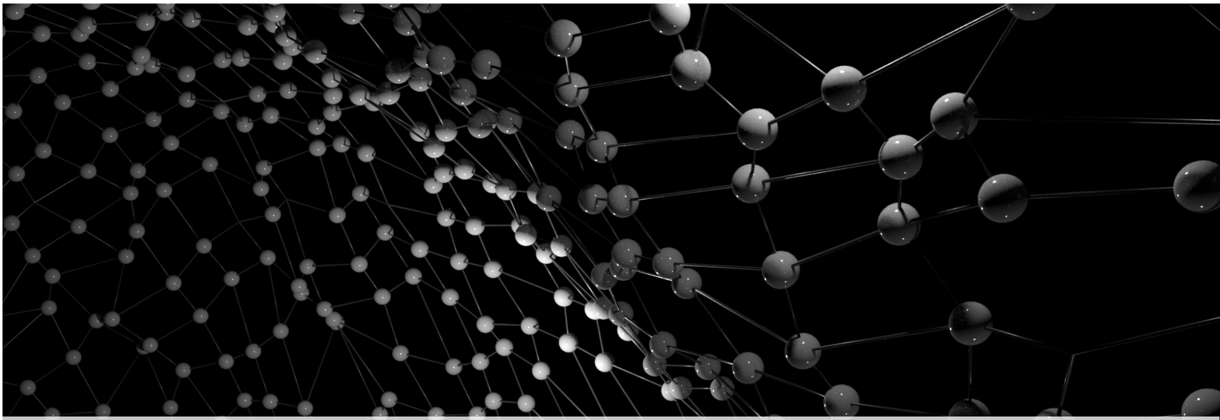
Book of Abstracts



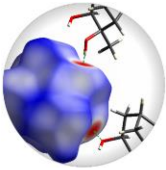
14
ENQF

14° ENCONTRO NACIONAL DE QUÍMICA-FÍSICA

3° Simpósio de Química Computacional

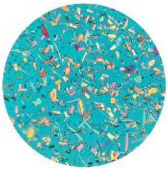
online • 29-31 MAR 2021 • U. Coimbra

Livro de Resumos



General Information

This book contains all the abstracts accepted for presentation in the 14th Meeting of Physical Chemistry and 3rd Symposium of Computational Chemistry. Authors are responsible for the scientific content of their abstracts, which were reproduced from the originals. The scientific program includes Plenary Lectures (PL), Invited Lectures (IL), Oral Communications (OC, or OCS for those assigned to the Symposium) and Poster Presentations. Both Oral Communications and Posters are presented in parallel sessions.



Welcome

The Portuguese Society of Chemistry (SPQ) and the Organizing Committee welcome all participants to the 14th Meeting of Physical Chemistry. Initially scheduled for June 2020 in Coimbra, it had to be postponed to March 2021 due to the covid-19 pandemic outbreak. Unfortunately, covid-19 disease is still not completely under control, which forced us to organize the Meeting as an online event.

Since the first national meeting held in Lisbon in 1993, this scientific event was regularly organized in several places of Portugal: Porto (1995, 2005, 2013), Monte da Caparica (1997), Coimbra (1999), Faro (2001, 2018), Lisboa (2003), Luso (2007), Aveiro (2009), Braga (2011) and Évora (2016). Since the 12th edition in 2016, it has been also associated with the organization of the Symposium of Computational Chemistry carried out by Computational Chemistry Group of SPQ.

The main objective of the 14th Meeting of Physical Chemistry is to bring together researchers from all areas of Physical Chemistry, in order to promote the discussion about the latest advances in this field, with special emphasis on the work developed by the national scientific community. The 3rd Symposium of Computational Chemistry, and a Training Action for Secondary School Teachers will be hosted in parallel to the main event.

From the very beginning, the Organizing Committee has encouraged researchers from diverse areas of physical chemistry to participate and present their most recent work in the Meeting. The significant number of participants and submitted contributions, even beyond our best expectations, are a clear sign of vitality of the physical chemistry community. We sincerely acknowledge the contributions from all authors and the financial support from the sponsors. We also thank the Department of Chemistry of the University of Coimbra and the Coimbra Chemistry Centre for the logistic and institutional support.

We hope that the 14th Meeting of Physical Chemistry will be a fruitful forum for discussion and sharing scientific knowledge. We wish all the participants a successful and pleasant online meeting.
Finally, and most especially for those who never visited Coimbra, we invite you to enjoy this video: https://www.youtube.com/watch?v=TSlf-ngo0tA

On behalf of the Organizing Committee,

Jorge Marques

Bem-vindos

A Sociedade Portuguesa de Química (SPQ) e a Comissão Organizadora dão as boas vindas a todos os participantes no 14º Encontro Nacional de Química Física. Inicialmente agendado para junho de 2020 em Coimbra, a pandemia de covid-19 fez com que fosse adiado para março de 2021. Infelizmente, com a pandemia de covid-19 ainda por controlar, fomos forçados a organizar o Encontro como evento online.

Desde o primeiro encontro nacional em Lisboa em 1993, este evento científico tem sido organizado regularmente em diversos locais de Portugal: Porto (1995, 2005, 2013), Monte da Caparica (1997), Coimbra (1999), Faro (2001, 2018), Lisboa (2003), Luso (2007), Aveiro (2009), Braga (2011) e Évora (2016). Desde a 12ª edição em 2016, tem sido também associado à organização do Simpósio de Química Computacional levada a cabo pelo Grupo de Química Computacional da SPQ.

O principal objectivo do 14º Encontro Nacional de Química Física é juntar investigadores de todas as áreas da Química Física, promovendo a discussão acerca dos avanços mais recentes neste domínio, com ênfase especial no trabalho desenvolvido pela comunidade científica nacional. Paralelamente a este evento, acolhemos o 3º Simpósio de Química Computacional, assim como uma Acção de Formação para Professores do Ensino Secundário.

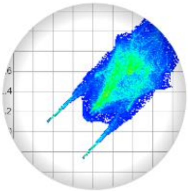
Logo desde o início, a Comissão Organizadora encorajou a participação de investigadores de áreas muito diversificadas da química física e a apresentação do seu trabalho mais recente no Encontro. O número significativo de participantes e contribuições submetidas, excedendo até as nossas melhores expectativas, são um claro sinal da vitalidade da comunidade dos químicos físicos. Agradecemos sinceramente as contribuições de todos os autores e o apoio financeiro dos patrocinadores. Agradecemos também ao Departamento de Química da Universidade de Coimbra e ao Centro de Química de Coimbra pelo apoio logístico e institucional.

Esperamos que o 14º Encontro Nacional de Química Física seja um fórum de partilha de conhecimento científico e de discussão frutífera. Desejamos a todos os participantes um encontro online agradável e com sucesso. Finalmente, e em especial aos que nunca visitaram Coimbra, convidamo-vos a desfrutar deste vídeo: https://www.youtube.com/watch?v=TSlf-ngo0tA

Em nome da Comissão Organizadora,

Jorge Marques

Organizing Committee



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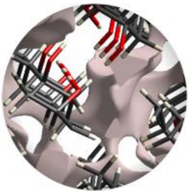

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Program

● Plenary Lectures

PL1 Manuel Yáñez 29 March (9:30-10:15)

An overview of the rich chemistry of electron-deficient compounds

PL2 Margarida Bastos 29 March (14:00-14:45)

Antimicrobial peptides: a multi-method approach for the development of new antibiotics

PL3 Eduardo Filipe 30 March (9:00-9:45)

(Semi) Fluorinated Soft-Matter

PL4 Sérgio Seixas de Melo 31 March (9:00-9:45)

Photophysics and Photochemistry in Molecules

PL5 Verónica Bermudez 31 March (14:15-15:00)

(Super)hydrophobic coatings inspired in the surface of plants leaves. The roles of chemistry and physics

PL6 Daniel Brandell 31 March (15:00-15:45)

Challenges for Li-Battery Polymer Electrolytes - Ion Transport, Electrochemical Stability and Predictability of Soft Matter

● Invited Lectures

ILS Miguel Jorge 29 March (16:15-16:45)

Accounting for polarization in non-polarizable force fields

IL1 Alexandre Magalhães 29 March (12:00-12:30)

Study of an S_N2-reaction under confinement

IL2 Helena Nogueira 29 March (14:45-15:15)

SERS studies for biodetection using hybrid nanostructures

IL3 Nuno Basílio 30 March (9:45-10:15)

From Micro to Picomolar Affinity: Photoactive Host-Guest complexes with Ultrahigh Stability in Aqueous Solution

IL4 Cláudio Nunes 30 March (11:45-12:15)

Molecular Manipulations under Cryogenic Conditions Controlled by Infrared Vibrational Excitation

IL5 Carlos Bernardes 30 March (14:00-14:30)

Rationalization of Crystallization Processes from the Study of the Organization of Molecules in Solution

IL6 Helena Passos 31 March (12:00-12:30)

From biocatalysis to metal separation: the versatility of ionic-liquid-based aqueous biphasic systems

● Oral Communications

3rd Symposium of Computational Chemistry

Code	Presenter / Title	Date
OCS1	Abeer Al Mohtar	29 March (10:15-10:30)
	First-Principles Model to Evaluate Quantitatively Long-Life Behavior of Cellulose Acetate Polymers	
OCS2	Amílcar Prata	29 March (10:30-10:45)
	How the structure of intermediate species influences selectivity in the photoreaction of 1-allyl-4-aryltetrazolones in solution	
OCS3	Luís Pinto da Silva	29 March (10:45-11:00)
	TD-DFT Study of Light-Absorption by Brown Carbon Over Three Southern European Cities	
OCS4	Vera Freitas	29 March (11:15-11:30)
	Energetic and structural properties of organic crosslinker molecules	
OCS5	Henrique Bastos	29 March (11:30-11:45)
	Rationalizing biomolecule solubilization mechanisms in colloidal systems through coarse-grained molecular dynamics	
OCS6	Nádia Figueiredo	29 March (11:45-12:00)
	New set-up force field for magnetic-ionic liquids	
OCS7	José Gouveia	29 March (15:15-15:30)
	Coarse-grained model of the synthesis of periodic mesoporous benzene-silica	
OCS8	Alexandre Pinto	29 March (15:30-15:45)
	The reaction mechanism of MHETase, a QM/MM MD study	
OCS9	Filipe Teixeira	29 March (15:45-16:00)
	Understanding the Topology of the Laplacian Field in Transition Metal Chemistry: From Chemical Insights to Specialized Molecular Descriptors	

OCS10 José Ferraz-Caetano 29 March (16:45-17:00)

Bias-Variation trade-off in Machine Learning modelling of the Jacobsen epoxidation process

OCS11 José Pereira 29 March (17:00-17:15)

ProtoSyn: an AI-powered tool for computational design of functional peptides

OCS12 Soraia Assis 29 March (17:15-17:30)

Characterizing psychoactive drugs by mining data from chemical databases and molecular simulations

OCS13 Natalia Osiecka-Drewniak 29 March (17:30-17:45)

Investigations of phase transitions in liquid crystals and pharmaceutical compounds using window clustering of infrared spectra

14th Meeting of Physical Chemistry

OC1 Fernando Pina 29 March (10:15-10:30)

The Evolution of the Color systems in Plants. A physical chemical approach

OC2 Daniela Nobre 29 March (10:30-10:45)

Photophysics and Photochemistry in N,N′-disubstituted indigo derivatives: Competition between ESPT and photoisomerization

OC3 Alberto Trevisan 29 March (10:45-11:00)

Supramolecular Approaches to Irreversible Thermochromic Systems

OC4 Luís Moreira 29 March (11:15-11:30)

Revisiting the Kamlet-Abraham-Taft Model Equation: The Separation Between Solvent Polarizability and Solvent Dipolarity

OC5 Ana Rufino 29 March (11:30-11:45)

Double-reversible aqueous biphasic systems based in protic and aprotic ionic liquids

OC6	Marisa Barros	29 March (11:45-12:00)
	High pressure Taylor setup – First results in supercritical carbon dioxide	
OC7	Ana Rita Carreira	29 March (15:15-15:30)
	Novel purine-based ILs and their behavior in aqueous solutions	
OC8	João Santos	29 March (15:30-15:45)
	Pharmaceutical Nanococrystals Synthesis: a novel mechanochemical approach	
OC9	Diogo Marinheiro	29 March (15:45-16:00)
	Encapsulation and enhanced release of resveratrol from mesoporous silica nanoparticles for melanoma therapy	
OC10	Małgorzata Jasiurkowska-Delaporte	29 March (16:45-17:00)
	Relaxation processes and crystallization behavior of liquid crystals: effects nanometric confinement	
OC11	Sara Fateixa	29 March (17:00-17:15)
	Textile based composites as substrates for Raman imaging and SERS detection	
OC12	Joana Martins	29 March (17:15-17:30)
	Supramolecular Sensors for Biologically Relevant Analytes	
OC13	Marcin Piwowarczyk	29 March (17:30-17:45)
	Influence of carbon chain length on properties of (E) 4((4alkyloxyphenyl)diazenyl) phenyl alkanoates	
OC14	Anna Drzewicz	30 March (10:15-10:30)
	How high pressure affects the crystallization kinetics of partially fluorinated chiral liquid crystal in its smectic phase?	
OC15	Estefanía Delgado Pinar	30 March (10:30-10:45)
	Aggregation Induced Emission from the interaction of polyamines with Cucurbiturils	
OC16	Gianluca Utzeri	30 March (10:15-10:30)
	Imidacloprid and Cymoxanil removal by mesoporous Poly(β-cyclodextrin)-based composites	

OC17 Natércia Martins 30 March (10:30-10:45)

Hydrophobic paper-based substrates for SERS detection of pesticides in spiked food products

OC18 Moisés Pinto 30 March (11:00-11:15)

Separation of ethylene from ethane with metal-organic frameworks

OC19 Marta Bordonhos 30 March (11:15-11:30)

Exploring periodic mesoporous organosilicas for ethane–ethylene adsorption–separation

OC20 João Nunes 30 March (11:30-11:45)

Supported ionic liquid materials for L-asparaginase immobilization

OC21 Miriam Colaço 30 March (11:00-11:15)

Kinetic control of host-guest binding with light

OC22 Isabel Oliveira 30 March (11:15-11:30)

Protein loading and release by temperature- and pH-sensitive tubule-based hydrogels

OC23 Roberto Aguado 30 March (11:30-11:45)

Release kinetics of monophenols from polysaccharides crosslinked with β-cyclodextrin

OC24 Aleksandra Deptuch 30 March (14:30-14:45)

Comparison of crystallization kinetics and molecular dynamics in liquid crystalline 3FmFPhH6 (m = 5, 7) compound

OC25 Joana Silva 30 March (14:45-15:00)

Co-amorphous nateglinide systems: screening and thermal behavior evaluation

OC26 Elodie Melro 30 March (14:30-14:45)

Enhancing lignin dissolution and extraction: The effect of surfactants

OC27 Bojan Kopilovic 30 March (14:45-15:00)

Ion Exchange in Aqueous Biphasic Systems

OC28 Carla Magalhães 31 March (09:45-10:00)

Development of chemiluminescent self-activating photosensitizers with selective anticancer activity

OC29 Artur Moro 31 March (10:00-10:15)

Dipicolylamine-based fluorescent chemosensors for ion detection in aqueous media

OC30 Ana Clara Rodrigues 31 March (10:15-10:30)

Tuning J-aggregate formation and emission efficiency in cationic diazapentacenium dyes

OC31 Dmitriy Moreira 31 March (10:30-10:45)

Photoresponsive catanionic vesicles for the effective encapsulation and release of an anticancer drug

OC32 Manuel Loureiro 31 March (09:45-10:00)

Absolute Photoluminescence Quantum Yield

OC33 Nuno Lousa 31 March (10:00-10:15)

Studying dangerous chemical reactions using calorimetry and thermal analysis

OC34 Isabel Barbosa 31 March (10:15-10:30)

3D-Printed Reactors for Photocatalytic Applications

OC35 Olivier Pellegrino 31 March (10:30-10:45)

Writing rules of the measurement results in Chemistry

OC36 Aleksey D. Lisenkov 31March (11:00-11:15)

Simulation of the electrowinning process using green renewable energy sources for industrial iron production

OC37 Daniela Pinheiro 31March (11:15-11:30)

All organic redox flow batteries with tryptanthrin sulfonic acid

OC38 Rui Pereira 31 March (11:30-11:45)

Silk-based materials showing prospects for the use of natural proteins in electrochemical devices

OC39 Hanane Boumeriame 31 March (11:45-12:00)

Photochemical H2 generation by a novel 2D/2D NiCeAl-LDH/g-C3N4 nanohybrid

OC40 Mirosław Gałązka 31March (11:00-11:15)

Study on electric conductivity and electric polarisation of electrodes as indicators of phase transitions

OC41 Bárbara Abreu 31March (11:15-11:30)

Carbon Nanotube/Transition Metal Dichalcogenide Composites via Surfactant-Assisted Dispersions as Electrocatalysts for Oxygen Reactions

OC42 Raquel Cristóvão 31 March (11:30-11:45)

Pristine carbon nanotubes for an efficient L-asparaginase immobilization

OC43 Joana Lopes 31 March (11:45-12:00)

Surface Studies on ZnS/Graphene Oxide Nanostructures Using 4-Mercaptopyridine as Molecular Probe

Poster Communications

P1-P10 30 March (15:00-15:45)

P1- Effect of poly(vinyl alcohol) on the water sorption and kinetics of tissue paper

P2 - Nickel separation via adsorption by an ORMOSIL aerogel modified with a Schiff base

P3 - Dancing with oils – The interaction of lipases with different oil/water interfaces

P4 - NaCl effect on the rheological properties and aggregates formation of anionic, non-ionic and amphoteric mixed surfactants systems

P5 - Data Driven Tools to Select Corrosion Inhibitors

P6 - Physical and chemical characterization of Cercis siliquastrum L. (Olaia) leaves

P7 - Langmuir Films of Ionic Liquids: Mono and Multilayers of (Cnmim)(X) n = 18,20 X^- = NTf_2^- ,Cl^- at the Air-Water Interface

P8 - Understanding the leaf surfaces of Phyllostachys nigra

P9 - Butler Equation for the Surface Tension of Liquid Mixtures: A re-examination

P10 - Catanionic vesicles from lysine-based surfactants for the delivery of bioactive plant extracts

P11-P20 30 March (15:00-15:45)

P11 - Surface modification of ZnS colloidal quantum dots with porphyrin: an approach to novel nanoassemblies

P12 - Coarse-Grained Reactive Silica Model for Classical Molecular Dynamics Simulations

P13 - On the calculation of diffusion coefficients of pesticides by employing molecular dynamics simulations

P14 - A molecular dynamics study of ionic interchange for (Zn_2Al) layered double hydroxides materials

P15 - H + O2 + M -> HO2 + M A Termolecular Reaction Pressure Dependence Study

P16 - Hydrogen combustion in carbon nanotubes: defining the nanotube behavior

P17 - DFT and TD-DFT studies of Ground and Excited State Properties of Free and Adsorbed Ru(II) Terpyridine Dyes

P18 - The OH + CH3OH → CH3O + H2O, a Barrierless Process at Low Temperatures

P19 - Hydrogen Combustion in Nanotubes

P20 - Energetic study of 5-methyl-1H-benzotriazole

P21-P29 30 March (15:45-16:30)

P21- Quasi-classical trajectory study of the O(1D) + H2O(X1A1) reaction

P22 - Mixed Hydrogenated and Fluorinated Ionic Surfactant Solutions: Towards designing compartmentalized nanostructures

P23 - New insights into BCRP efflux mechanism through Molecular Dynamics Simulations

P24 - Biotechnology for the degradation of plastics

P25 - Lyotropic Ionic Liquid Crystal Gels – Molecular Dynamics Simulations and Xenon NMR Spectroscopy

P26 - Interfacial Properties of Mixtures of Fluorinated and Hydrogenated Alcohols: Experimental and MD Simulations

P27 - Computational Modeling of drug recognition by cyclodextrin-based complexes

P28 - Predicting molecular similarity and toxicity using machine learning as a playground

P29 - Reversing multidrug resistance in cancer using indole alkaloid derivatives: in silico studies

P30-P38 30 March (16:45-17:30)

P30 - Investigations on the CFTR Ion Channel through Molecular Dynamics

P31 - Assessing the DFT low-energy landscapes of Li^+Kr_n clusters by employing machine learning techniques

P32 - Understanding conformational preferences and molecular interactions in co-amorphous drug systems: lurasidone combined with saccharin or cysteine.

P33 - From Experimentally Determined Enthalpies of Sublimation to the Validation of a Force Field for MD Simulations on Sulfur- and Halogen-Containing Active Pharmaceutical Ingredients

P34 - Comparative study on the thermochemistry of 2-mercapto- and 2-mercapto-5-methyl-1,3,4-thiadiazole

P35 - Self-assembled hemimicelles of semifluorinated alkanes: experimental and Molecular Dynamics simulations

P36 - Langmuir Films of Fluorinated Surfactants using Molecular Dynamics Simulations

P37 - Towards a simpler relation of electronic structure with molecular properties: historical findings

P38 - Basic education across Europe - A physical-chemical approach by the sea

P39-P48 30 March (15:45-16:30)

P39 - Linking Aggregation in Solution, Solvation, and Solubility of Simvastatin

P40 - Effect of sodium chloride on the behavior of the lactose in aqueous solution studied from diffusion experiments and molecular dynamics simulations

P41 - Energetics of Maleic acid-L-phenylalanine Bicomponent Crystals with Different Stoichiometry

P42 - Binary diffusion coefficients for hydrocarbons in supercritical carbon dioxide – Development of a Taylor dispersion setup for SFCs

P43 - Solubility enhancement of poorly water-soluble drugs with zwitterionic hydrotropes

P44 - Recovery of phenolic compounds from Kiwi waste with aqueous solutions of biobased solvents

P45 - Water Solubility in (n-Alkane + n-Perfluoroalkane) Mixtures and in n-Perfluoroalkylalkanes: Experimental and Modeling with the SAFT-γ Mie Group-Contribution Approach

P46 - Thermodynamic Stability of Fenclorim

P47 - Modeling Solvent Effects on Solution Enthalpies Using a Modified Version of the Kamlet-Abraham-Taft Model Equation

P48 - Thermodynamic characterization of anthranilate derivatives

P49-P58 30 March (16:45-17:30)

P49 - Sustainable cellulose-based floculants for microplastic remotion in aqueous media

P50 - New deep eutectic solvent assisted extraction of highly pure lignin from maritime pine sawdust (Pinus pinaster Ait.)

P51 - Equilibrium Constants and corresponding ΔG^0 in Heterogeneous Media

P52 -Temperature-responsive extraction of violacein using aqueous mixtures of a surfactant and an ionic liquid

P53 - Ionic liquids in the fractionation of terpenes and terpenoids

P54 - Lanthanide complexes with Valsartan: the influence of the metal center on the thermal decomposition of the ligand

P55 - Studies of Dual Drug Cocrystals: (1:1)-Diflunisal: Isoniazid and (1:1)-Lamotrigine:Ethosuximide

P56 - Vibrational dynamics of polar alcohols in various thermodynamic states

P57 - Excited state Decay Mechanisms of the Naphthoquinone Dye Shikonin

P58 - Luminescent aqueous inks and coating formulations with RGB-tunable emission

P59-P68 30 March (17:30-18:15)

P59 - TTA-UC emitter based on NIR excitable aggregated Pt(II) Chlorin immobilized with tetraphenylethylene in cellulose acetate films

P60 - Fluorescence Studies on a Thermo-responsive PNIPAM-Polyfluorene Graft Copolymer

P61 - Amino Acid-Based Fluorescent Nanomaterials Towards Nanohybrid Fabrication

P62 - BOTTOM-UP CARBON DOTS: Sensing and Imaging

P63 - Exploring the effect of hierarchical porosity in BEA zeolite in Friedel-Crafts acylation of furan and benzofuran

P64 - Synthesis of New BODIPYs for PET Diagnosis

P65 - The crystalline products of L–arginine and divalent metal ions

P66 - Synthesis and characterization of novel bio-based surface-active ionic liquids

P67 - Incorporation of porphyrins into SPEEK membranes: synthesis and characterization

P68 - Influence of acid-base properties of cobalt-lanthanide nanofibers on their catalytic activity for the methanation of CO_2

P69-P78 30 March (17:30-18:15)

P69 - Supported cerium-based catalysts on silica and carbon matrixes: redox properties

P70 - Activated carbons as active supports for bifunctional catalysts: exploring the surface chemistry and Pt immobilization method

P71 - Are ZnO- and TiO2- Carbon Nanocomposites Exciting for Photocatalytic Activity?

P72 - Optimising Reaction Conditions from Machine Learning Models

P73 - Decoding P-glycoprotein efflux mechanism: the role of substrate binding on signal transmission

P74 - Targeting the most common mutation in medium-chain acyl-CoA dehydrogenase with pharmacological chaperones: a breakthrough

P75 - Supra-amphiphiles based on chalcones and sulfocalix(4)arenes for drug delivery

P76 - LiNbO3 crystal as a test case for the correlation between experimental and theoretical polarized Raman spectra

P77 - Microwave spectroscopy of molecular switches

P78 - H-Tunneling Activated by Vibrational Excitation

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Plenary Lectures

An overview of the rich chemistry of electron-deficient compounds

Manuel Yáñez

Departamento de Química, Facultad de Ciencias, Módulo 13, and Institute of Advanced Chemical Sciences (IadChem), Universidad Autónoma de Madrid. Campus de Excelencia UAM-CSIC, Cantoblanco, 28049-Madrid. Spain

Electron-deficient derivatives, such as Be and B containing systems are paradigmatic examples of stable Lewis acids that lead to a drastic reorganization of the electron density of the compounds or clusters of compounds interacting with them. Such electron density reorganization results in a perturbation of the bonding patterns of all the compounds participating in the interaction, what is reflected in a significant disturbance of their intrinsic reactivity [1], to the point that conventional bases, such as ammonia, become stronger Bronsted acids than oxyacids like perchloric acid [2]. A high intrinsic acidity and the possibility of forming chelated structures is behind the behavior of 1,8-diBeX-naphthalene (X=H, F, Cl, CN, CF3, $C(CF3)_3$) derivatives as *anion sponges*, very much as 1,8-bis(dimethylamino)naphthalene derivatives behave as *proton sponges* [3], and on the ability of Be-compounds to trap electrons through the formation of three- and four-center bonds [4]. Similar mechanisms explain the exergonic and spontaneous formation of radicals [5], or the dramatic change in the intrinsic basicity of conventional acids [4]. Very interestingly, and in contrast with the aforementioned electron-deficient character of Be, Be_2 in complexes with C_nH_n-Be_2-C_nH_n (n=3, 5, 7) π-radicals may behave as an efficient electron donor [6]. More recently we were also able to show that Be_n clusters behave as very efficient Lewis acids when interacting with conventional Lewis bases such as ammonia, water or hydrogen fluoride, leading to a sequential dissociation of all the bonds of the Lewis base in a cascade of successive exothermic processes, which end up, spontaneously, in a global minimum in which the bonding patterns of both the base and the Be_n cluster are completely destroyed [7].

[1] M. M. Montero-Campillo, O. Brea, O. Mó, I. Alkorta, J. Elguero, M. Yáñez, Phys. Chem. Chem. Phys., **21**, 2222 (2019)
[2] M. M. Montero-Campillo, P. Sanz, O. Mó, M. Yáñez, I. Alkorta, J. Elguero, Phys. Chem. Chem. Phys. **20**, 2413 (2018)
[3] O. Brea, I. Corral, O. Mó, M. Yáñez, I. Alkorta, J. Elguero, Chem. Eur. J. **22**, 18322 (2016)
[4] I. Alkorta, M. M. Montero-Campillo, J. Elguero, M. Yáñez, O. Mó, ChemPhysChem **19**, 1068 (2018); O. Mó, M. M. Montero-Campillo. M. Yáñez, I. Alkorta, J. Elguero, J. Phys. Chem. A **124**, 1515 (2020
[5] O. Brea, I. Alkorta, O. Mó, M. Yáñez, J. Elguero and I. Corral, Angew. Chem. Int. Ed, **55**, 8736 (2016).
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Antimicrobial peptides: a multi-method approach for the development of new antibiotics

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Antimicrobial resistance is one of the major global health issues of the 21st century, as the current therapeutic strategies are no longer appropriate to fight infection and drug-resistant pathogens. In this combat, antimicrobial peptides (AMPs) are currently in the spotlight as a good alternative to the conventional therapeutics to overcome bacterial resistance, as their main target is the bacterial membrane and they induce significantly lower resistance.

AMPs present a diversity of functional and structural properties, but exhibit common basic features - they are usually cationic, with amphipathic structure, they have a small number of amino acids and they are active against Gram-positive and Gram-negative bacteria, fungi and viruses. Different mechanisms of action have been proposed for AMPs, all causing membrane perturbation and/or destruction. Their action is triggered by electrostatic interactions, the first driving force for interaction with the membranes, as the cationic AMPs interact with the anionic membrane surface (negative headgroups) of pathogens. Thereafter there is usually accumulation and rearrangement at the membrane, leading to membrane micellization, segregation/permeabilization, pore formation or aggregation.

Our group has been working with antimicrobial peptides for a number of years[1-6], using a range of biophysical techniques. An overview of the work done so far will be presented and discussed here.

Acknowledgements: M.B. acknowledges the financial support from Fundação para a Ciência e Tecnologia (FCT), Portugal, and FCT national funds and FEDER European funds, through COMPETE2020 program, project PTDC/BIA-BFS/30579/2017 (POCI-01-0145-30579) and UIDB/00081/2020.

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(Semi) Fluorinated Soft-Matter

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Perfluorinated compounds have become technologically important substances as a result of their peculiar properties, which ally chemical inertness and biocompatibility, high viscosity and low surface tension, with an enhanced hydrophobicity and the ability to dissolve large quantities of respiratory gases. Fluorinated surfactants, for example, are widely used as refrigerants, textile protection agents, fire-fighting foams, detergents and as precursors in the production of fluorinated polymers. Exciting applications can be found in biomedical field, as blood substitutes, oxygen carriers and drug deliverers.

In most cases supramolecular organization results from the coexistence of polar (hydrophilic) and apolar groups (hydrophobic) within the same molecule. Hydrophilic – hydrophobic amphiphiles are pervasive and can be considered the building blocks of soft-matter. Hydrogen bonding and hydrophobic effects play a central role in these systems, while apolar groups are almost always formed by hydrogenated alkyl chains.

However, there is a different type of apolar medium, formed by perfluorinated chains, which are known to be simultaneously hydrophobic and "organophobic". Indeed, mixtures of hydrogenated and fluorinated substances tend to phase separate and exhibit large positive excess properties, which is interpreted as a sign of weak intermolecular interactions between the two types of chains.

This phobicity between hydrogenated and fluorinated chains, leads to the formation of inhomogeneities and nano-domains in the fluid and opens the door to new levels of supramolecular organization. Observed examples include liquid crystalline phases in pure semifluorinated compounds, mixed hydrogenated and fluorinated micellar systems, hemi-micelles of semifluorinated alkanes at the surface of water and nano-segregated domains in ionic liquids.

The talk will describe some of these systems, which we have recently studied at IST, following a strategy that combines experimental results, theoretical calculations and atomistic molecular dynamic simulations.

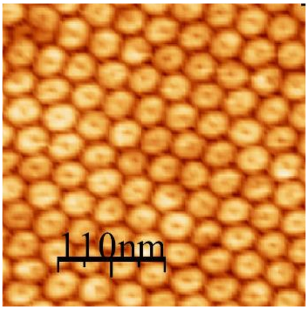

Figure 1. AFM image of a F8H16 monolayer spin-coated on a silicon wafer.

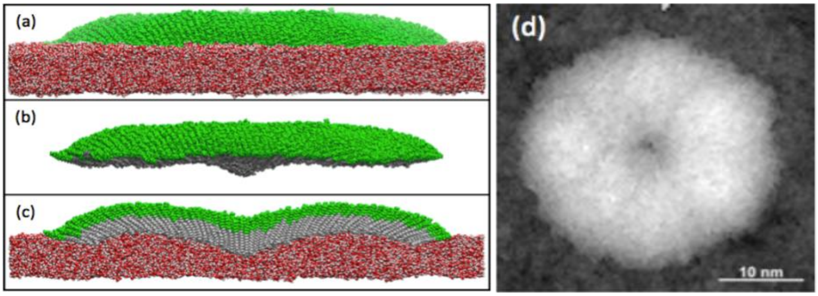

Figure 2. Simulated F8H16 hemimicelle: (a) side view; (b) side view with water molecules erased; (c) cross-section displaying the internal structure; (d) top-view topography (AFM-like) image.[1]

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Photophysics and Photochemistry in Molecules

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In the electronic excited state molecules gain a variety of properties that makes them unique entities different from those in ground-state. In the past years we have been involved in the study of molecules with a large variety of interests and applications. Amongst these are the molecules of color[1,2], see Fig 1, which include the timeless indigo, associated to its excited state proton transfer reaction (ESPT) which gives this molecule an additional photostability, the synthetic derivative thioindigo with its strong polarity dependence of the fluorescence and trypthantrin with Local Excited and Charge Transfer States and whose redox properties put them in the frontline for all-organic redox flow batteries. Indigo (as acceptor) can also be present in low bandgap polymers (e.g. with thiophene or fluorene derivatives as donors), in organic conjugated polymers and oligomers where, ESPT, intrachain energy transfer and conformational relaxation are competitive processes to the decay processes of the excited state both in solution and in the solid state, with relevance to the efficiency in displays.[3] One dominant current strategy for increase the emission in the solid state involves systems with aggregation induced emission, AIE. This effect goes back to an old concept in photochemistry: the loose bolt effect.[4] The photochemistry and photophysics of these, and other, molecules will addressed in this presentation.

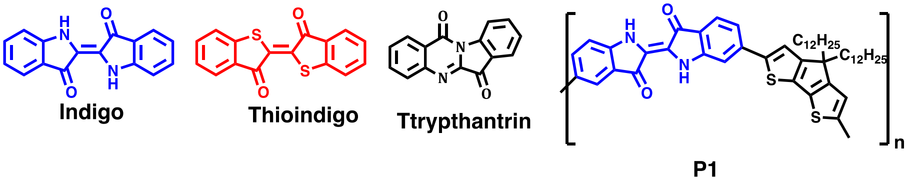

Figure 1. Chemical structures of indigo, thioindigo, trypthantrin, and a low bandgap co-polymer (P1).

Acknowledgements: The author acknowledges funding from FCT, FEDER and Compete Centro 2020 throughout projects Hylight PTDC/QUI-QFI/31625/2017, ROTEIRO/0152/2013, CQC (UIDB/00313/2020 and UIDP/00313/2020) and Laserlab-Europe (no. 284464, EC's 7th Framework Programme).

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(Super)hydrophobic coatings inspired in the surface of plants leaves: The roles of chemistry and physics.

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Superhydrophobicity[1] is an extraordinary wetting feature of many natural surfaces which has been a rich source of inspiration for the coating industry. Research in this field has been focused on the production of two types of advanced coatings: (1) “anti-icing”, “anti-fogging”, “anti-fouling”, and “anti-drag” coatings for the automobile, aeronautical, space, and naval industries, aiming safer transport, less fuel consumption, larger operational range, greater endurance, and higher achievable speeds; (2) “beading-effect” and “self-cleaning” coatings for the painting industry, aiming more aesthetic and cleaner building façades. In the last few years, a huge demand for stain-resistant, water-repellent, and self-cleaning advanced textiles has dominated the market of smart coatings.

Biomimetic applications of superhydrophobicity have been known for more than two decades.[2] The most successful superhydrophobic commercialized product is Lotusan®, a façade paint inspired in the “self-cleaning” properties of the Lotus leaf.[3] This is not surprising since more than half of the total surface area of our planet is covered by superhydrophobic leaves. In plants, water-repellency is the result of the synergy of surface physics (intricate hierarchical sculpturing) and surface chemistry (waxes).

In this presentation the (super)hydrophobic behaviour of the surface of several plant leaves from Northern Portugal will be highlighted.[4]

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Challenges for Li-Battery Polymer Electrolytes - Ion Transport, Electrochemical Stability and Predictability of Soft Matter

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Solvent-free polymer electrolytes (SPEs) will be vital for the realization of solid-state batteries with improved safety and high energy density, either as stand-alone electrolyte materials or in composites with ceramic electrolytes. Despite decades of research, however, there are still large uncertainties regarding the battery performance of Li-conducting SPEs: their ability to suppress dendrites, their interfacial chemistry with battery electrodes, their general chemical and electrochemical stability, electronically insulating properties, processing capabilities, transport mechanisms, etc.

While the performance of SPE is ultimately controlled by the properties of the resulting salt-solvent mixture, the generally most decisive component is the polymer host. There is a large variation of polymer which can dissolve Li-based salts: polyethers, polyesters, polycarbonates, polyalchohols, polyamines and polynitriles,[1] all with their different pros and cons. These possess strikingly different capabilities in terms of anodic and cathodic stability, ionic selectivity, conductivity, mechanical modulus, etc. Utilizing the possibilities of tailoring the polymer properties at the different electrodes separately, and combining this with the full range of tailoring the polymers synthetically, will provide novel strategies to design these materials to perfection. This will likely constitute the components for the next generation of SPE materials for use in Li-batteries.

The perhaps most underinvestigated field of SPE research is the material's interfacial stability at different electrodes. Large uncertainties exists on the potential decomposition mechanisms, the stability, conduction and dissolution of the different decompositions products, and how this varies among different SPE systems. Most conventional electrochemical techniques are also too crude to give useful estimates of the stabilities. The computational investigations of these systems are also in their infancy, with considerably less research work being performed than on liquid or ceramic electrolytes. Emerging research however shows that while there is significant room for improving this situation in future studies, these combined experimental-computational approaches will ultimately lead the design of the next-generation SPE materials.

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● ● ● ●

Invited Lectures

Accounting for polarization in non-polarizable force fields

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Classical non-polarizable models, normally based on a combination of Lennard-Jones (LJ) sites and point charges, are extensively used to model thermodynamic properties of fluids, including solutions and mixture. An important shortcoming of this class of models is that they do not explicitly account for polarization effects - i.e. a description of how the electron density responds to changes in the molecular environment. Instead, polarization is implicitly included, in a mean-field sense, into the parameters of the model, usually by fitting to pure liquid properties (e.g. density). Problems arise when trying to describe thermodynamic properties that involve a change of phase (e.g. enthalpy of vaporization), solutions/mixtures (e.g. solvation free energies), or that directly depend on the electronic response of the medium (e.g. dielectric constant)[1]. Fully polarisable models present a natural route for addressing these limitations, but at the price of a much higher computational cost. In this work, we combine the best of those two approaches, by running fast simulations using non-polarizable models and applying *post facto* corrections to the computed properties in order to account for polarization effects.

I will show how the application of polarization corrections allows for systematic improvements in the accuracy of classical non-polarizable models: i) they eliminate long-standing systematic deviations in predictions of the dielectric constant of liquids across the entire polarity range (from alkanes to water)[2,3]; ii) they offer a theoretically-grounded explanation as to why the dipole moments of effective non-polarizable models are much lower than real dipole moments in the liquid phase[4,5]; iii) they offer a route to simultaneously predict the vapourisation enthalpy and the hydration free energy of water[5]; iv) they allow for accurate predictions of thermodynamic properties of mixtures of compounds with different polarity (e.g. alcohols/alkanes), without *ad hoc* parameter adjustments[6]. I will finish by presenting very recent work on developing a new self-consistent approach for deriving both force field parameters and polarization corrections from simple QM/MM calculations. This paves the way for a new generation of classical models that combine high accuracy with low computational cost.

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Study of an S_N2-reaction under confinement

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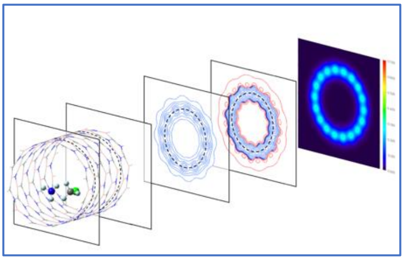
The thermodynamics and kinetics of chemical reactions can change dramatically when they occur under spatial/chemical confinement as compared to gas phase. Density Functional Theory (DFT) methods have been applied to carry out a systematic analysis of a simple Menshutkin S_N2 type of reaction between ammonia and methyl chloride within the confined inner space of several different carbon nanotubes. It was found that pristine carbon nanotubes can catalyze such type of chemical reaction as much as low-dielectric solvents, by lowering considerably the activation energy when compared to the gas phase. [1] Moreover, the magnitude of the effect depends on the radius of the nanotube and its structural type, namely armchair, zigzag or chiral. For example, the activation energy of the reaction drops from +35,4 kcal·mol^{-1} in gas phase to +17,9 kcal·mol^{-1} inside chiral (6,4) SWNT (diameter 6.8 Å).[2]



Moreover, when nanotubes become wider, they all converge to the value 28 kcal·mol^{-1} for the energy barrier regardless of chirality, which correspond to the reaction occurring near a graphene surface.

The effect of doping carbon nanotubes with different proportions of electron-deficient elements and electron-rich elements, such as B and N, respectively, has also been studied.[3] The change in the electronic structure of the nanotubes upon doping was analyzed and the impact on the energetics of the Menshutkin reaction was evaluated.

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SERS studies for biodetection using hybrid nanostructures

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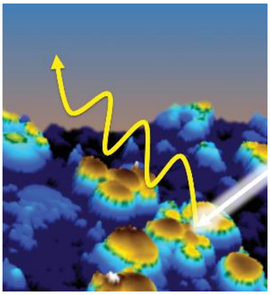
Surface-enhanced Raman scattering (SERS) allows selective detection that can be used for biological sensing, combining the capability of molecular fingerprinting with very high sensitivity. The assembly of metal nanoparticles, silver and gold in particular, into suitable substrates for SERS sensing has been intensively investigated [1]. We have been focused on the preparation of silver and gold nanocomposites, by supporting the metal nanoparticles in a variety of matrices such as graphene, polymers and textiles [2]. The current developments of techniques such as Raman imaging, through high resolution confocal Raman mapping with short measurement times, have brought a new look on nanocomposites and SERS applications. A Raman image can show either the chemical heterogeneity of the nanocomposite or a specific response such as SERS activity or a labeling process (Figure 1). In this communication, our latest results in the development of SERS active substrates will be presented together with its evaluation using Raman imaging. Illustrative examples of SERS applications will be provided along with perspectives of development in chemical detection applied to real contexts. There has been an interest in developing new SERS substrates that make this type of analysis handy, versatile and faster. Polymer based silver or gold nanocomposites can be used as SERS substrates in versatile solid films or in aqueous emulsions. The possibility to obtain SERS using Ag/PtBA (poly(tert-butylacrylate)) nanocomposites as substrates was investigated in detail. SERS activity for the detection of DNA nucleobases and DNA itself will be presented.



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IL3

From Micro to Picomolar Affinity: Photoactive Host-Guest complexes With Ultrahigh Stability in Aqueous Solution

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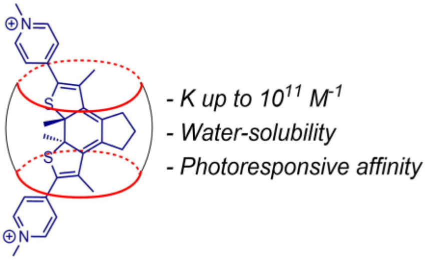
The development of synthetic small receptors that mimic the high affinity and selectivity displayed their biological counterparts (i.e. antibodies or the biotin-avidin affinity pair) is an important goal in supramolecular chemistry. However, while biological receptors typically bind their targets with dissociation constants in nanomolar range or below, most synthetic receptors display affinities below the micromolar range, especially in water. Amongst the rare examples of low molecular weight synthetic receptors that are reported to display high-affinity for complementary guest molecules in water, cucurbit[n]urils (CBn) are the most widely investigated with binding constants reaching 10^{17} M^{-1}.[1] Motivated by the exceptional binding properties displayed by CBn, our group became interested in the development of high-affinity binding pairs with photoresponsive properties. In the course of our investigations with several light-responsive molecules, which comprises both photolabile and photochromic compounds, we recently discovered that dithienylethene (DTE) photoswitches form highly stable 1:1 inclusion complexes with CB8.[2-4] In this presentation I will show some examples of photoactive host-guest systems developed in our laboratories with a focus in recent work in DTE:CB8 host-guest systems.



Acknowledgements: This work was supported by the Associate Laboratory for Green Chemistry - LAQV which is financed by national funds from FCT/MCTES (UIDB/50006/2020 and UIDP/50006/2020). N. B. thanks the FCT for his research contract CEECIND/00466/2017.

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IL4

Molecular Manipulations under Cryogenic Conditions Controlled by Infrared Vibrational Excitation

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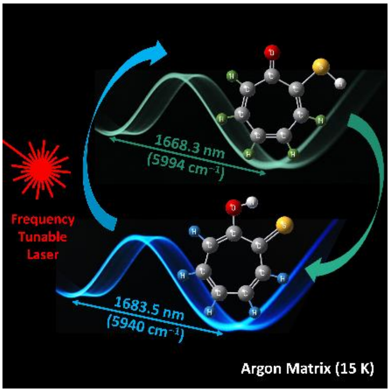
Infrared vibrational excitation is a promising approach for achieving exceptional control of molecular transformations, in ways that cannot be attained via thermal or electronic excitation. Until recently, most of the infrared-induced processes in cryogenic matrices concern the activation of conformational isomerizations of a light OH fragment by irradiation at its first stretching overtone. In this presentation, we will highlight our new advances in vibrationally induced chemistry. Namely, the experimental realization of the concept of remote vibrational antennas to achieve conformation control.[1] The demonstration of vibrational excitation of second stretching overtones to induce conformational isomerizations, opening the door to extend control over transformations separated by higher barrier.[2] Moreover, the demonstration that vibrational excitation can be harnessed to induce and control bond-breaking/ bond-forming reactions. Pioneer examples include an infrared-induced bidirectional tautomerization (as shown in the image) and a ring-opening reaction.[3,4]



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Rationalization of Crystallization Processes from the Study of the Organization of Molecules in Solution

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Crystallization from solution is one of the most important methods to purify and obtain crystalline materials. Even so, our current knowledge on the mechanism of molecular assembly in solution to form a crystal is incipient. Understanding how this process occurs is, therefore, not only a fundamental scientific question, but also a matter of technological interest, as it may allow the control of the molecular packing, morphology, and size distribution of precipitated materials.

In this communication, different aspects of the crystallization process will be discussed from an experimental and theoretical perspective. Three main topics will be addressed: (*i*) interplay between solute and solvent molecules; (*ii*) relation between solute organization and crystallization of different crystal phases; (*iii*) effect of impurities.

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From biocatalysis to metal separation: the versatility of ionic-liquid-based aqueous biphasic systems

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Aqueous biphasic systems (ABS) are liquid-liquid extraction systems composed of two aqueous phases. The development of novel ABS by using ionic liquids (ILs), combine all the advantages of these solvents, namely their tailoring ability, with the advantages of ABS, making them highly interesting to be used in extraction and separation processes of a wide range of compounds. The versatility of IL-based ABS has been repeatedly demonstrated since the first report about the application of ILs as phase-forming components in 2003.[1] Aiming at developing tailored systems with better extraction performance, we have been creating ABS that evolved from "simple" ABS used in the partition of small biomolecules, to multiphase-systems composed of three coexisting-phases, stimuli-responsive systems to act as integrated bioreaction–separation processes, and acidic ABS, which allowed to overcome the limited stability of ABS to the low pH and the "one pot" leaching and separation of critical metals. The development of these novel ABS was achieved by changing and/or adding new and tunable phase-forming components, resulting from a proper understanding of the mechanisms that rule their formation. In this presentation the development of a variety of versatile IL-based ABS will be addressed, along with the discussion of the mechanisms driving their formation.

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Oral Communications

First-Principles Model to Evaluate Quantitatively Long-Life Behavior of Cellulose Acetate Polymers

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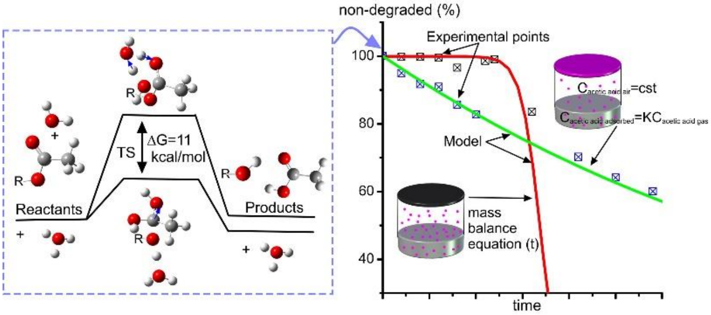
A significant part of the memoirs of the 20th century was recorded in films, photographs and audio tapes made with cellulose acetate that need to be preserved. We present in this work our contribution to this challenging degradation problem by establishing a first-principles model that can be used to estimate the polymer's stability under variable environmental conditions[1]. This approach can be externed to other polymeric materials.



the reaction mechanism of hydrolysis was investigated using electronic Density Functional Theory calculations with the B3LYP/6-31++G** level of theory to determine the energy barriers of the degradation reactions. This information was coupled with the Transition State Theory to establish the kinetics of the degradation for both the acid catalyzed and non-catalyzed degradation pathways. In this model, the dependence on the water concentration on the polymer as function of pH and the evaporation of acetic acid from the polymer is explicitly accounted. The accuracy of the developed approach was validated through comparison with experimental results of CDA accelerated aging experiments.

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OCS2

How the structure of intermediate species influences selectivity in the photoreaction of 1-allyl-4-aryltetrazolones in solution

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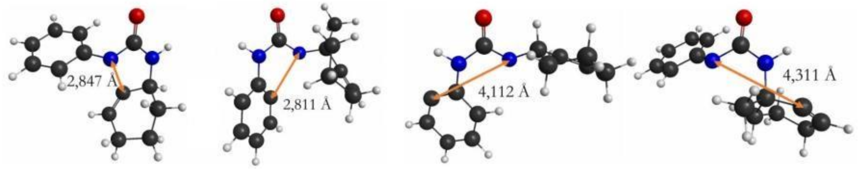
The photoreactions of 1-allyl-4-aryltetrazolones were already studied in solution and theoretically, with DFT(B3LYP/3-21G*) level of theory.[1] The postulated mechanism for these reactions, in methanol, involves the formation of a triplet biradical intermediate after N_2 photoextrusion. After the formation of this intermediate there are two possible pathways: if a proton is transferred from the allylic moiety, the photoreaction produces a pyrimidinone and if it is transferred from the phenyl moiety, the photoproduct is a benzimidazolone.

In this study, these photoreactions were characterized using time-dependent density functional theory to interpretate a postulated experimental-based mechanism, which relates structural constraints imposed by allylic moieties with the photoproduct selectivity.[1] No steric restrictions which could justify the selectivity observed experimentally were identified in the tetrazolones. The selectivity observed in these photoreactions is attributed to differences in the structures of the intermediate species present in the distinct pathways. We found that the orientation of the moiety involved in the cyclization favors or hinders the formation of the product. Structural differences involve smaller or larger reorganization of the solvent cage, which is directly related with the volumes of the different moieties.



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TD-DFT Study of Light-Absorption by Brown Carbon Over Three Southern European Cities

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Brown carbon is a strongly-light-absorbing type of organic aerosol with potential for significant regional radiative forcing. However, it has been neglected in climate models, which can justify differences between model predictions and measured data.[1] The analysis of the real effect of brown carbon is also difficult due to the uncertainty regarding the relationship between its chemical composition and optical properties.[2]
Herein, it was employed a Time-Dependent Density Functional Theory (TD-DFT) approach to model the "real-world" absorption of polycyclic aromatic hydrocarbons (PAHs) and their oxygenated (OPAHs) and nitrated (NPAHs),[3,4] which are main components of brown carbon.[3]
More specifically, TD-DFT calculations were performed to model the absorption spectra of 30 PAHs, 15 OPAHs and 10 NPAHs, present in the atmosphere over three Southern European cities (Porto, Florence and Athens).[4] The data were subsequently corrected both for "real-world" experimental concentration of these compounds over these cities, and for their theoretical fluorescence yield.[4]
The obtained results demonstrated that light-absorption by these molecules is more relevant for climate forcing at ~330, ~360 and ~440 nm. Even more, while absorption of ~330 nm is explained by both PAHs and OPAHs, the absorption at ~360 and ~440 nm is only attributed to OPAHs. The contribution of NPAHs appear to be negligible.
In conclusion, Porto appears to be the city most affected by radiative forcing induced by these molecules, while Florence and Athens appear to be similarly affected.

Acknowledgements: Projects PTDC/QUI-QFI/2870/2020 and UIDB/00081/2020.

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Energetic and structural properties of organic crosslinker molecules

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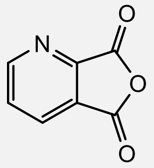
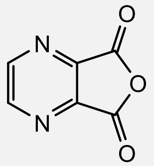
The structural characteristics of pyridine-2,3-dicarboxylic anhydride (**a**) and pyrazine-2,3-dicarboxylic anhydride (**b**) make them relevant organic crosslinkers. For this reason, they are important raw material and intermediates used in organic synthesis (pharmaceuticals, agrochemicals and dyestuff industries).[1]

The standard molar gas-phase enthalpies of formation, at T = 298.15 K, of the two organic crosslinkers were calculated in this work by means of the composite G3(MP2)//B3LYP approach, making use of several different group substitution reactions (isodesmic and homodesmotic reactions). According to our experience in the computational study of heteropolycyclic compounds,[2] this type of theoretical procedure generates reliable gas-phase enthalpy values of formation, in good agreement with the experimental data.



(a)



(b)

This computational study was also extended to the attainment of the dipole moments, electrostatic potential surfaces, and the frontier molecular orbitals for pyridine-2,3-dicarboxylic anhydride and pyrazine-2,3-dicarboxylic anhydride, allowing us to infer about their reactivity.

The main structural difference between the organic crosslinker compounds (the presence of pyridine and pyrazine rings in their structures) will be also compared in energetic terms.

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Rationalizing biomolecule solubilization mechanisms in colloidal systems through coarse-grained molecular dynamics

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The extraction of poorly soluble compounds from complex matrices often requires the use of solubilizing agents such as surfactants and hydrotropes, some of them tunable and responsive. However, the underlying mechanisms behind solubilization are still not fully understood. Molecular dynamics (MD) simulations can shed light into it by providing a detailed microscopic insight of the interactions between solutes and solubilizers.

In this work, three quaternary ammonium ionic liquids and salts (QAILS) were selected as solubilizers where the coarse-grained (CG) models were taken from the literature. These QAILS comprised a solubilizing mechanism spectrum: trimethyl-tetradecylammonium chloride ($[N_{1,1,1,14}]Cl$) as a surfactant, tetrabutylammonium chloride ($[N_{4,4,4,4}]Cl$) as an hydrotrope, and tributyl-tetradecylammonium chloride ($[N_{4,4,4,14}]Cl$) as an intermediate molecule sharing properties of both. Gallic acid (GA) was chosen as the poorly soluble compound, with a new CG model developed based on the MARTINI force field. A set of CG-MD simulations were carried out to study the mesophase behavior and the solvation of GA in aqueous QAILS solutions. Solute concentrations below and at the solubility limit in water were assessed as well as the GA speciation across the pH range.

The simulation results point out that dispersive interactions between QAILS and GA generally direct the solubilization. However, the speciation of GA depends on the pH, often not considered in CG-MD simulations. This affects the arrangement of the solute within the QAILS structures. When the GA charge is increased (deprotonation), the electrostatic interactions seem to play the main role. The hydrotropic solubilization mechanism displayed by the $[N_{4,4,4,4}]Cl$ corroborated recent hypothesis based on hydrotrope-solute aggregates formed through dispersive forces. This work opens the door to study the partition and solubilization mechanism using CG-MD computer simulations which can complement, guide and streamline experimental works and large-scale industrial processes.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. The authors acknowledge the research contract under the project CENTRO-01-0145-FEDER-000005: SusPhotoSolutions: Soluções Fotovoltaicas Sustentáveis. N.S. acknowledges financial support from the BATRE-ARES project (ERA-MIN/0001/2015) funded by ADEME and FCT. G. Pérez-Sánchez and N.S. acknowledge the national funds (OE), through FCT – Fundação para a Ciência e a Tecnologia, I.P., in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19.

New set-up force field for magnetic-ionic liquids

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Magnetic ionic liquids (MILs) are a new generation of ionic liquids that contain a transition metal or lanthanides in their cation or anion structure. In addition to their unique characteristics, such as high thermal stability, low flammability, and vapor pressure, MILs respond to an external magnetic field.[1] The presence of the external magnetic field makes them reusable and seems to improve the viscosity of this class of ILs.[2,3] So, a careful design of the MILs structure has yielded magnetoactive compounds with unique physicochemical properties. These properties can be tuned and turn these metal-based ionic liquids promising compounds in several areas such as analytical chemistry, catalysis, gas absorption, medicine, and sensing applications. [4]

This work aims to set-up a force field for anion-based-magnetic ionic liquids and study their thermodynamic, transport, and structural properties from molecular dynamics (MD) simulations. Therefore, based on this study, it will be possible not only to gather deep insights of these MILs and their mixtures but also to offer an efficient rational design of MILs forward enhancing their applicability.

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Coarse-grained model of the synthesis of periodic mesoporous benzene-silica

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We present a coarse-grained (CG) classical molecular dynamics model that reproduces the early stages of the templated synthesis of periodic mesoporous benzene-silica (PMO). We analyse the formation, growth and aggregation of hexadecyltrimethylammonium bromide (CTAB) micelles in aqueous benzene-silicate (BZS) solutions, which occurs during the synthesis of PMOs. Our model was calibrated to correctly reproduce the key features of the radial density profile of spherical micelles of CTAB and BZS in solution, previously calculated by our group, with an all-atom molecular dynamics approach.[1] In contrast with the AA method, our CG model considers groups of atoms, rather than individual atoms, as interaction centres. This allowed for a considerable increase in system size, from 100 surfactant molecules to 1000-3000, as well as an increase in simulation time, from around 50 nanoseconds to a few microseconds. Thus, we were able to observe more complex features of the synthesis of PMOs, such as the formation of CTAB spherical micelles, the aggregation of the micelles to form rods, and the final hexagonally ordered mesophase. We found that BZS is more than a spectator in this process – its presence hastens the formation of CTAB micelles and drives the transition to rods and their arrangement in a hexagonal pattern. In fact, the posterior removal of the BZS from the final PMO structure, which is only possible using computational approaches, caused the system to revert to the original spherical micelles. We determined experimentally relevant information, such a confirmation of the rod diameter and the minimum BZS/CTAB ratios required for the sphere-to-rod transition or to obtain the hexagonal mesophase.

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The reaction mechanism of MHETase, a QM/MM MD study

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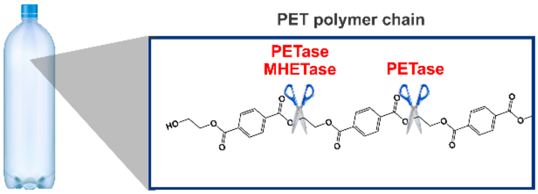
In 2016, one of the two enzymes involved in the polyethylene terephthalate (PET) degradation pathway of Ideonella sakaiensis 201-F6, MHETase, was found to exhibit a strong ability to degrade the PET monomer mono-(2-hydroxyethyl)terephthalate (MHET) at room temperature, converting it back into the precursors used in PET production.[1] MHETase engineering to improve efficiency is an active field that suffers from an incomplete characterization of its reaction mechanism.

Here, we analyze some protein dynamics and present a reaction mechanism proposal similar to the already reported in the literature, with the computational methodology B3LYP/MM-MD and umbrella sampling. The combination of a high theoretical level and extensive sampling generated a very robust computational prediction. We found that MHETase catalyzed the conversion of MHET in two steps with the rate-limiting step activation barrier $\Delta G\ddagger=17.49$ kcal.mol^{-1} (from the weighted histogram analysis). Our calculations are in line with the hypothesis that the reaction mechanism is mediated by a metastable tetrahedral intermediate, in each step, which is quite common in the serine hydrolase class.[2] The energy of the first tetrahedral intermediate was similar to that of the reactant state, while the tetrahedral intermediate of the deacylation step was observed to lie closer to the rate-limiting transition state.



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Understanding the Topology of the Laplacian Field in Transition Metal Chemistry: From Chemical Insights to Specialized Molecular Descriptors

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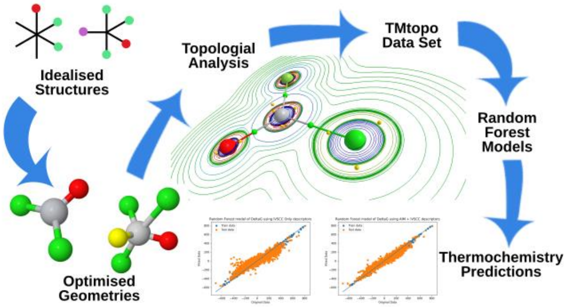
Transition metal (TM) chemistry is a challenging field for chemical modelling, due to the highly diverse behavior rooted in the partial filling of the d-hell orbitals. Nevertheless, a good predictive model opens huge opportunities for the development of novel compounds with useful properties. A long standing question in TM chemistry is the role of inner-Valence Shell Charge Concentrations in dictating the geometry[1,2] and reactivity[3] of TM complexes.

In this work, we present the preliminary results of a systematic survey of over 1000 first row TM complexes with respect to their geometry, energetics, electronic properties and the topology of their electron density, $\rho(\mathbf{r})$, with particular emphasis on the topological features of the Laplacian of $\rho(\mathbf{r})$. For this purpose, a collection of relevant topological features and quantum-calculated properties was curated into a data set, which was then used to train Random Forest models targeting ΔE, ΔH, and ΔG using different sets of molecular descriptors, for 22647 ligand-exchange reactions. All sets of descriptors yielded models with good predictive capabilities in both the training and validation states. In order to further test these models, they were coerced to predict ΔE, ΔH, and ΔG for 965 isomerization reactions. These results shown a remarkable resilience from the models trained using these new quantum topological descriptors when compared to the control models based on classical ones.



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Bias-Variation trade-off in Machine Learning modelling of the Jacobsen epoxidation process

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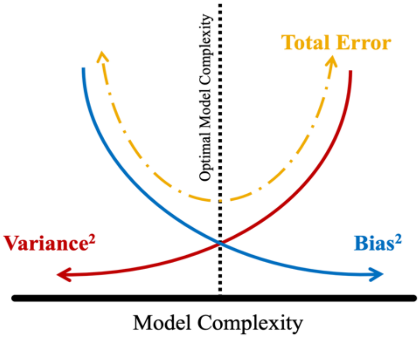
Machine Learning methods are a valuable asset in the development of industrial catalytic reaction models[1,2]. Working with very large datasets, Random Forest (RF) algorithms can handle numerous data from complex reaction systems, improving catalytic efficiency[3]. The catalytic epoxidation of olefins (Jacobsen epoxidation[4]) is one of such cases, providing valuable chiral intermediates for the production of fine pharmaceuticals and agrochemicals.

We have trained predictive RF models targeting the catalytic efficiency in the Jacobsen epoxidation process through a diverse set of published catalysts, substrates, reaction conditions, and theoretically generated molecular descriptors for the intervening species. These preliminary models successfully predict reaction yields and enantiomeric excesses (EE). Although the results are encouraging, there is still a pressing issue on the trade-off between bias and variance among these models. Hence, several techniques were implemented to reduce variance, but they often come at the cost of some increase in bias.



In this communication, we present a framework for evaluating the bias-variance trade-off in our catalytic models. The goal is to minimise together the bias and variance and thus improve combined predictions for both the yield and EE. The results from this evaluation strongly suggest that the data used in the catalytic assessments embody what the model might encounter when solving the problem it was designed for.

Acknowledgements: This work received financial support from FCT/MCTES through the projects UIDB/50006/2020, and PTDC/QUI-QIN/30649/2017.

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OCS11

ProtoSyn: an AI-powered tool for computational design of functional peptides

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Computer simulations have revolutionized the way new therapeutics, drugs, processes, and materials are researched and developed. Prototype candidates can be tested and screened a priori, cutting costs and development time in virtually all areas of science. One such application of computational chemistry is the rational design of custom-made peptides.

ProtoSyn has been developed over the past 2 years as a new software package for computational design of small peptides. ProtoSyn has been developed in Julia, a recent new programming language that aims to simplify the "two-language problem", where a scientific software often requires both the employment of a simpler scripting language, such as Python, for the user-interaction, and more dense and specific language for the computationally intensive work, usually C or C++. This has, historically, greatly reduced the accessibility of new developers to improve and build upon existing solutions in effective and meaningful ways. Besides aiming to have a much lower entry barrier to both new developers and contributors, ProtoSyn also intends to be a simple solution, tailored for non-specialized scientists who wish to employ computer simulations in their workflow. Moreover, ProtoSyn has native support for distributed computing, SIMD and GPU acceleration, among others, while implementing TorchANI[1], a machine-learning energy function able to accurately predict the correct position of atoms in a structure with DFT precision. Where a regular DTF calculation could take up to 50 hours of CPU time, ProtoSyn, empowered by the TorchANI AI, takes less than 0.3 seconds.

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Characterizing psychoactive drugs by mining data from chemical databases and molecular simulations

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Forensic science is currently faced with the challenge of classifying new psychoactive substances (NPS), which are designed to mimic established illicit drugs such as cannabis, cocaine, heroin, and others. NPS are relatively new, so there is little information on their health effects[1].

Since NPS are not controlled at International Drug Control Conventions, their legal status is undefined. Countries, where large numbers of different NPS have quickly emerged, invoke 'chemical similarity' to an already illicit substance to control those that are not explicitly mentioned in legislation[1].

There is therefore an urgent need to develop comprehensive databases for rapid characterisation of these substances, allowing them to be categorized, for example, according to their occurrence, molecular fingerprint, toxicity and consequent legal aspects.

In this work, we define a classification framework for NPS based on molecular and physicochemical descriptors, combining chemoinformatics tools, molecular modeling and simulation[2].

A set of 301 molecules containing licit and illicit drugs from 10 different NPS families is characterized using 287 descriptors.

Hierarchical and k-means clustering and Principal Component Analysis (PCA) reveal five natural clusters that match the known NPS families. The PCA results show that the discrimination between NPS is mainly determined by the main physiochemical descriptors of Lipinski's rule (e.g., number of H-bond donors and acceptors, molecular weight and hydrophobicity measured by logP, van der Waals surface area, molecular surface area, molecular solubility, number of rings, and number of rotatable bonds).

This study proved successful in classifying and characterizing NPS molecules that are not as well described in the literature.

Acknowledgements: The Coimbra Chemistry Centre (CQC) is supported by the Portuguese Agency for Scientific Research, “Fundação para a Ciência e a Tecnologia” (FCT), through Project UID/QUI/00313/2020.

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Investigations of phase transitions in liquid crystals and pharmaceutical compounds using window clustering of infrared spectra

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Infrared spectroscopy (IR) is a powerful experimental method which, if used to minor spectral changes along a trajectory of varying dynamic variable (such as temperature, pressure, etc.) requires advanced analytic tools of hyperspectral data such as two-dimensional correlation analysis.[1] In general, various chemometric methods are useful to spot and analyze minor spectral changes.[2] This presentation will show usefulness of cluster method in the investigations of phase transitions of several liquid crystals and pharmaceutical compounds.

Clustering methods are helpful tools in the detection of phase transitions, but do not provide information on the structural changes at the phase transitions. For this reason, window clustering analysis method has been proposed. Multivariate data has been divided into small windows of spectral regions, and then cluster analysis has been applied for each data window. This approach makes it possible to reduce the dimensionality of large data set, while reveals the spectral characteristic of given phase associated with various spectral regions. This method appears to be particularly sensitive when tracking the melting process of alkyl chains.[3]

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Oral Communications

14th Meeting of Physical Chemistry

The Evolution of the Color systems in Plants. A physical chemical approach.

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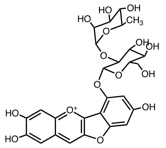
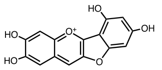
Anthocyanins are on the basis of the angiosperms colour, 3-deoxyanthocyanins play the same role in mosses and ferns and auronidins are responsible for the colour in liverworts. The separation of the ancestors of each of these lineages occurred in different periods of land plant evolution, therefore, our thesis is that chemical evolution of the color systems accompanied plant evolution.

The colour system of cyanidin-3-*O*-glucoside (kuromanin) as a representative compound of simpler anthocyanins was fully characterized by stopped flow. This type of anthocyanins cannot confer significant colour to plants without intra or intermolecular interactions, complexation with metals or supramolecular structures as in *Commelina communis*. The anthocyanin's colour system was compared to the one of 3-deoxyanthocyanins and riccionidin A the aglycone of auronidins. The three systems follow the same sequence of chemical reactions, but the respective thermodynamic and kinetics is dramatically different.

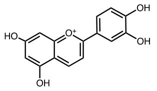
In this communication we compare the three systems and explain why anthocyanins were selected by angiosperms, the plants on the top of the evolution.



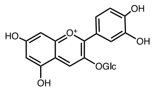
Aurodinin 2'-neohesperidoside



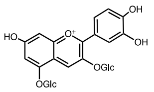
Riccionidin A (aglycone)



3-deoxyanthocyanidin (Luteolinidin)



Cyanidin-3-glucoside



Cyanidin-3,5—diglucoside

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Photophysics and Photochemistry in N,N'-disubstituted indigo derivatives: Competition between ESPT and photoisomerization

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Indigo is one of the lightest stable organic dyes known. Due to its natural origin it has been used as a dye for millennia, it acquired an almost mythical status. On the past recent years, its high stability has led to a renewed interest also in some of its synthetic derivatives. The photostability and low fluorescence has been imparted to the ESPT[1] involving a single N-H and C=O group of indigo leading to dominance of the internal conversion nonradiative process. This has also been used to explain the high photostability of this molecule.

With the indigo derivative N,N'-diacetylindigo (DAI) and N,N'-dibenzoilindigo (DBI) derivatives rotation around the central double bond was found in the excited state, with a conical intersection (CI) that makes this dark process highly efficient.[2] Steric hindrance prevents DBI from accomplishing full rotation with the formation of two conformers experimentally seen both from fs-TA and time-resolved emission measurements. For DAI, fs-TA indicates the presence of two species, with lifetimes, in 2MeTHF, of 33 ps and 2790 ps. The acyl derivative shows blue shifted absorption and emission from the parent indigo due to stabilization of the π HOMO orbital in the S1 $\pi^* \leftarrow \pi$ transition by delocalization to the acyl carbonyl. The extent of blue shift among the different acyl derivatives is found to depend on the geometric constraints imposed on the dihedral angle between indigo and the acyl group.[2]

For biomedical applications, these photo-switchable systems have become a key tool to remotely and noninvasively regulate processes in vivo, e.g. associated with photo-pharmacology, super-resolution fluorescence imaging, and optochemical genetics.

Acknowledgements: This work was supported by Project "Highlight" (no. 031625) 02/SAICT/2017, PTDC/QUI-QFI/31625/2017, which is funded by the Portuguese Science Foundation (FCT). The Coimbra Chemistry Centre is supported by FCT, through Projects UIDB/00313/2020, and UIDP/00313/2020. FCT is also gratefully acknowledged for a PhD grant to DCN - SFRH/BD/140890/2018.

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OC3

Supramolecular Approaches to Irreversible Thermochromic Systems

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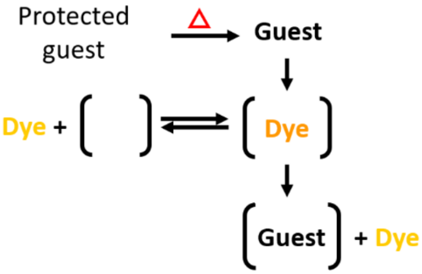
Flavylium compounds are versatile molecules whose rich complexity partially derives from their ability to switch between a variety of species by means of external stimuli, such as pH, temperature, and light.[1] They have found a wide range of applications in human technology, from paints to food additives, and organic electronics – particularly, smart-label technology - could be another interesting sector.

Irreversible thermochromic systems are made of materials able to change color upon application of a thermal stimulus; smart labels capitalize on a sensor responsive to temperature, which allows then irreversible color change of a chromogenic displaying unit.



By using our research-group's knowhow, we're investigating a thermosensitive host-guest competition (scheme aside) to eventually engineer smart-label applications. This approach relies on an equilibrium process between a colored molecule (*i.e.* dye) and a water-soluble macrocyclic receptor: the dye presents different colors when it's inside or outside the host. If in the same medium there is another molecule which can compete as guest, the dye gets out the macrocycle's cavity; this competitor arises from an irreversible thermo-induced deprotection reaction.

The deprotection kinetics of the competitor - in our case, an essential amino acid - has been investigating by testing different temperatures, pH values, and indicators (*e.g.* chalcones and flavylium compounds): all these variables can be tuned to design customizable systems depending on the desired situation.

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Revisiting the Kamlet-Abraham-Taft Model Equation: The Separation Between Solvent Polarizability and Solvent Dipolarity

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Multiple Linear Regression analysis remains one of the most popular methods to study solvent effects in physicochemical processes. In a recent paper, we have shown that the Kamlet-Abraham-Taft (KAT) model equation provided robust and predictive quantifications of the main solute-solvent interactions which prevail in the reaction processes of three heterolysis reactions.[1] However, a recent publication questioned the model's ability to adequately interpret the solvent-dependent behavior of several solvatochromic probes.[2] This failure was attributed to the combined quantification of the solvent's dipolarity/polarizability delivered by the π^* term used in the KAT equation.

We therefore decided to devise a method to split π^* into two independent contributions to separately quantify the solvent's polarizability and dipolarity. The potential capability of this modified version (KATm) was tested using five different solvent-dependent processes. Results show that the KATm model provides significant improvements over its predecessor, in particular for processes not dependent on specific solvent interactions – Fig. 1.

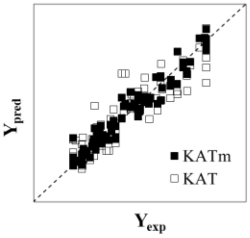

Fig. 1 – Performance of KATm *vs.* KAT model equations.

Other recently confronted[3] model equations were also tested but the overall better performance of KATm was observed.

Acknowledgements: The authors acknowledge support from Fundação para a Ciência e a Tecnologia, Portugal (UIDB/00100/2020).

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Double-reversible aqueous biphasic systems based in protic and aprotic ionic liquids

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Conventional liquid-liquid techniques commonly use volatile organic solvents. In this field, greener alternatives have been studied, such as aqueous biphasic systems (ABS) (1). ABS are mainly composed of water, and are formed by a combination of two hydrophilic solutes (two polymers, a polymer and a salt, or two salts) above certain concentrations. Nevertheless, these traditional combinations still present a limited polarity range, leading to the appearance of ionic liquid (IL)-based ABS to overcome this drawback (2). Aprotic ionic liquids (AILs) have been the most investigated as phase-forming compounds of ABS; however, protic ionic liquids (PILs) are gaining in this field in more recent years (3). In this work, both protic and aprotic ILs were synthesized and studied in the formation of IL-based ABS with PPG 400 $g.mol^{-1}$ at different temperatures (25 ºC, 35 ºC and 45ºC) and pH values (4,7 and 9). It was found that both classes of ABS are responsive to temperature, and that the increase in temperature favors the formation of two phases, therefore presenting a lower critical solution temperature (LCST) behavior. On the other hand, a pH response is also noticeable for both groups of IL-based ABS under study, however following different trends with the pH. In PILs-based ABS, the transition from the single-phase to the two-phase systems is favored with a decrease in the pH, whereas for the AILs-based ABS the two-phase formation is favored by the increase in pH. Therefore, ABS composed of ILs are of a double-reversible nature, switchable with temperature and pH, further following different trends according to the pH. This feature allows to use ABS as designed platforms for the separation and purification of (bio)molecules, with high relevance in separation processes.

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High pressure Taylor setup – First results in supercritical carbon dioxide

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Applications of the supercritical fluids (SCFs) in science and technology has expanded significantly in the past decades, at both academic and industrial level[1,2]. In this way, supercritical carbon dioxide is converting in one of the most used and important solvents due to its role in chemical extraction, low environmental impact and low price. So, information about diffusion of various compounds in supercritical CO2 is of high value for numerous applications.

The estimate of mass transfer rates, as well as empirically based models defining diffusion, are becoming increasingly important for simulating reactions under supercritical conditions. Diffusion coefficients of various compounds are essential to complete information about solutes in supercritical solvents, along with other transport properties.

This work presents the development of high-pressure apparatus for measurements of the diffusion coefficient in supercritical fluids, which is built using the principle of the Taylor dispersion method[3]. This set-up was tested by the measurements of binary diffusion coefficients D of various compounds at infinite dilution in supercritical carbon dioxide[4,5].

In order to test the set-up, have been measured the diffusion of a reference system in supercritical carbon dioxide, at temperatures in the range 306.15 K – 321.15 K and pressure 10.5MPa. The obtained diffusion coefficients are of order of 10^{-8} m^2 cm^{-1} and comparable to available literature data. The influence of several optimization parameters on the diffusion coefficient have been analyzed.

In a second part, binary diffusion for short chain alcohols in supercritical CO_2, were measured by the Taylor dispersion method in the range of 306.15 K- 321.15 K and at pressure of 10.5 MPa. The effect of molecular weight and temperature on the diffusion coefficients is examined.

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Novel purine-based ILs and their behavior in aqueous solutions

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Biobased ionic liquids (ILs) are being increasingly endorsed to design more ecofriendly ILs, with lower toxicity and better biodegradability.[1] Purines are the most widely distributed *N*-heterocycles in nature. Since most purines have low solubility in both water and organic solvents,[2] their application is restricted. Yet, the formation of salts of purines can improve their solubility.[3] In this work, four purines – theobromine, theophylline, xanthine and uric acid – were selected to design biocompatible ILs with tetrabutylammonium as a cation, aiming to simultaneously improve purine's solubility. The novel biobased ILs were characterized regarding melting and decomposition temperatures, water-solubility and microalgae toxicity against *Raphidocelis subcapitata*. The ILs display good thermal stability and aqueous solubility enhancement ranging from 659 to 2035-fold relative to their respective purines. The cation of the synthesized ILs seems to have a great impact on their toxicity, with no purine-based IL being classified as non-hazardous. The novel ILs application in the formation of aqueous biphasic systems (ABS) and as hydrotropes was also evaluated. The ILs were able to form ABS with both sodium sulfate (Na_2SO_4) and tripotassium citrate ($K_3C_6H_5O_7$) salts. The ability to form thermoresponsive ABS using Na_2SO_4 as a salting-out agent was successfully evaluated, with different ILs showing different behaviors, despite their structural similarity. The novel biobased ILs also displayed a hydrotropic effect, being able to greatly increase the solubility of ferulic acid in aqueous solution.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the Portuguese Foundation for Science and Technology/MCTES. This work was also funded by national funds through the Portuguese Foundation for Science and Technology within the scope of the bilateral Portuguese-French program Hubert Curien (Pessoa). Ana R. F. Carreira and Telma Veloso acknowledge FCT for the Ph.D. grants SFRH/BD/143612/2019 and SFRH/BD/147346/2019, respectively. H. Passos acknowledges FCT – Fundação para a Ciência e a Tecnologia, I.P. for the researcher contract CEECIND/00831/2017 under the Scientific Employment Stimulus - Individual Call 2017. JLP is funded by national funds (OE), through FCT, I.P., in the scope of the framework contract foreseen in article 23, of the Decree-Law 57/2016, changed by Law 57/2017.

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Pharmaceutical Nanococrystals Synthesis: a novel mechanochemical approach

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Pharmaceutical nanococrystals have recently been raising attention from the scientific community, being a young yet promising strategy applied on drug development to obtain new, revolutionary and pharmaceutically interesting solid forms.[1–4] This approach results from combining cocrystal formation, supramolecular structure composed by an active pharmaceutical ingredient (API) and an acceptable coformer, with known potential for drug physicochemical properties enhancement without compromising its biological function, with particle nanonization processes, also known to improve particles solubility and dissolution rate.

Herein, studies on a well documented cocrystal, (2:1) (S)-naproxen-nicotinamide,[5] were conducted, leading to the report of a novel in situ nanococrystal synthesis strategy based on liquid assisted grinding (LAG), with the application of two nonionic surfactants and PEG 6000 as stabilizers. Furthermore, studies regarding a top down wet milling procedure were also carried out.

The obtained nanosized co-crystals were characterized by differential scanning calorimetry, infrared spectroscopy, and powder X-ray diffraction. To confirm the presence of the aimed nanosized particles, scanning electron microscopy and laser diffraction were used, proving the successful obtention of a nanopowder by LAG and a nanodispersion by wet milling, stabilized by a mixture of Span® 85 and Tween® 85. LAG evolution as a one stepped and solvent free nanococrystal synthesis pathway promises to open new windows for drug development, not only by improving drug effectiveness but also by promoting greener pharmaceutical industries.

Acknowledgements: Coimbra Chemistry Center, CQC, is supported by national funds through the FCT – Foundation for Science and Technology, I.P., under the project UID/QUI/00313/2019.

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Encapsulation and enhanced release of resveratrol from mesoporous silica nanoparticles for melanoma therapy

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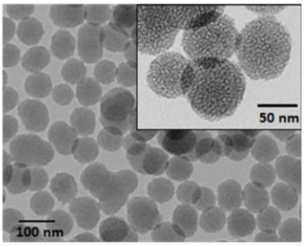

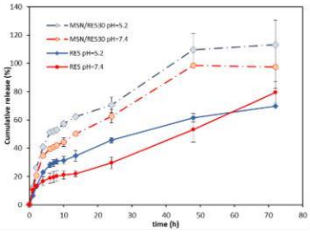

Chemotherapy has limited success in the treatment of malignant melanoma due to fast development of drug resistance and low bioavailability of chemotherapeutic drugs.[1] Resveratrol (RES) is a natural polyphenol with recognized preventive and therapeutic anti-cancer properties.[2] However, poor RES solubility hampers its bioactivity, creating a demand for suitable drug delivery systems to improve its bioavailability. This work aimed at assessing the potential of RES loaded mesoporous silica nanoparticles (MSNs) for human melanoma treatment. RES was efficiently loaded onto spheroidal (size ~ 60 nm) MSNs. The encapsulation promoted the amorphization of RES and enhanced the release *in vitro*, compared to non-encapsulated RES. The RES release was pH-dependent and markedly faster at pH 5.2 (acid environment in some tumorous tissues) than at pH 7.4 both in encapsulated and bulk form. The RES release from loaded MSNs was gradual with time, without burst effect. *In vitro* cytotoxic studies, on human A375 and MNT-1 melanoma cellular cultures, have shown a decrease in the cell viability with increasing concentration of RES loaded MSNs, indicating the potent action of released RES in both cell lines.

Acknowledgements: This work was developed within the scope of the projects CICECO (UIDB/50011/2020 & UIDP/50011/2020), and CESAM (UIDB/50017/2020 & UIDP/50017/2020), financed by national funds through the Fundação para a Ciência e a Tecnologia-FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. This work was supported by the project PTDC/BTMMAT/31794/2017 (POCI-01-0145-FEDER-031794) funded by FEDER, through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI), and by national funds (OE), through FCT/MCTES. FCT: IF/00405/2014; FCT: CEECIND/04050/2017.

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Relaxation processes and crystallization behavior of liquid crystals: effects nanometric confinement

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Liquid crystals (LCs), as other molecular systems, can either vitrify or crystallize (melt crystallization) upon cooling. Liquid crystalline materials, have been also found to undergo so-called cold crystallization on heating from a glassy state. This talk will present the relaxation dynamics and kinetics of isothermal and non-isothermal crystallization processes in the nematic phase of two mesogenic fluorene derivatives (5P-EtFLEt-P5[1] and 5P-Am*FLAm*P5[2]), and contrasts them with the highly-ordered smectic B phase (SmB) of 4-n-butyloxybenzylidene-4′-n′-octylaniline (BBOA). The studies combines broadband dielectric spectroscopy (BDS), differential scanning calorimetry (DSC), and polarized optical microscopy (POM) measurements. It was revealed that 5P-EtFLEt-P5 and 5P-Am*FLAm*P5 display different types of non-isothermal cold crystallization. Our experimental results obtained for the crystallization process under isothermal conditions are discussed in terms of dynamic and thermodynamic properties of a material.

The second part of the talk will focus on the effect of confinement imposed by nanopores on the molecular dynamics and phase behavior of BBOA liquid crystal[3]. The phase transition temperatures of bulk BBOA and enclosed in napores show linear dependence as a function of inverse pore diameter. The BDS investigations revealed new relaxation processes associated with gradual paranematic-to-nematic transition in nanopores. Special emphasis is given to the influence of geometrical restriction on the non-isothermal crystallization process upon cooling. Finally, the impact of spatial constraint on intramolecular vibrations of alkyl chains in the course of crystallization will be discussed in the context of Fourier transform-infrared spectral data.

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Textile based composites as substrates for Raman imaging and SERS detection

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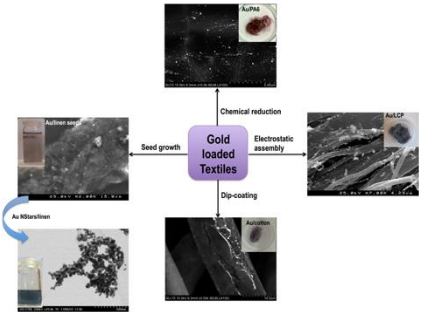
Analytical methods based on surface-enhanced Raman scattering (SERS) and Raman imaging are among the tools most exploited in recent years for the detection of vestigial amounts of organic compounds of environmental interest.[1,2] In particular, SERS has been largely improved due to considerable progress in the development of ultra-sensitive analytical platforms, which rely in our understanding of physicochemical phenomena occurring at the surfaces of nanomaterials. On the other hand, confocal Raman microscopy provides high resolution images with short measurement times in the analysis of nanoscale materials. Our interest in this field, led us to explore both methods in the development of nanostructured platforms for the SERS detection of organic pollutants in water.[3,4] This communication provides an overview of our research on the development of easy-handled SERS substrates based on textile fibres for analytical detection. Chemical strategies employed for the coating of textile fibres with metal nanoparticles will be also described. Illustrative examples of SERS applications together with its evaluation using Raman imaging will be provided along with perspectives of development in chemical detection applied to real contexts.



Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the FCT/MEC and when appropriate cofinanced by FEDER under the PT2020 Partnership Agreement. Sara Fateixa acknowledge the costs resulting from the FCT hirings funded by national funds (OE), through FCT-Fundação para a Ciência e aTecnologia, I.P., in the scope of the framework contract foreseen in the numbers 4, 5, and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19.

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Supramolecular Sensors for Biologically Relevant Analytes

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The study of peptides is of great interest, not only due to the variety of functions these molecules present in biological systems (e.g. in signalling, neuromodulation, immune response and metabolism)[1] but also as tools in biotechnology and as pharmacological agents, as is the case of antimicrobial cell-penetrating peptides[2]. Supramolecular receptors have had a rising application in the transport, modulation and sensing of these biomolecules, due to the strong interactions they can establish with affinities up to the nM range[3].

Our work focused on the development of a group of supramolecular dual emission sensors for cationic peptides. These consist of a modular amphiphilic system based on a p-sulfonatocalix[4]arene receptor, that can be monosubstituted in its lower rim with different functional groups, depending on the target application. The sensors SCnPy present an aliphatic chain of variable size (n = 4, 6), with a pyrene fluorescent moiety at its end. SCnPy have shown to have the pyrene's characteristic monomer emission at low concentrations and, when at high enough concentrations or in the presence of organic cations, they can form ground state dimers that emit at higher wavelengths. The variation of chain length successfully modulated the capacity of the SCnPy sensors to aggregate: SC4Py showed this dual emission for polyarginines of four or more residues, while SC6Py is able to aggregate in the presence of peptides with only 3 cationic residues. Furthermore, SC6Py showed selectivity for a fragment of the peptide Humanin, over a similar sequence of another mitochondrial signaling peptide, SHLP4, all the while presenting a dual emission that enables the correction of the measurement for instrumental factors and sensor concentration variations.

These results show that it is possible to mould the selectivity of a sensor towards similar target sequences, while maintaining high affinities and a self-correcting measurement.

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Influence of carbon chain length on properties of (E)-4-((4-alkyloxyphenyl)diazenyl)phenyl alkanoates

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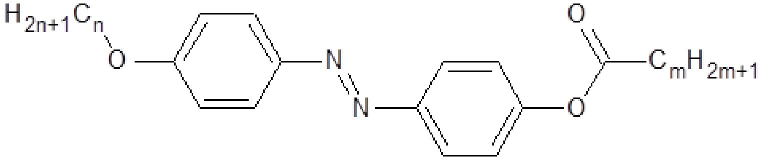
Thermotropic liquid crystals invariably arouse interest due to occurrence of variety of properties and wide application potential. Thousands molecules of this kind were synthesized and described in literature.[1] For instance, (E)-4-((4-alkyloxyphenyl)diazenyl)phenyl alkanoates (*n*OABOOC*m*, structure shown in *Figure*) homologues series with various numbers of carbon atoms in alkyloxy chain (*n*) and alkyl chain (*m*) were investigated. In this group of compounds presence of variety of mesophases was noted, e.g. crystal G and H, smectic C, nematic. Additionally, diazenyl group enables absorbance of UV-Vis light. [2,3]



This work emphasize on spectral studies of *n*OABOOC*m* (for *n* = 3,5,7,8,10), especially with fixed carbon atoms number in alkyl chain (*m* = 2). Measurements were conducted using Broadband Dielectric and FT-IR Spectroscopy methods. Main aim was to investigate and correlate influence of length of carbon chain on dielectric and infrared spectra (including moving window and 2D analysis). [4]

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How high pressure affects the crystallization kinetics of partially fluorinated chiral liquid crystal in its smectic phase?

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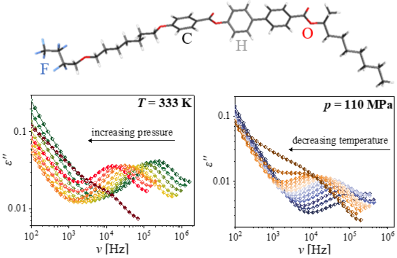
Crystallization of a soft matter under pressure or temperature is a very attractive scientific topic. Particularly in the field of molecular substances it is a subject of great importance to chemistry and material engineering. Many external factors may influence this transition, which often becomes a complex process. We mean thermal history, external pressure, the structure of the initial phase, or the geometry of the sample, just to name a few. Therefore, knowledge of the critical factors that enable the control over crystallization or vitrification facilitates the design and production of materials with extraordinary, often completely different attributes.

In our research we focus on the impact of hydrostatic pressure on the crystallization kinetics of a chiral liquid crystal in its smectic phase with antiferroelectric properties (SmC_A^*). The phase behaviour of the compound under study and its vibrational dynamics associated with particular thermodynamic states were recently described in Refs.[1,2] In this work, we examined the influence of varying: (i) temperature (T) at constant pressure or (ii) pressure (p) at a fixed temperature on crystallization of compound under study in its SmC_A^* phase, using BDS method. We also studied the melt crystallization along the trajectory of constant relaxation time τ on the (T,p) plane. The results of the isothermal melt crystallization kinetics studied at ambient[3] and elevated pressure[4] have been compared.



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Aggregation Induced Emission from the interaction of polyamines with Cucurbiturils

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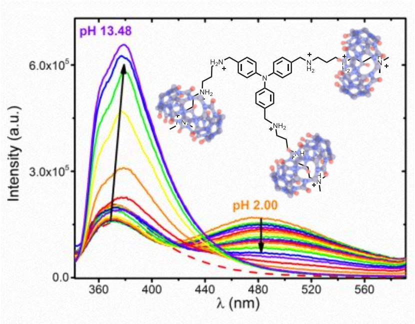
Aggregated induced emission (AIE) is a phenomenon that overcomes the quenching effect of traditional organic fluorophores at high concentration or in the solid state.[1, 2] Normally, this effect is accomplished with well-solubilize organic molecules after the addition of a variable percentage of a second solvent where the solubility is lower.[3. 4] However, in order to take advantage of this property, our approximation is to introduce macrocyclic chemistry into AIE-active systems by non-covalent interactions.

Macrocyclic receptors, such as cyclodextrins, calixarenes, and cucurbiturils, have received enormous attention owing to their ability to encapsulate non-covalently molecules and to release them by appropriate stimuli.

Herein, we present three ligands bearing triphenylamine as the aromatic core and one, two or three acyclic polyamine chains, TPA1p, TPA2p and TPA3p, respectively, which were found to be completely soluble in water and able to show AIE behaviour when pH and, more interestingly, when encapsulation inside cucurbit[7]uril, CB7 takes place.



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Imidacloprid and cymoxanil removal by mesoporous poly(β-cyclodextrin)-based composites

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Pesticides are widely used in agriculture to increase and protect crop production. A substantial percentage of the active substances applied is retained in the soil or flows into water courses, constituting a very relevant environmental problem. There are several methods for the removal of pesticides from soils and water; however, their efficiency is still a challenge. An alternative to current methods relies on the use of effective adsorbents in removing pesticides[1] which are, simultaneously, capable of releasing pesticides into the soil when needed. This reduces costs related to their application and waste treatments and, thus, overall environmental costs. In this paper, we describe the synthesis and preparation of mesoporous poly(β-cyclodextrin)-activated carbon composites[2]. The composites were characterized by different techniques such FTIR, ^{13}C CPMAS solid state NMR, TGA and dTG, SEM and BET. Their removal efficiency of pesticides was assessed by using two active substances: cymoxanil (fungicide) and imidacloprid (insecticide). Composites with 5 and 10 wt% of activated carbon showed very good stability, high removal efficiencies (>75%) and pesticide sorption capacity up to ca. 50 mg g^{-}1. The effect of additives (NaCl and urea) was also evaluated. Reusability of the sorbents was evaluated by sorption/desorption cycles observing release capability around 30% of the initial sorbed amount of pesticide without losing the capacity to keep the maximum removal efficiency in sorption/desorption cycles.

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Hydrophobic paper-based substrates for SERS detection of pesticides in spiked food products

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Monitoring trace levels of pesticides in food products is extremely important as a preventive measure for protecting public health. In the past years, surface enhanced Raman scattering (SERS) has been explored as a non-conventional method in the detection of trace chemical species in water and food, namely for the presence of vestigial pesticides.[1] The use of materials that act as highly sensitive substrates in SERS is a crucial requirement in this type of surface analysis. In particular, hydrophobic SERS substrates are attracting significant attention, because in certain conditions allow the analyte molecules to concentrate in a smaller area of the sensor, thereby increasing its sensitivity.[2]

Here, we propose an innovative strategy to prepare hydrophobic paper-based substrates for SERS analysis. The substrates have been manufactured by inkjet printing of formulations containing Ag colloids and polystyrene beads emulsions. The optimization of the substrates for SERS analysis was performed by varying parameters such as the type of paper and number of printing cycles. Several samples have been studied, including fruit juice and fruit peels spiked with the pesticide thiram. Using the new hybrid SERS substrates, thiram was detected in spiked apple juice at a level of 240 ppb, while in apple peel, the detection limit achieved was 600 ng/cm^2. As such, the paper-based SERS substrates allowed the detection of thiram in laboratorial samples at concentrations lower than the MRL established by the European Union (Commission Regulation (EU) 2016/1).

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Separation of ethylene from ethane with metal-organic frameworks

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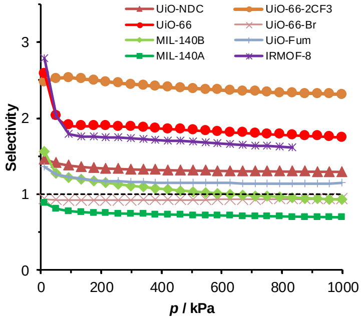
The separation of ethylene from ethane could be alternatively made by an adsorption process if the adsorbent would preferentially adsorb ethane over ethylene. Materials that exhibit this feature are scarce. Here we present our studies of metal-organic frameworks, IRMOF-8 and a series of zirconium-dicarboxylate based MOFs of the UiO-66 (tetrahedral and octahedral cages) or MIL-140 (triangular channels), for which the adsorption isotherms of ethane and ethylene were measured at 298 and 318 K up to pressures of 1000 kPa. Van der Waals interactions seem to be enhanced in the interpenetrated structure of IRMOF-8, favoring ethane adsorption in a wide pressure range. Results indicate that the 3D pores of the UiOs favor the adsorption of ethane due to the interactions between ethane with more spacers than in the case of the 1D channels of MIL-140s. The impact of the functionalization on the UiO-66 type revealed a very interesting increase of selectivity when two perfluoro groups are present on the aromatic ring (UiO-66-2CF$_3$) (value of 2.5 up to 1000 kPa). Indeed, UiO-66-2CF$_3$ revealed a unique combination of selectivity and working capacity at high pressures.



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Exploring periodic mesoporous organosilicas for ethane–ethylene adsorption–separation[1]

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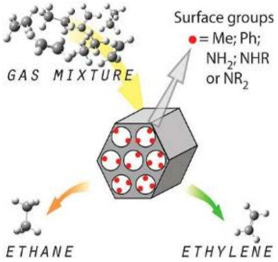
Ethylene is a core building block in the chemical industry and its separation from ethane is very challenging due to high energy requirements. Adsorption-based processes can be an alternative to current processes based on cryogenic distillation.

In this work, we explore for the first time the application of periodic mesoporous organosilica (PMO) materials, whose surface properties can be tuned with different functional groups. With the aim of correlating the PMO structure with ethane and ethylene adsorption, eight different PMO materials have been prepared, *viz.* the phenylene-bridged PMO, PMO aminated at the organic bridges, and PMO functionalized by silylation of free silanol (inorganic) moieties. High pressure adsorption isotherms were measured, and the separation selectivity and phase diagrams of a binary mixture of ethane and ethylene were estimated.



Results have shown that, overall, the PMO studied tend to be more selective towards ethylene than ethane probably due to the interactions between the quadrupole moment of ethylene and the free silanols in the samples. After silylation, the novel materials presented surfaces with higher affinity towards ethane than those of the pristine material. For the aminated samples, functionalization with primary amines originated materials displaying better selectivity towards ethylene than those functionalized with secondary or tertiary amines.

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Supported ionic liquid materials for L-asparaginase immobilization

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L-asparaginase (ASNase) (L-asparagine amidohydrolase EC 3.5.1.1) has been widely used as a therapeutic agent in the treatment of acute lymphoblastic leukemia (ALL) and in the food industry for the removal of toxic acrylamide (formed in foods cooked at high temperatures).[1] Accordingly, ASNase is also used in biosensors for leukemia diagnosis.[1] To improve the performance of ASNase and overcome the limitations of free enzymes, namely low stability and biocatalytic activity, enzyme immobilization is one of the most used strategies. Several supports as carbon nanotubes, graphene and chitosan have been reported for ASNase immobilization.[1] Among them, nanomaterials, and in particular silica, have emerged as a promising alternative support for enzyme immobilization due to their unique characteristics, such as biological compatibility and high surface to volume ratio,[2] being thus identified as promising supports for ASNase. In this work, supported ionic liquid materials (SILs) based on silica were used as novel immobilization supports for ASNase by a simple adsorption method. Different experimental conditions, namely contact time, medium pH and ASNase/SILs ratio were evaluated. The performance of the immobilized enzyme was studied by measuring its activity through the monitoring of the hydrolysis of the substrate, Lasparagine.[3] Characterization of the ASNase-SILs bioconjugate was carried out to evaluate the adsorption of the ASNase onto the supports. The immobilization of ASNase onto the SILs was successfully achieved with an activity of immobilized ASNase ranging from 0.6 to 0.86 U of enzyme per mg of SILs under the optimum immobilization conditions (60 min, pH 8.0 and 0.06 $mg.mL^{-1}$ of ASNase in 10 mg of SILs).

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Kinetic control of host-guest binding with light

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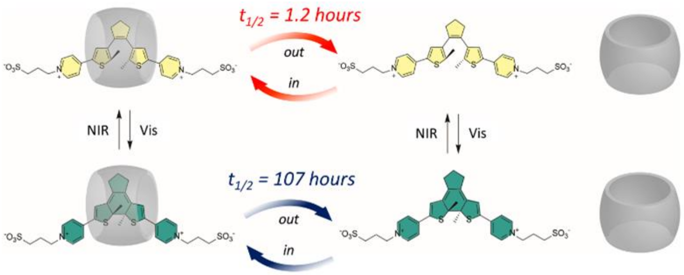
The design of host-guest pairs is mostly focused on its thermodynamic constants. However, an out of equilibrium control could be required to obtain more complex systems, such as advanced molecular machines. Therefore, a deep understanding in regulation of binding/displacement kinetics is crucial.

In this communication, we present a detailed study of the binding mechanism between a cucurbit[8]uril (CB8) host[1] and photoswitchable dithienylethene (DTE) guests in water.[2] We show that the introduction of two sulfonate side arms in the DTE, slows down the kinetic constants by at least 5 orders of magnitude, without significantly affecting the high affinity of the complex. The conformational flexibility of the DTE open isomer allowed the formation of a metastable complex in an unusual conformation that we call of *twisted* antiparallel. We also demonstrate that the closed isomer is both thermically[3] and kinetically more stable than the open form, allowing to control the displacement kinetics and complexation with light stimulus, including with near infrared light, that falls inside the "biological window".



Acknowledgements: This work was supported by the Associate Laboratory for Green Chemistry - LAQV which is financed by national funds from FCT/MCTES (UIDB/50006/2020 and UIDP/50006/2020). FCT/MCTES is also acknowledged for supporting the National Portuguese NMR Network (ROTEIRO/0031/2013-PINFRA/22161/2016, cofinanced by FEDER through COMPETE 2020, POCI, PORL, and FCT through PIDDAC) and for the grants PTDC/QUI-COL/32351/2017, PTDC/QUI-QFI/30951/2017 and CEECIND/00466/2017.

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Protein loading and release by temperature- and pH-sensitive tubule-based hydrogels

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Smart drug delivery vectors improve the efficiency of the delivery on the target cells, thereby minimizing the associated side effects in the treatment of patients. When constituted by amphiphilic molecules, these vectors present considerable advantages, namely versatility in physicochemical properties and sensitivity to stimuli. Amino acid-based surfactants are advantageous molecules because of their high biodegradability, reduced human cytotoxicity and aggregation versatility.[1-3]

In this work, we studied the interfacial and aggregation behavior of three families of novel anionic double-chained lysine-based surfactants, with variable degree of chain length mismatch. These compounds possess the ability to self-assemble into tubular structures, below a characteristic Krafft temperature (T_m). The effects of chain length mismatch and structural isomerism on surface activity and self-assembly in water were investigated. The tubules display various types of morphology and give rise to a swollen entangled 3D network, thus inducing gelation.[2] Cryo-TEM, cryo-SEM and SAXS show that they consist of long, multilamellar, hollow cylinders. Besides being temperature-sensitive, showing tubule-micelle and tubule-vesicle phase transitions, the lysine-based surfactants are also pH-sensitive, due to a carboxylate group in their headgroup.[2] The interactions of the tubular aggregates with a model protein, lysozyme (LZM), were also investigated with the aim of developing topical applications for the hydrogels.[3] The latter are efficient in entrapping LZM and show different release profiles, depending on temperature and/or pH. Cytotoxicity studies further show that the tubule-based hydrogels are biocompatible and promising for use in biological applications.

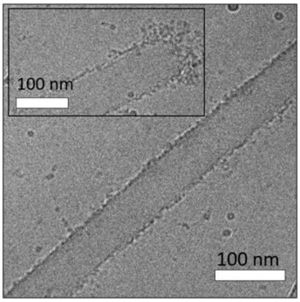

Fig. Cryo-TEM image of 10Lys14/LZM system, showing the protein surface-adsorbed at the tube outer wall.

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Release kinetics of monophenols from polysaccharides crosslinked with β-cyclodextrin

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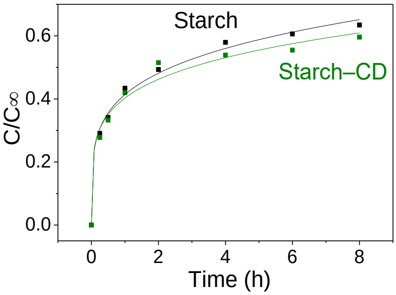
This communication considers the hypothesis that the functionalization of polysaccharides with β-cyclodextrin (β-CD) units improves their performance as carriers for bioactive compounds, slowing down the release rate to aqueous-alcoholic media. First, β-CD was esterified with 1,2,3,4-butanetetracarboxylic acid (BTCA) to yield BTCA–β-CD. Then, cellulose and starch were crosslinked to β-CD units by reaction of their hydroxyl groups with the free carboxyl groups of BTCA–β-CD [1]. The functionalized substrates, containing from 85 to 172 μmol of β-CD per gram, were loaded with cinnamaldehyde, carvacrol, hydroxytyrosol and cuminaldehyde. These compounds are highly valued due to their antimicrobial, antioxidant and antimutagenic properties[2].

The release kinetics to aqueous ethanol (10%, v/v) solutions was measured over the first hours, also taking samples over the following eight days to determine the concentration of active compound once the equilibrium is reached (C_∞). An example is given in the figure at the right, corresponding to the release of cinnamaldehyde. Kinetic data up to ~0.6 C_∞ were successfully fitted to a power law, whose parameters were used to compute the active substance mean dissolution time (MDT).



With the sole exception of carvacrol and cellulose, functionalized polysaccharides clearly resulted in longer MDTs than their native counterparts. These results allow us to claim that the insertion of β-CD units is a valid and feasible strategy to prolong the holding of monophenolic compounds in carbohydrate matrices.

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OC24

Comparison of crystallization kinetics and molecular dynamics in liquid crystalline 3FmFPhH6 (m = 5, 7) compounds

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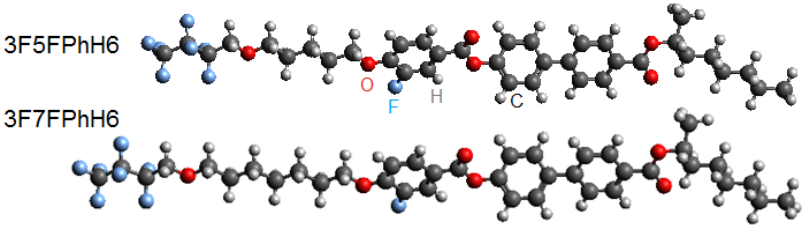
The influence of the -$OC_mH_{2m}O$- chain length on phase transitions, crystallization kinetics and dielectric relaxation processes of two chiral fluorinated 3FmFPhH6 homologues (m = 5, 7) is investigated. Both 3F5FPhH6 and 3F7FPhH6 are known to exhibit three liquid crystalline smectic phases, SmA^*, SmC^* and SmC_A^*.[1]



In this study it is shown that 3F5FPhH6 crystallizes during cooling even for fast 20 K/min rate, while 3F7FPhH6 crystallizes only during slow cooling and for rates ≥ 5 K/min a glass of the SmC_A^* phase is created instead. The crystallization kinetics studies in isothermal conditions show that the characteristic crystallization time is lower in 3F5FPhH6 than in 3F7FPhF6 and that the melt and cold crystallization of 3F7FPhH6 occur with similar characteristic times. The investigation of dielectric relaxation processes show a slight slowing down of collective phasons deep in the SmC_A^* phase of 3F5FPhH6 compared to 3F7FPhH6. The temperature dependence of the relaxation time of the α-process in the overcooled SmC_A^* phase of 3F7FPhH6 gives a high value of the fragility parameter $m \approx 144$ for this glassformer. The relaxation processes observed in the crystal phases of both compounds are interpreted as intra-molecular conformational changes, based on DFT-B3LYP/def2TZVPP calculations.

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Co-amorphous nateglinide systems: screening and thermal behavior evaluation

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Most of the new active pharmaceutical ingredients show low aqueous solubility, therefore facing the risk of reduced oral bioavailability and therapeutic efficacy.[1,2] Amorphization is a well-established strategy to enhance solubility as well as dissolution rate of these kind of drugs. However, amorphous phases are thermodynamically metastable, which makes amorphous drugs susceptible to crystallization. To overcome stability problems of these metastable phases, a new line of research has recently been pursued that involves co-amorphous systems of a drug and a small molecule excipient or of two complementary drugs.[3,4]

Diabetes disease is widespread in society, leading to an ever growing need to find more efficient therapeutics. Improvement of aqueous solubility of drugs increases their concentration in the systemic circulation, for better bioavailability and pharmacological response. This study aimed to design stable co-amorphous systems of the poorly water-soluble antidiabetic drug nateglinide and different small molecule co-formers. Two amorphization techniques were explored, namely quench cooling and milling, in different experimental conditions. The materials obtained were characterized by X-ray powder diffraction and FTIR spectroscopy, and their thermal behavior was evaluated. A preliminary assessment of the stability of the obtained co-amorphous phases was also carried out.

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Enhancing lignin dissolution and extraction: The effect of surfactants

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Lignin is a complex polyphenolic biopolymer, the second most available macromolecule on Earth, and works as a "natural glue" holding together cellulose and hemicellulose in the fibers of plant cell walls [1]. The dissolution and extraction of lignin from biomass represent a great challenge due to the complex structure of this natural phenolic biopolymer [2]. In this work, several surfactants (i.e., non-ionic, anionic, and cationic) were used as additives to enhance the dissolution efficiency of model lignin (kraft) and to boost lignin extraction from pine sawdust residues [3]. In the first part of this study, different cationic and anionic surfactants, are used in an aqueous solution to dissolve model kraft lignin. Non-ionic surfactants are also tested for comparison. In this first part, the interaction between lignin and a cationic surfactant is also followed, by electrical conductance. In the second part of this work, the most promising surfactants used for model lignin dissolution are tested as potential additives to improve the yield of lignin extraction from lignocellulosic biomass (maritime pine sawdust). It was found that ca. 20 wt. % of kraft lignin is completely solubilized using 1 M octyltrimethylammonium bromide and 0.5 M polysorbate 20, in an aqueous solution. Moreover, all surfactants used increased the lignin extraction with formic acid even at low concentrations, such as 0.01 and 0.1 M. Higher concentrations of cationic surfactants improve the extraction yield but the purity of extracted lignin decreases [3].

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Ion Exchange in Aqueous Biphasic Systems

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Ionic liquid-(IL)-based aqueous biphasic systems (ABS) are a well-known liquidliquid extraction technique with great interest in separation processes. ABS are majorly composed of water, thus presenting more biocompatible characteristics than conventional liquid-liquid extraction carried out with volatile organic solvents. However, it is still not clear if ion exchange occurs in systems composed of water and two salts, such as an inorganic salt and an IL. In this work, it is shown the extent of ion exchange occurring in ABS formed by protic ILs and inorganic salts, both by changes in the solubility curves and by the tie-lines composition. These systems are composed of 5 phase-forming components, instead of 3 as initially expected if no ion exchange occurs. Therefore, it is critical to determine the phase's composition in salt-salt ABS before their application in separation processes. Knowing the phase equilibrium data and the extent of ion exchange, it is possible to properly design separation processes in which all phase-forming components and the respective phases can be reused.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020 financed by national funds through the Portuguese Foundation for Science and Technology/MCTES. B. Kopilovic acknowledges the University of Aveiro for the PhD Grant Contrato de Bolsa (RH) 85281. E.V. Capela acknowledges FCT for the PhD grant SFRH/BD/126202/2016. C.M.S.S. Neves acknowledges FCT (Fundação para a Ciência e a Tecnologia), I.P., under the Scientific Employment Stimulus—Individual Call—CEECIND/01975/2017—under the CEEC Individual 2017.

Development of chemiluminescent self-activating photosensitizers with selective anticancer activity

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Cancer is a very challenging disease to treat, both in terms of treatment efficiency and side-effects[1]. To overcome these problems, there have been extensive studies regarding the possibility of improving treatment by employing combination therapy, and by exploring therapeutic modalities with reduced side-effects, such as photodynamic therapy[2]. While photodynamic therapy is known for having significant advantages over conventional cancer therapies, its dependence on light has limited it to treating tumors on or just under the skin or on the outer lining of organs/cavities[3].

Herein, we have developed new photosensitizers capable of intracellular self-activation with potential tumor-selectivity based on chemiluminescent reactions involving only a cancer marker. The photosensitizer is directly chemiexcited to a triplet excited state capable of generating singlet oxygen, without requiring either a light source or any catalyst/co-factor. So, this work had two aims: (i) development of a self-activating photosensitizer which can be used for light-free photodynamic therapy, eliminating light-related restrictions that this therapy currently possesses; (ii) assess their co-treatment potential when combined with reference chemotherapeutic agents[4,5].

Cytotoxicity assays with breast and prostate cell lines involving showed that the novel photosensitizers possess significant toxicity toward tumor cells, while not inducing toxicity toward normal cells. Analysis of co-treatment effects revealed significant improvements for both cell lines, producing better results than just for individual photosensitizers and the reference chemotherapeutic agents[4,5].

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Dipicolylamine-Based Fluorescent Chemosensors for Ion Detection in Aqueous Media

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Coordination chemistry has been strongly associated with ion sensors since the 1990s, particularly using chelating groups for binding metal cations. In the past ten to fifteen years, a stronger effort has been made to use these sensor systems for anions as well.[1] Binding anions in aqueous media is strongly hindered because of the high stability of the solvation sphere by water molecules. Pioneer work explored by Hamachi and co-workers has led to designing a series of sensors based on di-2-picolyl-amine (DPA) to complex with Zn^{2+} or Cd^{2+}, which can be subsequently used for detection of phosphates.[2] In this work, we present new fluorescent sensors based on DPA units, which are capable of working in aqueous environment.[3] Although detection mechanisms for cations and/or anions rely on interactions with DPA chelating moieties (see figure below), different behaviors are exhibited (luminescence quenching and/or enhancement, shift in absorption/emission wavelengths), which highlights both their complexity, as well as their potential for multiple analyte sensing applications.

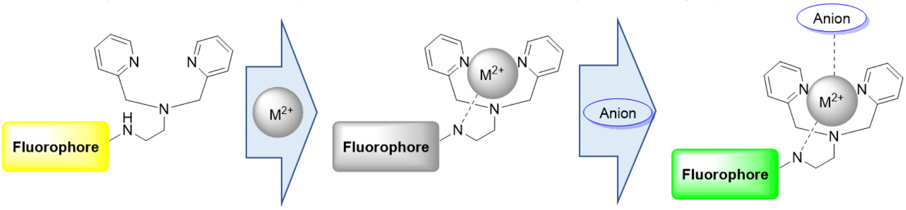

Figure 1. Example of binding and corresponding effect of metal and subsequent anion to a DPA fluorescent sensor.

Acknowledgements: DEFENSE project (PTDC/QUI-QFI/32007/2017) and the Associate Laboratory for Green Chemistry LAQV which is funded by national funds from FCT-MEC (UID/QUI/50006/2013) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER – 007265) are acknowledged for financial support.

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Tuning J-aggregate formation and emission efficiency in cationic diazapentacenium dyes

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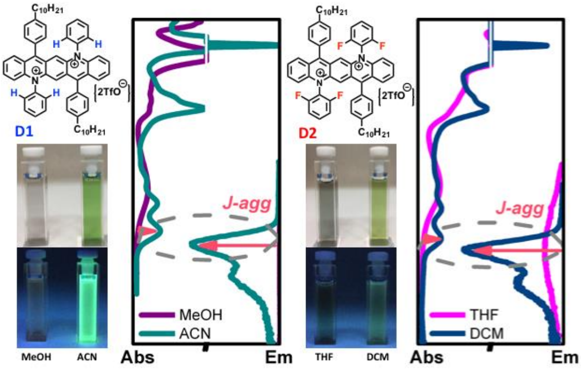
Aggregation induced emission (AIE) and AIE-luminogen systems are nowadays a topic of high interest and impact due to the increment of the emission properties in aggregate systems, which are usually poorly emissive[1,2].

In this work, we report the formation of J-aggregates in quaternized 5,12-diazapentacenium salts (**D1** and **D2**), coupled to an increase in fluorescence intensity (AIEE properties). Our data indicate formation of emissive J-aggregates in poor solvents, while in good solvents and in thin films, isolated molecules coexist with aggregates. This is evidenced by a strong increase of the fluorescence quantum yields along with the appearance of a narrow absorption band red shifted in poor solvents.



Enhancement of the luminescence efficiency of diazapentacenium salts, **D1** and **D2**, of more than 55 times for **D1** and 22 times for **D2** in poor solvents, acetonitrile (ACN) and/or dichloromethane (DCM), was observed in comparison to good solvents, methanol (MeOH) and tetrahydrofuran (THF), for **D1** and **D2**, respectively. The structural change of the N-aryl substituents from phenyl (**D1**) to 2,6-difluorophenyl (**D2**) also influences the optical properties. As an example, THF is found to be the best solvent for fluorinated derivative **D2**, while it is a poor solvent for **D1**. This illustrates that simple structural modifications in these compounds can dramatically change their optical properties, thus paving the way for a rational control of the supramolecular ordering, and consequently, of the luminescence efficiency.

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Photoresponsive catanionic vesicles for the effective encapsulation and release of an anticancer drug

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Stimuli-responsive drug delivery systems have been intensively investigated over recent times, due to their ability to provide activation-mediated drug release and hence potential increase in therapeutic efficacy. The stimuli can be either physiological, like pH or redox changes, or exogenous, such as light irradiation.[1-2] Among the myriad nanocarriers studied, mixed cationic/anionic surfactant vesicles display interesting physicochemical features, such as facile assembly, long-term stability and composition tunability.[3] Herein, we present recent work on the design and development of catanionic vesicles sensitive to UV irradiation and acidification, and on their ability to effectively entrap and release a model anticancer drug, doxorubicin (DOX). The catanionic vesicles are composed of an anionic amphiphile based on a 2-hydroxychalcone as the photosensitive unit, which presents an intricate chemical network combining the dynamics of other common photoswitches (e.g. spyropirans and azobenzenes),[4-5] and a cationic gemini surfactant. Upon irradiation in acidic media, a vesicle-to-bilayer transition is triggered and a 4-fold increase in release of incorporated DOX is observed compared to the non-irradiated system. The developed vesicles are a proof-of concept for a smart colloidal nanocarrier where the pH can be envisioned as a "lock mechanism", and light as the trigger.

Acknowledgements: We thank Fundação para a Ciência e Tecnologia, FEDER/COMPETE and P2020|COMPETE for financial support through projects POCI-01-0145-FEDER-032351 (PhotoSAN), UID/QUI/0081/2020, POCI-01- 0145- FEDER-006980, NORTE-01-0145-FEDER-000028, UID/QUI/50006/2013 and UID/QUI/50006/2019.

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Absolute Photoluminescence Quantum Yield

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Commercial talk from Hamamatsu Photonics. We will introduce our products related with spectroscopy for measuring absolute Photoluminescence quantum yield (PLQY) and photoluminescence lifetime.

Additionally, we will present with some measurement examples for our advanced PLQY system such as upconversion and NIR emissions.

Studying dangerous chemical reactions using calorimetry and thermal analysis.

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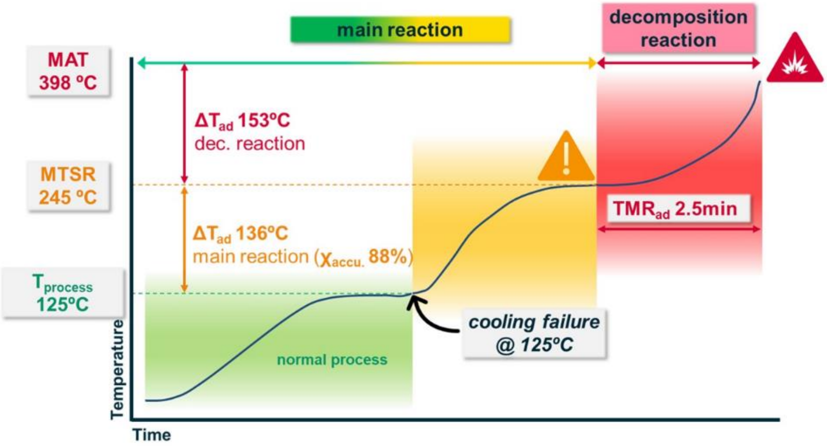
The overall hazard associated with chemical or transformation processes, arises from the combination of the chemistry involved, the intrinsic nature of the materials handled, and the operation/equipment's used. When handling exothermic chemical reactions at large scale, the main safety risk is associated with the loss of temperature control. Therefore, its important to understand how a reaction can shift from its normal course to a runaway condition ultimately leading to a major human and environmental catastrophe. This implies a thermodynamic and kinetic characterization of the reactive system at hand and to convert these results into the safeguards to be implemented at the manufacturing equipment train(1).
In the process safety laboratory at Hovione, our team experts focus on applying a systematic thermal hazards screening methodology to our projects, ensuring eventual dangerous reactions and/or decomposition events do not go unnoticed. A case study of a dangerous aromatic substitution under pressurized conditions at high temperature is presented. In this work, the main reaction and its contents decomposition was characterized using reaction calorimetry and thermal stability analysis. Using the heat flow data generated, two kinetic models were developed and used to predict the outcome of a chemical reaction runaway at manufacturing, thus allowing the selection of adequate safeguards for a safe and successful scale-up.



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3D-Printed Reactors for Photocatalytic Applications

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The interest in additive manufacturing (AM) technologies as a tool to develop and build highly adapted reactors increase with the number of available 3D printer models[1] and materials at lower costs. When projecting photocatalytic systems, some additional parameters must be considered, like radiation field, the interaction of the material of the reactor with the photocatalyst, and the optimization of photochemical reactions, which is more complex than the thermal-activated reactions. This plethora of physical phenomena raises a considerable number of hurdles when moving forward to industrial processes, raising the need for rapid prototyping technologies that enable research of a large number of technical solutions for process intensification in photoreactors.

In this work, a 3D structure was designed to achieve the best light distribution inside a cylindrical batch reactor and printed using the stereolithography (SLA) technique. A hybrid material composed of a commercial photoreactive resin (Formlabs Clear V4) and the benchmark photocatalyst TiO_2 P25 Evonik (1 wt%) was prepared and characterized by scanning electron microscopy (SEM) and rheological and mechanical methods.

To evaluate the photocatalytic activity of the materials, several experiments of the photocatalytic degradation of Rhodamine B (RB) were carried out using the 3D printed structure and its performance was assessed by monitoring the concentration at specific times.

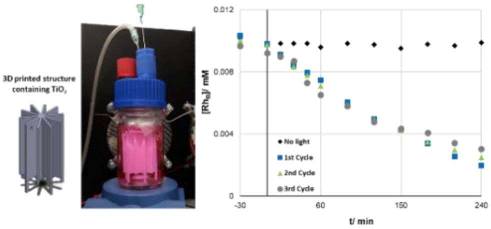

Figure 1. Experimental setup and photocatalytic degradation of RB over 3 consecutive cycles.

In the absence of light, no RB degradation was observed. However, when the reactor was irradiated by 370 nm LEDs, an 80% decrease in RB concentration after 240 min was observed (Fig. 1). Moreover, the photo-stability of the 3D structure was confirmed. Overall, the results demonstrate a simple, cost-effective and fast technique to immobilize catalysts used in photocatalytic applications.

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Writing rules of the measurement results in Chemistry

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The last revision of the International System of Units (SI), that was deeply changed by now being based on fundamental constants of Physics, has been followed with the publication of international documents in metrology[1,2,3]. Transposed at the national scale as national regulations[4], these documents enable also the diffusion of the writing rules for the measurement results, i.e. the good use of the scientific language. In the field of chemistry, the quantity calculus, the names and the symbols for the quantities and the units are displayed and discussed[5,6].

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Simulation of the electrowinning process using green renewable energy sources for industrial iron production.

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Nowadays, despite the rising demand of light materials, iron, namely steel, plays a crucial role in the modern world. Today, the EU is the 2nd largest steel producer globally with a production of 166 million tons of crude steel in 2015. For the time being, the main conclusion is that there are no economically feasible steelmaking technologies available that have the potential to meet the EU's climate and energy targets for 2030. At best, a 15% decrease in the overall CO2 intensity of the sector could be achieved throughout the widespread dissemination of technologies that could reasonably become cost-effective in the future. Therefore, breakthrough technologies are urgent and indispensable. An electrochemically based route is being already developed as a candidate for an alternative to conventional steelmaking processes for CO2-free iron production. Direct electrochemical reduction of iron oxides has been gaining attention as a process allowing in-situ reductions at the cathode, under strong alkaline media.

To find the feasibility of operation with long term interruptions (e.g. to seek preferential operation in low tariff periods), the experiments were performed with step changes in current rather than in potential. The selected experimental conditions comprise cycles with shut down interruptions, and other cycles with an impinged residual current (10%) to ensure cathodic protection. An important difference in deposit microstructure can be observed in subsequent interruption stages without and with cathodic protection. Shut down causes an increase in potential in the re-oxidation range and deeper decrease of potential in the cathodic range on resuming deposition, possibly implying an increase in power consumption. Nevertheless, there are no significant differences in Faradaic efficiency, possibly because potential remains in the safe range to suppress the evolution of hydrogen. Thus, it seems that microstructural changes are the prevailing effect of interruption without cathodic protection in these ranges of potential/current density. Coarser grain sizes observed for unprotected shutdown interruptions may be related to surface re-structuring of the top layer, by re-oxidation during the unprotected interruption and subsequent reduction. Investigation of the cross-sections of the deposits in both regimes doesn't reveal any layer structure. The only deposit where layers were observed was obtained in the regime, where the cathodic protection step lasted 8 times longer than the deposition.

All organic redox flow batteries with tryptanthrin sulfonic acid

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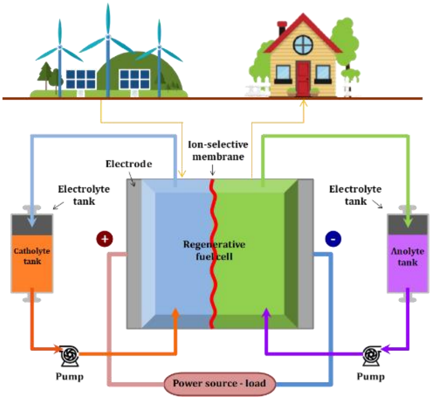
The global and economic population growth impels the increase of energy consumption. Resources formed over hundreds of millions of years have been burned in a relative short time, with substantial environmental impact.[1,2] To reduce the use of fossil fuels, an environmentally friendly route to generate and store electricity from renewable sources is thus mandatory to fulfill the world needs in a sustainable way.[1,3,4] A practical and modern application of storage of chemical energy with, an aqueous organometallic and an all-organic redox flow battery (RFB) with sulfonated tryptanthrin, working at neutral pH and with long-term stability, was developed.



The single cell tests showed reproducible charge-discharge cycles, with high coulombic, voltaic and energetic efficiencies stabilized over several working cycles.

The work paves the way to the promising development of new tryptanthrin based structures for environmentally friendly aqueous all-organic RFBs working at neutral pH values.

Acknowledgements: D. Pinheiro acknowledge FCT for the PhD grant SFRH/BD/74351/2010 and the project "SunStorage - Harvesting and storage of solar energy" for a research grant POCI-01-0145-FEDER-016387. The Coimbra Chemistry Centre is supported by the FCT, Portuguese Agency for Scientific Research, through the Projects UIDB/00313/2020 and UIDP/00313/2020. We also acknowledge the UC-NMR facility for obtaining the NMR data (www.nmrccc.uc.pt).

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Silk-based materials showing prospects for the use of natural proteins in electrochemical devices

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Silk biopolymer has a long history of use in the textile industry and in the biomedical science. The exceptional intrinsic properties of these fibers (e.g., self-assembly, biocompatibility, non-toxicity, and unique mechanical properties) offer a wide range of attractive applications. The incorporation of silk, either as silk fibroin (SF), the core protein of the silk fiber, or as a silk cocoon (obtained literally from nature), in the design of high-tech devices provides significant advantages with respect to traditional materials, including an enhanced eco-friendly label, reliability, and improved safety.

Recently, the use of silk-based materials in lithium ion batteries (LIBs)[1,2] and smart windows (SWs)[3,4] was proposed. The tested LIBs, composed of separators made of *Bombyx mori* SF[1] and cocoons,[2] exhibited good electrochemical performance. Interestingly, the device including a cocoon separator showed self-extinguishing ability thus imparting safety to the battery, minimizing fire or explosion hazards in the presence of flammable organic electrolytes, or even suppressing them in the presence of an ionic liquid.[2] A bioinspired strategy was also employed for the synthesis of green SF-based polymer electrolytes (PEs)[2,3] with outstanding filmogenic properties, very high transparency, and suitable adhesion to glass. Their potential use in electrochromic devices (ECDs) for SWs was demonstrated for the first time.[3] The present bio-inspired approach opens exciting new avenues in materials research, highlighting the potential of natural proteins in energy storage devices and SWs.

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Photochemical H_2 generation by a novel 2D/2D NiCeAl-LDH/g-C_3N_4 nanohybrid

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Photocatalytic hydrogen (H_2) generation via water splitting is considered an ideal approach for clean and sustainable energy. g-C_3N_4 (GCN) is a two-dimensional (2D) optical semiconductor with great potential for water splitting.[1] Still, it presents limited absorption in the visible region (band gap of 2.7 eV) and fast charge carriers recombination. Therefore, the present work aims to enhance the photocatalytic activity of GCN towards H_2 generation by assembling it with NiCeAl-layered double hydroxide (NiCeAl-LDH). Bulk g-C_3N_4 was thermally exfoliated (GCNN) and impregnated with *x*NiCeAl-LDH (x = 0.5, 1, 1.5, 3, and 7 wt%). The photochemical H_2 generation was assessed in an aqueous solution using Pt as a cocatalyst and EDTA as a sacrificial electron donor under vis-LED irradiation (λ = 420 nm, 3 h). In these conditions, NiCeAl-LDH plays a fundamental role in improving the photocatalytic performance of g-C_3N_4. The 1.5NiCeAl-LDH/GCNN nanohybrid presented the highest rate of H_2 evolved, 2035 µmol g^{-1} h^{-1}, *i.e.*, 2 times more than GCNN. The enhanced photocatalytic activity was attributed to efficient interfacial contact between both materials, facilitating the separation of the photoinduced charge carriers. The charge transfer process will be thoroughly discussed, considering the photoluminescence response (steady-state and time-resolved) and photoelectrochemical measurements.

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Study on electric conductivity and electric polarisation of electrodes as indicators of phase transitions

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Broadband Dielectric Spectroscopy allows one to study dielectric relaxation of disordered systems – a gradual return of a system to its equilibrium state after removal of the external disturbance, as the electric field. The dielectric response of systems under study gives information about contributions to the dielectric permittivity from: relaxation process/processes $\varepsilon_{(R.P.)}*(\omega)$, electric conductivity $\sigma*(\omega)$ (contributing to permittivity by $\varepsilon_\sigma*(\omega) = \sigma*(\omega)/i\omega\varepsilon_0$, ε_0 is the permittivity of the vacuum) and, in some cases, electrode polarization of electrodes $B'(\omega)$.[1-3] For the ohmic electric conductivity, its real part does not depend on the frequency and imaginary part equals zero. For the non-ohmic conductivity, the electric conductivity depends on the frequency and its contribution $\varepsilon_\sigma''(\omega)$ is a power function of frequency with an exponent n, for $0 < n \leq 1$.[2,3] The electrode polarisation is an unwanted effect during dielectric experiments. The molecular origin of the electrode polarisation is a partial (or a whole) blocking of charge carriers at the interface between the sample and electrode areas, leading to a separation of positive and negative charges giving a rise to an additional polarisation. The contribution of the electrode polarisation to the real part of the dielectric permittivity is a power law of the frequency with an exponent m, for $0 \leq m \leq 2$.[2,3] It will be shown that the exponents n and m take the appropriate values depending on a thermodynamic phase. Thus, they are excellent indicators of phase transitions. Analyses will be presented for various phases of different liquid crystals and soft matter compounds.

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Carbon Nanotube/Transition Metal Dichalcogenide Composites via Surfactant-Assisted Dispersions as Electrocatalysts for Oxygen Reactions

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Long-lasting and clean energy devices, such as fuel cells and metal air batteries, are crucial to the development of future energetic sustainability. These devices are dominated by the oxygen-based reactions, oxygen evolution reaction (OER) and oxygen reduction reaction (ORR), which exhibit slow kinetics and require the use of catalysts.[1-2] In this work, we prepared nanocomposites based on multiwalled carbon nanotubes (MWNTs) and transition metal dichalcogenides (TMDs), namely WS_2 and MoS_2, and evaluated their performance as electrocatalysts for the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR). First, the 1D and 2D building blocks were exfoliated and non-covalently functionalized by surfactants of opposite charge in aqueous media, using an optimized and strictly controlled methodology.[3] This step was followed by the assembly of the 3D composites via surfactant-mediated electrostatic interactions.[4] SEM imaging show relevant structural differences between the prepared nanocomposites. Electrocatalytic studies indicate that, although WS_2@MWNT and MoS_2@MWNT show moderate ORR performance, the latter exhibits promising results for OER, with the composite showing better activity than the individual building blocks. This work paves the way for further electrocatalyst performance optimization, using a cost-effective, robust and versatile methodology.

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Pristine carbon nanotubes for an efficient L-asparaginase immobilization

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The enzyme L-asparaginase (ASNase) presents effective antineoplastic properties for acute lymphoblastic leukemia treatment, besides their potential use in the food sector to decrease acrylamide formation. Considering their applications, the improvement of these enzyme properties by efficient immobilization techniques is in high demand. Carbon nanotubes are promising enzyme immobilization supports since these materials have increased surface area and effective capacity for enzyme loading. Accordingly, in this study, multi-walled carbon nanotubes (MWCNTs) were explored as novel supports for ASNase immobilization by a simple adsorption method. The effect of pH, the contact time of immobilization, and the ASNase to nanoparticles mass ratio were optimized according to the enzyme immobilization yield and relative recovered activity. The enzyme-MWCNTs bioconjugation was confirmed by thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and transmission electron microscopy (TEM) studies. MWCNTs have a high ASNase loading capacity, with a maximum immobilization yield of 90%. The adsorbed ASNase retains 90% of the initial enzyme activity at the optimized conditions (pH 8, 60 min, and 1.5×10^{-3} $g.mL^{-1}$ of ASNase). According to these results, ASNase immobilized onto MWCNTs can find in several areas improved applications, namely biosensors, medicine, and the food industry.

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Surface Studies on ZnS/Graphene Oxide Nanostructures Using 4-Mercaptopyridine as Molecular Probe

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Graphene oxide (GO) has been widely explored as a platform for producing hybrid materials exhibiting synergistic properties of interest in heterogeneous (photo)catalysis. However, there has been less emphasis in demonstrating that such properties are intrinsic to the nature of the hybrid material. In this work, we demonstrate that surface-enhanced Raman scattering can be easily explored to probe certain regions of GO sheets decorated with a semiconductor (ZnS). In particular, our studies reveal an enhancement of the Raman signal of 4-mercaptopyridine (4-MPy), which was used as a molecular probe, upon adsorption on ZnS@GO materials when compared to adsorption on the separated parent ZnS powders or GO flakes. The GO sheets in the composite play an important role in the enhancement of the Raman signal observed for this molecular probe because they create energy levels within the ZnS energy gap. This hypothesis was further confirmed by electronic density functional theory calculations employed to investigate the adsorption mechanism of 4-MPy on both ZnS and ZnS@GO substrates. The calculated results are in accordance with the experimental data, predicting the adsorption mode on both S and Zn surface sites, with preference toward the sulfur atom due to the influence of GO.

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Poster Communications

Effect of poly(vinyl alcohol) on the water sorption and kinetics of tissue paper

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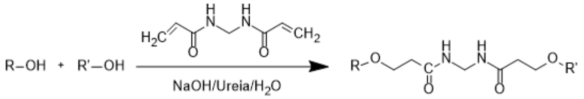
The tissue paper market has been growing. The consumers increasing health and hygiene awareness, along with better living standards have been driving the global growth on this market.[1] However in order to meet consumer's demand, on this increasingly competitive market, tissue papers need to be improved and exhibit differentiative performance on their key properties. Among all properties water absorption is a key property, that defines the ability of tissue paper to absorb and contain water. In order to enhance this key parameter, we have studied the effect of modifying pulp with poly(vinyl alcohol) – PVA. PVA is non-toxic and non-carcinogenic and is easily processed. Additionally, PVA gels exhibit a high degree of swelling in water and a rubbery and elastic nature. [2] Our approach was based on the use of PVA, with different molecular weights: 61000 g mol^{-1} and 27000 g mol^{-1}, which was crosslinked with pulp fibers using *N,N'*-methylene-bis-acrylamide as crosslinker. Scheme 1 represents the crosslinking reaction.



Scheme 1: Chemical crosslinking between two polymers, using MBA as crosslinking agent.

The obtained blends were characterized by FTIR, TGA and SEM. The water absorption capacity was evaluated by the basket method (ISO 12625-8) using a Frank-PTI equipment. The water desorption kinetic was also obtained and the results were discussed on the basis of kinetic models. The results have shown that the handsheets containing PVA with the lower molecular weight increase their water absorption capacity by 23%.

Acknowledgements: This work was carried out under the Project inpactus – innovative products and technologies from eucalyptus, Project N. º 21874 funded by Portugal 2020 through European Regional Development Fund (ERDF) in the frame of COMPETE 2020 nº246/AXIS II/2017. Financial support from Coimbra Chemistry Centre, which is supported by the FCT through the programmes UID/QUI/00313/2020 and COMPETE, is gratefully acknowledge.

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Nickel separation via adsorption by an ORMOSIL aerogel modified with a Schiff base

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A Schiff base modified silica aerogel was developed as a selective nickel adsorbent by including a salen ionophore in the silica network. Nickel is a good example of a heavy metal used as raw material in different industries [1-2] and thus, has increasing commercial value [2-3]. The recovery of this metal from wastewaters is worthwhile, and, in this work, it was investigated by adsorption. This process was shown to be efficient for metal cations in general [4].

Schiff bases are the most common family of nickel ionophores [5] and their inclusion in the silica network was confirmed by NMR analysis. Adsorption isotherms and kinetics with single and binary mixtures of cations were studied to assess the selectivity of the adsorbent. It was found that nickel adsorption is higher than for the remaining cations and is well described by a BET isotherm model. This trend was found for most cations and the likelihood of cation multilayers formation is discussed. The adsorption of binary mixtures revealed a high affinity for both copper and nickel by the Schiff base modified aerogel. Nickel removal is not affected by the presence of competing species (Cu, Pb, Cd), showing a significant selectivity adsorption onto the adsorbate.

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Dancing with oils – The interaction of lipases with different oil/water interfaces

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The use of enzymes as biocatalysts in industrial applications has received much attention during the last years. Lipases are on the forefront of this topic.[1] These enzymes are widely employed in the food and cosmetic industry, and more recently have been used for the synthesis of novel biomaterials and as a greener solution for the treatment of waste cooking oils (WCO). The latter topic has been widely explored in the literature, comprising the use of enzymes from several origins and types, for the treatment of used and non-used cooking oils from different origins.[2] The experimental conditions of these works are also quite broad. As a consequence, it may be difficult to extract a consolidated knowledge from these data. In this work we provide a clear picture of the interaction process taking place in many of these studies by presenting a detailed characterization for the interaction of commonly used lipases with several types of vegetal oils and food fats through coarse-grained molecular dynamics simulations. The work includes nine proteins and eight different types of oil/water (O/W) mixtures. First, the molecular details of the O/W mixtures, namely at the O/W interface, are described. The O/W interface was found to be enriched in triglyceride molecules with higher polarity. Then, the interaction of the lipases with oil mixtures is characterized from different perspectives, including the identification of the most important protein residues for this process. The lipases TLL, RML and CALB were found to bind to the O/W interface in a manner that makes the protein binding site more available for the oil molecules. These enzymes were also found to efficiently bind to the O/W interface of all oil mixtures, which in addition to reactivity factors, may explain the efficient applicability of these enzymes to a large variety of edible oils, such as WCO.

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NaCl effect on the rheological properties and aggregates formation of anionic, non-ionic and amphoteric mixed surfactants systems

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Surface-active molecules, such as surfactants are one of the most important type of molecules in life, due to their specific amphiphilic properties in aqueous solutions. They are present in the most of the personal care products of daily life, like shampoos, soaps, and also foods, among other examples. It is well known that many amphiphilic self-assembled structures, have in their constitution anionic, cationic, non-ionic or amphoteric surfactants, in their isolated form or in mixtures. In the literature, relevant systems of surfactant mixtures with improved properties are described. Most of these studies are related to binary systems, an only a few ternary systems are described. The knowledge about these system are of great importance for many industries. [1,2] The present study focuses the effect of NaCl addition to aqueous solutions containing different surfactants systems: Sodium laureth sulfate (SLES – anionic), alkyl polyglycoside (APG – non-ionic) and betaine (amphoteric), mixed in different concentrations. The study was performed in terms of rheological properties and microstructure analysis.

It was concluded that the concentration of different surfactants and the presence of an electrolyte have a clear influence on the type and shape of the surfactant aggregates formed, as well as the viscosity dependence on shear rate. [3,4]

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Data Driven Tools to Select Corrosion Inhibitors

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Metallic corrosion control and mitigation is key for many high-performance applications, including automotive and aeronautical industries, as well as in biomedical engineering, having the potential to reduce its cost, which every year is equivalent to 3-4 % of the global GDP.

Organic corrosion inhibitors embedded in coatings play a crucial role substituting traditional anti-corrosion pigments, which can cause acute toxicity problems to human health and the environment. However, why some organic compounds inhibit corrosion and others do not, is still not well understood. Therefore, we are currently developing two complementary technological approaches to help corrosion scientists and engineers working in academia and across different industries choose the optimal inhibitor for each specific problem: 1) build an interactive exploratory data tool for the selection of the ideal corrosion inhibitor taking into account different conditions (type of alloy, electrolyte, pH, etc.) based on previously published information (https://datacor.shinyapps.io/cordata/), and 2) develop machine learning models and an online tool to perform an initial virtual screen of potential molecules for the design of more efficient organic corrosion inhibitors (1). These two approaches will contribute to the digitalization of inhibitor search, helping speed up research in the corrosion science and tailor corrosion protective technologies in a more efficient and condition specific manner.

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Physical and chemical characterization of *Cercis siliquastrum* L. (Olaia) leaves

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Superhydrophobicity is one of the most fascinating water-wetting features of the surface of many plants. In recent years the interest for the production of superhydrophobic synthetic surfaces inspired in the surface of plant leaves and petals has not ceased to increase.[1,2] Superhydrophobic features, such as “self-cleaning”, “anti-acing”, “anti-fogging”, “anti-fouling”, and “anti-drag” offer excellent prospects for the design of new materials with high technological interest and high added value for specific targeted applications, opening challenging new directions in materials science and related technologies.

This work has been focused on the study of the physical-chemical properties of the leaf surfaces of *Cercis siliquastrum* L. (Olaia, family Fabaceae), a small deciduous tree from Southern Europe and Western Asia, and often found in European gardens. The adaxial (top) and abaxial (bottom) leaf surfaces feature hydrophobic and *quasi* superhydrophobic behaviour, respectively, with contact angle values of 131.4±0.2º-135.6±0.2º and 134.6±0.7º-152.9±0.2º, respectively. The morphology and chemical composition of the waxes, and the optical properties of the leaf surfaces have also been analyzed.

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Langmuir Films of Ionic Liquids: Mono and Multilayers of [$C_n$mim] [X] n = 18,20 X^- = NTf_2^-,Cl^- at the Air-Water Interface

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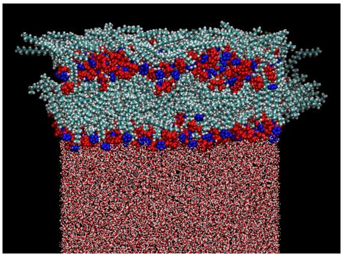
Room-temperature ionic liquids have received a rapidly increasing interest as a new type of fluids and a promising environmentally friendly alternative to conventional solvents, to be used in a large number of applications. Many of these applications involve processes that take place at interfaces, either at the liquid-vapour interface of a pure IL or solution, or at the liquid/solid interface between an IL and a solid surface. The study of the interfacial properties of ILs, pure or in solution, is therefore of utmost importance for the development of these technological applications, since their properties can be significantly different from those of the bulk liquids. Despite its importance, the knowledge of the structural properties of ILs at the air/water interface is still quite poor. A better understanding of the behaviour of ILs at this interface can be obtained studying the formation of thin films through the Langmuir and Langmuir-Blodgett techniques. To date this is a largely unexplored field.

In this work we have studied the behaviour of films of ILs of the methyl-imidazolium family at the air-water interface using a Langmuir trough. The films were characterized by Brewster angle microscopy (BAM), Grazing Incidence X-ray diffraction (GIXD) and X-ray reflectometry (XRR). In the case of [C_{18}mim][NTf_2] and [C_{20}mim][NTf_2] we have direct evidence of the formation of mono and multi layers of these ILs at the air-water interface. Molecular Dynamics simulations provide a molecular level interpretation of the experimental results.[1]



Simulation snapshot (side view) of a Langmuir film of [C_{20}mim][NTf_2] at 0.24 nm^2/molecule.

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Understanding the leaf surfaces of *Phyllostachys nigra*

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Using nature as inspiration, Biomimetics studies its models and then adapts them to design artificial materials and sustainable systems, such as nanomaterials, nanodevices, and smart coatings.[1] Green plants, very abundant in nature, are characterized by a diversity of hierarchical surface structures that can be employed as models for the development of biomimetic surfaces.[2] The wettability behavior, one of the most extraordinary properties exhibited by a plant surface, results from the interplay between the leaf's morphology (physics) and wax composition (chemistry).

The present work is focused on the wetting behavior of the leaves of *Phyllostachys nigra* specimens (black bamboo), one of the most popular Bambusoideae (family Poaceae) from eastern and center China, very frequent in the European gardens. *P. nigra* plays an important role in therapeutics and folkloric medicine. The fresh plant material was collected at the UTAD Botanical Garden.[3] The current study is fundamental for a comprehensive study of the wetting phenomena of natural structures and the pursuit of the correlation between multiscale structures and wettability. Such approach allows using plant surfaces as biotemplates for the production of advanced materials with enhanced features.

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P9

Butler Equation for the Surface Tension of Liquid Mixtures: A re-examination

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The surface tension and interface composition in equilibrium with underlying liquid mixtures has been determined, over the last century, using Butler equation.[1] Several analyses[2,3] prompted its re-examination seeking for concealed approximations. An independent derivation of Butler equation allowed the identification of a shortcoming, which is not allowing surface standard values to vary with surface tension by virtue of changing composition was identified.

This alternative derivation accounts for the variation of standard chemical potentials with changing surface tension from its value for pure components, to its value at the composition of interest. Furthermore, it reduces to the classical Butler equation for incompressible surface phases, as argued by Rusanov.[4]

A quantitative evaluation of this hidden approximation effect was performed for the molecular liquid mixture water–ethanol at 298.15 K and for the metallic liquid alloy cooper–tin at 1400 K, and shown to be within experimental error in terms of ideal surface tension and irrelevant in terms of surface phase compositions (<15%) .

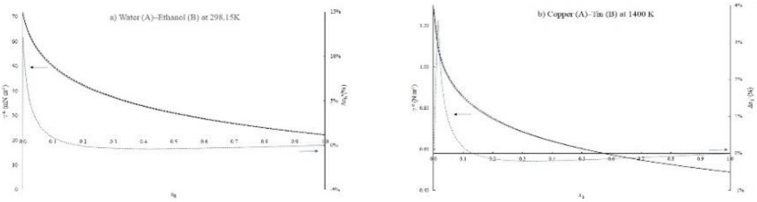

Figure 1. a) Ideal surface tension, γ^{id}, versus bulk mole fraction of component B, x_B. Solid lines for alternative model and broken lines for Butler's model; b) Difference between estimated surface mole fractions by the alternative and Butler´s equation, expressed as % deviation from the alternative model

Butler equation is shown to provide an explicit and simple mathematical expression for the ideal surface tension and surface phase composition of liquid mixtures, which can be confidentially used in view of the inconsequential deviations it encompasses.

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Catanionic vesicles from lysine-based surfactants for the delivery of bioactive plant extracts

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The use of colloidal nanocarriers in drug delivery applications has been steadily growing over the years with a constant demand for ever more effective vectors and novel bioactive compounds. Amino acid-based surfactants are interesting building blocks due to their reduced cytotoxicity, versatile aggregation properties and stimuli sensitivity.[1,2] In this work, we studied several anionic surfactants based on the amino acid lysine (designated as *m*Lys*n*) in a mixture with a varying molar fraction (x_+) of either cationic 12-*n*-12 gemini or cationic single-tailed surfactants (DTAB or CTAB) with the intent of forming spontaneous and stable catanionic vesicles. These vesicles are aimed at encapsulating a *C. cardunculus* extract enriched in cynaropicrin, a sesquiterpene lactone with great therapeutic potential.[3]

The phase behavior of the *m*Lys*n*/gemini and *m*Lys*n*/single tailed was characterized so as to select the most promising vesicular systems. The systems 10Lys12/12-3-12 (x_+=0.50), 12Lys8/12-3-12 (x_+= 0.30 and 0.50), 12Lys8/DTAB (x_+=0.50 and 0.60), 12Lys8/CTAB (x_+=0.50) and 14Lys8/CTAB (x_+=0.60) were selected and thus their interfacial properties were also studied by surface tension. All catanionic mixtures exhibit high synergistic effects, having reduced critical aggregation concentration than the neat surfactants. DLS assays provided the size, polydispersity and zeta potential of the catanionic vesicles. The 10Lys12/12-3-12 (x_+=0.50) and the 14Lys8/CTAB (x_+=0.60) show the largest vesicles, while the 12Lys8/single-tailed systems have the smallest and less polydisperse vesicles. Lastly, the encapsulation efficiency and loading capacity of the vesicular systems was evaluated, from which we concluded that the 10Lys12/12-3-12 (x_+=0.50) and 14Lys8/CTAB (x_+=0.60) vesicles show the most effective encapsulation properties.

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Surface modification of ZnS colloidal quantum dots with porphyrin: an approach to novel nanoassemblies

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Quantum dots (QDs) are semiconductor nanoparticles that show quantum size effects and exhibit a unique set of optical properties, as large absorption coefficients, size-tunable band structure and high fluorescent quantum yields[1]. QDs have been explored in broad application areas, including nanomedicine. QDs have been combined with organic dyes such as porphyrins for applications in biology and medicine [2] as well for nanosized sensors [3].

We decided to take advantage of the enhanced properties of these nanoassemblies quantum dots-porphyrins and evaluated their potential in luminescence thermometry. Here we will report the preparation of nanosized ZnS QDs reverse micelles and their conjugation with 5,10,15,20-tetrapentafluorophenylporphyrin by self-assembly processes. The optical properties of the hybrids by ultraviolet-visible spectrophotometry (UV-Vis), and steady fluorescence spectroscopy will be presented and discussed in detail. The preliminary studies of the hybrids as novel optical thermometers, where a dual sensing is observed, will be highlighted.

Acknowledgements: Thanks are due to FCT/MCTES for the financial support to CESAM (UIDB/50017/2020 + UIDP/50017/2020), CICECO (UIDB/50011/*2020* & UIDP/50011/*2020)* , QOPNA and LAQV-REQUIMTE (FCT UID/QUI/00062/2019, UIDB/50006/2020 and UIDP/50006/2020) through national founds and, where applicable, co-financed by the FEDER, within the PT2020 Partnership Agreement, and to the Portuguese NMR Network. This work was supported by the project [Corlutna (POCI-01-0145-031523)] funded by FEDER, through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI), and by national funds (OE), through FCT/MCTES.

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P12

Coarse-Grained Reactive Silica Model for Classical Molecular Dynamics Simulations

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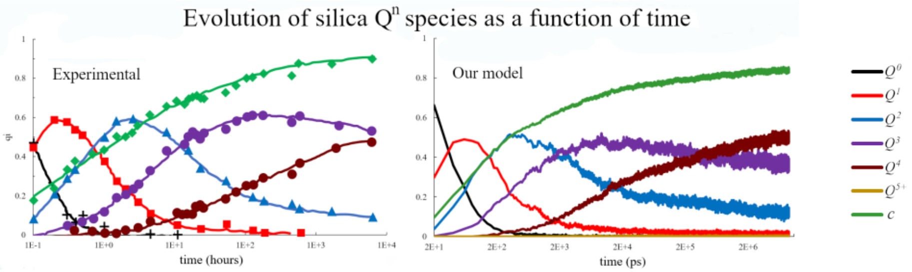
Tailoring the formation of ordered nanoporous materials, such as periodic mesoporous silicas (PMS), requires the understanding of the mechanistic details of their synthesis at the atomic scale. This is fertile ground for computer simulations but, unfortunately, current models cannot cope with the formation and breakage of chemical bonds in molecular systems constituted by many thousands of particles. Herewith, a new computational paradigm is presented, which is shown to handle the silica polymerization reaction in aqueous medium at room temperature. Encouragingly, the calculated temporal variation of the degree of silica polymerization agrees with that from nuclear magnetic resonance (NMR) experiments.

The simplicity of the model, which has been implemented within the MARTINI coarse-grained force field and the free and widely distributed Gromacs computer code, allows it to be applied to more complex systems like aqueous solutions of cationic surfactants and silicate monomers involved in PMS synthesis.



Acknowledgements: The research carried out at the CICECO – University of Aveiro Institute of Materials was developed within the scope of projects UIDB/50011/2020, UIDP/50011/2020 and CENTRO-01-0145-FEDER-31002 (SILVIA, ref. PTDC/QUI-QFI/31002/2017), financed by the Portuguese Fundação para a Ciência e a Tecnologia (FCT/MCTES), and co-financed by the European Regional Development Fund (FEDER) under the PT2020 Partnership Agreement. GPS acknowledges the national funds (OE), through FCT – Fundação para a Ciência e a Tecnologia, I.P., in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19.

P13

On the calculation of diffusion coefficients of pesticides by employing molecular dynamics simulations

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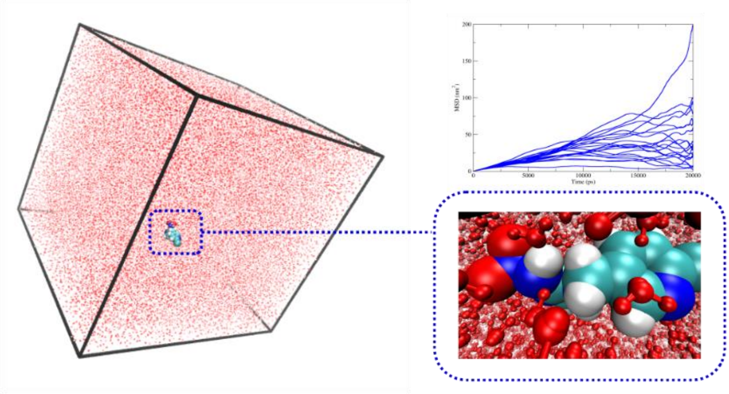
The use of pesticides leads to serious environmental problems, which requires insightful knowledge of their physicochemical properties. Diffusion has an important role in the transport of pesticides in the ground water. Thus the accurate values of the diffusion coefficients are relevant data to evaluate the impact of their use in agriculture. In this context, employing the best practices for computing transport properties, diffusion coefficients of pesticides (e.g. cymoxanil, imidacloprid and pirimicarb) in water were determined by molecular dynamics simulations.[1] Particularly, the effect of the concentration and simulation time on the calculated diffusion coefficients was investigated. The calculated results were compared with recent experimental data.[2,3] The analysis of radial distribution functions of water around pesticides and the number of hydrogen bonds provides a better understanding of the intermolecular interactions and their connection with the diffusion coefficients.



Acknowledgments: We acknowledge the support from the Coimbra Chemistry Centre (CQC), which is financed by the Portuguese "Fundação para a Ciência e a Tecnologia" (FCT) through the Project UIDB/00313/2020, co-funded by COMPETE2020-UE.

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P14

A molecular dynamics study of ionic interchange for (Zn_2Al) layered double hydroxides materials

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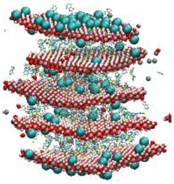
Corrosion inhibitors are playing an important role for protective technologies on a large number of applications. The smart materials for corrosion protection, particularly layered double hydroxide (LDH) nanocontainers provide an active protection effect.[1–6] The previous results of a MD study of a realistic Zn_2Al layered double hydroxide (LDH) model with intercalated MBT species was characterized with a great relation of experimental results.[7] Moreover, the simulation of nitrate intercalated in Zn_2AL layered double hydroxide was demonstrated a good stability in a corrosive sodium chloride water solution.[8]This smart material work a different mechanisms of protection, from the passivation by the occupation of surface to the caption of corrosive species, such as the Chloride. Different mechanism of protection would be happen, such as the delamination and reorder with other ions. The difficulty to characterize the interlayer of LDH with experimental techniques demands theoretical methods. In the interest of computational tractability, the choice for investigating these systems relies on the classical molecular dynamics (MD) simulation approach.



It this communication, we will present the results of a MD study of a realistic Zn_2Al layered double hydroxide (LDH) model with intercalated MBT and Nitrate species in a cluster model with a solution of Chloride. The analyses of the trajectories show the difference of mechanism occurs during the ionic interchange of ions of interlayer of LDH and the Chloride ions of solution. The ion-exchange is carried out by a rearrangement of the layers, the interlayer spacing being key for the kinetic ionic interchange.

This work was developed in the scope of projects CICECO – Aveiro Institute of Materials, refs. UIDB/50011/2020 and UIDP/50011/2020, financed by national funds through the Fundação para a Ciência e a Tecnologia (FCT/MEC) and co-financed by FEDER under the PT2020 Partnership Agreement, and in the framework of projects DataCor (refs. PTDC/QUI-QFI/30256/2017 and POCI-01-0145-FEDER-030256) and SELMA (ref. P2020-PTDC/QEQ-QFI/4719/2014), financed by Promover a Produção Científica e Desenvolvimento Tecnológico e a Constituição de Redes Temáticas and FEDER funds through COMPETE 2020.

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$H + O_2 + M \rightarrow HO_2 + M$ A Termolecular Reaction Pressure Dependence Study

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To study the rate of elementary reactions and their dynamics, we use Potential Energy Surfaces, being useful to compute state-to-state rate constants. The usual approach to study such system is to make use of all the system's available rate constants and build a system of master equations. This procedure assumes that reactants are in thermal equilibrium. Studies seem to indicate that the number of non-reactive collisions can be small and the energy distribution of the intermediate species may be far from the Boltzmann distribution. MreaDy[1] program (Multi-process Reactions Dynamics), aims to reproduce complex mechanisms, such as the hydrogen combustion, using accurate PES. We have introduced modifications on this program in order to study the pressure dependence of the reaction $H + O_2 + M \rightarrow HO_2 + M$. This reaction is one of the main sources of uncertainty when modelling hydrogen combustion chemistry, and being a termolecular reaction, it cannot be studied using normal classical trajectory programs. We start with hydrogen atoms and oxygen molecules, forming by collision excited HO_2* radicals. We can count how many of the excited HO_2* radicals are stabilized by collisions at 1500, 2000, and 2500 K and pressures of 10, 30 and 50 atm., and we calculate the formation rate of stable HO_2 radicals. We present results for this process showing a clear increase of the rate constant with pressure. We are also able to study the rate constants of the different reactions present in the system.

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Hydrogen combustion in carbon nanotubes: defining the nanotube behaviour

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Carbon nanotubes (CNTs) has attracted a widespread attention due to their intrinsic properties making them versatile materials with possible applications in a wide-range of fields[1-3]. Motivated by the application of these structures as nanoreactors[4], our research group has been recently developing theoretical studies to determine the effect of single-walled carbon nanotubes (SWCNT) in the hydrogen combustion process.

Modelling the hydrogen combustion reaction confined in the nanoscale environment implies the effective control of the initial conditions of position and velocity for the present particles so as to reproduce the pressure and temperature for the system. In the case of reactants, the initial velocities of the gas particles were randomly generated according to a Maxwell-Boltzmann distribution for a given temperature. In contrast, we did not find a standard procedure to define the initial conditions for the carbon nanotube, being this the subject of the present presentation.

Once specified the temperature, pressure and the number of reactive particles, the nanotube volume has been defined assuming a perfect gas behaviour of the mixture. The number of carbon atoms and nanotube length is then calculated from the nanotube diameter. Using the equilibrium distances between the carbon atoms their initial positions has been computed generating the carbon nanotube. The velocities of the carbon atoms are then randomly generated with the restrictions of zero total linear and angular moments of the nanotube and the total kinetic energy reproduce the nanotube temperature. To control this temperature, we propose a method that involves the application of Argon as a "thermometer".

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DFT and TD-DFT studies of Ground and Excited State Properties of Free and Adsorbed Ru(II) Terpyridine Dyes

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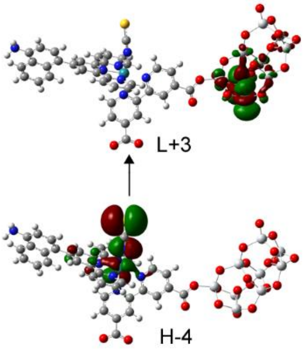
The performance of a series of Ru(II) substituted terpyridine dyes as sensitizers for TiO_2 dye-sensitized solar cells (DSSCs) was analyzed using a multidisciplinary approach. DFT and TD-DFT studies were carried out in order to rationalize and correlate the photovoltaic performance of the TiO_2 DSSCs with structural differences exhibited by the studied sensitizers.

In particular, geometries, frontier molecular orbitals and vertical electronic excitations of the complexes, both as free species as well as adsorbed on a $(TiO_2)_9$ cluster, were calculated. For all the studied chromophores, geometry optimization of the dye/TiO_2 system led to structures with a unidentate linkage between one of the COO^- groups of the dye and one Ti atom of the $(TiO_2)_9$ cluster. The DFT and TD-DFT results allowed to analyze the efficiency of the dyes in terms of electronic transitions involving charge transfer from the dyes into the semiconductor upon excitation.



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The OH + CH3OH → CH3O + H2O, a Barrierless Process at Low Temperatures

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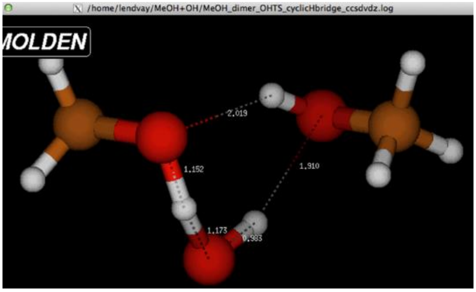
The removal of a hydrogen atom from a methanol molecule by the hydroxyl radical producing water and hydroxymethyl or methoxy radicals has been suggested[1] to be a possible source for the presence of methoxy radicals detected in interstellar space.[2] The experimental results display a peculiar behaviour: at temperatures above 200 K the formation of hydroxymethyl radical, CH2OH, dominates with a thermal rate constant that increases with temperature; however at temperatures below 200 K the product CH3O dominates, but the thermal rate constant decreases with temperature, halving its value when temperature increases from 50 K to 200 K. Theoretical calculations [3] on this system have shown that the production of CH2OH involves an energy barrier of 0.5 kcal mol-1, while the direct production of the methoxy radical, CH3O, involves a barrier of 2.54 kcal mol-1.

To explain the low temperature behaviour, Siebrand et al.[3] studied the role of the presence of the methanol dimer on this process. Here we present an alternative explanation to the experimental findings, keeping the idea of the importance of the presence of the dimer at low temperatures, which they showed to dominate at T < 100 K, being negligible at T > 150 K. We have carried out DFT calculations using B3LYP and MO8-SO functionals for the direct removal of the hydrogen atom from the dimer by the hydroxyl radical and found that this process occurs without barrier. Thus, the reaction rate will be dominated by the capture process known to have a negative temperature dependence.



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Hydrogen Combustion in Nanotubes

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We present preliminary studies on the effect of carbon nanotubes in the combustion of molecular hydrogen. The confinement of reactants in nanoscale media has been the subject of recent experimental and theoretical studies. In particular, the confinement of molecules in carbon nanotubes has shown to have considerable effect on increasing their reactivity at low temperatures. This has been justified by orientation effects of the confined reactants and to the increase of the collision probability due to reflection on the nanotube walls. Over the last years, it has been reported that small systems have properties that large systems have not.

According to the standard combustion theory[1], gas mixtures in small volume containers are not able to react. This is due to the absence of an ignition mechanism to produce initial radicals in the reactor and to the reaction inability to sustain itself, since the heat escapes too quickly. Despite that, recent work in nano and micro nanobubbles[2,3], produced in microsystems using electrochemical decomposition of water with a fast switching of voltage polarity, has demonstrated that nanobubbles containing the stoichiometric mixture of H_2 and O_2 disappear very quickly due to the spontaneous reaction and the short-lived microbubbles, formed by coalescence of H_2 and O_2 nanobubbles, ignite the reaction destroying the bubble in a short time provoking pressure jumps and temperature raise between 20 and 60 ºC. The pressure jumps have been proposed to be used in a new type of microengine[4]. According to the authors, the reaction mechanism is not yet clear, but it is obvious that the process is surface dominated and happens without significant temperature increase[2].

Recently, we have developed an innovative method to model complex systems. The MReaDy[5] program builds a global Potential Energy Surface (gPES), defined by integrating diverse PESs, each one of them representing an elementary reaction that is expected to play a role in the chemical process. The program MReaDy, which has shown to accurately model the gas phase combustion of a mixture of hydrogen and oxygen, has been adapted to study the same reaction confined in a carbon nanotube at different conditions of nanotube diameter, gas pressure and temperature. To accomplish this, we introduced a full potential for the carbon nanotube, including carbon-carbon vibrations and intermolecular forces between the carbon atoms and the reactant molecules.

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Energetic study of 5-methyl-1H-benzotriazole

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Triazole derivatives constitute an important class of compounds due to their applications in several fields, in particular in chemical pharmacology. It is possible to highlight studies of triazoles used as anti-cancer agents previously reported.[1]–Other applications of this kind of molecules include a wide range of fungicides[2] and also as explosives[3].

The thermodynamic characterization of these compounds, namely the knowledge of the respective thermophysical and thermochemical properties, is essential to evaluate and understand their reactivity. In this context, the present work reports an experimental and computational study of 5-methyl-1H-benzotriazole, presented in Figure 1.

The study of 5-methyl-1H-benzotriazole has been performed using static bomb calorimetry and high level ab initio calculations, at the G3(MP2)//B3LYP level of theory[4], leading respectively to its enthalpy of combustion and to the gaseous enthalpy of formation.

Furthermore, the energetic effect associated with the presence of a methyl group in the benzotriazole structure was evaluated. This enthalpic increment is compared with homologous substitutions in the benzene and naphthalene molecules.

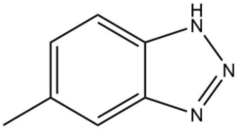

Figure 1 − Molecular structure of 5-methyl-1H-benzotriazole

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Quasi-classical trajectory study of the $O(^1D) + H_2O(X^1A_1)$ reaction

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The reactivity of the oxygen atom in the first excited electronic state, $O(^1D)$, is important in various fields of chemistry, and its reaction with water plays na important role in the HO_x chemistry, which in turn participates in the stratospheric ozone depletion.[1]

Several years ago a full dimensional potential energy surface (PES) for the ground state hydrogen peroxide molecule, H_2O_2, was developed by our group.[2] Recently, this PES was improved to accurately reproduce all the reaction channels and the minimum energy pathways for the different chemical reactions involved in the $O(^1D) + H_2O(X^1A_1)$ reaction system (see Figure 1). The aim of this work is to study theoretically the gas phase reactions involved in the $O(^1D) + H_2O(X^1A_1)$ system, considering this new full dimensional ground state PES.

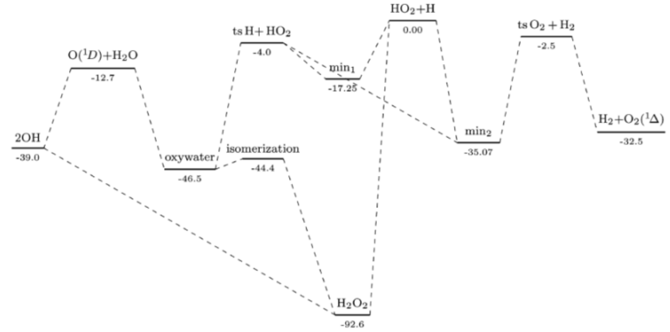

Figure 1. Energy diagram, in kcal ΔΔmol^{-1}, connecting the stationary points and dissociation channels for the ground state potential of the H_2O_2 system. The energies are given in relation to the H + HO_2 dissociation energy.

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Mixed Hydrogenated and Fluorinated Ionic Surfactant Solutions: Towards designing compartmentalized nanostructures

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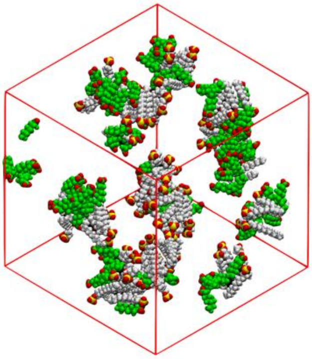
Perfluorinated compounds have found significant applications in industry, such as hydrophobic coatings, packaging, refrigerants, firefighting foams and lubricants. However, their use has been under scrutiny due to their environmental impact. Their high stability, conferred by the strongest known C-F single bond, although very useful, also means they accumulate in the environment at an alarming rate, either in animal tissues and eggs, in the atmosphere or in water basins. Thus, it is very relevant to study the behavior of these substances in water, in order to find suitable candidates for decontamination/separation processes.



Fluorinated surfactants are known to form micelles at very low concentration due to their enhanced hydrophobic character. Additionally, fluorinated chains also tend to segregate from hydrogenated chains, giving rise to interesting debates on the structure of aqueous micellar solutions containing fluorinated and hydrogenated surfactants. Indeed, the interpretation of experimental data on these systems (fluorescence[1], SANS[2] and NMR[3]) has not been consensual. While most authors agree on the large deviations to ideality of these mixed systems, some have proposed that there is intermicellar separation, while others defend that either partial or complete intramicellar segregation occurs. Relying on our accumulated experience on the experimental and computational studies of mixed hydrogenated and fluorinated systems, in this work we used atomistic molecular dynamics simulations to obtain molecular level information, which can help clarifying this controversy. Our simulation results seem to indicate that intramicellar segregation occurs in mixtures of hydrogenated and fluorinated surfactants with similar positive or negative charge. These results can have significant impact on the design of compartmentalized supramolecular nanostructures.

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New insights into BCRP efflux mechanism through Molecular Dynamics Simulations

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ABCG2 is an ATP-binding cassette (ABC) protein transporter closely associated with the development of multidrug-resistance (MDR) when overexpressed in cancer cells. The efficient modulation of the ABCG2 function has been pointed as a powerful therapeutic strategy to overcome MDR by improving the pharmacokinetics and efficacy of chemotherapeutic agents. However, the development of clinically useful modulators of ABCG2 has been hampered by the lack of knowledge about the structural and functional understanding of this efflux pump [1]. The publication of the first Cryo-EM structure of human ABCG2 (PDB ID: 5NJ3) in 2017 [2] brought new information and demanded new independent assays to get new insights on the ABCG2-efflux mechanism.

In this communication, we will present our contributions in clarifying key points of the mechanism of ABCG2-substrate recognition and ATP-driven transport as well as on the structural basis of small-molecule inhibition of ABCG2 efflux. A refined model of full-length ABCG2 was built based on the incomplete cryo-EM structure and our previous homology model[3] and refined through molecular dynamics (MD) simulations at physiological conditions. To understand how ABCG2 conformational changes lead to substrate efflux, the global motion patterns displayed by the apo ABCG2, and ABCG2 in the presence of specific subtracts or inhibitors during 500 ns MD simulations were comprehensively analyzed. Relevant differences were observed between the Apo and the substrate-bound structures, suggesting that substrate binding can induce specific conformational changes that could be part of the mechanism used by ABCG2 to change from inward-open to outward-open conformation. Distinct interactions and binding energies were also observed when comparing protein-inhibitor and protein-substrate simulations. The analysis of these interactions gives valuable information to identify a possible explanation for the mechanism of ABCG2.

Acknowledgements: This work was supported by projects PTDC/MED-QUI/30591/2017, SAICTPAC/0019/2015, and UID/DTP/04138/2019 from Fundação para a Ciência e a Tecnologia (FCT), Portugal.

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Biotechnology for the degradation of plastics

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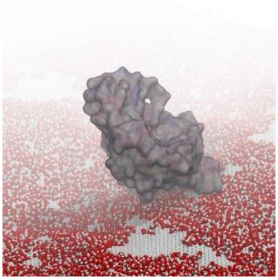
In a world where the use of plastics has become trivial, a big problem also appears, the accumulation of microplastics in the environment. This concern led to an interest in recycling it. Many methods for this have been developed, such as mechanical, chemical and biological process; the biological one being of greatest interest, due to its advantages at sustainable and industrial levels.

There are few reports on the degradation of plastics by biological method, specifically PET, one of the most present polymers in the world. But a microbial community aroused considerable interest, this being *Ideonella sakaiensis* 201-F6, which is capable of using PET as its main source of energy and carbon. When grown in the presence of this plastic, it produces two enzymes to hydrolyze PET and the intermediate of this reaction.[1, 2]

One of the two enzymes produced by *Ideonella sakaiensis* is the MHEtase, responsible for the final step of degradation of PET. With this protein, there is a lot of interest in isolation and immobilization on the surface, for use in industrial application. However, there may be limitations such as reducing its activity mainly, but with advances in biotechnology, these problems are being solved.[3]



A surface that is gaining prominence, due to its applicability, is the Oxide of Graphene (GO). It has a large area, with both sides accessible and possessing functional groups with oxygen, namely epoxide, hydroxyl and carboxylic. Additionally, it has good solubility in water, which is promising for many applications, especially enzyme absorption. The advantageous properties of enzyme immobilization triggered further investigation on the relationship between immobilization and surface, specifically that of nanostructured materials like GO sheet. [4] This concept led us to explore *in silico* the behavior of the MHEtase enzyme with the graphene oxide sheet. First, we made the assembly of the graphene sheet at different rates of oxidation, in order to explore the binding of the protein in the different oxidized media along the surface. The second step was to test the absorption of the enzyme at the molecular level by means of MD simulations. Preliminary tests have shown differentiation in the modes of interaction. The enzyme is able to adjust dynamically its spatial orientation over oxidized and non-oxidized parts of the surface in order to minimize the interaction energy. In all the interaction conformations obtained so far, the enzyme has kept the structural stability and its active site pointing towards the aqueous bulk.

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Lyotropic Ionic Liquid Crystal Gels – Molecular Dynamics Simulations and Xenon NMR Spectroscopy

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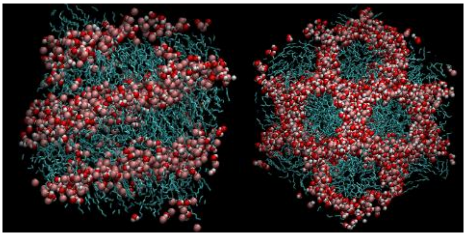
Ionic liquids (ILs) are usually defined as molten salts with melting points below 100 ºC. ILs show a variety of properties and structures, resulting from the countless possible cation-anion combinations. ILs are thus the ideal choice for a panoply of challenging applications. Some imidazolium-based ILs, such as the [$C_n$mim]X (n=8, 10; X=Br^-, Cl^-), are known for their self-assembly capabilities, in particular to form micelles and vesicles in aqueous solution.[1] Additionally, these ILs are known to form liquid crystals and gels upon addition of the appropriate amount of water. Liquid to gel transitions are accompanied by an extremely large increase of viscosity and have been observed within a narrow range of IL/water concentrations. Moreover, a variety of structures have been proposed for the gel phase depending on the water content.[2,3]

The xenon atom is in many aspects the perfect molecular probe. Moreover, ^{129}Xe NMR spectroscopy is a powerful technique to provide information on the structural properties of a range of systems, including ILs.[4]

In this work, the self-assembly and the gelation potential of systems containing [$C_n$mim]X and water were investigated. MD simulations, X-ray diffraction and ^{129}Xe NMR spectroscopy were performed for pure ILs and their aqueous mixtures. The results clarify the supramolecular structures of the gel phase and the role of the water molecules, the nature of the anions and the chain length of the cations.



Snapshots from MD simulations of [C_{10}mim]Br with water in the proportions of a) 1:1 and b) 1:4.

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Interfacial Properties of Mixtures of Fluorinated and Hydrogenated Alcohols: Experimental and MD Simulations

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The ability of fluorinated liquids to dissolve large quantities of respiratory gases, allied to their biocompatibility and chemical inertness and has triggered their potential use in biomedical and therapeutic applications such as perfluorocarbons-in-water emulsions for in vivo oxygen delivery (blood substitutes) and reverse water-in-PFC emulsions for pulmonary drug delivery in liquid ventilation. The knowledge of the surface and interfacial tension in presence of effective co-surfactants is obviously of utmost importance to control the stability and performance of both water-in-FC and in FC-in-water emulsions.

This work focuses on the study of interfacial properties of co-surfactants used to stabilize PFC/water emulsions. The interfacial properties of fluorinated alcohols and their mixtures with the corresponding hydrogenated alcohols have been investigated by three complementary techniques: experimental, Molecular Dynamics (MD) simulations and soft-SAFT-DGT calculations.[1] The surface tension of the pure fluorinated alcohols was measured as a function of temperature. The liquid-vapour surface tension of the mixtures was measured as a function of composition. Interestingly, most mixtures display aneotropes, i.e., minima in the surface tension vs composition curve, which is a very unusual behaviour. The water-liquid interfacial tension of binary mixtures was also experimentally measured. MD simulations were performed to obtain a molecular level insight of the structure of the bulk and interface.

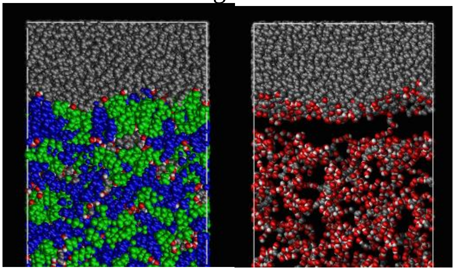

Figure 1. Simulation snapshots (side view) of the water-liquid interface of a (decanol + perfluorohexanol) mixture; (right) the hydrogenated chains (blue) and fluorinated chains (green) were omitted to visualize the hydrogen bonds network.

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Computational modeling of drug recognition by cyclodextrin-based complexes

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Cyclodextrin (CD)-guest interactions have been extensively explored to develop supramolecular smart materials that improve solubilization, transport, and targeting of therapeutic agents. A fundamental aspect to understand is the precise manner in which the binding process occurs. This includes the effect of the available volume in the cavity CD, the nature and size of the guest substituents, the role of solvation, and the reasons for conformational and thermodynamic characterization, both of which are experimentally accessible. The accurate description and quantification of the interaction patterns, energetics and binding affinities of CD-guest systems using molecular dynamics (MD) and free energy calculations have gained increasing interest in pharmaceutical technology and drug delivery applications. This work aims to develop a systematic modeling approach to understand the factors governing the formation of CD-based nanostructures, drawing on MD and potential of mean force calculations. Modulation of the inclusion complexes can be achieved by introducing different substituents on both guest and CD molecules. The results are investigated using a DoE-inspired approach. The role of the volume and flexibility of the CD guest in inclusion complexes with different model drugs is also investigated to obtain a general picture of the recognition behavior. The effect of different imposed properties on the stability of inclusion complexes between CD and different guests is thus investigated from structural, mechanistic and thermodynamic aspects. The complexation of the model guests is sensitive to changes in the basic framework and the available cavity volume, as the fit variations into the host cavity have a direct impact on the respective binding constants. These have a direct effect on the encapsulation and release of the guest from CD molecules and include substitution, size, conformation, orientation, flexibility, fit and contact, solvation and energy.

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Predicting molecular similarity and toxicity using machine learning as a playground

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The design of cost-effective strategies to simultaneously identify and eliminate toxic compounds from water requires knowledge of relevant molecular fingerprints, interaction patterns, co-occurrence, synergistic effects, and fungal sources, as this can be a gateway to an effective response to these societal obstacles.

This study aims to develop predictive models for molecular similarity and toxicity of mycotoxins based on molecular and physicochemical descriptors using chemoinformatics tools and machine learning approaches.[1] An efficient chemical data mining over 59 selected molecules described by 39 descriptors is proposed for virtual mycotoxin screening and toxicity prediction.

Hierarchical cluster analysis and k-means clustering reveal nine natural clusters consistent with the known mycotoxin families. PCA results show that discrimination between mycotoxins is largely determined by physiochemical descriptors of the Lipinski rule (apol, MW, LipinskiFailures, nHBAcc, MLogP and TopoPSA).[2]

A Neural Network model is combined with the molecular descriptors selected from PCA to improve the knowledge of the selected mycotoxins and develop models to predict their respective toxicity profiles. The optimal network structure consists of a two-layer model with 5 nodes in each layer.

This study allows the identification of relevant molecular and physiochemical descriptors for 1) the classification of structurally distinct molecules, and 2) the prediction of toxicity and respective nature of those molecules that are not so well described in the literature. This creates a gateway for the subsequent classification, identification, and rapid and efficient characterization of potential new and unknown mycotoxins. Bridging the gap between multivariate physicochemical data and the ability of models to predict and address relevant mycotoxin-related phenomena, such as co-occurrence and molecular recognition, and to develop improved classification and remediation methods remains a challenge, often limited by available experimental information.

Acknowledgements: The Coimbra Chemistry Centre (CQC) is supported by the Portuguese Agency for Scientific Research, "Fundação para a Ciência e a Tecnologia" (FCT), through Project UID/QUI/00313/2020. T.F Cova also acknowledges the Junior Researcher Grant CEECIND/00915/2018 assigned by FCT.

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Reversing multidrug resistance in cancer using indole alkaloid derivatives: *in silico* studies

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One of the major threats regarding the cancer treatment success is the multidrug resistance (MDR). The overexpression of ATP-binding cassette (ABC) transporters, responsible for the efflux of chemotherapeutic agents using ATP energy, is one of the most important factors behind MDR. P-glycoprotein (P-gp/ABCB1) is one of the main efflux pumps related with MDR. In order to search for effective P-gp inhibitors, dregamine indole alkaloid was firstly isolated in a large amount, from the methanol extract of the Mozambican plant *Tabernaemontana elegans*.[1] Afterwards, thirty new derivatives were obtained by derivatization in the indole alkaloid carbonyl. Their MDR reversal ability was assessed, using a human *ABCB1*-gene transfected L5178Y mouse lymphoma cell line, overexpressing P-gp.

The lack of information regarding the human P-gp structure, is another issue that has been hampering the development of effective P-gp inhibitors. In this regard, a deeper analysis using *in silico* tools was performed to gather further information on the drug-receptor interactions. All compounds were docked inside the P-gp's internal drug-binding pocket to classify the molecules as modulators (M-site) or substrates (R- or H-sites).[2] A QSAR model was built for a better understanding on which molecular descriptors could be correlated with the biological activity.

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Investigations on the CFTR Ion Channel through Molecular Dynamics

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ATP-binding cassette (ABC) proteins are ubiquitous super-family of membrane transporters present in all phyla with 7 sub-families (A-G) playing central roles in drug disposition, metabolism and pharmacokinetics. They are flexible transporters that efflux undesirable metabolites or xenobiotics from inside the cell providing this way a highly relevant protective role.

Cystic fibrosis (CF) is the most common life-shortening rare disease (median age at death ~28yrs). CF results from mutations in the gene encoding CFTR, an epithelial anion channel, member of the ABC family (ABCC7). The F508del mutation, occurring in 85% CF patients, causes CFTR protein to misfold. Thus, rescue of CFTR by pharmacological chaperones that correct basic defects is the much aspired alternative, but so far with limited success. Very few molecules have been approved that restore the function in mutant CFTR or rescue traffic to cell surface and together with a potentiator restores its function, but at low efficacy. Indeed, individual folding correctors provide only ~4% improvement in lung function.[1]

Here, we will present our recent findings resulting from studying the dynamic behavior of the CFTR ion channel using computational approaches in order to understand how selected mutations impact the gating mechanism, with the ultimate goal of identifying new leads/drugs which may improve the lives of CF patients carrying these mutations.

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Assessing the DFT low-energy landscapes of Li^+Kr_n clusters by employing machine learning techniques

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We report a computational study on the microsolvation of Li^+ with Kr atoms by employing an innovative methodology based on predictive machine learning (ML) techniques (see the figure). First, the interactions in the $Li+Kr_n$ clusters has been modeled with a potential energy surfaced (PES) involving two- and three-body terms [1]. By employing this analytical PES for $Li+Kr_n$ and an evolutionary algorithm (EA), we have obtained sets of low-energy structures for the cluster sizes n=2-14 and 16. The next main stage of the methodology is devoted to establish an adequate DFT approach to treat the microsolvation system, through a systematic benchmark study involving several combinations of functionals and basis sets. Among the basis sets and functionals tested against the previously optimized MP2 structures and CCSD(T) energies, the most competitive DFT approach was found to be the B3LYP-D3/aug-pcseg-1. In the next stage, we apply ML classification algorithms to predict how the low-energy minima of the analytical PES map to the DFT ones. An early and accurate detection of promising local minima from the analytical PES is extremely important to guide the choice of the low-energy minima of large clusters to be re-optimized at the DFT level of theory. The results have shown that the ML classifier was able to accurately predict most of the solutions to be re-optimized at the DFT level of theory, thereby greatly enhancing the efficiency of the process and allowing its applicability to larger clusters. The global predictive accuracy obtained was 80% for the $Li+Kr_n$ clusters with n = 2 -14 and 70% for those with n = 16 [2].

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Understanding conformational preferences and molecular interactions in co-amorphous drug systems: lurasidone combined with saccharin or cysteine.

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Co-amorphous drug systems have shown an increasing interest in the pharmaceutical field as a promising approach to improving the dissolution rate and potentially the oral bioavailability of poorly water-soluble drugs. Since amorphous forms have a higher internal energy, amorphous forms shows fast recrystallization kinetics to the low energy crystalline state. Then, to ultimately benefit from the solubility advantages of amorphous drugs, it is necessary to overcome their lower physical stability associated with the amorphous forms. In the co-amorphous formulation, the active pharmaceutical ingredient in its amorphous form is stabilized through strong intermolecular interactions with its co-amorphous low molecular weight partner molecule.[1]

In this study, two co-amorphous systems, proposed and studied experimentally, that include the drug lurasidone with saccharin and cysteine. First, the conformational landscape of lurasidone is explored by random search molecular mechanics to provide a varied set of initial conformations. Then, these conformations and the available X-ray diffraction crystal structures of the three component substances are subject to geometry optimization by a DFT method (B3LYP/def2-SVP), including corrections for dispersion. The same optimization procedure is applied to homodimers extracted from the crystal structures, and to heterodimers built using the evidence for the manner of aggregation provided by the published experimental studies. The intermolecular association is further explored with NBO analysis of the dimers, to better understand the electronic structure of the supramolecular drug–co-former entities and compare how they interact. It is concluded that faster, more approximate, methods were useful to deal with large and conformationally flexible drug molecules that are typical amorphous phase formers, and that the more rigorous quantum mechanical methods are necessary to rationalize and evaluate the molecular interactions in co-amorphous systems. The NBO analysis indicated that lurasidone has stronger hydrogen bonding with cysteine than with saccharin.

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From Experimentally Determined Enthalpies of Sublimation to the Validation of a Force Field for MD Simulations on Sulfur- and Halogen-Containing Active Pharmaceutical Ingredients

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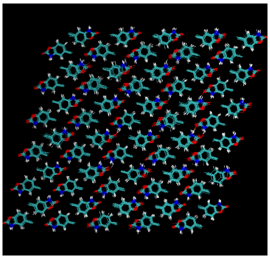

Molecular dynamics simulations provide a powerful tool to investigate many aspects of solid-state pharmaceuticals (e.g., crystallization, solubility, stability, polymorphism, phase transitions).[1-4] A pre-condition for the application of these methods is, however, the development of suitable force fields, which must be validated against reliable structural and energetic data. This work describes the determination of the enthalpies of sublimation of sulfanilamide, sulfapyridine, chlorzoxazone, clioquinol and triclosan by Calvet-drop microcalorimetry and their application in the development of a general purpose OPLS-AA based force field, to study sulfur- and halogen-containing APIs.

Acknowledgements: This work was supported by Fundação para a Ciência e Tecnologia (FCT), Portugal (projects PTDC/QUI-OUT/28401/2017, LISBOA-01-0145-FEDER-028401, UIDB/00100/2020, and UIDP/00100/2020). A PhD grant from FCT is also gratefully acknowledged by C.S.D. Lopes (SFRH/BD/128794/2017).

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Comparative study on the thermochemistry of 2-mercapto- and 2-mercapto-5-methyl-1,3,4-thiadiazole

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Thiadiazoles are five-membered heterocycles containing nitrogen and sulfur as heteroatoms and present wide applications in pharmaceutical, agricultural, and materials chemistry.[1] One of the most interesting properties of mercapto-substituted thiadiazoles is the possible existence of thiol and thione tautomeric forms, hence tautomerization influences the thiadiazoles reactivity.

One relevant goal in our research group is the study of the structural and the energetic properties of compounds with a pentagonal heterocyclic ring (two or three heteroatoms),[2] focusing on the establishment of energy-structural correlations, the conformational stability of the compounds and to provide a thorough insight on the thiol-thione tautomerism.

Therefore, we have performed an experimental and computational thermochemical study of two mercapto-thiadiazoles, namely 2-mercapto-1,3,4-thiadiazole (McT) and 2-mercapto-5-methyl-1,3,4-thiadiazole (McMT). The tautomeric equilibrium of each compound is presented in figure 1. The experimental data were determined from combustion calorimetry and from effusion method and used to derive the respective gas-phase standard molar enthalpy of formation. Additional quantum chemical calculations were carried out for both isolated molecules.

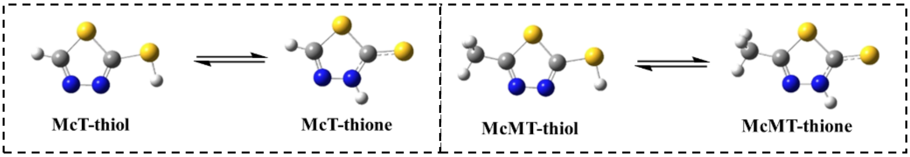

Figure 1. Thiol/thione tautomeric forms of 2-mercapto- and 2-mercapto-5-methyl-1,3,4-thiadiazole.

Acknowledgements: This work was developed under the funding of the project UIDB/00081/2020, awarded to CIQUP, financed by FCT, Lisbon, Portugal. Ana L.R. Silva thanks FCT/MCTES for her contract under Stimulus of Scientific Employment 2017 (CEECIND/01161/2017).

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Self-assembled hemimicelles of semifluorinated alkanes: experimental and Molecular Dynamics simulations

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Semi-fluorinated alkanes ($C_nF_{2n+1}C_mH_{2m+1}$, FnHm) are known to form nano-structured Langmuir films at the surface of water or an adequate solid substrate.[1,2] The films are formed by well-defined and mono-dispersed domains, hexagonally packed in highly organized 2D lattices, which make them very suitable to fabricate self-assembled templates for surface nano-patterning in a bottom-up approach. The tendency to spontaneously form dense, organized surface aggregates is a characteristic of the CF moieties, occurring even at very low surface density.[3]

Recently, we succeeded to model the formation, structure and size of F8H16 nano-domains using Molecular Dynamics (MD) simulations.[4] Herein, we extended the methodology to probe the influence of chain length on the size and aggregation number of the hemimicelles. The simulation results are in excellent agreement with experimental data. A geometric model was developed, based on the MD results, enabling an overall understanding of the self-assembling process. Preliminary studies were also performed to assess the properties of mixtures of FnHm, specifically their stability and domain size as a function of composition.

Current investigations are focused on elucidating these observations from first principles. Promising preliminary *ab initio* calculations highlight the prominent roles of the CH_2-CF_2 dipole and of the mutual phobicity between CH and CF chains in explaining the formation and internal structure of the observed hemimicelles.

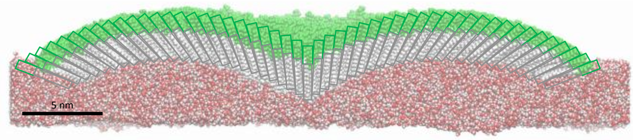

Figure 1. MD simulation snapshot (side view) of a F8H18 hemimicelle at the air-water interface.

Acknowledgements: CQE is funded by FCT through grant UIDB/00100/2020. P.S. acknowledges funding from FCT in the form of a PhD grant SFRH/BD/149192/2019.

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Langmuir Films of Fluorinated Surfactants using Molecular Dynamics Simulations

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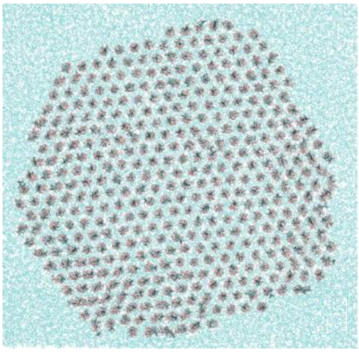
The interfacial properties of fluorinated amphiphiles are well known. Surfaces formed by perfluorinated chains, such as polytetrafluoroethylene or Teflon®, are simultaneously highly hydrophobic and lipophobic. Langmuir films (LB) are useful and well-established model systems. The organization and thermodynamic properties of LB films of hydrogenated fatty acids, alcohols, phospholipids, etc. are well established. On the contrary, studies of Langmuir films of fluorinated amphiphiles have been less systematic and scarcer.

In recent work we have studied Langmuir films of perfluorinated fatty acids and alcohols.[1,2] A combined experimental and computational methodology was used, bringing together experimental data (thermodynamic, atomic force microscopy (AFM), grazing incidence x-ray diffraction (GIXD)) and atomistic molecular dynamics simulations.

In this work, we have focused on long chain perfluorinated substances without a hydrophilic group. These are known to from stable Langmuir films at the surface of water in spite of the lack of amphiphilic character, which is remarkable.[3] Langmuir films of perfluoroeicosane ($C_{20}F_{42}$) have been simulated by atomistic molecular dynamics.

The simulation results are compared with experimental data, in particular GIXD, showing an excellent agreement that fully validates the simulation methodology and interpretations.



. MD simulation snapshot (top view) of an aggregate of $C_{20}F_{42}$ at the air-water interface

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Towards a simpler relation of electronic structure with molecular properties: historical findings

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The notions we have in general chemistry books are based on simpler ideas of Pauling and Coulson, complemented with others along the time, obtained in times were less access to computers or they were inexistent. They coined the used expressions based on the theory of valence bond and molecular orbitals and the hybrid explanations.
They had no access to the modern Density Functional Theory (DFT), except the Tomas-Fermi theory that is too qualitative and sometimes simply wrong to be used (as a matter of fact the incorrect idea that 3d orbitals com have energies lower than 4s is based on this theory). This work will be developed along these lines, and, hopefully, preliminary findings and suggestions will be presented in the meeting.

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Basic education across Europe - A physical-chemical approach by the sea

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Teaching continues to be a sharing of experiences and knowledge through a dynamic interaction that, according to UNESCO, “promotes quality of life for all”.

Old-fashioned studying methods and lack of critical thinking have often been seen as the causes of school failure in secondary education. The lack of a critical and entrepreneurial spirit has also conditioned the contribution of the younger population to the country's social and economic development.

In this investigation, I will focus on science teaching in Europe in elementary education. I also intend to compare the teaching contents, the teaching methods, and strategies used in different European countries. I intend to study the student's profile at the end of “elementary school education” in various European countries. Then I’ll make a comparative analysis of them to find out the students’ motivation to continue studying until secondary school.

As the Portuguese territory and the entire planet Earth are mainly constituted by water, part of my proposal will focus on the exploration of marine resources. These proposals should help change the way people perceive the resources of the ocean, to obtain a source of income, which can improve the quality of life and in which it is worthy to invest. Furthermore, this project intends to stir up the motivation to study and the will to enhance personal, economic, and social development in elementary education students, as well as to awaken the ability to act upon these situations.

Linking Aggregation in Solution, Solvation, and Solubility of Simvastatin

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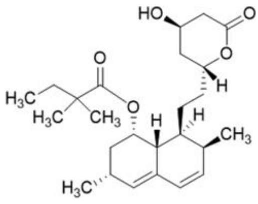
Understanding how organic compounds assemble in solution to form crystals remains a major chemical challenge.[1] The analysis of the solubility dependence on the solvent nature should, however, provide a window into how the aggregation of a particular solute is modulated by the solution environment at a particularly important point in the crystallization landscape, that of saturation.

In this work the aggregation of simvastatin (**1**), one of the most commonly prescribed antihyperlipidemic drugs, in three solvents differing in polarity and protic character (acetone, ethyl acetate, and ethanol), was analyzed through a combination of solubility versus temperature measurements and molecular dynamics (MD) simulations.

The results revealed a solubility order of acetone > ethyl acetate > ethanol, in the temperature range 283–308 K, with no observed changes in the crystal structure of the solid phase in equilibrium with the solution.[2,3] Solubility is generally thought to be higher if the solvent effectively solvates solute molecules that are well-separated from each other. However, an analysis of the structures of the different solutions on the basis of MD simulation results indicated that the observed solubility trend reflects a balance between the tendency for solute aggregation and the ability of the solvent to efficiently solvate the aggregate structures, regardless of their size, by effectively establishing solvent–solute interactions.



(**1**)

Acknowledgements: This work was supported by the Fundação para a Ciência e a Tecnologia (FCT), Portugal (projects PTDC/QUI-OUT/28401/2017, LISBOA-01-0145-FEDER-028401, UIDB/00100/2020 and UIDP/00100/2020), and by the FCT-DAAD program for cooperation in science. A postdoctoral grant awarded by the FCT to R.G.S. (SFRH/BPD/118771/2016) is also gratefully acknowledged.

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Effect of sodium chloride on the behavior of the lactose in aqueous solution studied from diffusion experiments and molecular dynamics simulations

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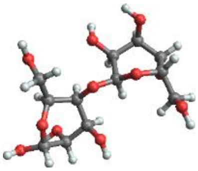
Taylor dispersion[1] has been used to measure ternary mutual diffusion coefficients (D_{11}, D_{12}, D_{21}, and D_{22}) for aqueous solutions of lactose (1) with added sodium chloride (2) at 25 ◦C and salt concentrations up to 1.00 mol dm^{-3}. From these data and by performing molecular dynamics simulations, it was possible to obtain a better understanding of the effect of sodium chloride on the transport of lactose in aqueous solutions, as well as to assume the importance of the Na$^+$-lactose short-range interaction, competing with the coulomb long-range interaction between the sodium and chloride ions, especially at low concentration of NaCl.



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Energetics of Maleic acid-L-phenylalanine Bicomponent Crystals with Different Stoichiometry

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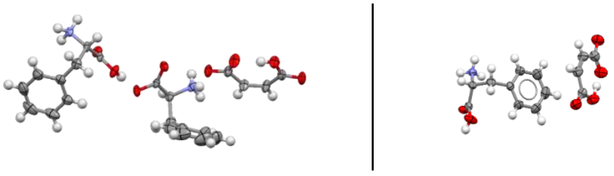
The synthesis of multicomponent crystals has emerged as a very convenient strategy to improve important physical properties of active pharmaceutical ingredients (e.g. bioavailability). A key aspect within this scope is the evaluation of the stability of the produced materials relative to their pure components, to ensure that they do not decompose during the storage period. A good indicator of that stability is the standard molar enthalpy, $\Delta_r H_m^o$, of the reaction $A_aB_b(cr) \rightarrow aA(cr)+bB(cr)$, which reflects the difference in lattice energy between the aA and bB precursors and the A_aB_b material. Based on this criterion A_aB_b will be stable if $\Delta_r H_m^o > 0$. An enthalpic only stability criteria can often be used because available experimental evidence [1,2] suggests, that, in most cases, close to ambient temperature, $|\Delta_r H_m^o| > -|T\Delta_r S_m^o|$.
The influence of stoichiometry of the stability of the A_aB_b species is a virtually unexplored topic. In this work the energetics of two organic salts consisting of maleic acid (MA) and L-phenylalanine (Phe) with 1:1 and 1:2 stoichiometries was investigated. The compounds were synthesized by mechanochemistry and structurally characterized by single crystal X-ray diffraction (Fig.1).[3] The $\Delta_r H_m^o$ determinations relied on enthalpy of solution measurements carried out with a newly developed calorimetric cell for the LKB 2277 Thermal Activity Monitor (TAM) and a previously described methodology.[1] The obtained results indicated that, at least in the present case, despite significant structural differences, $\Delta_r H_m^o(\text{MA:Phe}_2) \approx 2\Delta_r H_m^o(\text{MA:Phe})$.



(a) (b)

Fig. 1- Molecular structures of (a) zwitterionic salt MA:Phe$_2$ (determined in this work),[3] and (b) MA:Phe salt (CCD reference, EDAXIQ).

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Binary diffusion coefficients for hydrocarbons in supercritical carbon dioxide – Development of a Taylor dispersion setup for SFCs

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Supercritical technologies have become, in the last decades, a trending research topic due to the high increase of carbon dioxide in the atmosphere[1], especially the ones focused in Carbon Capture and Storage (CCS) that focus on the geological storage of large quantities of CO_2, and thus are potentially able of generating a positive impact on the environment[2]. The development of these technologies relies on the knowledge and understanding of the diffusion processes of supercritical fluids, therefore the study of substance diffusion in supercritical carbon dioxide is of major importance.

Currently, Taylor dispersion technique is one of the most commonly used methods for the study of transport coefficients in liquids. Our work consisted on adapting a Taylor dispersion apparatus to high pressure working conditions in order to obtain supercritical diffusion coefficients. The Taylor dispersion method involves the injection of a small volume of solute into a laminar flow of solvent streaming through a long dispersion tube. This solute pulse will broaden into a peak, due to the combined action of convection and molecular diffusion, being the diffusion coefficient of the solute calculated from the analytical analysis of the dispersion measured by the detector, an FT-IR Spectrometer[3], at different wavelengths.

The results of the measurements of the diffusion coefficients for pure toluene in supercritical carbon dioxide at 33ºC and pressure 10.5 MPa, are presented. The effects of flow velocity, spacer thickness, peak symmetry, and absorbance at different wave numbers on the diffusion coefficient have been analyzed and are discussed in detail.

Also, the effect of the pressure in the binary diffusion for toluene in supercritical CO_2, in the range of 7.5 to 12.5 MPa have been studied and are examined and discussed.

Acknowledgements:

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Solubility enhancement of poorly water-soluble drugs with zwitterionic hydrotropes

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One of the major limitations found in the development of new pharmaceutical products lies in the low solubility in water of oral drugs. The study on hydrotropes application – compounds with the capacity to increase the solubility of hydrophobic compounds in aqueous solutions – for molecules solubility enhancement has been increasing over the last years[1]. Several new types of hydrotropes have been identified and evaluated in order to develop more effective and biocompatible formulations. Nevertheless, and despite the large number of studies about hydrotropy, the mechanisms that rule hydrotropic effect is still not clearly understood.

In this work, aqueous solutions of novel zwitterionic compounds derived from ionic liquids were investigated to improve the solubility of poorly water-soluble drugs. Zwitterionic compounds present several chemical properties of high interest and are already widely used in the pharmaceutical industry[2]. The solubility of small bioactive molecules, such as gallic acid, vanillin and syringic acid, in aqueous solutions of sulfobetaines, carboxybetaines and other types of zwitterions, were ascertained. The effect of zwitterions cationic and anionic groups, spacer and alkyl chains length were evaluated. The collected data reveal a significant enhancement of bioactive molecules solubility in zwitterions solutions when compared to pure water and allowed for a better comprehension of the mechanisms that rule the hydrotropic effect.

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Recovery of phenolic compounds from Kiwi waste with aqueous solutions of biobased solvents

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Phenolic compounds are secondary metabolites in plants that display several biological activities, including antioxidant properties.[1] The extraction of these compounds from biomass wastes, and their reuse in new products, can be a sustainable way to valorize resources. However, one of the major limitations to the development of a sustainable extraction process for the recovery of phenolic compounds from biomass is their low solubility in water. To overcome this obstacle, additives such as hydrotropes can be used to increase the solubility of phenolic compounds in aqueous solutions.[2] Recently, it was demonstrated the ability of renewable solvents, such as biobased solvents, to act as hydrotropes, since they improved the solubility of hydrophobic compounds, like phenolic compounds, in water.[3] Thus, in this work, aqueous solutions of biobased solvents (gamma-valerolactone, cyrene and alkanediols), were investigated to improve the solubility and effectively extract phenolic compounds from Kiwi wastes, contributing this way to the development of a more sustainable extraction process. First, the solubility of phenolic compounds, such as ferulic acid, syringic acid and catechin, in aqueous solutions of biobased solvents was evaluated. The experimental data obtained showed a great enhancement in the solubility of these compounds in aqueous solutions of biobased solvents, compared to pure water. After proving the ability of biobased solvents to increase the solubility of phenolic compounds in water, these solutions were used to extract phenolic compounds from Kiwi waste, and to identify the best extractant solvent. The traditional Soxhlet extraction using volatile organic solvents (ethanol) was also carried out for comparison purposes.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the FCT/MCTES. H. Passos acknowledges FCT – Fundação para a Ciência e a Tecnologia, I.P. for the researcher contract CEECIND/00831/2017 under the Scientific Employment Stimulus - Individual Call 2017.

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Water Solubility in (*n*-Alkane + *n*-Perfluoroalkane) Mixtures and in *n*-Perfluoroalkylalkanes: Experimental and Modeling with the SAFT-γ Mie Group-Contribution Approach

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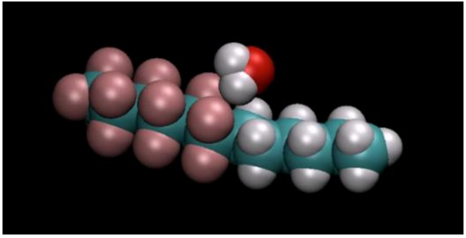
The solubility of water in liquid *n*-hexane, *n*-perfluorohexane and in their equimolar mixture was experimentally determined as a function of temperature. The solubility of water in the mixture is significantly higher than the average of the solubilities in the pure solvents, which lead to the suggestion, for the first time, that mixing hydrogenated and perfluorinated chains enhances the solubility of water in such systems.

A SAFT-γ Mie group-contribution approach that describes the phase behavior of *n*-alkanes, *n*-perfluoroalkanes, water and their binary combinations is used to calculate the solubility of water in the *n*-hexane + *n*-perfluorohexane mixture. This theoretical approach is used here to assess quantitatively how much the large deviations from ideality in the solvent mixture contribute to the water solubility behavior. The importance of a correct modelling of the non-ideality of the solvent mixture[1] is demonstrated by the quantitative prediction of the ternary behavior.

In addition, the same SAFT-γ Mie EoS is used to represent the solubility of water in a number of *n*-perfluoroalkylalkanes as a function of temperature, covering a range of relative lengths of the hydrogenated and perfluorinated chains. The theory can be used to correctly predict the relative extent of the solubility of water in the different solvents, in good agreement with experimental data. This is accomplished by using a single parameter to describe the strong attractive interaction between water and the CH_2CF_2 group at the junction between the hydrogenated and perfluorinated segments, which is known to be responsible for the increased solubility of water in these substances.[2]



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Thermodynamic Stability of Fenclorim

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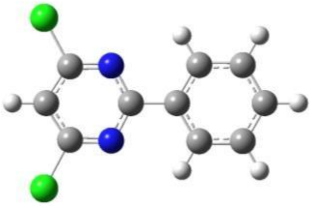
Pesticides are substances planned to prevent, destroy, repel, or mitigate pests with a harmful effect on agriculture, contributing drastically to reduce hunger in different areas of the planet.[1] The massive production and application of these compounds, however, can trigger serious biological and ecological imbalances, affecting the quality of the environment through contamination of water, air and soil, threatening human, animal and plant health. Thus, the knowledge of properties with important applications in environmental distribution of these compounds as well as the evaluation of their thermodynamic stability is essential information. In this work, the thermodynamic tendency of the herbicide Fenclorim to decompose into its constituent elements, under standard-state conditions, was evaluated considering the related values of $\Delta_f G_m^o$ (298.15 K, cr) – smaller values of this property correspond to larger thermodynamic stability. It was determined by subtracting from $\Delta_f G_m^o$ (298.15 K, g) the value of $\Delta^g_{cr} G_m^o$ (298.15 K). The result in the gas phase was calculated as [$\Delta_f G_m^o = \Delta_f H_m^o$ (298.15 K, g) − 298.15 $\Delta_f S_m^o$ (298.15 K, g)] and the values of $\Delta_f H_m^o$ (g) and S_m^o (g) (used to calculate $\Delta_f S_m^o$) were estimated, at $T = 298.15$ K, through G3(MP2) calculations. The results of $\Delta^g_{cr} G_m^o$ (298.15 K) were derived through vapor pressure measurements of the crystalline phase of Fenclorim, at different temperatures, using the mass-loss Knudsen effusion technique.[2]



Fenclorim

(4,6-dichloro-2-phenylpyrimidine)

Acknowledgements: Thanks are due to the project UIDB/00081/2020 awarded to CIQUP, financed by FCT (Portugal) with national funds of MEC. ARRPA acknowledges financial support through the FCT - I.P., in the framework of the execution of the program contract provided in paragraphs 4, 5 and 6 of art. 23 of Law no. 57/2016 of 29 August, as amended by Law no. 57/2017 of 19 July.

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Modeling Solvent Effects on Solution Enthalpies Using a Modified Version of the Kamlet-Abraham-Taft Model Equation

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Thermochemical data enclose valuable information regarding the nature of molecular interactions in solution which can be unraveled through Multiple Linear Regression (MLR) analysis. We have used an MLR approach to study solution enthalpies of several adamantane derivatives,[1] hydroxylic compounds[2] and 1,4-dioxane[3] in a wide set of both protogenic and non-protogenic solvents. Results have enabled us to assess and discuss the nature and magnitude of the major factors which influence these processes.

In a parallel communication in this conference, we show the superior capability of a modified version of the Kamlet-Abraham-Taft model equation (KATm) to study solvent effects upon several physicochemical processes. As so, we decided to also test the equation's ability to model the solution enthalpies of five different compounds.

Results show the excellent modeling capacity of the KATm equation - Fig.1. Still, the methodology failed to provide reliable predictions of the vaporization or sublimation enthalpies for the used compounds. Reasons for this drawback are pinpointed and discussed.

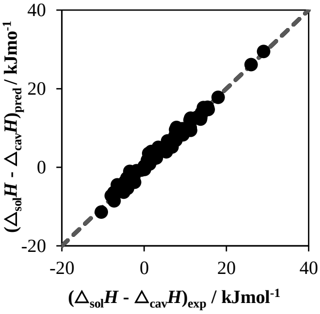

Fig. 1 – Performance of the KATm model equation.

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Thermodynamic characterization of anthranilate derivatives

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The everyday use of fragrances with olfactory properties, as well as their presence in various environments, constitute a concern, being the understanding their reactivity an important challenge.[1]

The aim of this work is to evaluate the energetic properties of methyl 2-amino-3methylbenzoate and methyl 2-amino-4,5-dimethoxybenzoate (Figure 1), performing experimental and computational studies, in order to provide reliable data for the analysis of their environmental risk assessment. This research follows a series of previous works.[2,3] This communication reports the massic energies of combustion of both compounds, measured by static bomb combustion calorimetry, the enthalpy of vaporization measured of methyl 2-amino-3-methylbenzoate, measured by Calvet microcalorimetry, and the enthalpies of sublimation of methyl 2-amino-4,5dimethoxybenzoate, measured by Calvet microcalorietry and Knudsen effusion method. These results are used to derive the enthalpy of formation of these anthranilate derivatives, in the condensed and gaseous phases, at T = 298.15 K. The values derived from the experimental measurements and from the complementary computational studies will be analysed in terms of their structural characteristics.

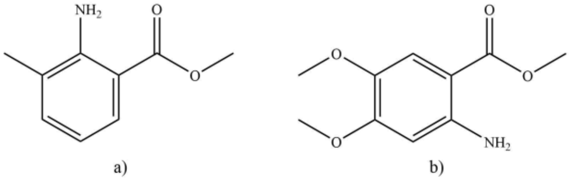

Figure 1 – Structural formulae of a) methyl 2-amino-3-methylbenzoate and b) methyl 2-amino-4,5-dimetoxymethylbenzoate.

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Sustainable cellulose-based floculants for microplastic remotion in aqueous media

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Plastics are widely used due to their excellent properties, inexpensiveness and versatility leading to an exponential consumption growth during the last decades. However, most plastic does not biodegrade in any meaningful sense; it can exist for hundreds of years. Only a small percentage of plastic waste is recycled, the rest being dumped in landfills, incinerated or simply not collected resulting quite often in a high load of microplastics in the environment. Waste-water treatment plants can only minimize the problem by trapping plastic particles of larger size and some smaller ones remain within oxidation ponds or sewage sludge, but a large amount of microplastics still contaminate water streams and marine systems [1]. Thus, it is clear that in order to tackle this potential ecological disaster, new strategies are necessary. In the present study, novel cationic hydrophobically modified cellulose derivatives have been developped, and their performance as bio-flocculants was accessed using a model system consisting of grinded polyethylene terephthalate particles. Laser diffraction spectroscopy was used in combination with microscopy to monitor the flocculation process in slight turbulent conditions, following previous developments from the group [2]. The developed biofloculants were found to successfully aggregate and remove the model microplastics from aqueous media. Moreover, the flocculation kinetics were observed to increase when adding the bioflocculation agent. Overall, this work demonstrates that “greener” approaches based on bio-based flocculants can be promising solutions for removing microplastics from aqueous media and minimize their potential negative effect on aquatic environments.

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New deep eutectic solvent assisted extraction of highly pure lignin from maritime pine sawdust (*Pinus pinaster* Ait.)

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Lignin is a natural aromatic polymer that has tremendous potential as a renewable and sustainable feedstock to produce fuels, chemicals and biomaterials. Its efficient extraction could expand the utilization of biomass and reduce the dependence on fossil fuels; however, the complex molecular structure of lignin makes its isolation from the other biomass components non-trivial[1]. In this work, novel acidic deep eutectic solvents (DESs) were prepared and screened for the fractionation of maritime pine (*Pinus pinaster* Ait.) sawdust to infer on their suitability for an efficient and selective extraction of lignin. DESs show several favorable features such as biodegradability, low cost and tunability that encourage their use as extraction solvents[2].

The extraction capacity was observed to be greatly affected by the DES composition. New DESs composed of ChCl and two acidic hydrogen-bond donors were prepared to achieve solvents with enhanced properties and superior extraction performance. Using a DES composed of lactic acid, tartaric acid and choline chloride in a molar ratio of 4:1:1, allows the recovery of 95wt% of the total lignin present in pine biomass with a purity of 89%. Moreover, the developed DES can be recycled and reused without compromising its performance for, at least, two additional cycles. The superior performance of the prepared DES and its “green” features makes the process highly appealing for biomass fractionation.

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Equilibrium Constants and corresponding ΔGº in Heterogeneous Media

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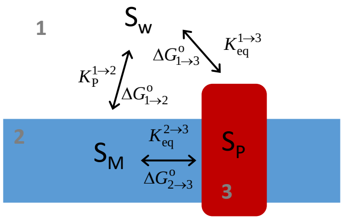
The distribution of small molecules between distinct environments in heterogeneous media is of fundamental importance on the overall effect of the solute on the system. This is of particular relevance in biological systems, where an active molecule (drug or biological ligand) may be in the aqueous media, associated with lipid bilayers, proteins or other macromolecules. The local concentration of the active molecule in a given environment depends on the affinity for and on the relative abundance of all binding agents. Association with proteins (or other macromolecules) is usually evaluated from the effect of increasing concentrations of the active molecule in a selected property of the protein, leading to a saturation curve from which the binding affinity may be calculated (K_{eq}). On the other hand, association with lipid bilayers is characterized as a partition coefficient (K_{P}), evaluated from the distribution of active molecules between the aqueous media and the lipid bilayer at increasing concentrations of the later. The intrinsic affinity of the active molecule to the distinct environments may be evaluated from variations in its free energy, and this may in principle be calculated from the association affinity. However, while the relation between ΔG^{o} and the dimensionless partition coefficient is immediate, its calculation from an equilibrium constant involves at least cancelation of the parameter units. Another difficulty in the calculation of the free energy of the active molecule when associated with macromolecules is that from the saturation curves it is not possible to distinguish between a single and several equivalent and independent binding sites.

In this work we propose an approach to calculate the relative free energy of an active molecule in the heterogeneous media containing biomembranes (lipid bilayers with embedded proteins) in aqueous media. With this approach, from the characterization of the protein saturation profile, the partition to the lipid bilayer, and the overall partition to the membrane, it is possible to calculate the intrinsic affinity for the distinct environments. With this information, the number of active molecules *per* protein at saturation may also be calculated.



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Temperature-responsive extraction of violacein using aqueous mixtures of a surfactant and an ionic liquid

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In thermoreversible systems, extraction or catalysis can occur under homogeneous conditions prior to the inducement of a biphasic regime by temperature adjustment leading to the separation of products and reactants. However, systems capable of undergoing phase transition are for the most part restricted to nonionic surfactants and polymers and rarely occur in ionic systems due to electrostatic interactions. This work successfully demonstrated the potential of aqueous solutions of the anionic surfactant sodium dodecylsulfate (SDS) with tetrabutylammonium ($[N_{4444}]Cl$) as an integrated platform for the solid-liquid extraction of violacein from biomass and its subsequent cloud-point extraction and separation from contaminant proteins. Through variations in the $[N_{4444}]Cl$ to SDS ratio, the character of the system could be selectively tuned from anionic to pseudo-nonionic. This greater degree of flexibility was applied to enhance the extraction and purification of violacein from real biomass. Finally, a bio-derived hydrophobic eutectic based on menthol:thymol was used to back-extract violacein and separate it from the dodecyl sulfate anion. (1)

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Ionic liquids in the fractionation of terpenes and terpenoids

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Terpenes and terpenoids include a vast number of compounds, with different functional groups, that find diverse application in the food, pharmaceutical, and chemical industries, mostly as flavours, organic solvents, and as raw materials for the synthesis of other compounds. Currently, novel fractionation and purification processes of these compounds are being developed, using green solvents, to increase their value and range of uses.[1,2]

In this work, the performance of a set of selected ionic liquids (ILs), as separation agents in deterpenation processes, was studied and compared to existing literature data.[1,2] Infinite dilution activity coefficient data of several organic solutes (alkanes, cycloalkanes, ketones, ethers, cycloethers, aromatic hydrocarbons, esters, acetonitrile, pyridine, thiophene, alcohols, terpenes and terpenoids) and water, obtained by gas-liquid chromatography, in different ionic liquids, were used to estimate selectivities and capacities values related to key separation problems involving terpenes and/or terpenoids mixtures such as limonene/linalool, α-pinene/β-pinene, borneol/camphor or menthone/menthol. Previous data using phosphonium-based IL ($[P_{6,6,6,14}]Cl$, $[P_{6,6,6,14}][(C_8H_{17})_2PO_2]$) and methylimidazolium-based IL ($[C_4mim][OAc]$, $[C_4mim]Cl$, $[C_4mim][CH_3SO_3]$, $[C_4mim][(CH_3)_2PO_4]$, $[C_4mim][CF_3SO_3]$)[1,2] were critically compared to new data obtained in this work for $[C_{12}mim]Cl$. The separation of terpene/terpene mixtures still remains a challenge, nevertheless suitable separation agents, in terms of selectivities and capacities, were identified for the fractionation of important mixtures containing terpenoids.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, and CIMO-Mountain Research Center, UIDB/00690/2020, both financed by national funds through the Portuguese Foundation for Science and Technology/MCTES. Sérgio M. Vilas-Boas also thanks FCT for the Ph.D. grant (SFRH/BD/138149/2018).

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Lanthanide complexes with Valsartan: the influence of the metal center on the thermal decomposition of the ligand

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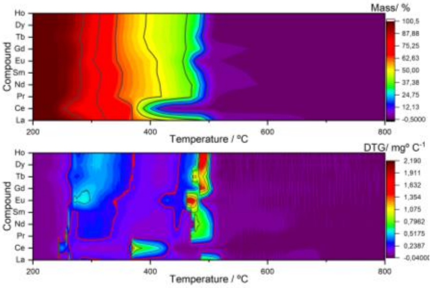
Trivalent lanthanide (La-Ho) complexes with Valsartan ligand were characterized by analytical, thermoanalytical and spectroscopic techniques. The bound between the ligand and the lanthanides were made through the tetrazole ring and the carboxylate groups, the last is made in a monodentate mode[1]. To facilitate the data visualization the thermal behavior of the compounds was compared by plotting a 2D contour map (Figure: TG - graph at the top, and DTG - graph at the bottom).

The changes in the thermal behavior can be assigned to three properties of the compounds: basicity and HOMO-LUMO orbitals of the lanthanides, and the strength of each bond in the molecule[2]. Therefore the pattern is the summation of the factors: how much the basicity affects the ligand, in the case of the present study higher basicity provided lower thermal stability; and higher differences between HOMO-LUMO orbitals provided higher stability. Finally, these factors affect the strength of the bonds in the ligand, showed by the changes in the decompotion during the heating.



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Studies of Dual Drug Cocrystals: (1:1)-Diflunisal: Isoniazid and (1:1)-Lamotrigine:Ethosuximide

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The present work describes the synthesis and characterization of two new dual drug cocrystals: (1:1)-diflunisal:isoniazid (DIF:ISO) and (1:1)-lamotrigine:ethosuximide (LAM:ETH). Diflunisal has anti-inflammatory, antipyretic and analgesic properties and isoniazid is an antibacterial agent, widely used in tuberculosis treatment. Lamotrigine and ethosuximide are anticonvulsants, but have different routes of action. Therefore, both cocrystals have great interest as they have potential to allow doubleaction therapy. Both cocrystals were synthesized using mechanochemistry, the first one through liquid-assisted grinding and the second through liquid-assisted and neat grinding. The cocrystals were characterized by attenuated total reflectance – Fourier transform infrared spectroscopy, differential scanning calorimetry and X-ray powder diffraction. Through these spectroscopic, thermal and diffractometric methods the formation of cocrystals was confirmed as well as their stoichiometry.

Although cocrystals have gained considerable importance in the pharmaceutical industry, there are still a number of challenges to be overcome[1]. The stability of cocrystals in the presence of excipients is still poorly investigated and the existing studies are quite recent[2]. Excipients can contain groups capable of forming hydrogen bonds and, since cocrystals are normally formed by these same bonds, their stability in the presence of excipients may be compromised. Thus, in this work preliminary results are also presented of compatibility studies of (1:1)-DIF:ISO and (1:1)LAM:ETH cocrystals with excipients commonly used in the development of solid dosage forms. Physical mixtures of the cocrystals were prepared with mannitol, microcrystalline cellulose, talc, sodium alginate, magnesium stearate, lactose monohydrate, anhydrous dibasic calcium phosphate and croscaramellose sodium (in different proportions). Differential scanning calorimetry confirms that only talc and anhydrous dibasic calcium phosphate did not cause a decrease in the melting temperature of DIF:ISO cocrystal. For the LAM:ETH cocrystal, talc was the only excipient that did not cause any alterations. Our research shows the interest in studying binary mixtures of cocrystals with pharmaceutical excipients for the development of the oral solid dosage forms, effective and safe.

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Vibrational dynamics of polar alcohols in various thermodynamic states

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The aim of our research is to determine the physicochemical properties of organic compounds with a single phenyl ring, present in various plants. Such compounds are also of much interest to the food, pharmaceutical or cosmetic industries, what stimulates their studies by complementary methods. In particular, amorphous forms are usually more biocompatible than crystal phases. Along this line, we embarked on the investigation of polymorphism and dynamics in various thermodynamic states that occur in these substances.

Results of calorimetric and spectroscopic studies (spectroscopy: broadband dielectric, infrared absorption and neutron spectroscopy, i.e., inelastic neutron scattering)[1,2] for this type of compounds will be presented. The results of our research will be compared with the literature data for similar molecular systems.

Through Inelastic Neutron Scattering we establish vibrational dynamic of proton group and the nature of hydrogen bond. Moreover, density of states G(ν), observed in a glass of liquid or plastic crystal phase (Debye vs. non-Debye G(ν) at small energy transfer and at helium temperature) will give information on the kind of glassy states. A combination of infrared and inelastic neutron scattering spectroscopies with the density functional theory and semi-empirical calculations was applied to propose an assignment of the vibrational spectra of trans-cinnamaldehyde and trans-anethole.

Acknowledgements: The work was partially supported by the Polish-Italy bilateral joint research project for years 2020 – 2021 “Multidisciplinary studies of glass-forming molecular materials”, and the funding from the JINR (Joint Institute of Nuclear Research, Dubna, Russia) research group and centres in Poland – project “Studies of selected soft materials and compounds in nanoporous materials”.

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Excited state Decay Mechanisms of the Naphthoquinone Dye Shikonin

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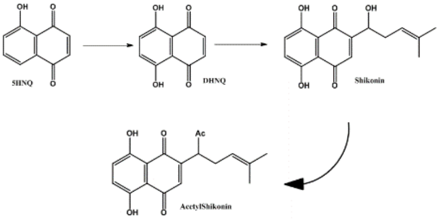
The year of 1453 is in mankind history not only associated to the beginning of the Roman's Empire fall, but also to the end of the use of mollusk purple – the Tyrian Purple - by the sultan Mehmet II. This was a very rare and desired color that could only be used by wealthy people: emperors, kings and popes. In 1828, near Thebes in Egypt, a papyrus was found, with some recipes regarding the use of purple dyes. Interestingly, this recipe for the "genuine purple secretion", indicated the use of alkanet, orchil and kermes, alone or mixed with woad to mimic the color "imperial purple" in dyestuff.[1]

Naphthoquinone dyes (present in anthraquinones, the constituent of madder), are therefore present since Ancient times in papyrus from Egypt, textiles and paintings from the Silk Road in China, etc. This carbonyl dyes class of molecules is one of the most popular for the natural red colour. Shikonin is considered a molecular marker for the presence of *Lithospermum erythrorhizon*, mainly found in Asia, and Alkannin a tracer for *Alkanna tinctoria* (also known as alkanet), is found in Europe.[2]

Shikonin has received some considerable attention in the past recent years. However, these are mainly theoretical studies involving DFT calculations.[3] In this work we study the spectral and photophysical behavior of the Shikonin, through a detailed investigation involving fast spectroscopic techniques (ps-TCSPC, fs-TA and fs-UC) together with the study of its quinones derivatives: 5-hydroxy-1,4-naphthoquinone (5HNQ), 5,8-dihydroxy-1,4-naphthoquinone (DHNQ) and acetylshikonin (AcShk), see Scheme 1, in order to understand the correct mechanism involved in the excited deactivation of Shikonin.



Scheme 2. Structures of the naphtoquinones investigated in this work.

Acknowledgements: The authors acknowledge funding from FCT, FEDER and Compete Centro 2020 throughout projects Hylight PTDC/QUI-QFI/31625/2017, ROTEIRO/0152/2013, CQC (UIDB/00313/2020 and UIDP/00313/2020) and Laserlab-Europe (no. 284464, EC's 7th Framework Programme). CMP gratefully acknowledges FCT by a PhD grant (SFRH/BD/140883/2018).

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Luminescent aqueous inks and coating formulations with RGB-tunable emission

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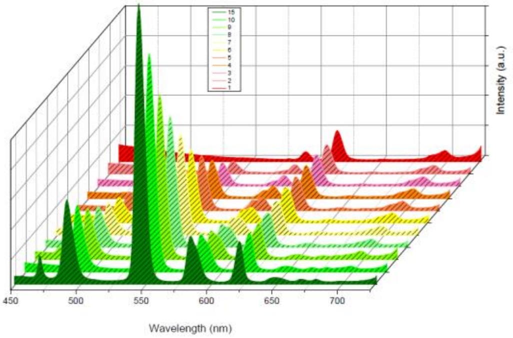
This communication reports the development of a luminescent complex, capable of RGB-tunable emission under UV radiation, to be used as a security tag in paper industry. For such type of paper, two main guarantees of security need to be present: a) the incorporation of a luminescent compound into the paper; and b) its reaction to a substance that would be responsive to it by proving its authentication. Several kinds of security ink formulations based on lanthanide doped luminescent nanomaterials, quantum dots (semiconductor and carbon based), organic conjugated materials, metal organic frameworks and plasmonic nanomaterials have been studied for their possible use in anticounterfeiting applications.[1]

A series of complexes based on europium and terbium salts, in the presence of a polyelectrolyte (PE), were synthesized. Under UV radiation (excitation wavelength 366 nm), different molar ratios of Eu(III)/Tb(III) led to spectra with luminescence emission ranging between red and green, including yellow and orange.[2] The figure at right shows the luminescence emission spectra, in the visible region, of those materials.



Furthermore, blue emission was attained by using a conjugated polymer with fluorescent properties, stabilized in water by an anionic surfactant. This polymer and the [≠(Eu^{3+}/Tb^{3+})(PE)] complex, enhanced by an organic ligand working as antenna, were successfully used to prepare tunable aqueous inks. These inks can be directly applied on sheets for painting or writing, or mixed with a thickener for paper coating. Finally, this work shows how the aforementioned conditions (a) and (b) of security paper are fulfilled.

Acknowledgements: This work was carried out under the Project inpactus – innovative products and technologies from eucalyptus, Project N. º 21874 funded by Portugal 2020 through European Regional Development Fund (ERDF) in the frame of COMPETE 2020 nº246/AXIS II/2017.

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TTA-UC emitter based on NIR excitable aggregated Pt(II) Chlorin immobilized with tetraphenylethylene in cellulose acetate films

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Fluorescence imaging is a powerful tool for diagnostic and medicinal therapy, however, is hampered by tissue absorbance and tissue autofluorescence. Thus, the development of new reagents that allow non-invasive imaging are of high value for tumor diagnosis and prognosis. Although, much attention has been paid to investigating in vivo targeted imaging using triplet-triplet annihilation photon upconversion (TTA-UC) emitters, the synthesis of better TTA-UC systems and formulations for efficient targeted delivery is currently undergoing.[1] The development of TTA-UC emitters is very attractive for the biomedical imaging field because these materials can be excited in the so-called NIR "imaging window" (650-1350 nm) where there is minimal tissue absorbance and autofluorescence and emit light in regions that are easily detected by existing equipment. One of the most important parameters to optimize in bioimaging techniques is the signal-to-noise ratio, which is usually hampered by the problem of autofluorescence of tissues. However, being an anti-Stokes process, TTA-UC overcome this drawback leading to biomedical imaging with high sensitivity. The rarity of anti-Stokes shifts ensures that light at the wavelengths being monitored should only arise from TTA-based processes. Furthermore, the long wavelengths used in excitation have greater penetration into tissue. Moreover, distinct from other upconversion approaches that typically require the use of lasers, TTA-UC can upconvert light from low-power, incoherent excitation sources, making it appealing for practical applications.

We successfully demonstrated that a Pt(II) complex of 4,5,6,7-tetrahydropyrazolo[1,5-a]pyridine–fused chlorin[2] (sensitizer) immobilized with tetraphenylethylene, TPE, (annihilator) in cellulose acetate films can act as a TTA-UC emitter. It was seen that the Pt-chlorin molecules can form J-aggregates that can be excited up to 900 nm yielding good TTA-UC efficiency (displaying the characteristic aggregation induced emission of the aggregated TPE moiety in the 400-600 nm range).

Acknowledgments: The Coimbra Chemistry Centre is supported by the Fundação para a Ciência e a Tecnologia (FCT), Portuguese Agency for Scientific Research, through the projects UIDB/00313/2020 and UIDP/00313/2020.

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Fluorescence Studies on a Thermo-responsive PNIPAM-Polyfluorene Graft Copolymer

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Polyfluorenes (PF) combine high photoluminescence (PL) quantum yields, good thermal stability and good solubility in a variety of solvents.[1] However, the PL efficiency of these organic conjugated polymers strongly depends on the properties and relaxation processes of electronic excited states, which has led to a considerable effort in characterizing their behavior in solution. Poly(*N*-isopropylacrylamide), **PNIPAM**, is as a well-known thermo-responsive polymer, that can display significant physical properties changes with temperature.[2] The lower critical solution temperature (LCST) behavior of **PNIPAM** (~ 32 ºC) has been attributed to the delicate balance between hydrogen bonding with water and hydrophobic hydration.[3]

In this work, the fluorescence behavior of a **PNIPAM**-grafted polyfluorene copolymer (**PF-PNIPAM**) was investigated by UV-Vis spectroscopy, DLS, steadystate and time resolved fluorescence techniques in DMF, MeOH and in an acetone:water (1:2) mixture over the temperature range from 5 to 70 °C. In acetone:water (1:2), absence of a significant temperature dependence of the decay time components between 5 and 20 °C indicates a dominant intra- and interchain hopping-type deactivation mechanism. However, non-Arrhenius behavior, especially for the acetone:water (1:2) mixture, is observed in the temperature range from 20 to 70 °C and is again attributed to the complete formation of aggregation around the LCST temperature.

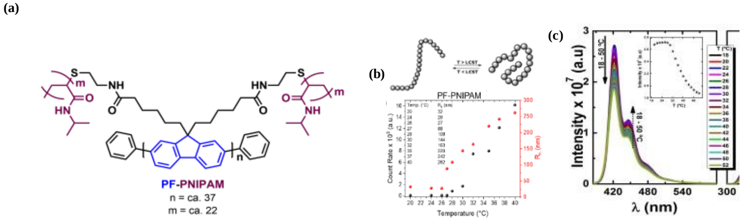

Figure 1. (a) Chemical structure of PF-PNIPAM, (b) DLS and (c) Fluorescence emission with temperature in acetone: water (1:2).

Acknowledgements: The authors acknowledge funding from FCT, FEDER and Compete Centro 2020 throughout projects Hylight PTDC/QUI-QFI/31625/2017, ROTEIRO/0152/2013, CQC (UIDB/00313/2020 and UIDP/00313/2020) and Laserlab-Europe (no. 284464, EC's 7th Framework Programme). CC gratefully acknowledges FCT by a PhD grant (2020.09661.BD).

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Amino Acid-Based Fluorescent Nanomaterials Towards Nanohybrid Fabrication

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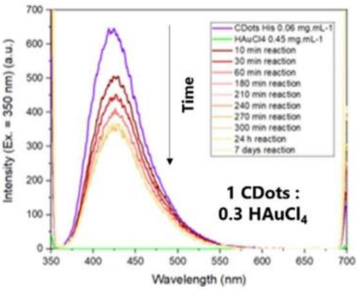
Amino acids consist of a carbon atom bonding to a carboxyl group, an amino group and alkyl chains. The nature of those groups influences the size, electric charge, and solubility of the amino acids. Thus, they can be very versatile molecules, with specific interactions and composition. Fluorescent nanomaterials with size-dependent electronic and optical properties, such as metal nanoclusters and quantum dots, are very interesting for their tunability, achieved by changing the synthetic path, precursor materials and ratio. Gold nanoclusters (AuNCs) have size comparable to the Fermi wavelength of electrons (< 2 nm) and display unique optical properties, although the atomically precise size control still remains a challenge in synthesis.[1] On the other hand, carbon quantum dots (Cdots) are easily produced and functionalized, but they show issues related to their heterogeneity. Our aim is to combine the ease of functionalization of GQDs with the tunable luminescent properties of AuNCs to build up novel hybrid particles. For that, we used the same starting material, an amino acid, to produce both nanomaterials.



Histidine has been chosen as reducer and stabilizing agent to produce stable gold nanoclusters, with maximum emission at 490 nm, through biomineralization using $HAuCl_4$ as source of gold ions. The same amino acid was used to produce carbon dots through hydrothermal synthesis. Both nanomaterials were mixed to form a hybrid with dual fluorescence emission. We also explored the different properties of the obtained Cdots as reducers and stabilizers to form in situ AuNCs by adding $HAuCl_4$ in various ratios. Cdots successfully reduced Au(III) to Au(0), as confirmed by fluorescence and absorbance measurements. These findings open the possibility to obtain one pot hybrids with tunable optical properties using amino acids as both carbon source and reducer.

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BOTTOM-UP CARBON DOTS: Sensing and Imaging

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In the last years, carbon dots (Cdots) have drawn tremendous attention from the scientific community because of their unique photoluminescence properties, high photostability, low toxicity and good biocompatibility.[1-3]
Structurally, Cdots are described as discrete, quasi-spherical zero-dimensional carbon nanoparticles (< 10 nm) with sp^2 hybridized carbon domains and a heterogeneous composition of functional groups at the surface. Several strategies have been proposed to synthesize Cdots that either follow a bottom-up approach, starting from natural organic precursors (citric acid and amines), or a top-down approach, starting from bulk carbon materials (e.g. graphite, carbon fibers, graphene oxide).
In this communication, we present our work on the preparation, characterization, and potential applications of Cdots. We discuss the optical properties of bottom-up Cdots prepared from citric acid and urea using a solvothermal approach. We present our latest results on the study of aggregation of coronene labelled in a push-pull arrangement with a carboxylic group at one end and an amine in the opposite side as a model to understand the formation of Cdots (**Fig.1**). We explore the use of europium doped Cdots as a luminescent sensor for metal ions in aqueous media. A noticeable effect of photoluminescence quenching of doped Cdots was observed only in the presence of silver and mercury. The two metals cause different effects on the emission of the dopped Cdots enabling identifications of the metal present in solution.

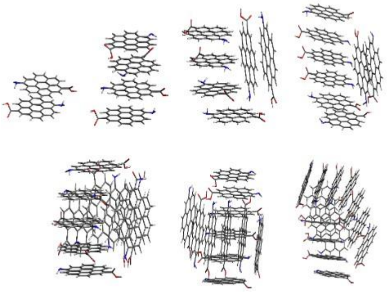

Figure 1. Global minimum structures of coronene clusters s clusters with the number n of coronene moieties (2<n<15)

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Exploring the effect of hierarchical porosity in BEA zeolite in Friedel-Crafts acylation of furan and benzofuran

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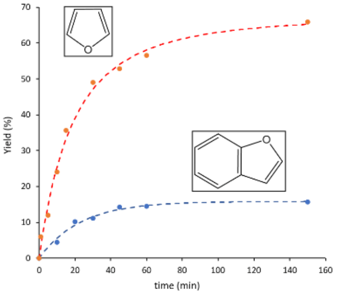
The acylation of aromatic compounds in organic synthesis can be achieved through Friedel-Crafts reactions. These reactions, especially interesting in the context of syntheses of fine and specialty products of pharmaceutical interest, occur usually in the presence of homogeneous catalysts such as strong Lewis or protonic acids. However, solid acid catalysts, such as zeolites, have several advantages over classical methods: they can be easily separated, offer some degree of regeneration and the side products are less toxic and corrosive[1].

In the last few years, we have studied the catalytic behavior of several substrates in Friedel Crafts acylation using hierarchical MCM-22[2] and BEA[3] zeolites, modified through alkaline treatment (0.1 M NaOH), followed, in some cases, by acid leaching with HCl. In this work we followed the same methodology, but extended the range of alkaline treatment to 0.2 and 0.4 M. To explore the effect of the hierarchical porosity we used two substrates with different molecular sizes, furan and benzofuran. All the kinetics results were modelled using a simplified Langmuir–Hinshelwood model equation from which rate constants and adsorption equilibrium constants were determined.



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Synthesis of New BODIPYs for PET Diagnosis

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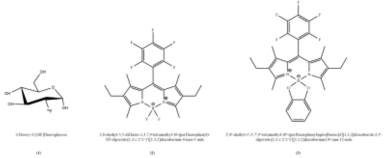
Positron Emission Tomography (PET) is a medical imaging methodology that can be used for diagnosis of several pathologies, namely cancer[1]. Its importance in the area of cancer diagnosis is growing due to its accuracy and ease of use. Most positron emitters are based on radioactive ^{18}F, which has a half-life of 109.7 minutes and is easily produced by proton bombardment of $H_2{}^{18}O$ in particle accelerators. The PET relevance in modern medical imaging diagnosis led to the search of new and efficient ^{18}F-containing molecules. The isotope exchange of ^{19}F for ^{18}F is one of the preferred ways to synthetize ^{18}F containing compounds, like the standard drug used in PET, the glucose derivative ^{18}F-FDG (**1**) showed in scheme 1. The isotopic exchange needs to be a fast synthetic procedure and therefore us and others are looking for new and faster alternatives for the SN2 substitution reactions as methods of incorporating ^{18}F in biocompatible molecules. One of the possible alternatives is the isotopic exchange on the boron instead on the carbon. That requires boron containing compounds like the BODIPYs. The BODIPYs (boron dipyrromethenes) have a large structural versatility that contributes to the definition of their unique spectroscopical, photophysical and chemical properties and are molecules that withstand large medium polarity or pH changes, besides presenting low self-aggregation in solution[2].



Scheme 1 - Structure of ^{18}F-FDG (**1**), BODIPY-*meso*-pentafluorinated (**2**) and BODIPY-catechol (**3**).

The BODIPY-*meso*-pentafluorinated (**2**) is formed by coupling the 3-ethyl-2,4-dimethyl-1*H*-pyrrole with the pentafluor-benzaldehyde in the presence of catalytic quantities of trifluoroacetic acid, resulting in the dipyrromethane that is oxidized to the corresponding dipyrromethene by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, followed by the addition of boron trifluoride. The synthesis of BODIPY-catechol (**3**) is based on the replacement of the fluorine atoms at the boron centre of compound (**2**) by a catechol molecule, in the presence of a Lewis acid catalyst. Our goal is to perform the incorporation of ^{18}F at the central boron atom. For that we are going to compare the efficiency of the process of ^{19}F to ^{18}F isotopic exchange *versus* the process of alcoxy by ^{18}F substitution, under several temperatures and solvents. Those data will provide us with a comparative kinetic study that can be used for the establishment of faster isotopic exchange pathways. This poster is going to present the synthesis of BODIPY-*meso*-pentafluorinated (**2**) and BODIPY-catechol (**3**) as well as a summary of its chemical and physical characteristics.

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The crystalline products of *L*−arginine and divalent metal ions

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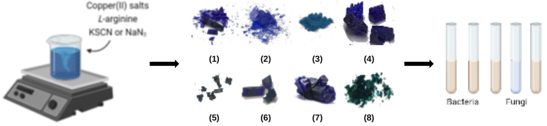
Two of the greatest goals in medicinal chemistry are to synthetize new drugs or to increase the quality/potency of the ones that are commercially available, while limiting side-effects.[1] Having this in mind, in the present work it was attempted the synthesis of new metal complexes (MC) with Ca(II), Mg(II), Cu(II) and Zn(II) ions as the central metal atoms, since it is known that metal-based compounds have, in general, noteworthy improved biological activities comparing to the parent drug.[2]

Eight MC with Cu(II) ions were successfully synthesized. The obtained single-crystals of formulae $\{[Cu(L{-}Arg)_2](NO_3)_2\cdot 3H_2O\}_n$ **(1)**, $[Cu(L{-}Arg)_2(SCN)_2]\cdot 2H_2O$ **(2)**, $[Cu(L{-}Arg)(SCN)_2]$ **(3)**, $[Cu(L{-}Arg)_2(N_3)_2][Cu(L{-}Arg)_2Cl](N_3)\cdot 7H_2O$ **(4)**, $\{[Cu_2(L{-}Arg)_2(N_3)_2(\mu{-}1,3{-}N_3)(\mu{-}1,1{-}N_3)][Cu(L{-}Arg)(N_3)(\mu{-}1,1{-}N_3)]\cdot 3H_2O\}_n$ **(5)**$[Cu(L{-}Arg)_2(N_3)_2][Cu(L{-}Arg)_2(N_3)](N_3)\cdot 6H_2O$ **(6)**, $[Cu(L{-}Arg)_2(H_2O)_2](N_3)_2$ **(7)** and $\{[Cu(L{-}Arg)(N_3)(\mu{-}1,3{-}N_3)]\}_n$ **(8)** were synthetized by slow crystallization from aqueous solutions. The products were characterized by the means of X-ray crystallography, infrared spectroscopy (FT-IR) and magnometry. The antimicrobial activity of the majority of the compounds was also evaluated. The tested compounds showed a strong activity against dermatophytes. In particular, **(3)**, **(7)** and **(8)** are highlighted for a much better MIC value comparing to the standard drug *Fluconazole*.



Acknowledgements: The support by a statutory activity subsidy from the Polish Ministry of Science and Higher Education for the Faculty of Chemistry, Wrocław University of Science and Technology is gratefully acknowledged. The authors are thankful to the Faculty of Pharmacy of University of Coimbra, FFUC, for supplying the antifungal and antibacterial strains used in this project.

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Synthesis and characterization of novel bio-based surface-active ionic liquids

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The continuous search for more environmentally friendly solvents, such as from biomass-derived chemicals, has been a target of research within the green chemistry area. The adequate solvent selection can significantly promote the sustainability of large-scale chemical processes. In this sense, the development of novel ionic liquids (ILs) able to boost the shift towards more sustainable industrial processes is an important contribution. Among these, ILs with surface-active characteristics play a significant role in food, cosmetic, pharmaceutical and several detergent-related industries. However, most surface-active ILs reported so far are imidazolium-based, which may raise health and environmental concerns. In this work, novel and more sustainable surface-active analogues of glycine-betaine ILs (AGB-SAILs), combined with the dodecylbenzenesulfonate ([DBS]) anion have been synthesized and characterized. The obtained AGB-SAILs were characterized by elemental analysis and spectroscopic methods. Their thermal properties, critical micellar concentration and ecotoxicity against *Allvibrio fischeri* were also determined. Their properties were compared with those of the commercial surfactant sodium dodecylbenzenesulfonate (SDBS). It was shown that all investigated AGB-SAILs are liquid at room temperature and thermally stable up to 216 ºC. Furthermore, most of them display a lower critical micellar concentration and lower toxicity towards *Allvibrio fischeri* than SDBS, thus being good alternatives to the commercial surfactant in a wide range of applications.

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Incorporation of porphyrins into SPEEK membranes: synthesis and characterization

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In the last decade, research on fuel cells has increased, aiming at developing commercially viable cells that can provide a cleaner and more efficient source of energy [1]. Proton exchange membranes (PEM) are one of the most expensive and important stack components influencing performance, durability and cost of fuel cells. PEMs function as electrolytes for transferring protons from the anode to the cathode, as well as providing a barrier to the passage of electrons and gas cross-leaks between the electrodes [2]. Perfluorinated sulfonic acid derivatives (e.g., Nafion, Aquivion, Aciplex, Flemion, Gore-Select) are the most used polymer membrane materials used in PEM fuel cells. Amongst these the Nafion series are the benchmark membranes due to their high mechanical strength, chemical and electrochemical stability and excellent proton conductivity. However, Nafion shows some drawbacks as, for example, high production costs. Looking to develop good alternatives to Nafion we prepared several porphyrin composite membranes using sulfonated poly ether ether ketone (SPEEK) and water soluble porphyrins, 5,10,15,20-*tetrakis*(4methylpyridyl)porphyrin (TPPy) and Cu(II)-5,10,15,20-*tetrakis*(4methylpyridyl)porphyrinate (CuTPPy). The TPyP and CuTPyP incorporation into SPEEK membranes, leading to the formation of porphyrin J-aggregates, does not modify the morphological properties of the SPEEK. However, the resulting composites present high chemical and temperature stability (increased range of operation temperature compared to Nafion), relatively high proton conductivity and low cost, which make them adequate to be used in fuel cells. The overall data will be discussed and preliminary studies on the potential use of SPEEK instead of Nafion membranes in Redox Flow Batteries will be presented.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support project nº UID/QUI/00313/2019. This work was supported by project "SunStorage - Harvesting and storage of solar energy", reference POCI-01-0145-FEDER-016387, funded by European Regional Development Fund (ERDF), through COMPETE 2020- Operational Programme for Competitiveness and Internationalization (OPCI), and by national funds, through FCT. L.D:D: thanks CNPq-Brasil for his PhD grant 232620/20148/6DG.

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Influence of acid-base properties of cobalt-lanthanide nanofibers on their catalytic activity for the methanation of CO_2

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Over the past centuries the intensive use of fossil fuels has caused an increase of CO_2 concentration in atmosphere, becoming the main carbon resource due to the decreases of limited resources such as coal, oil and natural gas, contributing to the 'greenhouse effect' and increasing the global temperature and climate change. [1] Efforts must be put forth to avoid the negative effects of climate change, such as, utilizing CO_2 (as C1 resource) in a catalytic process to manufacture valuable chemicals and fuels. [2,3]

The catalytic hydrogenation of CO_2 to methane, the *Sabatier* reaction, ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O; \Delta G = -130.8\ kJ/mol$), which associates the reaction of carbon dioxide with hydrogen, is performed over supported metals (e.g. noble metals, Ni, Co) and at atmospheric pressure. It is a reaction highly exothermic and thermodynamically favourable.[4] Cobalt-based catalysts exhibit a good performance in this reaction, being very active and selective for methane. The addition of promoters can improve their catalytic performance, increasing the activity and stability.[5]

The aim of this work was the preparation of nanofibers of cobalt-lanthanide bimetallic oxides (CoLn, Ln= La, Ce, Pr, Sm, Gd, Dy, Yb) by electrospinning technique (Figure 1) and evaluate their catalytic performance for the methanation of CO_2. The catalysts' acid-base properties seem to have an important contribution in their activity and selectivity, since an increase in basicity and oxygen's lability increases the catalyst activity. The nanofibers are basic and depending on lanthanide the strength of basic sites varies, and well correlate with catalytic performance. The best results were those obtained over CoYb.

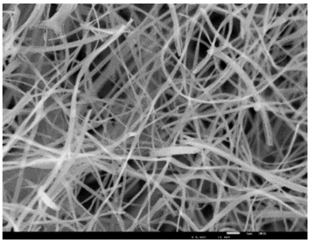

Figure 1. SEM image of nanofibers of cobalt-lanthanum bimetallic oxides

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Supported cerium-based catalysts on silica and carbon matrixes: redox properties

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The carbon dioxide (CO_2) concentration in the atmosphere continue to rise and efforts must be put forth to avoid negative environmental effects such as average global temperatures rise and ocean acidification [1-3]. The stabilization and decrease of atmospheric CO_2 levels requires significant reduction in emissions and increasing investment in its removal from the atmosphere taking at the same time advantage of the fact that CO_2 is at the same time an important C1 carbon source [4].

The most attractive way is to use CO_2 as raw material in catalytic process aiming the production of valuable chemicals and fuels, which is more desirable than sequestration because the amount of CO_2 mitigated by conversion with renewable energy is about 30 times better. Additionally, the value-added products of CO_2 conversion can be used to produce more complex chemicals and fuels. Among them, methane and higher hydrocarbons can be produced through direct CO_2 hydrogenation[4].

In this work, nanostructured Ni- or Co- cerium-based catalysts were synthesized and supported on two different matrixes: SiO_2 or carbon. There supports were prepared by the epoxide addition method or hydrothermal self-assembly in order to obtain aerogel structures and by the electrospinning technique to produce nanofibers. The catalysts were prepared by the incipient wetness impregnation technique and their catalytic performance studied for the hydrogenation of CO_2 to CH_4. The catalytic performance demonstrated to be dependent of the d-block element and catalysts' redox properties, better for Ni than for Co. The interaction between metal species and the different matrixes seems to be stronger for cobalt-cerium bimetallic oxides supported on carbon.

Acknowledgements: Authors gratefully acknowledge the support of the Portuguese "Fundação para a Ciência e a Tecnologia", FCT, through the PTDC/EAM-PEC/28374/2017 and UIDB/00100/2020 project.

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Activated carbons as active supports for bifunctional catalysts: exploring the surface chemistry and Pt immobilization method

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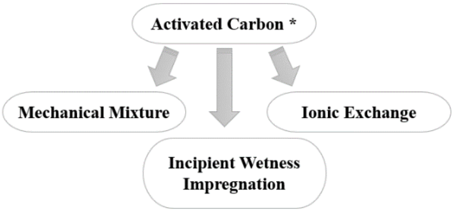
Activated carbons are porous materials with a wide range of applications, especially for adsorption in gas and liquid phase. However, the high porosity and rich surface chemistry of this class of materials makes them appealing for other applications such as heterogeneous catalysis[1]. In this work an activated carbon sample supplied by Ingevity, USA, was used as active support for the immobilization of Pt (1 wt.%) using several methods: mechanical mixture with commercial Pt/Al_2O_3, and incipient wetness impregnation and ionic exchange with $Pt(NH_3)_4Cl_2.xH_2O$. In some cases, prior to metal immobilization, the surface chemistry of the activated carbon was modified by performing oxidative treatments using optimized procedures[2].

The influence of the method of Pt introduction on the textural properties of the supported materials was studied through low temperature N_2 adsorption isotherms. The catalytic behavior of the bifunctional catalysts was explored in the hydroisomerization of long chain *n*-alkanes using *n*-decane as model molecule.



* Samples as received and after treatment with HNO_3 21% and 65% (w/w).

Simplified scheme of samples preparation

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Are ZnO- and TiO_2- Carbon Nanocomposites Exciting for Photocatalytic Activity?

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Water contamination is caused by thousands of different organic pollutants in very low concentrations, as a result of rapid urbanization and industrialization. There is a need to develop new nanomaterials for the efficient treatment of wastewater by means of photocatalysis processes powered by sunlight. Among several nanomaterials, zinc oxide (ZnO) and titanium dioxide (TiO_2) are two of the most used metal oxide semiconductors used in photocatalytic reactions. ZnO and TiO_2 have low toxicity, chemical stability, and wide band gap energy. An enormous effort has been put to improve the properties of these materials by the combination of their physicochemical properties with those of carbon nanotubes. These properties can be tuned according to the desired photocatalytic processes to subsequently improve the efficiency.

Herein, we present a controlled deposition of two metal oxides, ZnO and TiO_2, via atomic layer deposition (ALD) on high surface area supports, such as wave-like patterned carbon nanotube (w-VA-CNTs) arrays. From Figures 1a and 1b, it is possible to observe conformal, uniform and very thin films, with 26 and 11 nm layers of ZnO and TiO_2, respectively, which were obtained at 200 °C after 200 ALD cycles. The photocatalytic degradation of Rhodamine B using the synthesized nanostructures was assessed by following the absorbance of an aqueous solution of this dye over 240 min of irradiation (Figure 1c). Both materials show photocatalytic activity towards the degradation of Rhodamine B, which constitute very promising results towards their utilization in real wastewater streams.

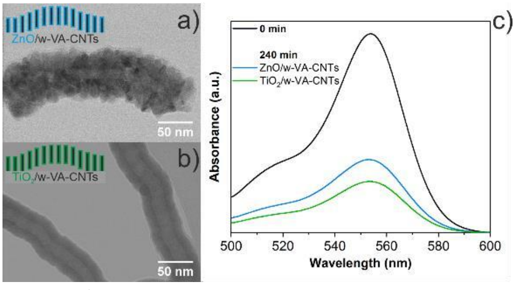

Figure 1: BF-TE-STEM images of carbon nanotubes decorated with (a) ZnO and (b) TiO_2 after 200 cycles. (c) Absorbance spectrum of Rhodamine B at the beginning and at the end of 240 min of irradiation using the ZnO and TiO_2 nanocomposites.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/ 50011/2020, financed by national funds through the FCT/MEC.

Optimising Reaction Conditions from Machine Learning Models

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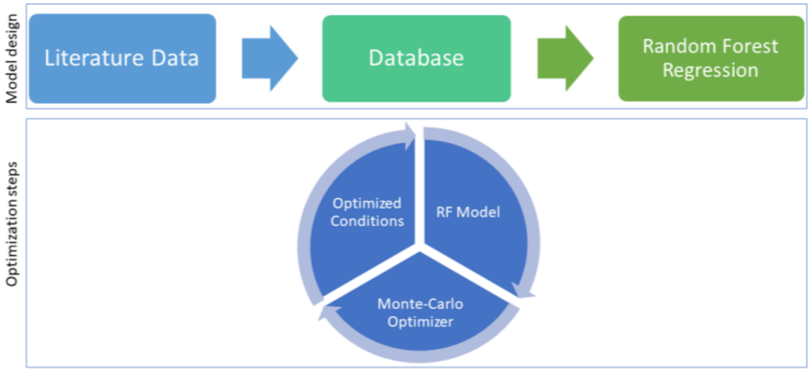
Aminoarenes are an important group of intermediates in the chemical industry. These compounds are usually produced by the reduction of nitroarenes (NA), and this reaction may be accomplished using catalytic routes with variable environmental impact and selectivity[1]. However, the proliferation of new catalysts, raises the question of which catalyst is better suited for a given substrate and/or deployment conditions.

In this work, we explore a database encompassing different reaction conditions, substrates, and catalysts, as well as a physicochemical characterisation of the latter.

The database was explored using a Random Forest regression scheme, to predict reaction speed from the variables selected as predictors.

Furthermore, to explore the Random Forest model, and find the optimised conditions, a Monte-Carlo optimiser was designed. Several cycles of this optimiser were executed, and the results of each run were stored and optimised on the next. The optimal conditions were assumed to be found when no significant optimisation between three consecutive runs was made.



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Decoding P-glycoprotein efflux mechanism: the role of substrate binding on signal transmission

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Multidrug resistance (MDR) to anticancer drugs is a significant contributor to cancer treatment failures, being P-gplycoprotein (P-gp) over-expression one of the most important MDR mechanism in tumor cells.[1] Thus, modulating drug efflux by P-gp is currently one of the promising approaches to overcome MDR. Nevertheless, and despite the increase on the number of published cryo-EM models, the mechanism of drug efflux is still unclear. To provide more insights on substrate specificity and signal-transmission mechanism between the transmembrane domains (TMD) and nucleotide-binding domains (NBD), computational studies were carried out. Starting from the previously published human wild-type (WT) P-gp model and four P-gp variants (G185V, G830V, F978A and ΔF335),[2] experimentally linked to changes in drug efflux and substrate specificity, the structural impact of these mutations on P-gp's architecture was assessed in the presence of substrates and modulators within the drug-binding pocket (DBP). The results upholded that while deep changes in the repacking of the transmembrane helices changes both i) the relative free-energies of binding (MM-PBSA) for most of the tested molecules, and ii) the mode and contact frequencies concerning protein-protein interactions, specifically at the TMD-NBD interfaces, but nonetheless similar to what was recently reported for cholesterol.[4] Taken together, all data points to the importance that both substrate binding and TMD-NBD interactions have in the mechanisms underlying the altered drug efflux observed in the above P-gp variants.

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Targeting the most common mutation in medium-chain acyl-CoA dehydrogenase with pharmacological chaperones: a breakthrough

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Medium-chain acyl-CoA dehydrogenase deficiency (MCADD) is the most common genetic disorder of the mitochondrial fatty acid β-oxidation pathway.[1] It results mostly from single amino acid changes (missense mutations) in the sequence of the human homotetrameric MCAD that can alter the enzyme's function and/or structure, impairing or fully abolishing its activity.[1]

Currently, the long-term treatment for MCADD is avoidance of fasting, being recommended a high-carbohydrate and reduced-fat diet, often supplemented with oral L-carnitine, in many countries.[1] Thus, the development of pharmacological chaperones able to specifically target MCAD and rescue the misfolded proteins are an attractive approach.[2]

For the most prevalent MCAD variant, p.K304E, previous computational studies identified the central β-domain as the most affected homotetramer region. Additionally, through molecular dynamics (MD) a distinct impact of the amino acid substitution on both dimers were also observed, along with severe disruption in the pockets' architecture and in the FAD and octanoyl-CoA binding affinities.[3]

A proof-of-concept concerning the discovery of pharmacological chaperones for MCADD treatment is herein provided through an optimization algorithm involving MD simulations, where free-energies of binding and ligand efficiency were evolved in a stepwise manner. Optimized compounds were experimentally evaluated for their effect on the p.K304E variant (using the WT as control). Some compounds show promising results in the thermal stability and enzyme inactivation assays, while others seem to increase the specific enzymatic activity of the variant protein.

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Supra-amphiphiles based on chalcones and sulfocalix[4]arenes for drug delivery

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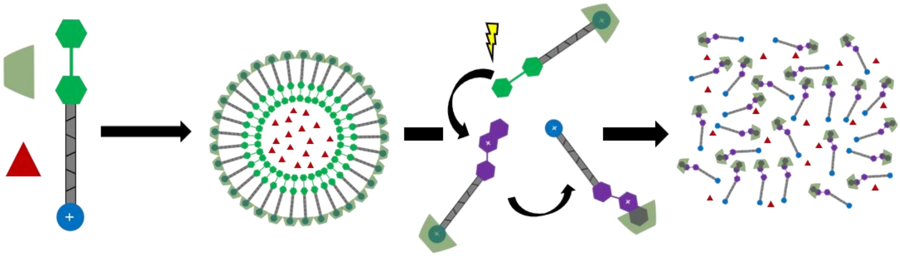
One of the major problems with drug administration is the unspecific delivery inside the organism. This causes that sometimes a larger dose must be given to the patient in order to achieve the desired local concentration. However, a larger dose comes with the problem of increased probability of undesired side-effects. In the last few years, some strategies to overcome this problem have been studied and one of them uses "smart" vehicles to deliver some specific cargo to some specific site within the organism. While there are many approaches in building these vehicles, one that we think to be of particular interest is the use of supramolecular amphiphiles that respond to external stimuli.[1]

The concept of supramolecular amphiphiles is, like "regular" amphiphiles, to have a polar head and an apolar tail that are bonded together by non-covalent interactions. This type of amphiphiles has some advantages since they can be more flexible and more prone to assembly/disassembly control via external stimuli. In this work we present a supramolecular type of amphiphile that can self-assemble into an ordered structure that could be used to control the delivery of payload cargo. To build this amphiphile 2-hydroxychalcone type molecules were employed since they can be interconverted into flavylium cations, thus disrupting the association with the calix-4-arene macrocycle. This interconversion is known to be controllable via light, pH and/or temperature stimuli with good conversion rates.[2]



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$LiNbO_3$ crystal as a test case for the correlation between experimental and theoretical polarized Raman spectra

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In this communication, the polarized Raman spectra of the *R*3*c* $LiNbO_3$ crystal is used as a benchmark test for DFT full periodic boundary conditions LCAO calculation of the Raman tensors, according to the implementation in the CRYSTAL software. The theoretical approach used provides excellent results regarding prediction of both wavenumbers and relative intensities for the transverse optical modes of both A_1 and E symmetry, considerably improving over previously reported data based on the plane-waves approach. Overall, the present investigation demonstrates that the LCAO approach, as implemented in the CRYSTAL software, gives excellent results regarding the calculation of Raman tensors and polarized Raman spectra. The possibility to put in correspondence the individual Raman tensors components and bands intensities in the different back-scattering experimental configurations revealed that the computed Raman tensors are very accurate, not only considering their average values (tensors invariant in the combination suitable for the description of Raman scattering of isotropic materials), but also when the tensors' individual components are considered. Based on the present results, a reassignment of the E (TO) modes of the *R*3*c* $LiNbO_3$ crystal is proposed, in particular for the 2 E and 9 E modes, which have been a matter of discussion over the years.

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Microwave spectroscopy of molecular switches

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Imine-based molecular motors and switches have been recently developed, and many of their properties remain largely unexplored.[1] With potential to perform multi-step unidirectional rotations, these systems are an important addition to the existing nano-motor toolbox.[2] Their photochemically-induced switching processes foresee applications in the regulation of chemical reactions, as well as performing mechanical functions. Microwave rotational spectroscopy appears as a technique which allows us to study the 3D structure of these molecules with incredible precision.[3] The pattern of rotational frequencies relates directly to the structure through the moments of inertia and can thus be compared to theoretical computations. In this contribution we will present rotational spectra for some simple molecular switches and the interpretation of these in order to demonstrate some of the applications of this technique.

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H-Tunneling Activated by Vibrational Excitation

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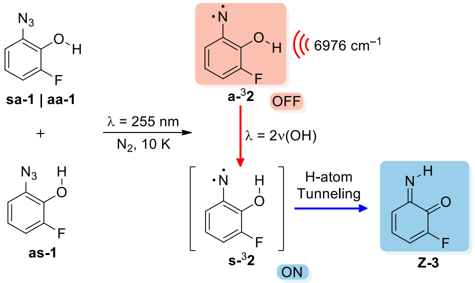
In the early days of quantum mechanics, Bell predicted theoretically that quantum tunneling could contribute significantly to chemical reactions involving the motion of hydrogen atoms.[1] Indeed, reports on the occurrence of H-tunneling are nowadays widespread in the fields of interstellar chemistry, biochemistry and catalysis.[2] Exciting studies aiming the control of tunneling have been carried out by modulating the reactant substituents, by isotopic labelling of key moving atoms, or by changing the reaction medium.[3,4] However, to the best of our knowledge, the control of tunneling activation by means of external radiation have never be achieved. We will demonstrate here a pioneer example of a tunneling reaction activated upon selective conversion of an unreactive to a reactive conformer by infrared vibrational excitation (Scheme 1). Experimental and theoretical results providing evidence of such achievement will be presented.



Scheme 1. Summary of the infrared induced conversion of an unreactive **a-^{3}2** to reactive **s-^{3}2** and subsequent spontaneous H-tunneling to **Z-3**.

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