiss. & Reut.), an underutilized leafy vegetable appreciated especially in salads due to its peculiar sensory properties [2]. Its revalorisation is therefore a sustainable strategy to improve the diversity of available foods and can be achieved by improving their shelf-life for an extended period of commercialization. Using modified atmosphere packaging (MAP), compositional changes associated with maturation and senescence can be delayed and the initial fresh state and quality prolonged. Inert gases such as argon and nitrogen have been tested, but the literature describing their application and benefits is still limited [3]. In this study, buckler sorrel specimens, sustainable wild harvested in the Northeast region of Portugal, were rinsed in tap water and submitted to different packaging atmospheres: MAP enriched with argon and nitrogen, air-packaging, and vacuum-packaging (no atmosphere). Colour, nutrients, hydrophilic and lipophilic compounds, and antioxidant properties were analyzed after gathering and past 12 days of storage at 4 ºC. The results were evaluated through a categorical principal components analysis (CATPCA) in order to find the most suitable atmosphere. Nitrogen-enriched MAP did not induced detachable effects on the evaluated parameters. Air-packaging preserved higher amounts of polyunsaturated fatty acids (mainly due to linoleic and linolenic acids). Vacuum-packaged samples showed higher amounts of γ-tocopherol, monounsaturated fatty acids and flavonoids and similar results were found for argon-enriched MAP, with the additional advantage of their higher antioxidant properties. Thus, this study highlights argon-enriched MAP as a suitable treatment to preserve the overall quality of buckler sorrel during cold storage.

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OC-26 DOXORUBICIN AND DAUNORUBICIN INTERACTIONS WITH NORMAL AND TUMORAL MEMBRANES: A COMPARATIVE STUDY USING LIPOSOMES

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Antracyclines (doxorubicin, daunorubicin) are among the most used drugs in cancer treatments. In order to be conducted to the desired intracellular targets (the DNA), these chemotherapeutic agents need to cross multiple barriers, including membranes of cancer cells. Therefore drug-membrane interactions are inevitable, play essential roles in drugs' therapeutic activity and profoundly influence the chemotherapy efficacy. In this sense, the present work aimed to mimic the tumor and normal cells external environment, using liposomes as model membranes, and to study the interactions between several anticancer drugs with such models (Figure 1). Regarding those interactions, different biophysical parameters were assessed using liposomes composed by DOPC:DMPC:DPPS:DOPE (1:3:1:2) (at pH 6.3) and DMPC:SM (4:0.9) (at pH 7.4) to mimic the tumor and the normal cell, respectively. Antracyclines partition within membranes was determined using a liposome/water system by derivative UV/vis spectrophotometry. Studies of drug location in the membrane were carried out using labeled liposomes with fluorophores that present a well-known membrane position and depth, by steady-state and time resolved fluorescence quenching.

The overall results obtained contributed to unveil the importance of drugs-membrane interactions in antineoplastic therapeutic action and side effects.

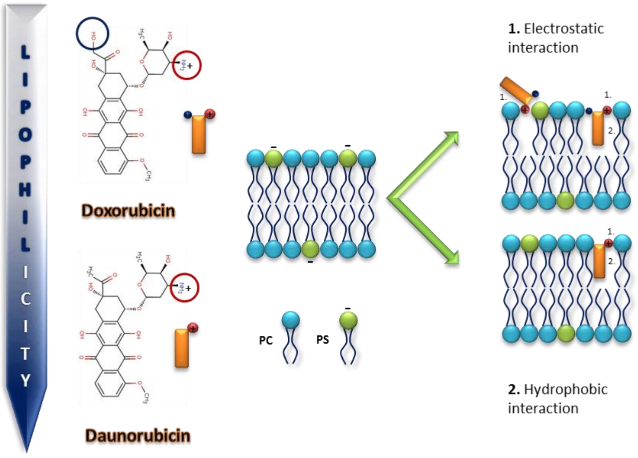

Figure 1: Schematic representation of the effects of drugs of different lipophilicity (daunorubicin and doxorubicin) on model membranes.

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OC-27 DEVELOPMENT OF TETRAPYROLIC MACROCYCLES AS MOLECULAR IMAGING PLATFORMS

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Tetrapyrrolic macrocycles such as phthalocyanines and porphyrins derivatives hold a remarkable variety of functional properties in natural and artificial systems. They represent one of the most widely studied chemical structures, particularly in biomedical applications. They possess favorable properties, such as long wavelength absorption and emission at an appropriate range of wavelengths (especially in the near infrared region, NIR); easy derivatization, preferential uptake in tumors and low in vivo toxicity.
Here we present the recent contributions of the Catalysis & Fine Chemistry and the state of the art on the synthesis and modulation of tetrapyrrolic macrocycles that show idealized properties for medical imaging, including Fluorescence Imaging, Magnetic Resonance Imaging and Positron Emission Tomography [i], discussing the role of structural modifications to encompass the suitable photophysical and amphiphilic properties required for the development of ideal photosensitizers for imaging oriented applications.

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OC-28 EVALUATION OF THE PH-SENSIBILITY OF DIFFERENT CHITOSAN-BASED HYDROGELS FOR THE CONTROLLED RELEASE OF DAPSONE

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Dapsone (DAP) is a bactericidal agent used in the treatment of leprosy, caused by *Mycobacterium leprae*. Despite its therapeutic potential, DAP has low solubility, which may result in low therapeutic index and a high microbial resistance. Recently, new approaches have been applied in order to increase DAP solubility. Nevertheless, the kinetic solubility profiles of some drug delivery systems based on water-soluble polymers generally exhibit an initial burst release of drug, followed by a sharp decline in drug concentration due to the nucleation and crystallization events under non sink conditions. In this context, controlled delivery systems provide an alternative approach to regulating the bioavailability of these kind of therapeutic agents. The use of hydrogel systems for the controlled release of drugs seems to be an advantageous strategy since they may exhibit dramatic changes in their swelling behaviors and network structures in response to environmental stimuli. Moreover, hydrogels derived from natural polymers, as chitosan (CS), have been widely used due to their advantageous properties, such as their non-toxicity, biocompatibility, and biodegradability [1-3]. Thus, the purpose of this study was to prepare and evaluate CS/Polymers hydrogel as a gastrointestinal drug-controlled release system. For this purpose, different polymers (PVP K30, PEG 6000 and HPMC) were used for the crosslinking, in different ratios. The hydrogels were evaluated regarding swelling degree in different pH (1.2 and 6.8) and the release profile of dapsone. Further, the obtained hydrogels were characterized by FT-IR and SEM.

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OC-29 DRUG-MEMBRANE INTERACTIONS: UNRAVELING DICLOFENAC'S BEHAVIOUR

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Nonsteroidal anti-inflammatory drugs (NSAID) represent one of the most widely consumed pharmaceuticals due to their anti-inflammatory, analgesic and antipyretic properties. Their chronic consumption is associated with a wide spectrum of unwanted effects (gastrointestinal, cardiovascular and renal adverse effects, among others). [1] Since the currently well-described NSAID main mechanism of action – inhibition of the prostaglandins (PG) biosynthesis – does not fully explain their therapeutic and toxic effects, other mechanisms such as their action at the membrane level must be explored. [2]

In this sense, this work intends to unravel diclofenac's interactions with biological membranes, using liposomes made of 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC) as membrane models. The preparation of large unilamellar vesicles of DMPC was accomplished through lipid film hydration, followed by extrusion. The drug's partition coefficient was assessed by derivative spectrophotometry and its effect on the thermal behaviour of DMPC was evaluated by differential scanning calorimetry and fluorescence anisotropy. To study the drug's location within the liposome, fluorescence quenching assays were executed. All experiments were performed under 3 pH conditions (7.4, 5.0 and 3.0) to mimic different microenvironments found *in vivo*, including the pH gradient of gastric mucosa and the pH of inflamed cells.

In general, diclofenac's interaction with phosphatidylcholine bilayers is highly dependent on its ionization state. As the protonated form of the drug has more affinity to the bilayer, major alterations of the lipid phase transition parameters as well as the ability to quench fluorescence probes (with well-known membrane location) are more notable at lower pH. Therefore, the medium pH is a key factor to understand the membrane effects of diclofenac *in vivo*. The gathered results will be discussed in terms of relevance for the enlightenment of the drug's therapeutic and toxic actions.

Acknowledgements: This work received financial support from the European Union (FEDER funds through COMPETE) and National Funds (FCT, Fundação para a Ciência e Tecnologia) through project Pest-C/EQB/LA0006/2013. The work also received financial support from the European Union (FEDER funds) under the framework of QREN through Project NORTE-07-0124-FEDER-000067.To all financing sources the authors are greatly indebted.

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OC-30 POxylated NANOCARRIERS FOR PULMONARY DELIVERY

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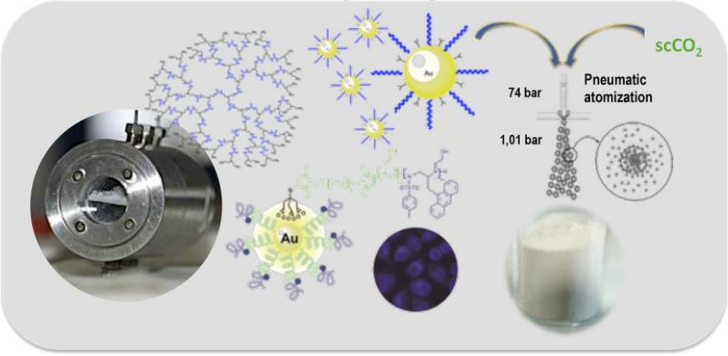
"Green" $scCO_2$-based methodologies are well suited to improve synthesis and materials processing leading to the assembly of three-dimensional multifunctional constructs. Novel routes are being explored to synthesize stimuli-responsive polymers, thus enabling the design of efficient platforms for sensing and delivery of therapeutic payloads. By using $scCO_2$, either as C1 feedstock or as solvent, simple, economic, efficient and clean routes can be designed to synthesize materials with unique properties such as PURE-type dendrimers, oxazoline- and based oligomers [1-3]. These new biocompatible, biodegradable, fluorescent and water-soluble polymeric materials can be engineered into multifunctional constructs with antimicrobial activity, targeting moieties, labeling units, and/or efficiently loaded with therapeutics. In particular, the remarkable features of POxylated polyurea dendrimers as potential theranostic nanodevices will be highlighted [4,5]. Additionaly, it will be described how $scCO_2$-assisted spray drying can be used to prepare controlled release formulations with improved regional targeting within the lungs (e.g., airway versus alveoli and vice versa) and containing active targeting moieties.



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OC-31 INORGANIC, ISOTOPIC AND MINERALOGICAL COMPOSITION OF URBAN $PM_{2.5}$ AT THE WESTERN EUROPEAN COAST

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Particulate matter (PM), especially with a diameter less than 2.5 µm ($PM_{2.5}$), has been a parameter of global concern within the field of atmospheric research due to its relation to serious health issues. A great deal of uncertainty still exists regarding the chemical diversity of $PM_{2.5}$, particularly in urban areas. This study aims at assessing the inorganic (major water-soluble inorganic ions (WSIIs)), isotopic ($^{86}Sr/^{87}Sr$), carbonaceous (organic carbon and elemental carbon), and mineralogical composition of $PM_{2.5}$ samples collected during a one-year period in an urban site at the Western European Coast (Aveiro, Portugal). The concentration of each component was found to be highly dependent on the seasonal events, with the carbonaceous component being the major constituent of the $PM_{2.5}$ in almost all seasons (Fig.1a). In warm seasons, the concentration of SO_4^{2-} is higher than during colder seasons, which is indicative of secondary formation (mediated by sunlight) in the atmosphere [1]. On the other hand, the concentration of the more volatile NO_3^- ion is highest for samples collected in colder seasons, which can be explained by the combined effects of lower air temperature and an increase of biomass burning and vehicles emissions during these seasons [1,2].

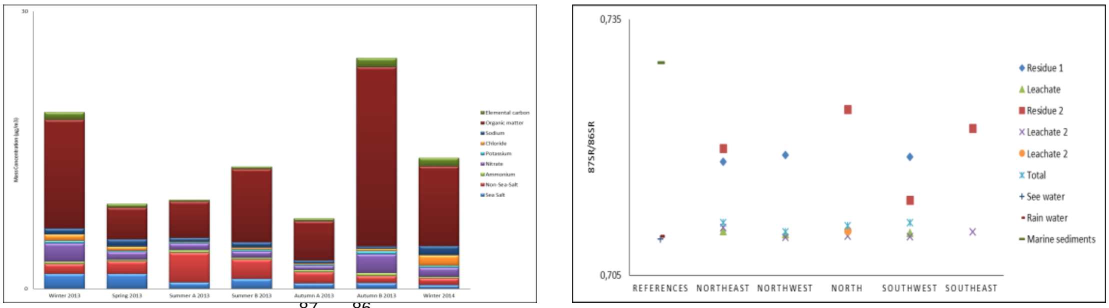

Figure 1: a) Seasonal distribution of the average mass concentrations of WSIIs, organic matter, and elemental carbon in $PM_{2.5}$; b) $^{87}Sr/^{86}Sr$ isotopic ratios in residues and leachates of $PM_{2.5.}$

The $^{86}Sr/^{87}Sr$ isotopic study showed a predominant marine influence (Fig.1b) for all $PM_{2.5}$ samples, which is in agreement with the X-ray diffraction results, which suggest the presence of gypsum with a clear marine origin, on almost all samples. Feldspar, with an anthropogenic origin, was also common to almost all $PM_{2.5}$ samples.

Acknowledgements: Centre for Environmental and Marine Studies (UID/AMB/50017/2013, University of Aveiro, Portugal) and the Portuguese Science and Technology Foundation (FCT), through the European Social Fund and “Programa Operacional Potencial Humano – POPH”, are acknowledged for financial support. This work was also funded by FEDER under the Operational Program for Competitiveness Factors – COMPETE and by National funds via FCT within the framework of research projects CN-linkAIR (PTDC/AAG-MAA/2584/2012) and ORGANOSOL (PTDC/CTE-ATM/118551/2010).

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OC-32 BIOGEOCHEMISTRY OF CANADIAN SUBARCTIC THERMOKARST THAW LAKES

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Rising temperatures are beginning to rapidly thaw the Arctic permafrost, and this may be a driving force for the release of trace elements, organic carbon and greenhouse gases into water and air. These inputs could have serious consequences for aquatic biota and may further accelerate global warming in the North.

Several studies have evaluated the concentrations of carbon compounds and trace elements in thaw lakes, and have examined some of the biogeochemical processes responsible for the partitioning, speciation and fate of certain elements on these lakes. However the chemical structure of the organic matter and its role in biogeochemical processes in thaw lakes remains unknown.

In order to contribute to the understanding of the role and organic matter structure in biogeochemical processes in thaw lakes, a field campaign was undertaken in the Canadian subarctic region of *Kuujjuarapik-Whapmagoostui* (QC) in June-July 2014 as a part of the Canadian ADAPT and the Portuguese PERMACHEM projects. Six thaw lakes and two rock basin reference lakes were sampled. Water samples were collected at different depths and analysed for labile and total dissolved metals. Duplicates were sampled for ^{1}H NMR and for mass spectrometry (HPLC-MS). Water samples were also collected for dissolved sulphur speciation. Lake sediments and nearby soils were also sampled and analysed using the equivalent techniques for water and also by X-ray diffraction analysis in powder, and solid-state ^{13}C NMR techniques. Finally, subsamples of soil and sediment were ^{14}C-dated.

Preliminary results showed that in thaw lakes the concentrations of some trace elements in general increase with the depth. The proportion of labile elements also varied, and it was more related with the anoxia of the water, assessed with a Hydrolab profiler and also by their HS^- content. In soils and sediments the sulphur composition also varied from lake to lake. In high carbon content lakes more than 50% of the total sulphur was in organic form, while in the reference rock basin lakes the contrary was observed. Interestingly the high trace element content was also proportionally higher in high organic sulphur anoxic lakes, suggesting precipitation of those elements from the water column. NMR and MS analyses are currently in progress.

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OC-33 NOVOS FOTOSSENSIBILIZADORES COM POTENCIAL ACTIVIDADE ANTIBACTERIANA

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A aplicação de sulfonamidas como agente antibacteriano encontra-se bastante consolidada, contudo, o desenvolvimento de resistência por parte dos microorganismos é a sua principal desvantagem [1].Deste modo, surge como um grande desafio, a descoberta de novas entidades moleculares capazes de promover a inativação de bactérias sem induzir resistência.

Motivados pelo conhecimento de que os derivados de porfirinas utilizados em terapia fotodinâmica (PDT) possuem estas propriedades [2], desenvolvemos métodos de síntese de novas moléculas que combinam na sua estrutura sulfonamidas [3] com porfirinas ou os seus derivados reduzidos [4], a fim de obter compostos que possam atuar simultaneamente como antibacterianos *per si* e como fotossensibilizadores para inativação de bactérias com recurso a PDT. A respectiva caracterização fotofísica (absorção, fluorescência, oxigénio singleto e fotodegradação) e os testes realizados *in vitro* com a linha celular de fibroblastos 3T3 são, também, apresentados e discutidos.

Agradecimentos: O autor agradece à FCT-Portugal e à QREN/FEDER (COMPETE Programa Operacional Factores de Competitividade) pelo financiamento (UID/QUI/00313/2013). Os dados de RMN foram obtidos num nmrccc (http://www.nmrccc.uc.pt; RECI/QEQ-QFI/0168/2012).

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OC-34 TURNING PERIODIC MESOPOROUS ORGANOSILICAS SELECTIVE TO CO_2/CH_4 SEPARATION: CONTROLLED DEPOSITION OF ALUMINUM OXIDE BY ALD

Mirtha A. O. Lourenço[1], Ricardo M. Silva[1], Rui F. Silva[1], Nicola Pinna[2], Stephane Pronier[3], João Pires[4], José R. B. Gomes[1], Moisés L. Pinto[5], Paula Ferreira[1]

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The upgrading of biogas via CO_2/CH_4 separation using an adsorbent material is a hot topic of research in the field of renewable energies. Periodic mesoporous organosilica (PMO) [1] has shown high potential to be applied in this process due to its ideal textural properties, but further optimization is required. With the purpose of tuning the properties of PMO, atomic layer deposition (ALD) [2] was used for the first time to modify a phenylene-based PMO with Al_2O_3. The number of deposition reaction cycles (from 2 to 100 cycles) were studied. The resultant composites were characterized by TEM/EDS, PXRD, N_2 adsorption isotherms and solid-state NMR, in an attempt to understand their final structural, physical and chemical properties. A clear correlation between the amount of deposited Al_2O_3 on the PMO and the number of deposition cycles was obtained. It was found that the increase of the number of deposition cycles promoted a decrease of the specific surface area and pore volume of the PMO material. In addition, different Al_2O_3 sites (e.g. tetra-, penta- and hexa-coordinated aluminum species) were obtained. The meso- and molecular-scale periodicity orders of the PMO were preserved. The prepared composites were tested in the adsorption of pure CO_2 and CH_4 gases and results indicated highest selectivity for CO_2/CH_4 separation for materials having larger amounts of tetrahedral (Al^{IV}) and pentacoordinated (Al^{V}) aluminum species.

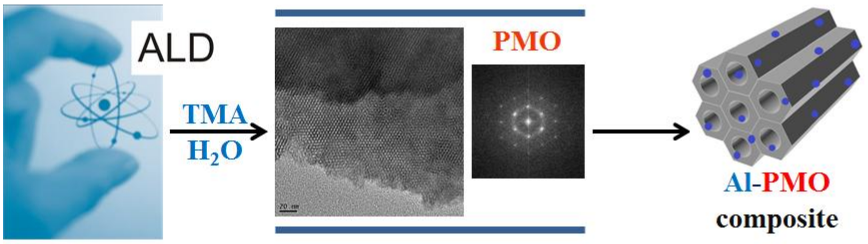

Figure 1: Preparation of Al-PMO composites.

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OC-35 SYNTHESIS OF NEW 2-HALO-2-(TETRAZOL-5-YL)-2H-AZIRINES

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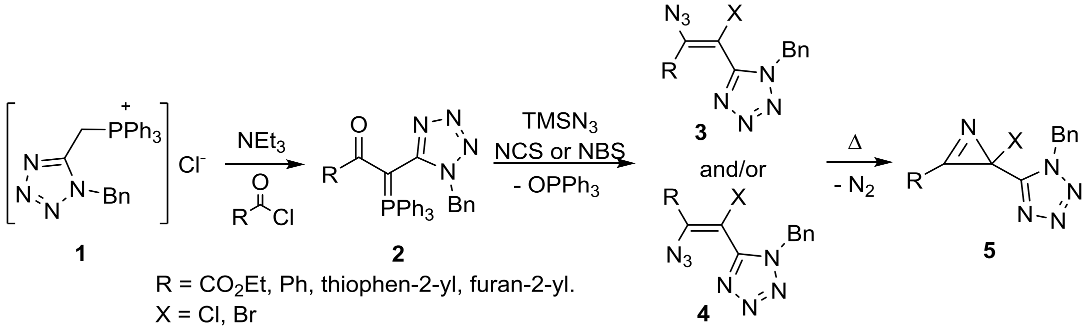
We have recently reported the synthesis of novel 2-(tetrazol-5-yl)-2*H*-azirines, using the Neber approach.[1] We envisaged that these three-membered heterocyclic compounds could be particularly interesting as building blocks for the synthesis of new 5-substituted tetrazoles. In fact, their reactivity towards imines has already been studied resulting in a novel and efficient route to 4-(tetrazol-5-yl)-1*H*-imidazoles, a class of compounds with potential biological activity.[2] Aiming to extend the reactivity of these 2-(tetrazol-5-yl)-2*H*-azirines we decided to prepare their 2-halo-2*H*-azirine derivatives, since the presence of the extra functional group could be particularly interesting.

Using the synthetic methodology previously developed in our group for the preparation of 2-halo-2*H*-azirines starting from haloazidoalkenes[3], we carried out reactivity studies of α-oxophosphorus ylides **1** bearing a tetrazole substituent. These ylides reacted with azidotrimethylsilane and *N*-halosuccinimides to afford 2-haloazidoalkenes **2** and/or **3**, which could be easily converted into the desired 2-(tetrazol-5-yl)-2-halo-2*H*-azirines **4** by thermolysis. Further details of this study will be disclosed.



R = CO_2Et, Ph, thiophen-2-yl, furan-2-yl.
X = Cl, Br

Scheme 1.

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OC-36 POLYPHENOLS & CARBOHYDRATES METABOLISM: COMPOSITION AND BENEFICIAL EFFECTS OF WILD ENDEMIC BERRIES FROM MADEIRA ISLAND

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In Madeira Island, several types of wild endemic berries are consumed fresh or processed as jam, juice or liquor. Here, we consider *Rubus grandifolius* Lowe and *Vaccinium padifolium* Sm. Local traditional medicine uses berries and leaves of these plants for several ailments, such as diabetes control and as depurative and diuretic.

This study aimed to investigate the components of these plants thus consumed, to confirm/dismiss their claimed health benefits.

A HPLC-DAD-ESI/MS^n validated method was used to establish phenolic profiles. Using ESI in negative mode, *O*-glycosilated flavonols (quercetin and kaempferol), quinic and caffeic acid conjugates were found in *Rubus,* while *Vaccinium* was characterized mainly by chlorogenic acids. In positive mode, several glycosylated anthocyanins were detected and quantified in both species

High antioxidant capacity is generally associated to berries species; in both cases, extracts of leaves presented a higher radical scavenger capacity (DPPH and ABTS assays) than berries.

Considering folk application, berries and leaves extracts were evaluated for their inhibitory activity towards key enzymes linked to type 2 diabetes using *in vitro* assays. Extracts showed stronger efficacy than acarbose (positive control) towards α-glucosidase and were less active towards α-amylase.

Acknowledgments: Thanks are due to FCT for a Ph.D. grant SFRH/BD/84672/2012 for Project PEst-OE/QUI/UI0674/2014; this work used equipments from the Portuguese National Mass Spectrometry Network (Contract RNEMREDE/1508/REM/2005) in the framework of the National Programme for Sicentific Re-equipment, with funds from POCI 2010 (FEDER).

OC-37 EDP - INOVAÇÃO PARA A SUSTENTABILIDADE NA EDP DISTRIBUIÇÃO

Pedro Carreira

A EDP Distribuição é a empresa que exerce a atividade de Operador de Rede de Distribuição, no território continental de Portugal, uma atividade regulada pela Entidade Reguladora dos Serviços Energéticos (ERSE), sendo titular da concessão para a exploração da Rede Nacional de Distribuição (RND) de Energia Elétrica em Média Tensão (MT) e Alta Tensão (AT), e das concessões municipais de distribuição de energia elétrica em Baixa Tensão (BT). A distribuição de energia elétrica é o nosso centro de atuação, a qual é pautada por elevados padrões de qualidade e eficiência, independência e transparência, consagrados no Código de Conduta da Empresa.

OC-38 INNOVNANO - INOVAÇÃO PARA A SUSTENTABILIDADE EM NANOMATERIAIS

Ricardo Gomes

A Innovnano é uma empresa de Nanotecnologia do grupo CUF, um grupo centenário na indústria química e o maior grupo Português com fabricas em Portugal e Espanha. A Innovnano desenvolve a sua actividade no campo dos materiais cerâmicos avançados e dos nanomateriais, com base num processo de síntese de micro e nanopartículas desenvolvido internamente, de carácter único e inovador a nível mundial. O nosso principal objectivo é ir ao encontro das necessidades do mercado em produtos de alta qualidade e os seus respectivos processos de produção. Sabemos que os pós de zircónica nanoestruturados são o futuro do alto desempenho das aplicações cerâmicas avançadas. Com a nossa tecnologia e experiência queremos explorar e desenvolver as suas propriedades no sentido de maximizar o seu potencial para aplicações inovadoras. A nossa tecnologia exclusiva de síntese é perfeitamente adequada para a produção na escala industrial de pós cerâmicos nanoestruturados para aplicações em materiais avançados. Além disso, o nosso processo de síntese usa precursores provenientes de matérias-primas de fontes sustentáveis, garantindo uma continuidade fiável e económica das matérias – primas e ainda apoia o crescimento sustentável da indústria de nanotecnologia.

OC-39 MARTIFER SOLAR - SU $\frac{N}{S}$TAINABILITY

José Alves

A Martifer Solar é uma empresa sediada em Portugal, presente em mais de 20 países em 4 continentes, tendo projectado e construído mais de 670 MW e gere mais de 600 MW em Serviços de O&M. Com base num track record comprovado e numa verdadeira presença mundial, a empresa oferece soluções completas 360º (desde a identificação do mercado e do local, passando pelo desenvolvimento, construção, até à ligação à rede e consequente operação das instalações), adaptadas às necessidades específicas de cada cliente, transformando a energia solar em activos “verdes” com rápido retorno financeiro garantido.

OC-40 EUROSPUMA - 50 ANOS DE SOLUÇÕES DE CONFORTO

Rui de Oliveira

A Eurospuma fabrica desde 1965 espumas de poliuretano de alta qualidade e também tecidos não tecidos desde 1979. A sua vocação claramente inovadora permite o desenvolvimento de produtos sustentáveis e de reconhecida qualidade em Portugal e no mundo. Nós fabricamos sensações!

OC-41 QUIMIJUNO - ALTERNATIVAS AOS SOLVENTES TRADICIONAIS DE USO INDUSTRIAL

Nuno Rebanda

Criada em 2005, a QUIMIJUNO opera na distribuição de produtos químicos industriais nas áreas de solventes e diluentes, lubrificantes, detergentes e produtos de manutenção industrial.

Com instalações na Zona Industrial de Condeixa que reunem todas as condições de segurança exigidas na sua atividade, a QUIMIJUNO é autónoma em termos de armazenamento de matérias-primas, formulação e embalamento. Possui também um laboratório devidamente equipado para as necessidades de controlo de qualidade dos produtos com que trabalha.

A QUIMIJUNO cobre todo o território continental e exporta para outros países na UE e também para África e Médio Oriente.

OC-42 AMORIM & IRMÃOS - CULTURA DE INOVAÇÃO - AMORIM E A UNIVERSIDADE

Paulo Gil

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OC-43 FUROSEMIDE AND p-AMINOBENZOIC ACID COCRYSTALS. A NEAR INFRARED SPECTROSCOPY STUDY

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This work presents a process analytical technology (PAT) approach to monitor on-line cocrystallizations. Cocrystals are a class of crystalline solids consisting of two or more molecular species that are solid at room temperature and held together by non-covalent bonds [1]. Pharmaceutical cocrystals offer a number of opportunities to modify physical properties (e.g. solubility) of an active ingredient without changing its structure [2]. The increase of drug solubility is very important since more than 40% of the drugs delivered in tablet form have solubility problems and furthermore, almost 80-90% of the drug molecules at advanced stages of development will present solubility problems [1]. Furosemide, an active pharmaceutic ingredient belonging to class IV [1] (low solubility/low permeability) of the Biopharmaceutics Classification System was used as case study. p-Aminobenzoic acid was used as coformer. The cocrystallizations were made by the solvent evaporation method. A 1:1 molar ratio of furosemide and coformer were added to 8 ml of methanol and 1 ml of water and stirred at 150 rpm in an orbital stirring table during 16 hours until complete solvent evaporation. The on-line monitoring of the cocrystallizations was performed with a FT-NIR spectrometer fitted with a diffuse reflectance fiber optic probe. The tip of the reflectance probe was fixed 1 cm above the cocrystallization medium. A NIR spectrum was taken every 5 minutes [1]. To analyze the NIR spectra, principal component analysis was used. Cocrystals were characterized off-line by near infrared and mid infrared spectroscopy, X-ray powder diffraction, differential scanning calorimetry and hot stage microscopy.

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OC-44 STRATEGIES FOR MULTICOMPONENT SEPARATION OF NADOLOL STEREOISOMERS BY PREPARATIVE LIQUID CHROMATOGRAPHY

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The Simulated Moving Bed (SMB) technology is receiving an increasing interest as an alternative technique for the production of fine chemicals and pharmaceuticals. However, the classic SMB process is limited to the separation of binary (or pseudo-binary) mixtures or to the recovery of one single component from a multicomponent mixture. Several configurations have been proposed in order to extend the SMB technology to the separation of multicomponent mixtures by using a cascade of SMBs in series or other complex SMB related techniques like multi-zone SMB, intermittent SMB and JO processes. The JO technology allows the separation of ternary mixtures through a cyclic process constituted by two discrete steps. [1,2]

Nadolol is a pharmaceutical drug marketed as a mixture of its four stereoisomers and its prescription is related with some severe risks such as heart failure. The nadolol stereoisomers will be used in this work as a case study for the development of chromatographic strategies for multicomponent separation.

Recently, our research group reported the pseudo-binary separation of nadolol stereoisomers by SMB chromatography [3]. A SMB pilot unit with Chiralpak AD chiral stationary phase (CSP) was used to obtained the more retained stereoisomer 100% pure in the extract and the mixture of the other three stereoisomers being co-eluted in the raffinate.

This work will show how different strategies for multicomponent separation can be implemented, using different CSP, solvent compositions and SMB related techniques, namely:

a) The use of a different CSP, the Chiralpak IA, allowing the use of a wider range of solvents and therefore better separation performances than Chiralpak AD;

b) To achieve a final ternary separation, using the mixture of the three stereoisomers co-eluted in the raffinate, previously referred, as the feed for a subsequent JO process;

c) The separation of the two pairs of nadolol enantiomers using an achiral C18 material, followed by two parallel classic SMB binary enantioseparation processes.

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OC-45 ANALYSIS OF RADIONUCLIDES IN URANIUM MINES WASTE AND ENVIRONMENTAL SAMPLES IN PORTUGAL

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There are about 60 old uranium mines and several ore processing facilities with contaminated waste piles in the central region of Portugal. The results of environmental radioactivity monitoring allowed the assessment of radioactive contamination of mining and milling waste materials, soil, and water in the Mondego River basin and other rivers of central Portugal and the evaluation of radionuclide transfer risk to the population with food and water intake [1]. Some of the old mining sites have been already the subject of environmental remediation measures in order to reduce the dispersion of contaminants. The analyzes of River Mondego water performed in 2013 with high water flow, showed that dissolved radionuclide concentrations were relatively low. Radionuclide concentrations in suspended particulate matter and riverbed sediments including those from several tributaries have shown the persistence of significant radioactive contamination in some locations. Table 1 illustrates radionuclide concentrations in environmental samples of the region. As many of former uranium mine sites were not intervened yet and waste heaps containing radioactive materials remain exposed to weathering, the current radioactive contamination and the main vulnerabilities of Mondego River basin are assessed. Continued environmental radioactivity monitoring and completion of environmental remediation are essential to support the sustainable development of this region.

Table 1: Radionuclide concentrations in mine waste, soil, river sediments and (fraction <63 µm) and filtered water.

Sample	^{238}U	^{234}U	^{230}Th	^{226}Ra	^{210}Pb	^{210}Po
Mine waste (Bq kg^{-1})	10534±518	9740±480	3584±300	2763±293	4387±228	4387±228
Agriculture soil (Bq kg^{-1})	830±20	854±20	747±53	1067±312	913±53	913±53
Sediment R.Pantanha (Bq kg^{-1})	5057±186	5208±192	6984±445	1922±172	2842±145	2842±145
Sediment Aguieira Dam (Bq kg^{-1})	146±5	145±5.4	135±9	145±19	123±8	123±8
Water R.Pantanha (mBqL^{-1})	6771±398	6707±394	2.3±0.4	13.1±1.5	<0.06	9.7±0.5
Water Aguieira Dam (mBqL^{-1})	10.8±0.5	10.6±0.5	0.36±0.04	5.1±0.5	1.22±0.08	2.9±0.2

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OC-46 RECOVERY OF PALLADIUM FROM A SPENT INDUSTRIAL CATALYST BY LEACHING AND SOLVENT EXTRACTION

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Palladium, platinum, and related rare metals (platinum-group metals, PGMs) are nowadays considered critical raw materials. They are extensively used in automobile, chemical and electronics industry due to their specific physical and chemical properties [1]. In the chemical industry, PGMs are widely used to catalyze the synthesis of various organic compounds.

Catalysts are usually composed by metals, normally supported on porous materials such as alumina/silica; those metals may appear in different proportions, with concentration ranges from 2.5 to 20% [2]. The problem of the scarcity of PGMs in natural mineral deposits, and their rather irreplaceable applications, has been motivating a wide research aiming to their efficient and selective recycling from secondary sources. Hence, the development of new and modified hydrometallurgical processes to achieve the separation and concentration of PGMs from specific industrial leaches or effluents is important [3], and hydrometallurgy may play an important role to accomplish those objectives. In literature [2-4] different studies about the selective recovery of metals from spent industrial catalysts, using hydrometallurgical processes, can be found.

In this communication, the experimental development of a leaching process of a spent industrial catalyst, from a petrochemical industry in Portugal, is presented. The investigated catalyst is composed by metals like aluminum, palladium and chromium. Several parameters were controlled under the leaching process, such as the temperature (40, 60, 80 and 90ºC), the reaction time, the hydrochloric acid concentration of the leaching solution (4 and 6M HCl), the concentration of the oxidizing agent (1M HNO_3), the liquid-solid ratio (L/S), and particle size. Leaching with 6M HCl, at 60ºC for 1 hour, with an L/S=2 and an average particle size of 176µm, was adequate to solubilize more than 85% of Pd and less than 4% and 2% of aluminum and chromium, respectively. The “best” liquors obtained in the leaching process have been tested for preliminary extraction studies aiming to the selective recovery of palladium by solvent extraction [5].

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OC-47 OPTIMIZATION OF NANOSTRUCTURE LIPID NANOPARTICLES LOADED WITH METHOTREXATE: APPLICATION OF BOX-BEHNKEN DESIGN

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The main goal of this study was to optimize and assess the potential of lipid based nanoparticles namely nanostructured lipid carriers (NLC) as capable of carrying drugs [1,2]. Preliminary screening drug/lipid solubility study, allowed us to select Witepsol® E85 and Migliol® 812 as the solid lipid and liquid lipid for the NLC loaded with methotrexate (MTX). Then, a 3^3 Box Behnken experimental design was developed in order to study the influence of three independent variables [3]: amount of liquid lipid (X_1), surfactant amount (X_2) and amount of drug (X_3) on the dependent variables as mean particle size, polydispersity index (PDI) and entrapment efficiency (EE) values. Optimized NLC loaded with MTX were produced with 45 mg of liquid lipid, 47 mg of surfactant polyvinyl alcohol (PVA) and 18 mg of drug and evaluate their physical-chemical properties such as morphology, size, zeta potential, EE, storage stability, *in vitro* drug release and cytotoxicity were investigated. NLCs loaded with MTX exhibited spherical shape with 252 nm, PDI around 0.06 ± 0.02, zeta potential of -14 mV and an EE of 87%. *In vitro* release studies revealed a fast initial release followed by a prolonged release of MTX from the NLC up to 24 h so in physiological and inflammatory environments that allow us to simulate some skin conditions. No toxicity was observed in fibroblasts up to 48h. Thus, the optimized MTX-loaded NLC have the potential to be exploited as delivery system such topical, oral or parenteral delivery.

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OC-48 $scCO_2$-PHASE INVERSION TECHNIQUE: A SUSTAINABLE METHOD TO PRODUCE WOUND DRESSINGS ABLE TO PROMOTE A FASTER SKIN WOUND HEALING

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Human skin, as the largest external organ in the body, is daily exposed to several toxic substances and pathogens, making it an easy target to be damaged. Indeed, skin wounds are a major social and financial burden and their healing process is extremely complex. Hydrogels seem to be promising dressings since they can absorb the wound exudate, protect it from infection and promote the healing process by providing a hydrated environment [1]. Nevertheless, the usual methods to produce hydrogels are very time consuming and in the majority of the cases demand the use of toxic crosslinking agents. Supercritical fluids technology is a feasible alternative to those methods [2]. In this study PVA/CS dressings were developed using $scCO_2$ phase inversion technique. This technique can tailor the final structure of the dressing by tuning the processing conditions allowing the development of high porous materials, without using toxic organic solvents. These highly porous membranes gel in contact with biological fluids, a property that is crucial to enhance the wound healing process. Moreover, the dressings were functionalized with poly(1,3-glycerol dimethacrylate) microbeads and β-cyclodextrins loaded with ibuprofen to further improve the drug release profile according to the demands of a good healing process. The *in vitro* physicochemical and biological characterization of the membranes revealed that they have a suitable water uptake ability, vapor permeability, biodegradability and biocompatibility, assets that are fundamental for their application as wound dressings. The data collected from *in vivo* assays showed that these membranes have an anti-inflammatory effect and are pain-relief for the host while promoting a faster skin healing.

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OC-49 KEY FINDINGS ON DRUG TRANSIT AND P-GYCOPROTEIN EFFLUX MECHANISM BY MOLECULAR DYNAMICS SIMULATIONS

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Multidrug resistance (MDR) to anticancer drugs has become a serious health concern due to increasing chemotherapy failures worldwide. Notwithstanding the central role that efflux pumps like P-glycoprotein (P-gp) have in MDR onset, experimental studies classified additionally the lipid micro-environment where P-gp is inserted as determinant for the increased efflux capability demonstrated in MDR cell lines [1].

Following our characterization of three drug-binding sites within P-gp's internal drug-binding pocket (DBP) [2] using the refined structure of mouse P-gp [3], a series of molecular dynamics (MD) studies were performed to further clarify how drug efflux occurs and how drug adsorption may affect P-gp activity.

In the first paper about the murine P-gp crystallographic structure it was hypothesized that molecules access the internal drug-binding pocket through entrance gates [4] but no experimental proof was given. Therefore, we have calculated the free energy profiles for the molecule transfer from water into the lipid bilayer, revealing greater propensity for efflux modulators to permeate into the membrane when compared to substrates. On the other hand, molecule transfer from the membrane's hydrophobic environment into the water-filled DBP revealed similar permeation profiles for both the substrate (colchicine) and the modulator (tariquidar), with a $\Delta\Delta G_{\text{entry}}$ between both molecules of 12 kJ.mol^{-1}. Nonetheless, tariquidar interacts strongly with P-gp, which may be related with its modulatory properties.

Our results show that drug efflux goes downhill in energy along the reaction coordinate, with drug permeation to the lipid, entry to the DBP and release to the extracellular medium being characterized as energetically favorable processes with no energy barrier for crossing the gate.

In addition, drug-membrane interactions are also predicted to affect ATPase function by inducing long-range mechanical alterations. However, drug adsorption also occurs at the nucleotide-binding domains where conformational changes driving efflux takes place. Thus, we assessed the effect of drug adsorption to both protein-water and lipid-water interfaces showing important differences in drug-protein interactions, protein dynamics and membrane biophysical properties for the different drug classes.

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OC-50 COMPUTER SIMULATION OF GAS ADSORPTION IN POROUS MATERIALS

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High demand for economically viable separation processes such as adsorptive separation for mixtures of hydrocarbons drives the need for understanding the interaction of gases with porous adsorbents, to replace the energy-intensive and expensive distillation processes. Computational studies based on either quantum or classical mechanics approaches and employing realistic structural models of porous materials have been found to provide key information on the microscopic interactions between adsorbates and adsorbents, which have a significant impact on macroscopic properties like adsorption capacity, selectivity, diffusion and molecular sieving. Selected examples of our recent computational studies on the adsorption of small molecules in Engelhard titanosilicates [1-3] and metal organic frameworks [4,5] will be presented in this communication. These studies reveal how a detailed description of the molecular-level interactions can be used to optimize the performance of these adsorbent materials.

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OC-51 TRYING TO UNDERSTAND THE ACTIVITY OF THE PHENANTHROLINE BASED INTERCALATION DRUGS

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Several flat ligands, alone or in coordination complexes (CCs), are active against tumor cells and can be used in chemotherapy.[1] Such activity is related to their mode of interaction with DNA and intercalation is a binding mode associated to cytotoxicity towards tumor cells.[1,2] Phenanthroline (phen) and Mo(II) CCs containing phen proved to be effective against different tumor cell lines.[3] phen derivatives also showed cytotoxicity, which was found to be deeply connected to the number and position of substituents.[2] Several works addressing the intercalation of small molecules in DNA have appeared recently in the literature.[4,5]. There is still some debate about the intercalation/deintercalation process [4-7] and the mechanism that could explain the modulation in cytotoxicity. We tried to rationalize the intrinsic forces and substitution patterns ruling the intercalation to get some insight on the relation with cytotoxicity by means of DFT methods including dispersion and models consisting on the intercalator and four DNA bases. Our results show that dispersion (ΔE_{disp}) is the most important contribution to the interaction energy (ΔE_{int}), but it is not enough to compensate Pauli repulsion (ΔE_{Pauli}), and the orbital contribution (ΔE_{orb}) and specially the electrostatic forces (ΔE_{elstat}) become crucial for the intercalation. For instance, for phen intercalated in Guanine-Cytosine/Cytosine-Guanine step via minor groove the contributions (in kcal mol^{-1}) to the interaction energy are the following: $\Delta E_{disp} = -48.6$, $\Delta E_{Pauli} = 56.4$, $\Delta E_{orb} = -11.4$, and $\Delta E_{elstat} = -25.5$. Such electrostatic contribution is also fundamental to understand the connection between substitution in number and position and cytotoxicity.

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OC-52 IMPROVING RECEPTOR-LIGAND SCORING FOR ENHANCED VIRTUAL SCREENING

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Protein-ligand docking can be used in Virtual screening to evaluate databases with millions of compounds to identify molecules that could bind to a particular protein or receptor of pharmacological interest [1,2]. This strategy if often used to limit the amount of molecules that has to be tested experimentally and to reduce the cost in the identification of new lead molecules for drug development.

Currently, one of the big problems in VS arises from the large number of false positives, i.e. molecules that are erroneously suggested, from docking, to bind strongly to the target. An even worse problem in VS comes from the large number of false negatives, i.e. molecules that docking fails to identify as strong ligands, despite their high affinity. Both problems result from the imperfections in the currently available scoring functions.

In this study we tested the performance of several scoring functions available in popularly used docking programs such as Autodock, Vina and GOLD and evaluate their ability in discriminating between real ligands and structurally similar decoy molecules, for different types of targets and ligands. Based on these results we highlight the strengths and weaknesses of different scoring functions and provide a set of guidelines on the limits of validity of currently available scoring functions with the type of target and ligand.

In addition, we present a strategy to obtain improved ligand/decoy discrimination in VS runs for particular types of targets and ligands, combining different scoring functions based on the idea of consensus scoring.

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OC-53 TRACKING THE PERIODIC CLASSIFICATION RECEPTION IN PORTUGAL THROUGH A MENDELEEV'S LETTER

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How and when was the periodic classification introduced in Portugal and what kind of notoriety was attained at the time, drove this research. The research involved the identification of remaining traces at different higher level teaching institutions as well as with books, textbooks and programs from beginner's level to advanced level that appeared in the period between 1876 and 1904. A notable finding gave emphasis to the research since its beginning: an unknown letter by Dmitri Mendeleev to a Portuguese professor, Balthazar Ozorio.[1] Other traces:

- 1876 - *The Theory of Atoms and the Limits of Science*
- 1880 - A student's perspective – *La loi périodique-de M. Mendéléjeff en ce qui concerne le problème de l'unité de la matière et la théorie de l'atomicité*
- 1881 - Ferreira da Silva – *Elementary Chemical Treatise*
- 1888-1889 - Lisbon Polytechnic School; Coimbra University – F.J. Sousa Gomes followed a German translation of Mendeleev's textbook, since it appeared in 1891.
- Secondary school teaching - the periodic classification only appears officially as a topic to be taught in 1948. But… as far as is known, its first presentation at this level was in 1906, in one of Achilles Machado's textbooks, as an extra reading material.
- Popularizing - Bibliotheca das Ideias Modernas; Bibliotheca do Povo e das Escholas
- Researching… - 1894 - *Funcção Chimica da Luz*; - 1904 – Mendeleev's letter

Based on printed (and handwritten) material it is possible to arrive at conclusions from four different aspects. The first is the acquaintance with a contemporary chemical topic and some reaction to it, either in support or not; the second pertains to the knowledge to be taught at two different levels: higher education and secondary education; the interest in popularizing the topic. A last aspect is based on some weaker research.

At first glance it seems that Mendeleev's classification was more or less commonly known in the 1880s Portuguese higher education, and by its more visible leaders. In some cases, the supporters consider it as a broad synthesis, a rational history of simple bodies, and especially a powerful affirmation of the unity of matter, while others don't go further in what concerns speculations on this last category as it doesn't fit positive science. This kind of discussion was more or less avoided when presenting chemistry to students, although it was a self-presented student that explicitly writes on the periodic table in one of the traces found. Disagreements do not emerge immediately from the textbooks. While a pedagogical tool, and by 1888, adoption of the periodic classification was deemed useful.

Populist books did not appear to immediately address Mendeleev's classification, preferring to focus on Wurtz or Berthelot's ideas on atoms and elements.

Mendeleev's letter, and the publication on the chemical function of light, offers some insight into research that may have been performed, not specifically on the development of the periodic classification but on subjects around elements, or at least some elements.

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OC-54 FROM NITRUM TO POTASH: THE HISTORY OF A SUBSTANCE

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Potash was a product with high commercial value mainly during the eighteenth century, as it was one of the raw materials used in the manufacture of soft soap, as a fluxing agent in the production of glass, and in the laundering of linen and cotton [1]. The use of potash in the arts dates back to antiquity. Pliny, the Elder, (23aC-79 AD) mentions the use of a substance called *nitrum*, which could be obtained through the ashes of certain plants, whose properties were extremely caustic. The *nitrum* is also referenced in the Proverbs of Solomon, by the prophet Jeremiah and by Herodotus when describing the Egyptian method of embalming corpses. Depending on the geographic location, *nitrum* received characteristic names, such as *nitri* among the Egyptians, *nitron* by the Greeks, *neteru* by the Acadians and *natron* by the Arabs [2]. As in that period the ancients have not mastered the methods of identifying materials, it is possible that they have given the same name to different substances, since both the soda and potash were obtained primarily through plant ashes. Until the eighteenth century, the concept of salt was quite unclear. Many substances were classified according to their macroscopic properties and both acids and alkalis were grouped in the class of salts [3]. Some properties of acid and alkali salts were studied by Boyle (1627-1691) that could distinguish between the fixed alkalis, obtained from plant ashes, and volatile alkali, those from the urine of animals [4]. With Duhamel du Monceau (1700-1782) and later with Marggraaf (1709-1782) it was identified that the fixed alkalis, vegetable (potash) and mineral (soda), were of a different nature. The name ‘potash’ was first approved in 1762 by the French Academy under John Murray’s (? -1820) proposal. According to Bergman (1735-1784), had its origin in the method used for the extraction of ashes in iron pots, from the German *pottasche* (ash pot) [5]. In the late eighteenth century the term potash was already disseminated through the scientific community. Nevertheless, depending on its purity and source of production, potash was receiving too some characteristic names, like gravel ashes [6], tartar salt, pearl ash or saline [7.8].

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OC-55 SCIENTIX: THE NEW INTERNET-BASED COMMUNITY FOR SCIENCE EDUCATION IN EUROPE

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The objectives of the Lisbon declaration (2000) and the affirmation of the European Commission that there is a need to promote more widely inquiry based science education methodologies in primary and secondary schools and to support teachers' networks (2007), were the basis for launch by European Schoolnet (EUN) of Scientix, a new web-based information platform for science education in Europe. Its aim is to ensure the regular dissemination and sharing of progress, know-how, and best practices in the field of science education and providing a feedback mechanism.

The portal (http://scientix.eu), available in six European languages, offers a resource repository containing hundreds of teaching materials from European projects, but also research reports and policy-making documents; a translation on demand service for the teaching materials towards any of the 23 languages of the European Union; a community including a forum and chat rooms; an online news service featuring international science education topics and a calendar of forthcoming events and training opportunities; and also a newsletter sent once a month to registered users. The portal allows interaction among the registered users in the public profiles directory and searching, commenting and rating the resources.

The Scientix main targets are teachers, providing teaching materials, scientific support and documentation that are able to give them some quality tools for the development and implementation of inquiry based science education teaching methodologies.

Besides the website, several events and workshops were organized across Europe to disseminate the portal's tools and services. Newsletters and workshops aim to inform science teachers, explain them how to make the best use of the Scientix platform in class and also give them the opportunity to meet other European science and maths teachers. An example of this was the two Scientix European Conference that took place in Brussels on 2011 and 2014, which had the participation of more then 400 teachers and education staff from 37 countries.

In this communication the Scientix platform and teachers and public rest will be invited to register on Scientix platform and to consult the resources available on the web page, specially in connection with chemistry will be presented; will also be given information on how to request the translation service for a specific feature.

[1] www.scientix.eu

OC-56 E-LAB CHEMISTRY ONLINE COURSES

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To meet the needs and challenges of nowadays students it is necessary to explore new ways of teaching and of catching the attention of students. Among those are the use of new platforms, simulations and remote labs [1,2].
The experimental nature of chemistry presents severe challenges for its teaching at distance. Many current online chemistry courses have no laboratory experiment at all [2]. However, the e-lab platform has been shown to contribute to the teaching of scientific subjects like chemistry since basic education until university.

Recently we started to elaborate and implement chemistry online courses for students using Moodle platform. With these e-learning courses on the practical implementation of e-lab, it is intended that the trainees can use e-lab properly within two weeks. These e-learning courses are also aimed to stimulate students and teachers to know, learn, explore and use technological resources to support the use of experimental methods in science education, in particular in chemistry. The starting point is the exploration of the online and remote laboratory e-lab [3]. There are results from a pilot study performed in May 2014 where 20 physics students of twelve grade showed interest, motivation and dedication in the various activities proposed. The results are available in [3].

This way of introducing science helps students to overcome the idea that Science subjects are complex and too difficult for them to understand and helps them to see e - lab as a tool that can be used to explore and understand the world around them. Today, a solution to this serious problem involves virtual and remote laboratories where simulated or real experiments can be conducted using the Internet [4].

Acknowledgements: Sérgio Leal wants to thank the Portuguese Foundation for Science and Technology a PhD grant (SFRH/BD/44889/2008) and Instituto Superior Técnico, the Portuguese University Institute that lodges the e-lab platform.

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OC-57 HANDS-ON CHEMISTRY: NEW PRESCHOOL CHALLENGE

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From the moment of his birth, any child begins to (re)construct the world around him [1] in different ways, with their five senses and through action. In a certain way, one could say that this is their first contact with science, being continuously strengthened by school and by their life experiences, as they grow.

Science is in the Portuguese preschool curriculum orientations, within one of the three major areas of the curriculum, «Conhecimento do Mundo», i.e., “World knowledge”, but it is not always well explored by teachers because they do not have specific training background. The topic includes developing basic knowledge through experiences in preschool or in their own surroundings, like at home. Steiner (1984) considered suitable to expose scientific concepts to children in the early years, with general ideas and terminology but without too much details [2]. The dialogue may be minimized, and the involvement of students should be maximized, because children’ thinking is closely linked to the action [3]. Environmental education and accidents prevention education are examples of scientific issues that could be included [4], and as a family educational process sequel.

Would chemistry help children in preschool? Chemistry, as other sciences, it is important to awake and strength the natural curiosity; to develop positive attitudes about science; to improve future learning by an early exposure [5], and especially to help solving problems and misunderstandings.

The methodology used in this ongoing work is action-research, with a holistic approach, involving 42 children aged between 3 and 6 years of one school at Esposende, in Portugal. Investigation had the participation of teachers, children, parents and other staff.

The hands-on chemistry experiments already developed focused on hazard warning labels of household chemicals, food preservation and water pollution.

The activities and the all participatory process is being well accepted by the community and has helped to increase the perceived relevance of chemistry education.

Acknowledgements: We have to thank to «Centro Escolar de Fão», belonging to «Agrupamento de Escolas António Correia de Oliveira – Esposende», for availability, consent and participation on this research.

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OC-58 CLORETO DE SÓDIO UM REAGENTE "VERDE" - A SUSTENTABILIDADE NO ENSINO DA QUÍMICA – O PROJETO SALCIÊNCIA

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Uma das missões do ensino da Química deve ser o combate ao mito de que esta área científica constitui a origem de todos os males que ocorrem no planeta. Para tal, é fundamental adotar práticas que promovam a formação de cidadãos cientificamente literatos e pró-ativos no que respeita ao desenvolvimento sustentável. As atividades laboratoriais, e a utilização de reagentes específicos, são uma das vias possíveis para demonstrar que a Química não é apenas fonte de problemas ambientais, mas sim também a via para encontrar uma solução para os mesmos.

Nesta comunicação apresentam-se um conjunto de experiências desenvolvidas no âmbito do Projeto SalCiência e que integram a utilização de um composto químico muito popular, nomeadamente o cloreto de sódio. O "sal comum", para além de ser muito barato e facilmente acessível ainda possui características que permitem a sua utilização como reagente químico ambientalmente "verde", pois não está classificado como substância perigosa na legislação da União Europeia.

O cloreto de sódio permite ainda introduzir muitos e variados conceitos de Química do estado sólido[1], estudar vários tipos de reações incluídas na química das soluções (complexação, oxidação-redução, precipitação) e ainda abordar diversas questões relacionadas com a química dos seres vivos. As experiências descritas podem ser utilizadas em ambiente de ensino formal e não formal e destinam-se a diferentes tipos de público, desde o ensino pré-escolar até à formação de adultos. As atividades propostas abordam as várias formas de utilização do sal, desde atividades lúdicas, passando também pela sua utilização no quotidiano dos portugueses, e nas atividades comerciais e industriais. Em termos pedagógicos as experiências estão dirigidas no sentido de promover a mensagem de que o cloreto de sódio é muito mais do que um condimento na cozinha, constituindo-se presentemente um recurso fundamental rumo ao desenvolvimento sustentável nas suas três vertentes (ambiente, economia e sociedade).

Agradecimentos: Agência Nacional para a Cultura Científica e Tecnológica, Projetos SalCiência I e II.

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OC-59 INTRODUÇÃO DA QUÍMICA VERDE, COMO SUPORTE DA SUSTENTABILIDADE, NO ENSINO SECUNDÁRIO

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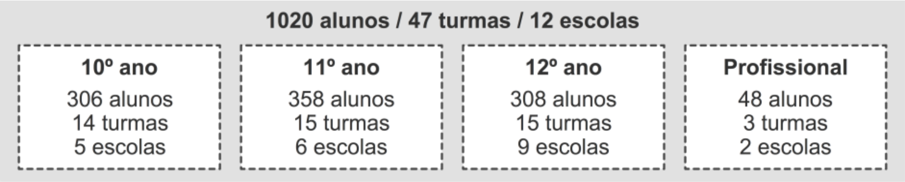
Nesta comunicação apresenta-se uma experiência para introduzir a Química Verde (QV) no ensino da química em escolas do ensino secundário, desenvolvida em um projeto [1] apoiado pelo programa "Escolher ciência" (Ciência Viva), implementado entre Abril de 2013 e Junho de 2014, em escolas da zona do Porto (Fig. 1).



1020 alunos / 47 turmas / 12 escolas

10º ano	11º ano	12º ano	Profissional
306 alunos	358 alunos	308 alunos	48 alunos
14 turmas	15 turmas	15 turmas	3 turmas
5 escolas	6 escolas	9 escolas	2 escolas

Figura 1: Universo de alunos envolvidos no projeto.

Primeiramente, apresentou-se uma introdução à QV, onde se abordaram os objectivos e os 12 princípios da QV, numa aula teórica de 45 minutos (realizaram-se 41 sessões). Em seguida, os estudantes realizaram atividades laboratoriais apoiados por elementos da equipa, nos tempos de aula destinadas a aulas práticas (280 sessões), com a presença e colaboração do professor responsável pela disciplina. Foram realizadas duas destilações e quatro sínteses, previstas nos programas,[2] com alterações nos protocolos experimentais de modo a aumentar a sua verdura química. Todas as atividades foram realizadas a microescala. Os estudantes avaliaram a verdura química de cada experiência com a métrica holística Estrela Verde [3] e, para as sínteses, calcularam algumas métricas de massa da QV (Fator E, Economia atómica, Eficiência de massa), bem como de energia (Intensidade de energia) e de tempo (Intensidade de tempo).

As avaliações do projeto por professores e estudantes sugerem que é exequível introduzir, nos currículos de química, uma abordagem desta segundo a QV. Todos os recursos desenvolvidos para o projeto estão publicados para utilização futura pelos professores,[1] com informações mais detalhadas acerca da QV e seu ensino em “Pedagogia da Química Verde - Educação para a Sustentabilidade”[4].

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POSTER
ABSTRACTS

COMUNICAÇÕES
EM PAINEL
(RESUMOS)

P-01 BIMETALLIC COPPER-LANTHANIDE/ACTINIDE CATALYSTS FOR CO_2 MITIGATION

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In the last decade the problem concerning the emission of greenhouse gases (GHG), namely CO_2, CH_4 and NO_x, has received increasing attention from the scientific community. One of the ways to mitigate its effects is their use as reagents aiming the production of value-added chemicals such as hydrocarbons and alcohols [1]. The production of CH_3OH became a major target since addresses two major problems: depletion of fossil fuels and GHG effect. Actinides and lanthanides based catalysts were already applied already with success in the partial oxidation of CH_4 and other catalytic reactions evolving hydrocarbons [2-5] as well as CH_3OH synthesis [6]. In these studies, CO_2 and CH_4 were used as reagents for the production of CH_3OH over Cu combined to *f* elements catalysts.

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P-02 SYNTHESIS AND CATALYTIC ACTIVITY OF PHOSPHONIC ACID PORPHYRIN-BASED NANO-METAL-ORGANIC FRAMEWORKS

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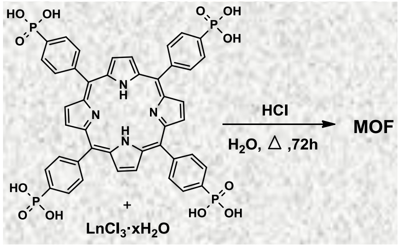
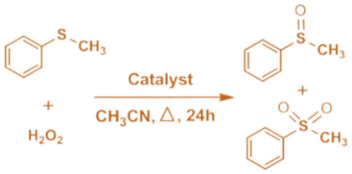
Porphyrins (Pors) and their derivatives are valuable compounds in different scientific fields, namely in medicine and catalysis, due to their unique physico-chemical properties [1]. Porphyrin-based Metal-Organic Frameworks (MOFs) are thermally stable, robust and permanently porous upon the removal of the solvent. In this way, these materials exhibit suitable structural features for catalysis and photocatalysis in industrial and/or environmental applications [2]. Following our research interests in this field [3a,b] we have developed phosphonic acid Pors to be employed as organic ligands in the construction of novel functional MOFs. Here we report the optimized synthesis of a tetra-phosphonic acid porphyrin and the corresponding lanthanide-based MOFs, as well as the oxidation profile obtained using this material and the corresponding primary building units as catalysts in the oxidation of sulfur compounds.





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P-03 PHOTOCHROMIC TEXTILES BASED ON SILICA NANOPARTICLES FUNCTIONALIZED WITH NAPHTHOPYRANS

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Photochromic textiles emerged as a new niche market for the production of smart clothing due to their switchable sensing properties and protection against the harmful effects of UV radiation; furthermore, they confer fancy color effects to fashion and interior design decoration [1]. These smart fabrics can be produced through the incorporation of inorganic or organic photochromic species into fibers by coating, dyeing and printing processes. Among organic photoactive molecules, naphthopyrans and spyropyrans have attracted much interest because they are easy to prepare, show an efficient color-changing ability and the color presented upon UV irradiation can be tuned through structural changes [2]. However, they present low thermal stability which can be improved through their immobilization onto silica nanoparticles (SNPs).

In this work, we produced a novel generation of light responsive textiles with enhanced photochromic properties based on (1) the preparation of photochromic nanomaterials through the immobilization of naphthopyrans onto SNPs followed by (2) their incorporation onto cotton fabrics by screen-printing technique which allows defining the desired printing pattern. All nanomaterials and corresponding textiles were characterized in terms of morphology/topology, chemical composition and bonding. The hybrid SNPs and functional textiles showed notable photochromic behavior, with a fast color change upon UV/visible light irradiation (within seconds) and good reversibility (a few minutes) (Figure 1).

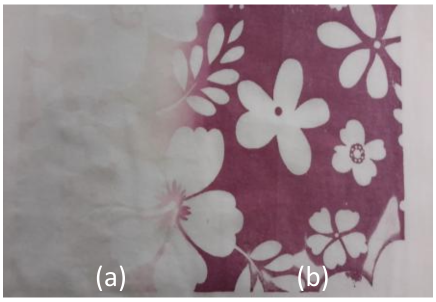

Figure 1: Photochromic textile coated with SPNs functionalized with a naphthopyran by screen-printing, (a) before and (b) after UV light exposure (1 min).

Acknowledgements: This work was funded by Fundação para a Ciência e a Tecnologia (FCT) and FEDER through project ref. PTDC/CTM-POL/0813/2012 and grants no. PEst-C/EQB/LA0006/2011 and UID/EQU/50020/2013 in the framework of Program COMPETE. The authors also acknowledge Operation NORTE-07-0124-FEDER-000067 – Nanochemistry. C. Sousa (SFRH/BPD/80100/2011), T. Pinto (SFRH/BD/89076/2012), P. Costa, and O.S.G.P. Soares (SFRH/BPD/97689/2013) thank FCT for their grants.

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P-04 PREPARATION OF NANOSTRUCTURED BIMETALLIC OXIDES CONTAINING f BLOCK ELEMENTS BY ELECTROSPINNING

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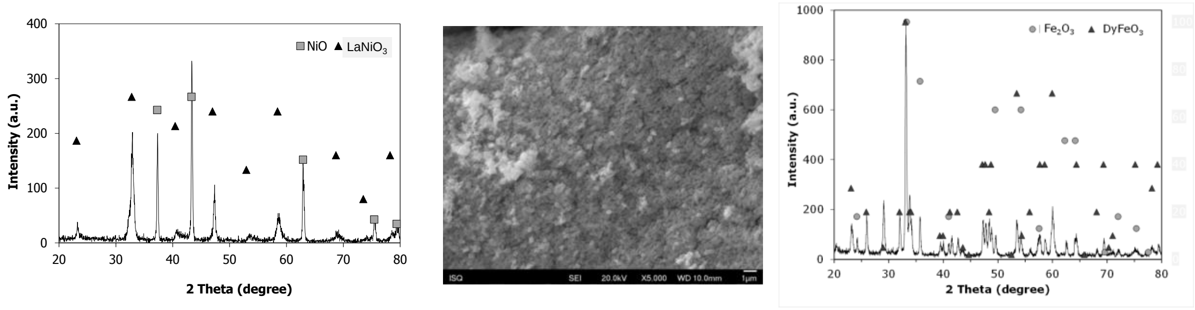
Electrospinning is a technique that has been originally developed to produce ultra-fine polymer fibers [1, 2]. This route enables low cost production of nanometer scale fibers with tunable surface properties. Such fibers have extremely high surface area, very high porosity, high permeability, low basic weight and the ability to retain electrostatic charges, among others properties [3]. Herein, we describe the use electrospinning for the preparation of bimetallic oxides nanofibers/nanoparticles containing *f*-block elements, who's expected high surface areas can bring benefits to their catalytic properties, namely, for the valorization of primary pollutants (e.g.CH_4, CO_2 or N_2O). So far, electrospinning was successfully applied to the preparation of bimetallic nanoparticles of $LaNiO_3$, $SmCoO_3$, La_2CuO_4, and $DyFeO_3$, with a particle size <30 nm. All nanostructured bimetallic oxides were characterized by XRD and SEM-EDS. Other parameters such as calcination temperature and the reducibility of these oxides were also studied. Figure 1 shows the he XRD patterns of $LaNiO_3$ and $DyFeO_3$ (A and C) and SEM image of $LaNiO_3$ (B).



(A) **(B)** **(C)**

Figure 1.Bimetallic oxide nanoparticles characterization (A) XRD pattern of La-Ni (B) SEM image. La-Ni (C) XRD pattern of Dy-Fe.

Acknowledgements: Ana C. Ferreira thanks FCT for her PhD Grant (SFRH/BD/ 69942/2010). This work was supported by FCT under contract number PTDC/AAG-TEC/3324/2012.

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P-05 MAGNETIC NANOPARTICLES MODIFIED WITH COPPER PORPHYRINS: MAGNETICALLY RECOVERABLE CATALYSTS FOR THE OXIDATION OF ORGANIC SUBSTRATES

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The oxidation of organic substrates is considered one of the most important topics for both academic and industrial research. Moreover, the development of environmentally friendly processes[1] using molecular oxygen as “green” and cost-effective oxidant, concomitantly with easy recoverable catalysts is still a great challenge.[2,3]

So, pursuing our goals of developing more sustainable synthetic methods for porphyrins[4] and its application as oxidation catalysts,[5] this work presents a synthetic methodology for the functionalization of metalloporphyrins, as well as their immobilization onto magnetic nanoparticles and full characterization using transmission electron microscopy, flame atomic absorption spectrometry, thermogravimetry, N_2 adsorption and infrared spectroscopy.

The use of the Cu(II)porphyrin based magnetic hybrid materials as oxidation catalysts, using cyclohexene as model substrate, molecular oxygen as oxidant, in absence of solvent is discussed. The magnetic nanocomposites were also evaluated for their recovery/reusability and the scope of the reaction was demonstrated by the oxidation of several organic substrates.

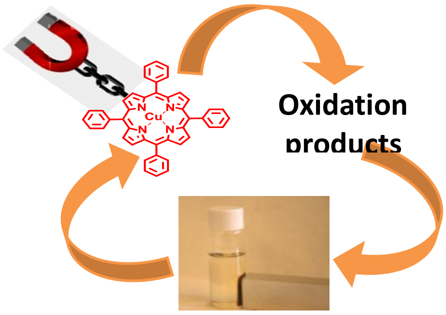

Figure 1: Schematic reutilization process.

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P-06 TOLUENE HYDROGENATION OVER BIFUNCTIONAL CATALYSTS COMPRISING Pt/AL$_2$O$_3$ MIXED WITH HBEA AND HUSY ZEOLITES

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Toluene hydrogenation over bifunctional catalysts is a structure-sensitive model reaction due to the contribution of both metal properties and support acidity to the overall activity [1]. The nature of the support and the balance between metal and acid sites influences the performances of Pt based catalysts used in refining industry. In this work, the catalysts are based on mixtures of Pt/γ -Al$_2$O$_3$ with HUSY, HBEA and a mixture of these two zeolites, with different metal/acid ratios. Acidity of zeolites and Pt/γ -Al$_2$O$_3$ was assessed by pyridine adsorption followed by FTIR. Metal dispersion was determined by H$_2$-O$_2$ titration. Turnover frequencies of fresh catalysts are not constant changing by ca. 2.4-fold and have different tendencies for each zeolite. For the same amount of accessible metal (e.g. 8,5 µmol/g), TOF values were 1666 h^{-1} (HUSY), 1444 h^{-1} (HBEA) and 2122 h^{-1} (mixture).

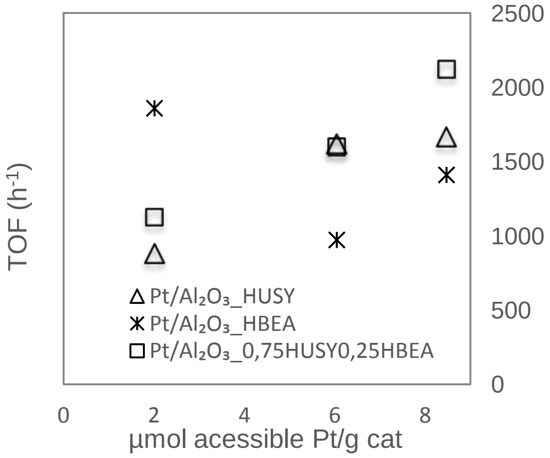

Figure 1. Accessible Pt and zeolite type influence changes on catalyst TOF´s values.

Taking into account the role of zeolite acidity, the catalysts series were compared by the activity per total adsorbing sites which was observed to increase steadily with metal/acid balance, with a similar positive tendency than impregnated catalysts series already published in literature. These results enlighten the relevance of the support on the hydrogenation activity [2].

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P-07 NANOSCALE-COPPER RESPONSES OF SEA PURSLANE (*HALIMIONE PORTULACOIDES L.):* SOME BIOCHEMICAL INSIGHTS

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In coastal areas, estuarine and salt marsh system can be the major sink of rapidly produced, multidisciplinary used and inevitably released engineered nanoparticles, where their obvious impact on inhabiting biota is least explored. In the hydroponic set-up, this study for the first time, evaluates the effects of nanoscale-copper oxide (nano-CuO) (<50 nm) concentrations (0, 20, 40, 80, 160 and 320 mg L-1) on the status, consequences and metabolism of H_2O_2 in salt marsh halophyte *Halimione portulacoides* L., and cross-talks the studied traits with the control of the health and services (Cu-accumulation/phytoextraction) of *H. portulacoides*. Cu-ions accumulated in *H. portulacoides* roots and shoots differentially disturbed the balance between H_2O_2-generation and its subsequent antioxidants-mediated metabolism therein, caused the oxidation of membrane lipids and cellular proteins, and elevated electrolyte leakage. A differential tuning among enzymatic (GSH reductase; GSH peroxidase; GSH-sulfo-transferase; ascorbate peroxidase, APX; catalase, CAT) and non-enzymatic antioxidants (as ascorbate, AsA; glutathione, GSH) was revealed that in turn controlled tissue-H_2O_2 status and consequences. Notably, a differential Cu-burden-mediated control of pools of AsA and GSH largely decided the effectiveness of non-GSH (such as CAT and APX) and GSH-requiring (such as GPX and GST)-requiring H_2O_2-metabolising systems. Thus, major ecological functions of the estuarine system can be hampered by the entry of nano-CuO and its subsequent and obvious impact on salt marsh halophytes. Notably, the status of root-Cu-burdens, and tolerance-strategies adopted therein indicated Cu-stabilization/immobilization potential of *H. portulacoides* that can be implicated in the remediation of nanoscale Cu in salt marsh/estuarine system.

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P-08 CARBONYLATIVE DIMERIZATION OF INDOLE: ONE-STEP SYNTHESIS OF CHIRAL DICARBOXAMIDE DIMERS

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The indole backbone is considered as one of the most relevant heterocycles in organic and medicinal chemistry.[1] The scientific interest on these “alkaloid” compounds is due to a number of factors, including their relevant structures, bioactivities and biomedical applications. An important subset of this family includes those made up of more than one indole subunit. For instance, bis-indoles (or indole dimers) constitute an important motif of aromatic compounds that are found in many natural products and pharmaceuticals.[2]

In this regard, the development of convenient synthetic procedures for dimeric indole molecules is an active research area. Particularly, the synthesis of indole dimers containing chiral dicarboxamide functionality remains a major challenge.

Prompted by our previous investigations on diaminocarbonylation reactions,[3,4] and considering the need for efficient and sustainable synthetic routes to prepare elaborate indole dimers with potential bioactivity, herein we report the one-step synthesis of indole-derived chiral dicarboxamides through Pd-catalyzed aminocarbonylation of 7-iodoindole with use of chiral diamines as N-nucleophiles (Figure 1). The effects of temperature and solvent on the reaction’s selectivity and on isolated yields are presented.

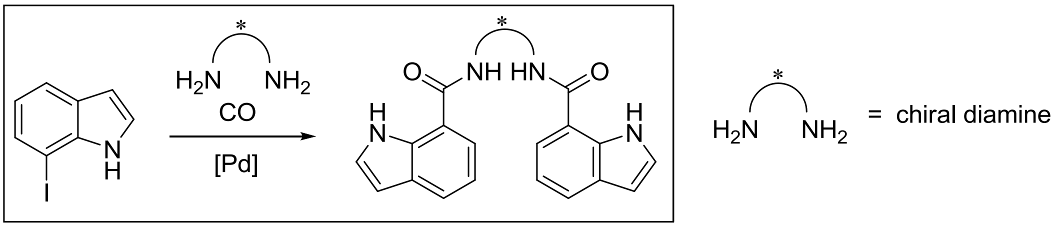

Figure 1: Pd-catalyzed carbonylative dimerization of indole.

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P-09 N, B AND P DOPED CARBON BLACKS FOR THE CWPO OF 4-NITROPHENOL SOLUTIONS

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A previous work has demonstrated that the Chemviron Carbon Black (CB, ref.:2156090) is a catalyst capable to combine a good activity with an adequate stability for long term use and high efficiency of H_2O_2 consumption in the CWPO of phenol [1]. In the current work, this catalyst was tested for the oxidation of 4-nitrophenol (4-NP). Furthermore, the catalyst was doped with nitrogen, boron and phosphorous in order to increase its activity. Doped Carbon Blacks (DCBs) were prepared by a single step heat-treatment of CB at 900 ºC in N_2 atmosphere during 24 h, using urea, boric acid or phosphoric acid as N, B and P sources, respectively. The CWPO runs were carried out in a magnetically stirred necked glass reactor equipped with a reflux condenser. The evolution of 4-NP was monitored by a Jasco HPLC system according to a previous work [2]. DCBs exhibited higher activity than the undoped CB (Fig. 1-A). Remarkably, CB doped with phosphoric acid (P-DCB) leads to total conversion of 4-nitrophenol after 24 h at 50 ºC. When the reaction is carried out at 80 ºC, only 4 h were needed to achieve the same conversion (Fig. 1-B).

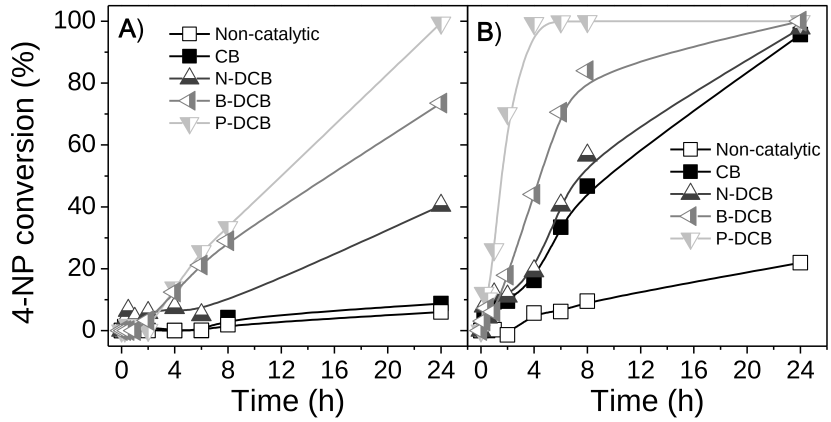

Figure 1: 4-nitrophenol conversion at pH = 3, 2.5 g/L of catalyst, 5 g/L of 4-nitrophenol, stoichiometric amount of H_2O_2 needed for the complete mineralization of 4-nitrophenol and (A) 50 ºC or (B) 80 ºC.

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P-10 IMPORTANCE OF BIOCHAR CHARACTERISTICS ON ITS ABILITY TOWARDS CO_2 CAPTURE BY ADSORPTION

Carlos M. F. Dias[1], Joana de A. e Silva[1], G. Ojeda[2], P. S. Pereira Silva[3], Manuela Ramos Silva[3], J. A. Paixão[3], L. A. E. Batista de Carvalho[4], V. F. Domingos[5], J. M. Gil[3], Abilio J. F. N. Sobral[1]

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The work presented in here is based on the study of the properties of biochar as an interesting biomaterial for the capture and sequestering of gaseous CO_2 [1,2]. Biochar (that results from the anaerobic pyrolysis of wood and wood related biomaterials) is being used as soil additive for agricultural activities from centuries and now the scientific community is showing that it can also act as a CO_2 adsorbent [3-5]. In this study we compared the behavior in CO_2 sequestering of two biochar samples from very distinct proveniences. The first samples correspond to gasified pine and the second ones to material resulting from the slow pyrolysis of urban sludge. The CO_2 adsorption studies were performed in a *Sievert* system and the interpretation of the results was based on their physicochemical properties using spectroscopic (FTIR, Raman), diffraction (LDS), scattering (XRPD) and microscopic (SEM) techniques. Pine samples revealed the highest capacity to adsorb CO_2. The samples present quite different physical and chemical characteristics depending on its origin, which may be responsible for the observed different adsorption behavior.

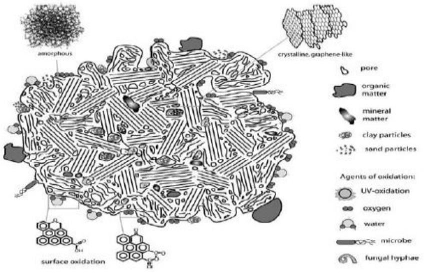

Figure 1: Chemical structure of a typical Biochar (adapted from [4])

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P-11 STABILITY OF CLAY-BASED CATALYSTS IN CONTACT WITH WATER VAPOUR

Isabel P. P. Cansado[1], M. Manuela L. Ribeiro Carrott[1], Peter J. M. Carrott[1], Paula Castilho[2], Cezar Catrinescu[2], César Fernandes[2,3], Chris Breen[4]

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The search for cleaner processes is one of the major challenges in modern chemical industries. In this context clay derived materials are environmentally friendly catalysts that can be easily tailored to optimize their catalytic activity for a precise reaction of interest. Furthermore, clay-based catalysts can be easily separated, recovered and reused and their versatility, low cost, high catalytic activity and/or selectivity render them very attractive materials.

Considering that the stability towards water vapour is a crucial aspect for catalytic performance and reuse of the catalysts, we present a study of the pore structure stability, in the presence of water vapour, of clay catalysts prepared by acid activation with HCl solutions and ion-exchange with sodium, aluminium and iron, from a natural clay collected at Serra de Dentro (Porto Santo Island, Portugal) [1]. For elucidating the influence of water vapour on the pore structure stability, water vapour adsorption--desorption isotherm, at 298 K, was determined on each sample by gravimetric method as well as n-pentane adsorption−desorption isotherms, at 298 K, which were determined before and after the corresponding water adsorption-desorption isotherms. Prior to the measurements, the samples were outgassed during 5 h at 473 K and the adsorptives were outgassed by repeated freeze–thaw cycles.

The results to be reported in the communication allow us to state that, upon contact with water vapour, the less acid activated catalysts suffered some reduction in pore volume reflecting changes in the pore structure, while the more acid activated catalysts and those prepared by ion-exchange presented excellent stability upon one cycle of water vapour adsorption-desorption. The results are corroborated by nitrogen adsorption-desorption isotherms determined, at 77 K, before and after the water and n-pentane adsorption-desorption measurements.

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P-12 CATALYTIC CONVERSION OF GLYCEROL OVER ACIDIC CLAYS

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Glycerol, a renewable feedstock from triglyceride saponification or trans-esterification in bio-diesel, requires new outlets to optimise the economy of biodiesel production and to rebalance supply and demand. Transformation by etherification, esterification, oxidation, dehydration and dehydroxylation are all interesting routes to valuable products from glycerol.

The acid-catalysed etherification of glycerol leads to mono-, di- and tri alkylglycerol ethers, which are the most suitable oxygenate additives to diesel fuels, decreasing cloud point.

In this study, we evaluated the catalytic capacity of modified clay material towards the conversion of glycerol into added value ethers, in 3 different kind of transformation:

- Acetalization of glycerol with acetone, leading to the formation of isopropylidene acetal (Solketal)
- Tert-butyl alkoxylation: The production of glycerol-tertiary-butyl-ether (GTBE), an antiknock additive for diesel by etherification with isobutene and tert-butanol were used as probe reaction.
- Etherification of limonene with solketal.

Acid activated clays and ion-exchanged clays previously prepared [1,2] were used as catalysts and their activity compared to that of homogeneous catalyst and synthetic resins.

The progress of reactions was followed by GC-FID and reaction products were identified either by mass spectrometry (GC-MS) or NMR.

The effect of reactant stoichiometry, temperature, glycerol purity, reaction time, catalyst characteristics and catalyst load in the conversion and selectivity as well as the reusability of catalysts were evaluated.

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P-13 SOLID CATALYSTS WITH SO_3H GROUPS TO PRODUCE BIO-PRODUCTS WITHIN SUGAR-PLATFORMS OF BIOREFINERIES

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Acid catalysis plays an important role in the conversion of biomass and derived intermediates for producing chemicals and fuels. Particularly, furanic ethers and levulinate esters (denoted bioEs) have wide application profiles and can be obtained by acid-catalysed reactions of, for example, fructose (FRU), 5-hydroxymethylfurfural (HMF) and furfuryl alcohol (FA), in alcohol media. For these reactions systems, carbon-based materials can be versatile catalysts since they have a modifiable surface composition, texture and acid properties. Strong acid catalysts based on carbon and carbon-silica (C/S) composites with sulfonic acid groups (SO_3H) were synthesized by chemical activation of *p*-toluenesulfonic acid (TSA) at low temperatures. Functionalised C/S composites based on a mesostructured cellular foam (MCF) and an ordered mesoporous silica (SBA-15) were also prepared by a similar procedure, in which TSA acted simultaneously as the carbon and SO_3H source. The nature and strengths of the acid sites were investigated by solid-state ^{31}P NMR studies of an adsorbed base probe, in combination with FT-IR and XPS spectroscopies. Increasing the ratio (R) between the activating agent and the organic precursor led to enhanced acidity, and thus enhanced reaction rates and yields of BioEs. For example, the C/S composites led to 95-99% BioEs yields from HMF, 44-53% from FRU and 79-86% from FA, and the results were superior to commercial sulfonic acid resin Amberlyst^{TM}-15 and zeolite H-beta.

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P-14 SURFACE FUNCTIONALIZED OF CORK BY OXIDATIVE TREATMENTS

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The chemical composition of cork has been studied since the 18th century [1]; however, the complete knowledge of its chemical properties is not yet established, and much less the potential of its functionalization.

Cork has several advantageous characteristics, but there is a restriction on its use for more elaborated applications due to its low surface energy. In order to ensure functional finishing, surface treatments can be applied to modify its properties.

In this work, cork particles with different origins were submitted to several oxidation treatments [2, 3] using different concentrations of HNO_3, H_2O_2 and O_3 to introduce chemical and physical functionalities on their surface. All the samples were fully characterized by several techniques. Table 1 shows the modifications in the contact angle of a cork sample after the functionalization treatments. The Fourier Transform Infrared spectroscopy - Attenuated Total Reflectance (FTIR-ATR) was used to identify the surface functional groups, and it was observed that the treatments with low concentrations of HNO_3 and H_2O_2 do not significantly change the surface chemistry of the cork particles, confirming the presence of suberin, lignin and polysaccharides, the major components of cork [4].

Table 1 **:** Contact angle for selected cork samples

Cork Sample	**contact angle /º**
Po Rt	128 ± 1.4
Po Rt with O_3	103 ± 1.1
Po Rt with HNO_3	101 ± 1.9
Po Rt with H_2O_2	102 ± 1.8

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P-15 POTENTIOMETRIC TITRATION DETERMINATION OF ACIDITY AND BASICITY OF CLAYS

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The potentiometric titration of clays is described in the literature but presents numerous issues due to the complexity of clay structure (change in water, with pH, etc.). These experimental biases usually present during clay potentiometric titration have been described [1] and a rational method to perform a potentiometric titration minimizing the experimental issues was proposed [2].

For the present work we designed and applied a modified method to evaluate acid and basic sites of several clays:

- SD-Na: montmorillonite clay from Porto Santo Island, purified and exchanged with Na. No acid properties.
- K10: a commercial (Aldrich) montmorillonite, acid-activated. Acid activity.
- Li-K10: the former after an ion-exchange with LiOH, with and without calcination. Basic properties expected.

For each clay, the titration is performed over the suspension and over the filtrate. A blank titration over a NaCl solution is also performed at each operating condition.

Ionic strength effects were determined with 3 different concentrations of NaCl.

The global acid sites number was determined using the Grant plot method: the curves $(V_0+V_{NaOH}) \times$ conc. $H^+ = f(V_{NaOH})$ and $(V_0+V_{NaOH}) \times$ conc. $OH^- = f(V_{NaOH})$ are drawn and the intersections with the abscissa are named V_{e1} and V_{e2}. With a perfect blank solution, $V_{e1} = V_{e2}$. Otherwise, the number of acid sites per gram of clay is calculated with the formula:

Grant plots were drawn for all the suspensions and filtrates. A corrected acid sites number was then calculated from the difference between the values obtained on the suspension and on the filtrate.

The number of acid sites obtained on K10 is in good correlation with the one obtained by another method (TPD-NH_3) [3].

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P-16 REMOVAL OF POLUTTANTS BY ACTIVATED CARBONS MADE FROM WOOD PRODUCED IN ANGOLA

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This work reports the production of activated carbons from novel precursors, namely wood produced in Angola (Benguela region), and its application to remove pollutants from aqueous solutions, namely an herbicide with a broad use in agriculture: Diuron (3-(3 4-dichlorophenyl)-1 1-dimethylurea).

Activated carbons have been used as adsorbents of excellence for many years. Additionally, the potential of the lignocellulosic materials as precursors for the production of activated carbons is also known. The novelty of this work is the use a novel precursor with the aim of creating added value products that can be used for environmental protection.

The activated carbons were produced by carbonisation under a nitrogen flow and activation with carbon dioxide at different temperatures and times. It was possible to produce materials with a range of porous and surface chemistry characteristics. The characterisation of the precursor and activated carbon samples were done by nitrogen adsorption at 77K, X ray diffraction, elemental analysis, FTIR, point of zero charge and thermal analysis.

We will present the results of the Diuron adsorption from aqueous solutions and we will correlate the results with the materials properties in order to better understand the adsorption mechanism. Based on the results we will also conclude on the best preparation condition to obtain a material tailored for the Diuron adsorption [1].

This work is relevant as the use of pesticides and herbicides are increasingly been used in Angola with the subsequent contamination of soils and water streams, river and lakes. The results of the reported work will help in fighting the negative impact of the contamination using activated carbons made from endogenous materials. This is also interesting from the economical point of view as we aim to create materials with an added value from agricultural residues [2].

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P-17 AMINOPROPYL-MODIFIED ORDERED MESOPOROUS SILICAS FOR CO_2 CAPTURE

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The production of energy from the burning of fossil fuels results in the emission of greenhouse gases, with one of the most important being carbon dioxide. Capture of this gas by adsorption, using selective adsorbents, is one of the most suitable alternatives that can help to minimize the amount of CO_2 released into the atmosphere. In this context, ordered mesoporous materials are interesting due to their pore structural features associated with hydroxyls on the surface inside the pores thereby allowing modification with organic compounds to increase favorable interactions with CO_2. This can be achieved, for instance, by impregnation with amines or by modification using aminoalkylalkoxysilanes. However, the properties of the final hybrid materials depend on the modification procedures, as well as on the silica precursors and organic functionalisation agents.

In this context, we present a study of the effect on the pore structure and CO_2 adsorption of modification with 3-aminopropyltriethoxysilane of ordered mesoporous silicas. We selected as silica precursors one MCM-41 and two SBA-15 obtained using some differences in the syntheses. The structure directing agents were removed by calcination in air and, subsequently, the materials were treated with dry toluene and variable amounts of 3-aminopropyltriethoxysilane. All the materials were characterized by nitrogen adsorption at 77 K, X-ray diffraction and thermogravimetric analysis (TGA), and CO_2 adsorption-desorption performance was evaluated using TGA. In all cases, the uptake of CO_2 was found to increase with increasing amount of nitrogen containing groups. Although this was accompanied by decrease in pore volume, the modified materials presented high specific surface areas and pore volumes, associated with uniform mesopore size distributions. Furthermore, the hybrid materials presented narrower pores than the corresponding unmodified silicas and high thermal stability indicating that aminopropyl groups are attached to the surface inside the channels. The larger mesopore sizes and pore volumes of the SBA-15 silicas enabled higher amounts of nitrogen in the final materials, with less disruption in pore structural features than for MCM-41. Furthermore, the increase in the initial amount of 3-aminopropyltriethoxysilane used in the modification procedure lead to interesting different effects on pore structure depending also on the SBA-15 silica precursor, and one allowed incorporation of more nitrogen containing groups into the channels and to reach higher total uptake of CO_2. Nevertheless, both SBA-15 modified with the larger initial amount of 3-aminopropyltriethoxysilane used in this work were stable upon two consecutive CO_2 adsorption-desorption cycles. The results to be reported in the communication illustrate successful preparation of ordered mesoporous materials as regenerable adsorbents with tailored surface chemistry for CO_2 capture.

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P-18 CARBON-COATED METALLIC MAGNETIC NANOPARTICLES: PREPARATION, CHARACTERIZATION AND APPLICATION ON BIOREMEDIATION

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Over the last few years, there has been an increased interest in studying superparamagnetic nanoparticles (SMNP) due to their unique magnetic properties and potential applications in several areas such as biomedicine/biotechnology, catalysis, magnetic sensors and magneto-optical devices [1]. Carbon materials are widely used as catalyst supports, but their use as a catalyst is attracting a great deal of attention [2]. MNP can be coated with a layer of different materials to improve their stability and to introduce new surface properties and functionalities. Therefore, the aim of this study was the synthesis and characterization of metallic magnetic nanoparticles coated with carbon (C-MNP) for subsequent application in catalysis. The use of magnetic nanoparticles coated with carbon will enable the catalyst recovery by magnetic separation and also taking advantage of the catalytic properties of the carbon materials.

In this work, the metallic (Fe, Co or Mn) MNP were based on FeO cores coated with carbon by chemical vapor deposition process (CVD) using ethane at different temperatures. The textural and chemical properties of the materials were characterized by N_2 adsorption at -196 ºC, temperature programmed reduction (TPR), elemental analysis (EA) and thermogravimetric analysis (TG).

The carbon content of the materials was determined from TG weight loss. The presence of carbon was observed in all of the materials prepared by CVD. It was also observed that the deposition of carbon decreases the surface area of the starting material.

The prepared materials exhibited high catalytic performance for the anaerobic bioreduction of azo dyes. Due to their magnetic character, at the end of the first cycle, materials could be removed from the reaction media and applied in successive bioreduction cycles without losing their catalytic properties.

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P-19 MAGNETIC N-DOPED AND UNDOPED CARBON NANOTUBES AS CATALYSTS FOR WET PEROXIDE OXIDATION

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Magnetic Fe-containing N-doped and undoped carbon nanotubes (N-CNT and CNT, respectively) have been prepared and tested in the catalytic wet peroxide oxidation (CWPO) of 4-nitrophenol (4-NP; 5 g L^{-1}) at relatively mild operating conditions (atmospheric pressure, T = 50 ºC, pH = 3, catalyst/adsorbent load = 2.5 g L^{-1} and $[H_2O_2]_0$ = 17.8 g L^{-1}).

The experimental results reveal that CNT have low affinity for H_2O_2, due to their hydrophobic nature, resulting in a controllable and efficient H_2O_2 decomposition to $HO^\bullet$ and $HOO^\bullet$ radicals, the first step in CWPO reactions, enabling the catalytic removal of 99% of the pollutant in about 12 h (Figure 1). The marked pH decrease observed during the reaction suggests the degradation of 4-NP through the formation of short-chain carboxylic acids. In addition, since Fe is confined inside the CNT structure, it is protected to some extent from leaching into the solution, making this catalyst very attractive for CWPO applications coupled with *in-situ* magnetic separation systems for catalyst recovery.

On the contrary, N-CNT comprise hydrophilic sections in their structure, strongly increasing the affinity of the material towards polar molecules like H_2O_2, which are then quickly decomposed into non-reactive O_2 and H_2O species. This inefficient H_2O_2 decomposition leads to almost no catalytic removal of 4-NP when using N-CNT. In addition, this process may also be assisted by oxidation of the Fe present in the N-CNT structure, as higher Fe leaching was observed.

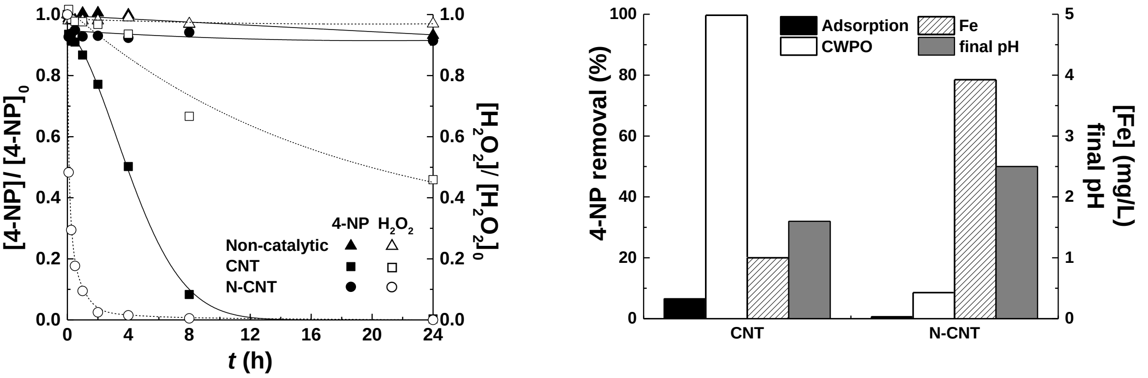

Figure 1: Concentration of 4-NP (solid) and H_2O_2 (open) during the CWPO experiments (left); 4-NP removal in adsorption and CWPO runs, Fe leaching and pH after 24 h (right).

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P-20 A COMPARATIVE STUDY OF COMPLEXATION OF 8-HYDROXYQUINOLINE-5-SULFONATE WITH In(III), Ga(III) AND Al(III) IN AQUEOUS SOLUTION

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8-Hydroxyquinoline and its derivatives are versatile chelating agents that complex a wide variety of cations, and have found applications in a broad spectrum of sciences ranging from advanced materials to biomedical uses in treating neurodegenerative disorders or as complexant for radionucleides in nuclear medicine. The observation at Kodak of electroluminescence from tris(8-hydroxyquinoline)aluminium (III) (Alq_3) [1] has led to its use in commercial organic light emitting devices, while metal quinolates also have potential as light absorbing and electron transport layers in photovoltaics for solar energy conversion. Multinuclear NMR, DFT calculations, UV-vis absorption and luminescence techniques have been used to study the complexation in aqueous solutions of 8-hydroxy-5-sulfoquinoline (8-HQS) with the trivalent metal ions, Al(III) and Ga(III) [2,3] and various other metal ions. These complexes may be used for solution based preparation of optoelectronic devices. Differences in structure have recently been reported for the 8-hydroxyquinolates of Al(III), Ga(III) and In(III) [4]. We, therefore, have extended our studies on 8-HQS complexation to the heavy atom In(III). As with the 8-hydroxyquinolates prepared in aqueous ethanol, marked differences are seen in the complexation behavior of In(III) with 8-HQS in aqueous solution compared with the other two trivalent metal ions.

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P-21 CATIONIC HALF-SANDWICH IRON(II) AND IRON(III) COMPLEXES WITH N-HETEROCYCLIC CARBENE LIGANDS

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Recently, the chemistry of piano-stool iron-N-heterocyclic carbene (NHC) complexes has been the subject of intensive research, including their successful application in reduction reactions, *eg*. hydrosilylation and hydrogen transfer, and in C-H activation processes and borylation reactions [1]. In our research group, we have developed an efficient catalytic system based on half-sandwich iron/silane for the reduction of carbonyl groups and sulfoxides [2]. Here, we present the synthesis of cationic Fe(II) complexes [(Cp*-NHC)Fe(CO)L][OTf] (Cp* = η^5-C_5Me_4; L = NCMe, DMSO; X = OSO_2CF_3) and their oxidation studies using silver salts and tert-butylhydroperoxide. The rare Fe(III) complex [(Cp*-NHC)Fe(NCMe)$_2$][BF_4]$_2$ was obtained by oxidation of [(Cp*-NHC)Fe(CO)(NCMe)][BF_4] with $AgBF_4$, Figure 1. These new complexes have been characterized by Mössbauer spectroscopy, and in some cases by X-ray diffraction studies. DFT calculations were used to rationalize the experimental results.

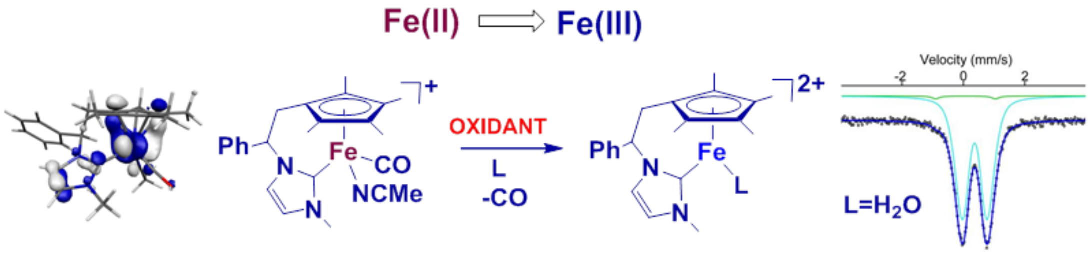

Figure 1: Fe(II)/Fe(III) Cp-NHC complexes: Mössbauer characterization and DFT studies.*

Acknowledgements: We gratefully acknowledge financial support from the FCT through project PTDC/QEQ- QIN/0565/2012, UID/Multi/04551/2013 and UID/Multi/00612/2013. B.R. thanks FCT for Consolidation contract F/00346/2013.

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P-22 MAGNETIC SILICEOUS/CARRAGEENAN HYBRIDS FOR THE UPTAKE OF WATER POLLUTANTS

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The discharge of toxic metal ions and dyes in water supplies is a matter of concern due their harmful impact on the environment. A number of nanoengineered materials have aroused as sorbents aiming the efficient and selective removal of pollutants from water. Examples of our own research include magnetic silica nanoparticles (NPs) functionalized with dithiocarbamate (DTC) groups for the removal of Hg^{2+} [1] and magnetite NPs coated with biopolymers [2]. Composites made of thermosensitive biopolymers loaded with iron oxide nanofillers are potentially useful as a new class of sorbents, with great practical interest for water treatment units using magnetic separation. Thus, the magnetic NPs allow fast magnetic separation, while the biopolymer provides an eco-friendly platform for chemical functionalization aiming targeted pollutants. In this context, biocomposites that form thermosensitive hydrogels [3] are particularly attractive since this feature can be exploited to recycle the magnetic NPs by thermo-magnetic treatment with the aim of decreasing the amount of contaminated sorbents and reuse the magnetic NPs in the production of new biocomposites.

The present communication reports the development of magnetic siliceous/biopolymer hybrids that merge the above described functionalities, aiming their application as thermosensitive sorbents in water purification processes with recycling capabilities. Hybrid materials comprising Fe_3O_4 NPs, siliceous DTC derivatives and the polysaccharide κ-carrageenan were synthesized, in the form of bulk materials and composite particles. The resulting materials formed gels at RT and undergo an endothermic transition upon heating, due to gel-to-sol transition, as seen by DSC. When exposed to an alternating magnetic field (AMF), the local temperature increased above the melting temperature due to the magnetocaloric effect of Fe_3O_4 NPs. The use of these materials for the magnetic removal of contaminants will be discussed, namely by considering the chemical functionalities associated to their composition: DTC groups are suitable chelating moieties for metal ions and sulfonate groups from carrageenan can attach electrostatically cationic dyes.

Acknowledgements: ncia e a Tecnologia) through the project PTDC/CTM-NAN/120668/2010, by FEDER through program COMPETE and by national funding through FCT in the frame of project CICECO - FCOMP-01-0124-FEDER-037271 (Ref. FCT Pest-C/CTM/LA0011/2013).

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P-23 NICKEL NANOWIRES AS EFFICIENT SORBENTS TO REMOVE MERCURY FROM WATER

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Water pollution by trace non-essential metal ions is an eco-toxicological hazard of prime interest that has raised the attention of the scientific community. In the last few decades, unprecedented progress on methods of synthesis of nanomaterials has been observed providing opportunities for the fabrication of materials with controlled properties desirable for water purification. In this context, nanoengineered particles have attracted a growing attention as new sorbents for water decontamination. This research describes a remediation technique based on a magnetically enhanced separation technology using nickel nanowires (NiNWs) as nanosorbents for the removal of aqueous Hg(II) ions [1]. Therefore, ferromagnetic NiNWs were prepared by Ni electrodeposition in an anodic aluminum oxide template. In order to act as efficient sorbents, the surface of NiNWs was chemically modified with siliceous shell containing dithiocarbamate groups to confer strong affinity for Hg(II) cations [2]. The efficiency of NiNWs@SiO_2/SiDTC to uptake Hg(II) from water was evaluated and this research has shown that such functionalized NiNWs have a removal capacity of about 99.8% for Hg(II). NiNWs offer an alternative in specific contexts of application such as in laboratorial monitoring and analysis of water quality.

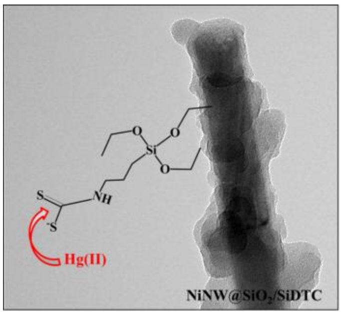

Figure 1: Illustration of the recovery of Hg(II) using modified NiNW.

Acknowledgements: P. C. Pinheiro thanks FCT for the grant SFRH/BD/96731/2013. This work was financed by national funding from FCT through the project PTDC/CTM-NAN/120668/2010, and by funding through FCT in the frame of project CICECO- Aveiro Institute of Materials (Ref. FCT UID/CTM /50011/2013), financed by national funds through the FCT/MEC and co-financed by FEDER under the PT2020 Partnership Agreement.

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P-24 ASSEMBLY OF METAL COLLOIDS ONTO SURFACE FUNCTIONALIZED MAGNETITE PARTICLES

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In the course of our research on new magnetic sorbents for metal species, we have recently described the preparation of dithiocarbamate functionalized magnetite particles that show high efficiency for mercury uptake from water [1] These materials comprise a ferromagnetic core (magnetite: Fe_3O_4) coated with silica shells enriched in dithiocarbamate moieties. Silica coated nanomaterials have been extensively used because confer robustness to the magnetic phases and offer a convenient platform for chemical derivatization, thus making easy the grafting of diverse functional groups at the surface of the nanoparticles. On the other hand, the magnetic cores confer ability for magnetic separation of the particles from the corresponding suspensions, just by employing an external magnetic field.

Taking advantage of the above properties of the surface modified magnetite particles, we have carried a series of experiments in which their sorption behavior for noble metal colloids (Ag, Au, Pt, Pd) was evaluated. This research demonstrates that the functionalization of silica coated magnetite particles with dithiocarbamate groups also confers affinity for such metal nanoparticles, thus allowing their uptake from hydrosols under a magnetic gradient. En route with these findings, we have varied several operational parameters in order to investigate this strategy as a new bottom-up assembly method for producing a range of coupled colloidal nanoparticles. The final properties of the assemblies will be discussed by taking into account the composition of the hybrid nanostructures and also their morphological characteristics.

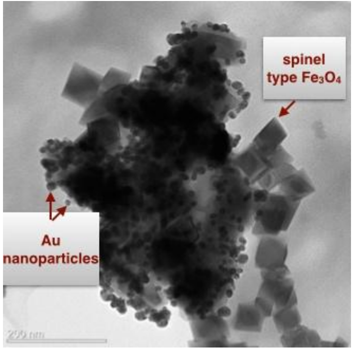

Figure 1: TEM image of Au nanoparticles attached to functionalized Fe_3O_4 particles.

Acknowledgements: This work was financed by national funding from FCT (Fundação para a Ciência e a Tecnologia) through the project PTDC/CTM-NAN/120668/2010, by FEDER through program COMPETE and by national funding through FCT in the frame of project CICECO - FCOMP-01-0124-FEDER- 037271 (Ref. FCT Pest-C/CTM/LA0011/2013).

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P-25 EXPLORING THE GAS-PHASE CHEMISTRY OF URANYL: NEW COMPLEXES WITH SUPEROXIDE AND AMINO ACID LIGANDS

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Electrospray ionization quadrupole ion trap mass spectrometry (ESI-QIT/MS) is currently used in our group to investigate several aspects of the gas-phase ion chemistry of actinide species, uranyl in particular.

1) Uranyl(VI) superoxide complexes: In actinide condensed-phase chemistry, uranyl(VI) generally forms η^2-peroxide complexes with dioxygen, but it has been proposed that superoxide complexes are intermediates in the oxidation of uranyl(V) species. Gas-phase reactions of the anionic uranyl(V) complexes $[UO_2X_2]^-$ (X = F, Cl, Br, I, OH, NO_3, ClO_4, HCO_2, CH_3CO_2, CF_3CO_2, CH_3COS, NCS, N_3) with molecular O_2 yielded the uranyl(VI) complexes $[UO_2X_2(O_2)]^-$, comprising a η^2-superoxo ligand, as confirmed by DFT and QTAIM computations on selected complexes [1]. The measured oxidation rates were diverse, ranging from relatively fast $[UO_2(OH)_2]^-$ to slow $[UO_2I_2]^-$; the effects of the basicity and number of vibrational degrees of freedom of the X^- ligands on the rates of O_2 addition were revealed. These gas-phase results suggest that formation of superoxo complexes of uranyl(VI) from reactions of uranyl(V) precursors with O_2 is within reach in the condensed phase.

2) Uranyl(VI) amino acid complexes: Uranyl(VI) is the predominant form of uranium in vivo and in natural environments, and gas-phase studies can provide information about its coordination to amino acids and help to illuminate its interactions with protein binding sites. The following types of uranyl complexes with neutral and deprotonated amino acids, with different side chain functional groups (aspartic acid, histidine and cysteine), were produced by ESI of solutions of uranyl(VI) and mixtures of two amino acids: $[UO_2(aa^1)_2(aa^2\text{-H})]^+$ or $[UO_2(aa^1)(aa^1\text{-H})(aa^2)]^+$, and $[UO_2(aa^1\text{-H})_2(aa^2\text{-H})]^-$ or $[UO_2(aa^1\text{-H})(aa^2\text{-H})_2]^-$ [2]. Collision-induced dissociation (CID) of the cationic species primarily showed loss of a neutral aa, followed by reaction with the background water in the QIT for some of the products; these competitive CID and hydrolysis experiments seem to indicate that the strength of the (neutral aa)-UO_2^{2+} interaction follows the order His>Asp>Cys, which is the trend of the gas basicity of these amino acids. In the negative mode, CID produced preferential loss of a neutral amino acid to form $[UO_2(aa\text{-H})(aa\text{-2H})]^-$ species in the order His~Cys>Asp, indicating particularly strong coordination of doubly-deprotonated Asp to UO_2^{2+}.

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P-26 CHARACTERIZATION OF HISTORICAL MORTARS OF CONVENT OF CHRIST IN TOMAR

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In this work we studied ancient masonry mortars samples from the monumental set known as Convent of Christ, located in Tomar, relating to various historical periods. For that purpose 9 samples were collected, corresponding to different locations and periods (centuries XII, XVI and XIX).

The physicochemical, mineral and microstructure characterization of these materials was achieved by a group of diverse and complementary analytical techniques, such as wet chemical analysis, X-ray diffraction, thermogravimetric analysis, atomic absorption spectroscopy and infrared spectroscopy by Fourier transform.

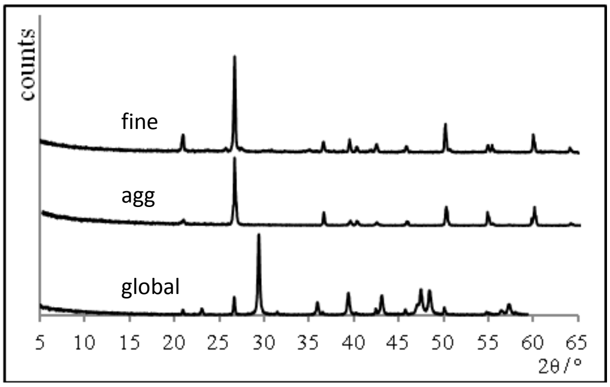

Figure 1: Example of X-ray diffractograms for one studied sample.

It was found that all samples are constituted mainly by quartz (SiO_2) and calcite ($CaCO_3$), the predominant compound being, in all cases, the quartz. Apart from these, other compounds, where they exist, are present in very small amounts.

Current weight composition was determined for each of the samples and, from this, considering how the mortars are prepared, the volumetric composition of the original mortars was deduced. The values obtained were relatively similar to each other (with the exception of the most recent sample, where the quartz content is slightly larger) and were within the expected range.

The results obtained have led to a set of information that may be used to better understand the monument in terms of construction techniques and suitability of possible restoration mortars.

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P-27 PEGYLATED DOTA-AHA-BASED Gd(III) CHELATES – A RELAXOMETRIC STUDY

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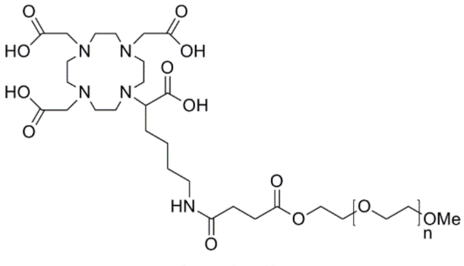
The need for magnetic resonance imaging (MRI) contrast agents with improved relaxivity maintains the development of new Gd(III) chelates as an intensive and demanding field of research. We report the synthesis and characterization of three DOTA-A(PEG)HA ligands (DOTA-AHA **=** 1,4,7,10-tetraazacyclododecane-1-((6-amino)hexanoic)-4,7,10-triacetic acid) differing in the molecular weight of the pendent PEG (poly(ethylene glycol)) chain.



DOTA-A(PEG)HA
n = 750, **L1**
n = 550, **L2**
n = 350, **L3**

Figure 1 - DOTA-A(PEG)HA (**L1**, **L2**, **L3**).

Their Gd(III) chelates were studied in aqueous solution using variable-temperature ^{1}H nuclear magnetic relaxation dispersion (NMRD) and ^{17}ONMR spectroscopy in view of the determination of their relaxivity and the parameters that govern it. The relaxivity values measured (varying from 5.1 to 6.5 $mM^{-1}.s^{-1}$, at 37 ºC and 60 MHz, with the increasing molecular weight of the PEG chain) are slightly higher than that of the parent chelate Gd(DOTA-AHA) [1] for which contributes long global rotational correlation times. A ^{1}H NMR study of several Ln(III) chelates of DOTA-A(PEG_{750})HA gave an insight into the dynamics and structural behavior of the chelates in solution.

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P-28 CRYSTAL STRUCTURE AND CATALYTIC PERFORMANCE IN OLEFIN EPOXIDATION OF A ONE-DIMENSIONAL TUNGSTEN OXIDE/BIPYRIDINE HYBRID

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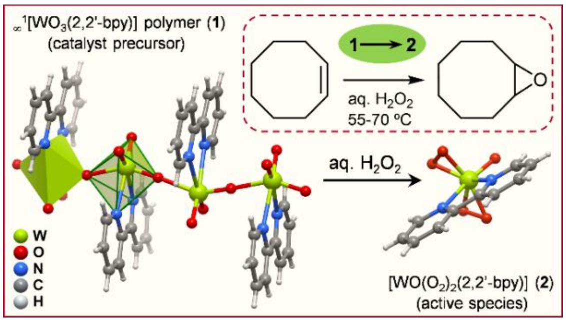
Metal oxide-organic hybrid materials have potential applications in many fields.[1] Group VIb (Mo, W) systems are of particular interest, especially those in which *N*-donor molecules are directly coordinated to the oxide substructure.[2] Depending on the structure and composition of the hybrid, as well as the catalytic reaction conditions, these materials can either act as sources of soluble active species, or as heterogeneous catalysts. In this study a new structural variant of a 1D tungsten oxide/2,2'-bipyridine hybrid material was prepared: ${}_{\infty}^{1}[WO_3(2,2'\text{-bpy})]$ (**1**). A search in the CSD reveals that only two polymeric structures are known: $[WO_3(2,2'\text{-bipy})]$[3], and $[WO_3(\text{en})]$[4] (en stands for ethylenediamine). Remarkably, none of these previous crystallographic reports concern the systematic search for this type of materials, *i.e.*, both polymers were obtained as secondary phases isolated during the search for other types of materials, and their structures determined using single-crystal XRD. In this work compound **1** was obtained in good yield as the principal product, characterized and its catalytic behavior studied in detail for the epoxidation of the model substrate *cis*-cyclooctene. When aqueous H_2O_2 is used as the oxidant, **1** is quickly converted *in situ* into the oxodiperoxo complex $[WO(O_2)_2(2,2'\text{-bpy})]$ (**2**) which was found to be the active species responsible for the selective epoxidation reaction in homogeneous phase. Hence, for this particular reaction, compound **1** is useful as a stable and easily storable, catalyst precursor.



Schematic representation of 1D neutral polymer **1**, the active species **2** and the catalytic reaction model.

Acknowledgements: The authors thank FEDER, COMPETE and FCT projects: CICECO (FCT UID /CTM /50011/2013), PTDC/EQUEQU/121677/2010 and FCOMP-01-0124-FEDER-029779 (FCT PTDC/QEQ-SUP/1906/2012). P.N. (SFRH/BPD/73540/2010) and T.R.A. (SFRH/BPD/97660/2013) thank the FCT and EU for postdoctoral grants cofunded by MCTES and the European Social Fund through the program POPH of QREN. This research was partially supported by the R&D FCT project FCOMP-01-0124-FEDER-041282 (FCT EXPL/CTMNAN/0013/2013).

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P-29 SOLID STATE SYNTHESIS OF *N*-HETEROCYCLES UNDER MECHANICAL ACTION

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LDAP, Mechanical Engineering Department, FCT-University of Coimbra

Organic Chemists had been looking for more sustainable methodologies and ways to improve de greenness of organic synthesis. Excluding solvent from the reaction medium, generally the main source of waste in a synthetic process, is probably the most efficient way to attain this objective. Mechanical activation, which is normally carried out in the absence of, or with minimal use of solvents, could be an alternative to improve the sustainability in organic synthesis, that in some cases proved to be more selective and efficient than the solvent-based versions in a wide range of reactions.(2) Mechanical activation can be carried out in a variety of ways. The simplest is the laboratory mortar and pestle, which is however; inappropriate for reactions that requires long reaction times, high energy or improvement of reproducibility. Therefore an ever-growing use of the higher energy ball-mill, laboratory vibrators, the Wiggle-Bug, high speed attritors or stainless steel ball mills of high impact (Spex type) has been adopted for prolonged high energy mechanical activation process [3].

N-heterocycles were selected as target compounds, considering that they hold a especial place among pharmaceutically important natural and synthetic meterials.

In this communication we report the solventless synthesis of *N*-heterocycles such as Hantzsch 1,4-Dihydropyridines, Biginelli and Biginelli type 3,4-dihydropyrimidine and thione derivatives, under mechanical action using a screw with different screw wall thickness developed by us to optimize the mechanical action. The intense shear stress of the reacting material was generated by the friction between turning screw and fixed wall.

Acknowledgements: Thanks are due to *Fundação para a Ciência e a Tecnologia* (FCT), Portuguese Agency for Scientific Research (Coimbra Chemistry Centre through the project UID/QUI/00313/2013) for financial support. We acknowledge the UC-NMR facility for obtaining the NMR data (www.nmrccc.uc.pt).

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P-30 PHENANTHROIMIDAZOLES AS FLUORIMETRIC AND COLOURIMETRIC CHEMOSENSORS IN AQUEOUS SOLUTION

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2,4,5-Triaryl-imidazoles are versatile compounds with application in medicine, due to their biological activity, and materials sciences, for their interesting optical properties. These properties can be tuned by careful selection of substituents at positions 2, 4 and 5: replacement of the aryl group by an heterocyclic group results in larger π-conjugated systems with improved optical properties for application in nonlinear optics, OLEDs, DNA intercalators, and chemosensors [1]. Moreover, it is expected that introducing more conjugation and rigidity into the resulting system will further improve its properties. The development of chromo/fluorescent probes that are capable of detecting ions with high sensitivity and selectivity in aqueous media is currently a topic of strong interest and the design of heteroditopic receptors that contain two or more different binding sites for the simultaneous complexation of cationic and anionic guests is a emerging field of supramolecular chemistry [2].

In this communication, we report the synthesis of new phenanthroimidazoles substituted at position 2 with arylthienyl or arylfuryl moieties possessing substituents of different electronic character, in order to tune the chromo/fluoro response in the presence of relevant anions and metal cations. Their photophysical properties and chemosensory ability were studied in acetonitrile and mixtures of acetonitrile and water, and selective detection of cyanide was achieved in aqueous mixtures for some of the derivatives.

Acknowledgements: Thank are due to *Fundação para a Ciência e Tecnologia* (Portugal) and FEDER-COMPETE for financial support through Centro de Química-UM (PEst-C/QUI/UI0686/2013 (FCOMP-01-0124-FEDER-037302)) and Centro de Física-UM [PTDC/CTM/105597/2008 (FCOMP-01-0124-FEDER-009457)], and a PhD grant to R.C.M. Ferreira (SFRH/BD/86408/2012). The NMR spectrometer Bruker Avance III 400 is part of the National NMR Network and was purchased with funds from FCT and FEDER. We are also grateful to Instituto da Educação-UM for providing the laboratory infrastructure necessary for the development of this work.

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P-31 SYNTHESIS OF NOVEL CHIRAL HEXACYCLIC STEROIDS DERIVED FROM 16-DEHYDROPROGESTERONE

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Steroidal compounds are widely existent in natural world and display a variety of biological activities.[1] The introduction of heteroatoms or heterocycles in the structure of the maternal steroids often results in alterations of its biological properties, for example, enhancing the cytotoxicity against some tumor cell lines.[2] Synthetic steroids fused to heterocyclic compounds possesses unique biological properties, along with high hormonal activity typical of steroids, they exhibit potent antimicrobial and anticancer activity.

We have previously demonstrated that diazafulvenium methides, generated from the SO_2 extrusion of 2,2-dioxo-1H,3H-pyrazolo[1,5-c][1,3]thiazoles, participate in [8π+2π] cycloaddition with 16-dehydropregnenolone acetate (16-DPA) giving the pyrazolo-annulated steroids in a stereoselective manner.[3a, 3b] Recently, the study was extended to new steroidal scaffolds such as 16-dehydropregnolone.[3b] In this communication, further cycloadditions of these diazafulvenium methides with 16-dehydroprogesterone, leading to new chiral hexacyclic steroids, will be presented. Future work will evaluate the activity of these new hexacyclic steroids in breast and prostate cancer cell lines.

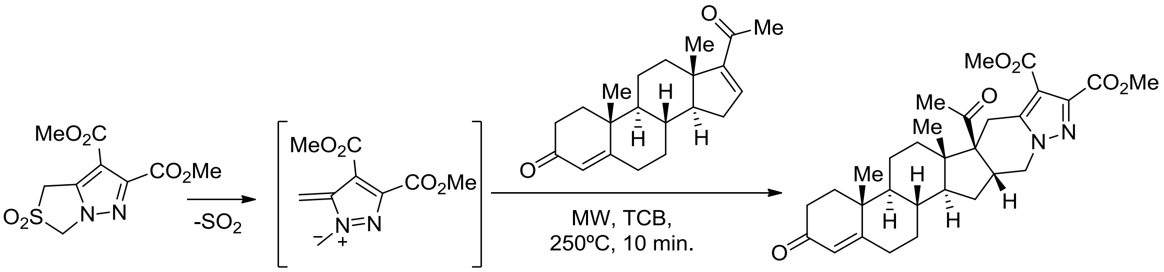

Figure 1: [8π+2π] cycloaddition of diazafulvenium methide with 16-dehydroprogesterone

Acknowledgements: Thanks are due to FCT (Centro de Química de Coimbra) through Project UID/QUI/00313/2013 and Grant SFRH/BPD/84423/2012) for financial support. We acknowledge the UC-NMR facility for obtaining the NRM data (www.nmrccc.uc.pt).

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P-32 NEW SYNTHETIC STRATEGY FOR THE SYNTHESIS OF CHIRAL TERTIARY CYCLOALKANOLS FOR TREATING NEURODEGENERATIVE DISEASES

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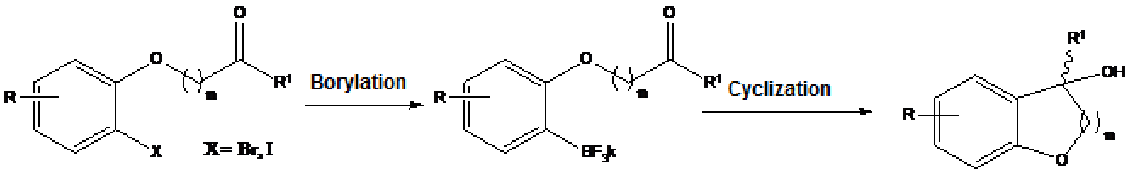
Neurodegenerative diseases such as Alzheimer's disease and Parkinson's disease are a significant threat to world health and particularly to the aging population [1]. Thus there has been a recent push in the research and development of new drugs that include molecules containing cyclic chiral amines and chiral cycloalkanols as the molecular core structure [2].

Rasagline (Parkinson's) [3] and rivastigmine (Alzheimer's) [4] are two drugs used to treat such diseases. MAO-B is the biological target for rasagiline [5] and acetylcholinesterase (ACH) for rivastigmine [6].

Intermolecular catalytic arylation methods using boronic acid precursors and derivatives are efficient methods for accessing these scaffolds [7].



In this communication we will discuss our efforts at synthesizing new bicylic tertiary cycloalkanols based on the strategy shown in the scheme above.

Acknowledgements: This work is supported by the project: INMOLFARM - Molecular Innovation and Drug Discovery (ALENT-57-2011-20) financed from the FEDER-INALENTEJO program ALENT-07-0224-FEDER-001743, as well as PEst-OE/QUI/UI0619/2014 (CQE-UE).

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P-33 SYNTHESIS OF DEHYDRODIPEPTIDES DERIVATIVES WITH A C , -DIMETHYLGLYCINE RESIDUE

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Non-proteinogenic amino acids are an important class of organic compounds some of which possess intrinsic biological activity. They are also found in peptides with known antiviral, antitumor, anti-inflammatory or immunosuppressive activities. Non-proteinogenic amino acids including *N*-alkylamino acids, dehydroamino acids and $C^{\alpha,\alpha}$-dialkylglycines, have a vast application in medicinal chemistry [1]. $C^{\alpha,\alpha}$-dialkylglycines, such as dimethylglycine, diethylglycine, isovaline and dipropylglycine are the main feature of peptaibols, a family of naturally occurring antibiotic peptides [2]. Recently, Monteiro et al. prepared dehydrodipeptide derivatives with a $C^{\alpha,\alpha}$-dimethylglycine residue that could additionally be *N*-alkylated at the amino terminal [3].

Herein, we describe the synthesis of dipeptides consisting of dimethylglycine and β-hydroxyamino acid residues. These dipeptides were subject to dehydration using the *tert*-butylpyrocarbonate [$(Boc)_2O$]/4-dimethylaminopyridine (Dmap) methodology developed by Ferreira et al. [4], to give dehydrodipeptide derivatives. These were treated with *N*-bromossuccinimide yielding β,β-dibromodehydrodipeptide and β-bromodehydrodipeptide derivatives. The β-bromo dehydrodipeptide derivatives were used in Suzuki-Miyaura cross-couplings reactions.

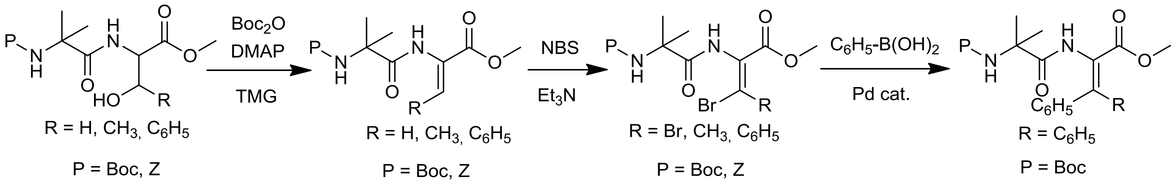

Figure 1: Synthesis of dehydrodipeptides derivatives with a *C*-dimethylglycine residue

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P-34 NOVEL GALACTODENDRITIC SILICON PHTHALOCYANINES

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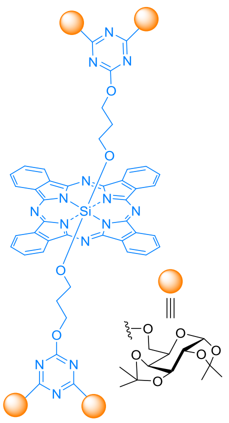
Photodynamic Therapy (PDT) combines a photosensitizer (PS), light at a specific wavelength and molecular oxygen present in the tissue to generate highly reactive (and toxic) oxygen species (ROS). In oncology, the PS needs to be: 1) preferentially accumulated in cancer cells; and 2) a good generator of ROS, especially singlet oxygen [1]. The development of phthalocyanines (Pcs) as PSs has been especially promising due to their high absorption bands in the PDT therapeutic window (600-800 nm), allowing the treatment of deep tumors [2]. Amongst several Pcs, the silicon ones have demonstrated potential pharmacological properties, since the silicon(IV) in the core allows the introduction of bulky groups, namely sugar units at axial positions, which can prevent the well-known self-aggregation associated with the stacking of the hydrophobic Pc core [3]. Previous studies demonstrated that a SiPc axially conjugated with two acetal-protected galactose substituents (**SiPcGal$_2$**) has high photodynamic potential against human hepatocarcinoma cells [4]. Recently, our research group developed new third generation PSs by conjugating porphyrins and Pcs with dendritic units of galactose [5]. These new PSs have demonstrated excellent photodynamic effect against human bladder cancer cells through mediated interaction with galactose binding proteins [6]. Thus, we decided to synthesize a SiPc containing two galactose-dendrimers in the axial positions (**SiPcGal$_4$**) and to study their photo-physical, -chemical and -biological properties against bladder cancer cells.



SiPcGal$_4$

Acknowledgments: Thanks are due to the University of Aveiro, Autónoma University of Madrid, IBILI-FMUC, FCT (Portugal), European Union, QREN, COMPETE and FEDER for funding QOPNA (Project PEst-C/QUI/UI0062/2013; FCOMP-01-0124-FEDER-037296) and IBILI (UID/NEU/04539/2013) Research Units. Patrícia M. R. Pereira (SFRH/BD/85941/2012) thanks FCT for his PhD grant.

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P-35 NEW PHOTOTRIGGERS BASED ON COUMARINS WITH EXTENDED -SYSTEMS

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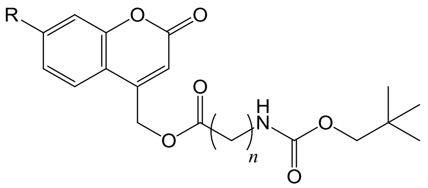
The 2*H*-1-benzopyran-2-one, commonly designated as coumarin, is a well-known oxygen heterocycle with several applications in various areas, including as food additive, in the preparation of insecticides and cosmetics, and exhibiting a broad range of therapeutic activities, such as anticancer, antimicrobial, analgesic, anti-HIV, anticoagulant and antioxidant.[1] In addition, coumarin derivatives have also been used as photocleavable protecting groups (PPGs), with particular importance in biological applications, due to their good molar extinction coefficients at high wavelengths. Also, they reveal a great potential in two-photon uncaging as the release of the target entity can occur under irradiation at wavelengths that are harmless to cells. [2]

Considering our research interest in the field of PPGs,[3] namely for the delivery of biologically relevant molecules, the present work describes the synthesis of new coumarin derivatives possessing an extended π-system, in order to bathocromically shift the wavelength of maximum absorption, and consequently of photolysis (Fig. 1). These compounds were tested as phototriggers of two neurotransmitter amino acids, glycine and β-alanine, at 254, 300, 350 and 419 nm, in a Rayonet RPR-100 photochemical reactor, and the release of the active compound was monitored by HPLC-UV detection, with collection of kinetic data.



1a: R= H, n=1
2a: R= NH_2; n=1
3a: R= C_6H_5; n=1
4a: R= p-OMe-C_6H_4; n=1
5a: R= CH=CH-C_6H_5; n=1

1b: R= H, n=2
2b: R= NH_2; n=2
3b: R= C_6H_5; n=2
4b: R= p-OMe-C_6H_4; n=2
5b: R= CH=CH-C_6H_5; n=2

Figure 1: Coumarin ester cages of glycine and β-alanine.

Acknowledgements: Thanks are due to the Fundação para a Ciência e Tecnologia (FCT, Portugal) for financial support to the NMR portuguese network (PTNMR, Bruker Avance III 400-Univ. Minho), FCT and FEDER (European Fund for Regional Development)-COMPETE-QREN-EU for financial support to Research Centre of Chemistry, CQ/UM [PEst-C/QUI/UI0686/2013 (FCOMP-01-0124-FEDER-037302)].

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P-36 SÍNTESE DE PIRRÓIS N-ARIL SUBSTITUÍDOS PARA ESTUDOS DE CAPTURA DE CO_2

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Após a Revolução Industrial, o aumento da emissão de CO_2 para atmosfera tem sido um dos maiores causadores de problemas ambientais, contribuindo para o efeito estufa, acidificação de rios e problemas respiratórios na população.

A síntese de novos materiais adsorventes de CO_2 que possam ser usados para diminuição destas emissões e, consequentemente levar a uma melhoria do ambiente, tem sido um grande desafio para a comunidade científica nas últimas décadas. O uso de pirróis N-aril substituídos, com diferentes grupos funcionais que permita estudar as interacções entre o CO_2, e os materiais moleculares onde pode ser aprisionado é um aspecto importante nesse desafio, já que nos permite planear e sintetizar novos e melhores compostos a serem usados no problema ambiental do sequestramento e captura do dióxido de carbono gasoso.

Neste trabalho sintetizámos vários pirróis usando a metodologia de Paal-Knorr, onde se faz reagir a 2,5 hexanodiona e uma amina aromática, tendo como catalisador o iodo [1]. Neste trabalho foram sintetizados pirróis com grupos funcionais diferentes para posterior estudo das suas capacidades na captura de CO_2 a pressões de até 5 bar, sendo avaliada a importância dos diferentes grupos funcionais no processo de captura de dióxido de carbono.

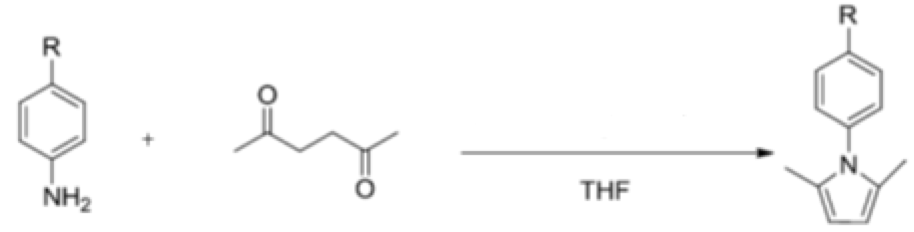

Figura 1. Esquema geral da reação de Paal Knorr para pirróis N-aril substituídos

Agradecimentos: Os autores agradecem o apoio FCT/QREN-COMPETE através dos projectos PEst-OE/QUI/UI0313/2014 e PTDC/AAC-CLI/118092/2010 também como o apoio da CAPES.

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P-37 RELAÇÕES ESTRUTURA/ACTIVIDADE NA CAPTURA DE CO_2 GASOSO EM MATERIAIS MOLECULARES BASEADOS EM PIRRÓIS

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Há algumas décadas a maioria das nações via o meio ambiente como um reservatório de matérias primas. Nesse período a exploração exagerada dos recursos naturais devastou as reservas de uma forma como nunca havia ocorrido. A consequência desses atos juntamente com o advento da máquina a vapor, crescimento industrial e utilização de combustíveis fosseis no sistema de transporte e geração de energia causou grandes impactos ao meio ambiente, como a destruição da camada de ozono e o efeito estufa. O grande desafio para o século XXI é tentar amenizar os danos que vêm sendo causados até o momento, criar novas formas de energias renováveis e diminuir a emissão dos gases nocivos ao meio ambiente, evitando um possível colapso climático. Pensando nisso o nosso trabalho centrou-se na síntese de novos materiais que consigam interagir com o CO_2, capturando-o na forma gasosa.

Assim, foram sintetizados pirróis N-aril substituídos, com diferentes grupos funcionais, usando o método de Paal-Knorr. Esses pirróis serão posteriormente estudados em captura de CO_2, de forma a serem estabelecidas relações estrutura-actividade, com o propósito de nos orientar na sintese de compostos poliméricos afim de otimizar a capacidade de adsorção do gás.

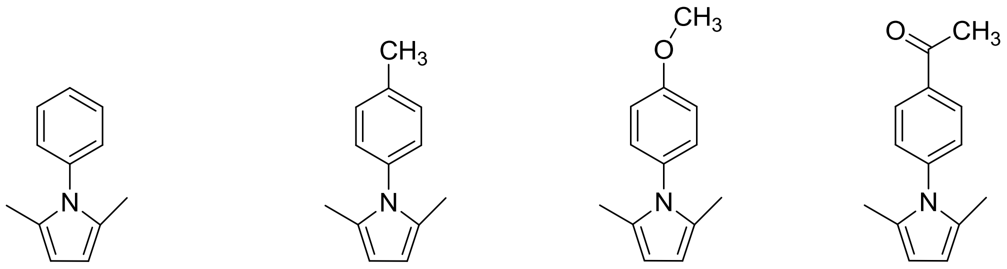

Figura 2- Pirróis N-aril substituídos

Agradecimentos: Os autores agradecem o apoio FCT/QREN-COMPETE através dos dos projectos PEst-OE/QUI/UI0313/2014 e PTDC/AAC-CLI/118092/2010 também como o apoio da CAPES.

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P-38 NEW THIAZOLIDINE-BASED ORGANOCATALYSTS FOR ENANTIOSELECTIVE CATALYSIS

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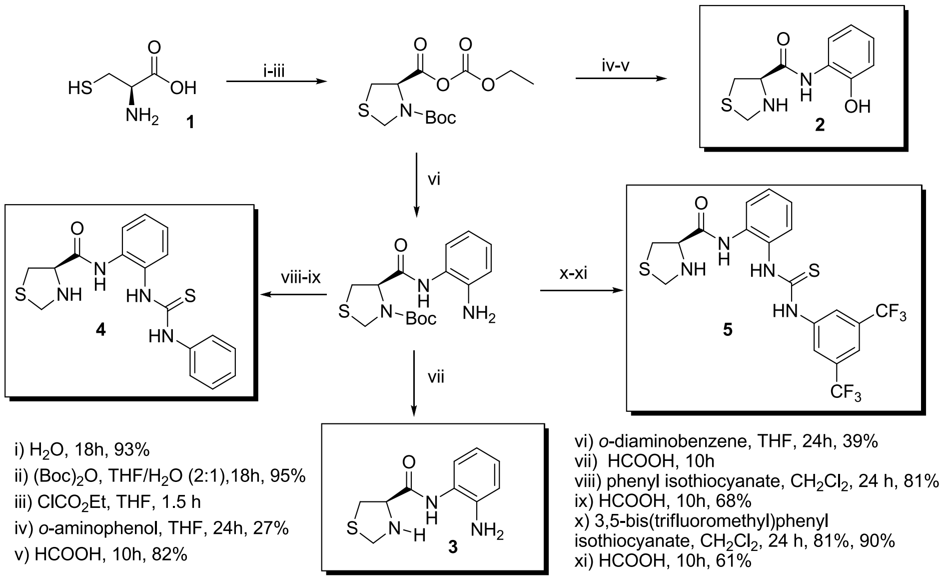
Asymmetric organocatalysis has emerged as a “green” alternative to organometallic catalysis, having experienced a rapid growth in recent years because it allows the metal-free synthesis of chiral compounds [1,2]. Thioureas have been used as organocatalysts in several asymmetric reactions with very good results [3,4]. However, as far as we know there are no references on the use of thiazolidine derived ureas as organocatalysts. This chiral scaffold is easily obtained from the condensation of cysteine with carbonyl compounds. In this context, several thiazolidine-based organocatalysts (**2**-**5**) were synthesized, starting from *L*-cysteine (**1**), according to the synthetic sequences described in Scheme 1. Compounds **2**-**5** were tested in asymmetric aldol and Strecker reactions with promising results.



i) H_2O, 18h, 93%
ii) $(Boc)_2O$, THF/H_2O (2:1),18h, 95%
iii) $ClCO_2Et$, THF, 1.5 h
iv) *o*-aminophenol, THF, 24h, 27%
v) HCOOH, 10h, 82%

vi) *o*-diaminobenzene, THF, 24h, 39%
vii) HCOOH, 10h
viii) phenyl isothiocyanate, CH_2Cl_2, 24 h, 81%
ix) HCOOH, 10h, 68%
x) 3,5-bis(trifluoromethyl)phenyl isothiocyanate, CH_2Cl_2, 24 h, 81%, 90%
xi) HCOOH, 10h, 61%

Scheme 1

Acknowledgements: The authors thank the FCT (projects Pest-C/QUI/UI0313/2011 and PEstOE/QUI/UI0313/2014), FEDER, COMPETE and QREN for financial support and the UC-NMR facility for NMR spectroscopic data (http://www.uc.pt/fctuc/dquimica/nmrccc).

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P-39 SYNTHESIS AND CHARACTERIZATION OF NOVEL HETEROCYCLIC – CONJUGATED SYSTEMS FOR DYE-SENSITIZED SOLAR CELLS (DSSCs)

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The quality of human life depends to a large degree on the availability of energy, which is threatened unless clean and renewable energy sources are developed in the future. Science is expected to make important contributions to identify environmental friendly solutions for the energy problem. One attractive strategy is the development of photovoltaic cells, a promising source of renewable energy able to convert sunlight to electricity and with high potential to contribute significantly for solving the energy problem [1].

Earlier, dye sensitizers applied in solar cells were mainly ruthenium complexes, consisting of the central metal ion with organic ligands containing an anchoring group. However, the lack of abundance of Ruthenium in nature, in addition with the latent risk to the environment, complicated synthetic processes and difficult purification methods, makes Ru-based dye sensitizers not suited in terms of cost efficiency and environmental friendliness. On the other hand, π-conjugated heterocyclic dyes of the type D-π-A are advantageous due to the structural diversity of the molecules that allows accurate adjustment of the photophysical and electronic properties, low cost of production, and environmental friendliness [2-3].

The present communication reports the synthesis and evaluation of the DSSCs performance of a wide range of novel π-conjugated heterocyclic dyes bearing bithiophene or thienothiophene π-bridges functionalized with (hetero)aryl donor groups and cyanoacrylic acid or rhodanine acetic acid as anchoring groups. This multidisciplinary study shows that the improvement of the DSSCs performance can be achieved through the rational design of the dye in which several modifications on the π-bridge and/or on the donor and anchoring groups were performed.

Acknowledgements: Thanks are due to *Fundação para a Ciência e Tecnologia* (FCT) and FEDER-COMPETE for financial support through the Centro de Química PEst-C/QUI/UI0686/2011 (F-COMP-01-0124-FEDER-022716) and a PhD grant to S. S. M. Fernandes (SFRH/BD/87786/2012). The NMR spectrometer Bruker Avance III 400 is part of the National NMR Network and was purchased within the framework of the National Program for Scientific Re-equipment, contract REDE/1517/RMN/2005 with funds from POCI 2010 (FEDER) and FCT. We are also grateful to the Instituto da Educação of Universidade do Minho for providing the laboratory infrastructure necessary for the development of this work. I. Mesquita acknowledges FCT for her PhD grant (Ref.: PD/BD/105985/2014); L. Andrade and A. Mendes acknowledge European Research Council (Contract no: 321315) for funding.

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P-40 AMINOCARBONYLATION AS NEW TOOL IN THE QUEST FOR BIOCOMPATIBLE PHTHALOCYANINES

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With the increasing number of applications of phthalocyanines and derivatives in the field of biomedicine, particularly in medical imaging techniques [1], research has been focused on the modeling of these macrocycles structures in order to increase their biocompatibility. Hence, the amide linkage (peptide bond) is one of the most natural conjugations available [2], present in many biological synthons, such as peptides, proteins or amino acids. Nevertheless, when compared with other functionalities, amide substituted phthalocyanines are quite rare [3].

In this study we present a new strategy for direct modulation of phthalonitriles through palladium catalysed amino-carbonylation reactions. Particularly, we have synthesised for the first time a phthalonitrile-DO$_3$A conjugate (DO$_3$A = amino functionalised 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic carboxylic acid ester), a versatile and easily accessible chelator, with great potential for the development of highly targeted contrast agents for optical imaging, namely magnetic resonance imaging (MRI) or positron emission tomography (PET). Additionally, we have also prepared and fully characterized the corresponding zinc phthalocyanine conjugates, as promising probes to be further exploited as suitable sensitizers in a variety of *in vivo* imaging techniques.

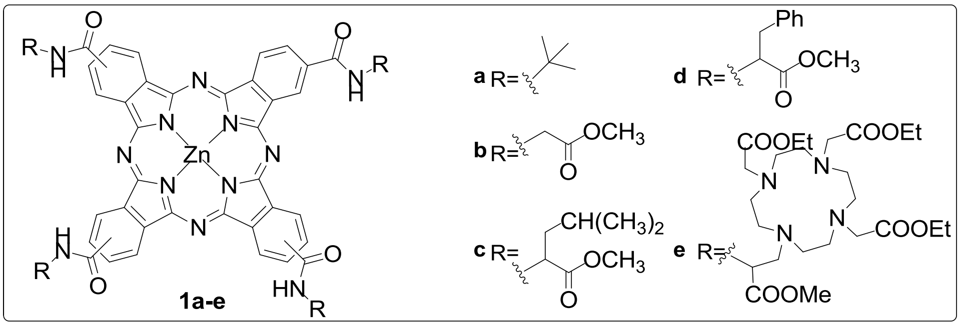

Figure 1: Amide substituted phthalocyanines.

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P-41 GLOBAL GEOMETRY OPTIMIZATION WITH EVOLUTIONARY ALGORITHMS: APPLICATION TO ATOMIC, MOLECULAR AND COLLOIDAL CLUSTERS

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Clusters are formed by a relatively small number of atoms or molecules, which leads such systems to have rather different properties in comparison to the condensed phase. These systems are somehow related with several phenomena, *e.g.*, nucleation and microsolvation, and develop an important role for the knowledge of fundamental properties of materials [1]. At the mesoscale, colloidal clusters may be visualized [2] by employing modern microscopy techniques and, hence, it is now possible to compare directly the experimental structures with those obtained with global optimization methods [3]. Due to the enormous number of local minima and the roughness of the potential energy surface, cluster systems are in general quite difficult to globally optimize. Because of this, several methodologies devoted to global optimization have appeared in the literature (see Ref. [4] and references therein). In the last decade, we have developed state-of-the-art evolutionary algorithms (EAs) to search for the global minimum of both atomic [5] and molecular clusters [6].

In this work, we showcase the successful application of the EAs developed in our group to different type of cluster systems. We present results on the structure and energetics of atomic, molecular and colloidal clusters. Specifically, we applied EAs to discover global minimum structures of binary atomic clusters [5], to study the microsolvation of alkali-metal ions with water [7], methanol [7], benzene [8] and hexafluorobenzene [9], and to get insight about charge-repulsion effects in colloidal clusters [4]. When available, we also compare the global optimization results with other theoretical and experimental data.

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P-42 DIFFUSION OF SMALL GASES INSIDE DIPEPTIDE NANOTUBES. A NON EQUILIBRIUM MOLECULAR DYNAMICS STUDY

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Crystalline dipeptides are excellent materials for storage or selective separation purposes, and they are also excellent candidates for use as permeation-selective barriers [1, 2].

This work is focused on the diffusion and flow of diatomic gases such as N_2 and O_2, through nanotubes of L-Leucyl-L-Serine (LS) crystals (Figure 1). To examine separation abilities of the studied structure (LS), Non Equilibrium Molecular Dynamics (NEMD) simulations were performed. The system of nine dipeptide nanotubes is considered and two boxes with different gases (N_2 and O_2) are introduced into the system separately. Simulations were carried out with the GROMACS 4.6 software, employing the General Amber Force Field (GAFF).

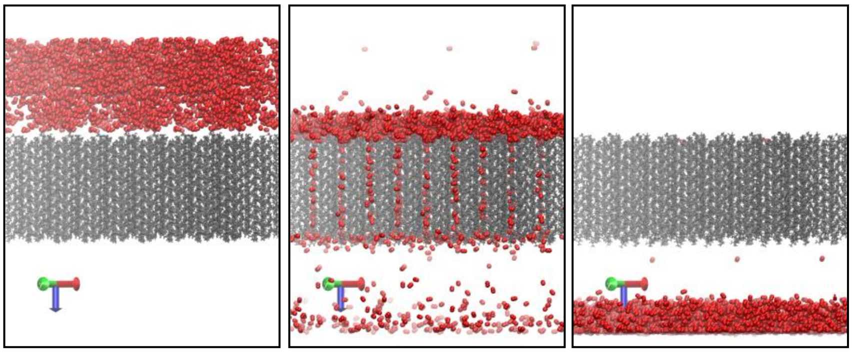

Figure 1

The results show that during the simulation the density of the oxygen inside the dipeptide nanotubes is higher than nitrogen, which correlate with their atomic radii. In addition, the rate of increasing density for oxygen inside nanotubes is higher than for nitrogen using two different values of force constant (10 kJ/mol·nm^2 and 100 kJ/mol·nm^2).

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P-43 QM/MM MD SIMULATIONS APPLIED TO IRREVERSIBLE INHIBITION OF *PLASMODIUM FALCIPARUM* CYSTEINE PROTEASE

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The increasing resistance of malaria parasite is a key factor in the persistence of malaria as a global major health concern. Therefore, novel, less toxic, and more specific inhibitors are urgently needed to control this infectious disease. The completed sequencing of *Plasmodium falciparum* genome allowed the identification of various potential biochemical targets, which are being pursued for the design of novel antimalarials. Among these targets are cysteine proteases (falcipains, FP) that hydrolise hemoglobin into amino acids in the food vacuole, essential to the survival of the parasite. [1]

The active site of FP consists of a catalytic dyad of cysteine and histidine, existing as an ion pair. Many of the reported FP inhibitors are able to block the enzyme's activity by forming an irreversible covalent bond with the active site cysteine. [1] Virtual screening has emerged as a powerful tool for identification of novel and diverse leads. However, it is extremely challenging to correctly score docked molecules that are covalently bound, as it is difficult to evaluate the contribution from the bond formation to the overall inhibitor potency. [2] Thus, understanding the covalent FP inhibition would be important: a) to define, at an atomic level, the mechanism of this inhibition process; b) to identify key active-site residues and c) to provide insights for the rational design of pharmacologically useful inhibitors. In this context, we performed a hybrid QM/MM MD simulation to reproduce the covalent FP inhibition by the peptidyl vinyl sulfone inhibitor. [3] The results permitted to determine the role of individual amino acids on the irreversible inhibition reaction by considering the interactions established along the process.

Acknowledgements: This work was supported by FEDER-COMPETE program (ref FCOMP-01-0124-FEDER-020963, FCOMP-01-0124-FEDER-041066 and PT2020 Partnership Agreement) and by Portuguese National Funds through FCT/MEC (ref EXPL/QEQ-COM/0927/2013, PTDC/QUI-QUI/116864/2010 and UID/CTM/50011/2013). CT and JRBG thank FCT for the post-doctoral grant (SFRH/BPD/62967/2009) and the Investigador FCT program, respectively.

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P-44 ANALYSIS OF THE VSPER MODEL USING COMPUTATIONAL QUANTUM CHEMISTRY CALCULATIONS

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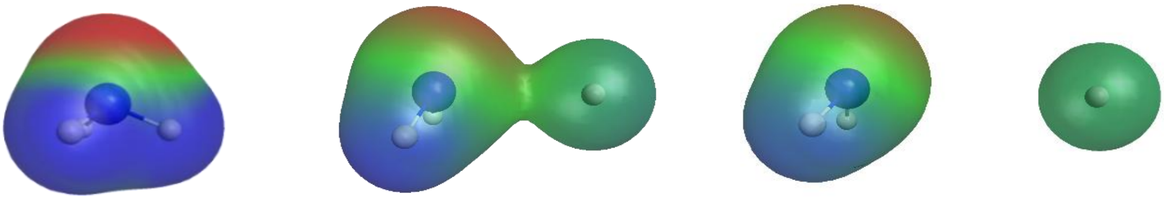

Figure 1: Electrostatic potential variation in NH_3 dissociation: a) equilibrium geometry; b) increase of NH distance c) dissociation in NH_2+H.

The main goal of the present work is to analyze the physical and chemical reasons why the VSPER model works (and sometimes fails) using accurate computational quantum chemistry calculations.

The VSPER model resulted from suggestions of Nevil Sidgwick and Herbert Powell before 1940 and was extended by Ronald Gillespie and Ronald Nyhoim [1-3]. This model is used to predict qualitatively bond angles in molecules with a central atom with chemical bonds and non-bonding pairs of electrons [3] (all this concepts referring to the generalized Lewis model). Although useful for interpreting the structure and geometry of many molecules, a rigorous quantum chemical explanation for its success is still lacking. Gillespie and coworkers [2] attribute this success to the Pauli principle and to the existence of electron pairs domains which are only qualitatively defined. Other authors, as Bent, refer to electron domains and advocate electrostatic and geometric reasons for the success of this type of models [4].

A detailed analysis of the electronic kinetic energy and total potential energy contributions (which are related by the virial theorem), as well as one-electron (nuclei-electrons attractions), two-electron (electron-electron repulsions), and nuclei-nuclei repulsion contributions in molecules such as H_2O, H_2S, NH_3, PH_3, CH_4 and SiH_4 are undertaken, using various *ab initio* and DFT methods with different basis sets. The variation of these quantities with geometry, as well as the evolution of electron densities and electrostatic potentials (see Figure 1), is analyzed and compared with VSPER model predictions.

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P-45 HINTS ON MACROCYCLIC DITERPENIC CORE DERIVATIZATION BY AN OPTIMIZED IN SILICO METHOD

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The increase number of chemotherapy failures reported worldwide has identified multidrug resistance (MDR) to anticancer drugs as a serious health concern, with long-lasting physical and psychological outcomes. As the over-expression of ABC transporters in cancer cell lines is one of the most reported MDR mechanisms [1] the selective inhibition of MDR-related efflux pumps as P-glycoprotein (P-gp) remains as a promising approach for overcoming MDR.

Macrocyclic and polycyclic diterpenes isolated from *Euphorbia* species have been the source of suitable P-gp efflux modulators [2]. Yet, their potency can be additionally improved through several chemical modifications of the different groups attached to the diterpenic core. To this matter, *in silico* approaches have been successfully applied in the identification of the most suitable chemical features for MDR modulation [3].

Through the combination of previously published computational and experimental data [4,5], a virtual screening procedure involving pharmacophoric identification and molecular docking over a refined murine P-gp structure was developed to evaluate the impact of the different chemical groups on MDR-reversal activity. Then, structure-based induced-fit docking followed by more accurately calculating free energies of binding (MM/PBSA) and ligand-based structure-activity relationship (QSAR) studies were used to characterize the relationship between chemical modifications and the respective modulation capabilities.

This computational workflow was originally developed from a small library of diterpenes, obtained from the chemical derivatization of compounds isolated from *Euphorbia boetica*. As this procedure was able to discriminate the most active from a set comprising 26 derivatives, it can be further used to guide chemical derivatization to avoid the synthesis of low-activity compounds. The developed *in silico* methodologies will allow a better identification of the chemical modifications suitable to increase the interaction towards P-gp, leading to more potent MDR reversers.

Acknowledgments: *Fundação para a Ciência e a Tecnologia* (FCT, Portugal) is acknowledge for financial support (project PTDC/QEQ-MED/0905/2012 and PhD scholarship SFRH/BD/84285/2012)

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P-46 NBO ANALYSIS OF SUBSTITUENT INTERACTION IN CYCLOHEXANE DERIVATIVES: EFFECTS ON MOLECULAR CONFORMATION AND SOLID PHASE STRUCTURE

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Hyperconjugation and steric hindrance have been extensively used to rationalize conformational preferences in flexible molecules, sometimes in conflicting views.[1,2] These factors can be analyzed by Natural Bond Orbital (NBO) theory. This tool offers a quantitative analysis of the wavefunctions, accounting relevant energetic terms in a chemically intuitive way based on localized Lewis-type orbitals.

The conformational equilibria of cyclohexane derivatives with different substitution patterns is dominated by the balance between axial and equatorial forms, and also by torsions of flexible substituents. In the case of hydroxyl substituents, the possibility of formation of intramolecular hydrogen bonds in some isomers can further influence the conformational distribution.

In this work, the conformational space of several cyclohexane derivatives is explored by post-Hartree-Fock ab initio calculations and the stability of the conformers is analyzed in terms of the contribution of different energetic terms accessible from NBO analysis, namely hyperconjugation and steric hindrance.

Both these factors are shown to by determinant, not only of the structure of isolated molecules, but also of condensed phases. Moreover, the shape and electron density of the individual molecules associated in the solid phases can be shown to be related to characteristic properties of cyclohexane diols such as plastic crystal formation and polymorphism.

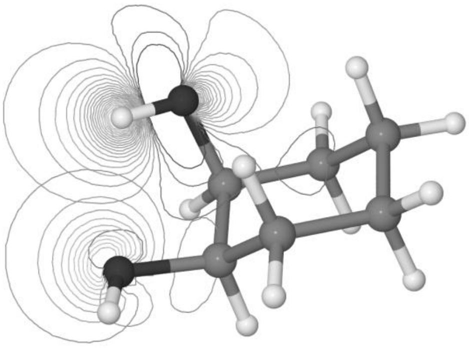

Figure 1: NBO interaction in a cyclohexanediol.

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P-47 VIBRATIONAL SPECTRA OF ClO_2 AND ClOO ISOMERS OF CHLORINE DIOXIDE: CALCULATION ON A NEW DMBE POTENTIAL ENERGY SURFACE AND MULTIPROPERTY FIT

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The goal of the present work is to calculate and analyze the vibrational spectra of C_{2v} ClO_2 and C_s ClOO isomers of chlorine dioxide on a new global DMBE potential energy surface for ClOO ground state system [1] taking into account the possible perturbations between the spectra of both isomers. In fact, although chlorine dioxide is a well known radical molecule with a dramatic role on the ozone depletion problem, there are still uncertainties on some aspects of its reactivity [2] and spectra [3].

In addition, it is aimed to improve the spectroscopic properties of the DMBE surface via a direct multi-property fit [4-7] to the available vibrational spetroscopic data [3] and *ab initio* energies [1].

Acknowledgements:This work has the support of Fundação para a Ciência e a Tecnologia, Portugal, under contracts PTDC/CEQ-COM3249/2012 and PTDC/AAG-MAA/4657/2012 as well as the support from the Coimbra Chemistry Center (UID/QUI/00313/2013).

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P-48 GLOBAL MINIMUM STRUCTURES OF NaK ALLOY CLUSTERS BY EMPLOYING AN EVOLUTIONARY ALGORITHM

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Clusters are intermediate species between a single atom or molecule and the bulk matter and, hence, they show peculiar properties with relevance for many disciplines. Because of this, cluster systems have been the subject of a great amount of theoretical and experimental work in the last decades (see Ref. [1] and references therein). In particular, metallic clusters develop an important role in many technological applications at the nanoscale (*e.g.*, in catalysis). In alloys, one may also modify the composition, which can be used to tailor materials with specific chemical and physical properties [2]. Recently, the growing pattern of the title alloy system has been studied by using global optimization methodologies [3,4]. In the present work, we have tested the evolutionary algorithm (EA) developed in our group [5] against the results given in Ref. [4]. From the 20 clusters of NaK considered by us, which include the largest ones of Ref. [4], we were able to reproduce the lowest-energy structures and, in addition, we improved the global minima of Na_2K_{53}, $Na_{35}K_{20}$ and $Na_{40}K_5$.

After benchmarking our EA, we have investigated the energetics and structure of all 38-atom NaK-alloy compositions using the Gupta empirical potential [6] with the same parameters employed in Refs. [3,4]. Whereas the corresponding homonuclear clusters present an octahedral geometry (which is observed in 38-atom clusters of many other systems), the mixed aggregates tend to show an icosahedral-type structure. In comparison with Na_{38} and K_{38}, the mixed $Na_{13}K_{25}$ cluster is the most stable one. Also, "magic-number" structures (*i.e.*, clusters that are particularly stable in relation to the neighbor-composition ones) arise for Na_2K_{36}, Na_9K_{29} and $Na_{13}K_{25}$. In the NaK alloy, the sodium atoms tend to occupy positions in the core, while the potassium ones segregate to the surface. Since our EA allows to freeze the core atoms during the optimization procedure, we have also studied the deposition of Na-atoms on a potassium core for the 38-atom size, which gives insight about the structural motifs arising in such doping process.

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P-49 TEORETICAL RATE CONSTANTS MAY NOT BE USEFUL FOR KINETICS MODELS: THE FATE OF OH IN THE COMBUSTION OF A HYDROGEN/OXYGEN MIXTURE

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Recently, we proposed a method to model complex reactive systems incorporating accurate potential energy surfaces, reactive and nonreactive, and concurrently integrating the equations of motion of the chemical species present in the bulk [1]. This is accomplished by defining a global Potential Energy Surface (gPES) combining various PESs, each one of them representing an elementary reaction that is expected to play a role in the chemical process. Multiple Reactions Dynamics, MREADY, is a program that builds an overall PES for the process in question and performs reactive classical dynamic calculations on it. Starting from a bulk mixture of H_2 and O_2 molecules, the program integrates the equations of motion in a total potential build from 17 accurate potential energy surfaces such as H_4, H_3O, HO_3, H_2O_2 and H_2O among others that should play a role in the combustion process. The overall results of this calculation have shown to be in reasonable agreement with similar kinetic model results [1].

In a gas phase combustion or explosion, reactants and intermediates can be far from thermal equilibrium, i.e., the number of non-reactive collisions can be small and the energy distribution of the intermediate species will be far from the Boltzmann distribution, depending on the energy distribution at the time of their formation and on the energy transfer in the non-reactive collisions. On the other hand, kinetics models use available kinetic data, rate constants and their variation with temperature, to model complex mechanisms and have been applied to model combustion processes. They rely on the assumption that the number of collisions between reactants and intermediates is large enough to achieve thermal equilibrium.

To test this last hypothesis we have followed the evolution of the hydroxyl radical, OH, which is an important and very reactive intermediate, during the combustion of a mixture of oxygen and hydrogen at 3000 K and 2 atm until 3 ns, using the MREADY program.

In this work we present preliminary results of that study. They show that, in spite of the occurrence of a large number of collisions, these are more efficient in rotational and translational energy transfer than in vibrational quenching. As a consequence, the OH radical seems to be vibrationally excited, having an average energy which is twice the rotational. This result, which is expected to have a significant contribution to the reaction rate constants involving this radical, has recently been confirmed experimentally [2].

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P-50 THERMOISOMERIZATION PRODUCTS OF INDIGO: EXCITED STATE CHARACTERIZATION

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Indigo was sublimated at a temperature of 950 ºc and a pressure of $9.7\text{x}10^{-3}$ mbar from which four major products have been obtained. These were analysed by column chromatography and HPLC-DAD. One of the products is identical to the one obtained under similar conditions (at 460 ºC) by Haucke and Graness. [1] However, under these experimental conditions, this was not found as the major compound.

The analysis of the four products, comprehensive electronic spectral and photophysical characterization is presented. It is shown that some of the products obtained have significant different photophysical properties with the radiative deactivation channel operative which contrasts with indigo. [2]

This work shows that indigo is not only photostable (a reason pointed for its longevity as a dye) but also thermostable. Indeed, albeit converted into other products, indigo is still one of the major compounds present upon.

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P-51 THE MATHEMATICAL STABILITY STUDY FOR THE PPy – CoO(OH) COMPOSITE SYNTHESIS

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Conducting polymers (CP) are one of the most studied classes of compounds during the 5 last decades. Their study is explained by their capacity to combine the properties of plastic with metal conductivity and by ease in their modification [1].

One of the important aspects of CP is their use in composites for different purposes. Some of them are corrosion protecting coatings, electrochromic devices and specific surfaces for photo and photoelectrodegradation.

In this aspect, other important substance may be oxy-hydroxycompound of cobalt (III), that is used as a specific surface because of its possibility of absorbing light, resulting in its extremely black color. Its composite with polypyrrole, polyfuran and polythiophene could have interesting behavior to be used in photodegradation and electroanalytical systems.

A possible scheme of its synthesis, including the PPy – Co composite cathodic deposition with $Co(NO_3)_2$ as an electrolyte, analogous to [2], as following:

$$NO_3^- + 4H^+ + 2e^- \rightarrow NO^+ + 2H_2O$$
$$NO^+ + Py \rightarrow Py^{+\cdot} + NO$$

with the following Co oxidation in alkaline media to CoO(OH). This synthesis may include electrochemical instabilities either on electropolymerization stage, or on the stage of cobalt oxidation [3 – 4]. Their phenomenological explanation may be based on logical arguments, but their rigid theoretic base may only be given by the analysis of the mathematical model of the system, capable to describe adequately its behavior. It is also capable to describe the similar systems (as a consequence of the third similarity theorem).

Two mathematical models, describing the first and the second step are represented. It is shown that at the second stage the appearance of time dissipative structures is more probable than at the first one.

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P-52 SYNTHESIS OF BIOCOMPATIBLE PHTHALOCYANINES

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Magnetic resonance imaging (MRI) has emerged in the last decades as one of the most powerful imaging techniques for pre-diagnostic of degenerative diseases. Currently Gd(III) based contrast agents (GBCA)s have been used in over 30% of MRI exams [1]. However, some recent studies show that certain Gd(III) chelates are not sufficiently stable within the intracellular space, toxic Gd^{3+} can be released in the organism and may favor the appearance of nephrogenic systemic fibrosis (NSF) [2]. The use of manganese chelates seems to be a good strategy to overcome the limitation of GBCAs. In the literature there are several examples of manganese porphyrins as potential contrast agents for MRI [3]. Manganese ions are less toxic than Gd(III), the probability of release of Mn^{3+} and Mn^{2+} is relatively low and also higher relaxivities can be achieved in higher field strengths because of the rigidity of the macrocycle, which seems to avoid internal rotation and can effectively lower the rotational diffusion rate. Herein we report the synthesis of novel water soluble phtalocyanines (Pcs), bearing either four PEG500 or four choline substituents at the macrocyclic periphery, and present photophysical properties and preliminary results of relaxivity properties of Mn(III)-PEG-phthalocyanine for development of MRI contrast agents.

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P-53 MICROBIAL STRESS TO REACTIVE OXYGEN SPECIES AND METALS

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The study of bacterial copper homeostasis, especially copper tolerance mechanisms, has gain interest due to the widespread use of copper compounds as bactericide in agriculture or as disinfectants in the food industry. This general use will undoubtedly lead to the selection of copper-resistance strains of bacteria and the dissemination of plasmid-borne copper resistance genes among different bacterial pathogens with important implications in disease control efforts. Moreover, mechanisms of copper tolerance have recently been linked to the molecular mechanism of pathogenesis. During infection, bacteria are exposed to different stresses, as reactive oxygen species and fluctuations in metal ions concentration. Under the scope of copper resistance, we have investigated the molecular mechanism of copper resistance in a bacterial system, *Marinobacter hydrocarbonoclasticus* [1].

Host immune response to pathogenic microorganisms, frequently employs oxidative stress in the form of reactive oxygen species (ROS). Some of the most common ROS found in biological systems involve the superoxide anion, hydrogen peroxide (H2O2) and hydroxyl radical. Pathogenic bacteria from the species *Neisseria gonorrhoeae* and *Neisseria meningitidis*, that cause gonorrhea and meningitis, respectively, have developed numerous defense mechanisms to cope with oxidative stress of the constant exposure to ROS. These mechanisms are essential for cell survival taking since ROS can cause damage to DNA, proteins and cell membranes. One of these mechanisms is based on the family of bacterial cytochrome *c* peroxidases. These periplasmatic enzymes catalyze the conversion of H_2O_2 to water using haem co-factors and *c*-type cytochromes or small type copper proteins of the respiratory chain as the electron donor [2].

Sulfate reducing bacteria are strictly anaerobic bacteria and some strains can tolerate low oxygen tension during short period of times. Therefore, these bacteria must have develop sensor proteins that upon oxygen exposure triggers mechanisms of defense. The Orange Protein Complex is a molecular system of still unknown function that is known to respond to oxygen and is involved in cell division of sulfate reducing bacteria. The proteins belonging to this complex have Fe-S centers or other heteronuclear Mo-Cu centers [3,4].

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P-54 DEVELOPMENT OF SOLID LIPID NANOPARTICLES OF DAPSONE AS A NOVEL DRUG RELEASE SYSTEM AGAINST *MYCOBACTERIUM LEPRAE*

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Dapsone (DAP) is a bactericidal agent used in the treatment of leprosy, an infectious disease caused by *Mycobacterium leprae*, which is transmitted through the bacilli present in the air. DAP is a class II drug, according to the Biopharmaceutical Classification System (BCS) (low solubility and high permeability), which may result in low therapeutic index and a high microbial resistance. Many technologies are available and have commonly been used to overcome drawbacks associated with poorly water-soluble drugs. Solid lipid nanoparticle (SLN) have attracted increasing attention in the last years as a colloidal carrier for controlled drug delivery system. These nanoparticles possess advantages such as good tolerability, high oral bioavailability, feasible scale-up, and less acute and chronic toxicity. The aim of the present work was to develop and optimize SLN for the increment of the therapeutic index of DAP. Firstly, a screening was performed in order to evaluate the suitable conditions as type and amount of lipid, time and amount of surfactant, amount of drug and time of sonication. The SLN were prepared by the ultrasonication method. The SLN were evaluated concerning the size, polidispersity, zeta potential, drugs' encapsulation efficiency, loading capacity and release. The developed SLN presented desirable characteristics, and seem to be a promise strategy to overcome DAP limitations in the therapy of leprosy.

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P-55 RECYCLING ANTIMALARIALS – A SUSTAINABLE APPROACH TOWARDS ANTIPARASITIC AND ANTIPROLIFERATIVE DRUGS

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Developing new drug products is a costly and time-consuming process, which is a delicate issue when addressing diseases of poverty; a low-cost reduced-risk strategy towards sustainable drug development may pass by performing simple chemical modifications on classical drugs (recycling), or by identifying new therapeutic uses for shelved drugs (rescuing), or for drugs approved to treat a specific disease while being potentially relevant against other therapeutic targets (repurposing) [1]. For the past few years, our group has been working on the recycling of classical antimalarials chloroquine (**1**) and mepacrine (**2**), whose originally thrilling antimalarial properties gave place to disappointing news about, respectively, emergence of parasite resistance and toxicity issues; starting from the heteroaromatic cores of these two antimalarial classics, we performed simple chemical transformations to obtain compounds **3** and **4** (Figure 1), whose remarkable antimalarial and antiproliferative properties will be presented [2-6].

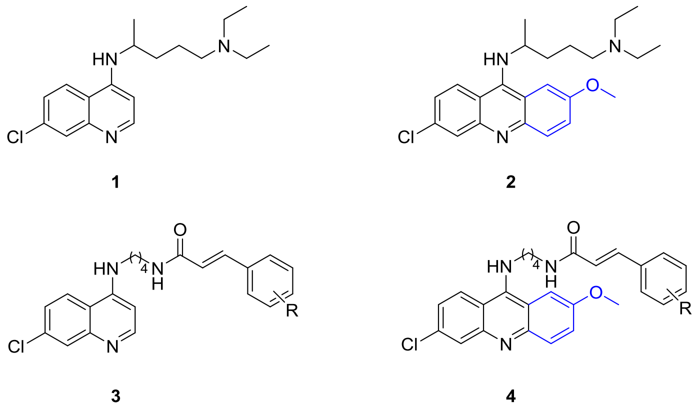

Figure 1: Chloroquine (**1**), mepacrine (**2**) and respective surrogates **3** and **4**.

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P-56 THE EFFECT OF THREE INHIBITORS IN THE INTRACELLULAR STAINING PATTERN OF TWO RECENTLY OBTAINED FLUORESCENT BENZO[a]PHENOXAZINES

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Oxazine derivatives have been reported as potential fluorescent probes, with uses as nucleic acid labels [1], showing a high tumor-specificity comparatively to normal cells [2,3]. In order to extend our studies regarding the applications of Nile Blue derivatives as fluorescent probes for assays employing intact, live cells, we evaluated the effect of three known inhibitors in the fluorescence intensity and in the intracellular distribution pattern of two benzo[*a*]phenoxazinium chlorides (Figure 1), recently prepared by our research group [4]. *N*,*N*-Dicyclohexylcarbodiimide was used as a F_0F_1-ATP synthase inhibitor, 2-desoxiglucose as a glycolysis inhibitor and the protonophore *m*-chlorophenylhydrazone as a mitochondrial uncoupling agent. It was shown that the last inhibitor had the most relevant effect both on the staining pattern and the intracellular fluorescence.

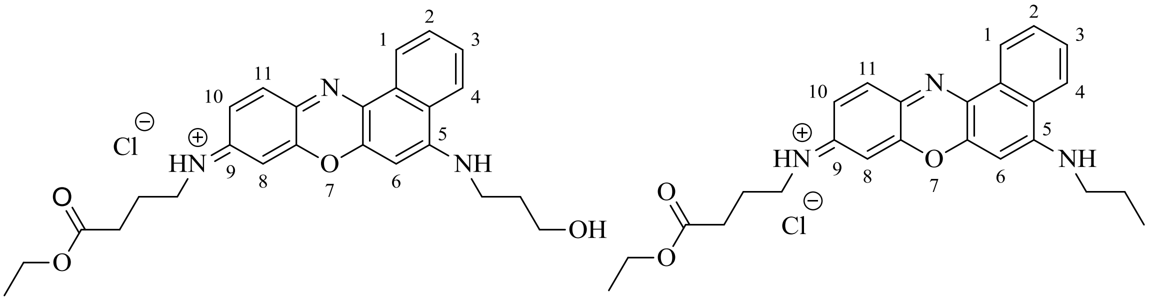

Figure 1: Structures of functionalised benzo[*a*]phenoxazinium chlorides.

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P-57 ITERATIVE OPTIMIZATION OF PACLITAXEL-LOADED NANOSTRUCTURED LIPID CARRIERS AND ITS CHARACTERIZATION

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Paclitaxel is one of the most effective broad-spectrum chemotherapeutic agent in the treatment of cancers. However, its clinical application has been limited due to its poor water solubility. Moreover, paclitaxel causes several side effects due to a wide biodistribution and has undesired pharmacokinetics. Therefore, there is a need of an effective incorporation of paclitaxel in a drug delivery system that can enhance its solubility, permeability and stability and promote a sustained, controlled and targeted delivery, increasing thereby the therapeutic effects and reducing the dosages and side effects.

The objective behind this study was to apply an iterative approach in the optimization of nanostructured lipid carriers' varied characteristics and assess its potential as Paclitaxel vehicles and therefore as anti-neoplastic drug delivery systems. Lipophilicity assays determined Gelucire® 43/01, Compritol® 888 ATO and Miglyol® 812 as the best lipid blend, among a wide variety of tested lipids, for Paclitaxel dissolution. From a starting composition the formulation's physicochemical properties, such as mean particle size, zeta potential and polydispersity index, were evaluated. The composition was iteratively changed as molar ratios between the lipids and the surfactant (Tween® 80) are concerned. Each and its composition was for the next one. At the current optimization step, a formulation with mean diameter of 245.5±1.0nm, polydispersity index of 0.113±0.008, zeta potential of -29.23±0.47 and entrapment efficiency of 76% was achieved. *In vitro* release studies were also performed. This optimized Paclitaxel-loaded nanostructured lipid carrier formulation already seems a potential candidate as a cheap and safer parenteral anti-neoplastic agent.

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P-58 DOES DRUG-IN-NANOPARTICLES-IN-ADHESIVE SYSTEMS ENHANCE TRANDERMAL DRUG DELIVERY?

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Nanostructured lipid carriers (NLC) are nanosystems considered a second and smart generation of lipid nanoparticles, consisting of a matrix composed of a blend of solid and liquid lipids (oils), stabilized by an aqueous emulsifier solution[1, 2].

PURPOSE In the present work, a patch based on NLC was used to simultaneously convey olanzapine (OL, atypical antipsychotic) and simvastatin (SV, antihyperlipidemic) for transdermal drug delivery.

METHODS Firstly, NLC were prepared by the hot high pressure homogenization (HPH). Secondly, drug-in-adhesive transdermal systems, combined with different chemical enhancers and adhesives were prepared. Finally, *in vitro* release, permeation and adhesion tests were carried out.

According to release profiles, the transdermal patches led to a significant increase in the amount of drug released, in comparison to liquid formulations. A higher lipid concentration resulted in a larger release, particularly for OL. A permeation synergistic effect was observed between NLC and propylene glycol for both drugs. Adhesives have also a marked effect upon permeation behavior and tack performance.

In conclusion, a new drug-in-adhesive transdermal system was successfully developed, being considered a promising nanoplatform for a future *in vivo* approach.

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P-59 NEAR-INFRARED DYES FOR NON-INVASIVE OPTICAL DIAGNOSIS

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Prevention and treatment of cancer are limited by the non-invasive detection capacity of the diseased tissue. Optical imaging has high sensitivity, high contrast and good spatial resolution but the imaging for deep tissues remains a challenge due to light scattering and strong attenuation in these tissues. The induced fluorescence endoscopy (IFE) has a higher sensibility than conventional endoscopy to identify precancerous and cancerous lesions of the larynx (95% vs. 73% [1]) but insufficient specificity. The development of IFE requires specific fluorescence probes for tumors [2] that must be biocompatible, absorb light in the therapeutic window (700 – 900 nm), have a high fluorescence quantum yield (Φ_F) and a considerable Stokes shift. Hydrophobic phthalocyanines are good candidates once they present high Φ_F and a biodistribution that reach (tumor) / (peritumoral tissue) ratios > 5 [3].

Several phthalocyanines were synthesized and characterized and developed a formulation to allow an intravenous administration. In addition pharmacokinetic studies were perfomed non-invasively in BALB/c. The phthalocyanine shown in figure 1 presented a strong absorption at 743 nm ($\varepsilon \approx 100.000\ M^{-1}\ cm^{-1}$) and fluorescence emission at 770 nm (with $\Phi_F = 0.2$).

Pharmacokinetic studies showed a maximum compound concentration in the liver 24 hours after administration. Preliminary *in vivo* biodistribution studies, with implanted subcutaneous tumors indicate that this phthalocyanine has the required characteristics for the non-invasive detection of hyperproliferative tissues by IFE. Currently detection limits are being studied.

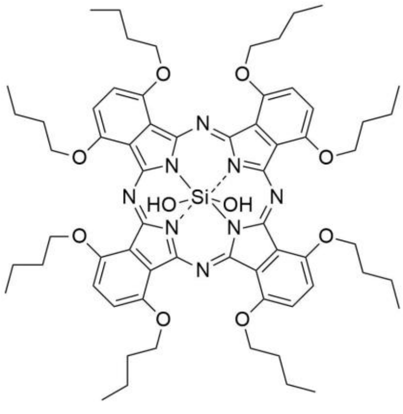

Figure 1: $Pc(Si(OH)_2(OBu)_8$

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P-60 CONTROLLING THE FLUORESCENCE BEHAVIOR OF 1-PYRENESULFONATE BY COINTERCALATION WITH A SURFACTANT IN A LAYERED DOUBLE HYDROXIDE

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Zn-Al layered double hydroxides (LDHs) containing solely 1-pyrenesulfonate (PS) or 1-heptanesulfonate (HS) anions, or a mixture of the two with HS/PS molar ratios ranging between *ca.* 7.5 and 80, were prepared by the direct synthesis method and characterized by powder X-ray diffraction, thermogravimetric and elemental analyses, scanning electron microscopy, FT-IR, FT-Raman and $^{13}C\{^{1}H\}$ CP MAS NMR spectroscopies. The materials obtained proved to be well-ordered with basal spacings of 18.8 Å for the LDH intercalated by PS and 19.2-19.4 Å for the other materials containing HS.

The photophysics of the solids, as well as the PS probe dissolved in water and common organic solvents (aiming to compare the behavior of the "isolated" molecule with that in the solid), were investigated by steady-state and time-resolved fluorescence techniques. The photophysical characterization of the resultant composites reveals the essential role of the surfactant in preventing PS aggregation and regulating the microenvironment within the LDH galleries. [1]

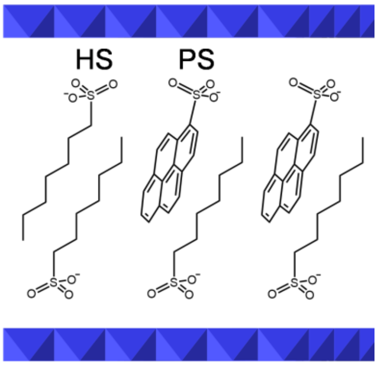

Figure 1: Schematic representation of PS and HS anions in LDHs.

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P-61 PHOTOPHYSICAL CHARACTERIZATION OF PORPHYRINIC DERIVATES FOR BIOMEDICAL APPLICATION

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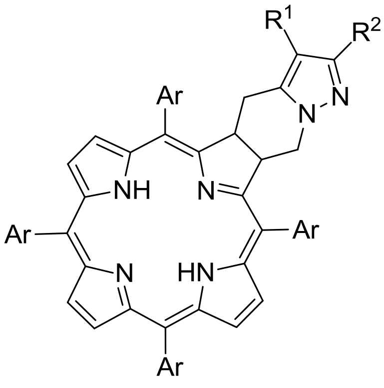
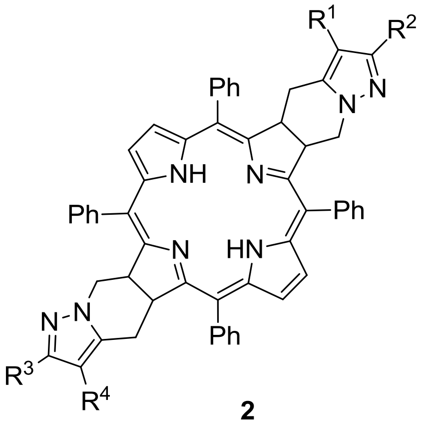
Porphyrins and their derivates (chlorins and bacteriochlorins) have a rich pattern of absorption bands particularly at red and near infrared region (NIR) of the spectra. Because of their red-shifted spectroscopic transitions, increasing interest exists in employing chlorins and bacteriochlorins in medicine. The most relevant applications of them are in medical imaging and in photodynamic therapy (PDT). The strong fluorescence in the NIR shown by these reduced forms of porphyrinic macrocycles within the phototherapeutic window (600-850 nm) is essential for their use as fluorescence markers for cancer lesions, making them valuable for tissue imaging. On the other hand, these macrocycles, when excited by light, are excellent singlet oxygen or superoxide ion producers that can destroy the diseased tissue, which is important in PDT [1a].

Recently the synthesis and photophysical characterization of new type of stable 4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyridine-fused chlorins and bacteriochlorins has been reported [1]. The first results regarding the *in vitro* study of some of these compounds showed that they will can be used as photossensitizers against melanoma cancer cells [2]. In this communication, details of photophysical characterization of novel chlorins and bacteriochlorins (*e.g* ***compounds 1-2)*** will be presented.



1

1a $R^1 = CH_2OH$, $R^2 = Ph$
1b $R^1 = H$, $R^2 = CH_2OH$
1c $R^1 = R^2 = CH_2OH$



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P-62 IMPACT OF PDT WITH LUZ11 IN DISTANT METASTASES

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Metastatic diseases are the main cause of death of cancer patients. Thus, treating cancer disease requires therapies capable of treating primary tumors but also able to eradicate distant secondary diseases [1]. Photodynamic therapy (PDT) with LUZ11 has revealed promising results, with high percentage of cures of subcutaneous tumors along with the ability to stimulate the immune system [2].

Our purpose is to develop a protocol for an animal model (BALB/c mice with orthotopic 4T1 mammary carcinoma tumor) that can be used to compare surgery against PDT in the elimination of the primary tumor and the control of metastasis.

BALB/c mice were inoculated with 4T1-luc2 cells in the abdominal mammary gland. The tumor kinetics of $1x10^4$, $2x10^4$, $5x10^4$ and $10x10^4$ inoculated cells was followed to assess the onset of metastatic disease. Metastization was monitored by bioluminescent imaging between days 27 and 41, and then the animals were sacrificed. Hereafter, metastases were confirmed by histological studies.

The first detection of metastases in the animals subjected to surgery was observed 27 days after inoculation. The higher percentage of metastization corresponded to the inoculation of $2x10^4$ cells. The inoculation of a smaller number of cells facilitates the metastization process, as described in literature [3].

The resistance of 4T1 cells and the location of the tumor are a challenge to PDT. Tumor kinetics, timing of surgery and PDT treatment parameters are being optimized to obtain an effective treatment of the primary tumor and to evaluate the impact of the treatment in metastases.

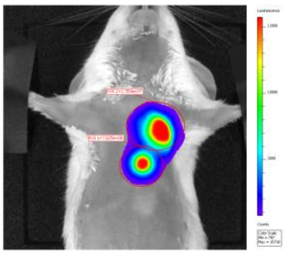

Figure 1: Bioluminescence imaging on day 41 of mice treated with surgery.

Acknowledgements: The Coimbra Chemistry Center is supported by the Fundação para a Ciência e a Tecnologia (FCT), Portuguese Agency for Scientific Research, through the project PTDC/QUI-QUI/120182/2010 and project PEst-OE/QUI/UI0313/2014.

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P-63 PDT-GENERATED ANTITUMOUR VACCINES

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Photodynamic therapy (PDT) is a well-known cancer treatment modality that requires the use of a photosensitizer (PS), light irradiation on a specific wavelength for each PS, and oxygen, in order to kill tumour tissue [1]. The development of PDT-generated antitumour vaccines [2, 3] takes advantage of the acute inflammatory response caused by PDT, which induces molecular changes associated with cell death such as damage-associated molecular patterns that stimulate the host immune system to destroy the cancer cells [1, 4]. The aim of this project is to generate effective prophylactic antitumour vaccines using PDT with the administration of the PS developed by Luzitin, F_2BMet [5], on a poorly immunogenic model (4T1 cell line).

The protocol for *in vitro* PDT was optimized to induce different types of cell death homogeneously, maintaining PS concentration while varying the light dose. It was possible to achieve 80-90% necrotic cell death at high light doses and 80-90% apoptotic cell death at lower light doses. This selectivity is important to assess which type of cell death is more relevant to stimulate the host immune system. Additionally, the cells were irradiated with a picosecond laser at 266 nm, 24h after the PDT procedure, to minimize the risk of tumour growth on the vaccine site. UV irradiation alone induced approximately 80% of cell death by apoptosis. After generating vaccines with $3x10^6$ treated cells, four groups of Balb/c mice (n=6) were subcutaneously inoculated: negative control (PBS), apoptosis, necrosis, and UV control (cells only treated with the UV irradiation). One week after vaccination, each group was inoculated with $3.5x10^5$ live 4T1 cells. The endpoint was the 33rd day after vaccination, or when the tumour's major axis reached 1.5 cm.

Calculated tumour volumes showed no statistical difference between negative control and vaccinated groups. The immunogenicity is lost 24 h post-PDT in vitro. Shorter periods between the preparation and inoculation of the vaccines are being tested.

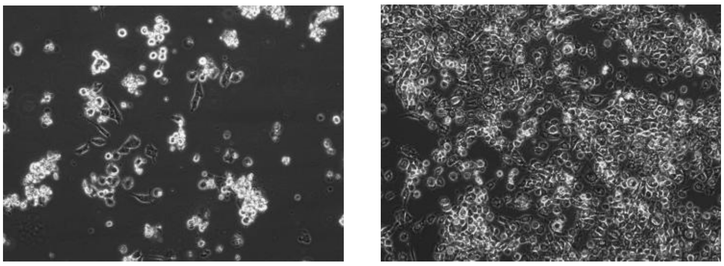

Figure 1: Different types of cell death 24h after PDT protocol: apoptosis (A) and necrosis (B).

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P-64 EFFECT OF TiO_2 ON THE DEGRADATION OF THE SUNSCREEN 2-ETHYLHEXYL p-METHOXYCINNAMATE UNDER SIMULATED SOLAR LIGHT IRRADIATION

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The public awareness of the health problems associated with UV radiation exposure (sunburn, cancer, photoaging) led to a dramatic increase in the use of sunscreen products. These products generally contain chemical (light absorbers) and physical (light reflectors) UV filters. One of the most commonly used chemical UV filter is the *trans*-2-ethylhexyl *p*-methoxycinnamate (EHMC) since present's absorption in the UVB region [1]. However, it lacks stability under UV irradiation as undergoes photoisomerization and phototransformation [2]. Physical filters include TiO_2 and ZnO but TiO_2 is the only physical filter allowed for commercial use in Europe. Though this material scatters and reflects UVA/UVB light, it also absorbs UV light and in aquatic environment this leads to the generation of reactive oxygen species (ROS) which can initiate oxidation, inducing DNA damage [3].

The aim of this study was to evaluate the effect of TiO_2 properties (particle size and crystal structure) on the degradation of EHMC aqueous solution under simulated solar light irradiation and find ways to stabilize its phototransformation. As so, the photodegradation of EHMC was carried out in absence (Fig. 1) and presence of the catalyst TiO_2. Furthermore, different tests were performed in order to ascertain which type of ROS ($^1O_2$, $^\bullet HO$, $O_2^{\bullet -}$) are formed upon UV illumination.

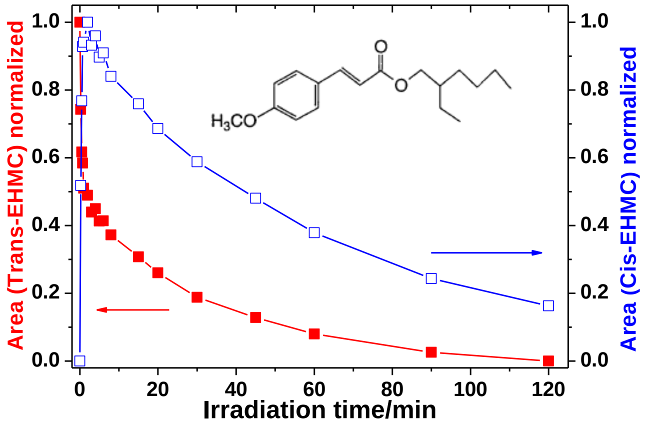

Figure 1: Photolysis of EHMC aqueous solution (10 % acetonitrile).

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P-65 ENHANCING PDT - TARGETING ENERGY METABOLISM OF TUMOR

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Photodynamic therapy has been used for cancer treatment with good results. The basic principle of this technique is based on the combined use of photosensitizer, light, and molecular oxygen to induce cell death. It starts by topical or systemic administration of a photosensitizer which preferentially concentrates in the tumor cells. The target tissue is subsequently irradiated with a light beam with a specific wavelength for the compound. When activated, the photosensitizer converts molecular oxygen to reactive oxygen species that react with vital cellular components, leading to cell death and culminating in the destruction of the tumor [1].

Understanding the biological differences between normal and tumor cells is essential for the design and development of therapies using selective anticancer activity. One of the most prominent metabolic alterations in tumor cells is an increased dependence on aerobic glycolysis and the glycolytic pathway for ATP generation, which provides a biochemical basis for the design of therapeutic strategies to preferentially kill cancer cells by pharmacological inhibition of glycolysis [2].

This work addresses the potentiation of PDT with the bacteriochlorin photosensitizer F_2BMet (or LUZ11), that recently entered clinical trials for head and neck cancer and was granted orphan drug designation for the treatment of biliary track cancer, with a specific inhibitor of glucose, 2-Deoxy-D-Glucose, in normal fibroblasts (3T3) and cancer (CT-26 and A549) cell lines by evaluation of the impact of the combination on the cellular survival.

We show promising results that PDT can be effectively enhanced by the combination between photodynamic therapy and anticancer drugs that alter the energy metabolism of the tumor. Currently, incubation times with inhibitor and range of concentrations are being optimized for a great impact of the therapy.

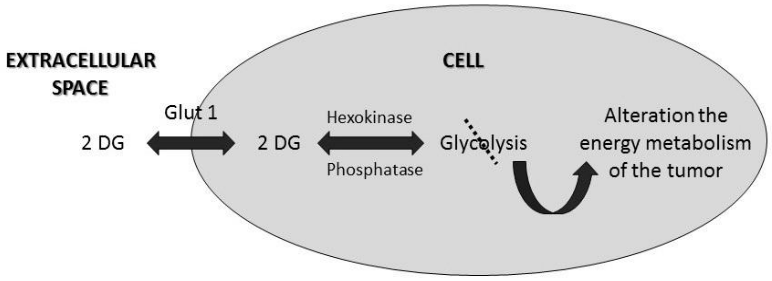

Figure 1: The inhibition of glycolysis and the preferential accumulation in cancer cells, are the basis for use 2-DG as an antitumor agent. Once inside the cell, the inhibitor will stop the glycolysis pathway and therefore alter the energy metabolism of the tumor. Adapted from [3].

Acknowledgments: This work was financed by FCT with project PEst-OE/QUI/UI0313/2014 and also supported with project PTDC/QUI-QUI/120182/2010.

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P-66 FAST pH JUMP INDUCED STRUTURAL CHANGES IN AMINOACIDS AND POLYCARBOXILIC ACID POLYMERS

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Bio polymers such as proteins can only continue their biological functions when properly fold into a particular shape, its "native conformation". Changes in kinetics of the folding process and transitions to states with wrong or non-functional conformations can be involved in the pathogenesis of many serious diseases, including Alzheimer's, Parkinson's, and Creutzfeldt-Jakob. Conformations in the folding process can have very short life times, being difficult to follow their dynamics with traditional methods. Kinetic, energetic and structural information about intermediate energy states in the folding process can be followed by time-resolved Photoacoustic Calorimetry. [1] The nature pH dependent conformational transitions in polyelectrolytes in aqueous solutions (from compact globules to more unfolded solvated chains) resemble the observed transitions in bio polymers.

In the present work we propose to follow the conformational changes in polycarboxilic acid polymers sensitive to sudden change of pH [2] promoted by photoexciting o-nitrobenzaldehyde with nanosecond pulsed laser. It is intended to obtain enthalpy data, kinetic and volume change associated with the protonation process and subsequent conformational changes. With the intention of studding how the polymer chain length influences the conformational behavior, polymethacrylic acids with distinct molecular weight were studied.

In addition, volume changes and fast heat deposition associated with amino protonation reaction in aqueous solution were studied. [3] This can be the first step in the unfolding process of peptides and proteins. The specific high starting pH for tyrosine and arginine protonation process possess the challenge of separating the photo release of H^+ and the aminoacid protonation reaction in competition with the protonation of OH^- ions present in solution at high concentration.

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P-67 NON INVASIVE ASSESSMENT OF COMPOUNDS SKIN PERMEATION THROUGH FLUORESCENCE METHOD

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In recent years fluorescence based methods have gained increased interest as non-invasive diagnostic tools in preclinical research and clinical practice.[1] In many circumstances, as in the field of *in vivo* pharmacodynamics studies,[2] real time quantification or relative quantification would be of considerable advantage. Optic fibers conveniently connected to excite and collect fluorescence can be used, allowing several non-invasive studies. Our study aims to optimize a fluorescence based method that uses an optical fiber and LED light sources to collect the fluorescence produced when the skin is permeated by a fluorophore, allowing quantification in real time.

In this work we prepared suitable gels of rhodamine-b and studied the fluorophore permeation in *ex vivo* pig skin. Fluorescence was measured using the fiber optics instrument and various parameters optimized in order to obtain satisfactory results in term of sensibility and exactness. In order to validate the methodology, results were compared invasive methods. Biopsy and extraction allowed absolute quantification of rhodamine-b that permeated the skin. The use of Franz cells gave us information on the fluxes of permeation. We also assessed the penetration depth by using fluorescence microscopy.

During this study we defined the excitation wavelength of the fluorophore so that the excitation light does not interfere with the fluorescence emission light in order to obtain a well-defined band. We could also establish a correlation of between the fluorescence in skin obtained by the non-invasive method and extraction and Cells Franz data. The method proved to be very promising for non-invasively quantify the permeation of fluorophores within skin and *in vivo* studies with active ingredients are foreseen in the near future.

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P-68 SELECTIVE PHOTOCATALYTIC OXIDATION OF BENZYL ALCOHOL TO BENZALDEHYDE UNDER LED IRRADIATION

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Benzaldehyde (BAHD) is the simplest representative of aromatic aldehydes and is a colorless liquid with a bitter smell of almond. BAHD has a variety of industrial applications, including in fine chemistry and in manufacture of polymers, fragrance compounds, dyes and pharmaceutical ingredients [1]. The global BAHD production capacity in 2009-14 was estimated at 100.000 tpy [2]. Therefore, efficient partial oxidation of benzyl alcohol (BA) to BAHD represents an important industrial process. Currently, partial oxidation generates a large volume of waste and the overall costs are high due to the use of severe operating conditions. Selective photocatalysis might reduce the inherent cost of the process by using ambient temperature, atmospheric pressure and environmentally friendly solvents such as water.

In this work, we have studied the effect of operating parameters, *i.e.* irradiance, pH and aeration/anaeration conditions in the selective photocatalytic oxidation of BA into BAHD under 390 nm LED irradiation (Fig. 1).

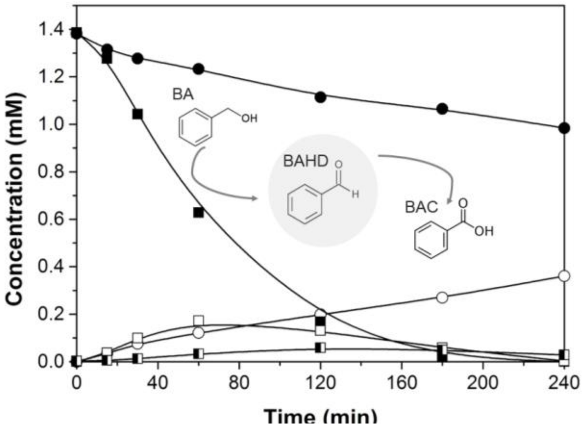

Figure 1: Conversion of BA (filled symbols) into BAHD (open symbols) and the sub-product benzoic acid (BAC, half-filled symbols).

Results demonstrated that BA conversion and selectivity towards BAHD greatly depends on the aeration/anaeration conditions. In the presence of Ar, at 4 h of irradiation, 29% of BA was selectively transformed into 90% of BAHD. On the other hand, under O_2 atmosphere, total conversion of BA was achieved; however, the formation of BAC was also observed, which may be attributed to the formation of high amounts of unselective superoxide radicals ($O_2^{\bullet -}$).

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P-69 CARBON-ZnO NANOMATERIALS FOR PHOTOCATALYTIC WATER DECONTAMINATION

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Water treatment has become unavoidable as result of increased standards of living and population growth. Heterogeneous photocatalysis is one of the most important environmental remediation technologies [1]. The massive use of TiO_2 as photocatalyst has triggered the interest on alternative materials with similar or even higher efficiencies, such as ZnO. Additionally, various studies have reported that carbon materials can provide beneficial effects on the photocatalytic activity of metal oxide semiconductors by inducing positive synergies between the two phases in composite photocatalysts. In the present work, we have explored the effect of coupling carbon nanotubes (CNT), nanofibers (NF), graphene (FLG), fullerene (C_{60}) and nanodiamonds (ND) with ZnO nanotetrapods in the photocatalytic degradation of phenol under simulated solar light irradiation (Table 1).

Table 1 – Apparent first order rate constants (k_{app}) and total organic carbon (TOC) removal for the photocatalytic reactions using ZnO and carbon/ZnO materials.

Photocatalyst	**k_{app} ($\times10^{-3}$ s^{-1})**	**TOC removal (%)**
ZnO	2.18	70
NC-CNT/ZnO	1.97	68
PYG-CNT/ZnO	2.03	66
AK-CNT/ZnO	2.43	72
ND/ZnO	2.52	68
C_{60}/ZnO	2.67	80
CNF/ZnO	3.08	76
FLGtk/ZnO	3.47	81
FLGtn/ZnO	3.88	70
N-CNT/ZnO	4.33	87

Results showed that the efficiency of the photocatalytic process depends on the nature of the carbon material used. Among the photocatalysts tested, the composite prepared using nitrogen-doped CNT as carbon phase (N-CNT/ZnO) showed the highest photocatalytic activity. An increase of 100 % in the k_{app} for phenol degradation was achieved when using N-CNT/ZnO instead of bare ZnO. The best performance shown by N-CNT/ZnO composite was attributed to the presence of electron-rich nitrogen groups in the CNT's structure.

Acknowledgements: Fundação para a Ciência e a Tecnologia (FCT), Fellowship SFRH/BD/79878/2011.

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P-70 NEW ERBIUM(III) BETA-DIKETONATE COMPLEXES AS NEAR-INFRARED EMITTERS

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New lanthanide complexes are attracting considerable attention due to their unique optical and magnetic properties, which include narrow emission in the visible and near-infrared regions, large Stokes shifts and long luminescence lifetimes presenting potential applications in medical imaging and optical telecommunications. Erbium ion (Er^{3+}) is of particular interest due to its emission in the C-band (1.53–1.565 μm) of the silica optical telecommunication window [1]. This work describes the synthesis and characterization of novel Erbium(III) based materials with different coordinating ligands.

The general synthesis procedure was as follows: a *β*-diketone methanol solution was added to $Er(NO_3)_3{\cdot}5H_2O$ in methanol, the resulting mixture was neutralized by adding potassium methoxide until KNO_3 precipitated, and the diimide ligand was finally added. Crystallization was conducted by slow solvent evaporation at RT. In those cases where single crystals were obtained, a full structural determination was performed. Luminescent properties were successfully measured, including emission in the NIR-region, confirming efficient ligand-mediated sensitization, in which complete energy transfer occurred by *antenna* effect. Structural, optical and magnetic properties of the new compounds will be presented and discussed.

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P-71 THE EFFECT OF IRON CHELATORS IN PHOTODYNAMIC THERAPY WITH LUZ11

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Photodynamic therapy (PDT) is a procedure that consists of generating reactive oxygen species (ROS) in a target tissue by a combination of light, a photosensitizer (PS) and molecular oxygen [1]. The photosensitizer absorbs light, preferably in the phototherapeutic window (650-850 nm, where tissues are the most transparent), and while in an electronically excited state it is capable of transferring an electron (Type I process) or electronic energy (Type II process) to molecular oxygen, to generate ROS. Thus, the therapeutic strategy followed in PDT is to produce a strong oxidative insult in the irradiated volume, sufficient to kill the target cells.

LUZ11 is a fluorinated sulfonamide bacteriochlorin with proved phototoxicity to several kinds of cancer cells. Its mechanism of action involves the formation of highly reactive oxygen species, such as singlet oxygen and other oxygen radicals [2]. It has been reported that PDT can promote the release of transition metal ions, such as cuprous (Cu^{2+}) and ferrous (Fe^{2+}), from storage proteins in biological systems [3].

Considering Fenton's reaction, it has been argued that the co-location of ferrous ions with LUZ11 may modulate the efficacy of PDT by production of hydroxyl radical ($OH^{\cdot}$), which is highly cytotoxic and may contribute significantly to the efficacy of PDT.

The presence of iron chelators, such as DFO (Deferoxamine) or thiosemicarbazones (TSCs) in the medium can control the availability of ferrous ions (Fe^{2+}) in biological systems.

The present study methodology involves the use of two distinct iron chelators (DFO and a novel synthesized TSC) on 3T3-type fibroblast cell cultures. Firstly, we assessed the toxicity of the chelators in the dark to establish a range of concentrations to work with, and then we analyzed the effect of the iron chelation in PDT with LUZ11.

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P-72 PHOTOPHYSICAL STUDIES AND INTERACTION WITH LOW-DENSITY LIPOPROTEINS OF (bis)PORPHYRIN-PEPTIDE CONJUGATES

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Porphyrins feature unique photophysical and photochemical properties which make them interesting for application in different fields: biomedicine, catalysis, and molecular electronics [1, 2].

In this contribution, we report on porphyrin-peptide conjugates formed by two porphyrin groups separated by a homo-oligo-[L-(αMe)Val]$_n$ peptide chain of variable length (n=2, 4, 6). (Figure 1). The two porphyrin groups were shown by circular dichroism measurements to be coupled by exciton interaction [3]. The extent of the exciton coupling strongly depends on 3D-structural, *i.e.* the conformations attained by the peptide chain, and dynamical, *i.e.* interconversion among the populated conformers, factors. In this work, the *bis*-porphyrin compounds were investigated by spectral and time-resolved spectroscopies (fluorescence and laser-induced transient absorption) to characterize the effects of the exciton-coupling interaction on the porphyrin excited states. Since porphyrins are currently used in photodynamic therapy of tumors (PDT) as photosensitizers [4], it will be also of interest to characterize the interaction of the porphyrin-peptide conjugate with low-density lipoproteins (LDL).

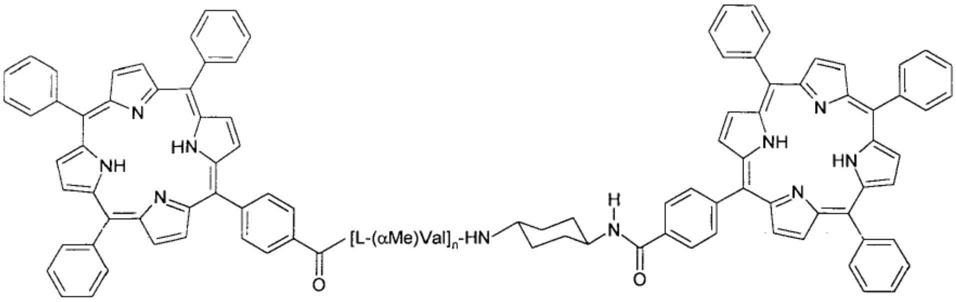

Figure 1: Chemical structure of the (bis)porphyrin-[L-(αMe)Val]$_n$ peptide conjugates (n=2, 4, 6).

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P-73 THE ROLE OF QUANTUM DOTS IN PEROXYOXALATE CHEMILUMINESCENCE REACTION

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Quantum dots (QDs) owning to their unique optical and electronic properties, which strongly dependent on size, shape and composition [1, 2, 3], have been the subject of extensive investigations. They found applications in several areas of science and technology such as optoelectronic, photovoltaic and biomedicine [4]. Recently, several studies involving quantum dots chemiluminescence behavior were also reported in the literature [5, 6]. Nevertheless, peroxyoxalate chemiluminescence (POCL) with QDs as activators has not yet been demonstrated.

In this work, the role of CdSe quantum dots in POCL reaction is discussed. In particular, this study is aimed at investigation of QDs' behavior in a system containing hydrogen peroxide and oxalic ester as oxidant and source of high-energy intermediates, respectively. Physicochemical and photochemical properties of the synthesised QD coated with various organic ligands are compared.

Figure 1: Image of CdSe QDs visible during CL reaction.

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P-74 PREPARATION AND OPTIMIZATION OF CLOFAZIMINE SOLID LIPID NANOPARTICLES VIA BOX-BEHNKEN DESIGN

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Clofazimine (CLZ) is an antibiotic drug which has been used in the treatment of multibacillary leprosy caused by *Mycobacterium leprae* [1]. It is a highly hydrophobic molecule (logP > 7) what enables its accumulation in several parts of the body, causing severe side effects as reddish-brown skin and gastrointestinal tract toxicity [1]. In humans, its absorption varies considerably (45%–62%) leading to a low oral bioavailability and gastric intolerance, limiting its activity. Once absorbed, it distributes primarily into fatty tissues, as well as cells of the mononuclear phagocyte system, forming intracellular precipitates or crystal-like deposits [1]. Many technologies are available and have commonly been used to overcome drawbacks associated with poorly water-soluble drugs [1, 2]. Solid lipid nanoparticle (SLN), has attracted increasing attention in recent years as a colloidal carrier for controlled drug delivery system [3]. It has advantages such as good tolerability, high oral bioavailability, feasible scale-up, and less acute and chronic toxicity [4]. The aim of the present work was to develop and optimize SLN for the improvement of CLZ, using a 3-level, 3-factor Box-Behnken design. The SLN were prepared by the ultrasonication method. Different formulation were prepared by varying: (X_1) time of sonication; (X_2) concentration of surfactant (Tween 80) and (X_3) amount of lipid (Precirol® ATO 55). The SLN were evaluated concerning the nanoparticle size (Y_1), zeta potential (Y_2) and polidispersity (Y_3). The design generated 15 samples, and the data were analyzed using ANOVA by STATISTICA 10 (Statsoft®, Inc) software, where the effects were considered significant when p<0.05. The graphical and numerical analyses were assessed in order to obtain optimum values of the variables based on the criteria of desirability. The optimized formulation was then characterized by scanning electron microscopy (SEM), and the encapsulation efficiency was evaluated.

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P-75 SEPARATION OF NADOLOL STEREOISOMERS BY LIQUID CHROMATOGRAPHY USING C18 COLUMNS

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Nadolol is a nonselective beta-adrenergic receptor antagonist (β-blocker) pharmaceutical drug, widely used in the treatment of cardiovascular diseases, such as hypertension, ischemic heart disease (angina pectoris), congestive heart failure, and certain arrhythmias. Its chemical structure has three stereogenic centers which allows for eight possible stereoisomers. However, the two hydroxyl substituents on the cyclohexane ring are fixed in the cis-configuration, which precludes four stereoisomers; in fact, two pairs of enantiomers. Nadolol is presently marketed as an equal mixture of the four stereoisomers, designated as the diastereomers “racemate A” and “racemate B” [1].

There are still few published works concerning the separation of nadolol stereoisomers. Most of these works refer the resolution at analytical scale and few refer the resolution at preparative scale using the simulated moving bed (SMB) technology. [2] This technology is normally based on the use of chiral adsorbents which must have enough recognition for all the chiral species.

In this work we propose an alternative strategy, implementing a first achiral separation step, which should be followed by two subsequent parallel chiral separation steps. Considering the first achiral step, common C18 columns will be used to perform a reversed-phase separation of the two pairs of nadolol enantiomers, the “racemate A” from the “racemate B”.

Extensive results will be shown considering the choice of the best solvent composition and the potentiality of this alternative strategy, in terms of SMB system performance under reversed-phase conditions and its comparison with a full chiral steps strategy.

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P-76 SEPARATION OF NADOLOL STEREOISOMERS BY LIQUID CHROMATOGRAPHY USING CHIRALPAK IA CHIRAL STATIONARY PHASE

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The separation of nadolol stereoisomers on CHIRALPAK® AD at both analytical and preparative scales was recently reported by Ribeiro et al. [1]. CHIRALPAK® AD is an amylose-based chiral stationary phase (CSP) and is produced by physical coating of the chiral polymer on a matrix. However, due to their coated nature, this CSP can only be used with a limited range of solvents such as the polar (e.g. alcohols) or non-polar solvents (e.g. alkanes). Immobilization of a polysaccharide-derivative on the support is an evolutionary strategy to make a CSP compatible with the whole range of organic solvents, which will consequently extend its application scope. CHIRALPAK® IA is a CSP containing amylose 3,5-dimethylphenylcarbamate immobilized onto silica gel [2].
This work will present a complete methodology concerning experimental, modelling and simulation results. Both the CHIRALPAK® AD and CHIRALPAK® IA CSPs will be evaluated using the nadolol stereoisomers separation as case study. The selection of the proper CHIRALPAK® IA/solvent combination for preparative operation will be fully study taking into account a complete screening strategy [3]. Additional results will include the measurement of the chiral mixture solubility's, equilibrium adsorption data and fixed bed (breakthroughs) experiments. The complete screening will lead to the choice of the better solution for the pseudo-binary separation of the nadolol most retained stereoisomer. Finally, experimental results will be presented for the preparative separation using a Simulated Moving Bed (SMB) pilot unit. The results obtained will be compared with previous published work using the CHIRALPAK® AD adsorbent.

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P-77 NEW POROUS MATERIALS FOR THE SELECTIVE REMOVAL OF GENOTOXIC IMPURITIES FROM ACTIVE PHARMACEUTICAL INGREDIENTS

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Many medical drugs are obtained by chemical synthesis using highly reactive reagents, and usually, low levels of reagents, fractions of catalysts, or by-products are present in the final active pharmaceutical ingredient (API) or drug product, as impurity. Some of those (referred as genotoxic impurities - GTIs), have unwanted toxicities, including genotoxicity and carcinogenicity, and therefore related API administration risks for patients' health has become an increasing concern of pharmaceutical companies [1]. API synthetic routes include intermediate and final product purification stages using conventional techniques, such as fractional crystallization, use of adsorbents, resins or column chromatography [2]. While adequate for partial removal of GTIs, the use of these techniques to reach authority regulated ultra-low GTI levels usually leads to API loss, with significant economic impact. Therefore, there is a demand for higher selective processes, specifically targeting the removal of GTIs from API post reaction streams.

Molecular imprinted polymers (MIPs) are generated by the interaction of functional monomers, a target molecule (template) and a cross-linking agent. They have the ability to recognize and bind specific target molecules and are robust and insoluble in most media [3]. The use of highly specific MIPs, for organic GTI removal, has been already reported [4,5].

In the present work, we developed a new MIP able to effectively remove the GTI 4-dimethylaminopyridine (DMAP) from an API solution (Mometasone furoate – Meta). Bulk polymerization based on non-covalent imprinting was employed to prepare the MIP with selectivity for DMAP corresponding to a high affinity porous material, organic solvent resistant, and able to remove, in a single stage, more than 90% of the GTI with minimal API loss.

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P-78 DEVELOPMENT OF ANTIMICROBIAL SURFACES USING GREEN TECHNOLOGIES

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Biocontamination of waters can lead to adverse health effects. Commonly used water disinfectants, such as chlorine or water-soluble biocides, encompass some drawbacks related with agents' residual toxicity that will result in environmental pollution and in the development of resistant microbial strains. It is crucial to develop new materials with self-desinfection properties and with the ability to kill microorganisms by contact, in order to avoid the development of resistant bacteria and the formation of biofilms, which could alter the performance of a material.

Our group has been developing clean methodologies to synthesize different antimicrobial oligo(2-oxazoline)s (OOXs) in $scCO_2$ [1] and to physically blend OOXs in different ratios with natural polymers (e.g. chitosan, CHT) [2]. More recently, a combined strategy using solvent-free plasma activation and supercritical fluid assisted method was developed to graft biocompatible microbial repellent OOX-based composites onto the surface of CHT scaffold. The grafting of antimicrobial OOXs did not alter the CHT scaffold morphology nor the stability in physiological conditions. However, an increased ability to resist bovine serum albumin adsorption was observed. OOX-grafted CHT scaffolds showed the ability to kill *S.aureus* and *E.coli* cells after only 3 minutes upon contact and to avoid bacterial adhesion to the materials surface preventing the formation of biofilms.

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P-79 QUANTITATIVE DETERMINATION OF ABIETIC ACID ON PINE ROSIN

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Rosin is an important natural resource, whose main components are resin acids. There are three kinds of rosin: gum rosin, wood rosin and tall oil rosin. Gum rosin occupies about 60% of the industrial market, wood rosin about 5% and tall oil rosin about 35%. The total world annual production volume of rosin has remained at 1.1-1.2 million tons since the 1990s. Rosin or modified rosin are widely used as sizes, adhesives, printing inks, emulsifiers, and these applications account for most of the rosin used in industry. Rosin are complex mixtures mainly constituted by diterpene acids. Among the acids present in rosins: abietic acid, dehydroabietic acid, pimaric acid and isopimaric acid, the quantification of abietic acid is determining for the manufacture of products with different commercial applications.

The analysis of the components of rosin could be achieved by GC-MS after derivatization (ASTM D5974-00 (2005), PCA-TEST Method PCTM27), but the quantification of abietic acid requires the use of high purity abietic acid as standard. Abietic acid could be purchase from Fluka with <75% purity and from Acros with >85% purity. We perform the purification of abietic acid trough isomerization reaction, solvent extraction and crystallization. The results from the different purification methods will be presented and the analysis of rosin samples will be presented

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P-80 AUTOMATION OF OXYGEN RADICAL ABSORBANCE CAPACITY-PYROGALLOL RED ASSAY TOWARDS ESTIMATION OF ANTIOXIDANT REACTIVITY

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An automated method based on programmable flow injection analysis for oxygen radical absorbance capacity (ORAC) measurement was developed for the estimation of antioxidant reactivity. In this assay, pyrogallol red (PGR) is employed as target molecule for peroxyl radicals, working simultaneously as spectrophotometric probe for reaction development at 540 nm (pH 7.4) [1]. Depending on their scavenging reactivity against peroxyl radicals, antioxidants will delay PGR oxidation (bleaching).

In this context, the present work describes a new format for ORAC-PGR assay that provides the *in situ* generation of peroxyl radicals from 2,2'-azobis(2-amidinopropane) dihydrochloride (AAPH) under strictly controlled conditions (temperature, reagent mixing and reaction time) along with real time monitoring of PGR bleaching within the first minute of reaction. ORAC-PGR values reflect initial antioxidant reactivity against peroxyl radicals, providing kinetic information about the initial interaction between them. Such information is particularly relevant to estimate whether a compound can neutralize peroxyl radicals at the initial stage of their formation, preventing chain reactions and further oxidative damage of biomolecules.

The features of the ORAC-PGR flow methodology will be discussed, namely the influence of PGR/AAPH concentrations and of programmable flow conditions on reaction development. Briefly, the applied strategy fostered the reduction of analysis time from 1 h to 60 s, by engaging on the initial kinetics of target molecule oxidation. After the selection of reaction conditions, peroxyl-scavenging reactivity of diverse antioxidants and pharmaceutical compounds was estimated. The applicability towards real samples (green tea, coffee and saliva) was also demonstrated. The detection limit calculated using the standard antioxidant compound Trolox was 8 µM. RSD values were < 3.4 and < 4.9 %, for intra and inter-assay precision, respectively. The developed system also afforded a high sampling frequency (29 h^{-1}), low operating costs and low generation of waste.

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P-81 OPTIMIZATION OF MICROWAVE-ASSISTED SYNTHESIS OF N-DOPED CARBON DOTS

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Fluorescent carbon dots (CDs) are a new class of carbon nanomaterials that have harvested increasing interest as alternatives to semiconductor quantum dots [1]. In addition to their incomparable optical properties, CDs possesses the desired low toxicity, biocompatibility, low cost and chemical inertness [1]. Moreover, their bandgap can be easily engineered either by chemical doping or by surface functionalization. Doping CDs with heteroatoms, namely with nitrogen atoms, has been widely used as a means to alter their optical properties [2].

Synthetic approaches for CDs are classified into two categories – “top-down” and “bottom-up” [3]. “Top-down” involves breaking down larger carbon structures whereas the “bottom-up” uses small organic molecules as precursors for CDs. Usually, the “bottom-up” approach allows the synthesis of CDs with higher yields and taking advantage of inexpensive materials in simple experimental set-ups. When combined with microwave heating, it provides the route for fine control over the optical properties of CDs [4].

Herein, we report the optimization of microwave-assisted synthesis of N-doped CDs. Citric acid and several amines were used as carbon and nitrogen sources. The formation of CDs and their luminescence behavior under various conditions were investigated. For reaction conditions optimization several parameters, such as molecular ratios between carbon and nitrogen sources, temperature and reaction time, were took into consideration. This effort allowed the preparation of N-doped GQDs in short reaction times, with high quantum yield and making use of easily available precursors.

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P-82 HEAVY METALS CONTENT IN CIGARETTES FROM THE PORTUGUESE MARKET

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Tobacco smoking is the major cause of preventable death and disease in developed countries. According to European Public Health Alliance (EPHA), over 650 000 Europeans are killed every year because of smoking-related diseases, and 13 million more are suffering as a result of their smoking [1].

For 2015, the World Health Organization (WHO) estimates as about 20% the percentage of the Portuguese population aged 15 years and over (approximately 1.8 million persons) with smoking habits [2].

Tobacco use or exposure to tobacco smoking is usually associated with chronic diseases, such as cancers and heart and respiratory diseases [2]. Smoking-related diseases can be attributed to the inhalation of many different substances. Tobacco smoke contains a long list of more than 7,000 chemicals, hundreds of them with recognized toxicological potential, including several metals and metalloids. About 70 of those chemicals are recognized as carcinogenic [3].

The metals present in tobacco that are most commonly associated with health effects are arsenic (As), cadmium (Cd), chromium (Cr), nickel (Ni) and lead (Pb). However, several other metals such as beryllium (Be), manganese (Mn), cobalt (Co) antimony (Sb), silver (Ag), thallium (Tl) and uranium (U) have detrimental effects on human health and can also be found in tobacco [3].

Based on this background, a comprehensive study was conducted in order to assess the content of heavy metals in the best-selling tobacco brands of the Portuguese market (n=19 different brands). Cigarettes samples were digested through a microwave-assisted acid digestion procedure and sample solutions were analyzed by ICP-MS.

The obtained results (mean±SD / maximum) were: As (0.11±0.06 / 0.36 µg/g), Cd (0.92±0.72 / 5.61 µg/g), Cr (1.50±0.51 / 2.72 µg/g), Ni (1.93±0.45 / 3.61 µg/g), Pb (0.55±0.11; 0.97 µg/g), Be (0.031±0.004 / 0.044 µg/g), Mn (148.7±16.8 / 179.0 µg/g), Co (0.82±0.08 / 0.97 µg/g), Sb (0.017±0.010 / 0.069 µg/g), Ag (0.024±0.006 / 0.044 µg/g), Tl (0.074±0.013 / 0.104 µg/g) and U (0.078±0.025 / 0.0133 µg/g).

These results are in good agreement with data from a recent study on the US market [3] and highlight the contribution of toxic metals for the smoking related pathologies.

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P-83 WHAT DO FINGERNAIL AND TOENAIL SAMPLES TELL US ABOUT ENVIRONMENTAL EXPOSURE TO METAL(LOID)S?

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The Estarreja Chemical Complex (NW Portugal) has been operating since the thirties of the XX century. This complex produces aniline and derivatives (nitric acid, sulfanilic acid, cyclohexylamine, cyclohexanol and nitrobenzene), “chlor-alkalis” (hydrochloric acid, chlorine, sodium hypochlorite, caustic soda), aluminum sulfate and aluminum polychloride, sodium and chlorate compounds from salt through electrolysis using Hg cathodes, polyvinyl chloride resins and methylene diphenyl diisocyanate. In the past it were also produced ammonium sulphate, ammonium nitrate, and sulphuric acid from arsenopyrite roasting, which has led to the disposal of a large volume of toxic waste solids and liquid effluents in areas not prepared for such purpose. This intense industrial activity has caused significant negative impacts on the environment, affecting a population that historically depends on groundwater as a source of water for human and agricultural uses. During the 1990's, several rehabilitation actions resulted in an important reduction of the negative environmental legacy, but groundwater still have heavy metals levels well above the international (EPA, WHO) and Portuguese recommended limit values [1-3].

This study involved the determination of a wide panel of metals and metalloids in paired fingernail and toenail samples from Estarreja inhabitants (n=55) in order to assess the extent to which their elemental profile provides information on exposure.

Median Hg levels were elevated, above literature data [4]. For other elements (As, V, Cr, Mn, Ba, Al and Pb) median metal content was below literature data, but some subjects presented values clearly above reported ranges. For several subjects, significant differences were found between the results found in fingernail and toenail samples (typically higher in fingernail).

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P-84 TRACEABILITY TO COMMON REFERENCES - REQUIREMENT TO COMPARABILITY OF RESULTS

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Traceability of results to common references is a key issue for ensuring comparability and enabling interpretation of measured values of physical-chemical quantities. Lack of observation of this fundamental principle has turned many data practically useless. This is often the case of oceanographic data, namely on what concerns pH. Assessed by either potentiometry with the glass combination pH electrode, or by other recommended instrumental method for evaluation of hydrogen ion signal, values measured for unknown samples will always be affected by an uncertainty equal or higher than the one respectively associated to the reference pH (S) values assigned to the calibrating solutions, S. UV-Vis spectrophotometry, with m-cresol purple indicator, has gained support as an alternative to potentiometry with pH electrodes [1]. While the spectrophotometric signal is related to concentration, H^T, the electrode potential responds to activity, . This work aims at illustrating the materialization of the traceability chain of seawater pH by the two methods, *Figure 1*.

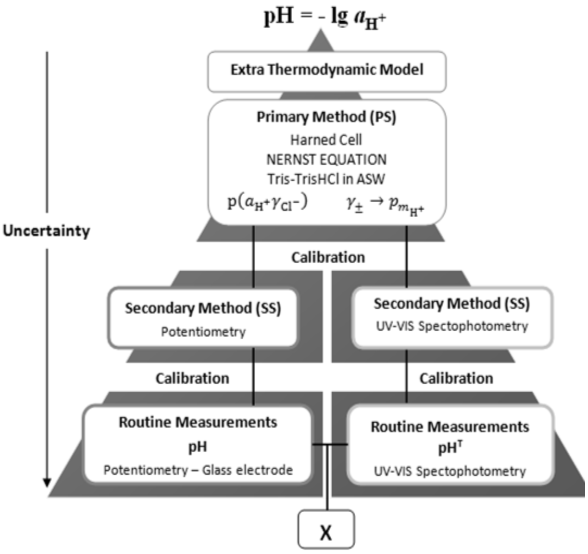

Figure 1: Schematic representation of a double traceability chain, showing traceability of two different types of analytical signals pertaining to hydrogen ion, H^+, to common references of pH.

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P-85 ELECTROCHEMICAL STUDY OF Fe(III) ORGANOPHILIC MONTMORILLONITE

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The electrochemical behavior, spectroscopic, thermal and XRD of the SWY-1-8HQ composite was investigated in the absence and in the presence of Fe (III) ions. Composite films were prepared by mechanical deposition of the SWy-1-8HQ suspension on the surface of a Pt disk electrode. The spectrophotometric techniques, thermal analysis and X-ray diffraction were used to characterize the composite in the absence and presence of ions Fe (III). From the experimental results could be noted: **1.** The platinum electrode was effectively modified with the mechanical deposition of a composite film (SWy-1-8HQ) for five depositions (n = 5), with a peak in the anodic branch and the other in cathodic branch, with adsorptive characteristic and low current intensity; **2.** the presence of four peaks present to $C_{Fe(III)} > 4.87 \times 10^{-6}$ mol L^{-1}, dependent each other. These peaks were identified as belonging to two types of mechanisms: **a)** Peaks A and D - EC mechanism, complex formation taking place $\{Pt / [> Si - O]_n[Fe(III) - (8HQ)_k]\}^{3-nk}$, and reduction of Fe(III) ions to Fe(II) inside the complex; **b)** peaks B and C - CE mechanism occurring the reduction of aqueous Fe (III) species by the complex $\{Pt / [> Si - O]\ n\ [Fe(II) - (8HQ)_k]\}^{2-nk}$, and partial oxidation reaction of aqueous Fe (II) ions by O_2. **3-** the electrode presents linear relation $I_p^a \times C_{Fe(III)}$ to $((2,4 \leq C_{Cu(II)} \leq 49,8)$ µmol L^{-1} and LOD = $(5,69 \pm 0,10)$ µmol L^{-1}; **4-** the results of spectroscopic and thermal studies corroborated the presence of ternary complex species $[>Si\text{-}O]_n[Fe(III)\text{-}(8HQ)_k]\}^{3-n-k}$; **5-** the modified electrode is stable, mechanically and electrochemically.

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P-86 CdTe-MPA QUANTUM DOTS PACKED REACTOR FOR CHEMILUMINESCENCE APPLICATIONS

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Despite hazardous effects upon humans and environment, zinc or cadmium with oxygen, sulfur, selenium or tellurium quantum dot nanostructures (QDs) seeded numerous publications last years. The high photostability, luminescence quantum efficiency, and wide emission tenability make them excellent candidates as fluorophores for immobilization[1], thus promoting safer use and recycling of out of use materials. In this work a novel procedure for the immobilization of CdTe quantum dots, capped with mercaptopropionic acid (MPA), in silica mesoporous xerogel is described. The procedure consisted in the addition of a CdTe-MPA colloidal solution to pre-hydrolized tetramethyl orthosilicate sol in an acidic medium containing Triton X100 as surfactant. Sol optimization and gelification monitoring through addition of crystal violet molecular rotor as fluorescent probe. The characterization of the luminescent film was performed by SEM-EDS, confirming uniform distribution of QDs agglomerates in vicinity of the surfactant vesicles. The confinement effect in immobilized QDs remained practically unchanged, as well as particles quantum yield (QY), but excitons lifetime increased almost 185 %. The additional ability of QDs to generate reactive oxygen species (ROS)[2,3] is then explored. To this, a small column packed with 100 mg of immobilized QDs was inserted in a continuous flow-system, and was continuously irradiated with commercial LED illumination lamp. Deionized water was made to flow through the column and down stream merged with a luminol alkaline solution to yield reproducible luminescence. The immobilization of CdTe-MPA QDs as packed reactor avoided the use of expensive reagents for ROS and provided a start point for future analytical applications.

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P-87 DESIGNING VALID AND OPTIMISED STANDARD ADDITION CALIBRATIONS: APPLICATION TO THE DETERMINATION OF ANIONS IN SEAWATER

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A strategy for designing valid standard addition calibrations and for optimising their uncertainty is presented.

Although standard additions calibrations are performed where instrumental sensitivity vary with the sample matrix, the general trends of the variation of the signal with the analyte concentration in matrix not matching accurately the sample one, can be used to define strategies for producing valid calibrations with optimal measurement uncertainty. The design of calibrations involves the development of models of the sensitivity and precision of the instrumental signal, in a wide range of analyte concentration (or any other studied quantity), and the definition of sample dilution and standard addition procedures that allow fulfilling the assumptions of the linear unweighted regression model [1] in, typically, a smaller range of standard addition calibrations. Calibrators are prepared by diluting the sample and adding analyte with negligible uncertainty to fit in a concentration range where signals are homoscedastic. The minimisation of the uncertainty is supported on detailed measurement uncertainty models function of the calibrators preparation procedure and of analytical instrumentation performance. The number of collected signals replicates is defined by balancing their impact on the estimated expanded uncertainty, the resources needed and the target (maximum) uncertainty for the intended use of measurements.

The calibration design strategy was successfully applied to the determination of the mass concentration (mg L^{-1}) of Cl^-, Br^-, NO_3^- and SO_4^{-2} in seawater by ion chromatography. A target expanded uncertainty of 20 % was defined for the determination of Cl^-, NO_3^- and SO_4^{-2}, or 40 % for the determination of the smaller mass concentration of Br^-. The developed measurement model produced reliable predictions of the measurement uncertainty from approximate concentration of the analyte in the sample, before its accurate quantification, thus proving optimisation is effective. Predictions are more prone to the variability of the measurement uncertainty estimation if based on low number of calibrators signals. The reported relative expanded uncertainty ranged from 7.1 % to 49 %.

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P-88 SIMULTANEOUS DETERMINATION, BY HPLC, OF ETHANOL AND ORGANIC ACIDS IN WINE

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A chromatographic method, HPLC, with UV and RI detection was developed, for the determination of ethanol and tartaric, malic, lactic and acetic acids in wines [1, 2]. From calibration curves some relevant analytic parameters were determined, namely, the detection limit and the linearity range. For tartaric acid the detector response was confirmed to be linear up to 500 ppm with a detection limit of 24 ppm. For the other acids the linear response was confirmed up to 1000 ppm with a detection limit of 42, 38 and 55 ppm for the malic, lactic and acetic acids, respectively.

The wine samples were submitted to a pre-treatment [3] aiming the elimination of the compounds which are strongly retained by the chromatographic column reducing the elution time to three analysis - hour. In the chromatograms the identification of the ethanol and of the organic acids was achieved using standards addition.

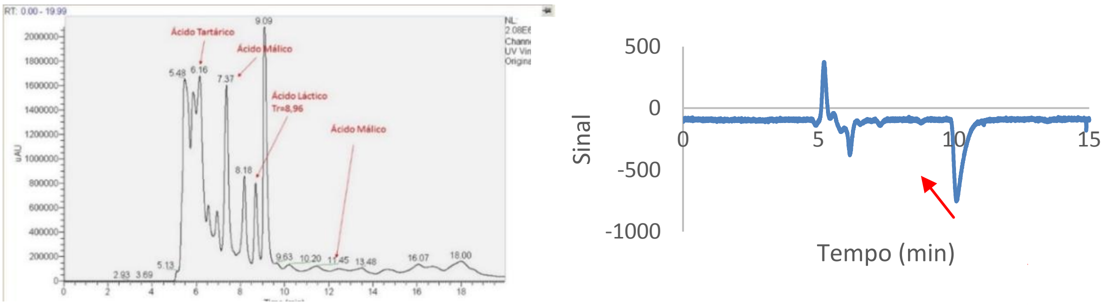

Figure 1(a) and 1(b) - Chromatogram of white wine sample without dilution. Column C18 ODS-AQ; T: 40ºC; Mobile Fase 8 mM Na_2SO_4 + 1 mM H_2SO_4: pH = 2.8; Flow- 0,5 mL min^{-1}; (a) Detector UV (λ=214 nm) - Organic Acids; (b) Detector RI - Ethanol.

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P-89 DIRECT ESTIMATION OF DISSOLVED ORGANIC CARBON USING SYNCHRONOUS FLUORESCENCE AND INDEPENDENT COMPONENT ANALYSIS (ICA): ADVANTAGES OF A MULTIVARIATE CALIBRATION

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Dissolved organic carbon (DOC) is frequently used as a diagnostic parameter for the identification of environmental contamination in aqueous systems [1]. This matter is evolving and decaying over time, thus, if samples are collected under environmental conditions, they require the use of some sample stabilization process until the corresponding analysis can be made. This may affect the analysis results. In this work we propose an in situ method for direct determination of DOC using synchronous fluorescence spectra, with independent component analysis used to retrieve relevant major spectral contributions and the respective component contributions.

Fluorescence spectroscopy is a very powerful and sensitive technique to evaluate vestigial organic matter dissolved in water, and is thus suited for the analytical task of directly monitoring dissolved organic matter in aqueous bodies [2,3], avoiding the need for the stabilization step.

In this work we report the development of an accurate calibration model for dissolved organic carbon determinations using environmental samples of humic and fulvic acids. The method described opens the opportunity for a fast, in locus, DOC estimation in environmental or other field studies using a portable fluorescence spectrometer with the benefits for the use of fresh, unpreserved samples.

This also allows the interpretation of various additional spectral contributions based on their respective estimated properties. Independent component analysis [4,5] may be used to describe tyrosine, tryptophan, humic acid and fulvic acid spectra and, thus, to retrieve respective individual component contribution information no DOC.

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P-90 ROLE OF TiO_2 NANOPARTICLES ON CADMIUM DYNAMIC SPECIATION IN FRESHWATER SYSTEMS

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Titanium dioxide nanoparticles ($nTiO_2$) are among the most produced nanomaterials, mainly due to their phtotocatalytic properties and ability to absorb UV-light, being widely used in personal care products (sunscreens, cosmetics) and dye solar cells (photovoltaic panels) [1]. Since these nano-enabled materials will undoubtedly end-up in the environment, a growing concern about their interaction with natural waters components, such as metal ions and organisms, has led to an increased discussion about their environmental impact in the ecosystems.

In this work cadmium dynamic speciation in the presence of two commercial $nTiO_2$s was evaluated under physicochemical conditions that can be found in freshwater systems using the newly developed electroanalytical techniques: absence of gradients and nernstian equilibrium stripping (AGNES) [2] and scanned stripping chronopotentiometry (SSCP) [3].

The results showed that in the presence of Cd, 1:1 $CdTiO_2$ homogeneous surface complexes were formed, independently of the $nTiO_2$ used. These complexes are labile, as could be concluded by the results of the electroanalytical techniques used that combine adequate sensitivity for environmental samples with the potential to perform dynamic speciation. Since the $CdTiO_2$ complexes formed has a labile nature, Cd will be available for the aquatic organisms, independently of the $nTiO_2$ presence in the media. These results are in agreement with the ones recently published by our group [4], where in similar physicochemical conditions Cd bioconcentration on the freshwater bivalve *Corbicula fluminea* depended solely on the dissolved metal irrespective to the $nTiO_2$ presence.

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P-91 SELENIUM AND MERCURY IN THE HUMAN BRAIN TISSUE

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The interaction between mercury (Hg) and selenium (Se) is one of the best-known examples of biological antagonism, yet the underlying mechanism remains unclear [1]. Several studies indicate that the toxic effects of Hg exposure increase when Se status is low. It is widely accepted that the toxicity is inversely proportional to Se:Hg molar ratios in specific tissues (e.g., brain) and increases dramatically for Se:Hg molar ratios < 1 [2].

Based on this background, we performed a study aiming to determine the Se and Hg levels in the human brain. Considering that human brain is a highly complex and heterogeneous organ at the functional and anatomical levels, 14 different the anatomical region were individually studied.

From neurologically and psychiatrically healthy individuals submitted to autopsy (n=42; 71±12, range: 50–101 years old) the following brain areas were sampled: frontal cortex, superior and middle temporal gyri, caudate nucleus, putamen, globus pallidus, cingulated gyrus, hippocampus, inferior parietal lobule, occipital lobe, midbrain, pons, medulla and cerebellum. After samples microwave-assisted acid digestion in closed vessels, Se and Hg were determined by ICP-MS.

Considering the whole data set (n=588; 42 individuals x 14 brain areas), Se and Hg levels (on a dry weight basis) were 0.63±0.08 μg/g (range: 0.46–0.98 μg/g) and 0.15±0.09 μg/g (range: 0.05–0.41 μg/g), respectively. The distribution of Hg within brain tissue showed to be homogeneous, but not the Se distribution: highest levels were found in the putamen (a region mainly related to motor functions), and the lowest in the cerebellum. Selenium levels tended to a slight increase with Hg levels. Se:Hg molar ratios < 1 were not found in any brain region. Values ranged from 11.6±9.1 in the midbrain to 30.0±23.0 in the caudate nucleus, suggesting that some brain regions may be more susceptible to Hg toxicity. Furthermore, Se:Hg molar ratio was not correlated with age, which suggests that individuals experience the same protective advantages of Se against Hg toxicity irrespective of their age.

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P-92 ELECTROCHEMICAL SENSORS BASED ON SCREEN-PRINTING TECHNOLOGY

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Over the past decades, there has been an increasing trend towards miniaturization of biological and chemical sensors and their integration with miniaturized sample pre-processing and analysis systems [1]. In this context, intensive research activity has been focused on the development of miniaturized electrochemical sensors intended for extracellular fluid measurement, clinical diagnosis and micro total analysis [2]. Electrochemical detection methods are fast, cheap and easy to perform, enabling the accurate quantification of the levels of several compounds in a wide range of samples. Particularly, the use of screen-printing technology in the serial production of screen-printed electrodes (SPEs) for the electrochemical determination of a wide range of substances is currently undergoing widespread growth [3]. Screen-printing techniques offer high-volume production of inexpensive, highly reproducible and reliable sensors, providing precise control over the SPEs dimensions, excellent uniformity, high reproducibility and potential for mass production [4, 5]. Moreover, SPEs can be easily modified, resulting in highly versatile devices that can be applied to *in situ* analysis with industrial and clinical interest. Due to their advantageous material properties, such as disposability, simplicity, and rapid responses, the development of electrochemical sensors based on SPEs for pharmaceutical analysis has received massive consideration since they enable the rapid screening of pharmaceutical compounds in complex matrixes, requiring small volumes of samples and no pre-treatment steps.

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P-93 METHODOLOGIES FOR MEASURING THE INTERACTION BETWEEN DRUGS AND ALBUMIN

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According to the "Harmonised methods of the European Honey Commission" [1], it is Albumin, the most abundant protein in the blood, has several functions such as osmotic pressure's maintenance, transport of hormones and lipids or pH control. This study is focused on methodologies for the measurement of the interaction between drugs (NBD-Cn, the fluorescent NBD group attached to an alkyl chain with n carbons, used as a model drug) and bovine serum albumin (BSA). The binding of drugs to albumin slows down their permeability through the endothelium because only the fraction of free drug is available to interact with the endothelial membranes. The drug hydrophobicity is also an important parameter because, in general, it increases the efficiency of binding to albumin [1]. In this work, this effect is evaluated by comparing the binding constants of NBD-C4 and NBD-C8.

The binding constants may be obtained with two distinct approaches: i) fixing the concentration of drug and varying that of albumin (evaluating the association to the binding center with the highest affinity), and ii) varying the drug's concentration while maintaining that of albumin (to evaluate the existence of several binding sites and their affinity). For fluorescent drugs, the two approaches may be followed focusing on the variations of drug's fluorescence upon binding to albumin and on the quenching of albumin fluorescence by the drug, respectively. When the drug's concentration is varied, care must be taken to guaranty that the optical density at both albumin excitation and emission wavelength is low to avoid artifacts, namely the inner filter effect [2]. Failure to do so leads to an incorrect evaluation of the number and affinity of the distinct binding centers.

In this work we have characterized the association of NBD-C4 and NBD-C8 to BSA following the two approaches. The comparison of the results for the two drug-like molecules allows us to critically evaluate the validity of the two approaches. The influence of experimental artifacts when following albumin fluorescence was also assessed through the use of a complementary technique, Isothermal Titration Calorimetry (ITC). This technique measures the heat evolved due to binding of the drug to the protein and may be used up to relatively high concentrations of both drug and protein. Due to the much lower sensitivity of ITC, when compared with fluorescence, the drug and protein concentrations used must be relatively high. Therefore, this methodology could only be followed for the less hydrophobic drug (NBD-C4).

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P-94 HYPOGLYCEMIC ACTIVITY OF ASTERACEAE SPECIES ENDEMIC OF MADEIRA ARCHIPELAGO: A RELATION TO THEIR POLYPHENOLIC COMPOSITION

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The vascular flora of Madeira Archipelago is exuberant and diverse, comprising over 1220 species of which 10% are endemic [1]. In this work, nine endemic *Asteraceae* plant species were studied for their phenolic profile and anti-hyperglycemic effects. The interest and selection of these species are related to their use in folk medicine. Two main groups of plants were analyzed: *Helichrysum* subspecies (*H. devium* Johns, *H. melaleucum* Rchb. ex. Holl, *H. monizii* Lowe and *H. obconicum* DC.) and other five endemic species: *Argyranthemum pinnatifidum* Lowe, *Artemisia argentea* L'Her, *Calendula maderensis* DC, *Cynara cardunculus* var. *ferocissima and Phagnalon lowei* DC.

Methanolic extracts were evaluated for their inhibitory activity towards key enzymes linked to type 2 diabetes using *in vitro* assays. Six extracts showed stronger inhibitory efficacy than commercial drug acarbose (positive control) towards α-glucosidase; exceptions were *H. monizii*, *C. maderensis* and *C. cardunculus.* However, all extracts were less active towards α-amylase. Caffeoylquinic acid derivatives (esterified with several acyl groups) whose anti-diabetic properties are extensively reported [2,3] were found as the main compounds in all plant species under analysis.

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P-95 TRACE ELEMENT DISTRIBUTION IN SOILS FROM FILDES PENINSULA (KING GEORGE ISLAND, ANTARCTIC PENINSULA)

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Compared to the Arctic, much less is known about sources, biogeochemistry and fate of contaminants in Antarctica. The frozen continent is considered pristine; however human presence in Antarctica has resulted in a sharp increase in anthropogenic pressure, leading to pollution problems, predominantly near scientific stations. The South Shetland Islands may be particularly vulnerable to human impacts as they contain one of the highest concentrations of research stations on the continent. Consequently, appropriate environmental monitoring is essential to inform the actions of Treaty Parties and national programme managers active in this region.

In the austral summer season of 2012/2013 and 2013/2014 two field campaigns were performed on Fildes Peninsula. Sediment/soils, water, ice/snow and vegetation were sampled at several sites in the Bays of Fildes, Great Wall, Elephant and Collins and analyzed for particulate and dissolved As, Cd, Cu, Hg (including MeHg), Pb and Zn. Some other interpretative parameters were also determined (e.g. organic carbon). In the laboratory trace element chemical and biological availability tests were also performed.

Results from the 2012/2013 campaign, showed Hg (and MeHg) concentrations to be low; however, high levels up to 2000 ppm of Pb, 15 ppm of Cd and/or 418 ppm of Cu were determined in soils samples from two locations on Fildes Peninsula. In water samples from the same area, a maximum concentration of 0.58 ppb of Pb was found, which is considerably higher than other reported values for Antarctic waters. For all trace elements analyzed, concentrations in the lichen *Usnea antarctica* reflected the concentrations on the corresponding soils, indicating efficient uptake.

These results point to the importance of a field campaign, that took place February in 2014, the results of which will be presented at this meeting.

Our work, in agreement with the evidence of earlier researchers, suggests a potential contamination problem in Fildes bay. It is hoped that environmental managers operating in the area will note these data and take appropriate action.

P-96 STUDY OF THE INTERACTION OF METAL CATIONS WITH FUCOIDAN

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Fucoidan is a polysaccharide found in the cell wall matrix of several species of brown algae. It is mainly constituted by L-fucose monomers with sulfate ester and carboxylic groups in different proportions that vary with algae species, place of cultivation, harvesting time and extraction methods [1, 2, 3]. It has been shown to exhibit a wide variety of biological activity - antibacterial, anticoagulant, antiviral, and so on [4].

Brown algae are recognized by their biosorption performance and capacity to bind cations. These attributes are related to their cell wall constituents, being fucoidan one of the main intervenient in the metal chelation process [1]. In the context of wastewater remediation, have proven to be an effective, low-cost and non-toxic substrate. Experiments carried out on fucoidan has shown that besides wastewater treatment, the fully controlled process of binding of divalent metal cations to fucoidan can lead to the production of seaweed extracts enriched with micronutrients that can be used in micronutrient supplementation.

In this study, the fucoidan was obtained commercially (Marinova) and two forms of fucoidan were applied: fucoidan in aqueous extracts and fucoidan in aqueous suspension. The degree of the fucoidan chelation for both forms was assessed by potentiometry and UV spectrophotometry. Experimental data was treated by using Gran's method and the results revealed that fucoidan-metal interaction is strongly dependent on the experimental imposed conditions such as ionic strength and pH.

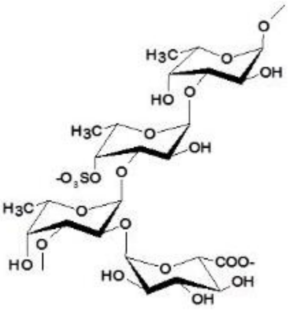

Figure 1: Structure of fucoidan.

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P-97 DEFATTED RICE BRAN VINEGAR: PRODUCTION AND EVALUATION OF ANTIOXIDANT ACTIVITY

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Rice bran is a by-product of rice industry produced on a large scale in Brazil, with high levels of carbohydrates and Phytic acid, which presents antioxidant capacity (1). The major applications of rice bran comprise the oil extraction and animal feed (2). One of the possible ways to add value to this residue is the application as substrate for fermentation processes, as the vinegar production. In this way, the aim of this work was to obtain vinegar from defatted rice bran (DRB) and the evaluation of their antioxidant activity by the DPPH method. The DRB was hydrolyzed enzymatically by commercial enzymes (Alcalase, α-amylase and AMG). Alcoholic fermentation was conducted with a culture of *Saccharomyces cerevisiae* (commercial dehydrated yeast). The "wine" was submitted to the acidification process in a 4,5 L batch stirred reactor, which was started using stronger ethanol vinegar and *Acetozyn* (mixed salts industrially used with nutrients for the bacteria's growth). The conditions used in the fermenter were 1.0 VVM (volume of air/volume of medium x min.), 500 rpm and 28 ºC (aeration, agitation and temperature). The product was considered ready when ethanol concentration was less than 1%, as recommended by the Brazilian law. The acetic fermentation was evaluated by the yield and process productivity. The DPPH method was applied to determine the total antioxidant activity. In addition, the physicochemical characterization was held in accordance with the Brazilian legislation. It was possible to obtain the DRB vinegar, and only the ash content not attended the parameters of Brazilian law. The yield based on the total concentration (TC = sum of the concentration of ethanol and acetic acid in a medium) was satisfactory, whereas ranging from 83.5% to 90.5% to four replicates of the experiment. For the total antioxidant activity, the result which corresponds to the sample required to reduce by 50% the initial DPPH concentration (EC_{50}) was 110 ± 1.4 g/mL, less than that found in the literature for other kinds of vinegars such as rice and grape, confirming the potential of antioxidant activity of the DRB vinegar produced.

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P-98 EFFECTS OF THE PARTICLES SIZE AND PLASTICIZER CONCENTRATION ON SOME PHYSICAL AND BARRIER PROPERTIES OF FILMS BASED ON CHITOSAN AND NATURAL DEEP EUTECTIC SOLVENTS

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Food packaging concerns preservation and protection of all types of foods and their raw materials, as preserving them from oxidative and microbial spoilage. Increased use of petrochemical based plastics such as polyolefins, polyesters, polyamides, etc. has led to serious ecological problems due to their non-biodegradability.

The use of biodegradable materials, especially from renewable agriculture feedstock and marine food processing industry wastes is currently of prime interest due to their ecofriendly and biodegradable nature. Among many natural biomaterials that can be used to produce biodegradable and/or edible packaging, chitosan is one of the most promising materials due to its biodegradability, biocompatibility, antimicrobial activity, non-toxicity and versatile chemical and physical properties; however, its transparent films present poor mechanical response and high sensitivity to moisture. In order to overcome this problem, plasticizers are added to provide the necessary workability to this biopolymer.

Here, Natural Deep Eutectic Solvents (NADES) were chosen as potential biodegradable plasticizers for investigation.

Specifically, natural deep eutectic solvent using choline chloride/Lactic acid was added on the mixture of fibrous (F) and nanoparticles (N) chitosan solutions so as to evaluate its plasticizing effect on physical and barrier properties of the chitosan films. Knife-coating technique was used for chitosan biofilms production. Different F/N mixing and plasticizer ratios were used. Significant differences on the hygroscopic behavior and on mechanical properties of biofilms were observed for the different mixtures and NADES contents considered.

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P-99 PHYSICO-CHEMICAL EVALUATION OF OLIVE PASTES PACKED IN TUBES OVER STORAGE

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Olive production has an increasing economic importance and a valuable tradition in Portugal. Despite the increased olive production, table olive industries sometimes find it difficult to sell small caliber fruits, as well as to find applications for fruits that are physically damaged or defective. Therefore it is necessary to look for alternatives to reduce or minimize economic losses and at the same time to add value to this important agricultural product.

One alternative explored in this work, is the development of olive pastes. This study had the collaboration of meia.dúzia®, a company specialized in the production of fruit jams packed in tubes, whose goal is to achieve sustainability through the constant introduction of new products in the market. Packaging in tubes has the advantage that light does not interact with the product. Also, after opening the exposure to air is reduced in comparison to other types of packages, minimizing oxidation processes and maintaining the original colors.

The raw materials used in this study were green and black olives (*Olea europaea L.)* in brine. The olives were washed in water to remove the brine and were subsequently crushed in a blade mill until a homogeneous paste was obtained. This initial olive paste was divided into 4 parts, two with green olives, one condiment with garlic, the other with rosemary, and the other two parts with black olives, one with honey and the other with rosemary. After mixing all ingredients, the pastes were packed in tubes, sealed and pasteurized at 85ºC for 10 min. The physic-chemical changes of the four types of pasteurized olive pastes was evaluated over 120 days of storage.

pH, water activity, color (L, a, b, ΔE), soluble solids (only in green olive pastes with honey) and texture were monitored at 0, 6, 15, 30, 62 and 90 days of storage. Sensory evaluation was also performed using quantitative descriptive analysis and acceptability (consumer) tests.

Slight changes were registered over storage time, namely an increase in Lightness (L*) observed in green olive pastes. pH was quite constant during the storage time, The pH of green olive pastes was always below 4, except on the 90th day, when pH exceeded 5. All samples had high water activity (aw) until the 6th day of storage (aw>0.92), and afterwards a decrease to aw = 0.84 was observed. After the 30th day of storage, brix of olive green pastes started to decrease. Regarding sensory analysis, olive pastes that showed better results and less loss of organoleptic characteristics were black olive pastes with garlic and rosemary with an estimated shelf life of 30 days.

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P-100 DETECTION OF A PEANUT ALLERGEN (ARA H 6) USING A VOLTAMMETRIC IMMUNOSENSOR

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Food allergies are based on an immunological hypersensitivity against some food proteins and/or glycoproteins, generally mediated by immunoglobulin E. Symptoms usually involve the gastrointestinal tract, skin and the respiratory system. Anaphylactic reactions are rare but they constitute a life threat [1].

Peanut (*Arachis hypogaea*) is one of the most allergenic foods. Even very small amounts of its allergens can originate severe reactions in some allergic individuals. Ara h 1, Ara h 2, and Ara h 3 have been recognized as major allergens. More recently, Ara h 6 also emerged as an important allergen since it has a similar seroprevalence as Ara h 2, and has also been associated to clinical peanut allergy. Ara h 6, a conglutin (2S albumin), is heat-stable and resistant to food processing and gut digestion [2]. Due to its stability, it has been considered a suitable marker to identify the presence of peanut in food products and production lines.

In this work, a voltammetric immunosensor for Ara h 6 detection in food samples is presented. Gold nanoparticle-modified screen-printed carbon electrodes were used to develop a sandwich-type immunoassay using two different monoclonal antibodies. The antibody-antigen interaction was monitored through the electrochemical detection of enzymatically deposited silver. The developed immunosensor presented a linear range between 1 and 100 ng/ml, limits of detection and quantification of 0.27 and 0.88 ng/ml, respectively, high intra- and inter-day precision (RSD ≤ 9.8%) and good accuracy (recoveries ≥ 97%). It was also successfully used to detect small amounts of Ara h 6 in complex food matrices.

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P-101 TEA FROM AZOREAN *CAMELLIA SINENCIS*: ANTIOXIDANT PROPERTIES, POLYPHENOL AND FLUORIDE CONTENTS

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Nowadays, tea is the most widely consumed beverage after water. A lot of people drink tea and studies suggest that infusions of *Camellia sinencis* leaves have many health benefits. Depending on the maturation stage of leaves and the process used in tea production, it is possible to find different varieties of this product in market today.
In this work, different types of tea from azorean *Camellia sinencis* such as, green tea (Hysson and Encosta de Bruma) and black tea (Pekoe, Orange Pekoe and Broken Leaf) were studied to carry out comparisons between its antioxidant properties, polyphenol and fluoride contents with aim to know about the influence of the processing method and type of leaves used in the production of these teas [1,2].
The infusions were prepared using 1.5 g of leaves in 200 mL of hot water (a cup of tea with an usual strength). Milled leaves are also used trying to improve extraction efficiency. The FRAP assay was applied for evaluation of the antioxidant compounds that can reduce Fe^{3+} to Fe^{2+}. From the reduction reaction, a blue complex of Fe^{2+}-tripyridyltriazine that absorbs at 593 nm was obtained. The quantification was performed using Trolox calibration curves (2.5 - 500 µmol/L). The total phenolic content was determined by Folin-Ciocalteau method using a galic acid calibration curve (12.5 – 500 mg/L). Direct potentiometry was applied for the quantification of fluoride ion using the corresponding ion selective electrode and an Ag/AgCl reference electrode. The calibration curve was built with standard solutions of NaF (0.01 – 5 mg/L).
Using milled leaves, the efficiency of extraction could increase two times depending on the tea sample and the type of quantified analyte. The fluoride content was in the range 1.42 to 2.39 mg/L and strongly related with the maturation state of leaves. Moreover, it was found that the antioxidant activity and total phenolic content of the tea samples were affected by the processing method of *Camellia sinensis* leaves.

Acknowledgements: To Gustavo França, student from Escola Profissional de Setúbal for the contribution in the potentiometric assays.

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P-102 THE ANTIOXIDANT PROPERTIES OF PORTUGUESE WINES: GOOD QUALITY THROUGHOUT THE COUNTRY

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Wine is one of the most important commercial products in the Mediterranean area and is one of the essential components of the Mediterranean diet. Antioxidant properties of wine depend on its content in antocianidins and resveratrol [1].In Portugal wine is produced all over the country but organoleptic characteristics are quite different from region to region.

In this communication we present the results of the evaluation of radical scavenging activity (RSA) of 12 commercial Portuguese wines, from 10 different regions, and also two wines provided by local producers. RSA was evaluated using the DPPH test [2].

Three of the commercial wines were produced using only one variety of grapes, *Arinto* and *Castelão*, the others were obtained from two or more varieties. Wine samples provided from a local producer from Torres Novas were also obtained from a single variety each, *Trincadeira*, *Aragonez (Tinta Roriz)* and *Touriga Nacional*.

Results obtained showed red wines were the more active and RSA ranged from 75% to 81%, being the most actives those from the south of Portugal, Alentejo and Algarve. White wines showed poor activity, but for the same producer and the same variety of grapes, RSA was very dependent on the year, in 2011 RSA = 15% and in 2012 RSA = 6%.

Since they were produced from a single variety of grapes each, wine provided from the local producer from Torres Novas was also investigated on what concerned their ability to prevent or minimize lipid peroxidation. This property was evaluated using the beta-carotene/linoleic acid bleaching test [3].

Wines obtained from the single varieties of *Aragonez* and *Touriga Nacional* were the more active in both tests. Results of the DPPH test were 89.0% and 84.8% respectively. Results of the beta-carotene/linoleic acid bleaching test were 63.5% and 60.9% respectively. Wine obtained from *Trincadeira* grapes were quite active in the DPPH test, 56.3%, but less active in the beta-carotene/linoleic acid bleaching test, 19.2%. These results indicate that the antioxidant activity of red wines is strongly dependent on the variety of the grapes used.

Acknowledgements: The authors acknowledge Quinta da Murta, Dra. Paula Oliveira and Dr. Armindo Jorge Ferreira de Oliveira for kindly provide wine from Bucelas, Cernache do Bonjardim (Sertã) and Torres Novas, respectively. This work was founded by Fundação para a Ciência e Tecnologia (FCT) Portugal (UID/MULTI/00612/2013).

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P-103 CAROTENOID COMPOSITION OF UNDEREXPLOITED BRAZILIAN FRUITS: FLACOURTIA JANGOMAS AND SOLANUM DIPLOCONOS

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Dietary carotenoid ingestion from food has been associated to the improvement of the immune system and decrease of the risk of development of chronic degenerative diseases, such as cardiovascular diseases, cataract, macular degeneration and certain types of cancer. In this preliminary study, our focus was directed to elucidate the carotenoid composition of two underexploited Brazilian fruits: *Flacourtia jangomas* (Lour.) (Brazilian name: “cereja-de-cametá”), from Flacourtiaceae family, and *Solanum diploconos* (Mart.) (Brazilian name: “tomatinho-do-mato”), from Solanaceae family. The carotenoids of whole fruit of *F. jangomas* and peel and pulp of *S. diploconos* were tentatively identified and quantified (μg/g, dry basis) by HPLC-DAD (Figure 1). All-*trans*-lutein (peak 2), all-*trans*-zeaxanthin (peak 3), all-*trans*-β-cryptoxanthin (peak 4) and all-*trans*-β-carotene (peak 7) were positively confirmed through the retention times, co-elution and UV-vis spectra feature as compared to authentic standards. The assignments of 13-*cis*-lutein (peak 1), 15-*cis*-β-carotene (peak 5), 13-*cis*-β-carotene (peak 6) and 9-*cis*-β-carotene (peak 8) were done considering that spectral fine structure (%III/II) decreases and the intensity of *cis*-peak (%AB/AII) increases as the *cis*-double bond is getting closer to the centre of the molecule as compared to its parent all-*trans*-carotenoid. The pulp of *S. diploconos* fruit presented the highest carotenoid content (47 μg/g) and β-carotene was the major carotenoid in both fruits (1.4-38 μg/g), followed by lutein (0.8-7 μg/g).

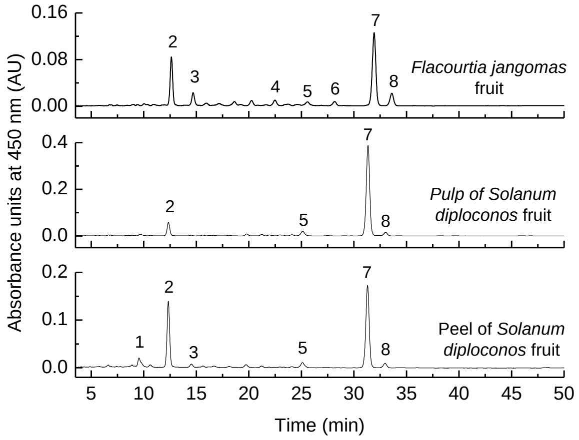

Figure 1: Carotenoid profiles obtained by HPLC-DAD at 450 nm.

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P-104 LEAF MATURATION MONITORING USING NEAR INFRARED SPECTROSCOPY

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There are many complex environmental factors within a vineyard that create its viticultural potential. Among those, vineyard leaf area and general health are important management tools. The overall status (nutrient, health) of leaves will directly affect total biomass production including the allocation of mineral nutrients to the fruits [1]. Furthermore, the analysis of the chemical composition of leaves will provide precious insight on grape characteristics and ultimately wine quality. Vineyard leaf area has been reported to be related to fruit ripening rate, infestation and disease, water status, fruit characteristics and wine quality. Management methods for leaf area regulation are numerous and include pruning, shoot thinning, leaf removal, cover crop cultivation, irrigation scheduling and application of soil and crop amendments. However, producers have no efficient way of mapping and monitoring leaf area, in absolute terms, during the growing season. Direct measurement of leaf area by leaf removal is accurate, yet time-consuming and destructive. Indirect methods include measurement of canopy-intercepted solar radiation, regressions based on shoot length and shoot number, and post-season collection of pruning weights (prior season woody production). While reasonably quick and accurate, these point-based techniques are not designed for mapping applications [2]. Near-infrared Spectroscopy (NIRS) is a rapid, non-destructive, inexpensive and accurate analysis technique. It has been widely used in various fields of the wine industry, providing specific information about plant composition, such as chlorophyll, nitrogen concentrations (N) and water content, among others. In this study, grapevine leaves from a vineyard, located in the Douro Wine Region of Portugal (*Quinta do Mourão*) were scanned over time, at different maturation stages of the plant, using a FieldSpec 4 Wide-Res (ASD Inc, Boulder, CO) in diffuse reflectance mode over a spectral range of 350-2500 nm. The objective of this work was to assess if, after processing of the spectra through chemometric tools, multivariate analysis would yield satisfactory results regarding leaf (and consequently plant) maturation monitoring. This knowledge will provide valuable insight to the winemaker and will constitute a useful management tool for more successful and cost effective future harvests.

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P-105 CHEMICAL CHARACTERIZATION AND BIOACTIVE EFFECTS OF DECOCTED MELISSA OFFICINALIS L. AND THE POSSIBILITY OF FOOD INCORPORATION

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Melissa officinalis L. (lemon balm) has been consumed as infusions and decoctions for hundreds of years. Its consumption is linked with various health benefits like the relief of headaches, rheumatism, digestion, neurodegenerative disorders and also antitumor, antioxidant and anti-inflammatory effects [1]. Herein, the chemical characterization (polyphenols, free sugars, tocopherols and organic acids) of its decoctions is presented, along with the reports of its antimicrobial, antioxidant and antitumor activity. The most abundant polyphenols, detected through HPLC-DAD-ESI/MS, were rosmarinic and lithospermic A acids, while fructose was the only free sugar detected by HPLC-RI. The most abundant tocopherol was γ-tocopherol detected through HPLC-FL, while in terms of organic acids, quinic acid was the most representative one (HPLC-PDA). Furthermore, after antimicrobial and antifungal screening, the most sensitive species were *Pseudomonas aeruginosa*, *Salmonella thyphimurium*, and *Penicillium funiculosum*. The inhibition of the growth of two human tumor cell lines, MCF-7 and HepG2, was also observed, along with very high free radical scavenging activity and reducing power. *M. officinalis* aqueous extracts, namely obtained by decoction, could be strong candidates to be incorporated into foodstuffs regarding antioxidant and antimicrobial effects, working as natural additives, substituting the synthetic ones which have been losing interest due to consumer preferences to natural and healthier products. Furthermore, our research group is working in this proof-of-concept incorporating *M. officinalis* extracts in "Serra da Estrela "cheese.

Acknowledgements: The authors are grateful to the company Mais Ervas, Lda, for providing the *M. officinalis* samples. Further acknowledgements to the PRODER project No. 46577-PlantLact, the foundation for Science and Technology (FCT, Portugal) for financial support to CIMO (Pest-OE/AGR/UI0690/2014) and L. Barros, and the Serbian Ministry of Education, Science and Technological Development for the Grant No. 173032.

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P-106 OPTIMISATION OF CHROMATOGRAPHIC CONDITIONS FOR AFLATOXINS M_1 AND B_1 DETECTION BY HPLC

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High Performance Liquid Chromatography (HPLC) is an outstanding analysis method for aflatoxins in milk and dairy products because of its sensitivity and accuracy of quantitative measurement [1]. However, standard approaches to development of HPLC methods have been through trial and error or intentional variation of experimental factors. These approaches to method optimisation fail to take into account interactions between experimental factors [2]. Recognizing this fact, this study considered another approach to optimisation. It was through the use a multivariate design to achieve multi-objective optimisation in HPLC, selecting the optimal conditions for the mobile phase composition, its flow into the chromatographic system and the column temperature in order to simultaneously identify, separate and quantify B_1 and M_1 aflatoxins in milk. Mixture experimental design was used with three components, with restrictions combined in a 2^2 factorial design for the process variables (column temperature and flow) with a total of 40 chromatographic runs performed on Acclaim PA2, 5 µm analytical (4.6 x 250 mm) C_{18} column with fluorescence detector (excitation and emission wavelengths of 360 and 450 nm, respectively). After model definition for the dependent variables, a search for optimum conditions was performed using the sequential simplex method and the Derringer and Suich desirability functions [3]. The variables evaluated were: mobile phase composition (acetonitrile, methanol and aqueous solution of 1% acetic acid); mobile phase flow rate (0.5 to 1.5 mL min^{-1}); and column temperature (30 to 40^oC). The chromatographic parameters obtained as responses and determined by the experimental design were: time (9.3 and 14.6 min for AFM_1 and AFB_1, respectively), retention factor ($0.5 > Rf > 1.0$), separation factor and column resolution (> 1.5), and height of the peaks (13816 and 5220 counts for AFM_1 and AFB_1, respectively). The models for all the responses evaluated showed highly significant regression ($p < 0.0001$) demonstrating that the models were well suited to the experimental data. The optimal conditions found were 35% acetonitrile, 10% methanol and 55% of acetic acid (1%) as components of the mobile phase with flow rate of 0.5 mL min^{-1} and 40^oC of column temperature, producing suitable results of retention time, retention factor, separation factor and column resolution, and intensity of peaks. The established optimal conditions were validated and all the obtained results were within the range established by experimental design. Therefore the design was able to produce reliable models ($R^2 > 0.96$) which enabled the estimation of the best conditions meeting the multiple objectives.

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P-107 PHOTOSENSITIZER/BIOMATERIAL LOCAL DRUG DELIVERY SYSTEMS WITH POTENTIAL APPLICATION IN CANCER PHOTODYNAMIC THERAPY

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In the last few years, new drug delivery systems based on polymeric biodegradable substrates have been investigated aiming to achieve high loadings and maintain therapeutic concentrations of the drug at the tumour site for an extended time period [1]. The development of a photosensitizer/polymer system is determined by the need to overtake the major limitations of Photodynamic Therapy of Cancer (PDT) [2]. The adsorption onto biopolymers may lead to new local delivery systems that can act as theranostic agents for simultaneous diagnosis and therapy. Recent studies show that fluorescence lifetimes, quantum yields and the stability of squarylium dyes [3,4] adsorbed onto powdered chitosan increases, promoting their use as implants for local delivery and therapy. Porphyrin dyes [5] were also studied in solution and adsorbed onto chitosan/PEG/Gelatin formulation films presenting very promising results to be applied as drug delivery systems. Nowadays we are also developing new hydrogel formulations to delivery drugs such as cardiogreen also known as IR125 [6].

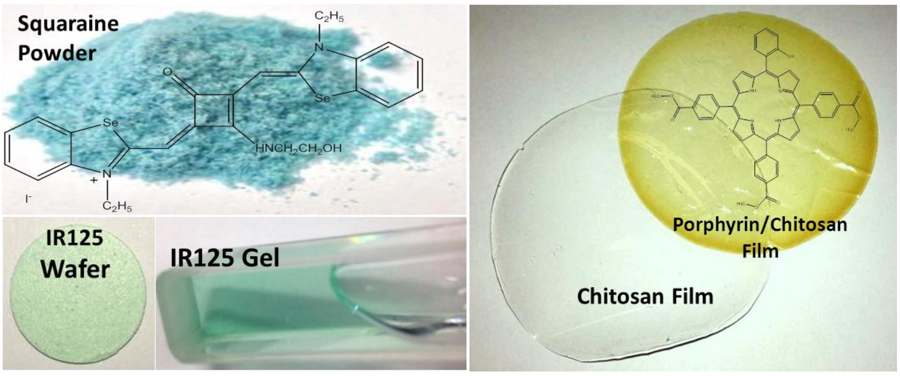

Figure 1: Examples of the systems: squaraine adsorbed onto chitosan powder, IR125 wafer/gel and chitosan films with and without porphyrin dye.

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P-108 EXPERIMENTAL AND COMPUTATIONAL THERMOCHEMICAL STUDY OF 2-METHYLINDOLE-3-CARBOXALDEHYDE

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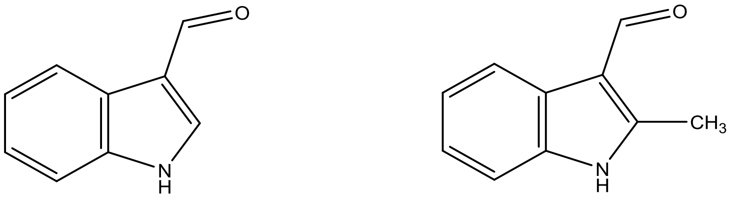
The indole ring, abundant in nature, is the basic structure of a number of heterocyclic compounds with high relevance due to their biological activity. In fact, indole derivatives have an important role in the preparation of many drugs, namely antifungal, antiviral, anti-inflammatory and have been involved in several studies aiming to evaluate the anticancer activity in human cells. They are also used in the production of heterocyclic Schiff bases adopted as catalysts in many reactions such as carbonylation, hydroformylation, among others. These aspects justify the interest on the knowledge of the thermodynamic properties of this class of compounds, due to their relevance on the evaluation of the respective reactivity. The standard (p^o = 0.1 MPa) molar energy of combustion of 2-methylindole-3-carboxaldehyde, in the crystalline state, was determined, at T = 298.15 K, using a static bomb combustion calorimeter. The vapor pressures as a function of the temperature were measured by using the Knudsen effusion technique and the standard molar enthalpy of sublimation of the compound, at the mean temperature of the range of vapor pressure measurements, was derived from the Clausius-Clapeyron equation. From the experimental results, the standard molar enthalpies of formation, in the condensed and gaseous phases, at T = 298.15 K, of 2-methylindole-3-carboxaldehyde were derived. Using the previous reported gas-phase enthalpy of formation for indole-3-carboxaldahyde [1] the energetic effect inherent to the presence of a methyl group at the 2-position of the indole ring has been evaluated. Additionally, the gas-phase enthalpies of formation of 2-methylindole-3-carboxaldehyde and also of indole-3-carboxaldehyde were determined by G3(MP2) calculations. The gaseous enthalpies of formation, were obtained using appropriate working reactions and the results were compared with the data obtained experimentally.



indole-3-carboxaldehyde   2-methylindole-3-carboxaldehyde

Figure 1: Structural formula of the compounds under study

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P-109 ENCAPSULATION OF CURCUMINE IN TRIBLOCK COPOLYMER PLURONIC® P-123 AS SEEN BY SELF DIFFUSION AND UV-VIS SPECTROSCOPY

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Curcumine (CUR) is a natural antioxidant isolated from the rhizome of *curcuma longa.* CUR presents a great potential against several kinds of cancers[1]. However, the hydrophobicity of CUR inviabilizes its use in pharmaceutical applications. Thus, in this work, the encapsulation of CUR in a copolymeric micelle of triblock copolymer Pluronic® P-123 has been done[1],[2]. The effect of different media (water and biological media as simulated intestinal (SIF) and gastric (SGF) fluids) on the P123/CUR interactions has been studied by spectroscopy and NMR. Diffusion Ordered Spectroscopy (DOSY) experiments were carried out to have an assessment on the effect of CUR encapsulation in the size of the micelle: furthermore, bi-dimensional NMR studies will provide information on the location of CUR into P-123 micelle. Diffusion coefficients for P-123 formulation in simulated gastric fluid (pH* 1.2) and simulated intestinal fluid (pH* 6.8) were 2.46×10^{-7} and 1.03×10^{-6} cm^2s^{-1}, respectively, showing the influence of media in diffusion patterns. NMR and spectroscopic studies showed that the formulation of Curcumine in P-123 is promising to use in pharmaceutical applications.

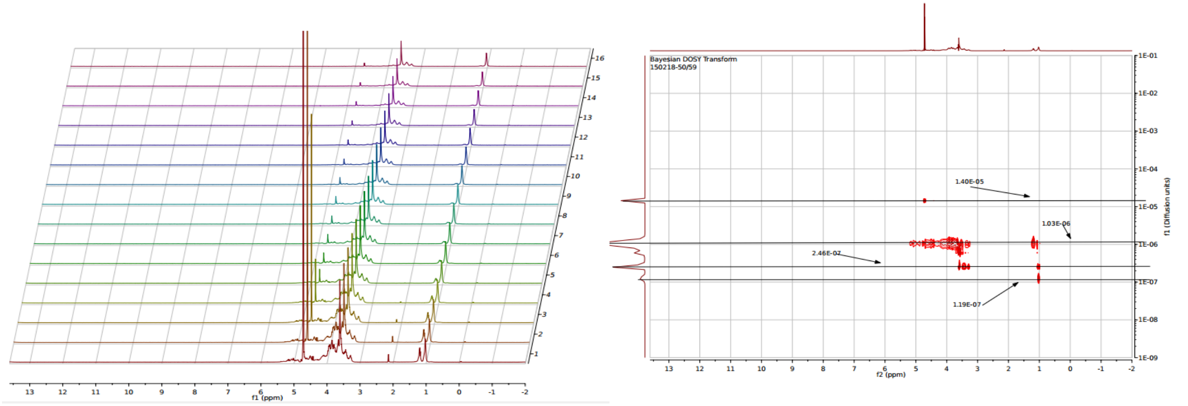

Figure 1: DOSY of formulation CUR/P-123 in SGF media, T: 25,0 °C, pH: 1,2.

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P-110 VAPOUR PRESSURES AND PHASE DIAGRAMS OF FOUR METHYL p-SUBSTITUTED BENZOATES

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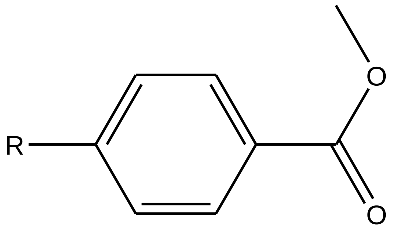
A simple approach for estimating vapor pressures of substituted benzenes with 30 different substituents was recently proposed [1]. In order to extend our data base of accurate results of benzene derivatives, a thermodynamic study of sublimation and vaporization of methyl *para*- cyano, nitro, formyl and (methylamino) benzoates, was achieved. A static method based on capacitance diaphragm gauges [2] was used to measure the vapor pressures of both condensed phases of the four compounds referred to above in the temperature ranges (303.9 to 363.6) K, (319.0 to 415.8) K, (303.2 to 388.2) K and (338.9 to 392.4) K, respectively. The results obtained enabled the determination of the standard molar entropy, enthalpy and Gibbs energy of sublimation and of vaporization, at T = 298.15 K, as well as a phase diagram representation of the (p,T) experimental data near the triple point. The temperatures and molar enthalpies of fusion were determined using differential scanning calorimetry and were compared with the values derived indirectly from the vapor pressure measurements.



R = CN, NO_2, CHO, $NH(CH_3)$

Figure 1: Structural general formula for the four methyl *p*-substituted benzoates studied.

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P-111 DEVELOPMENT OF pH-RESPONSIVE GUM ARABIC HYDROGELS FOR CONTROLLED RELEASE OF METHYLENE BLUE

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Hydrogels are three-dimensional cross-linked polymer networks capable of imbibing large amount of water or biological fluids used in several applications as tissue scaffolds, microfluid devices, biosensors and drug delivery sistems [1]. It is known that the polyssacharide Gum Arabic (GA) can be modified by chemical reaction, forming responsive superabsorventes hydrogels which can be used, e.g., for removal of dyes or as devices for biomagnetic materials [2]. In this work, GA with different methacrylation/substitution degrees (GAm) have been synthesized; The Afterwards those monomers have been used for the preparation of hydrogel matrices for transport and delivery of a photosensitizer compound: Methylene Blue (MB). GAm as well as the corresponding hydrogels were characterized by ^{1}H NMR (Figure 1-a), IR, thermal analysis as well the mechanism of sorption of MB by hydrogels. Adsorption studies showed a complex interaction involving MB and hydrogel matrices. The sorption isotherms have been discussed in terms of different models (such as, Langmuir and Freundlich (Figure 1-b)). The sorption isotherms and the corresponding equilibrium parameters, including the maximum amount of MB encapsulated into GA gel matrices, are dependent on the degree of substitution of GA. Release kinetics of MB from GA-based hydrogel matrices for SIF and SGF was also evaluated. It has been found that the mechanism and release kinetics of MB, from these gels, are dependent on the pH, enabling this system for controlled release of MB in biomedical applications.

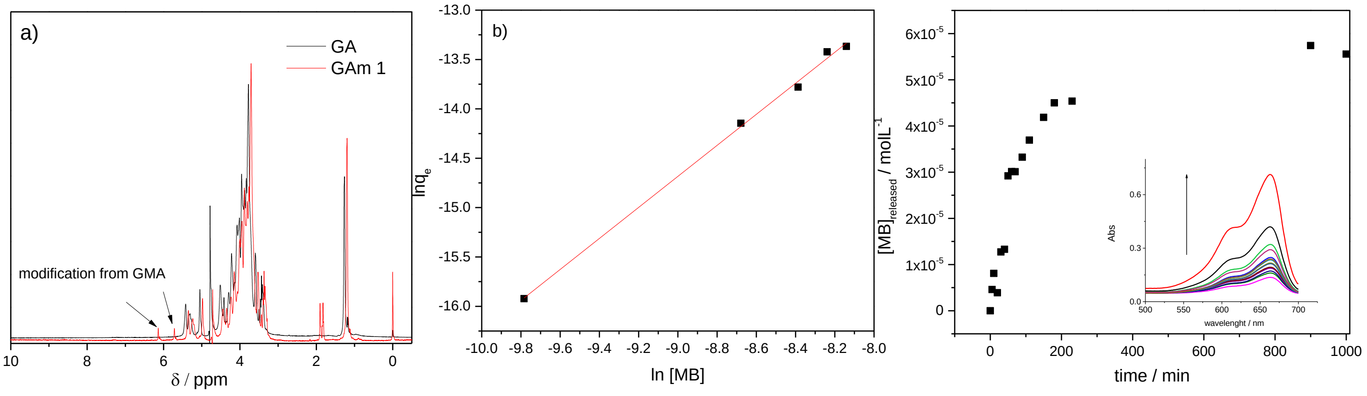

Figure 1: a) ^{1}H NMR spectra of GA and GAm. b) Sorption isotherm of MB by GAm hydrogels – the solid line has been obtained by fitting the Freundlich equation to the experimental data. c) Release kinetics of MB from GAm hydrogel to SIF media, as seen by UV-Vis spectroscopy.

Acknowledgements: Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Fundação para a Ciência e Tecnologia (FCT), University of Coimbra and State University of Maringá.

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P-112 SYNTHESIS AND CHARACTERIZATION OF PHYSICALLY CROSS-LINKED HYDROGELS BASED ON CHITOSAN/POLYVINYL ALCOHOL/MALEIC ANHYDRIDE-BETA-CYCLODEXTRIN

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Chitosan is a nontoxic, biodegradable and biocompatible polysaccharide derived from chitin and consisting of (1,4)-linked amino-2-deoxy-□D-glucan [1]. On the other hand, PVA gels are also nontoxic, show bioadheside characteristics. Furthermore, PVA gels exhibit a high degree of swelling in water and a rubbery and elastic nature. Because of all these features PVA is an excellent basis for biomaterials [2]. PVA and chitosan blend cryogels, prepared by the freezing/thawed cyclic method, show good mechanical strength and lack of toxicity [3]. The synergetic effect of those two polymers associated with the functionalization through the incorporation of maleic anhydride-beta-cyclodextrin monomer, will provide a new material with amphiphilic features. The objective of this study is to synthesize physically cross-linked hydrogels based on PVA/chitosan/maleic anhydride and beta-cyclodextrin monomer, using the freezing/thawing technique. The hydrogels will be characterized by different techniques, including thermogravimetry (TG), differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). These hydrogels may have applications as biodegradable and selective adsorbents in wastewater treatment.

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P-113 PHOTOCHEMICAL STUDIES OF MESOPOROUS AND NANOSTRUCTURED TiO_2 MATERIALS

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Mesoporous titanium oxide (TiO_2) materials, with high superficial areas and with controllable pore sizes, have been extensively studied in the past, due to its wide range of applications such as photovoltaics, photocatalysis, sensors, and even cosmetics [1,2]. To project and to synthetize a material formed by particles with different shapes and sizes can be as important and determinant as the selection of its structure and composition. In that sense, one of the biggest challenges is the synthesis of new TiO_2 based mesoporous and nanostructured materials, with specific morphologies and sizes, for a concrete application. Within the scope of this work, we present some TiO_2 based nanomaterials, synthetized by the hydrothermal method, complementary to the traditional sol-gel approach (Figure 1). For the same composition/structure, new properties can be obtained by changing its morphology. However, the opposite is also valid, either by the adsorption of fluorescent molecules that extend the absorption profile of the material to the visible range, or by doping with specific elements that can influence the electronic structure and retard the recombination of excited states [3]. For that purpose, we also studied and characterized new fluorescent squaraines and rhodamine-like dyes, both in solution and adsorbed in solid substrates. In the latter case, we used and compared electronically neutral substrates, such as cellulose, with the electronically active matrix, TiO_2.

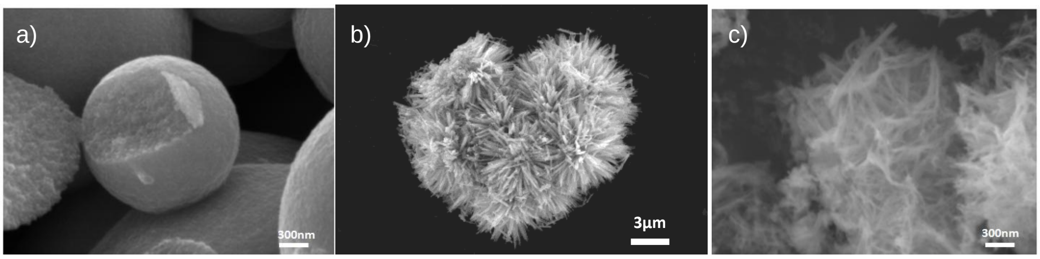

Figure 1: SEM image of a) Mesoporous TiO2 microspheres, b) 'Star'-like nanostructured TiO_2, and c) TiO2 nanowires.

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P-114 PHASE TRANSITION PROPERTIES OF 2-FLUOROFLUORENE AND 2-FLUOROFLUORENONE

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Polycyclic aromatic hydrocarbons (PAHs) with a fluorene core have attracted much attention given their appealing photo and electroluminescent properties, leading to an increase in their use in electronic devices. These compounds present high thermal and electrochemical stability and allow tuning of the compounds' properties by functionalization in the 9-position of the fluorene unit. The successful application of these materials depends greatly on the volatility of their solid phases, among other thermodynamic properties.

Following our previous reports on thermodynamic characterization of PAHs derivatives with a fluorene core [1,2], the present work focuses on the vapor pressure study of 2-fluorofluorene, using a static method based on capacitance diaphragm manometers, and 2-fluorofluorenone, using both a static method and a mass effusion method. Sublimation and vaporization properties (standard molar enthalpies, entropies and Gibbs energies) were determined and DSC measurements were performed in order to determine the enthalpy and temperature of fusion.

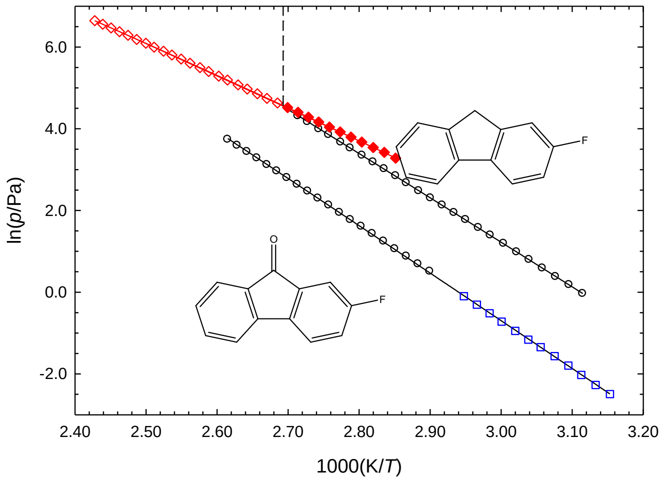

Figure 1: Plots of ln(p/Pa) against 1000(K/T) of 2-fluorofluorene and 2-fluorofluorenone: □ - effusion crystalline vapor pressures; ○ - static crystalline vapor pressures; ◇ - stable liquid vapor pressures; ◆ - super-cooled liquid vapor pressures.

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P-115 POLYMER-BASED SENSORS FOR DETECTING EXPLOSIVE VAPOURS FROM LANDMINES

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Current security and environmental concerns have forced the development of new devices, capable of rapid and cost-effective detection of explosives. These sensors must fulfill a number of criteria, namely sensitivity, reversibility and capability for real-time signal processing. For nitroaromatic explosives, sensing of a few parts per billion or less of the analyte vapour is required, with rapid and, ideally, reversible changes in the sensor. For in-field applications, a portable system would be advantageous. Conjugated polymers (CP) have emerged as promising chemosensory material for detecting nitroaromatic explosive vapours, as they readily transform a chemical interaction into an easily measured optical output with high sensitivity. The explosive vapour analyte consists of nitrated molecules, which are strongly electron-deficient, while the conjugated polymer sensing materials are luminescent and electron-rich. As a result, photoexcitation of the conjugated polymer is followed by electron transfer to the analyte, leading to quenching of the light-emission from the conjugated polymer.

The best conjugated polymer in our studies was found to be poly(9,9-dioctylfluorene-2,7-diyl]-co-bithiophene] (PF2T). This is stable, has a good absorption between 400 and 450 nm, a strong and structured fluorescence around 550 nm, and up to 96 % quenching of fluorescence, accompanied by a decrease in fluorescence lifetimes, is seen on exposure of films of PF2T in ethylcellulose to nitrobenzene (NB) or 1,3-dinitrobenzene (DNB) vapours. The effects of matrix, plasticizer and temperature have been studied, and the morphology of films determined by scanning electron microscopy (SEM) and confocal fluorescence microscopy. We also used ink jet technology to structure this sensor. In addition, a dedicated, high dynamic range, intensity-based fluorometer, with laser diode and filtered photodiode has been developed for use with this system.

We have also been working on an insoluble patterned cross-linkable poly(9,9-diocthyl-alt-bithiophene) (PF8T2). The columnar, spike and porous structures obtained lead to a significantly improvement in the detection of TNT- like compounds.

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P-116 INFLUENCE OF FRUCTOSE ON THE DIFFUSION OF HYDROGEN PHOSPHATE IONS AT 298.15 K

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Fructose is a monosaccharide found *in natura* in fruits and honey. However, exponential use of high fructose corn syrup (HFCS) as a sweetener in processed foods (e.g. yogurt, bread, ketchup or beer), appeared on the focus of recent scientific literature as a main cause of both obesity epidemics and a growing number of fructose-correlated diseases and conditions. [1]

Phosphates are critical for human life because they fulfil important roles like pH buffering or ATP/ADP energy management. So, mobility of phosphates is paramount and degradation of this parameter will certainly promote metabolic changes.

In order to establish new mobility data, mutual binary diffusion coefficients for potassium hydrogen phosphate in aqueous solutions (0.100 mol dm-3) containing fructose at various concentrations (from 0.001 to 0.200 mol dm-3) have been measured at 298.15 K, by using a conductimetric Lobo cell coupled to an automatic data acquisition system to follow the diffusion.

This cell proved itself to be very useful when studying interactions between an electrolyte and a non-electrolyte as it can measure the system transient response using a pseudo-binary approach while maintaining the concentration changes of the non-electrolyte component transparent to the conductimetric measure. [2]

The analysis of the fructose-limited K_2HPO_4 diffusion coefficient values obtained should prove useful in modelling mechanisms of metabolic syndrome and other fructose-correlated diseases and conditions recently reported.

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P-117 THERMOCHEMICAL STUDY OF 4-METHYLMORPHOLINE

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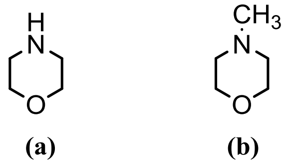
Combined experimental and computational studies were performed aiming the evaluation and the understanding of the energetic effect of the substitution of the hydrogen's amino group by an alkyl group in the morpholine scaffold. This goal has been performed studying the 4-methylmorpholine (structure depicted in figure 1) and comparing it with morpholine [1].

This communication reports the enthalpy of vaporization and the massic energy of combustion of the title compound, measured by Calvet microcalorimetry and static bomb combustion calorimetry techniques, respectively. These quantities were used to derive the enthalpy of formation of the 4-methylmorpholine in the liquid and gaseous phases, at T=298.15 K.

The experimental study was complemented computationally with the composite G3MP2//B3LYP method, based on the Gaussian-*N* theory. This approach was used in the optimization of the structure and calculation of the frequencies of vibrations for the different conformers in the gas-phase. The lowest energies were corrected for T=298.15 K with the zero-point energy and the thermal corrections. These energy values were used to calculate the enthalpies of the hypothetical working reactions involving the morpholine derivative. The average value of the calculated enthalpies was combined with the experimental standard molar gas-phase enthalpies of formation of the other compounds included in those reactions used to estímate the gas-phase standard molar enthalpies of formation at 298.15 K of 4-methylmorpholine.

The values of the experimental and computational gas-phase enthalpy of formation obtained for 4-methylmorpholine will be compared and discussed. The structural changes and the energetic effects, associated with the substitution of the hydrogen's amino group by a methyl group will be analyzed.



(a) **(b)**

Figure 1. Structural formulae for morpholine (a) and 4-methylmorpholine (b).

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P-118 SOLID STATE INVESTIGATION OF METHYLCYCLOHEXANOL STEREOISOMERS

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Cyclohexane derivatives are a class of compounds known for their polymorphism. Some of them undergo a solid–solid phase transition from an ordered crystalline phase to a high temperature orientationally disordered mesophase known as plastic crystal phase [1-3]. This solid–solid phase transition is characterized by an unusually large enthalpy compared to the enthalpy of fusion. Plastic crystals were described in detail by Timmermans [4]. This early work on a range of molecular plastic crystalline materials identified a number of features of plastic crystal behaviour, such as low entropy of melting, $\Delta_{\text{fus}}S < 20\ \text{J·K}^{-1}\text{·mol}^{-1}$.

The work presented in this communication is part of a systematic study we have been carrying out on the effect of the nature of the substituent and of its position in the cyclohexane ring, on the ability of disubstituted cyclohexanes to give rise to plastic crystal mesophases.

Polymorphism of *cis* and *trans*-1,2-methylcyclohexanol, and *cis* and *trans*-1,4-methylcyclohexanol is investigated by a multidisciplinary approach, combining differential scanning calorimetry (DSC), polarized light thermal microscopy (PLMT) and X-ray diffraction analysis and also different methodologies for solid form generation from the undercooled liquid.

Plastic crystal mesophases were identified for *cis*-1,2 and *cis*-1,4-methylcyclohexanol. In opposition, no such phase could be observed in the corresponding *trans* stereoisomers. These observations are discussed by comparison to the phase behavior of the corresponding cyclohexanediols [1-3,5].

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P-119 INTERACTIONS BETWEEN LEVODOPA AND CYCLODEXTRINS AS SEEN BY TRANSPORT AND NMR TECNHIQUES

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L-Dopa, L-3,4-dihydroxyphenylalanine, is one of the most used drugs in the treatment of the Parkinson's disease [1,2]. It is usually administered orally, and is rapidly absorbed. However, the extent of absorption and its clinical response is largely dependent on its low solubility.

With the objective of studying the ability that two cyclodextrins (β-CD and HP-β-CD) have of forming inclusion complexes with L-dopa, we have carried out a study combining diffusion measurements, with the Taylor dispersion technique, at 298.15 K and 310.15 K, and NMR spectroscopy.

It has been possible to obtain information about the influence of these macromolecular solutes on the diffusion of L-dopa by comparison between the ternary diffusion main coefficients, D_{11} and D_{22}, the binary diffusion coefficients of aqueous solutions of these drugs, and the values of the cross coefficients, D_{12} and D_{21}, for all these systems. From the ratios D_{21}/D_{11} and D_{12}/D_{22} it was possible to obtain information concerning the number of moles of each component transported per mole of the other component driven by its own concentration gradient.

Further insight on these interactions in solution has been obtained from ^{1}H NMR spectroscopy, which indicates relatively weak binding at low pH values, but significant increases in interaction with increasing pH. This information helps understanding the structure and properties of these important pharmaceutical systems, and may be important in the design of novel formulations.

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P-120 SORPTION OF PESTICIDES IN DEPOSITS FROM DRINKING WATER NETWORKS

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Pesticides are compounds of great importance to sustainable agriculture, in the prevention and control of harmful organisms. Their utilisation led to the reduction of the adverse effects of diseases in crops and plants, which allowed an increase in the production [1]. Due to their highly persistent properties and toxicity, pesticides pose a serious risk to the environment and human health [2]. Also, owing to their availability and low cost, pesticides should be regarded as possible contaminants in a scenario of a deliberate (or even accidental) contamination event of a drinking water distribution system (DWDS). In the case of such an incident, these contaminants may interact with the deposits formed in the pipe walls, and accumulation might occur. Therefore, it is important to understand the sorption process of pesticides in inorganic deposits from water distribution systems. Furthermore, the possibility of using real deposits as low-cost adsorbents can also be explored, as a mean to take benefit of a material usually considered useless after cleaning/maintenance operations in DWDS.

The aim of this work was to study the interaction of a real deposit, collected from a DWDS, with two pesticides, representative of different classes: carbofuran (carbamate) and chlorfenvinphos (organophosphate). This study is important to understand the behaviour and fate of these pesticides in the water distribution systems. Kinetic sorption experiments were performed in order to evaluate the time necessary to reach the equilibrium in the partition solvent/sorbent and the sorption process kinetics. The sorption isotherms for each pesticide were also described. The sorption of these pesticides onto the deposit appears to be a slow process. Considering the event of a deliberate contamination, in which the contact time between the contaminant and the deposit should be low, it might indicate that most of the contaminant should remain in the water stream. Excepting the cases where there is a stagnation point in the DWDS, the deposits might not represent a serious risk of accumulation of such contaminants.

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P-121 DELAYED FLUORESCENCE IN XANTHENE DYES, PORPHYRINS, PAHS AND FULLERENES

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Thermally activated delayed fluorescence (TADF) is an uncommon type of molecular fluorescence resulting from both singlet and triplet state properties: The emission spectrum is identical to that of normal (prompt) fluorescence, whereas the lifetime is close to that of phosphorescence [1]. In the TADF mechanism, after excitation and once the S_1 state is reached, intersystem crossing (ISC) to the triplet manifold takes place, followed by a second ISC back to S_1, from which fluorescence ensues. The S_1-T_1-S_1 cycle can occur several times, however this mechanism is only operative for very low concentrations of molecular oxygen, otherwise the triplet state is quenched. Not too low temperatures are also required, as the reverse ISC is thermally activated. Owing to the temperature and oxygen dependences, TADF can be used both in molecular thermometry and in oxygen sensing [2]. TADF is a process of current interest as it is the basis of third generation of organic light-emitting diodes (OLEDs) [3].
In this work, the TADF of xanthene dyes (**1**-**3**), a silicon porphyrin (**4**), coronene [4] (**5**) and fullerene C_{70} (**6**), including the internal heavy atom and isotope (carbon-13 and deuterium) effects, is studied in detail.

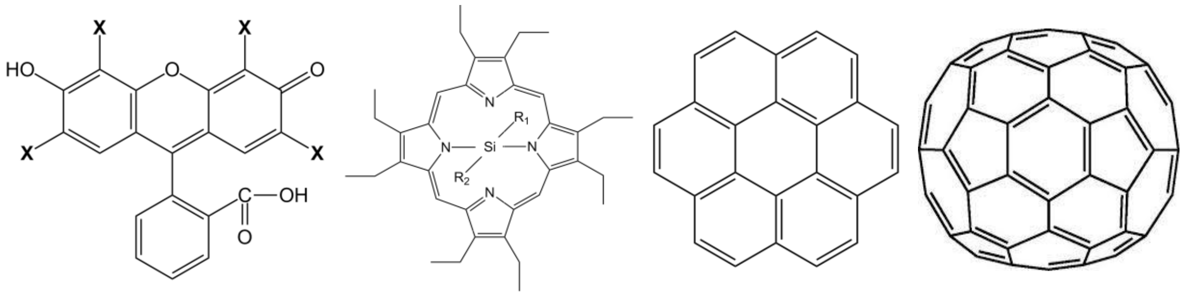

Figure 1: Molecular structures of fluorescein (**1**, X=H), eosin (**2**, X=Br), erythrosin (**3**, X=I), Si porphyrin (**4**), coronene (**5**) and fullerene C_{70} (**6**).

Acknowledgements: This work was carried out within project PTDC/QUI-QUI/123162/2010 (FCT, Portugal). TP was supported by a research grant from the same project.

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P-122 ENERGETIC AND STRUCTURAL EFFECTS RESULTING FROM CHANGING THE RING SIZE OF TRICYCLIC ANILINES

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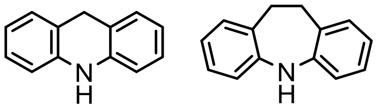
This work addresses an energetic and structural research, combining experimental and computational studies of two key anilines, 9,10-dihydroacridine and iminodibenzyl, whose molecular structures are presented in Figure 1.

The experimental thermochemical study was performed only for the iminodibenzyl compound, using the mass-loss Knudsen effusion and the static bomb combustion calorimetry techniques aiming the determination of the vapour pressures at different temperatures and of the massic energy of combustion, respectively. The data obtained for these properties were used to derive the enthalpies of sublimation and formation (crystalline and gaseous phases) of iminodibenzyl at T=298.15 K. The gas-phase enthalpy of formation of 9,10-dihydroacridine has been calculated and reported by Slayden and Liebman [1].

The computational study was developed using the composite G3(MP2)//B3LYP method, based on the Gaussian-*N* theory. This approach enabled the optimization of the 9,10-dihydroacridine and iminodibenzyl structures, as well as the computation of their vibrational frequencies and energies at 0 K, and their absolute enthalpies at 298.15 K. These data were combined with the calculated values of the absolute enthalpies of selected auxiliary compounds used in hypothetical reactions, allowing the estimation of the gas-phase standard molar enthalpies of formation, at 298.15 K, of iminodibenzyl and 9,10-dihydroacridine. Other issues were also addressed for the two compounds as the frontier orbitals, electrostatic potential energy maps and other gas-phase thermodynamic properties for ionic/radical species.

The experimental and computational results obtained for the enthalpies of formation will be discussed and compared with other related compounds, providing an opportunity to evaluate enthalpic contributions associated with changes in the ring size of this kind of key molecules.



(a) **(b)**

Figure 1. Structural formulae for 9,10-dihydroacridine (a) and iminodibenzyl (b).

Acknowledgements: Thanks are due to Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal and to FEDER for financial support given to CIQ-UP (PEst-C/QUI/UI0081/2013). VLSF thanks FCT for the post-doctoral grant SFRH/BPD/78552/2011.

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P-123 TEACHING CASE: A FORENSIC CHEMISTRY IN THE CLASSROOM

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In this work we present an exposition of as the Teaching Case was used to introduce students to the Forensic Chemistry and some techniques used (as chromatography, spectroscopy, electrophoresis, thermogravimery), apply the knowledge acquired in high school Chemistry and allow increasing the repertoire of abilities of the students, as comunication skill, critical analysis, collaboration and team-work.

Participants were 159 students from the Chemistry course of the 2nd year of high school Brasilian public school. The case method is a useful educational tool for teaching science, being a variant of the Problem-Based Learning method (PBL) [1], and has been widely disseminated by some websites and journals [1, 2]. The aim of the technique is to present a problem to students in the form of a narrative [3] and must contain some elements: be short, current, relevant, useful, generalist, awaken empathy and interest, contain dialogues, cause a conflict, force a decision [1, 4].

We conducted a survey of prior knowledge, through a questionnaire containing discursive and multiple choice questions. We discussed the death of a chemist working on a fuel company, a case of police expertise and one of the fields of Forensic Chemistry, a branch of Chemistry that caters to aspects of legal interest [5]. The tools commonly used in criminal forensics may be useful in teaching natural sciences [6] and can arouse great interest students, bringing desirable aspects as drama, suspense and impact. We used a short case, with activity in groups. The case was divided into 5 parts and posted weekly on a college blog page, aiming to create a clime of suspense. After the last activity an assessment of the acquired knowledge was performed and access in blog was monitored. The activty involved undergraduate students who were intern at high school.

The results obtained from the analysis of the questionnaires indicated a gain of knowledge in terms of content (forensic concepts and fingerprinting) and this proved to be recognized by the students themselves. The activity proved to be valid to integrate concepts from other areas and allowed the use of much of the knowledge acquired over the Chemistry course (as chemical bonds, solutions, stoichiometry). Furthermore it gave rise to a research project in which students of the college were involved in the creation of new teaching cases related to the area. The questionnaire results suggested that other types of expertise (environmental, industrial, doping) can be worked, increasing contact with the Forensic Chemistry. We suggest more investigation in monitoring the performance of students, for its improvement, and interdisciplinary projects, and not just multidisciplinary, should be encouraged.

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P-124 HOW FAR A SIMPLE MODEL CAN TAKE US?

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Measuring formation enthalpies of chemical compounds is a difficult and time consuming task. Estimations or calculations can be made and work quite well for gas phase and pretty well for liquid phase. For solid phase the calculations are more difficult, time and computer consuming and having a larger error. By using a simple ionic model it was possible to calculate reliable enthalpies of formation [1]. The model starts with the calculation of lattice energy and thus the thermochemical radii of the ions. These radii allow the calculation of other lattice energies and through a Born–Haber cycle the calculation of new enthalpies of formation.

Despite the simplicity of the model it allow the calculation of formation enthalpies for crystalline ionic liquids (for which experimental data are scarce), Table 1.

Table 1 – Enthalpies of formation for several crystalline ionic liquids (kJ/mol).

X^-	NH_4^+	Hmim$^+$	C_2mim$^+$	C_4mim$^+$
Cl^-	–316.6 ± 10.9	–136.8 ± 5.8	–169.6 ± 7.0	–212.8 ± 7.0
Br^-	–273.9 ± 10.5	–100.4 ± 5.9	–135.3 ± 7.1	–178.4 ± 7.1
I^-	–209.5 ± 9.6	–44.6 ± 5.7	–82.8 ± 7.0	–125.2 ± 7.0
NO_3^-	–376.1 ± 10.3	–201.3 ± 5.7	–235.7 ± 7.0	–278.8 ± 7.0
PF_6^-	–2240.5 ± 22.4	–2063.8 ± 18.5	–2097.6 ± 18.3	–2140.7 ± 18.3
CH_3COO^-	–607.9 ± 15.8	–425.0 ± 11.4	–456.8 ± 11.7	–500.0 ± 11.7
$ClCH_2COO^-$	–649.1 ± 15.0	–468.1 ± 11.1	–500.6 ± 11.6	–543.7 ± 11.7
$BrCH_2COO^-$	–606.4 ± 15.4	–425.3 ± 11.6	–457.6 ± 12.1	–500.8 ± 12.1
ICH_2COO^-	–555.6 ± 17.0	–375.1 ± 12.7	–407.7 ± 12.9	–450.8 ± 13.0

The published result deals only with binary compounds containing both simple and complex ions. In this contribution, the scope of the model is enlarged in order to cope with non-monocharged anions and non-homoleptic compounds. Whenever possible, the calculated values are compared with literature data.

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P-125 JOULE EFFECT FOR ERASING MEMORY IN PDLCs

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Polymer Dispersed Liquid Crystal (PDLC) have been intensively studied due to their great potential in several electro-optical applications, which are based on the ability of the liquid crystal (LC) micro-domains nematic director to align under an electric field. The PDLC behaves as a capacitor and in the absence of applied voltage, the director of each micro-domain is randomly oriented, allowing light scatter and the PDLC shows the characteristic opaque aspect. When a high enough voltage is applied, the associated electric field forces the directors to align with the field, reducing the dispersion of the light passing through the PDLC, and it shows a clear appearance. In some cases, after removal of the applied voltage the PDLC remains transparent, even when the electric field is off, being this known as permanent memory effect (PME). This effect can be removed reversibly by heating the electro-optical cell at a given temperature, in order to promote new random orientation of the directors. This leads to new and interesting PDLC applications, such as the use of these PDLCs as digital memory devices.

With the purpose of controlling the PME removal process, the heating of the cell was related with the capacitance's variation. In this study, Joule-heating effect generated by an electric current moving across the PDLC at a given time was tested. PDLC devices were prepared from a homogeneous mixture of monomers or oligomers and a nematic liquid crystal mixture, E7 from Merck. It is possible to observe the dependence of capacitance with the current used when the PDLC is heated or cooled within an electro-optic cell.

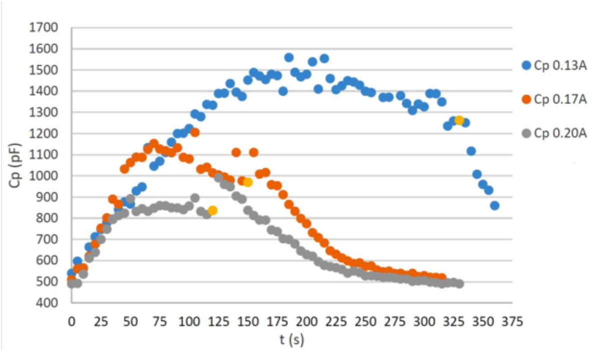

Figure 1: Capacitance dependence on electric current.

These findings can be seen as alternative routes to the improvement of sustainable and innovative liquid crystal devices which increasingly tend to become of high importance in the technological industry.

Acknowledgements: This work was supported by Fundação para a Ciência e Tecnologia through project PTDC/CTM-POL/122845/2010.

P-126 MOLTEN SALTS AS ENGINEERING FLUIDS - A REVIEW

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Molten salts are engineering fluids with a large range of applications (fig.1). In this presentation we will review some of the recent progresses in this field of science, with special emphasis on they utilization as heat storage/ heat transfer fluids or molten baths.

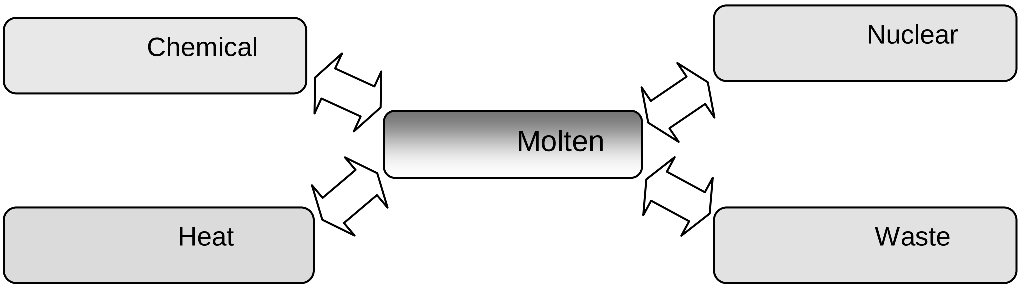

Figure 1: Some applications of molten salts

Energy and environment are key issues in every modern society and the search for renewable sources of energy and environmental protection are decisive factors. Among other technologies, using molten salts, concentrated solar power plants (CSP) or molten salt oxidation (MSO) received special attention in recent years [1-4]. This kind of technologies uses molten salts as heat transfer or heat storage fluids. An important aspect is the selection of the working fluids. Data on the thermophysical and thermal properties of the molten salts are reported and critically evaluated, since accuracy of data can have a severe impact in the dimensioning of equipment's [5].

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P-127 REAÇÕES DE OBTENÇÃO DO IODETO DE CHUMBO PARA A COMPREENSÃO DOS NÍVEIS MACRO, SIMBÓLICO E MICRO NA APRENDIZAGEM DA QUÍMICA

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Depois de compreendido um fenómeno químico observável (nível macroscópico) e sua representação (nível simbólico) torna-se necessário que os alunos façam esquemas que ilustrem de modo explicativo o fenómeno ao nível sub-microscópico para a compreensão deste nível não-observável. A exploração articulada dos três níveis de análise deve ser incentivada por forma a ajudar os alunos na apropriação sucessiva mas integrada da linguagem específica da química como sistema interpretativo. [1]

O conjunto de atividades laboratoriais apresentadas integra-se no estudo da unidade didática “Reações Químicas” do currículo de química do 8.º ano de escolaridade e foi desenvolvido de modo a orientar os alunos para proporem e desenvolverem um procedimento experimental que lhes permita testar as suas previsões e dar resposta às questões-problema manipulando com rigor e segurança o material de laboratório na obtenção do iodeto de chumbo, por dois processos diferentes. O primeiro processo consiste na obtenção do produto em resultado da reação de precipitação entre as soluções de nitrato de chumbo e de iodeto de potássio. Os alunos realizam a reação e são questionados acerca da possibilidade de solubilizar o precipitado amarelo formado; sugerem e executam procedimentos na consecução da atividade, registam observações e tiram conclusões.

O segundo processo visa a previsão e realização de uma atividade que permita a obtenção do iodeto de chumbo a partir dos mesmos reagentes, mas em estado sólido, com recurso à fricção num almofariz, podendo, depois, juntar-lhe água para se obter um resultado semelhante.

Partindo de duas diferentes formas de usar os dois reagentes para obter a mesma situação final, a escrita da equação química torna-se mais intuitiva e racional pois evidencia a formação, que, mesmo não sendo visível, era previsível. Assim sendo, fica facilitada a passagem à representação do nível sub-microscópico através de esquemas ilustrativos.

O objetivo das atividades apresentadas é, portanto, a compreensão articulada dos três níveis de análise de uma reação química através de uma estratégia didática centrada numa abordagem diferente da tradicional reação de precipitação do iodeto de chumbo sem outra interpretação associaida. Os resultados evidenciam que os alunos: identificaram a ocorrência de uma reação química através de evidências (nível macroscópico), sugeririam procedimentos experimentais para dar resposta às questões problema, escreveram corretamente a equação química relativa à reação em causa (nível simbólico) e, embora alguns alunos tenham evidenciado dificuldades, melhorou a compreensão da reação química também ao nível sub-microscópico.

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P-128 A PRODUÇÃO DE BIODIESEL E SUA CARACTERIZAÇÃO EM PERCURSOS EDUCATIVOS DISTINTOS

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A produção de biodiesel e posterior caracterização do produto obtido foi proposta a dois grupos de alunos de escolas diferentes e com percursos educativos distintos. Envolveu-se neste projeto uma turma de alunos de Química do 12º ano, do curso científico-humanístico de Ciências e Tecnologias dos Salesianos de Lisboa, tendo todo o trabalho laboratorial sido desenvolvido nas instalações da escola. O mesmo desafio foi proposto a um formando-estagiário do Curso Técnico de Análise Laboratorial – Curso EFA de nível 4, da Escola Secundária José Afonso. Neste caso, o trabalho constituiu o estágio profissional e foi desenvolvido nos laboratórios do Departamento de Química e Bioquímica da Faculdade de Ciências de Lisboa.

Nas duas situações o processo iniciou-se com uma investigação bibliográfica e posterior execução laboratorial, facto que conduziu à obtenção de amostras de biodiesel. Este foi posteriormente sujeito a um conjunto de análises – avaliação visual, cromatografia em camada fina, cromatografia em camada fina bidimensional e determinação da densidade – cujos resultados permitiram a sua caracterização.

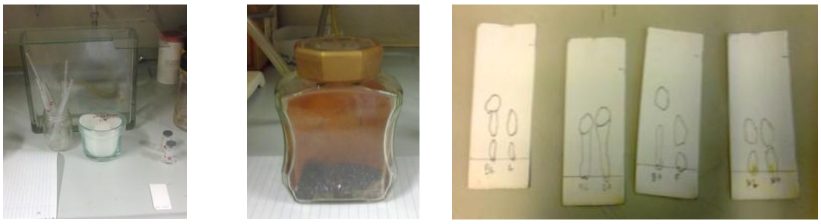

Figura 1: Avaliação do biodiesel preparado por cromatografia em camada fina

O desenvolvimento deste trabalho tornou possível enfatizar a necessidade de produção de combustíveis alternativos, a partir de óleos alimentares usados. Simultaneamente, as distintas análises a que o produto foi sujeito permitiram que os alunos contextualizassem aprendizagens, no domínio laboratorial, realizadas ao longo de toda a escolaridade.

Cabe realçar que os resultados obtidos permitiram concluir ser este um trabalho investigativo com grande potencial no que respeita não só à ilustração de um processo de síntese. Por outro lado, constituiu uma ferramenta de consolidação de aprendizagens do domínio laboratorial, independentemente do percurso educativo e nível etário dos alunos.

Agradecimentos: Agradece-se o contributo de todos os alunos do 12º ano dos Salesianos de Lisboa que, no ano letivo de 2013/2014, frequentaram a disciplina de Química e estiveram envolvidos neste projeto e ao formando-estagiário Pedro Empadinhas, da ESJA de Loures, que realizou o seu Estágio em 2013/2014.

P-129 A UTILIZAÇÃO DE SENSORES NO ENSINO EXPERIMENTAL DE QUÍMICA: UM CONTRIBUTO PARA UMA UTILIZAÇÃO SIGNIFICATIVA

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O estudo desenvolvido traduziu uma preocupação sobre a forma como são utilizados os sensores, nas aulas experimentais de Química do ensino secundário. Procurou-se implementar uma metodologia de trabalho experimental, de modo que a utilização destes equipamentos proporcionasse aprendizagens significativas. Constituiu-se um grupo de professores que frequentaram uma ação de formação acreditada, de modo a testarem as atividades experimentais de Química, que envolvessem a utilização de sensores, em que todas as atividades partissem de uma questão-problema. Deste modo foi necessário pesquisar informação que conduzisse à sua resposta, seguida de elaboração de um protocolo experimental, montagem de todo o equipamento e por último elaboração do relatório da atividade, com recurso ao “V” de Gowin. Esta metodologia foi posteriormente aplicada, pelos professores participantes, aos seus alunos.

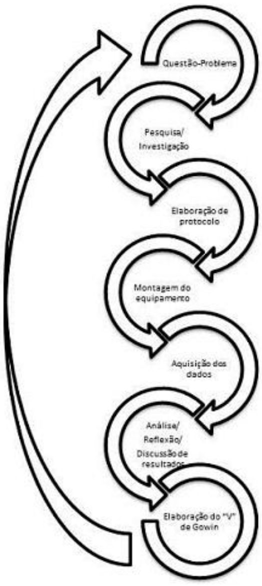

Figura 1: Esquema de trabalho experimental com recurso a sensores.

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P-130 PROVA DE APTIDÃO PROFISSIONAL DO CURSO PROFISSIONAL DE TÉCNICO DE ANÁLISE LABORATORIAL: UMA OPORTUNIDADE PARA O DESENVOLVIMENTO DE COMPETÊNCIAS DE TÉCNICO DE LABORATÓRIO

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A Escola Secundária de Fonseca Benevides tem uma longa e bem conhecida tradição na formação de técnicos de laboratório. Mais recentemente, nos últimos sete anos, com a implementação do curso profissional de técnico de análise laboratorial, esta escola tem vindo a desenvolver novos projetos experimentais em parceria com o Instituto Superior de Engenharia de Lisboa, ISEL [1,2].

Os projetos experimentais desenvolvidos em colaboração com o ISEL têm sido realizados no âmbito dos vários programas Ciência Viva em que ambas as instituições participaram, envolvendo os alunos do curso profissional de técnico de análise laboratorial [1,2].

Por outro lado, o trabalho de colaboração no contexto da Formação em Contexto de Trabalho, FCT e, sobretudo, no acompanhamento dos projetos experimentais conducentes à Prova de Aptidão Profissional, PAP, que se realiza no último ano do curso, tem-se revestido de grande importância na formação dos alunos, futuros técnicos de laboratório. Assim, o trabalho de colaboração desenvolvido no contexto da PAP tem contribuído para reforçar competências profissionais, melhorando a sua autonomia, o espírito crítico, a capacidade de análise e de vencer dificuldades, características reconhecidas como importantes em técnicos de laboratório pelas instituições em que os alunos têm realizado a FCT.

Nesta comunicação será dado conhecer o trabalho que tem vindo a ser desenvolvido e realizado em parceria entre as duas instituições no contexto da consecução dos projetos experimentais conducentes a PAP.

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P-131 UMA VIAGEM PELA HISTÓRIA DA QUÍMICA

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A necessidade de contextualizar a formação para professores realizada no Departamento de Química e Bioquímica da Universidade de Lisboa e o facto do estudo da História da Ciência ser fundamental para alunos que frequentam o ensino secundário na área das Ciências, justificou que tivesse sido proposto a uma turma de Química, do 12º Ano, como trabalho de pesquisa, o tema "Uma Viagem pela História da Química".

Apresenta-se, na Figura 1, a título de exemplo, um poster construído por um dos grupos de trabalho.

Os alunos, em grupo, começaram por desenvolver um trabalho de pesquisa sobre o tema, tendo cada grupo dedicado a atenção a um Cientista nas vertentes vida e obra científica.

Posteriormente, apresentaram em sala de aula, ao grupo-turma, o resultado do investimento na pesquisa e na documentação que permitiu contextualizar a Química da época que cada grupo optou por retratar.

É importante enfatizar que os alunos prepararam, de forma bastante empenhada, a apresentação oral dos seus trabalhos o que lhes permitiu expor o seu conteúdo perante os outros e por outro lado investiram na sua capacidade de síntese que culminou com a elaboração de um poster por cada grupo de alunos.

NIELS BOHR

Introdução

O objetivo deste trabalho foi compreender o contributo dado por alguns cientistas na evolução da ciência, neste caso, o de Niels Bohr. Bohr foi um importante físico e desempenhou um papel de relevo na área das ciências, introduzindo novos conceitos e aperfeiçoando outros.

Biografia

- Nasceu em Copenhaga a 7 de Outubro de 1885;
- Em 1912 casou-se com Margrethe Nørlund;
- De 1914 a 1916 foi professor de Física Teórica na Universidade de Victoria em Manchester;
- Em 1920 fundou o Instituto de Física Teórica;
- Em 1922 ganhou o Prémio Nobel da Física;
- Em 1957 ganhou o U.S. Atoms for Peace Award (Prémio Átomos para a Paz);
- Morreu a 18 de Novembro de 1962, em Copenhaga.

Conclusão

Este trabalho permite o aprofundamento do conhecimento acerca de determinadas teorias de Bohr, e também a aprendizagem de novos conceitos por ele trabalhados.

Trabalho Realizado Por:
Maria Brinco
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14.11.2014, Salesianos de Lisboa

Contributo Científico

O trabalho científico de Bohr inicia-se quando este era ainda estudante, com uma investigação teórica e experimental sobre a tensão da superfície provocada pela oscilação de jatos fluídos que lhe valeu uma medalha de ouro da Academia de Ciências dinamarquesa.

No Outono de 1911, Bohr mudou-se para Cambridge, onde trabalhou no Laboratório Cavendish sob a orientação de J. J. Thomson. Na Primavera de 1912, Niels Bohr passou a trabalhar no Laboratório do Professor Rutherford, em Manchester. Aí realizou um importante trabalho sobre a absorção de raios alfa.

Para solucionar os problemas originados pelo modelo atómico de Rutherford, Bohr propôs adicionar a este a nova ideia quântica, elaborada por Max Planck. Assim, os eletrões existiam apenas em determinados níveis de energia, ou seja, a distâncias fixas do núcleo. Se o átomo absorvesse energia, o eletrão transitava para um nível mais afastado do núcleo; se o átomo emitisse energia, o eletrão transitava para um nível mais próximo do núcleo. Recebeu pelo trabalho o prémio Nobel da Física em 1922.

Elaborou ainda a teoria de que o núcleo seria como uma gota líquida, e também a ideia de "complementaridade" e aprofundou a teoria da fissão, evidenciando o papel fundamental do urânio 235. Em 1939, Bohr visitou os EUA trazendo consigo a notícia vinda de Lise Meitner de que os cientistas alemães estavam a trabalhar na fissão do átomo. Tal levou ao lançamento, por parte dos EUA, do Manhattan Project para a produção da bomba atómica.

Figura 1 – Poster sobre Niels Bohr

Este trabalho permitiu aos alunos ganhar maior consciência de que a Ciência é uma força cultural no mundo moderno que pode influenciar o modo como as pessoas pensam e agem.

Vários foram os cientistas, que nos têm mostrado como a Ciência influencia profundamente a nossa visão do mundo.

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Agradece-se à Professora Doutora Raquel Gonçalves Maia, todo o apoio dado ao projeto e aos elementos nele envolvido.

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P-132 CHARACTERIZATION OF DRUG-MEMBRANE INTERACTIONS BY SURFACE PLASMON RESONANCE SPECTROSCOPY

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The interaction of drugs with biomembranes is of fundamental importance for their pharmacokinetics as it determines the concentration of drug available to interact with the biological target. During the last years we have characterized the interaction of fluorescent drug-like molecules with membranes of distinct lipid composition with the goal of obtaining the relationships between its structure and the kinetics and equilibrium of the interaction with biological membranes. Fluorescence is a very well suited methodology due to its high sensitivity. However, drugs are not usually fluorescent and the introduction of fluorescent moieties affects their properties. To overcome this difficulty we have recently explored alternative methodologies based on ubiquitous properties of molecular interactions. In this context we have developed methodologies to obtain the equilibrium and kinetics of drug-membrane interactions using Isothermal Titration Calorimetry (ITC) [1]. However, the time response of ITC equipments available is slow (~15 s) and only relatively slow processes may be quantitatively characterized.

Surface Plasmon Resonance (SPR) is an alternative label-free method based on changes in the mass of the binding agent and on variations in the refractive index of the media that occur upon ligand binding. This method has been successfully used to characterize ligand-protein interactions and may in principle be used to characterize drug-membrane interactions occurring in the time scale from 10 to 10 000 s [2]. Several drawbacks of this method have however hindered its application to ligand-membrane interactions, namely uncertainty regarding the topology of the lipidic phase (individual vesicles or a single bilayer spread on the chip active surface) and adsorption of the ligands to the microfluidic system.

In this work we use the SPR technique to characterize the interaction of several drug-like molecules with lipid bilayers. The molecules chosen (NBD-C_n and CPZ) have been previously characterized using different methodologies [1,3] and the comparison of the results obtained allows the establishment of validation protocols.

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P-133 SYNTHESIS OF N-DOPED TITANIUM DIOXIDE (TiO_2-xNx) AS AN EFFICIENT PHOTOCATALYST FOR POLLUTANT DEGRADATION

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Nanocrystals of nitrogen doped titanium dioxide powders were prepared by a wet method, involving the hydrolysis of tetra-butyl titanate promoted by nitric acid and ammonia solution, followed by calcination at temperatures about 400°C [1]. Undoped titanium dioxide was prepared by the same way. By diffuse reflectance spectroscopy (DRS) we observed an absorption onset of $TiO_{2-x}N_x$, which was shifted to longer wavelengths than TiO2, moving into the visible region (Figure 1). Good crystallinity of the powder was observed by X-ray diffraction (XRD), with only an anatase phase. The material proved to be an efficient photocatalyst for the photodegradation of methomyl and ibuprofen that are wastewater pollutants [2]. The kinetics was followed by UV/Vis. Photoproducts are underway by GC-MS.

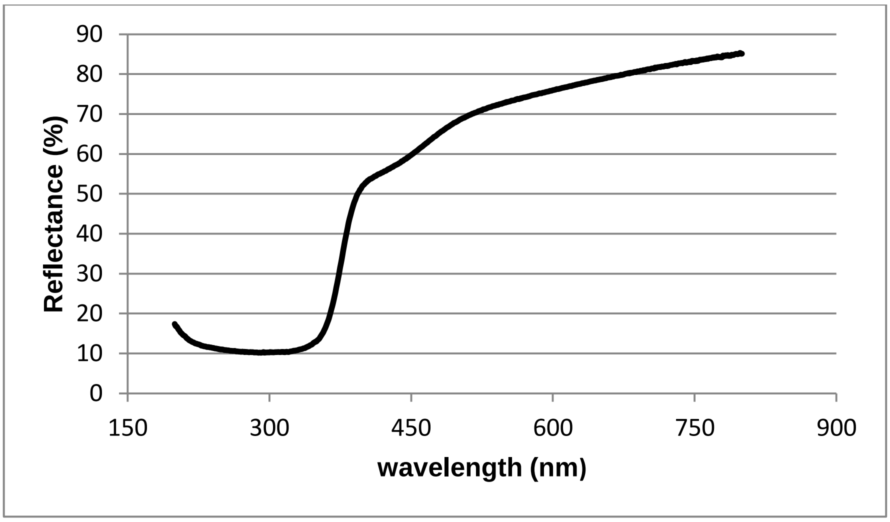

Figure 1: Diffuse Reflectance Spectrum.

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P-134 BRASIL: RESPONSABILIDADES E FUNCIONALIDADES DA "MASS BURNING", (CUSTOS/BENEFÍCIOS), TRATAMENTOS DOS RESÍDUOS SÓLIDOS URBANOS NO BRASIL: MEIO AMBIENTE, SUSTENTABILIDADE E POLÍTICA NACIONAL DE RS (PNRS). SOMANDO PT/BR

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A necessidade de ser sustentável é mais que clara, porém ainda tem inúmeras discussões em aberto sobre qual forma sustentável adotar. O presente artigo reabre as discussões e esclarece algumas dúvidas a cerca da MASS BURNING (PRODUÇÃO DE ENERGIA ATRAVÉS DO USO DE RESÍDUOS SÓLIDOS URBANOS (RSU)), levantando as possibilidades para que uma empresa de tal porte seja implantada no Brasil, apresentando dados fornecidos pelo Ministério do Meio Ambiente (MMA), Acessória de Assuntos Internacionais (ASIN) e de algumas Secretarias Estaduais do Meio Ambiente dos Estados de Mato Grosso (MT), Goiás (GO), Pernambuco (PE) e São Paulo (SP). Também manteve-se contato com uma empresa Portuguesa (VALORSUL), a qual é pioneira no ramo de produção e gestão integrada de RSU (Valorização Energética e Bioenergética).

Este artigo tem como objetivo, mostrar a necessidade sustentável de destino final dos (RSU), diante disso defende-se como uma opção de descarte final e de ganho econômico, a implantação do sistema Mass Burning, uma vez que a demanda e ganho são proporcionalmente positivos para o Brasil . O Brasil, possui a necessidade de inovar no ramo de reaproveitamento, usando o "lixo" a seu favor, neste caso como fonte de energia.

Na Política Nacional de Resíduos Sólidos (PNRS), um dos objetivos é a redução da quantidade de RSU. Como solução à redução de deposição em Aterros Sanitários (AS) - teoricamente -, na prática o sistema Mass Burning é capaz de fazer tamanha redução e gerar lucros e economia. Logicamente ainda existe algumas falhas que devem ser estudadas para que não haja transtorno ambiental e econômico. Assim, a importante tarefa é realizar a defesa da aplicação de novas e possíveis formas sustentáveis para o RSU, visando sempre o melhor para o Homem e o Meio Ambiente. Com isso, mostrar também que o método MASS BURNIG vai além da produção de energia através de RSU, como: tratamento dos gases gerados; tratamentos das escórias (cinzas) e dos metais que sobram na incineração; construção de rodovias; aterros sanitários que visam pela sua manutenção correta; queima do biogás; tratamento dos lixiviados e do metano. Além disto, a empresa que trabalha no ramo pode ser uma empresa autossuficiente, pois cerca de 15% da energia produzida é capaz de mantê-la funcionando, sem a necessidade de utilizar energia fornecida por vias externas de produção terceirizada. Bioenergia e valorização energética, são hoje, umas das formas de produção de energia mais limpas e, tratando-se do custo/beneficio, são economicamente viáveis.

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P-135 COMPARISON OF DIFFERENT METHODS TO ASSESS THE VIABILITY OF HUMAN NEUTROPHILS

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Neutrophils are the most abundant leukocytes, representing 70% of the circulating white blood cells. These cells play an important role in the complex immune defense system, and are responsible for the modulation of the inflammatory process. Due to these important roles, neutrophils are commonly used as an *in vitro* cellular model to evaluate the immunogenicity and/or pro-inflammatory effect of different compounds, as nanoparticles, metals, plants extracts, among others. Cellular viability assays are mandatory in these studies. There are several methods routinely used in the laboratory to assess the neutrophils' viability. Nevertheless, the information in literature comparing the different methods in what concerns the mechanism of action, the time-consuming, the ease of handling and possible interferences, is very scarce.

In this work three viability assays were tested to evaluate the toxic effect of silver nanoparticles on human neutrophils, namely trypan blue, propidium iodide and the neutral red.

The results obtained showed a high variability, depending on the viability test used. Among the studied methods, propidium staining method was the more accurate, rapid and reproducible test to study the effect of silver nanoparticles on human neutrophils viability.

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