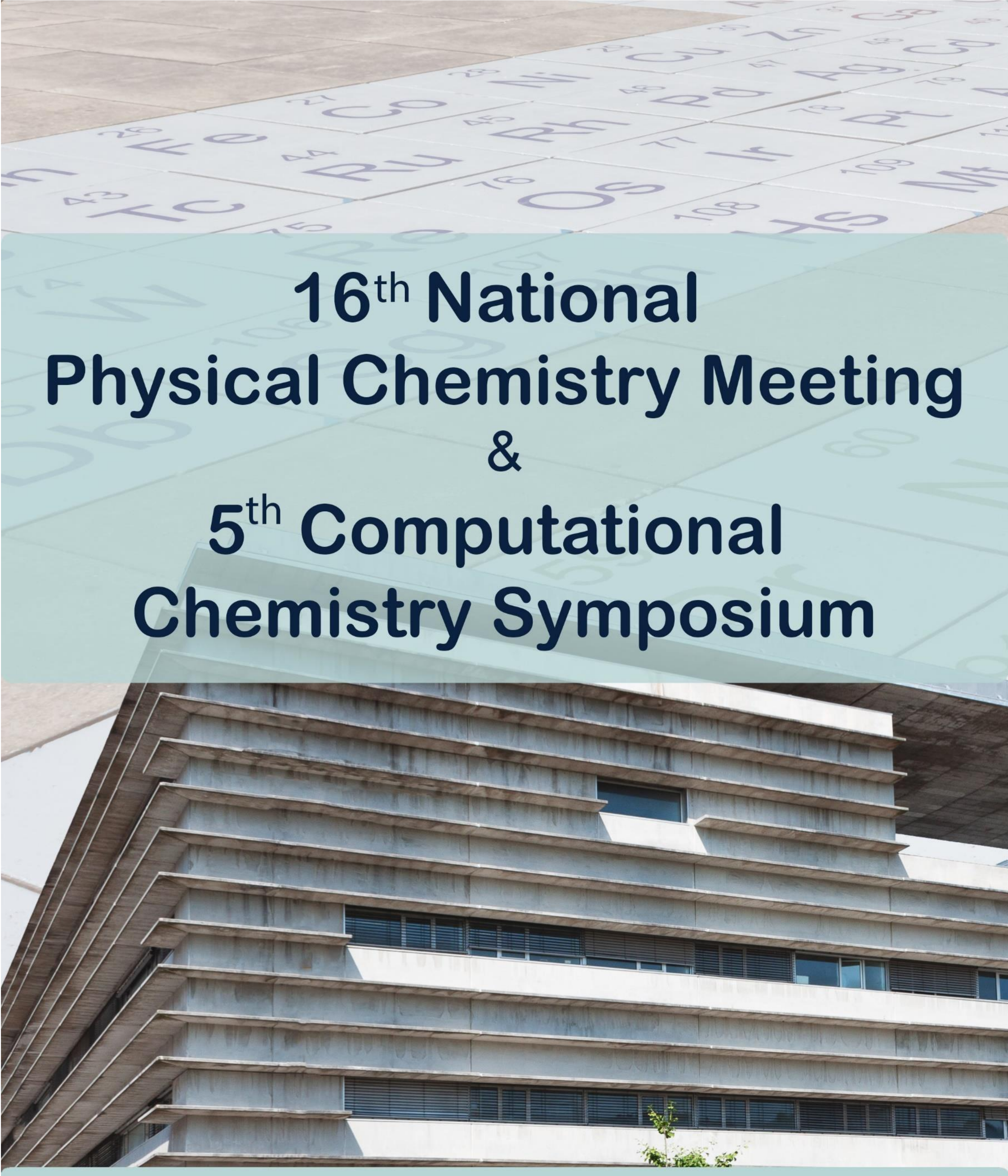


16th National Physical Chemistry Meeting & 5th Computational Chemistry Symposium

BOOK OF ABSTRACTS

PLENARY & KEYNOTE LECTURES
ORAL & POSTER COMMUNICATIONS

JULY 17-19, 2024
FACULDADE DE CIÊNCIAS
UNIVERSIDADE DE LISBOA

16th National Physical Chemistry Meeting (ENQF)
&
5th Computational Chemistry Symposium

Sociedade Portuguesa de Química

Book of Abstracts of the ENQF 2024
17 – 19 July 2024, Lisbon, Portugal

Sponsors

LABOR
SPIRIT, Lda.

ERT

mtb
PRECISION TECHNOLOGY

izasa
scientific
a werfen company

paralab

BRUKER

Dias de Sousa
INSTRUMENTAÇÃO ANALÍTICA E CIENTÍFICA, S.A.

photochem

SOCIEDADE PORTUGUESA DE QUÍMICA

FC
Ciências
ULisboa
Faculdade
de Ciências
da Universidade
de Lisboa

Contents

Foreword 1

Timeline of the ENQF 2

Committees 3

Programme 7

Plenary Lectures 13

Keynote Lectures 18

Sponsored Talks 23

Oral Communications 25

Poster Communications 69

List of communications 135

List of Participants 144

Foreword

Physical Chemistry is a wide and ever-growing research field, concerned with the study of macroscopic and microscopic chemical phenomena in terms of physical laws and concepts. It is a central discipline in Chemistry, essential to address not only blue-sky science, but also current societal challenges, such as food security, access to clean water, energy production and management, environmental pollution, and human health.

Organized by the Physical Chemistry Division of the Portuguese Chemical Society (SPQ), the National Physical Chemistry Meeting (ENQF), has, since its first edition in 1993, been an essential vehicle to bring together the national Physical Chemistry community, showcase ongoing research, and stimulate exchange of ideas and collaborations. Reflecting the importance of Computational Chemistry in the Portuguese Physical Chemistry scene, from 2016 on, the meeting has been held together with a Computational Chemistry Symposium.

The pandemic we have experienced in recent years forced the two previous meetings to be held online. Despite the great success of those meetings, it is pleasant that we can now return to in-person mode, which is irreplaceable to create opportunities for informal fruitful discussions, and connections that transcend the limitations of digital communication.

The considerable number of participants and submitted contributions gives a clear indication that the Portuguese physical chemistry community is strong and highly active. The present book of Abstracts highlights the wide range of topics covered in the meeting.

Last but not the least, I would like to thank CIÊNCIAS ULisboa, SPQ, and all sponsors for supporting the meeting, those involved in the organization and scientific committees for their contributions to bring the conference together, the invited speakers for kindly accepting to present lectures, and all national and international participants who are the true reason of the 16th ENQF.

Manuel Minas da Piedade

Conference Chair

Timeline of the ENQF

	Date	Chairman	Venue
I	1993 (June 2-4)	Sílvia Costa (IST-UTL)	Lisboa
II	1995 (June 21-23)	José Ferreira Gomes (UPorto)	Porto
III	1997 (November 20-22)	Manuel Nunes da Ponte (FCT-UNL)	Caparica
IV	1999 (October 1-2)	Hugh Burrows (UCoimbra)	Coimbra
V	2001 (September 12-14)	João Brandão (UAlgarve)	Faro
VI	2003 (August 31 – September 4)	Fernando Fernandes (FCUL)	Lisboa
VII	2005 (May 5-7)	Alexandre Magalhães (UPorto)	Porto
VIII	2007 (June 21-22)	Rui Fausto (UCoimbra)	Luso
IX	2009 (June 15-16)	João Coutinho (UAveiro)	Aveiro
X	2011 (July 3-6)	João Paulo André (UMinho)	Braga
XI	2013 (May 9-10)	Maria das Dores Ribeiro da Silva (UPorto)	Porto
XII	2016 (June 22-24)	João Paulo Ramalho (UÉvora)	Évora
XIII	2018 (June 4-6)	João Brandão (UAlgarve)	Faro
XIV	2021 (March 29-31)	Jorge Marques (UCoimbra)	online
XV	2023 (April 4-5)	Manuel Minas da Piedade (Ciências-ULisboa)	online
XVI	2024 (July 17-19)	Manuel Minas da Piedade (Ciências-ULisboa)	Lisboa

Committees

Organizing Committee

Manuel Minas da Piedade, Conference Chair (Universidade de Lisboa)
Alexandre Magalhães (Universidade do Porto)
Ana Viana (Universidade de Lisboa)
Carlos Bernardes (Universidade de Lisboa)
Ermelinda Eusébio (Universidade de Coimbra)
Filomena Martins (Universidade de Lisboa)
Herminio Diogo (Universidade de Lisboa)
João Paulo Leal (Universidade de Lisboa)
Jorge Marques (Universidade de Coimbra)
Luis Belchior Santos (Universidade do Porto)
Maria da Soledade Santos (Universidade de Lisboa)

Scientific Committee

João Paulo Ramalho (Universidade de Évora)
Jorge Parola (Universidade Nova de Lisboa)
José Nuno Canongia Lopes (Universidade de Lisboa)
Manuela Silva (Universidade do Minho)
Margarida Bastos (Universidade do Porto)
Paulo Fialho (Universidade dos Açores)
Rosa Perestrelo (Universidade da Madeira)
Rui Borges dos Santos (Universidade do Algarve)
Rui Fausto (Universidade de Coimbra)
Tito Trindade (Universidade de Aveiro)
Verónica Bermudez (Universidade de Trás-os-Montes e Alto Douro)

Local Organizing Committee

Manuel Minas da Piedade, Conference Chair (Ciências, Universidade de Lisboa)
Afonso Gonçalves (Ciências, Universidade de Lisboa)
Afonso Gordo (Ciências, Universidade de Lisboa)
Alejandro Ornelas (Ciências, Universidade de Lisboa)
Ana Maria Rosa (Ciências, Universidade de Lisboa)
Ana Viana (Ciências, Universidade de Lisboa)
Carlos Bernardes (Ciências, Universidade de Lisboa)
Catarina Sousa (Ciências, Universidade de Lisboa)
Filomena Martins (Ciências, Universidade de Lisboa)
Herminio Diogo (Ciências, Universidade de Lisboa)
Inês Feliciano (Ciências, Universidade de Lisboa)
João Paulo Leal (Ciências, Universidade de Lisboa)
Johan Korsnes (Ciências, Universidade de Lisboa)
José Fonseca (Ciências, Universidade de Lisboa)
Leonor Pedrosa (Ciências, Universidade de Lisboa)
Marco Fialho (Ciências, Universidade de Lisboa)
Maria da Soledade Santos (Ciências, Universidade de Lisboa)
Maria João Pintassilgo (Ciências, Universidade de Lisboa)
Mariana Ventura (Ciências, Universidade de Lisboa)
Ricardo Simões (Ciências, Universidade de Lisboa)
Rui Furtado Nunes (Ciências, Universidade de Lisboa)
Tomás Lourenço (Ciências, Universidade de Lisboa)

Venue

The location of the 16-ENQF Meeting is the **C6 Building** at Faculty of Science of Lisbon University (FCUL). The oral presentations will take place in rooms 6.1.36 and 6.2.53. The FCUL campus can be easily accessed.

Arriving by plane

From the airport take the METRO (Red line - Linha Vermelha) and change at ALAMEDA for the Green line (Linha Verde) direction TELHEIRAS and get off at CAMPO GRANDE station (~30min + 5 min walk to the meeting).
Taxi is also a good option (takes 15-20 minutes).

Arriving by train

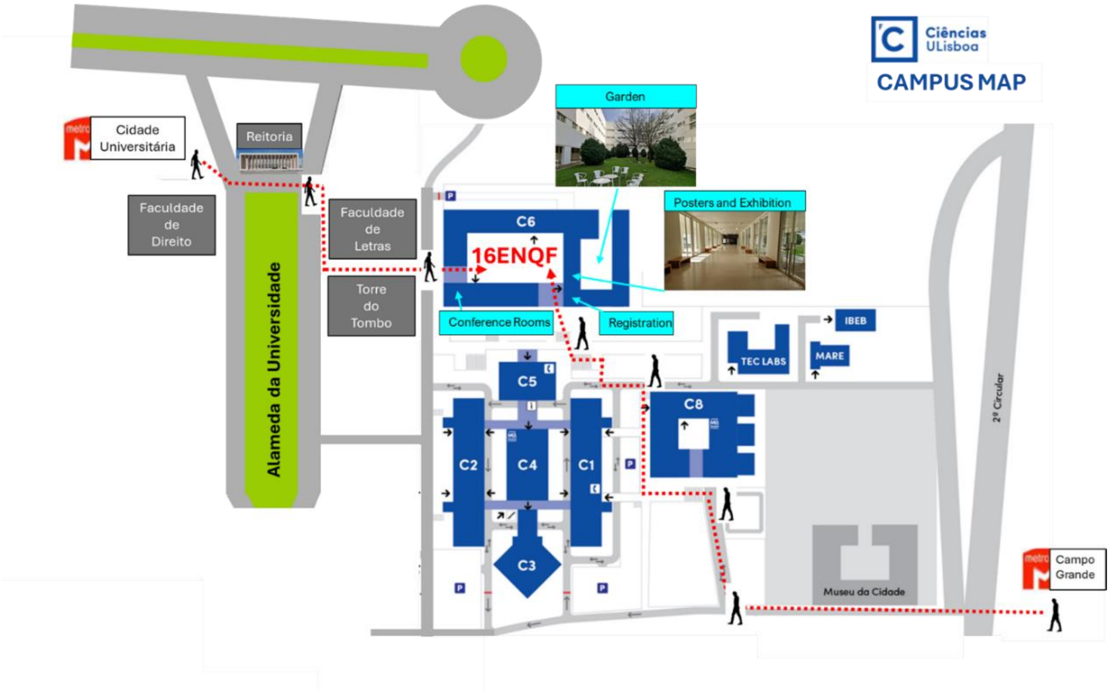
If you arrive by train from a European country, you will get off at GARE DO ORIENTE station. There take the METRO line and change at ALAMEDA for the Green line (Linha Verde). Get off at CAMPO GRANDE (5 min walk to the meeting).

Arriving by car

Take the 2ª Circular to Campo Grande / Cidade Universitária. Parking information: public pay-and-display car parks nearby.

Arriving from other parts of Lisbon

From other parts of Lisbon, we particularly recommend the use of public transportation. Buses stopping at FCUL: 7, 21, 31, 35, 36, 47, 64, 78, 83, 106, 108, 701, 738, 745, 750, 755, 767, 768, 777. Nearest METRO stations: Campo Grande (Green and Yellow lines) and Cidade Universitária (Yellow line). Buses: www.carris.pt/; Metro: www.metrolisboa.pt/eng.



Programme

JULY 17

11:00	Opening of Registration	
14:00-14:15	Opening Session Manuel Minas da Piedade (Conference Chair) Jorge Parola (General Secretary of SPQ) **Room 1: 6.1.36**	
14:15-15:00	PL1 Gérard Coquerel Université de Rouen Normandie *Controlled and spontaneous symmetry breaking by means of crystallization* **Chair:** Ermelinda Eusébio **Room 1: 6.1.36**	
	Room 1: 6.1.36 **Chair:** Filomena Martins	**Room 2: 6.2.53** **Chair:** João Paulo Leal
15:10-15:25	OC1.1 Vera L.S. Freitas *Enthalpic mapping of anthranilate and cinnamate Derivatives: An Experimental and Computational Approach*	OC2.1 Carlos F.R.A. Costa Lima *Reactivity patterns in the decomposition of fullerene derivatives via the retro-Diels-Alder reaction*
15:25-15:40	OC1.2 Inês Feliciano *Thermodynamic study of polymorphism in the nicotinamide+adipic acid co-crystal system*	OC2.2 Miriam Colaço *Supramolecular catalysis of diazocine isomerization*
15:40-15:55	OC1.3 Jorge Martins *For hydrophobic free energy (HFE) of linear alkylic molecules, not only size matters*	OC2.3 Bruno D.A. Pinheiro *Assessment of the mobility and fate of halogenated substituted benzonitriles and benzaldehydes*
15:55-17:40	Poster Session and Coffee Break	

17:40-18:10	KL1 Mara Freire Universidade de Aveiro *Ionic liquids, water and proteins: Favorable vs. competitive interactions to design separation processes* **Chair:** José Nuno Lopes **Room 1: 6.1.36**	
	Room 1: 6.1.36 **Chair:** Paulo Fialho	**Room 2: 6.2.53** **Chair:** Jorge Martins
18:15-18:30	OC1.4 Maria S.M. Mendes *Enhanced cancer biomarker detection in microfluidic devices using ionic liquid-based aqueous biphasic systems for serum pretreatment*	OC2.4 Liliana Gomes *Exploring coumarin-3-carboxamide derivatives as fluorescent metal cation detectors*
18:30-18:45	OC1.5 Rodrigo M.A. Silva *Thermodynamics of cation-fluorinated ionic liquids*	OC2.5 Artur F. Moreno Farinha *Optimizing vapor deposition of pentacene for inverted perovskite solar cells*
18:45-19:00	OC1.6 Carlos A. Nieto de Castro *Thermal conductivity of ionic liquids - A reappraisal*	OC2.6 Maria C.M. Sequeira *Seeking new low temperature energy storage systems: n-alkanes as phase change materials*

JULY 18

9:30-10:15	**PL2** Ana Aguiar-Ricardo Universidade Nova de Lisboa *Empowering sustainable development with supercritical CO_2 technologies* **Chair:** Luis Belchior Santos **Room 1: 6.1.36**	
	Room 1: 6.1.36 **Chair:** Ricardo Castro	**Room 2: 6.2.53** **Chair:** Karina Shimizu
10:25-10:40	OC1.7 Güliz Akyüz *Extraction of proteins from Tenebrio molitor flour using deep eutectic solvents*	OC2.7 Inês S. Fernandes *Modeling CO_2 electrochemical reduction in porous cathodes for liquid-phase electrolyzers*
10:40-10:55	OC1.8 Pedro C. Xavier *Improving niraparib's solubility using a deep eutectic solvent as a drug delivery system*	OC2.8 João Brandão *Studying the hydrogen combustion in carbon nanotubes*
10:55-11:10	OC1.9 Cláudio C. Fernandes *Varnishes? Paints? Why use toxic solvents in their formulation when there are eutectic systems?*	OC2.9 Joana R.S. Figueiredo *Experimental and theoretical insight into structural, energetic and electronic properties of 4-MPy adsorption onto zinc chalcogenide-based substrates*
11:10-11:30	Coffee Break	
	Room 1: 6.1.36 **Chair:** Manuela Silva	**Room 2: 6.2.53** **Chair:** Jorge Marques
11:30-11:45	OC1.10 Joana F.M. Sousa *Chitosan and naphthaldehydes derivatives composites: adsorptive remove of tetracycline from water*	OC2.10 Hugo Marques *A robust method for property prediction via artificial neural networks: Incorporating key structural features for carbon dioxide-ionic liquid mixtures*
11:45-12:00	OC1.11 Alexandre C.P.M. Alves *Sputtering of silver in thin films of long-chain imidazolium-based ionic liquids: An efficient approach to metal nanoparticle stabilization*	OC2.11 José Ferraz-Caetano *Making sense of data: Intelligible machine learning analytics for VOC vaporization enthalpy prediction*
12:00-12:15	OC1.12 Pedro M. Cruz Matias *Triazine porous organic polymers for simultaneous removal and sensing of antibiotics in water*	OC2.12 Hajer Bouznif *A combined structural, spectroscopic, and theoretical investigation of a water-soluble Schiff base: stability and enol-imine/keto-enamine tautomerism*
12:20-12:50	**KL2** Manuela Pereira Universidade de Lisboa *Energy transduction by biological systems* **Chair:** Margarida Bastos **Room 1: 6.1.36**	
12:50-14:15	Lunch	

14:15-15:00	PL3 Eduardo Marques Universidade do Porto *Self-assembled colloids: When physical chemistry interfaces with nanomedicine and nanomaterials* **Chair:** Cristóvão S. Dias **Room 1: 6.1.36**	
15:00-15:10	Sponsor presentation - PARALAB	
	Room 1: 6.1.36 **Chair:** Rosa Perestrelo	**Room 2: 6.2.53** **Chair:** João Brandão
15:15-15:30	OC1.13 Patrícia Sousa *MALDI-TOF MS-based urinary peptidomics biosignature of breast cancer as a powerful approach for diagnosis*	OC2.13 Andreia Fortuna *Halogen anisotropy in solvation and membrane permeability: implications for protein-ligand binding and drug efficiency*
15:30-15:45	OC1.14 Marta Giza Serra *Metrological study on a relationship between salinity and surface tension of buffered artificial seawaters*	OC2.14 Wahi Noor *Eutectic mixture formation and relaxation dynamics of co-amorphous mixtures of two antifungal imidazole drugs*
15:45-16:00	OC1.15 Teresa Abreu *Volatilomic fingerprint of grape pomace as a sustainable approach for its valorization*	OC2.15 Cristóvão S. Dias *Structural criterion for the onset of rigidity in a colloidal gel*
16:00-17:10	Poster Session and Coffee Break	
17:10-17:40	KL3 Sérgio Melo Universidade de Coimbra *Bright and dark molecules: A photophysical journey* **Chair:** Jorge Parola **Room 1: 6.1.36**	
	Room 1: 6.1.36 **Chair:** Tito Trindade	**Room 2: 6.2.53** **Chair:** Nuno Bandeira
17:45-18:00	OC1.16 Lydia dos Orfãos *Exploring the ^{19}F NMR and photoluminescence of fluorinated dendrimers for gene delivery*	OC2.16 Diogo José Lopes Rodrigues *Open subsystem-based partition of molecular energies into resonance structure-resolved contributions*
18:00-18:15	OC1.17 Nuno Basílio *Exploring the kinetic and thermodynamic stability of photoresponsive cucurbituril-dithienylethene inclusion complexes*	OC2.17 Joana Ribeiro da Silva *Computational venom whispering to decode molecular insights of bee and snake-secreted phospholipases A2*
18:15-18:30	OC1.18 Duarte Fernandes *Properties of proton and metal-ion bound to PAMAM dendrimer primary and tertiary amines*	OC2.18 Joana R.S. Santos *Unveiling pesticide interactions: Insights from the Aplysia californica AChBP-imidacloprid complex*
18:35	Meeting of the SPQ Physical-Chemistry Division **Room 1: 6.2.52**	
19:30	*Dinatoire*	

JULY 19

9:30-10:15	**PL4** Chiara Cappelli University of Pisa ***Multiscale modeling of complex systems: from solvation to nanoplasmonics*** **Chair:** Alexandre Magalhães **Room 1: 6.1.36**	
	Room 1: 6.1.36 **Chair:** Ricardo Franco	**Room 2: 6.2.53** **Chair:** João Paulo Ramalho
10:25-10:40	OC1.19 Daniel J.V.A. dos Santos *A new road to discover ABC transporter modulators*	OC2.19 César Mogo HO_2* *stabilization in the presence of argon*
10:40-10:55	OC1.20 Luís P. Viegas *Constrained transition state randomization: A general transition state sampling method for bimolecular reactions*	OC2.20 Nuno A.G. Bandeira *Beyond DFT: Tackling the strong correlation problem in noble gas chemistry*
10:55-11:10	OC1.21 André Seco *How cucurbit[7]urils allow the formation of a highly stable and stimuli responsive hexacationic flavylium-based quaternary rotaxane*	OC2.21 Leonardo José Duarte *Investigation of the IVR isomerization of nitrous acid*
11:10-11:30	Poster Session and Coffee Break	
11:30-12:00	**KL4** António José Candeias Universidade de Évora *For nothing is secret that will not be revealed, nor anything hidden that will not be known and come to light … or when Science meets Art* **Chair:** Rui Fausto **Room 1: 6.1.36**	
12:00	Awards and Closing Session	

Plenary Lectures

PL1 Controlled and spontaneous symmetry breaking by means of crystallization

G. Coquerel,[1] *W.-S. Kim,*[2] *B. J. Park*[2]

[1] *SMS UR3233Université de Rouen Normandie, Place Emile Blondel 76821 Mont-Saint-Aignan CEDEX FRANCE*
[2] *Functional Crystallization Center, Department of Chemical Engineering (BK21 FOUR Integrated Engineering Program), Kyung Hee University, Yongin, Gyeonggi-do 17104, Republic of Korea Country*
Email: gerard.coquerel@univ-rouen.fr

Crystallization offers a variety of methods for spontaneous macroscopic chiral symmetry breaking.[1] The corresponding processes are run close to equilibrium for Deracemization Induced by a Flux of Energy Crossing the Suspension (Viedma[2] ripening, TCID and other deracemization variants where a single flux or several fluxes of energy pass through a suspension) or with a significant departure from equilibrium for the Kondepudi[3] experiment with preferential secondary nucleation, or even very far from equilibrium in the case of Preferential Enrichment[4] (PE). Those processes include an important amplification of local fluctuations and their mechanisms are currently the focus of many studies. Interestingly, as the system departs more from equilibrium, the mechanical stress imposed on the system has to be softened in order to observe the spontaneous chiral symmetry breaking. Indeed, in Viedma ripening performed close to equilibrium, all sorts of abrasions, breakages, defects induced by shear forces, etc., are beneficial to the advancement of chiral symmetry breaking. In the Kondepudi experiment, the mechanical stress must be softer to avoid primary and secondary heteronucleation in the system. In the case of Preferential Enrichment (PE), the very large departure from equilibrium has to be associated with almost stagnant conditions. Indeed, for the latter case a simple magnetic stirrer is sufficient to return the solution to normal conditions of crystallization without macroscopic chiral symmetry breaking. The latest results on systems close to equilibrium, suggest that the nature of the stirring can also impact on the symmetry breaking.[5] Indeed, coherent motions of the suspension (in a Couette-Taylor reactor) is more efficient than chaotic stirring such as that in a mixed tank. Size also matters:[6] small systems like sessile drops, offer a facile and spontaneous symmetry breaking.

References

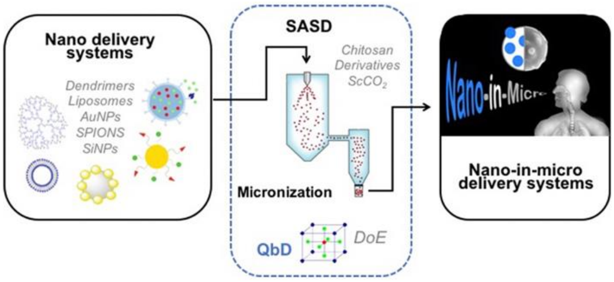
1. G. Coquerel, M. Hoquante; *Symmetry* **2020**, *12*, 1796
2. C. Viedma; *Phys. Rev. Lett.* **2005**, *94*, 065504
3. D.K. Kondepudi, K.L. Bullock, J.A. Digits, J.K.Hall, J.M. Miller; *J. Am. Chem. Soc.* **1993,** *115*, 10211-10216
4. C. De Saint Jores, C. Brandel, M. Vaccaro, N. Gharbi, I. Schmitz-Afonso, P. Cardinael, R. Tamura, G. Coquerel; *Molecules* **2022**, *27*, 8652.
5. Z, Bowen, G. Coquerel, B.J. Park, W-S. Kim; *Cryst. Growth Des.* **2024**, *24*, 5893-5897.
6. S.Y. Bak, G. Coquerel, W.-S. Kim, B. J. Park; *J. Phys. Chem. Lett*. **2023**, *14*, 785-790

PL2 Empowering sustainable development with supercritical CO_2 technologies

A. Aguiar-Ricardo

LAQV-REQUIMTE, Department of Chemistry, NOVA School of Science and Technology, Universidade NOVA de Lisboa, 2829-516, Caparica, Portugal
Email: air@fct.unl.pt

All member countries of the United Nations committed to 17 Sustainable Development Goals for promoting inclusive well-being in the world. The need for sustainable approaches is invading all fields and steps of manufacturing. From the choice of a green solvent and natural materials to the use of safe chemical reactions and processes, many efforts are described in literature. This lecture will address specific challenges on the bottom-up assembling of complex composite formulations. Special attention will be given to the integration of supercritical fluid assisted spray drying with other technologies for the generation of precision formulations, for the delivery of small molecule therapeutics to biologic drugs and nucleic acids, namely: i) nano-in-microparticles solid dosage forms for pulmonary delivery;[1] ii) micronized layer-by-layer siRNA powders;[2] iii) nano-in-micro POxylated polyurea dendrimer solid dosage forms;[3] iv) liposomal dry powder formulations with hydrophobic and hydrophilic compounds.[4,5] Our results demonstrate the potential of $scCO_2$-assisted technologies for particle engineering of pharmaceutical materials, especially in the manufacture of pulmonary drug delivery systems, considering the tight requirements necessary for the final aerosol properties.



Acknowledgements: This work was financed by national funds from FCT – Fundação para a Ciência e a Tecnologia, I.P., in the scope of the project, Associate Laboratory for Green Chemistry – LA/P/0008/2020 (DOI: 10.54499/LA/P/0008/2020), UIDP/50006/2020 (DOI: 10.54499/UIDP/50006/2020) and UIDB/50006/2020 (DOI: 10.54499/UIDB/50006/2020) and CA18224 GREENERING ("Green Chemical Engineering Network towards upscaling sustainable processes"). COST Actions are funded within the EU Horizon 2020 Program.

References

1. A. Aguiar-Ricardo; *Curr. Opin. Green Sust. Chem*. **2017**, *5*, 12-16.
2. A.S. Silva, K.E. Shopsowitz, S. Correa, S.W. Morton, E.C. Dreaden; T. Casimiro, P.T. Hammond, A. Aguiar-Ricardo, *Int. J. Pharm.* **2020**, *591*, 119989.
3. R.B. Restani, M.T. Tavares, R.F. Pires, P.V. Baptista, A.R. Fernandes, T. Casimiro, V.D.B. Bonifácio, A. Aguiar-Ricardo; *Part. Part. Syst. Charact.* **2020**, *37*, 1900447.
4. C. Costa, B. Nobre, A.S. Matos, A.S. Silva, T. Casimiro, M.L. Corvo, A. Aguiar-Ricardo; *J. CO_2 Util.* **2021**, *53*, 101709.
5. C. Costa, T. Casimiro, M. L. Corvo, A. Aguiar-Ricardo; *J. Supercrit. Fluids* **2023**, *200*, 105991.

PL3 Self-assembled colloids: when physical chemistry interfaces with nanomedicine and nanomaterials

E. F. Marques

Centro de Investigação em Química (CIQUP)/IMS, Departamento de Química e Bioquímica, Faculdade Ciências, Universidade do Porto, Portugal
Email: efmarque@fc.up.pt

Self-assembled colloids are nano-scale fluid systems spontaneously formed from amphiphiles, such as surfactants, lipids, or certain polymers like poloxamers. Amphiphiles are very versatile molecules, helping to bridge "things" and bring some order to the molecular world. They organize at surfaces, forming Gibbs and Langmuir monolayers, impacting properties like surface tension and wettability, and in bulk, they form various nanostructures from micelles to liquid crystals, influencing mixing, transport and flow. Physical chemistry provides the framework and experimental toolbox to understand these phenomena, connecting with fields like nanomedicine and materials science.

This talk will discuss recent research in our group characterizing different surfactant-based systems, including amino acid-based[1] and gemini surfactants, [2] as well as cationic/anionic[2] and polymer/surfactant mixtures (Fig. 1). We'll explore the interplay between electrostatic and hydrophobic interactions driving self-assembly. We'll demonstrate then how self-assembled colloids can enable smart, stimuli-responsive delivery of therapeutic molecules into cells.[1,2] Additionally, we'll show how amphiphiles can be key to the exfoliation and non-covalently functionalization of nanomaterials (e.g. carbon nanotubes and 2D materials),[3,4] facilitating the fabrication of nanocomposites, such as novel electrocatalysts for energy-related reactions (like oxygen reduction and evolution) critical for fuel cells and water splitting.[5]

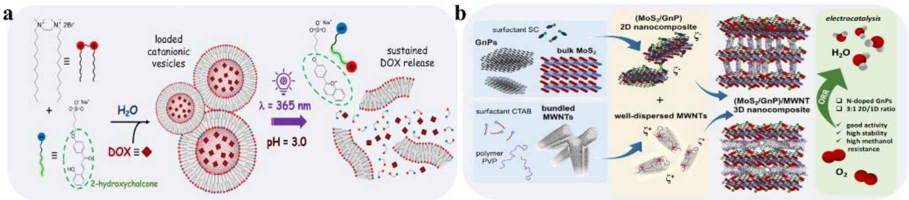


Fig. 1. Self-assembly driving: a) photo-triggered drug delivery; b) nanocomposite fabrication.

Acknowledgements: Thanks are due to FCT for funding through CIQUP (UIDB/00081/2020), Institute of Molecular Sciences - IMS (LA/P/0056/2020) and grant 2022.05543.PTDC.

References

1. I.S. Oliveira, R.L. Machado, M.J. Araújo, A. Gomes, E.F. Marques; *Chem. Eur. J.* **2021**, *27*, 692-704.
2. D. Moreira, O. Regev, N. Basilio, E.F. Marques; *J. Colloid Interface Sci.* **2023**, *650*, 2024–2034.
3. R.M.F. Fernandes, B. Abreu, B. Claro, M. Buzaglo, O. Regev, I. Furó, E.F. Marques; *Langmuir* **2015**, *31*, 10955-10965.
4. B. Abreu, B. Almeida, P. Ferreira, R.M.F. Fernandes, D.M. Fernandes, E.F. Marques; *J. Colloid Interface Sci.* **2022**, *626*, 166-167.
5. B. Abreu, M. Rocha, M. Nunes, C. Freire, E.F. Marques; *J. Mater. Sci.* **2021**, *56*, 19512-19527.

PL4 Multiscale modeling of complex systems: from solvation to *nanoplasmonics*

C. Cappelli

Scuola Normale Superiore, Piazza dei Cavalieri, 7, 56126, Pisa, Italy
Email: chiara.cappelli@sns.it https://embedlab.sns.it

The conventional notion of complexity in chemistry often pertains to intricate molecular structures. However, complexity can also manifest when chemical species interact with their environment or radiation, individually or in combination. Even apparently simple molecules exhibit a significant degree of complexity when embedded in the external environment and responding to electromagnetic fields.

In modeling complex systems in the condensed phase, fully atomistic multiscale approaches have demonstrated considerable success. A particularly effective strategy for solvated systems involves focusing on a specific portion described at the Quantum Mechanical (QM) level, while treating the remaining portion classically using tailored Molecular Mechanics (MM) forcefields.[1] The extension of such methodologies to complex plasmonic nanostructured materials poses additional challenges because resonance with external probing fields must be considered.[2]

In this lecture, I will present my recent contributions to the development of fully atomistic multiscale approaches, showcasing pilot applications that underscore the potential of these methods. Through these discussions, I aim to shed light on the challenges and opportunities in modeling solutions[3-8] and complex plasmonic nanostructured materials[9-14] within the framework of multiscale approaches.

References

1. H. M. Senn, W. Thiel; *Angew. Chem. Int. Ed.* **2009**, *48*, 1198.
2. T. W. Odom, G. C. Schatz; *Chem. Rev.* **2011**, *111*, 3667.
3. T. Giovannini, F. Egidi, and C. Cappelli; *Chem. Soc. Rev.* **2020**, *49*, 5664.
4. T. Giovannini, C. Cappelli; *Chem. Comm.* **2023**, *59*, 5644.
5. T. Giovannini, F. Egidi, C. Cappelli; *Phys. Chem. Chem. Phys.* **2020**, *22*, 22864.
6. F. Egidi, S. Angelico, P. Lafiosca, T. Giovannini, C. Cappelli; *J. Chem. Phys.* **2021**, *154*, 164107.
7. P. Lafiosca, S. Gómez, T. Giovannini, C. Cappelli; *J. Chem. Theory Comput.* **2022**, *18*, 1765.
8. P. Lafiosca, F. Rossi, F. Egidi, T. Giovannini, C. Cappelli; *J. Chem. Theory Comput*. **2024**, *20*, 266.
9. T. Giovannini, M. Rosa, S. Corni, C. Cappelli; *Nanoscale* **2019**, *11*, 6004.
10. T. Giovannini, L. Bonatti, M. Polini, C. Cappelli; *J. Phys. Chem. Lett.* **2020**, *11*, 7595.
11. L. Bonatti, L. Nicoli, T. Giovannini, C. Cappelli; *Nanoscale Adv.* **2022**, *4*, 2294.
12. T. Giovannini, L. Bonatti, P. Lafiosca, L. Nicoli, M. Castagnola, P. Grobas Illobre, S. Corni, C. Cappelli; *ACS Photonics* **2022**, *9*, 3025.
13. S. Zanotto, L. Bonatti, M. F. Pantano, V. Miseikis, G. Speranza, T. Giovannini, C. Coletti, C. Cappelli, A. Tredicucci, A. Toncelli; *ACS Photonics* **2023**, *10*, 394.
14. P. Lafiosca, L. Nicoli, L. Bonatti, T. Giovannini, S. Corni, C. Cappelli; *J. Chem. Theory Comput.* **2023**, *19*, 3616.

Keynote Lectures

KL1 Ionic liquids, water and proteins: Favorable vs. competitive Interactions to design separation processes

M.G. Freire,

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

Ionic liquids (ILs) have gained recognition as “greener” solvents compared to conventional volatile organic solvents, primarily due to their non-volatile nature at ambient conditions. The extensive variety of possible ion combinations, each with distinct chemical structures, allows ILs to be tailored for specific applications, offering a unique set of properties. This versatility has spurred significant research into their potential as media for the separation and purification of bioactive compounds from diverse sources. ILs have been explored as solvents, co-solvents, co-surfactants, electrolytes, and adjuvants in liquid-liquid systems, as well as in the development of IL-supported materials.

This presentation will review the major outcomes achieved using IL-water-based processes for protein separation and purification. It will deeply discuss the role of specific interactions in determining the selectivity and performance of these processes. Additionally, the key accomplishments in the field will be highlighted, along with future challenges and directions for research and technology transfer.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI 10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MEC (PIDDAC).

KL2 Understanding proton exchange membrane fuel cells by advanced transmission electron microscopy

M. Pereira

Departamento de Química e Bioquímica and BioISI – Biosystems & Integrative Sciences Institute
Faculdade de Ciências, Universidade de Lisboa, Portugal
Email: mmpereira@fc.ul.pt

Life relies on the constant exchange of different forms of energy. Therefore, organisms have evolved in a way to be able to harvest the energy made available by external sources (such as light or chemical compounds) and convert it into biological useable energy forms, such as the transmembrane difference of electrochemical potential ($\Delta\tilde{\mu}$). Respiratory proteins contribute to the establishment of $\Delta\tilde{\mu}$ by coupling exergonic catalytic reactions to the endergonic translocation of charges (electrons/ions) across the membrane. We have been exploring the respiratory alternative complex III – ACIII and here I will discuss it as an example of an energy transducing machine.

Acknowledgements: The work in the group was funded by Fundação para a Ciência e a Tecnologia (DOI 10.54499/PTDC/BIA-BQM/2599/2021 to MMP) and further supported by UIDB/04046/2020 (DOI: 10.54499/UIDB/04046/2020) and UIDP/04046/2020 (DOI: 10.54499/UIDP/04046/2020) Centre grants from FCT, Portugal (to BioISI).

KL3 Bright and dark molecules: A photophysical journey

S. Melo

University of Coimbra, CQC-IMS, Department of Chemistry, Rua Larga, 3004-535 Coimbra, Portugal
Email: sseixas@ci.uc.pt

Upon light absorption, molecules can undergo decay by a variety of pathways. Some molecules are non-emissive and contribute to photoprotective mechanisms, while others become emissive upon aggregation. Molecules of Colour belong to the former category. In contrast, AIEgens, which exhibit aggregation-induced emission (AIE), and molecular systems capable of efficient emission across the entire visible spectrum, known as white light emission (WLE), belong to the latter group. For example, aggregates formed by diphenylbenzofulvene (DPBF) derivatives exhibit WLE, and structural modifications can lead to an approximation of pure white light emission.[1] The implications of studying these molecules range from practical applications in light capture and storage to the preservation of cultural heritage.[1-2] Examples of dark (non-emissive) molecules are indigo and indirubin, which have different excited state decay mechanisms. In the excited state, these molecules efficiently undergo a radiationless deactivation process related to their extraordinary molecular stability. These excited state decay mechanisms include ESPT, conformational isomerism and trans-cis photoisomerisation. Photostability can be conferred by ESPT involving the N-H...O=C groups of indigo and indirubin, but also by the introduction of other functional groups.[3] In the case of highly emissive molecules, we find the synthetic derivatives such as tioindigo[4] or substituted TPE derivatives[5] in solution and in solid state.

The interplay between these different deactivation mechanisms and their resulting properties will be presented and discussed.

Acknowledgements: We acknowledge support from the Coimbra Chemistry Centre-IMS, which is supported by FCT through Projects UIDB/00313/2020 and UIDP/00313/2020.

References

1. A. C. B. Rodrigues and J. S. Seixas de Melo; in *Aggregation-Induced Emission: From Small Molecules to Polymers—Historical Background, Mechanisms and Photophysics*, Eds.: Y. Tang and B. Z. Tang), Springer International Publishing, Cham, **2022**, 209-246.
2. a) D. Pinheiro, M. Pineiro and J. S. Seixas de Melo; *Comm. Chem.* **2021**, *4*, 89; b) C. Clementi, M. J. Melo, A. Romani and J. S. Seixas de Melo in *Organic Dyes and Lake Pigments*, Eds.: A. Romani, A. Nevin, D. Comelli and M. J. Melo), Springer International Publishing, Cham, **2024**, 1-38.
3. a) J. S. Seixas de Melo; in *The molecules of colour. The real blue indigo: photostability mechanisms, new functional derivatives, and hybrids*, *Vol. 49* Eds.: S. Crespi and S. Protti, The Royal Society of Chemistry, **2022**, 31-52; b) D. C. Nobre, E. Delgado-Pinar, C. Cunha and J. Sérgio Seixas de Melo; *Phys. Chem. Chem. Phys.* **2024**, *26*, 7416-7423.
4. R. C. Pereira, M. Pineiro, A. M. Galvão and J. S. Seixas de Melo; *Dyes and Pigments* **2018**, *158*, 259-266.
5. A. C. B. Rodrigues, I. S. Geisler, P. Klein, J. Pina, F. J. H. Neuhaus, E. Dreher, C. W. Lehmann, U. Scherf and J. S. Seixas de Melo; *J. Mat. Chem. C* **2020**, *8*, 2248-2257.

KL4 For nothing is secret that will not be revealed, nor anything hidden that will not be known and come to light … or when Science meets Art

A. Candeias

IN2PAST Associated Laboratory, HERCULES Laboratory and City University of Macau Chair in Sustainable Heritage, Evora University, Portugal
Email: candeias@uevora.pt

For nothing is secret that will not be revealed, nor anything hidden that will not be known and come to light…explores the fascinating realm where scientific techniques intersect with the world of art. This communication highlights the innovative methods employed by scientists to explore artworks. Utilizing various complementary analytical techniques and electromagnetic radiations chemistss reveal hidden layers and structures, stratigraphies and material compositions, offering a deeper understanding of artistic masterpieces and cultural heritage.

Particularly relevant are the recent advances in imaging and non-invasive point and mapping analytical techniques that allow the development of comprehensive non-invasive studies and integrated conservation projects. In this talk we will explore the use of multi-analytical methodologies and the integration of new non-invasive and imaging techniques with application in conservation and heritage science showcasing collaborative projects at HERCULES Laboratory on easel paintings, mural paintings, illuminated manuscripts, polychrome sculptures, textiles, among others.

Fig. 1. Old Goa Revelations project (2022.10305.PTDC) field mission snapshots, Goa, January 2023.

Acknowledgements: The author wishes to acknowledge HERCULES Lab team for the work developed under the collaborative projects, the Portuguese Foundation for Science and Technology through the contracts UIDP/04449/2020 and UIDB/04449/2020 (HERCULES Laboratory) and the National Key R&D Program of China (2021YFE0200100).

Sponsored Talk

ST1 Optimization of supercritical fluid extraction (SFE) and reaction systems

J. Carvalheira, S. Cardoso

Paralab, S.A., Portugal
Email: joao.carvalheira@paralab.pt

Supercritical fluids (SCFs), with their unique properties and tunability, are powerful alternatives to traditional organic solvents, enabling a wide range of chemical and biological engineering processes. They facilitate the selective extraction of valuable or undesirable compounds from solids, the fractionation of liquids, and the impregnation of porous materials. SCFs also support particle formation processes and increase chemical reaction rates with improved selectivity. Their potential to inactivate microorganisms is valuable for sterilization in medical and food applications. In addition, supercritical CO_2 offers a "green" solution by replacing toxic solvents and minimizing the need for solvent clean-up operations. By customizing equipment design, we can fully exploit the unique properties of supercritical fluids for specific applications. We can fine-tune systems to match the scale of operation, desired throughput, and particular compounds in focus. As a result, the inherent versatility of SCFs is used to meet a wide range of application requirements, providing customized, efficient, and environmentally sustainable solutions.

Fig. 1. Customized compact SFE system up to 600 bar.

Oral Communications

OC1.1 Enthalpic mapping of anthranilate and cinnamate derivatives: An experimental and computational approach

V.L.S. Freitas, C. A. O. Silva, M. D. M. C. Ribeiro da Silva

CIQUP-IMS, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre, P-4169-007 Porto, Portugal

Email: vera.freitas@fc.up.pt

Anthranilate and cinnamate derivatives are widely used in cosmetics for their perfuming and UV protection functions.[1] The present communication is concerned with the effect of different substituents on the energy of seven esters derived from anthranilic and cinnamic acids (Fig. 1), being this work part of a research project, whose main purpose is the development of studies to provide accurate structural, thermodynamic and electronic properties of fragrances.[2]

The experimental studies involved the use of static-bomb combustion calorimetry and Calvet microcalorimetry, to obtain, respectively, the enthalpy of formation in the condensed phase and the phase transition enthalpy (condensed to gaseous phases) for each compound. These experimental data enabled the calculation of the gas-phase standard molar enthalpy of formation, at T=298.15, of the corresponding compounds. Additionally, this parameter was estimated from theoretical studies employing the G3(MP2)//B3LYP composite computational method.

The data gathered allowed the development of an enthalpic increment scheme useful for the estimation of properties of structurally related compounds.

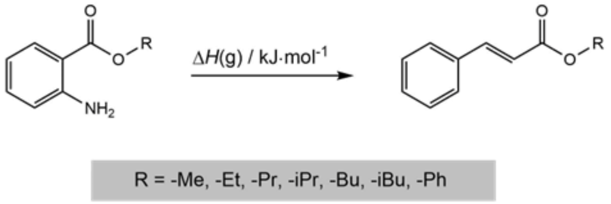


Fig. 1. Enthalpic increment scheme for anthranilate and cinnamate derivatives.

Acknowledgements: The authors acknowledge Fundação para a Ciência e Tecnologia (FCT) for the financial support through the projects UIDB/QUI/00081/2020 (https://doi.org/10.54499/UIDB/00081/2020) and IMS-(LA/P/0056/2020). C.A.O.S. thanks FCT for the doctoral grant SFRH/BD/137672/2018. VLSF thanks FCT for founding with the reference https://doi.org/10.54499/DL57/2016/CP1454/CT0019.

References

1. A. Gunia-Krzyżak, K. Słoczyńska, J. Popiół, P. Koczurkiewicz, H. Marona, E. Pękala; *Int. J. Cosmet. Sci.* **2018**, *40*, 356.
2. C.A.O. Silva, V.L.S. Freitas, M.D.M.C. Ribeiro da Silva; *Molecules* **2023**, *28*, 6686.

OC1.2 Thermodynamic study of polymorphism in the nicotinamide+adipic acid co-crystal system

I. O Feliciano, C.E.S. Bernardes, M. Fátima M. da Piedade, M.E. Minas da Piedade

Centro de Química Estrutural, Institute of Molecular Sciences, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal

Email: idfeliciano@fc.ul.pt

Crystal engineering is a relatively new field of research, focused on the design of functional materials through control of the molecular organization in solids. This area attracted industries like pharmaceuticals and agrochemicals, offering solutions to common challenges in product development such as solubility, stability, and tabletability. Key strategies include the production of co-crystals (materials including two or more different molecules in the crystal lattice) and polymorphs (crystal phases where the molecules pack with different arrangements). Polymorphism can also occur in co-crystals, as previously found in the case of a system consisting of nicotinamide (NIC) and adipic acid (AA), with 1:1 stoichiometry (NIC:AA).[1] The two different NIC:AA polymorphs were synthesized in this work via mechanochemistry and structurally characterized by X-ray diffraction. Insights into their thermal stability domains and relative thermodynamic stability were obtained from differential scanning calorimetry, solution calorimetry, and solubility measurements. The obtained results showed that the system is enantiotropic with form I (triclinic), the thermodynamically stable polymorph at 298.15 K, converting into form II (monoclinic) at 358 K.

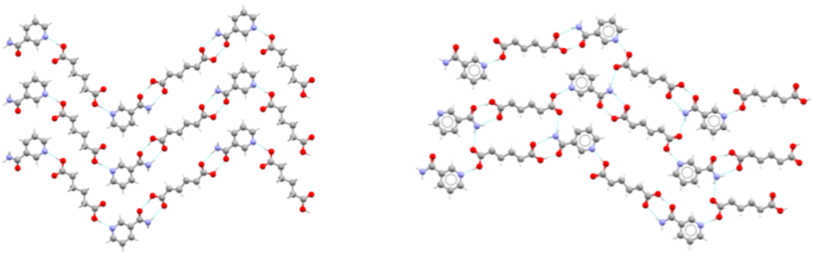

Form I
Form II

Fig. 1. Crystal structures of the two NIC:AA polymorphs studied in this work.

Acknowledgements: Centro de Química Estrutural is a Research Unit funded by FCT through projects UIDB/00100/2020 (https://doi.org/10.54499/UIDB/00100/2020) and UIDP/00100/2020 (https://doi.org/ 10.54499/UIDP/00100/2020). Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020 (https://doi.org/10.54499/LA/P/0056/2020). This work was further supported by 2021.03239.CEECIND (https://doi.org/10.54499/2021.03239.CEECIND/ CP1650/CT0003) and a doctoral grant awarded by the FCT to I. Feliciano (2021.04637.BD). Thanks, are finally due to Dr. Franziska Emmerling (BAM, Berlin) for the SCXRD data measurements used in this work to determine the form I structure.

References

1. L.S. Germann, M. Arhangelskis, M. Etter, R.E. Dinnebier, T. Friscic; *J. Chem. Sci.* **2020**, *11*, 10092-10100.

OC1.3 For hydrophobic free energy (HFE) of linear alkylic molecules, not only size matters

J. Martins[1-3]

[1] *CCMAR– Universidade do Algarve, Campus de Gambelas, Faro, Portugal*
[2] *CIMAR LA, Campus de Gambelas, Faro, Portugal*
[3] *DCBB-FCT – Universidade do Algarve, Campus de Gambelas, Faro, Portugal*
Email: jmartin@ualg.pt

The major thermodynamic process driving the hydration of structurally nonpolar solutes is the hydrophobic effect. This process depends on the size, shape, and polar/ionic features of nonpolar or amphiphilic molecules.[1] The hydrophobic effect was first perceived by Isidor Traube in 1891,[1] when describing the effect of linear methylenic chain solutes (fatty acids, fatty amines, and fatty alcohols), in lowering the surface tension of water: the relative magnitude increasing for each methylene group in the alkyl chains ("Traube's rule"). Aliphatic linear hydrocarbons are structurally nonpolar and therefore their hydration process was soon[2] settled as the hallmark for the study of hydration for homologous amphiphilic molecules. In this work, the quantitative analysis of "Traube's rule" is outlined. The linear dependency of HFE on the length of linear methylenic molecules is analyzed for fatty acids, amines, and alcohols, and hydrocarbons. This set of linear molecules comprises the main nonpolar and amphiphilic alkylic molecules in biological systems: acid, base, polar and nonpolar, respectively.

Henry's law constant values were obtained from a database accessible both in literature [3] and online (here: http://www.henry-law.org). In this work, only experimental values are used in the dimensionless solubility formulation (gas to water equilibrium transfer process),[4] and only consistent sets of at least 2 independent experimental values were considered, allowing the estimation of mean values and standard deviations. The calculation of HFE values [4] allows the study of its relationship with the length (n_{CH2}) of linear alkylic molecules.[5] It is a thermodynamic analysis based on a linear equation for the relationship of HFE vs. n_{CH2}: the slope is the incremental augment arising from each methylene group and the intercept is the contribution from both terminals (*e.g.* two CH_3 in hydrocarbons), for HFE values.

For hydrocarbons from propane to decane, the HFE vs. n_{CH2} correlation is linear (R=0.998) and provides a slope of 0,808 kJ/mol per CH_2 group and an intercept value of 7.30 kJ/mol. This value is similar to the 7.51 kJ/mol for ethane. For the amphiphiles, the outcomes are in accordance with their respective ionic or polar features. The critical discussions about their hydration properties based on the HFE analysis will appear elsewhere (under submission).

Acknowledgements: This study received Portuguese national funds from FCT - Foundation for Science and Technology, through projects UIDB/04326/2020 and LA/P/0101/2020.

References

1. C. Tanford; *The Hydrophobic Effect: The Formation of Micelles and Biological Membranes*; 2nd Edition, John Wiley and Sons: New York, 1980.
2. C. McAuliffe; *J. Phys. Chem.* **1966**, *70*, 1267-1275.
3. R. Sander; *Atmos. Chem. Phys.* **2023**, *23*, 10901-12440.
4. R. L. Baldwin; *FEBS Lett.* **2013**, *587*, 1062-1066.
5. D. Marsh; *Biophys. J.* **2016**, *110*, 188-196.

OC1.4 Enhanced cancer biomarker detection in microfluidic devices using ionic liquid-based aqueous biphasic systems for serum pre-treatment

M.S.M. Mendes,[1,2] V. Chu[2], F.A. Silva[1], M. G. Freire[1], J. P. Conde [2,3]

[1] *CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.*
[2] *Instituto de Engenharia de Sistemas e Computadores-Microssistemas e Nanotecnologias (INESC MN), Rua Alves Redol 9, Lisbon, 1000-029, Portugal*
[3] *Department of Bioengineering, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1, Lisbon, 1049-001, Portugal*
Email: msilvinamm@ua.pt

Cancer is a major global health issue with low survival rates often due to late diagnoses. Early detection is crucial for effective treatment and monitoring. Human serum cancer biomarkers are important for indicating cancer development, treatment efficacy, and disease recurrence. However, detecting these biomarkers is challenging due to interferences from abundant proteins like human serum albumin (HSA) and immunoglobulin G (IgG). Thus, a sample pretreatment step is necessary to remove these proteins before quantification. Ionic liquid-based aqueous biphasic systems (IL-ABS) are promising for sample pretreatment and biomarker extraction.[1] In this study, IL-ABS were used to extract and purify prostate specific antigen (PSA) and human epidermal growth factor receptor 2 (HER2), biomarkers for prostate and breast cancer, respectively, prior to detection via a bead-based sandwich immunoassay in a microfluidic device. Initially, the impact of biological matrices on biomarker detection was evaluated using an on-chip immunoassay. Comparing the fluorescence intensity of biomarkers in human serum versus phosphate-buffered saline revealed significant interference from serum, highlighting the need for an extraction technique for accurate PSA and HER2 detection. Various ILs in ABS were tested, with IL-ABS effectively reducing serum interference. This point-of-care system provided reliable results within the clinical ranges for PSA and HER2, relevant for prostate and breast cancer diagnosis.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI 10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC). This work was developed within the project ILSurvive, PTDC/EMD-TLM/3253/2020 (DOI 10.54499/PTDC/EMD-TLM/3253/2020), funded by national funds (OE), through FCT/MCTES. M.S.M.M. acknowledges FCT for the doctoral grant 2022.11229.BD. F.A.eS. acknowledges FCT for the researcher contract CEECIND/03076/2018/CP1559/CT0024 (DOI 10.54499/CEECIND/03076/2018/CP1559/CT0024) under the Scientific Employment Stimulus – Individual Call 2018.

References

1. M.S.M. Mendes, M.E. Rosa, F. Ramalho, M.G. Freire, F.A. e Silva; *Sep. Purif. Technol.* **2023**, *317*, 123875.

OC1.5 Thermodynamics of cation-fluorinated ionic liquids

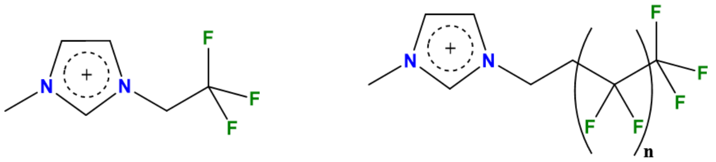
R. M. A. Silva, A.I. M.C. Lobo Ferreira, L.M.N.B.F. Santos

CIQUP, Institute of Molecular Sciences (IMS) – Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua Campo Alegre, 4169-007 Porto, Portugal
Email: rodrigo.m.a.silva98@gmail.com

Fluorinated ionic liquids (FILs) present an enhanced capability of absorbing gases when compared with archetypal alkyl-based ILs. This has made them especially interesting for gas capture and separation.[1] With this work we aimed to understand the phase behavior, thermal stability, heat capacity and volatility of several cation-fluorinated ILs. These FILs are composed of imidazolium cations with perfluorinated *n*-alkyl chains, paired with the bis(trifluoromethylsulfonyl)imide ($[NTf_2]$) anion. General structures are presented in Fig. 1.

The phase behavior of the FILs was studied through differential scanning calorimetry (DSC), while the thermal stability was investigated using thermogravimetric analysis (TGA). The heat capacity was measured, from T = 283 K up to T = 333 K, using a customized differential scanning microcalorimeter. Additionally, a high precision drop calorimeter[2] was used to determine the heat capacity at T = 298.15 K. Knudsen effusion coupled with quartz crystal microbalance (KEQCM)[3] was used to study their volatility.

The FILs presented higher glass transition temperature and melting point than their alky-based analogs. Through the heat capacity results, it was possible to estimate the contribution of each difluoromethylene group, $-CF_2-$, to the heat capacity of the liquid phase, at T = 298.15 K. The KEQCM studies revealed that the FILs are more volatile than their hydrogenated analogs.



$[(CH_2CF_3)C_1im][NTf_2]$

$[(CH_2)_2(CF_2)_nCF_3)C_1im][NTf_2]$
n = 1, 3, 5, 7

Fig. 1. General structures and nomenclature of the studied fluorinated cations Magnetic and Luminescent Ionic Liquids based on choline derivatives

Acknowledgments This work was supported by the Fundação para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020), IMS-Institute of Molecular Sciences (LA/P/0056/2020). RMAS is grateful to FCT for the award of his PhD grant (U1/BD/153093/2022). AIMCLF is also financed by national funds 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.

References

1. A. B. Pereiro *et al.; ACS Sustainable Chem. Eng.* **2013**, *1*, 427-439.
2. L. M. N. B. F. Santos *et al; J. Chem. Thermodyn.* **2011**, *43*, 1818-1823.
3. L. M. N. B. F. Santos *et al.*; *J. Chem. Thermodyn.* **2018**, *126*, 171-186.

OC1.6 Thermal conductivity of ionic liquids - A reappraisal

C. A. Nieto de Castro,[1] *M.J.V. Lourenço*,[1] *W.A. Wakeham*[2]

[1] *Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal*

[2] *Faculty of Engineering, University of Southampton, Highfield Road Southampton, UK*

Email: cacastro@ciencias.ulisboa.pt

Ionic liquids are still icons for different applications as green or not-so-green chemicals. Apart from the necessary regulations protecting their safe use and impact on the environment and living beings,[1] they have particular physicochemical properties, pure, mixed, or with dispersed nanomaterials that make them potentially attractive and efficient thermal energy transfer and storage engineering fluids.

Among the properties studied, one of them, thermal conductivity is essential for many developing heat transfer applications. Still, it is challenging owing to the difficulties of performing rigorous experiments and in modeling, whether theoretically or empirically based.[2] The experience of our research group in the field, one of few existing in the world with high-quality work, will be exemplified, with pure ionic liquids, IoNanofluids, and aqueous mixtures,[3-5] with special emphasis on the most recent publications, contributing to the United Nations Sustainable Development Goals and a 2050 solar-powered and sustainable society.

References

1. M. J. Lourenço, J. Alexandre, C. Huisman, X. Paredes, C. Nieto de Castro; *Nanomaterials,* **2021**, *11*, 1871.
2. X. Paredes, M. J. V. Lourenço, C. A. Nieto de Castro, W.A. Wakeham; *Fluids* **2021**, *6*, 116.
3. F.E.B. Bioucas, C.S.G.P. Queirós, D. Lozano-Martín, M. Ferreira, X. Paredes, A.F. Santos, F.J.V. Santos, M.L.M. Lopes, M. I. Lampreia, M.J.V. Lourenço, C. A. Nieto de Castro and K. Massonne; *Ind. Eng. Chem. Res.* **2022,** *61*, 2280–2305.
4. R. M. Almeida, M.J.V. Lourenço, C. Nieto de Castro; *J. Mol. Liq*. **2024**, *397*, 124123.
5. C. A. Nieto de Castro, A. Lamas, X. Paredes, F.J.V. Santos, M. J.V. Lourenço, T. Graber; *J. Chem. Eng. Data* **2024**, *69*, 2227–2235.

OC1.7 Extraction of proteins from *Tenebrio molitor* flour using deep eutectic solvents

G.Akyüz,[1] E. V. Capela,[1] V. Vieira,[1] L.C. Branco,[2] A. P. M. Tavares,[1] M. G. Freire[1]

[1] *CICECO-Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal*

[2]*Associated Laboratory for Green Chemistry (LAQV) of the Network of Chemistry and Technology (REQUIMTE), Faculdade de Ciência e Tecnologia, Universidade Nova de Lisboa*

Email: gulizakyuz@ua.pt

The growth of global population will significantly impact the demand for meat protein with raising critical concerns regarding sustainability, environmental degradation, and resource inefficiency.[1] Therefore, it is crucial to identify alternative protein sources, where insects have a high potential in contributing to food sustainability. Current methodologies mostly focus on application of conventional alkaline aqueous solutions for the protein extraction. However, alkaline conditions can lead to the formation of phenolic compound-protein complexes. This cause to a maillard reaction which affects the color of the product and resulting a bitter or astringent taste. Also, extraction of proteins with alkaline aqueous solutions are followed by long and expensive precipitation steps.[2] To overcome the described drawbacks, deep eutectic solvents (DES) emerge as alternative solvents for protein extraction,[3] since they are considered as green solvents, due to the low toxicity, high biodegradability and lower energy consumption during the process.[4] In this work, we aimed to develop a sustainable technology to extract and purify proteins from edible insect flour (*Tenebrio molitor*), envisioning their application in food products, using aqueous solutions of DES. Several DES were prepared, and their aqueous solutions were applied in the extraction of proteins from *Tenebrio molitor* flour. The operation conditions were optimized to maximize the extracted protein content. Based on this, DES were successfully applied, for the first time, in the extraction and purification of proteins from insects, revealing improved features when comparing with the conventional methods.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI 10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MEC (PIDDAC). This study was funded by the PRR - Recovery and Resilience Plan and by the NextGenerationEU funds at Universidade de Aveiro, through the scope of the Agenda for Business Innovation "InsectERA" (Project no. 20 with the application C644917393-00000032).

References

1. E. Fukase, and W. Martin; *World Develop.* **2020**, *132,*104954.
2. F.N. Abd Rahim, et al.; *Int. J. Biol. Macromol*. **2023**, *242,* 3, 124908.
3. P. Suthar, et al.; *J. Agric. Food Res.* **2023**, *14,* 100678.
4. T. Negi, et al.; *Heliyon* **2024**, *10*, e28784.

OC1.8 Improving niraparib's solubility using a deep eutectic solvent as a drug delivery system

P. Xavier,[1-3] F. Martins,[1,2] N. Galamba[1,3]

[1] *Department of Chemistry and Biochemistry, Faculdade de Ciências, Universidade de Lisboa, Portugal*
[2] *Centro de Química Estrutural - Institute of Molecular Sciences, Universidade de Lisboa, Portugal*
[3] *Biosystems and Integrative Sciences Institute (BioISI), Faculdade de Ciências, Universidade de Lisboa, Portugal*
Email: fc49256@alunos.ciencias.ulisboa.pt

Niraparib is a poly(adenosine diphosphate [ADP]-ribose) polymerase (PARP) inhibitor with a high selectivity.[1] Clinical trials have shown that niraparib is an active pharmaceutical ingredient (API) in the treatment of recurring epithelial ovarian, fallopian tube, or primary peritoneal cancers.[1,2] However, this API has a low predicted solubility, in water, of ~ 0.015 mg/mL, and a predicted logP of 2.45.[3] Ethaline is a well-known deep eutectic solvent that has been described as a solubility enhancer in some pharmaceutical applications.[4] In this work, we study the possibility of improving the solubility of niraparib using this DES through an hybrid approach, both experimental and computational. On the computational side, a general AMBER force field was optimized to reproduce the density, viscosity, and the diffusion coefficients of the DES. The solvation of the API was then investigated in water and ethaline through molecular dynamics simulations. Additionally, experimental assays were performed to assess the API solubility in ethaline, in a phosphate buffered saline (PBS) solution, and in water. Our results show a significant increase of the solubility of the API in the DES relative to water and PBS alone. A solubility enhancement is also observed in the latter solutions upon addition of the DES. These results are discussed in terms of the solvation of the API in the distinct solvents.

Acknowledgements: Centro de Química Estrutural is a Research Unit funded by FCT, Portugal, through projects UIDB/00100/2020 (https://doi.org/10.54499/UIDB/00100/2020) and UIDP/00100/2020 (https://doi.org/10.54499/UIDP/00100/2020). Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020 (https://doi.org/10.54499/LA/P/0056/2020). NG also acknowledges financial support from Fundação para a Ciência e a Tecnologia, Portugal, through project CEECIND/00821/2017. This work was likewise supported by BioISI UIDB/04046/2020 (doi: 10.54499/UIDB/04046/2020) and UIDP/04046/2020 centre grants.

References

1. M.R. Mirza, B.J.Monk, J. Herrstedt, *et al.*; *New England J. Med.* **2016**, *375,* 22, 2154-2164.
2. DA. Highlights of Prescribing Information - Niraparib. Food and Drug Administration (FDA), 2017.
3. VCCLAB VCCL: ALOGPS 2.1. https://vcclab.org/about/about1.html accessed January 4th, 2024.
4. M. Moradi, P. Jafari, E. Rahimpour, *et al.*; *J. Drug. Deliv. Sci. Tech.* **2023**, *90*, 105143.

OC1.9 Varnishes? Paints? Why use toxic solvents in their formulation when there are eutectic systems?

C.C. Fernandes, A. Quirino, A. Paiva, R. Marques, A. R. C. Duarte

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

Email: cco.fernandes@campus.fct.unl.pt

Toxic, hazardous, cancerogenic, inflammable and corrosive, that is how many of the organic solvents used in conservation and restoration are classified (e.g., toluene, xylene, white spirit, turpentine, etc).[1,2] Despite knowing all this, conservators are reluctant to use other alternatives mainly due to the said good effectiveness at low cost provided by these conventional solvents. Additionally, there is very little information regarding the properties, behaviour or applicability of the current solvents categorized as "potential green solvents". Therefore, this work aimed to evaluate and compare the performance of eutectic systems[3,4] (fluids with versatile applications, formed by mixing bio-based compounds in specific molar ratios), when implemented in varnish formulations. Through the use of many different techniques, it was possible to screen and select the most potential eutectic systems; formulate new eutectic systems-based varnishes; to finally, assess and compare them with traditional solvents in terms of spectral and rheological analysis. The results have shown that one of the found eutectic systems-based varnishes has comparable behaviour to some organic solvents-based varnishes.

Acknowledgements: This project has received funding from the European Union's Horizon 2020 – European Research Council (ERC) – under grant agreement No ERC-2016-CoG 725034. This work received financial support from FCT/MCTES (UIDB/50006/2020 DOI 10.54499/UIDB/50006/2020) and FCT/BDCEE (PRT/BD/154656/2023), through national funds.

References

1. H. H. Morgan; *J. R. Soc. Arts* **1926,** *74*, 271–291.
2. A. Phenix, K. Sutherland; *Stud. Conserv.* **2001,** *46*, 47–60.
3. C.C. Fernandes, C. C., *et al; Chem. Eng.* **2021,** *9*, 15451–15460.
4. A. Paiva, *et al.*; *ACS Sustain. Chem. Eng.* **2014,** *2,* 1063–1071.

OC1.10 Chitosan and naphthaldehydes derivatives composites: adsorptive remove of tetracycline from water

J. F. M. Sousa, D. Murtinho, A. J. M. Valente, J. M. C. Marques

University of Coimbra, CQC-IMS, Department of Chemistry, Rua Larga,3004-535, Coimbra, Portugal
Email: uc2011141774@student.uc.pt

Contamination of aquatic environments negatively impacts ecosystems, wildlife, and human health. Because antibiotics and their metabolites are excreted in urine and faeces, improper disposal and excessive use in agriculture result in the presence of these compounds in wastewater treatment plants (WWTPs).[1] Continued exposure of bacteria to low levels of antibiotics in WWTPs leads to the development of antibiotic-resistant bacteria, which constitutes a high risk to human health. Antibiotics in WWTPs can also lead to disruption of microbial communities and potential harm to aquatic organisms. These factors make antibiotics one of the emerging pollutants that have received particular attention in recent decades.[2] Among the various methods for antibiotic removal, adsorption has proven to be the most economical, feasible and highly effective. Commercial adsorbents used for adsorption have high costs and potential sustainability issues.[3] To overcome these issues, chitosan has been used in our work. Indeed, chitosan is an animal-derived polysaccharide that can be recycled from crustacean waste and is very abundant, non-toxic, inexpensive and biodegradable. The presence of free hydroxyl and amino groups makes the chitosan a good adsorbent. However, chitosan has poor mechanical properties (e.g. rigidity and brittleness) and it is poorly soluble in many solvents and unstable in acidic medium.[4] To overcome these drawbacks, naphthaldehyde (RCN) and 2-hydroxy-1-naphthaldehyde (RCN1) were used to functionalize chitosan in order to be used as an adsorbent for tetracycline (TC) in aqueous media. Computational techniques such as density functional theory (DFT) and molecular dynamics simulations were employed to get molecular-level insight about the interactions between TC and chitosan-based derivatives. These calculations indicate that the TC-RCN1 complex is the one among all with the lowest binding energy, thus anticipating a high removal efficiency. Electrostatic interactions, hydrogen bonding and π -π electron donor–acceptor (EDA) contributions may be relevant for the adsorption of tetracycline onto chitosan derivatives. In agreement with such calculations, the experimental TC removal efficiency is greater for RCN1 than for RCN and chitosan, and the highest adsorption capacity occurs at pH=6. The study of isotherms indicated that the data were better fitted with the Langmuir model while the adsorption kinetics followed the PSO model.

Acknowledgements: We thank Fundação para a Ciência e Tecnologia (FCT), Portugal for the Ph. D Grant UI/BD/150803/2020 with DOI 10.54499/UI/BD/150803/2020 (https://doi.org/ 10.54499/UI/BD/150803/ 2020) and the Coimbra Chemistry Center (CQC), supported by the FCT through grant ref. UIDB/QUI/00313/2020, for supporting this work.

References

1. R. K. Mishra, S. S. Mentha, Y. Misra, N. Dwivedi; *Water-Energy Nexus* **2023**, *6*, 74–95.
2. S. T. Odonkor, K. K. Addo; *Int. J. Microbiol*. **2018**, *2018*, 7.
3. S. Das and S. Sengupta*; Water Conserv. Sci. Eng*. DOI:10.1007/s41101-023-00180-5.
4. X. Qi, X. Tong, W. Pan, Q. Zeng, S. You, J. Shen; *J. Clean. Prod.* **2021**, *315*, 128221.

OC1.11 Sputtering of silver in thin films of long-chain imidazolium-based ionic liquids: An efficient approach to metal nanoparticle stabilization

A. C. P. M. Alves, *L.M. N. B. F. Santos, J.C. S. Costa*

CIQUP, Institute of Molecular Sciences (IMS), Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Porto, Portugal

Email: up201503618@up.pt / alexandrecostapalves@gmail.com

This study aimed to investigate the sputter deposition of silver nanoparticles (AgNPs) onto films of three symmetric imidazolium-based ionic liquids (ILs) that share the same anion (bis(trifluoromethylsulfonyl)imide) but differ in cation alkyl side chain lengths. The investigated ILs included [C7C7im][NTf2], [C8C8im][NTf2] and [C10C10im][NTf2]. This study extends previous research, concluding that symmetric alkyl side chains of the cationic moieties had better results when these chains were longer.[1] Not only were the ILs effective as a medium to capture the metal atoms but also as stabilizers during the formation of NPs, as they tend to form small aggregates of uniform sizes.[1-3] Different conditions were evaluated by modifying the thickness and deposition rate of the IL, as well as the silver deposition time and discharge current. Thermal vacuum evaporation was used to obtain IL films as microdroplets and was conducted by carefully controlling the effusion temperature, deposition rate, and deposition time. The use of Knudsen cells provided a means to achieve precise and reproducible control over the mass flow rate.[4,5] The sputtering process of the metal onto ILs, when conducted simultaneously with argon plasma, promoted the coalescence of IL microdroplets and the incorporation and stabilization of AgNPs in the coalesced IL films. The formation/stabilization of the AgNPs was confirmed through high-resolution scanning electron microscopy (SEM), UV-Vis spectroscopy, and X-ray photoelectron spectroscopy (XPS). Previous findings demonstrated that both the size and symmetry of the alkyl side chain significantly influenced the formation of droplets on ITO, subsequently impacting the formation and stabilization of AgNPs.[1] This study achieved significantly improved results with ionic liquid films of very long alkyl chains attached to the cation. The longer chains promoted the formation and dispersion of AgNPs, resulting in higher stabilization even after several days of deposition.

Acknowledgements: This work was supported by the Fundação para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020: DOI 10.54499/UIDP/00081/2020), IMS-Institute of Molecular Sciences (LA/P/0056/2020)) A.C.P.M.A. also thanks the FCT and the European Social Fund (ESF) for the award of a Ph.D. Research Grant (ref. 2022.11108.BD).

References

1. A. C. P. M. Alves, L. M. N. B. F. Santos, M. Bastos, J. C. S. Costa; *Molecules* **2023**, *28*, 3029.
2. L. Calabria, J. A. Fernandes, P. Migowski, F. Bernardi, D. L. Baptista, R. Leal, T. Grehl, J. Dupont; *Nanoscale* **2017**, *9*, 18753–18758.
3. T. Torimoto, K. I. Okazaki, T. Kiyama, K. Hirahara, N. Tanaka , S. Kuwabata; *Appl. Phys. Lett.* **2006**, *89*, 243117.
4. J. C. S. Costa, A. C. P. M. Alves, M. M. H. M. Bastos, L. M. N. B. F. Santos*; Phys. Chem. Chem. Phys*. **2022**, *24*, 13343.
5. J. C. S. Costa, A. F. S. M. G. Coelho, A. Mendes, L. M. N. B. F. Santos; *Appl. Surf. Sci*. **2018**, *428*, 242–249.

OC1.12 Triazine porous organic polymers for simultaneous removal and sensing of antibiotics in water

P.M.C. Matias, A.C.B. Rodrigues, D. Murtinho, A.J.M. Valente

University of Coimbra, CQC-IMS, Department of Chemistry, Rua Larga, 3004-535 Coimbra, Portugal
Email: petermatias1998@gmail.com

Water pollution, particularly with antibiotics, contributes to the induction and spread of antimicrobial resistance, which are two of the main problems that mankind is facing today.[1] Therefore, new solutions must be found to detect polluted environments early and promote their decontamination. For this purpose, this communication describes three highly stable amine-rich triazine-based mesoporous organic materials (T-POP1-3, Fig. 1), as advanced platforms belonging to the family of porous organic polymers (POPs), which have promising application properties because they are custom-built through a rational design at the molecular level.[2] T-POPs exhibited good performances for sulfamethazine (SMT) and tetracycline (TC) removal, with efficiencies up to 97% and 79% and maximum adsorption capacities (q_m) between (0.33 – 0.40) and (0.133 – 0.154) mmol g^{-1}, respectively, which are similar or better to those obtained with other materials. Good reusability was also observed, particularly for T-POP2, despite being the polymer with the lowest surface area and q_m values. At the same time, T-POPs acted as fluorescent chemosensors. On the one hand, T-POP1 underwent linear Stern-Volmer fluorescence quenching in the presence of both antibiotics. On the other hand, the enhanced-fluorescent T-POP2 and T-POP3 experienced fluorescence extinction through a sphere of action mechanism in contact with TC, and bathochromic shift accompanied by a hyperchromic effect on fluorescence at the new emission region with the increase in SMT concentration. Overall, T-POP2 and T-POP3 have better performance, as they can both promote a selective on-site monitoring of the two antibiotics and a more efficient remediation of waters with lower pollutant contents.

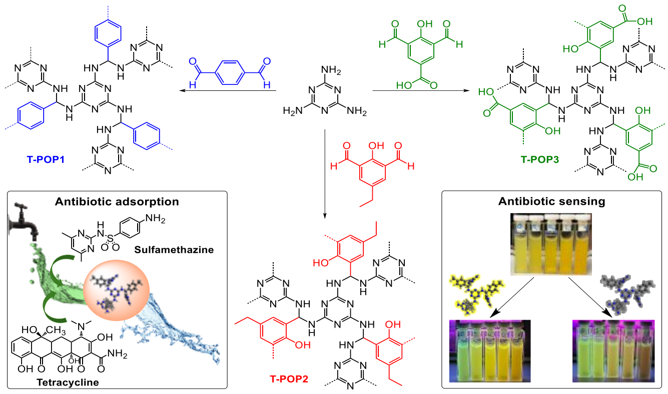


Fig. 1. Synthesis of T-POPs and their application for antibiotic adsorption and sensing.

Acknowledgements: To the Coimbra Chemistry Centre (CQC-IMS), supported by FCT through the program UID/QUI/00313/2020. Pedro M. C. Matias also thanks FCT for the PhD Grant 2022.12425.BD.

References

1. A. K. Singh, R. Kaur, S. Verma, S. Singh; *Front. Environ. Sci.* **2022**, *10*, 830861.
2. P. M. C. Matias, D. Murtinho, A. J. M. Valente; *Polymers (Basel)* **2023**, *15*, 1815.

OC1.13 MALDI-TOF MS-based urinary peptidomics biosignature of breast cancer as a powerful approach for diagnosis

P. Sousa,[1] J.S. Câmara,[1,2] R. Perestrelo[1]

[1] CQM – Centro de Química da Madeira, Universidade da Madeira, Campus da Penteada, 9020-105 Funchal, Portugal

[2] Departamento de Química, Faculdade de Ciências Exatas e Engenharia, Universidade da Madeira, Campus da Penteada, 9020-105 Funchal, Portugal

Email: patricia.sousa@staff.uma.pt

According to GLOBOCAN 2020, a database developed by the International Agency for Research on Cancer (IARC), breast cancer (BC) is the most frequently diagnosed heterogeneous tumor among women worldwide, followed by lung (11.4%), colorectal (10.0%), prostate (7.3%), and stomach (5.6%) cancers, since nearly 2.3 million women (11.7% of all cancer cases) were affected in 2020.[1] In this sense, the development of a rapid and highly sensitive diagnostic method for breast cancer (BC) has been the focus of intense research to improve treatment efficacy through early detection of the disease, which affects millions of women worldwide.[2] However, the identification of specific biomarkers faces challenges in the preparation of urine samples for peptidomic analysis due to their highly variable composition and the presence of proteins in low abundance or modified forms.[3] This study aims to identify potential urinary peptide biomarkers for BC using a combination of one-dimensional sodium dodecyl sulfate-polyacrylamide gel electrophoresis (1D SDS-PAGE) and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) for diagnosis and therapy monitoring, Fig. 1.

The results show an increase in total protein concentration after precipitation, with healthy controls (HC, 160 to 318 µg/mL, 142 µg/mL, on average) showing higher concentrations than BC patients (140 to 311 µg/mL, 115 µg/mL, on average). MALDI-TOF MS analysis revealed four peptide ion signatures (*m/z* 1046.5, 1062.4, 1237.7, and 1727.9) capable of discriminating between BC patients and HCs. The discrimination efficiency and accuracy of the biomarkers were confirmed by ROC curve analysis, demonstrating high sensitivity (88%) and specificity (98%). These findings highlight MALDI-TOF MS as a powerful tool for disease biomarker identification, but further studies with larger sample sizes are needed to validate these findings.

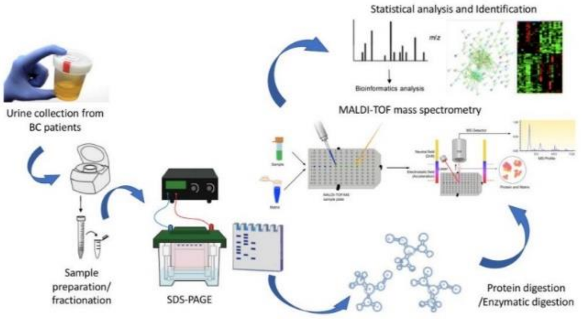


Fig. 1. Workflow of the urinary BC peptidomic biosignature.

Acknowledgements: This research was funded by FCT-Fundação para a Ciência e a Tecnologia through the CQM Base Fund - UIDB/00674/2020, and Pro- grammatic Fund - UIDP/00674/2020, by Interreg MAC 2014–2020 Cooperation territorial through AD4MAC project (MAC2/1.1b/350), and by ARDITI-Agência Regional para o Desenvolvimento da Investigação Tecnologia e Inovação, through the project M1420-01-0145- FEDER-000005 - Centro de Química da Madeira - CQM$^+$ (Madeira 14–20 Program). The authors also acknowledge FCT and Madeira 14–2020 program to the Portuguese Mass Spectrometry Network (RNEM) through PROEQUIPRAM program, M14-20 M1420-01-0145- FEDER-000008). Patrícia Sousa thanks the Rubina Barros fellowship 2023 supported by NRM-LPCC.

References

1. P. Sousa, I. Camacho, J.S. Câmara, R. Perestrelo; *Separations* **2023**, *10*, 291-308.
2. R.L. Siegel, K.D. Miller, H.E. Fuchs, A. Jemal; *CA Cancer J. Clin.* **2022**, *72*, 7-33.
3. N. Joshi, K. Garapati, V. Ghose, R. Kandasamy, A. Pandey; *Clin. Proteomics* **2024**, *21*, 14-34.

OC1.14 Metrological study on a relationship between salinity and surface tension of buffered artificial seawaters

M. Serra, S. Moura, R. Quendera, O. Pellegrino

IPQ, Instituto Português da Qualidade, I.P., 2829-513 Caparica, Portugal
Email: smoura@ipq.pt

This work displays the preliminary results of a metrological study on a relationship between surface tension, γ, contact angle, θ, density, ρ, and absolute salinity, S_A, of buffered artificial seawater. Indeed, whereas natural seawater exhibits high variability in temperature, pressure and dissolved organic matter composition, playing a significant role in ocean water circulation,[1] its inorganic matter content remains relatively constant. Seawater samples density results measured with an oscillation-type densimeter, and refractive index results displayed a direct correlation to absolute salinity,[2] due to the total dissolved salt content. Concomitantly surface tension, linked to contact angle by the Young equation,[3] tends to depend on S_A and temperature, t, mainly due to intermolecular interactions within these systems. Tris(hydroxymethyl)aminomethane (TRIS) buffers and hydrochloric acid in artificial seawater matrix (ASW) within [35; 70] g/kg S_A interval and Standard Seawater were tested to assess the mathematical relationship between seawater γ and S_A and t relatively to that of ultrapure water, as evidenced by the International Association for the Properties of Water and Steam (IAPWS).[4] TRIS buffered ASWs are considered primary standards, traceable to the Harned cell, matching the composition of natural seawater, according to the International Association for the Physical Sciences of the Oceans (IAPSO) 2008 recommendations, and used to calibrate pH measurement instruments in oceanographic studies.[5-7] In this work, web-based software applications[8,9] were used to estimate measurement uncertainties, allowing the quantities of interest to characterize potential certified reference materials.

References

1. R. Pawlowicz; *Nature Education Knowledge* **2013***, 4*,13.
2. A. Furtado *et al; Int. J. Metrology Quality Eng*. **2022**, *13*, 10.
3. I. Gao *et al.*; *Langmuir* **2006***, 22*, 6234.
4. IAPWS, Revised release on surface tension of ordinary water substance, 2014. available from http://www.iapws.org.
5. T.A. DelValls, *et al.; Res. Papers* **1998**, *45*, 1541-1554.
6. G. M. Marion, *et al.; Marine Chem.* **2011**, *126*, 89-96.
7. A. G. Dickson *et al.; Metrologia* **2015,** *53*, R26.
8. National Institute of Standards and Technology (NIST), *NIST Uncertainty Machine*, available from https://uncertainty.nist.gov/.
9. Laboratoire National de Métrologie et d'Essais (LNE), *LNE Uncertainty software*, available from https://www.lne.fr/en/software/lne-uncertainty-evaluating-measurement-uncertainties-using-gum-and-monte-carlo.

OC1.15 Volatilomic fingerprint of grape pomace as a sustainable approach for its valorization

T. Abreu,[1] J.S. Câmara,[1,3] J. Teixeira,[2] R. Perestrelo[1]

[1] CQM – Centro de Química da Madeira, Universidade da Madeira, Campus da Penteada, 9020-105, Funchal, Portugal
[2] Justino's Madeira Wines, S.A., Parque Industrial Da Cancela, Caniço, 9125-042, Santa Cruz, Portugal
[3] Departamento de Química, Faculdade de Ciências Exatas e Engenharia, Universidade da Madeira, Campus da Penteada, 9020-105, Funchal, Portugal
Email: teresa.abreu@staff.uma.pt

Agri-food waste is a global problem that continues to pose challenges. The huge amount of grape pomace (GP) produced each year worldwide, especially in Europe, has negative economic and environmental impacts. To reduce and minimize these concerns, it is necessary to implement conversion strategies that allow the transformation of agricultural waste into a variety of marketable end products with added value.[1] In this context, this research aimed to establish the volatilomic fingerprint of GP obtained from different grape varieties of *Vitis vinifera* L. cultivated on the Island of Madeira, using solid-phase microextraction (HS-SPME) coupled to gas chromatography-mass spectrometry (GC-MS), to reveal the characteristics of the most dominant volatile organic metabolites (VOMs) in the context of their application on marketable products, in the food, pharmaceutical and cosmetic industries. A total of 52 VOMs belonging to different chemical families were identified, namely alcohols (14), esters (14), carbonyl compounds (10), terpenoids (11), acids (2), and hydrocarbons (1), 18 of which were common to all GPs analyzed, Fig. 1. The results obtained revealed the potential of some GP VOMs to replace synthetic antioxidants, anti-inflammatories, and antimicrobials with great potential for industrial applications, meeting the increasing consumer demand for natural alternative compounds, and promoting its use in the context of a circular bio-economy.

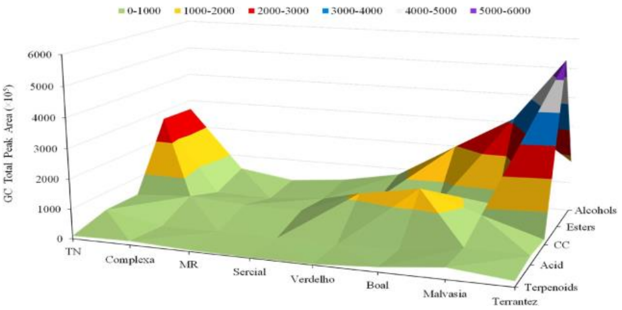


Fig. 1. The total peak area of chemical families identified in GP of investigated grape varieties. MR: Malvasia Roxa, CC: Carbonyl compounds.

Acknowledgments: This research was funded by FCT- Fundação para a Ciência e a Tecnologia through the CQM Base Fund - UIDB/00674/2020, and Programmatic Fund - UIDP/00674/2020, by Interreg MAC 2014–2020 Cooperación territorial through AD4MAC project (MAC2/1.1b/350), and by ARDITI-Agência Regional para o Desenvolvimento da Investigação Tecnologia e Inovação, through the project M1420-01-0145- FEDER-000005 - Centro de Química da Madeira - CQM⁺ (Madeira 14–20 Program). The authors also acknowledge FCT and Madeira 14–2020 program to the Portuguese Mass Spectrometry Network (RNEM) through PROEQUIPRAM program, M14-20 M1420-01-0145- FEDER-000008). Teresa Abreu thanks for the PhD fellowships FCT 2022.11323. BDANA supported by FCT.

References:

1. T. Abreu, G. Jasmins, C. Bettencourt, J. Teixeira, J. S. Câmara, R. Perestrelo; *Curr. Res. Food Sci*. **2023**, *7*, 100608.

OC1.16 Exploring the ^{19}F NMR and photoluminescence of fluorinated dendrimers for gene delivery

L. dos Orfãos,[1] F. Lahoz[2], J. Rodrigues[1]

[1] *CQM – Centro de Química da Madeira, Universidade da Madeira,*
Campus da Penteada 9020-105 Funchal, Portugal
[2] *Dpto. Física, IUdEA, Universidad de La Laguna, 38200, Tenerife, Spain*
Email: joaor@uma.pt

Fluorinated compounds have been studied for a plethora of applications in imaging, therapeutics, and the environment.[1] The high sensitivity and the absence of background signals make them very interesting for applications on ^{19}F MRI.[2,3]

The aim of this work was to functionalise generation 4 PAMAM (G4PAMAM) dendrimers with the fluorine compound, 2,3,5,6-tetrafluoro-4-hydroxybenzoic acid (TFHBA), to enhance their photoluminescence and explore their potential in ^{19}F NMR. Additionally, we examine the ability of these dendrimers as a carrier for drugs or genes.[4]

The conjugation of TFHBA to the dendrimer was performed by adding different ratios of the aqueous fluorine molecule solution into a stirring G4PAMAM dendrimer in water. After stirring the reaction for 2 days, a purification step by dialysis was performed, and the dry compound was obtained by freeze-drying. Characterisation was performed to evaluate the success of the functionalisation using NMR, FTIR, UV/Visible, and Photoluminescence. The functionalisation degree (FD) of the prepared dendrimers was also assessed by the NMR signals integrations of the ^{1}H and ^{19}F NMR spectra using the 1-fluoro-2,4-dinitrobenzene as the standard. FTIR and UV/Visible further confirmed the successful conjugation of the dendrimer with the fluorine compound. Photoluminescence studies showed a stock-shift of 1.37 ± 0.03 eV and an unusual increase in emission through time. Biological studies such as cytotoxicity and transfection were also performed, revealing that the conjugated dendrimer can deliver genes into cells and have a low cytotoxicity.

Acknowledgments: This work was supported by the Fundação para a Ciência e a Tecnologia (FCT) with Portuguese Government funds through the CQM Base Fund - UIDB/00674/2020 (DOI: 10.54499/UIDB/00674/2020) and Programmatic Fund - UIDP/00674/2020 (DOI: 10.54499/UIDP/00674/2020), and Ph.D. grant UI/BD/152860/2022 (LdO); and project PID2022-136566NB-I00 funded by Ministerio de Ciencia e Innovación/Agencia Estatal de Investigación from Spanish Government and by "ERDF (FEDER) A way of making Europe".

References

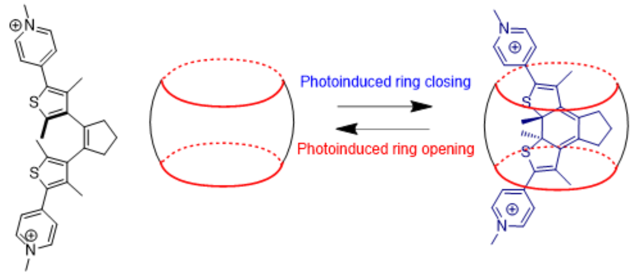
1. C. Zhang, K. Yan, C. Fu, H. Peng, C. J. Hawker, A. K. Whittaker; *Chem. Rev.* **2022**, *122*, 167–208.
2. D. Perumal, J. Krishna, K. S. Harikrishnan, G. Raj, J. Kalathil, M. Saji, K. M., R. Varghese; *Nanoscale* **2023**, *15*, 8972–8977.
3. W. Yu, Y. Yang, S. Bo, Y. Li, S. Chen, Z. Yang, X. Zheng, Z. X. Jiang, X. Zhou; *J. Org. Chem.* **2015**, *80*, 4443–4449.
4. H. Tomás, J. Rodrigues; In *New Trends in Smart Nanostructured Biomaterials in Health Sciences*; Elsevier, **2023**; pp 41–78.

OC1.17 Exploring the kinetic and thermodynamic stability of photoresponsive cucurbituril-dithienylethene inclusion complexes

N. Basílio, A. J. Parola, P. Máximo, M. Colaço

Laboratório Associado para a Química Verde (LAQV-REQUIMTE), Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516, Caparica, Portugal
Email: nuno.basilio@ fct.unl.pt

Host-guest pairs provide promising binding motifs for the construction of sophisticated supramolecular systems, molecular machines, and self-assembled materials. However, and despite the increasing number of new host-guest systems, the development of complementary binding pairs showing high affinity (below the micromolar range) and selectivity in water is challenging. Our group has recently discovered new host-guest affinity pairs based on cucurbit[8]uril (CB8) and photochromic dithienylethene (DTE) guests reaching binding affinities of log K > 11 in water.[1–3] Importantly, this remarkable affinity can be modulated with light stimulation owing to the exceptional selectivity (Kclosed/Kopen up to 10000-fold) displayed by CB8 towards the closed DTE isomers. In this communication I will present results from our recent work on the binding kinetics and thermodynamics of CB8:DTE host-guest systems, to provide important hints towards the design of novel host-guest pairs with photomodulated binding stability and dynamics.



- *Picomolar affinity*
- *Water-solubility*
- *Photoresponsive binding*
- *All-photonic operation*
- *Visible light excitation*

Fig. 1. A photoswitchable CB8:DTE inclusion complex.

Acknowledgements: This work was supported by the Associate Laboratory for Green Chemistry - LAQV (projects UIDB/50006/2020 and UIDP/50006/2020), which is financed by national funds from FCT/MCTES. FCT/MCTES is also acknowledged for the project 2022.02538.PTDC.

References

1. P. Máximo, M. Colaço, S. R. Pauleta, P. J. Costa, U. Pischel, A. J. Parola, N. Basílio; *Org. Chem. Front.* **2022**, *9*, 4238–4249.
2. M. Colaço, P. Máximo, A. Jorge Parola, N. Basílio; *Chem. – A Eur. J.* **2021**, *27*, 9550–9555.
3. P. Ferreira, B. Ventura, A. Barbieri, J. P. Da Silva, C. A. T. Laia, A. J. Parola and N. Basílio; *Chem. – A Eur. J.* **2019**, *25*, 3477–3482.

OC1.18 Properties of proton and metal-ion bound to PAMAM dendrimer primary and tertiary amines

D. Fernandes,[1] C. S. Alves,[1,2] P. Pires[1]

[1] CQM – Centro de Química da Madeira, Campus Universitário da Penteada, 9020-105 Funchal, Portugal
[2] Centre of Technology and Systems, CTS, UNINOVA, 2829-516, Caparica, Portugal
Email: pedro.pires@staff.uma.pt

Copper (Cu) has the potential to be an appealing alternative in many different applications (*e.g.*, electronics,[1] antimicrobial,[2] imaging,[3] anticancer[3]) for more scarce, more expensive, less biocompatible/toxic, or less performant (*e.g.,* electric conductivity) metals like gold,[2] silver,[1,2] platinum,[2,3] gallium,[1-3] *etc*. For metallic Cu, these advantages come with the major disadvantage of instability to the moister in air, thus, overcoming this instability is the target of many works.[1,4] One example is using polyamidoamine (PAMAM) dendrimers as a capping agent.[4,5]

This preliminary work focuses mostly on the analysis of the effect of copper ion ratios on the properties of fourth generation PAMAM dendrimer with OH-terminus (*i.e.*, tertiary amine binding sites), but also explores on occasion, the NH_2-terminus variant (*i.e.*, primary amine binding sites), the effect of protons (*i.e.*, pH), ionic strength, temperature, etc. Samples were characterized with techniques such as potentiometry and spectroscopy (*e.g.*, UV-Vis, photoluminescence, and proton nuclear magnetic resonance).

The main goal of this study was to learn more about these complexes as they are used as precursors for metal dendrimer entrapped nanoparticles (DENPs). Insights from this work can help optimize the synthesis of Cu-DENPs, which has been difficult to achieve in the past.

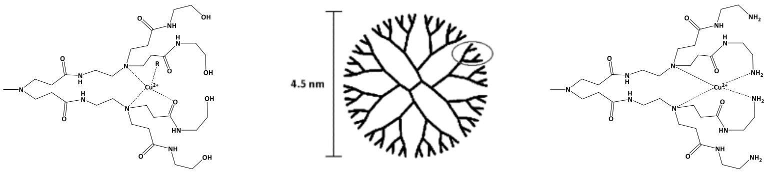


Fig. 1. Example how (**Left**) OH and (**Right**) NH_2-terminous dendrimer can complex ions.

Acknowledgements: This work was supported by FCT (Fundação para a Ciência e a Tecnologia) through the CQM Base Fund - UIDB/00674/2020 (DOI: 10.54499/UIDB/00674/2020) and Programmatic Fund - UIDP/00674/2020 (DOI 10.54499/UIDP/00674/2020). DF also acknowledges the FCT (Fundação para a Ciência e a Tecnologia) through the PhD Grant FCT UI/BD/154492/2022.

References

1. Y. Kamikoriyama, H. Imamura, A. Muramatsu, K. Kanie; *Sci. Rep.* **2019** *9*, 899.
2. A. Frei, A.D. Verderosa, A.G. Elliott; *Nat. Rev. Chem.* **2023**, *7*, 202-224.
3. Y. Fan, J. Zhang, M. Shi, D. Li, C. Lu, X. Cao, C. Peng, S. Mignani, J.-P. Majoral, X. Shi; *Nano Lett.* **2019**, *19*, 1216-1226.
4. M. Nemanashi, R. Meijboom; *J. Colloid Interface Sci.* **2013,** *389*, 260-267.
5. Z. V. Feng, J. L. Lyon, J. S. Croley, R. M. Crooks, D. A. Vanden Bout, K. J. Stevenson; *J. Chem. Educ.* **2009,** *86*, 368-3720.

OC1.19 A new road to discover ABC transporter modulators

D. J. V. A. dos Santos,[1,3] *R. J. Ferreira,*[2] *M. J. U. Ferreira,*[3] *J.-P. Gillet,*[4] *M. N. D. S. Cordeiro,*[5] *C. A. Bonito*[6]

[1] *CBIOS— Research Center for Biosciences & Health Technologies, Universidade Lusófona de Humanidades e Tecnologias, Lisbon, Portugal.*
[2] *Red Glead Discovery AB, Medicon Village, Lund, Sweden.*
[3] *Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Portugal.*
[4] *Laboratory of Molecular Cancer Biology, URPhyM, NARILIS, Faculty of Medicine, University of Namur, Belgium.*
[5] *LAQV@REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.*
[6] *Medicinal Chemistry, Research and Early Development, Cardiovascular, Renal and Metabolism (CVRM), BioPharmaceutical R&D, AstraZeneca Gothenburg Sweden*
Email: daniel.dos.santos@ulusofona.pt

The estimated number of new cancer cases is expected to grow 33% by 2030, with an estimated increase of 35% in the total number of deaths. Although having a multifactorial origin, multidrug resistance (MDR) can be achieved through efflux pump-mediated resistance in which the ATP-binding cassette transporters superfamily (ABC transporters) like P-glycoprotein (Pgp/ABCB1), Multidrug Resistance Protein 1 (MRP1/ABCC1), and Breast Cancer Resistance Protein (BCRP/ABCG2) were found to be markers of overall poor chemotherapy response and prognosis.

To date, three distinct generations of P-gp modulators were developed, but all failed to demonstrate efficacy and safety in the clinical environment. Furthermore, the development of more selective and effective modulators, using structure-based approaches, was also hampered by the polyspecificity of the drug-binding pockets (DBPs).

Therefore, novel strategies for efflux modulation are extremely important to reverse MDR in cancer cells. In this communication, we will present and discuss our research on computational approaches used in the study of ABC transporters involved in multidrug resistance in cancer like Pgp and BCRP. We will focus our attention on the efflux mechanism[1,2] and on a novel approach aiming at designing modulators that bypass drug-binding at the DBPs of ABC transporters.[3]

Acknowledgements: This research was funded by the Portuguese Fundação para a Ciência e a Tecnologia (FCT), under contracts UIDP/04567/2020, UIDB/04567/2020, UIDP/04138/2020 and UIDB/04138/2020, and project 2022.05718.PTDC. ILIND is also acknowledged for funding through project: ABC-MDR-REVERSAL– Multidrug Resistance Reversal in Cancer Through a Novel Allosteric Mechanism.

References

1. C. A. Bonito, R. J. Ferreira, M. J. U. Ferreira, J.-P. Gillet, M. N. D. S. Cordeiro, D. J. V. A. dos Santos; *Sci. Reports* **2020**, *10*, 9823-9835.
2. C. A. Bonito, R. J. Ferreira, M.-J. U. Ferreira, J.-P. Gillet, M. N. D. S. Cordeiro, D. J. V. A. dos Santos; *J. Biomol. Struc. Dyn.* **2023**, *41*, 14428–14437.
3. C. A. Bonito, R. J. Ferreira, M.-J. U. Ferreira, J.-P. Gillet, M. N. D. S. Cordeiro, D. J. V. A. dos Santos; *ACS Omega* **2023**, *8*, 11281–11287.

OC1.20 Constrained Transition State Randomization: A general transition state sampling method for bimolecular

L. P. Viegas

Coimbra Chemistry Centre-Institute of Molecular Sciences (CQC-IMS), Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal

Email: lpviegas@ci.uc.pt

Transition state sampling is a crucial step in computational protocols that require a careful analysis of the energy barriers controlling the reaction flux. The calculation of rate coefficients through transition state theory is a typical example of such protocols, particularly if the reactant(s) exhibit conformational complexity. We have found this to be critical in obtaining accurate rate coefficients for atmospherically important bimolecular oxidation reactions, such as the OH-initiated reactions of fluorinated volatile organic compounds.[1-4] We have, since then, upgraded our sampling procedure with the development of a method called Constrained Transition State Randomization (CTSR),[5] which has now been improved, expanded to the Cl and NO_3 oxidants and made available[6] for the community.

Here, we will present the new features and capabilities of this new version of the CTSR method, along with its impact on the calculated rate constants. We will also present preliminary results of the generalization of this method to any two reactants, covering a wide range of fundamental bimolecular substitution reactions such as electrophilic substitution (S_E2), nucleophilic substitution (S_N2) and homolytic substitution (S_H2), where the CTSR code can greatly facilitate the calculation of transition states for increasingly complex substitution reactions.

Acknowledgements: The Coimbra Chemistry Centre-Institute of Molecular Sciences (CQC-IMS) is supported by the Portuguese Foundation for Science and Technology (FCT) through projects UIDB/QUI/0313/2020, UIDP/QUI/0313/2020 and LA/P/0056/2020 (national funds). L. P. V. acknowledges FCT for an Assistant Researcher grant (2021.01367.CEECIND/CP1656/CT0002).

References

1. L. P. Viegas; *J. Phys. Chem. A* **2021**, *125*, 4499-4512.
2. L. P. Viegas; *J. Phys. Org. Chem.* **2023**, *36*, e4470.
3. L. P. Viegas, F. Jensen; *Environ., Sci. Atmos.* **2023**, *3*, 855-871.
4. L. P. Viegas; *ChemPhysChem* **2023**, *24*, e202300259.
5. L. P. Viegas; *Chem. Phys. Lett.* **2022**, *803*, 139829.
6. L. P. Viegas, B. R. L. Galvão; *Atmos. Environ.* **2024**, *328*, 120515.

OC1.21 How cucurbit[7]urils allow the formation of a highly stable and stimuli responsive hexacationic flavylium-based quaternary rotaxane

A. Seco,[1] N. Mcclenaghan,[2] A. J. Parola,[1] N. Basílio[1]

[1] *NOVA School of Science and Technology, Lisbon, Portugal*
[2] *CNRS/Univ. Bordeaux, Institut des Sciences Moléculaires, Bordeaux, France.*
Email: am.seco@campus.fct.unl.pt

Rotaxanes are among the most well-known families of host-guest systems. Simply put, they consist of an axle to which a macrocycle binds and the presence of stoppers in the axle mechanically prevents the dissociation of the complex.[1] In this work we present a rather novel rotaxane, assembled in aqueous solution, in which the tetracationic blue box[2] binds to a dicationic flavylium guest having two cucurbit[7]urils acting as supramolecular stoppers. The flavylium/chalcone photoswitch[3] is explored and when in chalcone form, the axle binds one macrocycle of each type. Upon irradiation and formation of the flavylium cation, a second CB7 binds the axle, locking the blue box in place with a very high binding constant (>1x10^{7} M^{-1}) accompanied by a drastic increase in fluorescence quantum yield (12x, QY=0.78). In the absence of cucurbiturils no interactions between the flavylium axle and blue box are observed. Furthermore, in the axle, we explored two different tail groups appended to the flavylium/chalcone moiety. One has a cationic trimethylammonium, another has an anionic sulfonate and we found that only the one with the cationic tail forms this hetero[4]rotaxane since it provides a binding site for the second CB7.

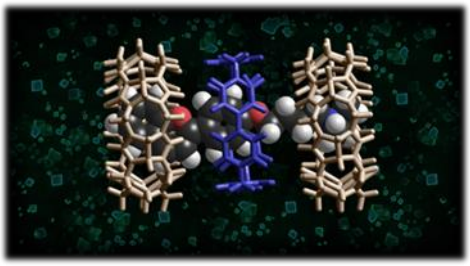


Fig. 1. Representation of the quaternary rotaxane with a flavylium-based axle inside a blue box and two cucurbit[7]uril macrocycles. On the background, a picture of crystals of this complex under a microscope.

Acknowledgements: This work was supported by the Associated Laboratory for Sustainable Chemistry, Clean Processes and Technologies – LAQV through national funds from Fundação para a Ciência e Tecnologia, FCT/MCTES, under project UIDB/50006/2020. A.S. also acknowledges FCT for his doctoral grant (2020.07313.BD).

References

1. C. Bruns, J. F. Stoddart; The Nature of the Mechanical Bond. From Molecules to Machines; Wiley VCH, 2016.
2. P. L. Anelli, N. Spencer, J. F. Stoddart; *J. Am. Chem. Soc.* **1991**, *113*, 5131-5133.
3. A. Seco, *et al*; *Chem. Eur. J.* **2021**, *27*, 16512.

OC2.1 Reactivity patterns in the decomposition of fullerene derivatives via the retro-Diels-Alder reaction

C.F.R.A.C. Lima, D.J.L. Rodrigues, C.S.T. Pinto, L.M.N.B.F. Santos

CIQUP, Institute of Molecular Sciences (IMS), Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Rua do Campo Alegre, P4169-007 Porto, Portugal
Email: carlos.lima@fc.up.pt

The peculiar geometry of fullerenes (spherical shape, high symmetry, curvature of the carbon skeleton) has long amazed chemists. Seeking to broaden the understanding of the reactivity of fullerenes, this work involves the kinetic and thermodynamic study of indene derivatives of C_{60} and C_{70} fullerenes in the solid phase: IC60MA (indene-C60-mono-adduct), IC60BA (indene-C60-bis-adduct), IC60TA (indene-C60-tris-adduct), IC70MA (indene-C70-mono-adduct), IC70BA (indene-C70-bis-adduct) and IC70TA (indene-C70-tris-adduct). The kinetic study focuses on measuring the decomposition temperatures, via Retro Diels-Alder reaction (RDA) of these adducts by thermogravimetry (TGA) and determining the respective kinetic parameters. The thermodynamic study involves the determination of the solid phase heat capacities of the compounds by Drop microcalorimetry and the analysis of the decomposition reaction by differential scanning calorimetry (DSC). These results are complemented by the characterization of the final fullerene products by various methods. With the results obtained, we seek to understand the RDA reaction mechanism, in the solid phase, of the fullerenes, focusing on the effects of the central fullerene (C_{60} *vs* C_{70}) and the number of indene addends (1 *vs* 2 *vs* 3). The results highlight the impact of the crystal packing of the solids on the activation energies, E_a, of the RDA reactions, and the pre-exponential values, A, were found to reflect the statistical weight of the C60–Indene bonds that can be broken.[1] Reaction mechanisms were proposed for the decomposition of the fullerene adducts.

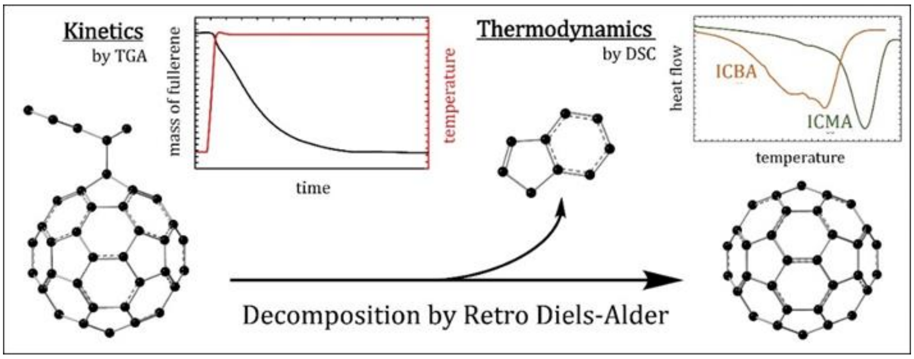


Fig. 1. Molecular structure representation of the four dichlorobenzonitrile isomers studied.

References

1. D.J.L. Rodrigues, I.B.O.M. Pina, L.M.N.B.F. Santos, C.F.R.A.C. Lima; *Diam. Relat. Mater.* **2023**, *136*, 110031.

OC2.2 Supramolecular catalysis of diazocine isomerization

M. Colaço,[1] J. Ewert,[2] U. Pischel,[3] R. Herges,[2] N. Basílio[1]

[1] Laboratório Associado para a Química Verde (LAQV), Rede de Química e Tecnologia (REQUIMTE), Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal

[2] Otto Diels-Institute of Organic Chemistry, Christian Albrechts University Kiel, Otto Hahn Platz 4, 24118 Kiel, Germany

[3] CIQSO – Centre for Research in Sustainable Chemistry and Department of Chemistry, University of Huelva, Campus de El Carmen s/n, E-21071 Huelva, Spain

Email: mr.colaco@campus.fct.unl.pt

Diazocines (DAC) can be described as azobenzenes with an additional bridge linking the phenyl rings, becoming a less flexible tricyclic molecule.[1] Hence, the *Z*-isomers are the most stable in DAC, unlike what happens to the well-known azobenzenes. This complementarity of properties between them allows the overcoming of each limitation. In this communication, we present new host-guest pairs, composed of a water-soluble diazocine derivative as photoactive guest and synthetic macrocycles called cucurbit[n]urils (CBn, in this work n = 7 or 8) as hosts. The host-guest affinities were determined by NMR, UV-Vis absorption spectroscopy and ITC, through direct or competitive titrations. The CB7 host binds selectively the E-isomer with a micromolar affinity (Figure 1). Furthermore, CB8 bind strongly both isomers, but prefers the Z-isomer, as it forms a tighter complex. The photochemical conversion of DAC from Z to E isomer is mainly unaffected by CBn complexations, but the thermal recovery rates were found to be accelerated by these hosts. This effect is remarkable in the presence of CB7, decreasing the half-life from 23 h to 36 min. When catalytic amounts of CB7 are present, the kinetics is of zero-order, so it acts as a supramolecular catalyst in a system comparable to Michaelis-Menten enzymes. To better understand those catalytic effects, the activation enthalpies and entropies were also studied. To apply these systems, we added the pesticide fuberidazole[2] to the CB7:DAC assembly to develop a supramolecular photoacid.

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, co-financed 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, CEECIND/00466/2017 and the PhD grant 2021.07205.BD.

References

1. P. Lentes, P. Frühwirt, H. Freißmuth, W. Moormann, F. Kruse, G. Gescheidt, R. Herges; *J. Org. Chem.* **2021**, *86*, 4355-4360.
2. A. L. Koner, I. Ghosh, N. Saleh, W. M. Nau; *Can. J. Chem.* **2011**, *89*, 139-147.

OC2.3 Assessment of the mobility and fate of halogenated substituted benzonitriles and benzaldehydes

B.D.A. Pinheiro, A.R.R.P. Almeida, M.J.S. Monte

Research Center in Chemistry of University of Porto (CIQUP), Institute of Molecular Sciences (IMS), Department of Chemistry and Biochemistry (DQB), Faculty of Sciences of University of Porto (FCUP), Rua do Campo Alegre, P-4169-007 Porto, Portugal
Email: bruno.pinheiro44@gmail.com

Accurately assessing the environmental risks posed by organic compounds requires a thorough understanding of their physical and chemical properties. The extensive production and use of these substances can lead to significant environmental pollution, as they disperse across soil, water, air, and biota, thereby impacting biodiversity and human health. Their distribution among these environmental compartments is governed by their properties, namely volatility and solubility.[1] Therefore, this research aims to furnish crucial data on the experimental determination and subsequent prediction of important physical-chemical properties of several halogenated substituted benzonitriles and benzaldehydes. The research covers the volatility study (vapor pressures) using a capacitance diaphragm manometer static method[2] and a Knudsen mass-loss effusion technique.[3] The solubility in water (Sw) of those compounds was also determined at 298.15 K using the shake-flask method[4] and UV-Vis spectroscopy. The sublimation properties obtained through vapor pressure measurements[2,3] were combined with those obtained through solubility experiments resulting in additional crucial properties such as Henry's constants and Gibbs energy of solvation. All the obtained results will be useful to expand a database, reported before for halogenated benzenes, that enabled to develop simple equations to predict those environmental mobility properties, at 298.15 K, for benzene derivatives integrating only halogen atoms.[1]

Acknowledgements: This work was supported by the Fundacão para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Sciences, University of Porto (Project UIDB/00081/2020) and IMS - Institute of Molecular Sciences (LA/P/0056/2020)). BDAP thanks FCT for the award of a PhD research grant (UI/BD/152715/2022). ARRPA is financed by national funds through the FCT-I.P: DL57/2016/CP1454/CT0006: https://doi.org/10.54499/DL57/2016/CP1454/CT0006

References

1. M.J.S. Monte, A.R.R.P. Almeida; *Chemosphere* **2017**, *189*, 590.
2. M.J.S. Monte, L. M. N. B. F. Santos, M. Fulem, J.M.S. Fonseca, C.A.D. Sousa; *J. Chem. Eng. Data* **2006**, *51*, 757.
3. M.A.V. Ribeiro da Silva, , M.J.S. Monte, , L.M.N.B.F. Santos; *J. Chem. Thermodyn*. **2006**, *38*, 778.
4. A. Veseli, S. Žakelj, A. Kristl; *Drug Dev. Ind. Pharm*. **2019**, *45*, 1717.

OC2.4 Exploring coumarin-3-carboxamide derivatives as fluorescent metal cation detectors

L.J. Gomes,[1] *C.S.B. Gomes,*[1-3] *A.C. Tomé* [4], *A.J. Moro*[1]

[1] *LAQV-REQUIMTE, Department of Chemistry, Nova School of Science and Technology / FCT-NOVA, Monte de Caparica, Portugal FCT-NOVA*
[2] *UCIBIO, Department of Chemistry, Nova School of Science and Technology / FCT-NOVA, Monte de Caparica, Portugal FCT-NOVA*
[3] *i4HB, Department of Chemistry, Nova School of Science and Technology / FCT-NOVA, Monte de Caparica, Portugal FCT-NOVA*
[4] *LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal*
Email: lj.gomes@campus.fct.unl.pt

The desire of detecting and quantifying different metals in a matrix by the scientific community is enormous.[1] Indeed, some industries have a high demand for new tools towards detection of raw materials (e.g. heavy metal ions in the mining industry), while having the necessity for monitorization of surroundings water and soil deposits. On the other hand, given the intrinsic toxicity of some metals, new methods for testing biological samples are key for controlling levels of these elements in vivo. Although several methods are available, such as Atomic Absorption Spectroscopy (AAS) or Inductively Coupled Plasma Optical Emission Spectrometry (ICP-AES), they are considered expensive, and their samples are hard to prepare and analyze.[2] For this purpose, fluorescence spectroscopy stands out since it is a faster tool, while having a high sensitivity. Moreover, it is regarded as more cost-effective technique.

Fluorescent chemosensors emerge as a solution since in the presence of an analyte, these molecules are capable of produce a different signal from the original one, being selective even at low concentrations.[3]

Having this in mind, a new family of 3-acetylcoumarin derivatives is herein presented as potential metal fluorescent chemosensors. The derivatives of 3-acetylcoumarin could be divided into two moieties, being the coumarin structure the fluorophore or signalling moiety, and the receptor/recognition moiety an aza-crown (1,4-Oxazinane, 1-Aza-12-crown-4, Aza-15-crown-5 and others).

In order to study the photophysical characteristics of these compounds, UV-Vis and fluorescence titrations were carried out with several ions (Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Mg^{2+}, Fe^{2+}, Ca^{2+}, Li^{+}, Pb^{2+} and K^{+}). The outcome of these experiments, some of the synthesized coumarins demonstrate selectivity to lead, calcium and cobalt.

Acknowledgements: FCT/MCTES for a Ph. D. grant (UI/BD/153617/2022).

References

1. J. Zhao et al.; *Coord. Chem. Rev.* **2019**, *378*, 415–444.
2. M. N. Sweilam et al.; *ACS Sens.* **2018**, *3*, 1802.
3. T. Sakamoto, A. Ojida, I. Hamachi; *Chem. Comm.* **2009**, 141–152.

OC2.5 Optimizing vapor deposition of pentacene for inverted perovskite solar cells

A.F.M. Farinha, R.A.S. Pinto, L.M.N.B.F. Santos, J.C.S. Costa

CIQUP, Institute of Molecular Sciences (IMS), Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Portugal
Email: up201506214@fc.up.pt

The vapor deposition methods are highly relevant in developing perovskite solar cells (PSCs), particularly in forming planar films for devices with an inverted architecture (see Fig. 1). In this project, we investigated the deposition of perovskite (PVK) films employing a thermal evaporation apparatus with multiple Knudsen cells, each featuring independent temperature control.[1-3] Simultaneous evaporation of two perovskite precursors, methylammonium iodide (MAI) and lead iodide (PbI_2), resulted in the formation of a hybrid organic-inorganic PVK film ($MAPbI_3$). This method offers exceptional purity, crystallinity, homogeneity, and thickness control.[2-3] A hole transport layer (HTL) based on a pentacene (PENT) film was incorporated into the PSCs. The HTL significantly improved device performance with PENT deposited at a slower rate, demonstrating the best crystallinity and enhancing charge transport properties. Current-voltage (I-V) curves were analyzed, and the morphological, structural, and optical characteristics of the various layers were assessed using scanning electron microscopy (SEM), X-ray diffraction, and UV-vis spectroscopy, respectively. To complete the device, a fullerene derivative (PCBM) was utilized as the electron transport layer (ETL) deposited atop the PVK layer, while silver served as the cathode. Compact and homogeneous PVK films were successfully produced, and devices with highly crystalline pentacene showed decent stability and efficiency, suggesting potential for further optimization of the pentacene-PVK interface.

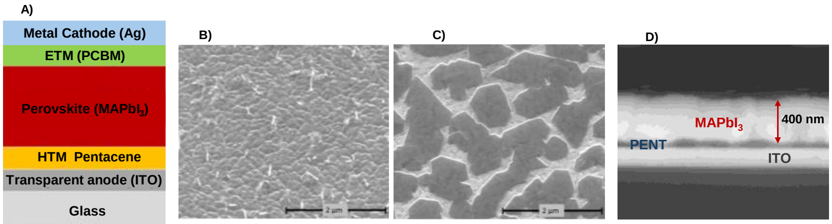


Fig. 1. Architecture of an inverted perovskite solar cell (A); SEM images of pentacene films obtained at fast (B) or slow (C) deposition rates. Cross-sectional SEM image of $MAPbI_3$/Pentacene/ITO (D).

Acknowledgements: This work was supported by the Fundação para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020: DOI 10.54499/UIDP/00081/2020), and IMS-Institute of Molecular Sciences (LA/P/0056/2020)). A.F.M. Farinha also thanks the FCT and the European Social Fund (ESF) for the award of a Ph.D. Research Grant (ref. 2022.11342.BD). The authors also thank J.R. Sánchez-Valencia and F.N. Gálvez for their support in the deposition of the ETL and characterization of the PSC.

References

1. J.C.S. Costa, R.M. Rocha, I.C.M. Vaz, M.C. Torres, A. Mendes, L.M.N.B.F. Santos; *J. Chem. Eng. Data* **2015**, *60*, 3776.
2. J.C.S. Costa, J. Azevedo, L.M.N.B.F. Santos, A. Mendes; *J. Phys. Chem. C* **2017**, *121*, 2080.
3. J.C.S. Costa, J. Azevedo, J.P. Araújo, L.M.N.B.F. Santos, A. Mendes; *Thin Solid Films* **2018**, *664*, 12.

OC2.6 Seeking new low temperature energy storage systems: *n*-alkanes as phase change materials

M.C.M. Sequeira,[1] *B.A. Nogueira,*[2] *T. Nikitin,*[2] *F.J.P. Caetano,*[3] *H.P. Diogo,*[1] *J.M.N.A. Fareleira,*[1] *R. Fausto*[2,5]

[1] *Centro de Química Estrutural, Institute of Molecular Sciences, Dep. de Engenharia Química, Instituto Superior Técnico, Univ. de Lisboa, Av. Rovisco Pais, 1049-001, Lisbon, Portugal*
[2] *Centro de Química de Coimbra, Institute of Molecular Sciences (IMS), Dep. de Química, Univ. de Coimbra, Portugal*
[3] *Dep. de Ciências e Tecnologia, Univ. Aberta, R. da Escola Politécnica 147, 1269-001, Lisboa, Portugal*
[4] *Centro de Química Estrutural, Institute of Molecular Sciences, Instituto Superior Técnico, Univ. de Lisboa, Av. Rovisco Pais, 1049-001, Lisbon, Portugal*
[5] *Faculty of Sciences and Letters, Dept. of Physics, Istanbul Kultur Univ., Ataköy Campus, Bakirköy 34156, Istanbul, Turkey*
Email: maria.sequeira@tecnico.ulisboa.pt

Over the last decades, the increasing need for energy has been a tremendous challenge. Until now, fossil fuels have been the dominant energy source, however, due to their environmental consequences, renewable energies are the promising solution for the future.[1] Nevertheless, the intermittent nature of most renewable energy sources often leads to a discrepancy between the energy produced and its consumption, which highlights the crucial role of energy storage technologies in enhancing clean energy utilization.[2] From all energy storage solutions, thermal energy storage (TES) is one of the most promising options, showing substantial energy storage capacity at an acceptable cost.[3] For these applications, phase change materials (PCMs) are particularly important, especially for low temperature energy storage systems. Linear alkanes (*n*-alkanes) have been studied as good candidates for TES applications mainly due to their singular phase transition performance, among others.[4] In the present work, it has also been studied the differences due to the odd-even carbon chain number on the solid-liquid equilibrium properties that these materials can present, which is a key aspect to characterize the systems for an upcoming use as PCMs.[4,5]

For TES applications, solid-liquid phase equilibrium is determinant to characterize the phase transitions which are more important for the application of these systems, as new PCMs. As an example, in the logistics associated to the transport of perishable consumables, like vaccines and other pharmaceutical products, TES plays an important role. In the present context, this work aims the characterization of some selected *n*-alkane binary systems that can be used for energy storage applications at low temperatures, including the construction of the solid-liquid binary phase diagrams at sub-zero temperatures using differential scanning calorimetry (DSC), hot stage microscopy (HSM) and Raman spectroscopy. The studied systems composed by odd and even *n*-alkanes, have showed different solid-liquid equilibrium behaviour. The HSM and Raman spectroscopy were fundamental to obtain the binary phase diagrams, but also to visualize the changes taking place in real time as a function of temperature and often the identification of the different solid and liquid phases exhibited by these systems.

This work presents some preliminary phase equilibrium data, which, to the knowledge of the authors, are not available in the literature, and are presently being prepared for publication in an international scientific journal. The presentation will also include comparisons with spread literature data, when available. All these studied systems have promising characteristics for low temperature energy storage. With this work, it is also demonstrated how solid-liquid phase equilibrium studies are a central key to select the most adequate phase change material for a specific TES application.

Acknowledgements: This work was supported by Fundação para a Ciência e a Tecnologia (FCT), Portugal, Projects UIDB/00100/2020 (https:// doi. org/ 10. 54499/ UIDB/ 00100/ 2020), UIDP/00100/2020 (https://doi. org/ 10. 54499/ UIDP/ 00100/ 2020), UIDB/00313/2020 (https:// doi. org/ 10. 54499/ UIDB/ 00313/ 2020), UIDP/00313/2020 (https:// doi. org/ 10. 54499/ UIDP/00313/ 2020) and IMS-LA/P/0056/2020UIDB/00100/2020 (https:// doi. org/ 10. 54499/ LA/P/ 0056/ 2020). M.C.M. Sequeira acknowledges the PhD grant funded by FCT ref. UI/BD/152239/2021.

References

1. G. Wang, Z. Tang, Y. Gao, P. Liu, Y. Li, A. Li, X. Chen; *Chem. Rev.* **2023**, *11*, 6953–7024.
2. European Commission, Energy storage – the role of electricity, Comm. Staff Work Doc., 25, 2017. https://ec.europa.eu
3. EASE, Thermal Energy Storage, Brussels, 2023. https://ease-storage.eu
4. H. Yan, H. Yang, J. Luo, N. Yin, Z. Tan, Q. Shi; *Chinese Chem. Lett.* **2021**, *32*, 3825–3832. https://doi.org/10.1016/j.cclet.2021.05.017
5. D. Mondieig, F. Rajabalee, V. Metivaud, H.A.J. Oonk, M.A. Cuevas-Diarte; *Chem. Mater.* **2004**, *16*, 786–798.

OC2.7 Modeling CO_2 electrochemical reduction in porous cathodes for liquid-phase electrolyzers

I. S. Fernandes, R. Martins, M. J. Mendes, A. S. Reis-Machado

i3N/CENIMAT, Department of Materials Science, NOVA School of Science and Technology, and CEMOP/UNINOVA, Campus de Caparica, 2829-516 Caparica, Portugal

Email: isd.fernandes@alumni.fct.unl.pt

The CO_2 electrochemical reduction (CO_2R) powered by green energy is crucial for "defossilizing" the production of fuels and added-value chemicals, aligning with the UN and EU Sustainable Development Goals.[1] Since the early 2000s, numerous studies have employed finite element (FEM) and finite difference (FDM) modeling to simulate the performance of CO_2R electrolyzers with different configurations, electrolytes, and electrode types.[2] These experimentally validated models enhanced process understanding and device optimization over time.

This work aims to advance CO_2R technology by developing representative models for the parametric analysis and optimization of zinc porous cathode electrolyzers. Simulations consider steady-state operations with various temperatures, inlet pressures, and flow rates of liquid CO_2, including different configurations of the electrolyzer components (cathodic porosity, fiber diameter, pore length, fiber cross-sectional geometry, electrode thickness, and electrolytic chamber dimensions).[3] Validated with experimental data from state-of-the-art literature,[4,5] the models were implemented using mesh-based software designed for multiphysics phenomena simulation, considering species transport in aqueous solutions, flow in the Reynolds regime, and secondary current distribution.[6] This methodology significantly improved CO production, achieving a record partial current density of 263.6 mA/cm² at -1.1 V vs. RHE,[3] a 486% increase over the reference case.[4] The results underscore the remarkable potential of computational modeling in guiding the manufacture of electrolytic structures. Optimized CO_2R conditions demonstrate the possibility of producing green fuels economically interestingly when integrated with renewable energy sources such as photovoltaic electricity.

Acknowledgements: This work received funding from FCT (Fundação para a Ciência e a Tecnologia, I.P.) under the projects LA/P/0037/2020, UIDP/50025/2020 and UIDB/50025/2020 of the Associate Laboratory Institute of Nanostructures, Nanomodelling and Nanofabrication—i3N, and by the project CO2RED, DOI 10.54499/PTDC/EQU-EPQ/2195/2021. The work was also supported by the European project SYNERGY (H2020-WIDESPREAD-2020-5, CSA, Grant No. 952169), M-ECO2 – Industrial cluster for advanced biofuel production, Ref. C644930471-00000041, co-financed by PRR – Recovery and Resilience Plan of the European Union (Next Generation EU), and by the European Union via the project X-STREAM (Horizon EU, ERC-2023-COG, Grant No. 101124803).

References

1. A. C. Lourenço, A. S. Reis-Machado, E. Fortunato; *Mater. Today Energy* **2020**, *17*, 100425.
2. O. A. El-Shafie, R. M. El-Maghraby, J. Albo; *Ind. Eng. Chem. Res.***2020**, *59*, 20929–20942.
3. I. S. Fernandes, D. Antunes, R. Martins; *Heliyon* **2024**, *10*, e26442.
4. W. Luo, J. Zhang, M. Li; *ACS Catal.* **2019**, *9*, 3783–3791.
5. M. Morimoto, Y. Takatsuji, K. Hirata; *Electrochim. Acta* **2018**, *290*, 255–261.
6. C. Ma, X. Li, L. Lin; *J. Energy Storage* **2018**, *18*, 16–25.

OC2.8 Studying the hydrogen combustion in carbon nanotubes

J. Brandão, C. Mogo, C. M. A. Rio, W. Wang, D. V. Coelho

CEOT, Universidade do Algarve, Portugal
Email: jbrandao@ualg.pt

We present 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 a considerable effect on increasing their reactivity at low temperatures. This has been justified by orientation effects of the confined reactants and 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,[1-3] 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 the reaction's inability to sustain itself since the heat escapes too quickly. Despite that, work in nano and micro nanobubbles[4,5] 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.
Recently, we have developed an innovative method to model complex systems. The MReaDy[6] program builds a global Potential Energy Surface (gPES), defined by integrating diverse PESs, each 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. The results strongly depend on the type of the nanotube.

Acknowledgments: FCT under the PTDC/QUI-QFI/31955/2017 research project, co-financed by the European Community Fund, FEDER and the COST Action CA18212 "Molecular Dynamics in the GAS phase".

References

1. A. C. Fernandez-Pello; *Proc. Combust. Inst*. **2002**, *29*, 883.
2. B. Lewis, G. von Elbe; *Combustion, Flames and Explosions of Gases*, Academic Press: New York, NY, USA, 1987.
3. F. A. Williams; *Combustion Theory*, The Benjamin/Cummins: Prinston, NJ, USA, 1985.
4. V. Svetovoy, A. Postnikov, I. Uvarov, R. Sanders, G. Krijnen; *Energies* **2016**, *9*, 94.
5. A. V. Postnikov, I. V. Uvarov, A. V. Prokaznikov, V. B. Svetovoy; *Appl. Phys. Lett.* **2016**, *108*, 121604.
7. C. Mogo, J. Brandão; *J. Comp. Chem.* **2014**, *35*, 1330.

OC2.9 Experimental and theoretical insight into structural, energetic and electronic properties of 4-MPy adsorption onto zinc chalcogenide-based substrates

J.S. Figueiredo, S. Fateixa, J. Lopes, A. C. Estrada, J. D. Gouveia, J. R. Gomes, T. Trindade

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

Raman spectroscopy is a technique with great detection and identification potential, but whose low sensitivity renders its use impractical in many situations. Some materials provide signal enhancement through the surface-enhanced Raman spectroscopy (SERS) effect, making the technique more generally viable. SERS was originally thought to be exclusive to plasmonic metals, most notably gold and silver, but further theoretical and technological developments unveiled new types of SERS-active materials, including nanostructures of distinct morphologies and compositions.[1] Fully understanding non-plasmonic SERS would potentially be revolutionary, as these materials are highly customizable, cheaper, and tailorable for a multitude of purposes.[2]

In this communication, we explore the properties of ZnO and its interaction with 4-mercaptopyridine (4-MPy) through first principle calculations and compare it with those of ZnS in the same role. The basis for these studies was our recent research on ZnS/GO, which was found to enhance the Raman signal of chemisorbed 4-MPy, compared to isolated ZnS or GO flakes. Via computational methods, we concluded that the observed synergistic effect was the result of the appearance of intragap energy levels upon adsorption of ZnS on GO, assisting charge-transfer mechanisms and resulting in signal enhancement.[3] Despite the similarities between ZnS and ZnO, ZnO behaves very differently, barely interacting with GO and enhancing the Raman signal unaided. The influence of diverse parameters in the morphological characteristics of the substrates is discussed, thereby gaining a better understanding on the application of zinc chalcogenide semiconductors as SERS substrates.

Acknowledgements: J.J.L thanks FCT for the doctoral grant (SFRH/BD/126241/2016). A.C.E. and S.F. acknowledge the costs resulting from the FCT hirings funded by national funds (OE), through FCT. This research was funded through the FCT Project UTAP-ICDT/CTM-NAN/0025/2014 in the framework of the UT Austin/Portugal Program and project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by the FCT/MEC and co-financed by FEDER under the PT2020 Partnership Agreement. We thank Dr. Rosário Soares, Marta Ferro, and Manuela Marques for technical support.

References

1. M. Moskovits, B.D. Piorek; *J. Raman Spectr.* **2021**, *52*, 279–284.
2. B. Yang, Y. Wang, S. Guo, S. Jin, E. Park, L. Chen, Y.M. Jung; *Bull. Korean Chem. Soc.* **2021**, *42*, 1411–1418.
3. J.L. Lopes, S. Fateixa, A.C. Estrada, J.D. Gouveia, J.R.B. Gomes, T. Trindade; *J. Phys. Chem. C* **2020**, *124*, 12742–12751.

OC2.10 A robust method for property prediction via artificial neural networks: Incorporating key structural features for carbon dioxide-ionic liquid mixtures

H. Marques, J. N. Canongia Lopes, A. A. Freitas, K. Shimizu, P. S. F. Mendes

Centro de Química Estrutural, Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
Email: hugo.s.marques@tecnico.ulisboa.pt

The literature on carbon dioxide (CO_2) and ionic liquid (IL) mixtures lacks comprehensive data, especially for flow properties, hindering practical applications.[1,2] This study develops an efficient method to predict CO_2-IL mixture densities across various conditions and IL families using artificial neural networks (ANN). Three models trained on (1) IL critical properties, (2) IL structural descriptors, and (3) a combination of both showed relative deviations below 3%, with the combined model achieving an R^2 of 0.986 for the testing dataset. Post-processing outlier removal was applied, which resulted in further enhanced accuracy. Molecular Dynamics simulations validated the ANN models, demonstrating excellent accuracy even beyond the training range and for ILs not included in the dataset. This approach offers a faster and broader alternative to traditional thermodynamic tools, setting a robust foundation for future Machine Learning-based property predictions.

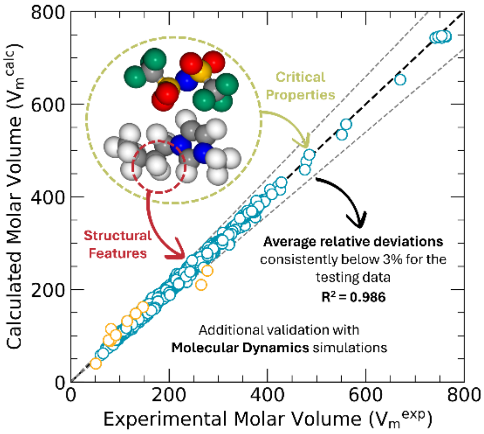


Fig. 1. Illustration of the methodology and results used to obtain mixture molar volume.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by FCT through projects UIDB/00100/2020 (10.54499/UIDB/00100/2020) and UIDP/00100/2020 (10.54499/UIDP/00100/2020). Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020 (10.54499/LA/P/0056/2020). This work was funded through the grant 2022.10217.BD (H. Marques) and through CEEC contract IST-ID/93/2018 (A. A. Freitas) and IST-ID/100/2018 (K. Shimizu).

References

1. M.E. Hamzehie, M. Fattahi, H. Najibi, B. Van Der Bruggen, S. Mazinani; *J. Nat. Gas Sci. Eng.* **2015**, *24*, 106–114.
2. J.A. Lazzús; *J. Taiwan Inst. Chem. Engineers* **2009**, *40*, 213–232.

OC2.11 Making sense of data: Intelligible machine learning analytics for VOC vaporization enthalpy prediction

J. Ferraz-Caetano,[1] F. Teixeira,[2] M. N. D. S. Cordeiro[1]

[1]LAQV-REQUIMTE – Department of Chemistry and Biochemistry – Faculty of Sciences, University of Porto – Rua Campo Alegre, S/N, 4169-007 Porto, Portugal
[2]CQUM – Centre of Chemistry, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal
Email: jose.caetano@fc.up.pt

Precise prediction of standard molar vaporization enthalpy ($\Delta_{vap}H_m°$) for volatile organic compounds (VOCs) holds critical significance in environmental chemistry, industrial usage, and regulatory compliance. To relinquish conventional, time-consuming, experimental approaches for estimating $\Delta_{vap}H_m°$ of VOCs, machine learning (ML) models offer an efficient and cost-effective alternative. However, despite increasing adoption, current ML algorithms face property prediction challenges: statistical accuracy, wide applicability, and data availability, materialized in the lack of an explainable model to overcome these issues.

In this communication, we present our *in-house* explainable, data-driven ML model, designed to predict $\Delta_{vap}H_m°$. It was built upon a constructed experimental database comprising 2410 unique molecules and 106 open-source physico-chemical descriptors. Our model can accurately predict the $\Delta_{vap}H_m°$ of VOCs, achieving a mean absolute error of 3.02 kJ mol^{-1} and a test accuracy of 95%.[1] Model validation was conducted by $\Delta_{vap}H_m°$ prediction with external datasets (including an established VOC database), and through molecular group hold-out tests.

This study underscores the critical role in deciphering the physical significance of chemical open-source descriptors for $\Delta_{vap}H_m°$, demonstrating their predictive power and interpretability. Chemical feature importance analysis demonstrated that factors such as VOC polarizability, connectivity indexes, and electrotopological state play critical roles in the model’s predictive accuracy. We emphasize the model's significant potential in streamlining chemical property predictions, accelerating the identification of chemical behaviors.

Acknowledgements: The authors thank the Fundação para a Ciência e Tecnologia (FCT/MCTES) support to LAQV-REQUIMTE (UIDP/50006/2020) and CQUM (UID/QUI/00686/2020). JFC’s PhD Fellowship is supported by the doctoral Grant (ref. SFRH/BD/151159/2021) financed by the FCT, with funds from the State and EU Budget through the Social European Fund and Programa Por_Centro, under the MIT Portugal Program. FT is supported by FCT through contract CEECINST/00156/2018/CP1642/CT0011.

References

1. J. Ferraz-Caetano, F. Teixeira, M.N.D.S., Cordeiro, *Chemosphere* **2024**, 142257.

OC2.12 A combined structural, spectroscopic, and theoretical investigation of a water-soluble Schiff base: stability and enol-imine/keto-enamine tautomerism

H. Bouznif,[1,2] *L.L.G. Justino,*[2] *M.I.L. Soares,*[2] *T. Costa,*[2] *M. L. Ramos,*[2] *T. Nikitin,*[2] *T.M.V.D. Pinho e Melo,*[2] *N. Zouari*[1], *R. Fausto*[2,3]

[1] *Laboratory Physico-Chemistry of the Solid State, Department of Chemistry, Faculty of Sciences of Sfax, B. P. 1171, Sfax 3000, University of Sfax, Tunisia*
[2] *CQC-IMS, Department of Chemistry, University of Coimbra, Rua Larga 3004-535 Coimbra, Portugal*
[3] *Faculty of Sciences and Letters, Department of Physics, Istanbul Kultur University, Ataköy Campus, Bakirköy 34156, Istanbul, Turkey*
Email: bouznif.hajer@uc.pt

Schiff bases were first synthesized in the mid-19th century by condensing primary amines with aldehydes or ketones.[1] Since then, they have been intensively investigated due to their straightforward synthesis and relevance in various fields, such as catalysis, medicinal chemistry, materials science,[2] etc. Among them, the salen-type (*N*,*N'*-ethylenebis(salicylimine)) Schiff bases have attracted considerable interest due to their versatility and tunability. In these compounds, the existence of intramolecular proton transfer between the imine nitrogen atom and the ortho phenolic oxygen is favored, resulting in two tautomeric structures: the enol-imine and the keto-enamine forms.

Here, we report a water-soluble di-Schiff base *N*,*N*'-bis(3-methoxy-5-sulfonatosalicylidene)-1,2-ethylenediamine disodium salt (**MSS**), derived from the condensation of 3-methoxy-salicylaldehyde-5-sulfonate sodium and 1,2-ethylenediamine in 2:1 molar ratio, synthetized using both conventional and microwave methods. **MSS** was characterized using NMR, HRMS, UV/vis, fluorescence, Raman, and FTIR spectroscopies, complemented by density functional theory (DFT) calculations. To assess the stability, over time, of **MSS** in aqueous solution, we conducted a series of experiments. Moreover, a detailed exploration of the enol-imine // keto-enamine tautomerism in different solvents and in the solid state was conducted, along with an analysis of the impact of intramolecular interactions on the tautomeric preferences in different media. Based on theoretical calculations, the enol-imine tautomeric form was found to be preferred in the gas phase. Nevertheless, the keto-enamine form was determined to be the predominant tautomer in several solvents, as well as in the solid state. The optical band gap of polycrystalline **MSS** was determined to be 2.63 eV, revealing its wide band gap semiconductor character.

Acknowledgments: The CQC-IMS is supported by FCT (projects UIDB/00313/2020, UIDP/00313/2020, LA/P/0056/2020). The authors also thank the UC Laboratory for Advanced Computing and the UC-NMR facility (supported by FEDER through COMPETE, National Funds from FCT through grants REEQ/481/QUI/2006, RECI/QEQ-QFI/0168/2012, CENTRO-07-CT62-FEDER-002012, and RNRMN).

References

1. H. Schiff, J. Justus; *Liebigs An. Chem.* **1864**, *131*, 118–119.
2. S. Kagatikar, D. Sunil; *J. Electron. Mater.* **2021**, *50*, 6708–6723.

OC2.13 Halogen anisotropy in solvation and membrane permeability: implications for protein-ligand binding and drug efficiency

A. Fortuna,[1,2] Paulo J. Costa[2]

[1] *Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, University of Lisbon, Av. Professor Gama Pinto, 1649-003 Lisbon, Portugal*
[2] *BioISI - Instituto de Biossistemas e Ciências Integrativas and Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Lisboa, Portugal*
Email: ajfortuna@fc.ul.pt

Halogenation is a widely used strategy in drug discovery to optimize absorption, distribution, metabolism, and excretion properties. Moreover, halogenated compounds can interact with biological targets, such as proteins[1] and membranes,[2] through halogen bonds (XBs) and hydrogen bonds (HBs). This ability arises from the anisotropic electrostatic potential of covalently-bonded halogens (X), which generates a positive region (σ-hole) on the opposite side of the X atom along the R–X bond axis. Consequently, halogens can interact with negatively charged species, such as the carbonyl oxygens in protein backbones, by forming XBs while also serving as acceptors for HBs with electropositive molecules. Describing this anisotropy is challenging when using force field methods that rely on atomic charges, which typically represent X atoms as negative, precluding the possibility of XB formation. To address this, our group has been developing and testing force field parameters to improve the representation of halogens in significant biological phenomena such as solvation, receptor binding, and membrane permeability. Indeed, the role of these odd noncovalent interactions is often overlooked, with the focus being mainly on HBs. This communication presents the recent advances in the validation of various halogen parameters to calculate hydration free energies (ΔG_{hyd}) using both implicit (fast)[3] and explicit (more detailed) solvent models.[4] Furthermore, and considering the importance of the desolvation process in protein-ligand and membrane-ligand interactions, these parameters were also evaluated in determining binding free energies (ΔG_{bind}) and the calculated membrane permeability coefficients (P_{calc}) of halogenated compounds. We will show that better correlations between the experimental and calculated values are obtained when the halogen anisotropy is modeled, highlighting the importance of XBs in drug permeation and binding and providing a robust methodology for future studies.

Acknowledgements: /BD/146447/20119 (AF), UIDB/04046/2020 (DOI: 10.54499/UIDB/04046/2020) and UIDP/04046/2020 (DOI: 10.54499/UIDP/04046/2020) to BioISI,2021.00381.CEECIN(DOI: 10.54499/2021.00381.CEECIND/CP1650/CT0004) to PJC. EU: project TWIN2PISPA - Twinning for Excellence in Biophysics of Protein Interactions & Self-Assembly (GA 101079147.

References

1. P. J. Costa, R. Nunes, D. Vila-Viçosa; *Exp. Expert Opin. Drug Discov.* **2019**, *14*, 805-820.
2. R. Nunes, D. Vila-Viçosa, P. J. Costa; *J. Am. Chem. Soc*. **2021**, *11*, 4253–4267.
3. A. Fortuna, P. J. Costa; *J. Chem. Inf. Model.* **2021***, 7,* 3361-3375.
4. A. Fortuna, P. J. Costa; *J. Chem. Inf. Model.* **2023**, *23*, 7464–7475.

OC2.14 Eutectic mixture formation and relaxation dynamics of co-amorphous mixtures of two antifungal imidazole drugs

W. Noor, C.D.R. Macovez, M. Romanini, J.L. Tamarit

Grup de Caracterització de Materials, Department of Physics & Barcelona Research Center in Multiscale Science and Engineering, Universitat Politècnica de Catalunya, Barcelona, Spain
Email: wahi.noor@upc.edu

Amorphous forms of active pharmaceutical ingredients (APIs) exhibit enhanced water solubility and, as a result, greater bioavailability compared to their crystalline counterparts. However, they tend to be prone to recrystallization. Creating co-amorphous mixtures of two compatible APIs is a promising approach to enhance a drug's water solubility while also increasing the kinetic stability of the resultant glass. This method also enables the simultaneous administration of both drugs.[1] We present kinetically stable amorphous binary combinations of two marketed antifungal imidazole medicines, bifonazole and clotrimazole, with comparable melting points and glass transition temperatures. The equilibrium phase diagram of this binary system, as determined by calorimetry, aligns with the Schroeder-Van Laar-Le Chatelier model, which is typical for compounds that are miscible in the liquid state but immiscible in the crystalline state. The experimental eutectic composition is close to an equimolar ratio, with a eutectic melting point $T_e = 392$ K. The glass transition temperature T_g varies linearly with composition, indicating that the two APIs form ideal liquid mixtures. Dielectric spectroscopy is utilized to analyze the relaxation dynamics of each amorphous API individually, as well as the amorphous mixtures in both the supercooled liquid and glass states. A single structural α relaxation is observed in all amorphous samples, suggesting homogeneity. Each pure amorphous API exhibits intramolecular secondary relaxations. For pure bifonazole, the secondary relaxation arises from the rigid torsional rotation of the imidazole ring. In pure clotrimazole, the secondary relaxation is considerably slower than in bifonazole and is attributed to small-angle torsional motions of the imidazole and/or chlorobenzene rings, hindered by intramolecular steric interactions (clotrimazole is a methane derivative with four geminal rings). These secondary relaxation processes are also detected in binary mixtures, with their intensity varying based on the chemical composition.

References

1. S. Valenti, C. Cazorla, M. Romanini, J.L. Tamarit, R. Macovez; *Pharmaceutics* **2023**, *15*, 196.

OC2.15 Structural criterion for the onset of rigidity in a colloidal gel

C.S. Dias,[1,2] *J.C. Neves,*[1,2] *M.M. Telo da Gama,*[1,2] *E. Del Gado,*[3] *N.A.M. Araújo*[1,2]

[1] *Centro de Física Teórica e Computacional, Faculdade de Ciências,*
Universidade de Lisboa, 1749-016 Lisboa, Portugal
[2] *Departamento de Física, Faculdade de Ciências,*
Universidade de Lisboa, 1749-016 Lisboa, Portugal
[3] *Department of Physics, Institute for Soft Matter Synthesis and Metrology,*
Georgetown University, Washington, D.C. 20057, USA
Email: csdias@fc.ul.pt

Identifying the necessary conditions for the onset of rigidity in a gel remains a challenge. It has been suggested that local particle coordination could be used to establish such conditions, but rigid gels occur for various coordination numbers. Combining simulations, oscillatory rheology, and a percolation analysis, for particles where the valence can be controlled, we find that the onset of rigidity coincides with the percolation of particles with three or more bonds, which arises after the connectivity percolation. We show that the rigidity results from an interplay of bonding and non-bonding interactions, providing insight into low-valence colloidal gel rigidity.[1]

Acknowledgements: We acknowledge financial support from the Portuguese Foundation for Science and Technology (FCT) under Contracts no. PTDC/FIS-MAC/28146/2017 (LISBOA-01-0145-FEDER-028146), PTDC/FIS-MAC/5689/2020, EXPL/FIS-MAC/0406/2021, CEECIND/00586/2017, UIDB/00618/2020, and UIDP/00618/2020. EDG acknowledges financial support from NSF DMR-2026842 and ACS Petroleum Fund. The authors also thank Minaspi Bantawa for support with the rheological tests.

References

1. C.S. Dias, J.C. Neves, M.M. da Gama, E. Del Gado, N.A.M. Araújo, *arXiv preprint arXiv:2307.13315*.

OC2.16 Open subsystem-based partition of molecular energies into resonance structure-resolved contributions

D.J.L. Rodrigues, E. Francisco, A.M. Pendás

Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, 33006-Oviedo, Spain
Email: diogojlrodrigues@gmail.com

A convenient route to updating the chemical bonding paradigm with a quantum mechanically rigorous treatment is considering molecular groups as Open Quantum Systems (OQSs),[1] which are interacting subsystems that are able to exchange particles and energy with their environment. This can be accomplished using real space molecular partitions, by resorting to Quantum Chemical Topology (QCT)[2] tools. The combination of both these ideas[3] has paved the way to new developments and interpretations in chemistry (ex: in [4]). One route for this combination is endowing the atoms of the Quantum Theory of Atoms in Molecules (QTAIM)[2] with a new fine-grained layer of OQS descriptors, based on electron sectors that possess an integer number of electrons.

On the other hand, the total energy of any molecular system (which can be obtained solely from the one- and two-particle components of the Hamiltonian and the one- and two-particle reduced density matrices (1- and 2-RDMs)), given a partition of space into chemically meaningful regions, can be exactly decomposed as a sum of intra and inter-atomic components. This is what the Interacting Quantum Atoms (IQA) partitioning provides, fed only the 1- and 2-RDMs written in the orbital basis. The OQS-QCT treatment can then be combined with the IQA approach to provide an even thinner energetic partition than that of current-state IQA, in which the intra and inter-atomic components of the energy are further partitioned into OQS sector atomic contributions, based on the sector compliant 1- and 2-RDMs. In this study we work towards achieving precisely that and define the OQS sector decomposition of the IQA energy components into real space resonance structures (which we call the resonance-structure resolved IQA (rsr-IQA)). This sector-energy partition is thereafter applied to simple academic examples, covering the standard types of bonds: ionic, covalent, polar-covalent, etc., with the goal to upgrade and redefine our understanding of the chemical bond. Furthermore, the rsr-IQA should provide an orbital invariant equivalent to Valence-Bond structures.

Acknowledgements: We thank the support of the Spanish MCIU (Ministerio de Ciencia, Inovación y Universidades), grant MCIU-22-PID2021-122763NB-I00. DJLR is financed by Fundação para a Ciência e Tecnologia (FCT), through PhD grant 2023.00844.BD.

References

1. H.-P. Breuer, F. Petruccione; The Theory of Open Quantum Systems. *Oxford University Pres*s, 2007.
2. P.L.A. Popelier; *Struct. Bond.* **2016**, *170*, 71-117.
3. M. A. Pendás, E. Francisco; *J. Chem. Theory Comput.* **2018**, *15*, 1079-1088.
4. M.A. Pendás, E. Francisco; *Phys. Chem. Chem. Phys.* **2021**, *23*, 8375-8392.

OC2.17 Computational venom whispering to decode molecular insights of bee and snake-secreted phospholipases A_2

J.R. da Silva, J. Castro-Amorim, M.J. Ramos, P.A. Fernandes

LAQV/Requimte, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, s/n, 4169-007 Porto, Portugal
Email: up201805310@fc.up.pt

Beyond its ubiquitous role in numerous biological processes, the secreted phospholipase A2 (sPLA2) plays a crucial role in envenoming. This enzyme is a prominent component across many animal venoms, contributing significantly to the manifestation of some of the most severe side effects associated with envenoming.

While the role of sPLA2 in envenomation is well-established, the mechanism underlying its action may vary among different venomous species. This study will focus on the bee and snake venom sPLA2 because, despite the notable differences in their tertiary structures, the enzymes present identical catalytic residues, thus indicating functional similarity despite evolutionary divergence.

To carry out this in-depth assessment, molecular docking calculations followed by molecular dynamics (MD) simulations were performed to compare the target specificity between the snake venom $sPLA_2$ ($SV\text{-}PLA_2$) and the bee venom $sPLA_2$ ($BV\text{-}PLA_2$).

Secondly, to understand both the quaternary structure and the behavior of these enzymes in solution, the structural stability was analysed through MD simulations, which were performed for 1 microsecond.

In a subsequent step, a $BV\text{-}PLA_2$:membrane system was built to study the interaction between the enzyme and a 50:50 POPC:POPS eukaryotic cellular membrane. Simultaneously, by having a POPC substrate bound to the active site of BV-PLA2, RMSD-clustering analysis allowed the selection of an MD conformation for Quantum Mechanics/Molecular Mechanics calculations, aiming to elucidate the catalytic mechanism of $BV\text{-}PLA_2$. Like in the initial assessments, these final steps were compared with the results of $SV\text{-}PLA_2$ enzyme.[1,2]

By providing detailed insights into the molecular interactions, structural dynamics, and catalytic mechanisms of $sPLA_2$ enzymes from both bee and snake venom, this work challenges the status quo of antidote development with newfound perspectives that could be implemented in more effective treatments for envenomation.

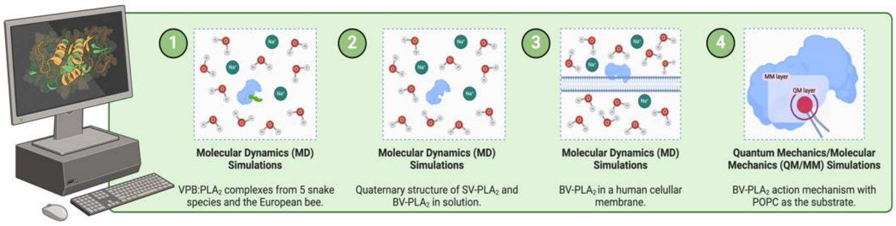


Fig. 1. Schematic representation of the research pipeline implemented in this study.

References

1. J. Castro-Amorim, et al.; *J. Med. Chem*. **2023**, *66*, 5364-5376.
2. A.L.N. de Oliveira, et al.; *Toxins* **2024**,*16*, 71.

OC2.18 Unveiling pesticide interactions: Insights from the *Aplysia californica* AChBP-imidacloprid complex

J.R.C. Santos, P.E. Abreu, J.M.C. Marques

CQC-IMS, Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal
Email: joanarcs95@gmail.com

Pesticides have been designed to control pests or regulate plant growth, nonetheless, their widespread use has led to serious environmental problems, in particular water pollution. A comprehensive understanding of the physicochemical properties of pesticides and the elucidation of their interactions with target proteins in living organisms is crucial for the design of new materials for pesticides remediation from water.[1] Imidacloprid (IMI), a neonicotinoid insecticide, stands out as one of the predominantly utilized pesticides, leading to its prevalent occurrence in high concentrations within aquatic environments. Previous research have reported the IMI mode of action as an insecticide, which entails its binding to the nicotinic acetylcholine receptor (nAChRs) present in various insect species. This interaction disrupts the transmission of stimuli within the insect nervous system.[2] *Aplysia californica* acetylcholine-binding protein (Ac-AchBP), due to chemical and pharmacological similarities, has been used as a surrogate structure to model the interaction between neonicotinoids and the extracellular ligand-binding domain of the nAChRs.[3]

In this work, we explore the interaction of the IMI with the Ac-AchBP in water by employing molecular docking, electronic structure calculations, classical molecular dynamics simulations, and molecular mechanics/Poisson−Boltzmann (Generalized-Born) surface area (MM/PB(GB)SA) method for the calculation of the binding free energies of the complexes.[4] To characterize the IMI-protein interactions during the molecular dynamics simulations, several properties were calculated, such as root mean square deviation, number of hydrogen bonds, ligand interaction network with the protein, distances between atoms or molecules, interaction energies, and visual inspection of the trajectories. The results allowed the detection of several interaction sites and the identification of key amino acids directly involved in the binding such as Ile118/Tyr188 and their respective energetic contribution. The important role of water molecules in the stabilization of the binding pocket was also evaluated.

Acknowledgements: We thank the support from the Coimbra Chemistry Centre (CQC-IMS), 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. FCT is also gratefully acknowledged for a PhD grant to J.R.C. Santos – 2022.12451.BD. This publication is also based upon work of COST Action CA21101 "Confined molecular systems: from a new generation of materials to the stars" (COSY) supported by COST (European Cooperation in Science and Technology).

References

1. I.A. Saleh, N. Zouari, M.A. Al-Ghouti; *Environ. Technol. Innov.* **2020**, *19*, 101026.
2. B. Selvam, J. Graton, A.D. Laurent, Z. Alamiddine, M. Mathé-Allainmat, J. Lebreton, O. Coqueret, C. Olivier, S.H. Thany, J.-Y. Le Questel; *J. Mol. Graphics Model.*, **2015**, *55*, 1.
3. B. Lin, H. Meng, H. Bing, D. Zhangsun, S. Luo; *Biomed Res. Int*., **2014**, 691480.
4. R.P.D. Bank, https://www.rcsb.org/structure/3C79 (accessed June 2023).

OC2.19 HO_2* stabilization in the presence of argon

C. Mogo, J. Brandão, W. Wang, D. Coelho, C. Rio

CEOT, Universidade do Algarve, Portugal
Email: cfmogo@ualg.pt

Our dynamic molecular simulations, coupled with accurate potential energy surfaces, have proven to be a powerful approach for gaining detailed insights into complex reaction mechanisms. Recently, we presented detailed results of the collisional stabilization of the HO_2 complex in a mixture of hydrogen atoms and oxygen molecules.[1,2] We pointed out in great detail the results of the temperature and pressure dependencies of this process and the role of each collider, providing specific rate constants and their temperature dependence. Now, we include Argon in the system and close the gap to experimental conditions.

The cage effect enables a significant increase of 5 to 10% in complex formations. Still, Argon's main contribution is allowing more H and O_2 encounters, potentiating more complex formations.

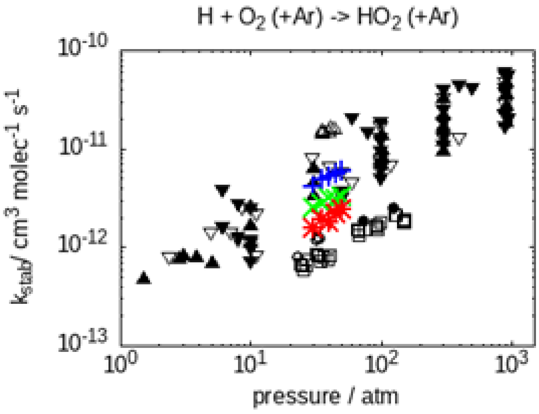


Fig. 1. H + O_2 (+ M) →HO_2 (+ M) stabilization and comparison with experimental data. This work: 1500 K (+), 2000 K (x) and 2500 K (*); Bates et al. using: Ar (1019–1264 K) (□), N_2 (1119–1222 K) (◦) and H_2O (1082–1262 K) (▵); Getzinger and Blair using Ar (1300–1600 K)(■); Davidson et al. using Ar (1325) (•) and Fernandes et al.: using He (300–700 K) (▴), Ar (300–700 K) (▿) and N_2 (300–900 K) (▾).

Acknowledgements: This document results from the research started in the PTDC/QUI-QUI/100089/2008 project, funded by the Fundação para a Ciência e a Tecnologia.

References

1. C. Mogo, J. Brandão, W. Wang, D. Coelho, C. Rio; *Comput. Theor. Chem.* **2023**, *1224*, 114123.
2. C. Mogo, J. Brandão, W. Wang, D. Coelho, C. Rio; *Comput. Theor. Chem*. **2022**, *1209*, 113614.

OC2.20 Beyond DFT: Tackling the strong correlation problem in noble gas chemistry.

N.A.G. Bandeira,[1] S. Oliveira,[2] L. Maria,[2] B.Monteiro,[2] J.M. Carretas,[2] J.P. Leal,[2] J. Marçalo[2]

[1] BioISI, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal.
[2] Centro de Química Estrutural, Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa, Estrada Nacional 10, 2695-066 Bobadela LRS, Portugal.
Email: nuno.bandeira@ciencias.ulisboa.pt

The chemistry of noble gases still affords great opportunities for exploration[1,2] particularly from a fundamental perspective. In this communication the reactivity of Xe^+ cations will be studied computationally to account for the experimental evidence (mass spectrometry) of the following transformations (with X=N,O):

$$Xe^+(g) + X_2O(g) \rightarrow XeO^+(g) + X_2(g) \qquad (1)$$

The reaction mechanism will be analysed through a state specific CASPT2 approach for geometries and multi-reference coupled cluster MR-CCSD for the final energies. The results explain why the N_2O reaction does not proceed whereas the one with O_3 does.

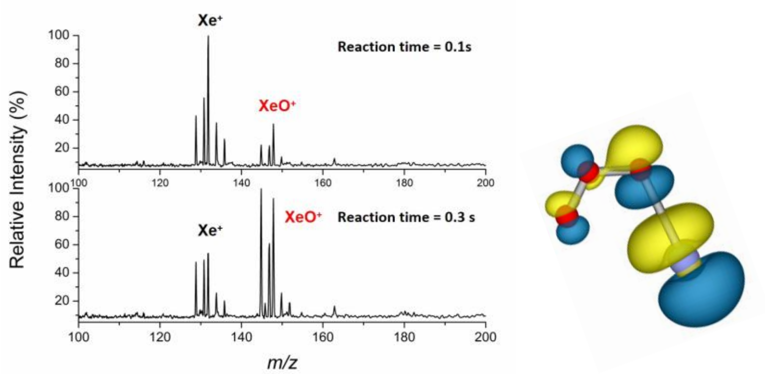


Fig. 1. Mass spectrometry cationic peaks after O_3 addition to Xe^+(left) and SOMO of the adduct intermediate XeO_3^+.

Acknowledgements: The authors thank FCT for funding through grants PTDC/QUI-QFI/31896/2017, doi:10.54499/UIDB/04046/2020 (BioISI) and doi:10.54499/UIDB/00100/2020 (CQE).

References

1. F. Grandinetti; *Noble Gas Chemistry: Structure, Bonding, and Gas-Phase Chemistry*; 1st ed. Wiley, Weinheim, Germany, 2018.
2. N.A.G. Bandeira, J. Marçalo; *Phys. Chem. Chem. Phys.* **2023**, *25*, 14084-14088.

OC2.21 Investigation of the IVR isomerization of nitrous acid

L. J. Duarte,[1, 2] *C. M. Nunes,*[2] *R. Fausto,*[2] *A.A.C. Braga*[1]

[1] *Institute of Chemistry, University of São Paulo, Av. Prof. Lineu Prestes, 748 -Butantã, 05508-900, São Paulo, Brazil*

[2] *Department of Chemistry, University of Coimbra, P-3049 Coimbra, Portugal*

Email: ljduarte@iq.usp.br

The isomerization of Nitrous Acid (HONO) in noble gas cryogenic matrix (around 20K) is the first observed case of an infrared photochemical reaction where the excitation of the O-H or the N=O stretch normal coordinate triggers a conformational change from the *cis* to the *trans* isomer. Experimental observation suggests that the radiation energy, captured by the normal mode of a functional group (acting as an antenna), is redistributed into a highly excited vibrational level of the torsion normal coordinate, which is also the isomerization reaction coordinate. Such level is delocalized between the *cis* and *trans* minimum points on the double well potential energy surface, thus allowing for the system to decay to a lower energy vibrational level of either isomer.[1]

To investigate such mechanism, we present simple numerical methods to qualitatively investigate the coupling between the normal coordinates and the possible gateways for vibrational energy redistribution leading to the isomerization process. Our methodology involves the generation of the 2D Potential Energy Surface (PES) at the B3LYP/aug-cc-pVTZ level of theory by spanning the reaction coordinate and one of the five projected normal coordinates along the IRC. Once the PES has been obtained, the time-independent wavefunctions are obtained using the standard Discrete Variable Representation (DVR) approach. The vibrational eigenspace obtained with such an approach provides a good description of the system, reproducing the experimental infrared intensities and frequencies.

The reaction barrier was investigated using the Interacting Quantum Atoms (IQA) decomposition scheme, evidencing an important contribution from exchange-correlation energy to the isomerization. The energy contribution for the barrier is localized in the central N-O bond and is not correlated with any internal coordinate of the antenna normal modes.

Thermally activated tunneling rates are calculated using the vibrational eigenstate of the torsion normal mode. Considering the low temperature of the matrix, tunneling processes are negligible and the reaction can only proceed by the vibrational energy captured by the antenna.

Results from the IQA analysis suggests that the shape of PES is more important than its energetic origins when selecting the possible functional groups that will capture and redistribute the vibrational energy, at the same time coupling between normal coordinates indicates preferential normal modes to redistribute the vibrational energy. The main factor behind the IVR isomerization mechanism is the existence of delocalized IRC eigenstates, which acts as gateways allowing transitions between normal modes of the *cis* and *trans* isomers.

Acknowledgments: L.J.D. (grant #2022/09269-1) and A.A.C.B. (grant#2015/01491-3) are grateful to the São Paulo Research Foundation (FAPESP) for financial support. C.M.N and R.F acknowledge the Project PTDC/QUI-QFI/1880/2020, funded by National Funds via the Portuguese Foundation for Science and Technology (FCT). The Coimbra Chemistry Centre – Institute of Molecular Sciences (CQC-IMS) is supported by FCT through projects UIDB/00313/2020 and UIDP/00313/2020 co-funded by COMPETE and the IMS special complementary funds provided by FCT.

References

1. R.T. Hall, G.C. Pimentel; *J. Chem. Phys* **1963**, *38*, 1889–1897.

Poster Communications

P1 Spice volatilomic pattern – A suitable approach to explore their antioxidant and anti-inflammatory properties

N. Hontman,[1] J. Gonçalves,[1] A. Soares,[1] J.S. Câmara,[1,2] R. Perestrelo[1]

[1] CQM – Centro de Química da Madeira, Universidade da Madeira, Campus da Penteada, 9020-105, Funchal, Portugal
[2] Departamento de Química, Faculdade de Ciências Exatas e Engenharia, Universidade da Madeira, Campus da Penteada, 9020-105, Funchal, Portugal
Email: rmp@staff.uma.pt

Spices have been used throughout the world for a variety of purposes across the world since ancient times. From natural flavouring and preservatives in beverages, pharmaceuticals, and foods, to ingredients in cosmetics and perfumes, to their use as preventive agents with potential benefits for human health.[1] Their composition contains natural phytochemicals including volatile organic metabolites (VOMs), polyphenols, and vitamins, among others. Several studies have reported the bioactive properties of these natural phytochemicals, namely antioxidant, antimicrobial, anti-inflammatory, antidepressant, anticancer, cardioprotective and neuroprotective effects, which help to explain the effects of spices and other rich foods.

This study aimed to establish the volatilomic pattern of six spices using solid phase microextraction combined with gas chromatography-mass spectrometry (HS-SPME/GC-MS), as well as explore their antioxidant activities (ABTS, DPPH, ORAC) and inhibition of protein denaturation by *in vitro* methods. A total of 85 VOMs were identified. Semi-quantitative assessments revealed that monoterpenoids and sesquiterpenoids amounted to the major chemical families in the investigated spices. Most of the studied spices comprised key health bioactive compounds, e.g., α-phellandrene (24.3 % of total volatile fraction) in curcumin, myristicin (20.4 %) in nutmeg, cuminaldehyde (81.8 %) in cumin, 3-carene (30.3%) in black pepper, (*Z*)-methyl isoeugenol (51.3 %) in Jamaica pepper and β-myrcene (32.1 %) in Juniper berry. In addition, the *in vitro* assays demonstrated that Jamaica pepper, cumin and Juniper berry had the highest DPPH, ABTS, ORAC antioxidant activities. The results demonstrated the potentiality of these spices to act as antioxidant and anti-inflammatory agents.

Acknowledgements: This research was funded by FCT- Fundação para a Ciência e a Tecnologia through the CQM Base Fund - UIDB/00674/2020, and Programmatic Fund - UIDP/00674/2020, by Interreg MAC 2014–2020 Cooperación territorial through AD4MAC project (MAC2/1.1b/350), and by ARDITI-Agência Regional para o Desenvolvimento da Investigação Tecnologia e Inovação, through the project M1420-01-0145- FEDER-000005 - Centro de Química da Madeira - CQM$^+$ (Madeira 14–20 Program). The authors also acknowledge FCT and Madeira 14–2020 program to the Portuguese Mass Spectrometry Network (RNEM) through PROEQUIPRAM program, M14-20 M1420-01-0145- FEDER-000008).

References

1. S. Izcara, R. Perestrelo, S. Morante-Zarcero, I. Sierra, J. S Câmara; *Molecules* **2022**, *27*, 6403.

P2 Enhancing potato starch beads for effective sorption of toxic metals: the role of crosslinking degree

T.B. Costa,[1,2] *P.M.C. Matias,*[1] *D.S. Rosa,*[2] *D.M.B. Murtinho,*[1] *A.J.M. Valente*[1]

[1] *Coimbra Chemistry Centre, Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal*

[2] *Center for Engineering, Modeling and Applied Social Sciences, Federal University of ABC, 09280-560, Santo André, SP, Brazil*

Email: joanacl@fe.up.pt

Potentially toxic elements (PTEs) are widely used in various industrial activities and are frequently found in effluents. The presence of these elements in water resources is related to risks to the environment and human health. The use of three-dimensional porous systems, such as hydrogels/aerogels, is an alternative for the removal these contaminants from water.[1] In this study, we investigated the effect of the degree of crosslinking on the development of potato starch-based hydrogels/aerogels beads and their performance in the removal of PTEs. The experimental conditions for the synthesis of hydrogels/aerogel beads are presented in Fig. 1. The covalent crosslinking of the hydrogels/aerogels beads was carried out by monitoring the intensity of the carbonyl peak around 1725 cm^{-1}, which is characteristic of the ester moiety, identifying the occurrence of esterification. The results showed that increasing the citric acid content up to 15 g/L promoted the appearance of a new band at 1725 cm^{-1} (—C═O), which was not observed in the spectra of the other formulations. In fact, there was an increase in the degree of substitution (DS) ranging from 2.656 to 2.879 mmol/g (hydrogel beads) and 2.844 to 3.214 mmol/g (aerogel beads), with increasing citric acid concentration (6 to 15 g/ L). A decrease in the bead's solubility between 25.48-1.89% (hydrogel beads) and 36.9-5.15% (aerogel beads) was also observed, indicating that the increase in citric acid content promoted greater interaction between the polymer chains during crosslinking. The hydrogel/aerogel beads with higher citric acid content presented a higher potential for PTEs sorption with the following affinity order: Pb^{2+} (0.528 ± 0.005 mmol/g) > Cu^{2+} (0.315 ± 0.026 mmol/g) > Cd^{2+} (0.184 ± 0.007 mmol/g) > Ni^{2+} (0.086 ± 0.008 mmol/g) > $HCrO_4^-$ (0.014 ± 0.001 mmol/g) (hydrogel beads) and Pb^{2+} (0.555 ± 0.008 mmol/g) > Cu^{2+} (0.335 ± 0.030 mmol/g) > Cd^{2+} (0.175 ± 0.003 mmol/g) > Ni^{2+} (0.049 ± 0.012 mmol/g) > $HCrO_4^-$ (0.011 ± 0.001 mmol/g) (aerogel beads). Thus, potato starch-based materials can be promising for the removal of PTEs from contaminated water flows.

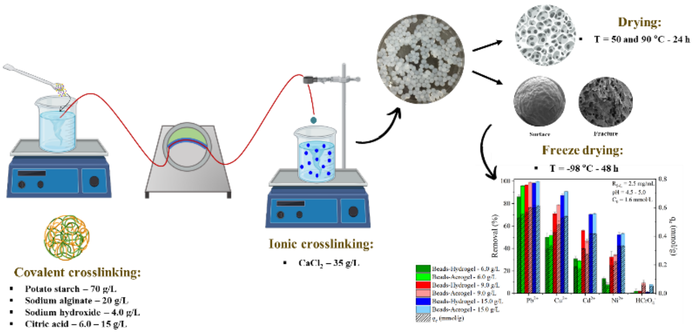


Fig.1. Synthesis of hydrogel/aerogel beads based on potato starch and potential for removing PTEs.

Acknowledgements: The work was funded by the Coimbra Chemistry Centre, which is supported by the Fundação para a Ciência e a Tecnologia (FCT, Portugal), through the program UID/QUI/00313/2020. Talles B. Costa thanks Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, Brazil) for the grants #2022/11133-0 and #2023/11783-8, and Pedro M. C. Matias acknowledges FCT, Portugal for the PhD Grant 2022.12425.BD.

References

1. T. B. da Costa, T. L. da Silva, M. G. C. da Silva, M. G. A. Vieira; *J. Environ. Chem. Eng.,* **2023**, *11*, 109222.

P3 Fluorescence/phosphorescence imaging lifetime microscopy study on a ratiometric Pt(II)-chlorin oxygen sensor

T. Costa,[1] *M. Pineiro,*[1] *M. Laranjo,*[2-4] *B. Serambeque,*[2] *M.F. Botelho,*[2-4] *N.A M. Pereira,*[1]
A.J.S. Alves,[1] *T.M.V. D. Pinho e Melo,*[1] *J.S. Seixas de Melo*[1]

[1] *University of Coimbra, CQC-IMS, Department of Chemistry, Coimbra P-3004-535, Portugal.*
[2] *University Coimbra, iCBR -CIMAGO, Institute of Biophysics, Faculty of Medicine, Coimbra, 3000-548, Portugal.*
[3] *University Coimbra, CIBB, Coimbra, 3004-504, Portugal*
[4] *Clinical Academic Center of Coimbra (CACC), Coimbra, 3004-561, Portugal*
Email: tcosta@qui.uc.pt

A platinum(II) 4,5,6,7-tetrahydropyrazolo[1,5-a]-pyridine-fused chlorin derivative, Pt(II)-chlorin, has been recognized as a promising ratiometric oxygen sensor in chemical and biological media.[1] At room temperature, Pt(II)-chlorin exhibits simultaneous fluorescence and phosphorescence emissions.[1]

In this study, we investigate the effect of aggregation on the photophysical properties of Pt(II)-chlorin and its sensitivity to oxygen. The investigation was carried out in different environments, including different solvent mixtures, polymer thin films and in vitro (using human melanoma A375 cells), using fluorescence/phosphorescence lifetime imaging microscopy (FLIM/PLIM). Our findings revealed significant insights of the interplay between the presence of oxygen, photoluminescence properties and aggregation. It was shown that although the presence of oxygen does not have a significant influence on fluorescence, aggregation-induced quenching has a pronounced effect. In addition, both dissolved oxygen and aggregation significantly quench phosphorescence. In cellular environments, phosphorescence decay times correlate with oxygen levels, while fluorescence decay times provide insight into the occurrence of Pt(II) chlorin aggregation. Moreover, we highlight the reversible nature of aggregation in aqueous solutions upon cellular uptake. This phenomenon significantly affects the sensitivity of the phosphorescence lifetime to oxygen concentration and the generation of reactive oxygen species (ROS), ultimately affecting the efficacy of photodynamic therapy (PDT).

Acknowledgements: CQC was supported by the Portuguese Agency for Scientific Research, "Fundação para a Ciência e Tecnologia" (FCT) through project UIDB/00313/2020, cofounded by COMPETE2020-UC. CIBB was funded by FCT Strategic Projects UID/NEU/04539/2019, UIDB/04539/2020, and UIDP/04539/2020. This work was part of the project CENTRO-45-2021-30 - SAICT - 01/SAICT/2021 - Projetos de Prova de Conceito (PdC); Project nº 180078. The authors acknowledge the UC-NMR facility (www.nmrccc.uc.pt) and the support of Teresa Ribeiro-Rodrigues at iLAB. iLAB is supported by POCI-01-0145-FEDER-022122. BS acknowledges the PhD Scholarship from FCT (2020.07672.BD).

References

1. N.A.M. Pereira, M. Laranjo, J. Casalta-Lopes, A.C. Serra, M. Piñeiro, J. Pina, J. S. Seixas de Melo, M.O. Senge, M.F. Botelho, L. Martelo, H.D. Burrows, T.M.V.D. Pinho e Melo; *ACS Med. Chem. Lett.* **2017**, *8*, 310-315.

P4 Structural, vibrational and photochemical data of simple hydantoins – common features and substituents effects

G. O. Ildiz,[1,2] *B.A. Nogueira,*[2,3] *R. Fausto*[1,2]

[1] *CQC-IMS, Department of Chemistry, University of Coimbra, Portugal*
[2] *Department of Physics, Faculty of Sciences and Letters, Istanbul Kultur University (IKU), Turkey*
[3] *International Iberian Nanotechnology Laboratory (INL), Braga, Portugal*
Email: assel.amine@gmail.com

Characteristic features of the structure (geometries, electronic structures), vibrational spectra (infrared) and photochemistry of a series of simple hydantoins (parent hydantoin, 1-methylhydantoin, 5-methylhydantoin, and 5-acetic acid hydantoin; Fig. 1), and effects of substituents on these properties, are described. It is shown that the hydantoin moiety shows a general trend to planarity (or quasi-planarity) that is mostly determined by the π-electron delocalization in the system, in which the two nitrogen atoms participate extensively and, in the studied molecules, also counts with the involvement of the π-type orbitals of the -C_5H_2- or -C_5HR- (with R= CH_3 or CH_2COOH, respectively in 5-methylhydantoin, and 5-acetic acid hydantoin, respectively) fragment (hyperconjugation). The geometries and charge density analyses of the compounds also reveal that the main electronic effects in the hydantoin ring are the N-to-(C=O) π electron donation, and the σ system back-donation from the σ lone electron pairs of the oxygen atoms to the ring. The frequencies of the bands observed in the matrix-isolation infrared spectra (Ar; 10 K) of the different compounds that are assigned to the carbonyl and amine fragments are discussed in a comparative way, and substituent effects assessed. Finally, the UV-induced (λ = 320 nm) photochemistry of the hydantoins is shown to share a common pattern, leading to the concerted extrusion of isocyanic acid and carbon monoxide, accompanied by an imine derivative that depends upon the specific hydantoin reactant. An additional photofragmentation pathway, most probably involving nitrene intermediacy, takes also place for 1-methylhydantoin, indicating a specific effect of the substitution at position 1 of the hydantoin ring on the photofragmentation of hydantoins.

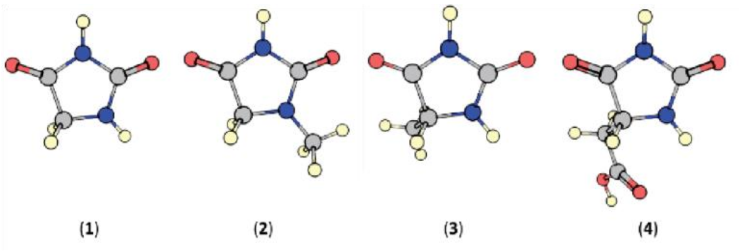


Fig. 1. DFT(B3LYP)/6-311++G(d,p) optimized structures of hydantoin, 1-methylhydantoin, 5-methylhydantoin and the most stable conformer of 5-acetic acid hydantoin.

Acknowledgements: This work has run within the research project PTDC/QUI-QFI/1880/2020. The CQC-IMS is supported by the Fundação para a Ciência e a Tecnologia (FCT), through projects 10.54499/UIDB/00313/2020), 10.54499/UIDP/00313/2020 and LA/P/0056/2020. The authors also acknowledge the Laboratory for Advanced Computing at University of Coimbra (https://www.uc.pt/lca), for providing computing resources, and LaserLab Coimbra for experimental facilities.

P5 Are Kamlet-Taft parameters sufficient to model the solution enthalpies of different APIs?

M. Chorão,[1,2] *N. Nunes,*[1,3] *R. Elvas-Leitão,*[1,3] *F. Martins*[1,2]

[1] *Centro de Química Estrutural – Institute of Molecular Sciences, Universidade de Lisboa, Portugal*
[2] *Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Portugal*
[3] *Departamento de Engenharia Química, Instituto Superior de Engenharia de Lisboa, IPL, Portugal*
Email: fc58479@alunos.fc.ul.pt

An active pharmaceutical ingredient (API) is the biologically active component of a given drug, responsible for producing a desired therapeutic effect. Elucidating the behavior of an API in different solvents can be crucial to develop strategies to enhance its solubility, a critical factor for the pharmaceutical industry.[1] One such methodology involves the study of interactions between solute and solvent, which can be achieved through the determination of solution enthalpies.

In this work, we studied four well-established APIs: acetylsalicylic acid and ibuprofen, two non-steroidal anti-inflammatory drugs; acetaminophen, a widely used analgesic and antipyretic drug; and salicylic acid, commonly employed in the cosmetic industry.

The solution enthalpies of the above APIs were measured at 298.15 K and infinite dilution, in a diverse set of 19 hydroxylic and non-hydroxylic solvents using a Thermometric precision solution calorimeter. Solvent effects were reasoned on the basis of quantitative-structure property relationships (QSPR) using different solvent descriptors, namely the Kamlet-Taft solvatochromic parameters α, β and π^*, that describe the solutes' acidity, basicity and dipolarity/polarizability, respectively.[2] The effect of an additional cavity parameter, a term that measures the energy involved in the creation of a cavity in the solvent to accommodate the solute, was also considered. The pros and cons of using a QSPR approach were critically evaluated.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by FCT through projects UIDB/00100/2020 (https://doi.org/10.54499/UIDB/00100/2020) and UIDP/00100/2020 (https://doi.org/10.54499/UIDP/00100/2020). Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020 (https://doi.org/10.54499/LA/P/0056/2020).

References

1. S. Nusim (ed.) *Active Pharmaceutical Ingredients*; 2nd Ed., CRC Press : New York, 2016.
2. M. Reis, N. Nunes, R. E. Leitão, F. Martins; *Thermochim. Acta* **2015**, *604*, 140-144.

P6 Revolutionizing stroke diagnosis with silver nanostars and SERS analysis

C. Freitas,[1] *M. Enea,*[2] *R.L. Carvalho,*[1] *M. Ozório,*[3] *H. Águas,*[3] *E. Pereira,*[2] *H.L.A. Vieira,*[1] *R. Franco*[1]

[1] *Associate Laboratory i4HB—Institute for Health and Bioeconomy, and UCIBIO - Applied Molecular Biosciences Unit, Depart. Chemistry, NOVA FCT, 2819-516 Caparica, Portugal.*
[2] *LAQV /REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, 4169-007, Portugal.*
[3] *CENIMAT-i3N, Departamento de Ciência dos Materiais, NOVA FCT, and CEMOP/UNINOVA, 2829-516 Caparica, Portugal.*
Email: cmt.freitas@campus.fct.unl.pt

Stroke is a major medical issue affecting cerebral vessels and disrupting blood circulation, affecting around 12 million individuals annually.[1] Accurate Stroke diagnosis is crucial for therapeutic choice, early interventions, and the success of patient recovery. Surface-Enhanced Raman Spectroscopy (SERS) is a potential approach for precise stroke diagnosis, using silver nanostars (AgNS) to create intense Raman signals from analytes adsorbed at 'hotspots'.[2] This study aims to develop a point-of-care test (PoCT) for stroke diagnosis employing a SERS-based method to analyze plasma samples. This is achieved by mixing plasma samples with a AgNS colloid, formation of bioconjugates that are applied to innovative plasmonic paper substrates, and analysis of the unique sample fingerprints by SERS (Fig. 1). Principal Component Analysis (PCA) was used to compare SERS spectral features and obtain meaningful information for Stroke diagnosis. In conclusion, SERS utilizing AgNS and PCA analysis is a valuable technique for rapidly identifying and discriminating plasma samples, particularly suitable for PoCT applications due to the simplicity of AgNS synthesis and potential for handheld Raman spectrometers.[3] PoCT can be used with machine learning (ML) techniques for Stroke diagnosis, improving patient outcome by enabling early and tailored treatment.

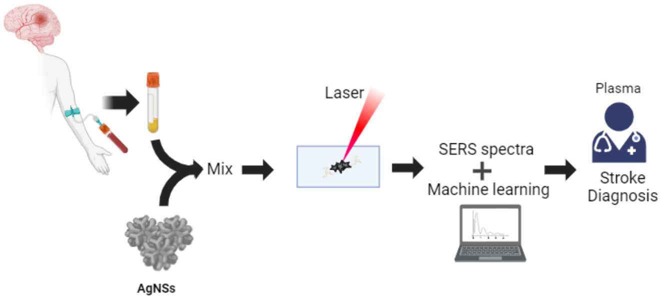


Fig. 1. Stroke diagnosis using SERS detection and machine learning for data analysis.

Acknowledgements: Prof. Marco Silva and MSc. Flavia Freitas from LAQV/REQUIMTE (Caparica, Portugal), are acknowledged for their assistance on using PCA software. Funds by FCT, I.P. in the scope of Projects UIDP/04378/2020 and UIDB/04378/2020 of UCIBIO; LA/P/0140/2020 of i4HB; UIDB/50006/2020 and UIDP/50006/2020 of LAQV; and LA/P/0037/2020, UIDP/50025/2020 and UIDB/50025/2020 of i3N. M.E. acknowledges LAQV for her Post-Doc grant ref. REQUIMTE 2022-06.

References

1. R.G. Kowalski, *et al.; Stroke* **2023,** *54*, E52–E57.
2. M.P. de Almeida, *et al*.; *Front. Chem.* **2019**, *7*. doi:10.3389/fchem.2019.00368.
3. M.P. de Almeida, *et al*.; *Biosensors (Basel)* **2023**, *13.* doi:10.3390/bios13020149.

P7 Partition of isoniazid derivatives active against tuberculosis to membrane mimetic systems: Octanol-water (log $P_{oct/w}$) *vs.* micelle-water (log K_p)

M. Reis[1,3], *T. Luan*[2], *V. Leandro*[2], *M. Mendes*[2], *F. Martins*[1,2], *M.S.C.S. Santos*[1,2]

[1] *Centro de Química e Estrutural (CQE), Institute of Molecular Sciences (IMS) Campo Grande, 1749-016 Lisboa, Portugal*
[2] *Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa (DQB-FCUL), Ed.C8, Campo Grande, 1749-016 Lisboa, Portugal*
[3] *Instituto Superior de Educação e Ciências (ISEC Lisboa), Alameda das Linhas de Torres, 179, 1750-142 Lisboa, Portugal*
Email: marina.reis@iseclisboa.pt

Tuberculosis (TB) is a worldwide infectious disease, that despite the 2035 eradication goal established by WHO, has not seen major advances. The increasing number of multi-drug resistant strains (MDR) of *Mycobacterium tuberculosis* (*Mtb*), and the absence of efficient therapeutic regimes account for the perpetuation of high mortality levels.[1] The clinical efficacy of isoniazid (INH) against *Mtb* was thoroughly demonstrated in the second half of last century. INH is a pro-drug that upon activation by *Mtb* catalase-peroxidase enzyme *KatG* leads to mycolic acids biosynthesis inhibition and cell lysis. Notwithstanding the efficacy-toxicity balance of INH, a strong *Mtb* resistance to this 1st-line drug has emerged through the years. This downside led to the development of quantitative structure−activity relationships (QSARs), based on INH core structure, and afforded the synthesis and evaluation of some potentially active INH derivatives.[2]

Being generally accepted that pharmacological processes involve penetration, binding, and activation steps, the interaction of new drug-like candidates with membranes, the first barrier, may determine their *in vivo* activity. Thus, the lipophilicity evaluations is an extremely useful parameter in a preliminary screening of potential new drugs. Lipophilicity, conventionally expressed in the pharmaceutical industry in terms of the octanol-water partition coefficient ($P_{oct/w}$), was also evaluated in terms of partition coefficients (K_p) toward membrane mimetic systems to identify eventual specific interactions or anisotropy effects of lipid membrane bilayers on drugs' partition. Several authors have correlated log $K_{p(NaDS/w)}$ (sodium dodecyl sulfate micelles/water) to log $P_{oct/w}$ data for various solutes.[3,4] In this study, 7 isoniazid derivatives, active against *Mtb*, evidenced a linear dependence between these two parameters, supporting a diffusion driven partition process, mainly determined by hydrophobic interactions, for all hydrazides.

Acknowledgements: The authors acknowledge financial support of Fundação para a Ciência e a Tecnologia, (FCT) in projects PTDC/MED-QUI/29036/2017, UIDB/00100/2020, UIDP/00100/ 2020, LA/P/0056/2020.

References

1. World Health Organization, *Global tuberculosis Report 2023* (https://www.who.int/teams/global-tuberculosis-programme/tb-reports/global-tuberculosis-report-2023).
2. F. Martins, S. Santos, C. Ventura, et al.; *Eur. J. Med. Chem.*, **2014**, *81*, 119-138.
3. C. Treiner and M.H. Mannebach; *J. Colloid Interface Sci.*, **1987**, *115*, 243-251.
4. M.S.C.S. Santos, A.M. Matos, M. Reis, F. Martins; *Colloids Surf. A: Physicochem. Eng. Asp.*, **2020**, *599*, 124820.

P8 Temperature increase in activated T-cells detected by quantum dots 655

M.F. Antunes,[1] R.M. Almeida,[1] H. Soares,[1,2] C.E.S. Bernardes,[1] M.E. Minas da Piedade,[1] F. Antunes[1]

[1] *Centro de Química Estrutural, Institute of Molecular Sciences, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal.*

[2] *Escola Superior de Tecnologia da Saúde de Lisboa, Instituto Politécnico de Lisboa*

Email: fc55119@alunos.fc.ul.pt

Quantum dots (QDs) are semiconductor nanocrystals, which can be excited with a light source and subsequently undergo fluorescence decay. They are being used to detect temperature changes in neuronal and fibroblast cells, based on temperature dependent shifts observed in the fluorescence spectra.[1,2] In this work we investigated if the fluorescence from QDs 655 could be used to detect temperature changes associated with T-cell activation. QDs 655 were incorporated in activated and non-activated T-cells (Fig. 1A) and, after excitation with a 450 nm laser, fluorescence spectra were recorded in the wavelength range 590-730 nm, at 37 ºC. To determine if there was a shift between the QDs spectrums of activated and non-activated T-cells, a fluorescence intensity (FI) ratio was calculated by dividing the integrated fluorescence intensity values in the 656-676 nm range by those in the 636-656 nm range. Previous calibrations carried out in the absence of cells showed that an increase in temperature leads to a red shift in the QDs 655 spectrum, which results in an increase in FI ratio. The results obtained with the cell samples kept at 37ºC, showed that the FI ratio increases after T-cell activation, thus suggesting that activation is probably accompanied by an increase in cell temperature (Fig. 1B).

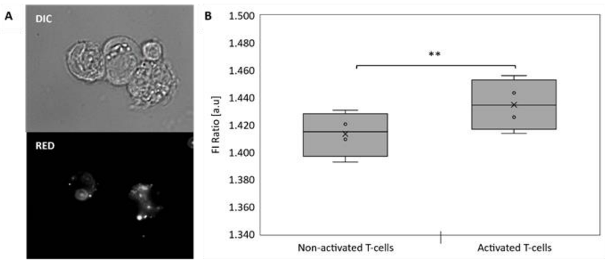


Fig. 1. (A) Fluorescence microscopy images of cells containing QDs 655. (B) Fluorescence intensity ratio obtained for samples with activated (*n*=4) and non-activated (*n*=4) T-cells. **p-value <0.05.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by FCT through projects UIDB/00100/2020 (https://doi.org/10.54499/UIDB/00100/2020) and UIDP/00100/2020 (https://doi.org/ 10.54499/UIDP/00100/2020). Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020 (https://doi.org/10.54499/LA/P/ 0056/2020). This work was further supported by the FCT project 2022.06098.PTDC (http://doi.org/10.54499/2022.06098.PTDC), and a PhD. grant awarded by FCT to Marisa Antunes (UI/BD/154824/2023).

References

1. T. Nakamura, J. Sakamoto, K. Okabe, A. Taniguchi, T. G. Yamada, S. Nonaka, Y. Kamei, A. Funahashi, M. Tominaga, N. F. Hiroi; *Opt. Continuum* **2022**, *1*, 1085-1097.
2. R. Tanimoto, T. Hiraiwa, Y. Nakai, Y. Shindo, K. Oka, N. Hiroi, A. Funahashi; *Sci. Rep.* **2016**, *6*, 22071.

P9

Hierarchical Pt/Y zeolite prepared through surfactant mediated technology: the effect of ionic strength

B. Matos,[1,2] N. Nunes,[2,3] A. Martins,[2,3] J. Coelho,[3,4] M.S. Santos,[1,2] A.P. Carvalho[1,2]

[1] *Departamento de Química e Bioquímica, FC, ULisboa, Lisbon, Portugal*
[2] *CQE, Institute of Molecular Chemistry, Fac. Ciências ULisboa, Lisbon, Portugal*
[3] *DEQ, Instituto Superior de Engenharia de Lisboa, IPL, Lisbon, Portugal*
[4] *CQE, Institute of Molecular Chemistry, IST, ULisboa, Lisbon, Portugal*
Email: fc54692@alunos.ciencias.ulisboa.pt

Zeolites are crystalline aluminosilicates with a wide range of applications as catalysts or adsorbents. However, as they are microporous their use in the presence of large molecules is hindered by diffusional limitations. Surfactant mediated technology comprises an alkaline treatment assisted by a surfactant, followed by a thermal treatment under autogenous pressure. This procedure allows the development of ordered mesopores with sizes, tuned by the type and size of the surfactant used as template. In this work, Y zeolite (Zeolyst Si/Al=5.4) was submitted to an alkaline treatment with a 0.37 M NaOH solution in the presence of CTAB (0.7 g CTAB / 1 g zeolite) and, the ionic strength adjusted adding variable amounts of NaBr (0.1-0.7 wt.%). The zeolite suspensions were kept under autogenous pressure at 150 °C for 6 h, dried and calcined at 550 °C. The metal loading was made using $Pt(NH_3)_4Cl_2{\cdot}xH_2O$ as metal precursor through incipient wetness impregnation (IWI) or by direct introduction of the Pt precursor on the zeolite suspension prior to the hydrotreatment. The materials were characterized by powder X-ray diffraction and low temperature N_2 adsorption isotherms. Fig. 1 presents the effect of ionic strength on the textural properties of the hierarchical zeolites. As can be observed, the presence of NaBr slightly shifts the mesopore distribution for lower ranges, especially for HYC6_0.23 sample, probably because of the ionic strength effect on the micellar aggregates' shape.[1] The catalytic behavior of Pt loaded samples will be evaluated in hydrodeoxygenation reaction using as reactants molecules with distinct sizes to probe the effect of the textural modifications.

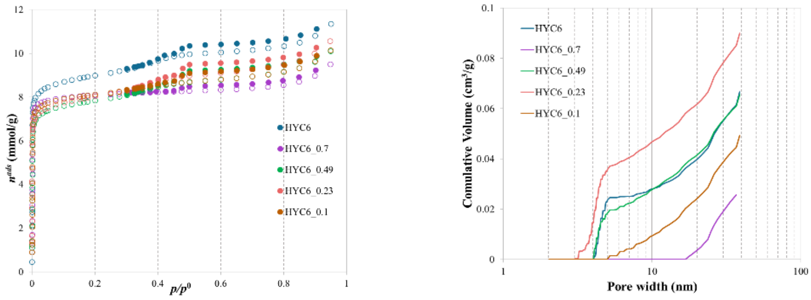


Fig. 1. N_2 adsorption isotherms (left) and mesopore size distribution (right) for parent and treated samples with NaOH + CTAB (C) + NaBr for 6 h.

Acknowledgements: This research was funded by FCT through UIDB/00100/2020, https://doi.org/10.54499/UIDB/00100/2020 UIDP/00100/2020 https://doi.org/10.54499/UIDP/00100/202 and LA/P/0056/2020 https://doi.org/10.54499/LA/P/0056/2020 and IPL through Project IPL/2023/Zeo@BioRef ISEL

References

1.T. Imae, R Kamiya, S. Ikeda; *J. Colloid Interface Sci.* **1985**, *108*, 215–222.

P10 Mechanochemistry: an effective method to produce metal loaded HY catalysts for HDO reaction

M. Matos,[1,2] *N. Nunes*,[1,2] *R. Miguéis*,[2,3] *M.S. Santos*,[2,3] *A.P. Carvalho*,[2,3] *J. Coelho*,[1,4] *A. Martins*[1,2]

[1] *DEQ, Instituto Superior de Engenharia de Lisboa, IPL, Lisbon, Portugal*
[2] *CQE, Institute of Molecular Sciences, Fac. Ciências, ULisboa, Lisbon, Portugal*
[3] *Departamento de Química e Bioquímica, Fac. Ciências, ULisboa, Lisbon, Portugal*
[4] *CQE, Institute of Molecular Sciences, IST, ULisboa, Lisbon, Portugal*
Email: mariana.matos@isel.pt

Mechanochemistry has become a powerful tool in the past few decades to change the properties of zeolites and related materials promoting several types of modifications, depending on parameters such as ball size, milling speed and time. It also brings the advantage of being solvent-free, allowing to suppress solvent elimination and drying steps.[1] In this work, Pt/HY, Ni/HY as well as bimetallic Pt-Ni/HY were prepared by mixing HY zeolite (Zeolyst Si/Al=5.4) with $Pt(NH_3)_4Cl_2{\cdot}xH_2O$ and/or $NiNO_3{\cdot}6H_2O$ in a planetary ball mil (Resch) using an agate vase with 5 spheres of 20 mm diameter for 30 min and 200 rpm. The samples were calcined, reduced with H_2 at 450 ºC, and named *a*Pt, *b*Ni or *a*Pt-*b*Ni/HY, where *a* is the amount of Pt (0.1-1 wt.%) and *b* is the amount of Ni (1-5 wt.%). The samples were characterized through powder XRD, N_2 adsorption at -196 ºC and laser diffraction particle sizing (LSD) measurements. The catalytic behavior in hydrodeoxygenation (HDO) was explored using model compounds such as guaiacol in a high-pressure batch reactor Parr 4843 using 200 mg of catalyst and 25 mL of 5 % vol. of guaiacol in *n*-heptane, at 250 ºC, 20 atm and 350 rpm. Samples were collected after 60 min and analyzed by GC-FID and GC-MS.

The diffraction patterns show that milled samples keep the crystal pattern typical of Y zeolite whereas LSD measurements evidence some decrease on the particle size. Preliminary catalytic results indicate that bimetallic zeolites present improved catalytic performance

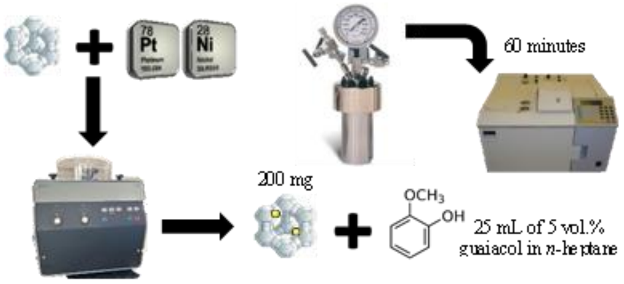


Fig. 1. Metal loaded HY in ball mill and HDO reaction in a high-pressure batch reactor.

Acknowledgements: This research was funded by FCT through UIDB/00100/2020, https://doi.org/10.54499/UIDB/00100/2020 UIDP/00100/2020 https://doi.org/10.54499/UIDP/00100/202 and LA/P/0056/2020 https://doi.org/10.54499/LA/P/0056/2020 and IPL through Project IPL/2023/Zeo@BioRef ISEL

References

1. G. Majano, L. Borchardt, S. Mitchell, V. Valtchev, J. Pérez-Ramírez; *Microporous Mesoporous Mater*. **2014**, *194*, 106–114.

P11 Stoichiometrically diverse cocrystals of nicotinamide with dicarboxylic acids: studies of solubility behavior

A.R. Mendonça,[1] I.O. Feliciano,[2] M. F. M. Piedade[1,3]

[1] Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Lisboa, Portugal
[2] Centro de Química Estrutural, Institute of Molecular Sciences, Faculdade de Ciências, Universidade de Lisboa, Lisboa, Portugal
[3] Centro de Química Estrutural, Institute of Molecular Sciences, IST, Universidade de Lisboa, Lisboa, Portugal
Email: fc55343@alunos.ciencias.ulisboa.pt

In pharmaceutical industry, the solubility of active pharmaceutical compounds (APIs) plays a critical role in drug development since it directly impacts their bioavailability and efficacy. Traditional methods of enhancing solubility often involve complex chemical modifications or the addition of co-solvents, which can introduce unwanted side effects or regulatory hurdles.[1]

Cocrystallization, the process of combining two or more compounds in a crystalline lattice bonded together by noncovalent bonds, has emerged as a promising approach to improve the solubility of APIs. Interest in cocrystals continues to grow due to their enhanced properties when compared to the starting materials.[2] The establishment of hydrogen bonds between the API and the coformers leads to a distinct crystalline structure compared to the original, thereby modifying both physical and chemical attributes. If a coformer possesses greater solubility, it can elevate the solubility of the resultant cocrystal, whereas a coformer with lower solubility tends to diminish the solubility of the API.

The aim of this study was to model the solubility of nicotinamide, a frequently used active pharmaceutical ingredient (API), through its cocrystallization with five precursor acids: malonic acid, glutaric acid, pimelic acid, azelaic acid, and sebacic acid, at ratios of 1:1 and 2:1. Following thorough characterization, the solubility of the resulting materials was determined using dynamic measurement techniques.

Acknowledgements: Centro de Química Estrutural is a Research Unit funded by FCT through projects UIDB/00100/2020 (https://doi.org/10.54499/UIDB/00100/2020) and UIDP/00100/2020 (https://doi.org/10.54499/UIDP/00100/2020). Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020 (https://doi.org/10.54499/LA/P/0056/2020). A doctoral grant awarded by the FCT to I. Feliciano (2021.04637.BD) is also gratefully acknowledged.

References

1. *Bioavailability Enhancement Techniques for Poorly Aqueous Soluble Drugs and Therapeutics - PubMed*. https://pubmed.ncbi.nlm.nih.gov/36140156/ (accessed 2024-04-22).
2. M. Karimijafari, L. Padrela, G. Walker, D. Croker; *Cryst. Growth Des.* **2018**, *18*, 6370–6387.

P12 Experimental and theoretical study of the crystallization process of paracetamol from solution

I. Calheiros, C.E.S. Bernardes

Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal
Email: fc56593@alunos.ciencias.ulisboa.pt

Crystallization has been employed for millennia to obtain and refine compounds, yet our comprehension of this process remains incomplete.[1] At this critical stage, the crystal structure of the material is defined, setting many crucial properties of final materials like the fusion temperature, thermal stability, solubility, and tabletability, profoundly impacting production, processing, stability, and product delivery. Our limited understanding of crystal formation in solution hampers our ability to replicate and control material properties consistently. Therefore, it is imperative, particularly in industries like pharmaceuticals, to develop strategies facilitating informed design and control of crystallization processes.

The formation of a macroscopic crystal necessitates the initial development of a nucleus, a microscopic structure comprised of a few molecules. While these structures can be studied experimentally, a promising opportunity lies in theoretical methods, such as Molecular Dynamics (MD) simulations, which allow for the exploration of the dynamics of thousands of molecules over time. Consequently, MD simulations can enable the identification of key steps in the formation and evolution of initial structures formed during crystallization, as well as the prediction of material properties, such as crystal structure.

This study presents both experimental and theoretical investigations into the crystallization of paracetamol, a widely prescribed drug (Fig. 1), from methanol, ethanol, and propanol. Experimentally, induction times of crystallization were obtained as a function of solution supersaturation levels. The interpretation of these findings, including the influence of solvent on the ability to obtain different crystal phases of paracetamol (polymorphs) and the microscopic structural alterations occurring in solution with varying supersaturation levels, will be discussed using MD simulations.

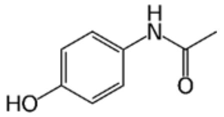


Fig. 1. Paracetamol molecular structure.

Acknowledgements: This work was supported by FCT, Portugal, through projects UIDB/00100/2020 (https://doi.org/10.54499/UIDP/00100/2020), UIDP/00100/2020 (https://doi.org/10.54499/UIDB/00100/2020), LA/P/0056/2020 (https://doi.org/10.54499/LA/P/0056/2020), 2021.03239.CEECIND (https://doi.org/10.54499/2021.03239.CEECIND/CP1650/CT0003).

References

1. C.S.D. Lopes, C.E.S. Bernardes, *Boletim SPQ,* **2023**, *46*, 266-271.

P13 Enhancing the baricitinib intrinsic dissolution rate by co-crystallization and amorphization

M. I. G. Silva,[1] T. M. R. Maria,[1] R. A. E. Castro,[1,2] M. E. S. Eusébio,[1] J. Canotilho[1,2]

[1] Coimbra Chemistry Center/Institute of Molecular Sciences, Department of Chemistry, University of Coimbra, Rua Larga, 3004-535 Coimbra, Portugal
[2] Faculty of Pharmacy, University of Coimbra, Azinhaga de Santa Comba, 3000-548 Coimbra, Portugal
Email: mariaines.g.silva20@gmail.com

Baricitinib (BAR) acts as a suppressor for the Janus kinase enzymes, specifically targeting JAK1 and JAK2. Initially approved for treating moderate to severe cases of rheumatoid arthritis (RA), it has also demonstrated notable effectiveness in managing the inflammatory responses associated with various diseases.[1,2] This compound falls under class II of the Biopharmaceutical Classification System, notable for its limited solubility in aqueous solutions but high permeability through membranes.[1] The growing necessity to address the challenge of poor solubility in active pharmaceutical ingredients (APIs), has led researchers to study new solid forms of the compounds, such as, co-crystals and co-amorphous.[3,4] This API was selected to investigate the possibility of obtaining new solid forms with enhanced properties.

This research was carried out using mechanochemistry in order to study the possible association between this API and four other compounds of pharmaceutical interest: flurbiprofen (FBP), oxalic acid (OA), folic acid (FA) and nicotinamide (NIC). The solids obtained were characterised using differential scanning calorimetry, attenuated total reflectance infrared spectroscopy and powder X-ray diffraction. In addition, the intrinsic dissolution rate of these multicomponent systems was analysed.

Grinding baricitinib with these co-formers made it possible to obtain BAR co-crystals with FBP and OA. The association of BAR+FA led to the formation of an amorphous system. The BAR+NIC mixture give rise to the formation of an eutectic mixture. These multicomponent systems show higher intrinsic dissolution rates compared to the pure API, according to the following order: BAR+FA > BAR:OA > BAR+NIC > BAR:FBP > BAR.

Acknowledgements: Coimbra Chemistry Center- Institute of Molecular Science (CQC-IMS), is supported by national funds through the FCT – Foundation for Science and Technology, I.P., under the project UID/QUI/00313/2020. The authors would like to thank Unidade de Controlo de Qualidade de Produtos Farmacêuticos, UCQFarma, Faculty of Pharmacy of the University of Coimbra for the use of the XRPD and intrinsic dissolution tests equipment.

References

1. A. Markham; *Drugs*, **2017**, *77*, 697-704.
2. S. Assadiasl, Y. Fatahi, B. Mosharmovahed, B. Mohebbi, M. H. Nicknam; *J. Clin. Pharmacol*. **2021**, *71*, 1274-1285.
3. A. V. Yadav, A. S. Shete, A. P. Dabke, P.V Kulkarni, S. S. Sakhare; *Indian J. Pharm Sci*. **2009**, *71*, 359-370.
4. S. J. Dengale, H. Grohganz, T. Rades, K. Löbmann; *Adv. Drug. Deliv*. Rev. **2016**, *100*, 116-125.

P14 Energetics and structures of borophene nanoclusters

J. M. C. Marques,[1] *F. Zergani,*[1] *M. Bartolomei,*[2] *F. Pirani*[3]

[1] *CQC-IMS, Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal*
[2] *Instituto de Física Fundamental, Consejo Superior de Investigaciones Científicas (IFF-CSIC), Serrano 123, 28006 Madrid, Spain*
[3] *Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, 06123 Perugia, Italy*
Email: qtmarque@ci.uc.pt

Boron and carbon are neighbor elements in the second period of the Periodic Table and, consequently, they have similar valence orbitals. However, boron is not expected to form graphene-like structures due to its electron deficiency that leads to displaying aromaticity and antiaromacity character.[1,2] Thus, borophene structures, such as B_{12} and B_{36}, show special properties,[3] which may be of great interest for building up new nanomaterials.

In this work, we have investigated the aggregation of $(B_{12})_n$ and $(B_{36})_n$ clusters by developing and exploiting an analytical potential energy surface (PES) that has been calibrated with accurate electronic-structure calculations. The analytical PES is formed by an antiaromatic contribution, that decreases exponentially with the distance between the centers of the planes defined by the uppermost atoms of two monomers, and a non-electrostatic term whose components are described through improved Lennard-Jones functions.[4,5] The novel PES was, then, used in a global geometry optimization study carried out with an evolutionary algorithm[6] to discover the lowest-energy structures of the $(B_{12})_n$ and $(B_{36})_n$ (n=2-10) clusters.

The results from this work[7] show that both $(B_{12})_n$ and $(B_{36})_n$ clusters present particular stability for n=6 and n=8. In general, $(B_{12})_n$ structures tend to maximize close contacts between the edges of the monomers, thus leading to the formation of cage-like clusters, while $(B_{36})_n$ are mainly composed of stacked or herringbone structures.

Acknowledgements: We thank the support from the Coimbra Chemistry Centre (CQC–IMS), which is financed by "Fundação para a Ciência e a Tecnologia" (FCT) through the programmes UIDB/00313/2020 and COMPETE. This contribution is also based upon the work of COST Action CA21101 supported by COST. This work was mostly carried out with the computational resources hosted at the Molecular Modeling and Computational Simulation Laboratory (Department of Chemistry, University of Coimbra). M.B. also acknowledges the support of the Spanish MICINN PID2020-114654GB-I00 grant.

References

1. D. Y. Zubarev, A. I. Boldyrev; *J. Comput. Chem.* **2007**, *28*, 251-268.
2. A. P. Sergeeva, B. B. Averkiev, H.-J. Zhai, A. I. Boldyrev, L.-S. Wang; *J. Chem. Phys.* **2011**, *134*, 224304.
3. A. J. Mannix, X.-F. Zhou, B. Kiraly, J. D. Wood, D. Alducin, et al.; *Science* **2015**, *350*, 1513-1516.
4. F. Pirani, M. Albertí, A. Castro, M. M. Teixidor, D. Cappelletti; *Chem. Phys. Lett.* **2004**, *394*, 37-44.
5. F. Pirani, S. Brizi, L. F. Roncaratti, P. Casavecchia, D. Cappelletti, F. Vecchiocattivi; *Phys. Chem. Chem. Phys.* **2008**, *10*, 5489-5503.
6. J. Llanio-Trujillo, J. M. C. Marques, F. Pereira; *J. Phys. Chem. A* **2011**, *115*, 2130-2138.
7. F. Zergani, J. M. C. Marques, M. Bartolomei, F. Pirani; in preparation.

P15 Modeling preferential solvation in binary aqueous mixtures using a solvatochromic probe

A. Pinção,[1,2] L. Moreira,[1,3] R. Elvas-Leitão,[1,4] F. Martins [1,2]

[1] *Centro de Química Estrutural - Institute of Molecular Sciences, Universidade de Lisboa, Portugal*
[2] *Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Portugal*
[3] *Instituto Superior de Educação e Ciências, ISEC Lisboa, Portugal*
[4] *Departamento de Engenharia Química, Instituto Superior de Engenharia de Lisboa, IPL, Portugal*
Email: fc58482@alunos.ciencias.ulisboa.pt

Most chemical reactions and general physicochemical phenomena take place in solution and the path they follow, the equilibrium position they reach and the rate at which they occur depend heavily on a complex, and difficult to quantify, phenomenon generally called polarity. The devise of empirical solvent polarity scales, based on the response of solvent-sensitive solvatochromic probes is an effective way of tackling the problem and the subject still attracts the attention of researchers.[1] Despite the profusion of solvent polarity scales, the best known and most used is the one proposed by Dimroth, Reichardt and collaborators, based on the transition energy of the probe 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinium)phenolate, also known as betaine(30) or Reichardt betaine – $E_T(30)$.[2] In the case of mixtures, just as important as determining the polarity of the solvent, it is crucial for researchers to understand and quantify how solvent-solvent interactions alter the behaviour of the medium, distancing it from ideality. Several models have been developed over the years to explain and quantify preferential solvation in solvent mixtures. One of those is the Bosch and Rosés model, originally applied to binary mixtures[3] and later extended to ternary and higher order mixtures.[4]

In this work, Bosch and Rosés's model was applied to the obtained or collected $E_T(30)$ *vs*. x_w (mole fraction of water) values in 13 protic-water and aprotic-water binary mixtures. The results are presented and discussed. A less common approach is used to analyze and choose the best models.

Acknowledgements: Centro de Química Estrutural is a Research Unit funded by FCT through projects UIDB/00100/2020 (https://doi.org/10.54499/UIDB/00100/2020) and UIDP/00100/2020 (https://doi.org/ 10.54499/UIDP/00100/2020). Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020 (https://doi.org/10.54499/LA/P/0056/2020).

References

1. A. B. Hosseinbakhi , A. Mirabi, M. R. Zardoost, H. Zhao, A. Farajtabar; *J. Mol. Liq.* **2024**, *404*, 124948.
2. K. Dimroth, F. Bohlmann, C. Reichard, T. Siepmann; *Annalen Der Chemie-Justus Liebig* **1963**, *661*, 1-37.
3. E. Bosch, M. Rosés; *J. Phys. Org. Chem* **1996**, *9*, 403–410.
4. N. Nunes, C. Ventura, F. Martins, R. E. Leitão; *J. Phys. Chem. B* **2009**, *113*, 3071-3079.

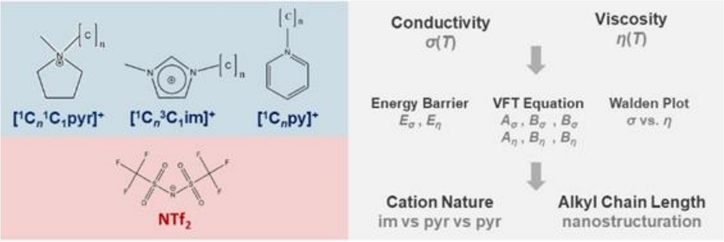
P16 Cation effect on the viscosity and electrical conductivity of ionic liquid

C.F.P. Miranda, L.M.N.B F. Santos

CIQUP, Institute of Molecular Sciences (IMS)- Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre S/N, Porto, Portugal

Email: carlospesqueiramiranda@gmail.com

This work presents a study concerning the effect of the cation structure on the viscosity and electrical conductivity of ionic liquids (ILs). Three cationic series were studied coupled with the bis(trifluoromethylsulfonyl)imide anion: 1-alkyl-3-methyl-imidazolium, $[\mathrm{C}_n\mathrm{C}_1\mathrm{im}]^+$,1-alkyl-1-methylpyrolidinium $[\mathrm{C}_n\mathrm{C}_1\mathrm{pyr}]^+$, 1-alkylpyridinium $[\mathrm{C}_n\mathrm{py}]^+$. Additionally, for each series the effect of increasing the alkyl chain was also evaluated. The electrical conductivity measurements were performed between 283 and 333 K using a customized impedance methodology to scan the resistance, *R,* and reactance, *X*, from 20 Hz to 500 kHz. The resistance of the solution was derived from the extrapolation to infinite frequency in order to avoid polarization effects.[1] The viscosity and density were measured between 273 and 373 K using an automated SVM 3001 Stabinger viscometer-densimeter based on the concentric cylinders and vibrating tube methods. The dependence of electrical conductivity, $\sigma(T)$, and dynamic viscosity, $\eta(T)$, with the temperature was found to be well represented by the Vogel-Fulcher-Tammann (VFT) equation. The combination of the $\sigma(T)$ and $\eta(T)$ data, along with the derived VTF coefficients, energy barrier, Walden plots and the resistance-reactance spectra were used to elucidate the effects of cation structure on the transport properties, ion association and structuration of the ILs. Overall, the following trends were found, η: im < py < pyr, σ: pyr < py < im. Furthermore, for all series it was found a shift on the variation of conductivity, viscosity, and other derived properties with the increase of the number of carbons on the alkyl chain, *n*. This trendshift is an evidence of the intensification of IL nanostructuration that happens around η = 6.



Acknowledgements: This work was supported by the Fundacão para a Ciência e Tecnologia (FCT) through the FCT/MCTES (PIDDAC) to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020), IMS-Institute of Molecular Sciences (LA/P/0056/2020). Carlos F. P. Miranda is grateful to FCT for his research grant (Reference: 2020.05717.BD).

References

1. X. Paredes, C. S. G. P. Queirós, C. A. N. Castro; *J. Phys. Chem. Ref. Data* **2020**, *49*, 043101-51.

P17 Thermodynamics of fumaric acid polymorphism

A.S. Pereira, R.G. Simões, M.F.M. Piedade, M.E. Minas da Piedade

Centro de Química Estrutural, Institute of Molecular Sciences, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal
Email: alexandre.sabio1@gmail.com

Molecular organic solids can often adopt multiple crystal structures, a phenomenon known as polymorphism. Due to the different arrangements of the molecules in the lattice, the solid-state properties (e.g. melting point, compressibility, solubility, color) of each polymorph can be significantly different. Thus, once polymorphism has been established, the stability domains and stability hierarchy of the different forms must be determined.

In this work, forms I and II (monoclinic and triclinic, respectively)[1,2] of fumaric acid (FA) were prepared and characterized by single crystal X-ray diffraction, and their stability relationship investigated by differential scanning calorimetry (DSC) and solubility measurements.

The results revealed that the system is enantiotropic, with form II converting to form I upon heating, at T_{trs} = 471.2±1.0 K with $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$ = 1.58±0.18 kJ mol^{-1} (Fig. 1). Solubility studies in ethanol confirmed that form I is metastable at 298 K, changing into form II after 5-10 minutes under stirring. The Gibbs energy of the crII → crI phase transition could, nevertheless, be determined as $\Delta_{\mathrm{trs}}G_{\mathrm{m}}$ = 0.15±0.03 kJ mol^{-1} from solubility measurements.

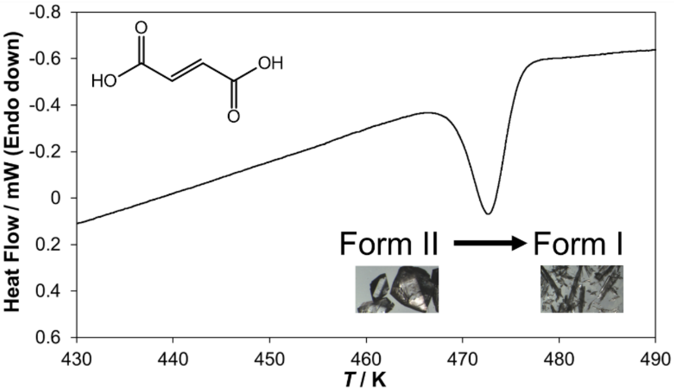


Fig. 1. Solid-solid transition observed by DSC.

Acknowledgements: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia (FCT) through projects UIDB/00100/2020 (https://doi.org/10.54499/UIDB/00100/2020) and UIDP/00100/2020 (https://doi.org/10.54499/UIDP/00100/2020). Institute of Molecular Sciences is an Associate Laboratory which is funded by FCT through project LA/P/0056/2020 (https://doi.org/10.54499/LA/P/0056/2020).

References

1. A. L. Bednowitz, B. Post; *Acta Cryst*. **1966**, *21*, 566-571.
2. C. J. Brown; *Acta Cryst*. **1966**, *21*, 1-5.

P18 Metabolomic analysis of endogenous *Saccharomyces cerevisiae* strains from Madeira Island

F. Pereira,[1] *M. Castillo,*[1] *J.S. Câmara*[1,2]

[1] *CQM - Centro de Química da Madeira, Universidade da Madeira, Campus Universitário da Penteada, 9020-105 Funchal, Portugal*
[2] *Departamento de Química, Faculdade de Ciências Exatas e Engenharia; Universidade da Madeira, Campus Universitário da Penteada, 9020-105 Funchal, Portugal*
Email: 2066121.student.uma.pt

The yeast species Saccharomyces cerevisiae (*S. cerevisiae*) has been essential since the oldest civilizations in the production of bread, wine, and beer, among other fermented drinks.1 It is currently used in the production of medicines, nutraceuticals, food preservatives, and biofuels, among other value-added products. In winemaking, during the selected preparation of grape must, yeasts, especially the species S. cerevisiae, metabolize glucose into ethanol and CO_2.[1] Several studies report the biosynthesis of diverse volatile organic metabolites (VOMs),[1,2] during mixed fermentation, products of secondary metabolism, important in the typicality of wine aroma, mostly esters, alcohols, fatty acids, and in smaller proportions carbonyl compounds and phenols.[3] In this sense, the genetic component of the strain, in close relation to environmental pressure, influences the VOMs produced. In this context, the main of this study was to characterize the volatilomic profile biosynthesized by four endogenous strains of *S. cerevisiae* through solid-phase microextraction in headspace mode (HS-SPME) followed by gas chromatography coupled to mass spectrophotometry (GC-MS). A total of 55 VOCs biosynthesized by each strain were identified. Overall, the specific majority of VOMs belong to the chemical families of alcohols and carbonyl compounds, while the minority ones include esters, terpenes, and sesquiterpenes. The greatest abundance found in all strains was phenylethyl alcohol. The main compounds synthesized by strains A, B, C, and D were isobutyl alcohol, benzaldehyde, and isoamyl alcohol, respectively. In the volatilomic profile of the experimental strains, a probable relationship with the grape variety and the location in which they were sampled was verified.

Acknowledgements: This research was funded by FCT- Fundação para a Ciência e a Tecnologia through the CQM Base Fund - UIDB/00674/2020, and Programmatic Fund - UIDP/00674/2020, by Interreg MAC 2014–2020 Cooperación territorial through AD4MAC project (MAC2/1.1b/350), and by ARDITI-Agência Regional para o Desenvolvimento da Investigação Tecnologia e Inovação, through the project M1420-01-0145- FEDER-000005 - Centro de Química da Madeira - CQM+ (Madeira 14–20 Program). The authors also acknowledge FCT and Madeira 14–2020 program to the Portuguese Mass Spectrometry Network (RNEM) through PROEQUIPRAM program, M14-20 M1420-01-0145- FEDER-000008). Mariangie Castillo thanks for the PhD fellowships SFRH/BD/147434/2019 supported by FCT.

References

1. G.M. Walker, G.G. Stewart; *Beverages* **2016**, *2*, 8-10.
2. M.G. Lambrechts, I.S. Pretorius; *S. Afr. J. Enol. Vitic*. **2019**, *21*, 101-117.
3. M. Castillo, E. Silva, J.S. Câmara, M. Khadem; *Processes* **2020**, *8*, 1058.

P19 Polymorphism and thermal behavior of succinic acid

P.M.S. Mateus, R.G. Simões, M F.M. Piedade, M.E. Minas da Piedade

Centro de Química Estrutural, Institute of Molecular Sciences, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal.
Email: pedro-miguel-mateus@hotmail.com

Succinic acid (SA, Fig. 1) is a dicarboxylic acid with a wide range of uses, from food additive to pharmaceuticals. It is also employed in the production of many other products, including surfactants, detergents, clothing fibers, flavors and fragrances, fungicides, and herbicides.[1]

SA has three known polymorphs:[2] *α* (triclinic, space group $P\bar{1}$), *β* (monoclinic, space group $P2_1/c$), and *γ* (monoclinic, space group $C2/c$). Both the *α* and *β* forms can be isolated and stored at room temperature, without conversion. The *γ* form was serendipitously discovered while purifying a leucine dipeptide by co-crystallization from methanol and is classified as a "disappearing" polymorph (i.e., this phase was identified but cannot be reproducibly prepared).[3]

In this work, the crystal structures of the *α* and *β* polymorphs, at ambient temperature, were revisited and their thermal behavior investigated. The results showed that the *β* form is the most stable polymorph at room temperature, as a stirred suspension of either *α* or *β* in acetone would result in conversion to this phase. Moreover, the two polymorphs displayed different thermal behaviors. Indeed, while only a single peak, corresponding to melting, could be observed upon heating the *β* form, the *α* phase experienced multiple endothermic events prior to fusion.

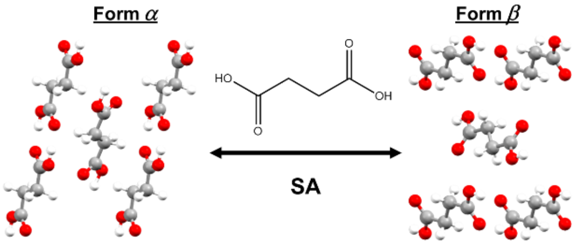


Fig.1. Molecular and crystal structures of the *α* and *β* polymorphs of the succinic acid.

Acknowledgements: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia (FCT) through projects UIDB/00100/2020 (https://doi.org/10.54499/UIDB/00100/2020) and UIDP/00100/2020 (https://doi.org/10.54499/UIDP/00100/2020). Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020 (https://doi.org/ 10.54499/LA/ P/0056/2020).

References

1. R.K. Saxena, S. Saran, J. Isar, R. Kaushik; *Current Developments in Biotechnology and Bioengineering*; Elsevier, 2017.
2. C.R. Groom, I.J. Bruno, M.P. Lightfoot, S.C. Ward; *Acta Cryst.* **2016**, *B72*, 171-179.
3. P. Lucaioli, E. Nauha, I. Gimondi, L. S. Price, R. Guo, L. Iuzzolino, I. Singh, M. Salvalaglio, S. L. Price, N. Blagden; *CrystEngComm* **2018**, *20*, 3971–3977.

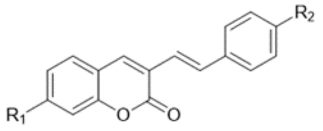
P20 Synthesis of vitrimers doped with solvatochromic coumarins

T. Sousa, C.A.T. Laia, P.S. Branco, J. Sarrato, A. Pinheiro

LAQV-REQUIMTE, Departament of Chemistry, NOVA School of Science and Technology, FCT NOVA, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal
Email: tfm.sousa@campus.fct.unl.pt

Vitrimers are plastic materials that behave like a viscoelastic fluid at high temperatures (above 100 ºC). This is due to transesterification reactions, which create a three-dimensional polymeric network at room temperature. However, these covalent bonds break with increasing temperature, changing the internal structure of the polymer. [1] These materials possess unique properties, forming strong glasses and exhibit self-healing, shape memory, among others.

This work aims to synthetize these glasses doped with coumarins whose structure can be seen in Fig. 1. These coumarins exhibit high Stokes shifts, high fluorescence quantum yields and strongly solvatochromic fluorescence. [2] This combination is perfect for obtaining fluorescent vitrimer films using coumarins as probes of its inner structure. The study of the photophysical properties of both the vitrimers and coumarins as well as self-healing experiments by monitoring the fluorescence colour are currently being performed.



R_1 - $N(CH_2CH_3)_2$; OCH_3 R_2 - NO_2 ; OCH_3

Fig.1. Structure of the synthetized coumarins

Acknowledgements: This work received financial support from PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through the projects UIDB/50006/2020 and UIDP/50006/2020.

References

1. F.I. Altuna et al.; *Polymers* **2018,** *10*, 43.
2. J. Gordo, J. Avó, A.J. Parola, J.C. Lima, A. Pereira, P.S. Branco; *Org. Lett.* **2011,** *13*, 5112–5115.

P21 Diving the deep eutectic systems: The order on the water's addition

C. Sarmento, H. Monteiro, A. Santos, A. Paiva, A.R.C. Duarte

[1] *LAQV-REQUIMTE, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal*
Email: cc.sarmento@campus.fct.unl.pt

The interest in DES (Deep Eutectic Systems) has been growing in the past decades due to the fact that this kind of solvents are a green alternative able to replace hazardous organic solvents in various fields, namely extraction, pharmaceutical preparations, enzymatic reactions, textile or food industry, among others.[1] These solvents are characterized by their low melting point, low toxicity, eco-friendly, and low cost of production. The methods of production of DES are usually simple, being the most widely used based on heating and stirring.[2]

A great number of these systems are composed of highly hygroscopic compounds, e.g., choline chloride and betaine. In most cases, the water interacts with the DES components and consequently becomes a part of the network, thus making the water impossible to remove. On the other hand, water is also used to tailor DES physicochemical properties, in particular viscosity, and in these cases, it is normally considered as an additional component of the system.[3]

However, the role of water is not fully understood and there are different approaches to the preparation of these systems: in some cases, water is introduced as an initial component of the mixture, whilst in others, water is added after the formation of the DES. This work is aiming to analyze its differences on DES with compounds such as choline chloride, betaine, ethylene glycol, in order to understand the water role on DES. To provide answers to this pertinent question, macroscopic analysis were performed namely density, viscosity, and solvatochromic parameters.

Acknowledgements: This work received financial support from FCT/MCTES (UIDB/50006/2020 DOI 10.54499/UIDB/50006/2020) through national funds), through national funds and from the PhD grant 2021.07457.BD from FCT.

References

1 B. B. Hansen, S. Spittle, B. Chen, D. Poe, Y. Zhang, J. M. Klein, A. Horton, L. Adhikari, T. Zelovich, B. W. Doherty, B. Gurkan, E. J. Maginn, A. Ragauskas, M. Dadmun, T. A. Zawodzinski, G. A. Baker, M. E. Tuckerman, R. F. Savinell, J. R. Sangoro; *Chem. Rev.* **2021**, *121*, 1232–1285.

2 L. Meneses, F. Santos, A. R. Gameiro, A. Paiva and A.R.C. Duarte; *JoVE (Journal of Visualized Experiments)*, **2019**, e60326.

3 Y. Dai, G.-J. Witkamp, R. Verpoorte, Y. H. Choi; *Food Chem.* **2015**, *187*, 14–19.

P22 Investigation of solid forms of sotagliflozin

R. A. E. Castro,[1, 2] *L. Puppini*,[3] *J. A. Baptista*,[1] *J. Canotilho*,[1, 2] *M. E. S. Eusébio*[1]

[1] *Coimbra Chemistry Center/Institute of Molecular Sciences, Department of Chemistry, University of Coimbra, Coimbra, Portugal*
[2] *Faculty of Pharmacy, University of Coimbra, Coimbra, Portugal*
[3] *Faculty of Pharmacy, University of Bologna, Bologna, Italy*
Email: rcastro@ff.uc.pt

Based on the degree of order/periodicity, solids can be classified into three groups: amorphous, mesophases, and crystalline solids. Amorphous solids only can have short-range order and crystalline solids, on the other hand, have a long-range, translational, orientational, and conformational order.[1] Crystalline solids can be found in various forms, such as polymorphs, solvates and cocrystals.

The investigation of known solid forms and new solid forms of a drug is essential for optimizing its properties and to select the most suitable form for clinical use, ensuring maximum therapeutic benefit and manufacturability. This will lead to the development of more effective and safer pharmaceutical formulations.

Sotagliflozin (SGF), Fig. 1, takes part of the class of inhibitors of the transport protein sodium-glucose (SGLT1/2) also known as gliflozins, the latest approved class for the treatment of diabetes mellitus type II, with unique cardioprotective and nephroprotective effects compared to other oral antidiabetic drugs.[2, 3] Sotagliflozin is a crystalline solid; it has a low water solubility of 0.042 mg/ml[4] and high membrane permeability and is classified as class II in the Biopharmaceutical Classification System (BCS).

In this work solid forms of SGF were investigated and characterized by thermal analysis (differential scanning calorimetry, thermogravimetry and thermomicroscopy), spectroscopic methods (powder X-ray diffraction and Fourier transform infrared) and polythermal method for solubility determination in green solvents.

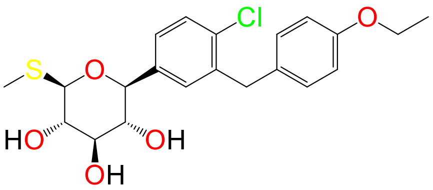


Fig. 1. Sotagliflozin, (2S,3R,4R,5S,6R)-2-[4-chloro-3-[(4-ethoxyphenyl)methyl]phenyl]-6-methylsulfanyloxane-3,4,5-triol.

Acknowledgements: Coimbra Chemistry Center- Institute of Molecular Science (CQC-IMS), is supported by national funds through the FCT – under the project UID/QUI/00313/2020. Thanks are due to UCQFarma, Faculty of Pharmacy of the University of Coimbra for XRPD and TGA. J. A. B. thanks FCT for financial support (grant UI/BD/150859/2021).

References

1. Y. Qui, Y. Chen, G. Zhang, L. Liu, W. Porter; *Developing Solid Oral Dosage Forms: Pharmaceutical Theory & Practice*; Academic Press: Burlington, MA, 2009.
2. A.R. Aguillón, A. Mascarello, N.D. Segretti, H.F.Z. de Azevedo, C.R.W. Guimaraes, L.S.M. Miranda, R. de Souza; *Org. Proc. Res. Develop.* **2018,** *22*, 467-488.
3. S. Shakil; *J. Cell. Biochemistry* **2017,** *118*, 3855-3865.
4. S.S. Tiwari, S.J. Wadher, S.J. Fartade, C.N. Vikhar; *Int. J. Pharm. Sci. Res.* **2019,** *10*, 4070-4077.

P23 Novel conformational changes in ABCG2 mediated by ATP binding

P. Suzano,[1] B. Gonçalves,[2] M. Ferreira,[2] D. dos Santos[1]

[1] *CBIOS – Research Center for Biosciences & Health Technologies, Universidade Lusófona de Humanidades e Tecnologias – Escola de Ciências e Tecnologias da Saúde, Campo Grande 376, 1749-024, Lisboa, Portugal*

[2] *iMed.Ulisboa - Research Institute for Medicines, Faculdade de Farmácia da Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal.*

Email: p7857@ulusofona.pt

The ABC (ATP-Binding Cassette) protein superfamily is a group of membrane transporters that bind to ATP to perform their function. Their upregulation is a defense strategy against administered drugs, leading to drug resistance, and poor chemotherapy response and prognostic factor.[1] Advances in experimental techniques, such as Cryo-EM, improved the resolution of structural details. However, the full transport mechanism of ABC transporters is still unclear.[2] Herein, we report the dynamics of the inward-facing conformation of the ABCG2 protein in its apo and ATP-bound states, and the effects of ATP binding.

Homology modelling was used to complete a structure of the ABCG2 protein, starting from a cryo-EM result available on the Protein Data Bank (pdb: 6ETI). Missing sequences were built using our previous BCRP model[3] as template along with the PredictProtein secondary structure prediction server.[4] The protein was then inserted into its native environment and under physiological conditions.

We analyzed and compared the conformational changes occurring in the transmembrane and nucleotide binding domains of the ABCG2 apo and ATP-bound forms, providing interesting insights. Our results appear to support a hypothesis proposed by Locher et al[5] for the ABCG2 efflux mechanism.

Although our research helped elucidate the ABCG2 structural differences between the Apo and ATP-bound forms, further research is required to completely characterize these mechanisms. Nevertheless, a complete understanding of these transporters is essential for anticancer research.

Acknowledgements: This research was funded by the Portuguese Fundação para a Ciência e a Tecnologia (FCT), under contracts UIDP/04567/2020, UIDB/04567/2020, UIDP/04138/2020 and UIDB/04138/2020, and project 2022.05718.PTDC. ILIND is also acknowledged for funding through project: ABC-MDR-REVERSAL– Multidrug Resistance Reversal in Cancer Through a Novel Allosteric Mechanism.

References

1 Y.G.. Assaraf, et al.; *Drug Resist. Update* **2019**, *46*, 100645.
2. C. Thomas, R. Tampé; *Annu. Rev. Biochem.* **2020**, *89*, 605–636.
3. R.J. Ferreira, C.A. Bonito, M.N.D.S. Cordeiro, D.J.V.A dos Santos; *Sci. Rep.* **2017**, *7*, 15534.
4. G. Yachdav, et al.; *Nucleic Acids Res.* **2014**, *42*, W337-43.
5. Q. Yu, et al.; *Nat. Commun.* **2021**, *12*, 4376.

P24 Improving the solubility of monomethyl fumarate through co-crystallization

R. Mané, M.F.M. Piedade, M.E. Minas da Piedade

Centro de Química Estrutural, Institute of Molecular Sciences, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal.
Email: rdmane@fc.ul.pt

Fumaric acid and alkyl fumarates have demonstrated a wide spectrum of potential or effective therapeutic applications. Monomethyl fumarate (MMF), the compound of interest here, was FDA-approved in April 2020 (tradename Bafiertam) as an oral medicine for treatment of relapsing forms of multiple sclerosis[1] and it is also being considered for the treatment of Parkinson disease type conditions.[2]

As observed for about 90% of drugs under development, MMF has poor aqueous solubility.[3] Because this normally has a strong negative impact on bioavailability, in this work co-crystallization was explored to improve solubility. Using nicotinamide (NIC) as co-former, a new MMF:NIC co-crystal of 1:1 stoichiometry was obtained by mechanochemistry. The material was characterized by powder X-ray diffraction, thermogravimetry, differential scanning calorimetry, Calvet microcalorimetry and single-crystal X-ray diffraction (Fig. 1). The solubility in water was determined using an in-house designed apparatus for clear point determination based on turbidity and imaging detection. The obtained results showed a considerable enhancement in mole fraction solubility when the co-crystal was compared with pure MMF. At 298 K a ca. two times increase was observed. A solubility increase of about 2.5 and 1.3 times was observed at pH 1.40 and 6.81, respectively, at 298 K.

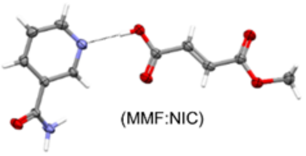


Fig.1. Molecular structure of the monomethyl fumarate-nicotinamide co-crystal.

Acknowledgements: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia (FCT) through projects UIDB/00100/2020 (https://doi.org/10.54499/UIDB/00100/2020) and UIDP/00100/2020 (https://doi.org/10.54499/UIDP/00100/2020). Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020 (https://doi.org/10.54499/LA/P/ 0056/2020).

References

1. A. A. Berger, E. R. Sottosanti, A. Winnick, J. Izygon, K. Berardino, E. M. Cornett, A. D. Kaye, G. Varrassi, O. Viswanath, I. Urits; *Neurol. Int*. **2021**, *13*, 207-223.
2. M. Ahuja, N. A. Kaidery, L. Yang, N. Calingasan, N. Smirnova, A. Gaisin, I. N. Gaisina, I. Gazaryan, D. M. Hushpulian, I. Kaddour-Djebbar, W. B. Bollag, J. C. Morgan, R. R. Ratan, A. A. Starkov, M. F. Beal, B. Thomas; *J. Neurosci.* **2016**, *36*, 6332-6351.
3. G. Bolla, B. Sarma, A. K. Nangia; *Chem. Rev*. **2022**, *122*, 11514-11603.

P25 Rate constants from elementary reactions fail for combustion kinetics models

C. M. A. Rio, J. Brandão, C. Mogo, W. Wang, D.V. Coelho

CEOT - Centro de Eletrónica, Optoeletrónica e Telecomunicações, Universidade do Algarve, Faculdade de Ciências e Tecnologia, DQF, 8005-139 Faro, Portugal
Email: crio@ualg.pt

Kinetics models use available kinetic data, rate constants and their variation with temperature to model complex mechanisms and have been successfully applied to model combustion processes. They rely on the assumption that the number of collisions between reactants and intermediates is large enough to achieve thermal equilibrium.

Recently, we proposed a method to model complex reactive systems incorporating accurate PESs, reactive and nonreactive, and concurrently integrating the equations of motion of the chemical species present in the bulk.[1] This is accomplished by defining a global Potential Energy Surface (gPES) integrating various PESs, each one of them representing an elementary reaction that is expected to play a role in the chemical process. Multi-process Reactions Dynamics, MReaDy, is a program that builds an overall PES for the process in question and performs reactive classical dynamic calculations on it.

To test the distribution of the reaction partners, we have followed the evolution of the hydroxyl radical in its ground electronic state, OH ($^2\Pi$), which is an important and very reactive intermediate during the combustion of a equimolecular mixture of oxygen and hydrogen, started at 3000 *K* and 2 *atm*, until 2 *ns*, using the MReaDy program. The overall results of this calculation have shown to be in reasonable agreement with similar kinetic model results.[1]

To follow the OH radical, the MReaDy program has been modified in order to print out the identification, the position and the velocity of each O and H atom of a OH radical, every time a OH radical is “formed” or “consumed”. Using this information, we have been able to decompose the energy of this radical in its translational, vibrational and rotational components.

In this work we present preliminary results of that study. They show that, despite the occurrence of a large number of collisions, these are more efficient in rotational and translational energy transfer than in vibrational quenching. Consequently, the OH radical has shown to be vibrationally excited, having an average energy which is twice the rotational. The non-thermal distribution of the internal energy of intermediate radicals in hydrogen combustion has recently been experimentally confirmed.[2]

Acknowledgements: FCT under the PTDC/QUI-QFI/31955/2017 research project, co-financed by the European Community Fund, FEDER and the COST Action CA18212 “Molecular Dynamics in the GAS phase”.

References

1. C. Mogo, J. Brandão; *J. Comput. Chem.* **2014**, *35*, 1330–1337.
2. O.V. Skrebkov; *J. Mod. Phys.* **2014**, *5*, 1806-1829.

P26 Multiprocess reaction dynamics program (MReaDy) and applications

W. Wang, J. Brandão, C. Mogo, C.M.A. Rio, D. V. Coelho

CEOT, Universidade do Algarve, Portugal
Email: wwang@ualg.pt

MReaDy [1] is a program for studying reactive dynamic systems using a global potential energy surface (gPES).

Potential Energy Surfaces (PES), based on ab initio calculations, is a powerful tool to study the rate of elementary reactions and their dynamics. It is indicated to compute state-to-state rate constants. In a more complex mechanism, we will be in the presence of different and simultaneous elementary reactions, corresponding to all the possible reactive and non-reactive collisions between the species present and leading to the respective products. Attempting to build a traditional PES for such a system quickly becomes impossible. To circumvent this problem, a global Potential Energy Surface (gPES) can be defined by integrating various PESs, each representing an elementary reaction expected to play a role in the chemical process. MReaDy is built in such a way that it performs reactive dynamic calculations based on such gPES.

We have already used MReaDy to study the combustion dynamics of hydrogen and oxygen mixtures with success.[2,3] Recently, MReaDy has been adapted for studying hydrogen and oxygen combustion confined within carbon nanotubes, as well as H + O_2 + M three-body reaction systems.

Acknowledgements: FCT under the PTDC/QUI-QFI/31955/2017 research project, co-financed by the European Community Fund, FEDER and the COST Action CA18212 “Molecular Dynamics in the GAS phase”.

References

1. C. Mogo, J. Brandão; *J. Comput. Chem.* **2014**, *35,* 1330-1337.
2. C. Mogo, J. Brandão, W. Wang, D. Coelho, C. Rio; *Comput. Theor. Chem.* **2023,** *1224*, 114123.
3. C. Mogo, J. Brandão, W. Wang, D. Coelho, C. Rio; *Comput. Theor. Chem.* **2022**, *1209*, 113614.

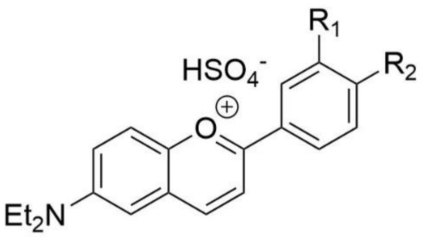
P27

Synthesis of 6-(*N,N*-diethylamino)-flavylium salts for application in dye-sensitized solar cells

A.J. Barbosa,[1,2] *C.A.T. Laia,*[1,2] *A. Jorge Parola*[1,2]

[1] *Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, Portugal*
[2] *LAQV-REQUIMTE, Portugal*
Email: marcin.piwowarczyk@ifj.edu.pl

The need for a more sustainable way of producing energy is a key subject in our current fast-growing world. Dye-Sensitized Solar Cells (DSSC's) aim to compete with the current silicon-based solar cells to provide a greener production of solar energy. Flavylium salts comprise a vast array of molecules found in nature with a characteristic 2-phenyl-1-benzopyrylium skeleton which include anthocyanins, the colorants found in most fruits and flowers[1]. These molecules have accompanied humanity throughout its history with various applications from paints to food additives and now as a partner in a greener future due to their intrinsic fluorescent properties. In this work three flavylium salts were synthesized, characterized by NMR, UV-Vis and Fluorescence spectroscopy in water at different pH values and in ethanol, and then applied to DSSC's. The salts' pK_a's were determined through the UV-Vis data using Solver[3] and are as follow: **1**: $\mathrm{pKa}_1<0$; $pK_{a2} = 5{,}3$; $pK_{a3} = 10{,}3$; **2**: $pK_{a1}<0$; $pK_{a2} = 5{,}8$; **3**: $pK_{a1}<0$; $pK_{a2} = 9{,}6$. The DSSC's presented a maximum efficiency around 0,5% for **1**, 0,2% for **2** and 0,1% for **3** (solvent: ethanol).



1: $R_1 = R_2 = OH$

2: $R_1 = H$; $R_2 = OH$

3: $R_1 = OH$; $R_2 = H$

Fig. 1. Synthesized compounds.

Acknowledgements: This work received support from PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through the projects UIDB/50006/2020 and UIDP/50006/2020.

References

1. F. Pina, M. J. Melo, C. A. T. Laia, A. J. Parola, J. C. Lima; *Chem. Soc. Rev.* **2012**, *41*, 869-908.
2. M. C. Moncada, D. Fernández, J. C. Lima, A.J. Parola, C. Lodeiro, F. Folgosa, M. J. Melo, F. Pina; *Org. Biom. Chem.,* **2004**, *2*, 2802-2808.
3. Pinto, A. (2022). *Flavylium dyes for Dye-Sensitized Solar Cell Applications* [Doctoral dissertation, Universidade Nova de Lisboa]. Repositório da Universidade Nova de Lisboa.
4. G. Calogero, A. Sinopoli, I. Citro, G. Di Marco, V. Petrov, A.M. Diniz, A.J. Parola, F. Pina; *Photochem Photobiol Sci.*, **2013**, *12*, 883-94.

P28 Investigation of the alkyl chain length effect on the energetic properties of γ- and δ-lactones

A. L. R. Silva,[1] G. P. León,[1] V. Lukeš,[2] E. Klein,[2] M. D. M. C. Ribeiro da Silva[1]

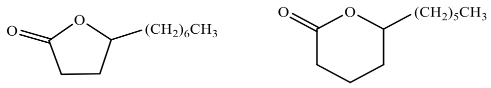
[1] Centro de Investigação em Química (CIQUP), Institute of Molecular Sciences (IMS), Faculty of Sciences of University of Porto, Portugal

[2] Institute of Physical Chemistry and Chemical Physics, Slovak University of Technology in Bratislava, Slovakia.

Email: analuisa.rs@fc.up.pt

An extensive thermochemical study of γ-undecanolactone and δ-undecanolactone has been performed using calorimetric techniques and computational methodologies. The combustion energy of each compound was determined by static-bomb combustion calorimetry, and the corresponding enthalpy of vaporization was determined by high-temperature Calvet microcalorimetry, being these properties reported at T = 298.15 K. The standard molar enthalpy of formation of each lactone, in the gas-phase, was derived using the experimental results obtained through the two calorimetric techniques. Additionally, high level computational calculations were carried out for both compounds, using composite ab-initio G4 and G4(MP2) methods, as well as DFT M06-2X/6-311++G(d,p) approach, to estimate the corresponding enthalpy of formation in the gas-phase. Thus, these theoretical results can be compared with the experimental ones, allowing to evaluate the performance of the different computational approaches.

The experimental results are discussed in terms of structural contributions to the thermochemical properties of the title lactones, as well as other alkylated γ- and δ-lactones[1,2], and empirical correlations are suggested for the estimation of the standard molar enthalpies of formation, at T = 298.15 K, for other alkylated γ- and δ-lactones, both in the liquid and gaseous phases, as well as for the respective enthalpies of vaporization.



γ–undecanolactone (γUL) **δ-undecanolactone (δUL)**

Fig. 1. Structural formulae of γ-undecanolactone and δ-undecanolactone.

Acknowledgements: This work was supported by the Fundação para a Ciência e Tecnologia (FCT) to CIQUP, Faculty of Sciences, University of Porto (Project UIDB/00081/2020) and IMS-Institute of Molecular Sciences (LA/P/0056/2020)). This work was also supported by Slovak Grant Agency (VEGA 1/0461/21). G.P.L. thanks CIQUP/FCUP for his contract under project CIQUP-UIDP/00081/2020 funded by FCT. A.L.R.S. thanks FCT/MCTES for her contract (CEECIND/01161/2017).

References

1. A. Ximello-Hernández, V. L. S. Freitas, M. D. M. C. Ribeiro da Silva; *J. Chem. Eng. Data* **2020**, *65*, 1968-1975.
2. V. N. Emel'yanenko, S. P. Verevkin, E. N. Burakova, G. N. Roganov, M. K. Georgieva; *Russ. J. Phys. Chem. A* **2009**, *83*, 598-603.

P29

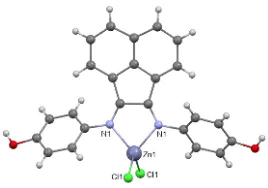
[Zn(Aryl-BIAN)Cl_2] based hybrid materials for visible light driven hydrogen production from water splitting

J. Maçãs,[1] V. Rosa,[1] C. S. B. Gomes,[1] I. Matos,[1] S. Gago[1]

[1] *LAQV-REQUIMTE, Department of Chemistry, NOVA School of Science and Technology, NOVA University of Lisbon, Portugal*
Email: j.macas@campus.fct.unl.pt

Nowadays around 95% of global production of hydrogen (H_2) comes from fossil fuels, resulting in H_2 with low purity and emission of harmful greenhouse gases. New technological energy approaches without carbon emissions are necessary to rapidly address the challenges of increasing energy needs, global warming, and limited fossil resources. Photocatalytic water splitting for H_2 production emerges as an environmentally friendly strategy utilizing clean and free sunlight as energy source. However, to be a competitive method, highly efficient, corrosion-resistant, recyclable and low-cost photocatalysts are required.[1]

In this work, a complex based on $ZnCl_2$ and a Aryl-BIAN (bis(*p*-hydroxyphenyl)acenaphthene) ligand was prepared and immobilized in different supports, such as onto mesoporous silica MCM-41 and onto a commercial sample of NORIT activated carbon GAC 1240W, through functionalization or adsorption. The complex was characterized by Single-Crystal X-ray Diffraction (SCXRD), Fourier Transform Infrared (FTIR), Nuclear Magnetic (NMR) and Diffuse Reflectance Spectroscopies (DRS) and the hybrid materials by powder X-ray diffraction (PRXD), Fourier Transform Infrared (FTIR) and Diffuse Reflectance Spectroscopies (DRS). Their photocatalytic activity for the production of H_2 from water splitting was tested using different sacrificial agents.[2]



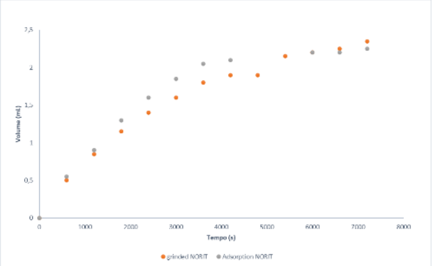


Fig. 1. [Zn(Aryl-BIAN)Cl_2] complex (left) and production of H_2 from water splitting, using zinc-based hybrid materials and a 300 W Xe lamp (right).

Acknowledgements: This work was supported by FCT/MCTES (LA/P/0008/2020 DOI 10.54499/LA/P/0008/2020, UIDP/50006/2020 DOI 10.54499/UIDP/50006/2020 and UIDB/50006/2020 DOI 10.54499/UIDB/50006/2020) through national funds.

References

1. X. Tao, Y. Zhao, S. Wang, C. Li and R. Li; *Chem. Soc. Rev*. **2022**, *51*, 3561–3608.
2. A. Koca and M. Sahin; *J. Chem. Educ.* **2003**, *80*, 1314–1315.

P30 Unveiling the potential of Zr- and Zn-MOFs as photocatalysts for H_2 production from water splitting

M. Lúcio, V. Rosa, C.S B. Gomes, S. Gago

LAQV-REQUIMTE, Department of Chemistry, NOVA School of Science and Technology, NOVA University of Lisbon, Portugal
Email: m.lucio@campus.fct.unl.pt

In this century, environmental pollution and global warming are some of impending issues plaguing the Human's future development and survival. The over-usage of fossil fuels is leading scientists to start looking for alternative energy sources, that are green, and sustainable, so hydrogen generated by water splitting is a promising candidate, using heterogenous photocatalysis and sunlight as its source, converting solar energy to chemical.[1]

The ultra-specific surface area, modifiable functionality, and tunable pores are a few characteristics that make metal-organic frameworks (MOFs) very attractive to use in several types of applications. However, they also present a few problems such as their low electronic conductivity, poor light absorption, and poor long-term cycling durability. Therefore, the choice in the metal node and functional groups in ligands are crucial for the catalytic performance of these porous compounds.[2,3]

In this work, we synthesized the Zr-MOFs (UiO-66 and UiO-66-NH_2) and other Zn-MOFs prepared from the reaction of triazine-tripyridine (TPT), a dicarboxylic acid (e.g. terephthalic acid, 2-amino-terephthalic acid, etc) and ZnI_2, and tested their performance in a photocatalytic system using Na_2S/Na_2SO_3 as sacrificial agent. These materials were characterized through powder X-ray diffraction (PXRD), infrared spectroscopy (IR), diffuse reflectance spectroscopy (DRS), and, when possible, by single-crystal X-ray diffraction (SCXRD).

These materials were also tested as crystalline sponges for the structural elucidation of non-crystalline compounds using the Crystalline Sponge Method.

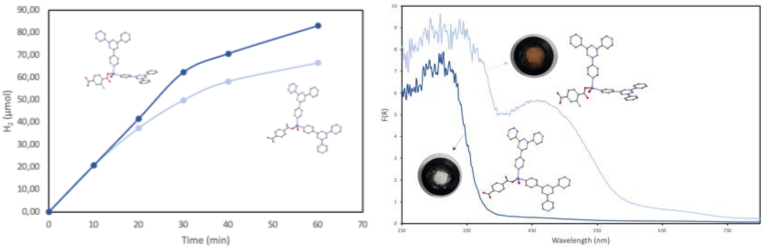


Fig. 1. (a) Zn-MOFs in H_2 production from water splitting, using Na_2S/Na_2SO_3 as a sacrificial agent and a 300 W Xe lamp. (b) Kubelka-Münk DRS for Zn-MOFs.

Acknowledgements: This work was supported by FCT/MCTES (LA/P/0008/2020 DOI 10.54499/LA/P/0008/2020, UIDP/50006/2020 DOI 10.54499/UIDP/50006/2020 and UIDB/50006/2020 DOI 10.54499/UIDB/50006/2020) through national funds.

References

1. L. Zeng, X. Guo, C. He, C. Duan; *ACS Catalysis* **2016**, *6*, 11, 7935-7947.
2. Y. Qian, F. Zhang, H. Pang; *Adv. Funct. Mater.* **2021**, *31*, 2104231.
3. L. Jiao, Y. Wang, H.-L. Jiang, Q. Xu; *Adv. Mater.* **2018**, *30*, 1703663.

P31 Polymer/tubule hydrogels: structural, thermodynamic and rheological characterization

R.L. Machado,[1] *E. Loureiro*,[1] *A.C. Gomes*,[2] *E.F. Marques*[1]

[1] *CIQUP, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre, 4169-007, Porto, Portugal*
[2] *Centre of Molecular and Environmental Biology (CBMA), School of Sciences, University of Minho, Campus of Gualtar, 4710-057, Braga, Portugal*
Email: com efmarque@fc.up.pt

Hydrogels are three-dimensional entangled networks with a myriad applications in areas such as drug delivery, tissue engineering, water purification and sensing. In drug delivery, they are used not only as active drug reservoirs but also as scaffolds for nanocarriers like micelles, vesicles or tubules. Herein, we have developed a thermosensitive polymer/tubule hydrogel for prospective localized drug-delivery based on an amphiphilic block copolymer (F127) and two lysine-based surfactants (14Lys10 and 10Lys14). F127 exhibits thermal gelation due to a micelle-to-cubic liquid crystal phase transition. The lysine-based surfactants also form a temperature-sensitive gel through a network of entangled tubular structures. These tubules exhibit a phase transition to micelles (10Lys14) or vesicles (14Lys10) upon heating, causing the destruction of the gel matrix.[1,2] In this work, F127 is employed as a scaffold for dispersing the surfactant nano/microtubes, hence leading to a hybrid polymer/tubule gel. This hybrid shows distinct physicochemical properties from the neat components. In presence of F127, the melting temperature of the tubules decreases significantly. Rheological studies provide further insight into the hybrid gel evolution as temperature is varied in the range 5-35 ºC. A complex variation of the storage (G') and loss (G'') moduli, with two crossover points, is observed, one related to tubule melting and another with the formation of the polymer cubic phase (Fig. 1), confirming the predominance of a surfactant-based gel at lower temperature and a polymer-based gel at higher. Despite the presence of surfactant, the polymer-based gel retains its structural recovery capabilities. Overall, these features are relevant for the desired delivery goal.

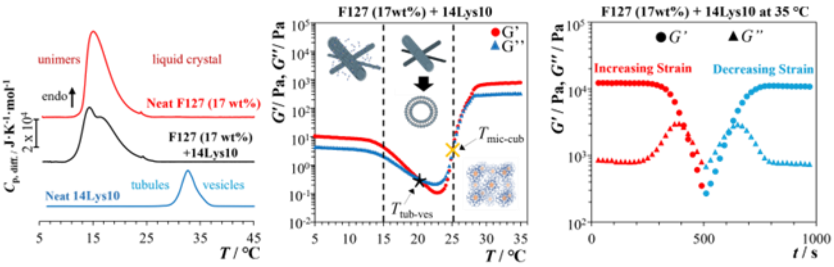


Fig. 1. (a) Zn-MOFs in H_2 production from water splitting, using Na_2S/Na_2SO_3 as a sacrificial agent and a 300 W Xe lamp. (b) Kubelka-Münk DRS for Zn-MOFs.

Acknowledgements: We thank FCT for financial support through CIQUP (UID/QUI/0081/2020), IMS (LA/P/0056/2020) and CBMA (UID/BIA/04050/2020), and PhD studentship 2021.06971.BD.

References

1. I. S. Oliveira, M. Lo, M. Araújo, E. F. Marques; *Soft Matter* **2019**, *15*, 3700-3711.
2. I. S. Oliveira, R. Machado, M. Araújo, A. Gomes, E. F. Marques; *Chem. Eur. J,* **2021**, *27*, 692-704.

P32 Research on the volatility and solubility of two methyl halogenated benzoates

G. P. León, B. D. A. Pinheiro, A. R. R. P. Almeida, M. J. S. Monte

Research Centre in Chemistry of University of Porto (CIQUP), Institute of Molecular Sciences (IMS), Department of Chemistry and Biochemistry, Faculty of Sciences of University of Porto (FCUP), Rua do Campo Alegre, P-4169-007, Porto, Portugal
Email: gaston.leon@fc.up.pt

Studying the volatility, phase transitions, and solubility of organic compounds is essential for understanding their environmental fate, enabling better management of pollution risks associated with their use. Knowledge of these properties is crucial for assessing the environmental mobility of these substances and implementing effective pollution control strategies.[1] This research aims to provide essential data on the experimental determination of those important physico-chemical properties, facilitating the assessment of mobility characteristics and environmental fate of Methyl 2,5-dichlorobenzoate and Methyl 2,5-dibromobenzoate (Fig. 1). The study involves measuring the volatility (vapor pressures) and phase transitions of these compounds, as well as their solubility in water (Sw) at 298.15 K. Vapor pressure measurements were carried out using a diaphragm manometer static method and/or a Knudsen effusion technique,[2] while solubility was determined using the shake flask method[3] and UV-vis spectrophotometry. The thermal analysis of the two compounds was performed using differential scanning calorimetry and their fusion properties and crystalline heat capacities were determined.

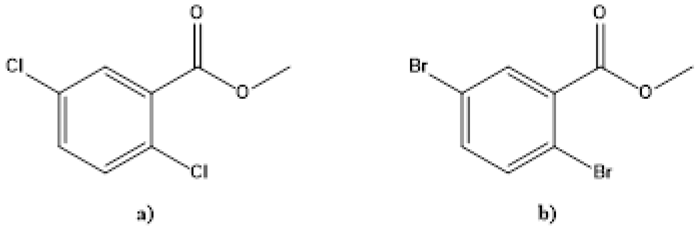


Fig. 1. a) Methyl 2,5-dichlorobenzoate and b) Methyl 2,5-dibromobenzoate

Acknowledgements: This work was supported by the Fundação para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Sciences, University of Porto (Project UIDB/00081/2020) and IMS - Institute of Molecular Sciences (LA/P/0056/2020)). GPL thanks CIQUP for his contract under project CIQUP-UIDP/00081/2020 funded by FCT. BDAP thanks FCT for the award of a PhD research grant (UI/BD/152715/2022). ARRPA is financed by national funds through the FCT-I.P. DL 57/2016/CP1454/CT0006: https://doi.org/10.54499/DL57/2016/CP1454/CT0006

References

1. M. F. F. Bernardes, M. Pazin, L. C. Pereira, D. J. Dorta; Impact of Pesticides on Environmental and Human Health. *Toxicology Studies - Cells, Drugs and Environment;* IntechOpen: London, 2015.
2. M. J. S. Monte, L. M. N. B. F. Santos, M. Fulem, J. M. S. Fonseca, C. A. D. Sousa; *J. Chem. Eng. Data.* **2006**, *51*, 757-766.
3. A. Veseli, S. Žakelj, A. Kristl; *Drug Dev. Ind. Pharm.* **2019**, *45*, 1717-1724.

P33 Sustainable technology for protein extraction from *Tenebrio molitor* flour

P. Moleiro,[1] *L.C. Branco,*[2] *A.Q. Pedro,*[1] *A.P. Tavares,*[1] *M.G. Freire,*[1]

[1]CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Aveiro, Portugal.
[2]Associated Laboratory for Green Chemistry (LAQV) of the Network of Chemistry and Technology (REQUIMTE), NOVA School of Science and Technology, Caparica, Portugal.

Introduction: Regarding the Earth's population growth rate, it is evident that the demand for protein will continue to increase, leading to impacts in terms of sustainability across many sectors. Due to this, it is urgent to find efficient alternative protein sources, where insects such as *Tenebrio molitor* (yellow mealworm) are prominent candidates. *T. molitor* is highly rich in proteins and other nutrients when compared to other usual sources of proteins (poultry and cattle). Another advantage is the low environmental impact and economic costs of production and maintenance, which are crucial to comply with the global protein needs. A concern when using insects as food is consumer acceptability, which in the West is still a hurdle. One way to overcome this concern is by carrying out protein extraction and formulating new food products with higher tolerance by the end user. **Methodology:** Design of experiments (DOE) was applied to optimize the extraction operating conditions, namely temperature, time of extraction, and salt concentration in aqueous solution. The solvent was mixed with the yellow mealworm flour, the solution was centrifuged, and the supernatant was collected for further analysis of the extracted proteins. After this, isoelectric precipitation was applied to recover the proteins in solution, followed by centrifugation, and freezing the pellet. Then, the samples were to be freeze-dried to obtain a pure dried protein powder. Protein in solution was quantified by the BCA method, whereas the precipitated protein was determined by weight. In the extracted samples, the total protein profile was analysed by SDS-PAGE. **Results:** The best results were achieved with an extraction yield in solution ranging between 44 and 49 g of protein per 100 g of insect flour. In the final protein powder form, the best results correspond to 25 g of protein per 100 g of insect flour. **Conclusion:** From the obtained results, the possibility of integrating insects' protein into new food products is a promising strategy. Scaling-up tests are being carried out to address the technology potential at the industrial level.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI 10.5499/UIDB/50011/2020), UIDP/50011/2020 (DOI 10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI 10.54499/PA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC). This study was funded by the PRR - Recovery and Resilience Plan and by the NextGenerationEU funds at Universidade de Aveiro, through the scope of the Agenda for Business Innovation "InsectERA" (Project no. 20 with the application C644917393-00000032). Augusto Q. Pedro and Ana P. M. Tavares acknowledge FCT for the research contracts under the Scientific Stimulus – Individual Call CEECIND/2020/02599 (DOI 10.54499/2020.01867.CEECIND/CP1589/CT0013) and CEECIND/2020/01867 (DOI 10.54499/2020.02599.CEECIND/CP1589/CT0023), respectively.

P34 Adsorption and release of NO and H_2S from a zinc BioMOF

J. Pires,[1] *M. Pinto,*[2] *T. K. Tajnšek,*[3,4] *M. Mazaj,*[3] *M. Lopes,*[2] *M. Batista*[1]

[1] *CQE, Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016, Lisboa, Portugal*
[2] *CERENA, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, 1049-001, Lisboa, Portugal*
[3] *National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia*
[4] *EaStCHEM School of Chemistry, Purdie Building, North Haugh, St Andrew, UK*
Email: jpsilva@ciencias.ulisboa.pt

Small gaseous molecules such as nitric oxide (NO) and hydrogen sulfide (H_2S) are gasotransmitters in the human body, where they accomplish a myriad of signalling functions. In this way, NO and H_2S play key roles in a variety of physiological processes, including vasodilation, angiogenesis, immune and inflammatory responses, and regulation of gene transcription.[1] This wide range of functions has triggered intensive research on the delivering of NO and H_2S. Exogenous administration of gases in controlled amounts and for a defined period of time may be beneficial as a potential therapeutic approach to replenish or regulate local NO and H_2S levels. Porous materials have emerged as a possibility of being carriers for NO and H_2S delivery. Following our previous studies in this field, [1,2] we herein study the properties of a zinc-based Metal-Organic Framework – BioNICS-1, whose structure and other characteristics are described elsewhere,[3] for the adsorption and release on NO and H_2S. Fig. 1 shows and example of a release curve of NO from BioNICS-1.

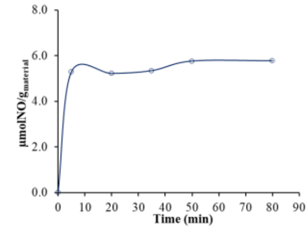


Fig.1 Release of Nitric Oxide from BioNICS-1 MOF using the Oxyhemoglobin Assay.[4]

Acknowledgements: This research was financed by Fundação para a Ciência e a Tecnologia (FCT) in the scope of the projects UIDB/00100/2020 (CQE), UIDB/04028/2020 (CQE), UIDB/04028/2020, and UIDP/04028/2020 (CERENA), and the Institute of Molecular Sciences (IMS) Associate Laboratory funded by FCT through project LA/P/0056/2020 and the project 2022.05605.PTDC (DOI 10.54499/2022.05605.PTDC).

References

1. R. V. Pinto, S. Carvalho, F. Antunes, J. Pires, M. L. Pinto; *ChemMedChem* **2022**, *17*, e202100429.
2. R. V. Pinto, S. Wang, S. R. Tavares, J. Pires, F. Antunes, A. Vimont, G. Clet, M. Daturi, G. Maurin, C. Serre, M. L. Pinto; *Angew. Chem. Int. Ed.* **2020** *59*, 5135-5143.
3. T. K. Tajnšek, E. S. Grape, T. Willhammar, T. A. Jelić, U. Javornik, G. Dražić, N. Z. Logar, M. Mazaj; *Commun. Chem.* **2022**, *5*, 24.
4. M. Feelisch, D. Kubitzek, J. Werringloer, In Methods in Nitric Oxide Research; Feelisch, M., Stamler, J. S., Eds.; John Wiley & Sons, Ltd.: New York, 1996; pp 455-478.

P35 Modification of carprofen palatability via formation of multicomponent solid forms

P. M. S. Inácio,[1,2] J. A. Baptista,[1] T. M. R. Maria,[1] R. A. E. Castro,[1,2] M. E. S. Eusébio,[1] J. Canotilho[1,2]

[1] Coimbra Chemistry Center/Institute of Molecular Sciences, Department of Chemistry, University of Coimbra, Portugal
[2] Faculty of Pharmacy, University of Coimbra, Portugal
Email: pedroinacio_95@outlook.com

Carprofen is a non-steroidal anti-inflammatory drug used in veterinarian medicine, most commonly in dogs, for the treatment of inflammation and pain relief. Oral administration of this medicine can be a challenge due to its inherent bitterness and overall low palatability.[1]

The main objective of this study is to investigate multicomponent molecular solids, such as cocrystals, using coformers with known pleasant flavors, in order to increase the palatability of carprofen.

From a local database, compounds that could act as coformers for co-crystallization with carprofen were selected using the *COSMOquick* software,[2] evaluating the number of rotatable bonds of the API and the coformer and the excess enthalpy of the undercooled melt made up of both components. The best screening results were filtered out, taking into account only flavoring agents, and the following candidates were selected: pyrazine, 2-methylpyrazine, 2,6-dimethylpyrazine, 2-acetylpyrazine, methyl nicotinate, vanillin, thymol, menthol and citric acid.

To attempt co-crystallization, mechanochemical methods, liquid-assisted and neat grinding, were applied, using a ball mill machine, mortar and pestle. Recrystallization by evaporation from ethanol solutions was also performed. The samples obtained were characterized by differential scanning calorimetry, Fourier transform infrared spectroscopy and powder X-ray diffraction.

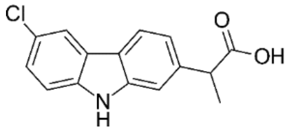


Fig.1 Chemical structure of carprofen [(RS)-2-(6-Chloro-9H-carbazol-2-yl)propanoic acid].

Acknowledgments: Coimbra Chemistry Center/Institute of Molecular Science (CQC-IMS) is supported by national funds, FCT–Foundation for Science and Technology, project UID/QUI/00313/2020. The authors thank Unidade de Controlo de Qualidade de Produtos Farmacêuticos, Faculty of Pharmacy, University of Coimbra, for the use of the XRPD facility. J.A.B. thanks FCT for financial support (grant UI/BD/150859/2021).

References

1. A. G. Thombre; *Adv. Drug Deliv. Rev*. **2004**, *56*, 1399–1413.
2. C. Loschen, A. Klamt; *J. Pharm. Pharmacol*. **2015**, *67*, 803–811.

P36 Computational-aided evaluation of repurposing pediocin-like bacteriocins as antifungal agents against *Candida albicans*

I.R. Blanco,[1,2] *R.P.S. Oliveira*,[1] *M.M. Pereira* [2]

[1] *Departament of Biochemical and Pharmaceutical Technology, Faculty of Pharmaceutical Sciences, University of São Paulo, São Paulo, Brazil*
[2] *University of Coimbra, CERES, Department of Chemical Engineering, Coimbra, Portugal*
Email: iagoblanco@usp.br

Over the last years, the search for safer and more efficient alternatives to the traditional antimicrobial strategies has led to great advances in peptide research. Bacteriocins, which are natural peptides produced by various microorganisms, are able to inhibit pathogens and induce health-promoting effects to their hosts, with better biocompatibility and reduced side effects. On the other hand, antimicrobial strategies such as currently applied antifungals, exhibit disadvantages including lower specificity, and higher toxicity and antimicrobial resistance. The class of pediocin-like bacteriocins is known for its high bioactivity against the foodborne pathogen Listeria. However, few studies investigate broader activity of these antimicrobials in different contexts. Based on this, the aim of this work is to evaluate the potential antifungal activity of pediocin-like peptides through molecular simulations. The receptor structure of secreted aspartic protease (SAP) from *Candida albicans* was retrieved from Protein Data Bank (PDB: 3PVK) and docked to four peptides (pediocin-like bacteriocins) produced by the probiotic *Pediococcus pentosaceus*: pediocin PA-1, penocin A, coagulin A and plantaricin 423, using HDock. Then, the interactions and surface accessibilities of protein-peptide complexes were assessed, and MM/GBSA was calculated to identify the binding energies of all complexes obtained. According to the results obtained, the complexes of pediocin-SAP display binding energies ranging from -19.97 to 5.30 kcal.mol^{-1}. The main interaction observed was electrostatic. Thus, the repurposing here proposed shows that pediocin-like bacteriocins exhibit great potential as antifungal agents targeting SAP from *C. albicans*.

Acknowledgements: M. M. Pereira acknowledges the financial support of FCT, Portugal, within the projects DOI:10.54499/UIDB/00102/2020 (Base funding) and DOI: 10.54499/UIDP/00102/2020 (Programmatic funding); I. R. Blanco and R. P. S. Oliveira acknowledge support of FAPESP projects 2023/17741-5, 2022/07304-4 and 2018/25511-1.

P37 Optimizing dopamine polymerization through enzymatic pathways in aqueous biphasic systems

F.F. Magalhães,[1] M.L. Alfier,[2] L. Panzella,[2] M.G. Freire,[1] A.P.M. Tavares[1]

[1] CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Aveiro, Portugal
[2] Department of Chemical Sciences, University of Naples Federico II, Naples, Italy
Email: aptavares@ua.pt

Laccase, a multicopper oxidase and eco-friendly biocatalyst, is attracting global interest for its diverse applications in biotechnology, particularly in synthesizing diverse polymers.[1] Among them, polydopamine (PDA) is a high-value biopolymer crafted through dopamine polymerization, prized for its role in modifying surfaces with biomedical benefits.[2] In contrast to the conventional methods of dopamine polymerization, which are generally time-consuming and may produce PDA films with poor stability, the production of PDA using laccase improves the efficiency and rate of the process while embracing green chemistry principles.[3] However, developing novel methods for biocatalyst recovery and reuse is relevant for industrial scale. In this field, aqueous biphasic systems (ABS), which are liquid-liquid systems mainly composed of water, appear a promising alternative since they provide a mild and biocompatible environment for biocatalysts.[4] This study dives into optimizing several parameters, including dopamine and laccase concentration, for the enzymatic production of PDA and film deposition into glass using ABS (composed of polymer and salt) as a reaction media. Biocatalyst recovery and reuse were explored in the ABS. Compared to traditional methods, ABS-driven enzymatic polymerization of dopamine proves more efficient, requiring lower dopamine concentrations for film formation. Using ABS in polymerization enzymatic reactions is a promising tool to elevate enzymatic polymerization processes.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials,UIDB/50011/2020(DOI10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC). Ana Tavares acknowledges FCT for the research contract CEECIND/01867/2020 (10.54499/2020.01867.CEECIND/CP1589/CT0013). Flávia Magalhães acknowledges the SPQ/FCT PhD grant SFRH/BD/150669/2020.

References

1. R. Debnath, et al.; *Biocatal. Agric. Biotechnol*. **2020**, *26*, 101645.
2. Y. H. Ding, et al.; *Biosurf. Biotribology* **2016**, *2*, 121–136.
3. O.Y. Milyaeva, et al.; *Colloids Surfaces A Physicochem. Eng. Asp*. **2020**, *599*, 124930.
4. M. G. Freire, et al.; *Chem. Soc. Rev*. **2012**, *41*, 4966–4995.

P38 Structural, optical, and thermal properties of $BiVO_4$

B. Norte,[1] *A. C. Estrada,[1] H. I. S. Nogueira,[1] T. Trindade[1]*

[1] *Department of Chemistry-CICECO, Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal*

Email: bernardonorte51@ua.pt

Bismuth(III) vanadate ($BiVO_4$) is a material of great technological relevance associated with several applications, namely as a yellow pigment with remarkable stability. $BiVO_4$ exists in three natural polymorphs - *pucherite*, *dreyerite* and *clinobisvanite*. The monoclinic *clinobisvanite* (or monoclinic *scheelite*) and tetragonal *dreyerite* (or tetragonal *zircon*) are also obtained synthetically, whereas the orthorhombic polymorph *pucherite* exists only naturally.[1] In addition to these polymorphs, synthetic $BiVO_4$ is also known to crystallize in the tetragonal *scheelite* structure, which shows a similar structure to monoclinic *scheelite* $BiVO_4$ with tetrahedrally coordinated V(V) and eightfold coordinated Bi(III).[2,3] The performance of $BiVO_4$ pigments can still be improved by acquiring a deeper understanding of its structural and optical properties, which are strongly dependent on the materials preparation.

In this work, we have revisited the structural, optical and thermal properties of $BiVO_4$ chemically deposited on distinct inorganic substrates.[2] A series of spectroscopic and diffraction studies have been carried out to probe structural modifications on $BiVO_4$ materials submitted to distinct experimental conditions, namely by varying the temperature and the nature of the underlying substrate. In particular, it will be discussed the application of Raman spectroscopy and confocal Raman spectroscopy to get new insights into such structural modifications, which have been associated to changes on the optical properties of $BiVO_4$ materials.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI 10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC). Ana C. Estrada also thanks FCT for her research contract funded by National funds (OE), in the scope of the framework contract foreseen in the numbers 4, 5, and 6 of article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19 (DL 57/2016/CP1482/CT0007; DOI 10.54499/DL57/2016/CP1482/CT0007).

References

1. D. Ke, T. Peng, L. Ma, P. Cai, K. Dai; *Inorg. Chem*. **2009**, *48*, 4685.
2. J. L. Lopes, A. C. Estrada, S. Fateixa, N. A. Sobolev, A. L. Daniel-da-Silva, T. Trindade; *J. Photochem. Photobio*. A **2024**, *447*, 115174.
3. D. Trung, T. Trinh, W. Khanitchaidecha, D. Channei; *Res. Chem. Intermed*. **2019**, *45*, 5217.

P39

Thermodynamic and kinetic parameters of the crystallization of probucol and structurally related compounds from ethanol solutions

J. A. Baptista,[1] R.A.E. Castro,[1,2] J. Canotilho,[1,2] M.T.S. Rosado,[1] M.E.S. Eusébio[1]

[1] *Coimbra Chemistry Center/Institute of Molecular Sciences, Department of Chemistry, University of Coimbra, Portugal*
[2] *Faculty of Pharmacy, University of Coimbra, Portugal*
Email: jabaptista@qui.uc.pt

Crystallization from solutions is widely used in the pharmaceutical industry, in the final steps of active pharmaceutical ingredients (APIs) synthesis and purification. The nucleation of an API is a key step in the development of a crystallization process, since it controls the crystal size, morphology, solid form obtained and the particle size distribution.

In this work, results are presented for thermodynamic and kinetic parameters of the nucleation processes of the antihyperlipidemic drug probucol (PROB) and two structurally related compounds, tetra(*ter*)butyl bisphenol F (TB-BPF) and tetramethyl bisphenol A (TM-BPA) (Fig. 1), in ethanol, obtained from experimental measurements of induction times (t_{ind}).

The solubilities of these compounds in ethanol were determined at various temperatures, using gravimetric or polythermic methods. The induction times were determined using a small volume of solution (1 mL), placed in a benchtop crystallization system (Technobis Crystal16), at different temperatures and for various supersaturation ratios. In order to determine the probabilistic distribution of t_{ind}, 80 to 100 crystallization experiments were performed for each temperature and supersaturation ratio. The nucleation rate (J), according to the classical nucleation theory,[1] as well as the thermodynamic exponential parameter (B) and the effective interfacial energy (γ_{EF}), were determined and a comparison is made of the results obtained for the three compounds.

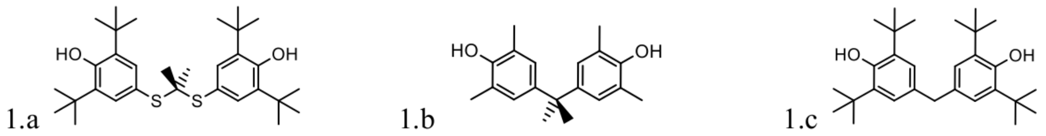


Fig.1 Structural formula of: 1.a. PROB; 1.b. TM-BPA; 1.c. TB-BPF.

Acknowledgements: J.A.B. thanks FCT - Fundação para a Ciência e a Tecnologia for financial support (grant UI/BD/150859/2021). Coimbra Chemistry Center/Institute of Molecular Science (CQC/IMS) is funded by national funds through FCT, project UIDB/00313/2020. Thanks are due to UCQFarma, Faculty of Pharmacy, University of Coimbra, for the use of the XRPD facility.

References

1. S. Jiang, J. H. ter Horst; *Cryst. Growth Des*. **2011**, *11*, 256–261.

P40 Superhydrophobic Materials for Oil/Water Separation based on Supported Ionic Liquids

J.C.F. Nunes, M.G. Freire, A.P.M. Tavares, M.C. Neves

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

Materials comprising a water contact angle (WCA) above 150° and a roll-off angle below 10° are designated as superhydrophobic.[1] These materials have high potential to several relevant applications, e.g., anti-bacterial and oil/water separation.[1]

Oil spill accidents and industrial oily wastewater have emerged as serious threats to the environment and public health.[1,2] Membrane separation is a widely used, easy, and environmentally friendly oil/water separation method.[2]

Supported ionic liquid (SIL), where the IL are covalently bonded to the support, enable unique interactions with target compounds.[3] These features and the capacity of ILs to be designed[3] make SIL suitable candidates for membrane separation.

In this study, SIL materials based on cellulose functionalized with quaternary ammonium cations with different alkyl chain lengths and chloride as the counterion were synthesized, and chemically, thermally, and morphologically characterized. The resulting SIL materials demonstrated superhydrophobic and oleophilic properties. The findings indicate that these cost-effective SILs can significantly contribute to oil/water separation.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI 10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC). This work was supported by the project POCI-01-0145-FEDER-031268-funded by FEDER through COMPETE2020, and by national funds (OE) through FCT/MCTES. Ana P. M. Tavares and Márcia C. Neves acknowledge FCT for the research contract CEECIND/2020/01867/CP1589/CT0013 (DOI 10.54499/2020.01867.CEECIND/CP1589/CT0013) and CEECIND/00383/2017/CP1459/CT0031 (DOI 10.54499/CEECIND/00383/2017/CP1459/CT0031), respectively. João C. F. Nunes acknowledges SPQ and FCT for the PhD fellowship SFRH/BD/150671/2020 (DOI 10.54499/SFRH/BD/150671/2020).

References

1. M. Z. Khan, J. Militky, M. Petru, B. Tomková, A. Ali, E. Tören, S. Perveen; *Eur. Polym. J*. **2022**, *178*, 111481.
2. A. Xie, J. Cui, Y. Chen, J. Lang, C. Li, Y. Yan, J. Dai; *Surf. Coat. Technol.* **2019**, *361*, 19–26.
3. E. V. Capela, J. Bairos, A. Q. Pedro, M. C. Neves, M. R. Aires-Barros, A. M. Azevedo, J. A. P. Coutinho, A. P. M. Tavares, M. G. Freire, *Sep. Purif. Technol.* **2023**, *305*, 122464.

P41 Phase behavior and structural characterization of photosensitive lipid/chalcone liposomes

D. Moreira,[1] *I. S. Oliveira*,[1] *N. Basílio*,[2] *E. F. Marques*[1]

[1] *CIQUP, IMS, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto 4169-007, Porto, Portugal*

[2] *LAQV-REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516, Caparica, Portugal*

Email: efmarque@fc.up.pt

Liposomes are self-assembled closed bilayers (vesicles) formed by lipids, which encapsulate a solvent pocket. These colloidal structures have enormous relevance as membrane models for biophysical studies and are also applied as nanoreactors and as scaffolds for synthesizing nanoparticles. Their most widespread application is in drug delivery, where they improve the efficiency and efficacy of therapeutic agents.[1] Stimuli-responsive liposomes, particularly those responsive to light, offer precise spatiotemporal control over drug release.[2] This work focuses on developing light-responsive liposomes composed of a zwitterionic phospholipid (DPPC) and novel chalcone-based amphiphiles. The latter act as stimuli-sensitive elements as they are part of the multistate chemical network of flavylium compounds, previously explored in smart drug delivery systems (Fig. 1a).[2] This study investigates the impact of the different light-sensitive chalcones, varying in charge and alkyl chain length (Fig. 1b), on the properties of the liposomes, resorting to microDSC, electrophoretic light scattering, light microscopy, and UV-vis and fluorescence spectroscopies. Results show that the chalcone compounds enhance the colloidal stability of the liposomes, decrease their gel-to-liquid crystal phase transition temperature, and enhance their loading properties towards a hydrophilic probe. Moreover, light irradiation further decreases the fluidization temperature of the liposomes, which could prove key to their potential as smart nanocarriers.

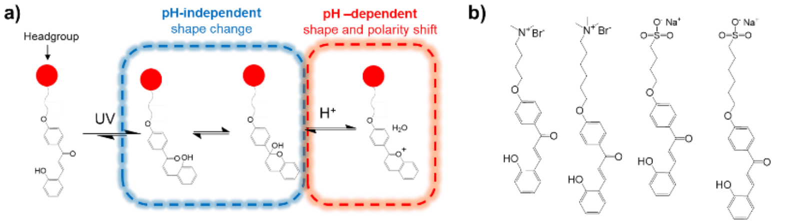


Fig. 1. a) chalcone/flavylium interconversion reactions; b) molecular structures of chalcone derivatives employed in this work.

Acknowledgements: We thank FCT, FEDER/COMPETE and P2020|COMPETE for financial support through projects POCI-01-0145-FEDER-032351 (PhotoSAN), 2022.05543.PTDC (Smart4Vir), UID/QUI/0081/2020, IMS (LA/P/0056/2020), and UID/QUI/50006/2019. Dmitriy Moreira also acknowledges financial support from FCT through the PhD grant 2021.06067.BD.

References

1. E. Rideau, R. Dimova, P. Schwille, F. R. Wurm, K. Landfester; *Chem. Soc. Rev.* **2018**, *47*, 8572-8610.
2. D. Moreira, O. Regev, N. Basílio, E. F. Marques; *J. Colloid Interface Sci.* **2023**, *650*, 2024-2034.

P42 The ROADMAP project – when Chemistry and Art meet for *the greater good*

C. Miguel,[1] S. Bottura-Scardina,[1] A.T. Caldeira,[1] P. Flor,[2] A. Candeias[1]

[1] HERCULES Laboratory, IN2PAST Associate Laboratory and City University of Macau Chair in Sustainable Heritage, University of Évora, Palácio do Vimioso, Largo Marquês de Marialva 8, 7000-809 Évora, Portugal

[2] Universidade Aberta, Rua da Escola Politécnica, n.º 147, 1269-001 Lisboa, Portugal and IHA-NOVA/FCSH, Instituto de História da Arte, NOVA University, Colégio Almada Negreiros, Campus de Campolide, 1099-032 Lisboa, Portugal

Email: cpm@uevora.pt

More than 450 years after the death of the great Renaissance artist António de Holanda (c. 1480-1557), a transnational multi-institutional research consortium – the ROADMAP project - is, for the first time, developing an integrated and interdisciplinary study of his illuminated masterpieces spread by several Libraries across Europe. From the study of iconographic references present in the codices to the underdrawings and the painting and material techniques, the project is profusely analysing and comparing the selected masterpieces for the establishment of a chronological perspective of the artwork of António de Holanda. For this, in-situ non-invasive analyses are being used, including elemental (h-EDXRF), molecular (UV-Vis-NIR-FORS) and chemical imaging (MA-EDXRF, hyperspectral imaging and IR reflectography) aiming at providing data to better understand the creative process of the painter and of his workshop. Special attention is being given to the analyses of the use of a possible binding media formulations transversal to Holanda's illuminated manuscripts, based on the analysis of UV-Vis-NIR spectra following a chemometric approach based on Principal Component Analysis, and to the evaluation of a special *modus opperandi* of creating illuminations and paints by the António de Holanda in the context of the art of illuminating manuscripts during the Renaissance period.

Fig. 1. MA-EDXRF analysis of the *Crónica de D. Afonso Henriques* (16th c., MCCG).

Acknowledgements: The authors thank the FCT – Fundação para a Ciência e a Tecnologia, I.P. for supporting the costs involving the research through the ROADMAP project (PTDC/ART-HIS/0985/2021) and the UIDB/04449/2020 and UIDP/04449/2020 projects. Catarina Miguel thank the DL57/2016/CP1372/CT0012 (Norma Transitória).

P43 The curious case of $[C_8C_1im]Cl+H_2O$ system

M. Tariq,[1] *J.M.S.S. Esperança,*[1] *J.N.C. Lopes,*[2] *L.P.N. Rebelo*[1]

[1] *LAQV/REQUIMTE, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, Portugal*
[2] *CQE, Instituto Superior Técnico, Universidade de Lisboa, Portugal*
Email: tariq@fct.unl.pt

Ionic liquids (ILs) with longer alkyl chain lengths and appropriate size of ions are known to show identical behavior as ionic surfactants in aqueous solutions.[1] One of the advantages of IL-type surfactants (especially those, which are liquid around room temperature) is that they can be mixed with water in the entire composition range. Such cases are very interesting from the fundamental point of view that allow to study various structural organizations in different concentration regimes.[2] In this work we have chosen one such amphiphilic IL, 1-octyl-3-methylimidazolium chloride, $[C_8C_1im]Cl$ that is completely miscible with water to demonstrate using several techniques that it forms distinct thermo-responsive structures while mixed in different proportions along the entire composition range covering from pure IL to water ($0>x_{IL}>1$).

In very dilute regimes ($0.1>x_{IL}$) the IL self-assemble and forms micelles like aggregates as shown by density measurements. On further increase of the IL concentration in the mixture ($0.10>x_{IL}>0.40$), we encountered a gel like structure that is thermo responsive and can be cleared off and brought back using thermal switching. The pure IL just shows a glass transition temperature and do not crystallize, however the phase behavior of the samples ($0.10>x_{IL}>0.40$), was characterized using differential scanning calorimetry (DSC). Extensive rheological characterization of gels and those of pre- and post-gel samples reveal that the gel is quite mature and has distinct structure and properties highly dependent on the composition and temperature. The water-rich mixtures show a Newtonian behaviour but the IL-rich mixtures ($0.7>x_{IL}>1$) exhibit shear-thinning effects, which seem highly temperature dependent. The polarized optical microscopy (POM) was used to record the images during sol-gel transitions, which provides further insights into the structures present during heating/cooling cycles. These gels were stored in air tight vials and were found stable over years.

Fig. 1. Thermoresponsive sol-gel transition of $[C_8C_1im]Cl+H_2O$ sample.

Acknowledgements: This work was partially supported by the Associate Laboratory for Green Chemistry - LAQV which is financed by national funds from FCT/MCTES (UIDB/50006/2020 DOI 10.54499/UIDB/50006/2020 and UIDP/50006/2020 DOI 10.54499/UIDP/50006/2020 and LA/P/0008/2020 DOI 10.54499/LA/P/0008/2020). Authors would like to thank Dr. Vitor Alves and Dr. Ana Duarte for providing access to Rheometer and POM.

References

1. K. Shimizu, M. Tariq, A.A. Freitas, A.A.H. Pàdua, J.N.C. Lopes; *J. Braz. Chem. Soc.* **2016**, *27*, 349-362.
2. M. Tariq, A. Podgoršek, J.L. Ferguson, A. Lopes, M.F.C. Gomes, A.A.H. Pàdua, L.P.N. Rebelo, J.N.C. Lopes; *J. Coll. Int. Sci,* **2011***, 360*, 606-616.

P44 Effect of isotopic substitution on the phase behaviour and nucleation of CO_2 hydrates

M. Tariq,[1] *M.R.C. Soromenho,*[1] *M.M. Piñeiro,*[2] *M. Pérez-Rodríguez,*[2] *D. Kumar,*[3] *A. Rodriguez, F.J. Deive, J.M.S.S. Esperança*[1]

[1] *LAQV/REQUIMTE, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, Portugal*
[2] *CINBIO, Departamento de Fisica Aplicada, Universidade de Vigo, España*
[3] *Department of Chemical Engineering, National Taiwan University, Taiwan*
[4] *Departamento de Enxeñería Química, Universidade de Vigo, España*
Email: tariq@fct.unl.pt

Gas hydrates (GHs) are crystalline inclusion compounds where small gas molecules (guests) are accommodated within the three-dimensional hydrogen bond network of water (host). GHs are generally stable at low temperatures and moderately high pressures. Different size of guest gas molecules forms different hydrate structures.[1] The effect of additives on hydrate phase behaviour and formation is well documented but studies concerning the effect of different hosts are scarce.[2]

In this work, we have studied the CO_2 hydrate phase equilibria and nucleation phenomena using H_2O, D_2O and their binary mixtures as hosts. It was found that the phase equilibrium shifts +2.3 K in H_2O compared to D_2O indicating a significant effect of isotopic substitution. These shifts were successfully calculated with triphasic equilibrium temperature variation estimated ones using the MD simulations and are found to be in good agreement.

A constant cooling method was used to obtain the onset nucleation temperatures at an initial pressure of 3.5 MPa which indicates that nucleation always occurs between the melting temperature and the temperature of the maximum density (TMD) of the corresponding system.

The results reported in this work indicates the magnitude of the isotopic effect on CO_2 hydrates formation and dissociation, which may have implications towards the application of hydrate technology for separation and purification processes.

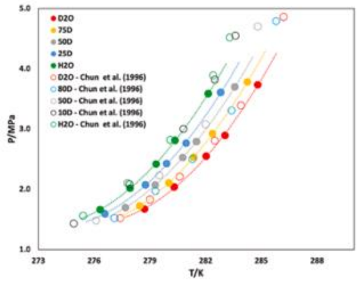


Fig. 1. CO_2 hydrate-liquid-vapour equilibria in H_2O, D_2O and their binary mixtures along with the values reported in the literature.[2]

Acknowledgements: Fundação para a Ciência e Tecnologia, FCT/MCTES (Portugal) for financial support through project PTDC/EQU-EQU/32050/2017. This work was partially supported by the Associate Laboratory for Green Chemistry - LAQV which is financed by national funds from FCT/MCTES (UIDB/50006/2020 DOI 10.54499/UIDB/50006/2020 and UIDP/50006/2020 DOI 10.54499/UIDP/50006/2020 and LA/P/0008/2020 DOI 10.54499/LA/P/0008/2020).

References

1. E.D. Sloan Jr.; *Nature* **2003**, *426*, 353-359.
2. M.K. Chun, J.H. Yoon, H. Lee; *J. Chem. Eng. Data* **1996**, *41*, 1114-1116.

P45 Experimental and computational study into the thermochemistry of furfurylamine and 5-methylfurfurylamine

L. M. P. F. Amaral,[1] *A. R. R. P. Almeida,*[2] *M. A. V. Ribeiro da Silva*[2]

[1]*LAQV/REQUIMTE*
[2]*Research Centre in Chemistry of University of Porto (CIQUP), Institute of Molecular Sciences (IMS) Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre, P-4169-007 Porto, Portugal*
Email: ana.figueira@fc.up.pt

The need to transition from fossil fuels to renewable energy sources is driven by factors such as fluctuating prices, resource depletion, and environmental concerns. Lignocellulosic biomass emerges as a compelling alternative for chemical production due to its renewable nature, abundant availability, and minimal impact on food resources. Furfural, a versatile chemical derived from biomass, holds significant commercial promise for producing sustainable chemicals and fuels.[1] The energy properties of two derivatives of this compound were investigated in the present work (Fig. 1). The standard ($p° = 10^5$ Pa) molar enthalpies of formation of furfurylamine and 5-methyl furfurylamine were derived at $T = 298.15$ K, in the liquid phase, from their standard massic energy of combustion measured by static-bomb combustion calorimetry. Using high-temperature Calvet microcalorimetry, the standard molar enthalpies of vaporization of both compounds were also determined, at the same temperature. From the experimental results, the standard molar enthalpies of formation in the gaseous phase were determined, at $T = 298.15$ K, for furfurylamine, and for 5-methylfurfurylamine and were compared with the ones estimated through a theoretical analysis using G3 level calculations.

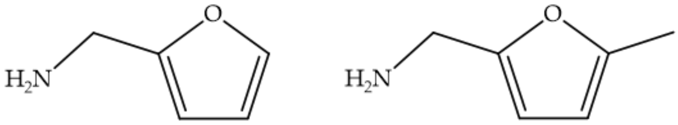


Fig. 1. Structural formulae of a) Furfurylamine and b) 5-Methylfurfurylamine.

Acknowledgements: This work was supported by the Fundacão para a Ciência e Tecnologia (FCT) to CIQUP, Faculty of Sciences, University of Porto (Project UIDB/00081/2020) and the Institute of Molecular Sciences (LA/P/0056/2020)). A.R.R.P.A. is financed by national funds through the FCT-I.P., in the framework of the execution of the program contract provided in the art. 23 of Law no. 57/2016, as amended by Law no. 57/2017. https://doi.org/10.54499/DL57/2016/CP1454/CT0006). L.M.P.F.A. acknowledges FCT/MCTES funding through the Individual Call to Scientific Employment Stimulus 2018. https://doi.org/10.54499/CEECIND/03202/2018/CP1545/CT0001).

References

1. J. Di, Q. Li, C. Ma, Y.-C He; *Bioresour. Technol*. **2023**, *369*, 128425.

P46 Understanding the influence of ionic liquids on carbonic anhydrase activity using molecular docking

M. Fraga,[1] *M.G. Freire,*[1] *M.M. Pereira*[2]

[1] *CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal*

[2] *University of Coimbra, CERES, Department of Chemical Engineering, Coimbra, Portugal*

Email: michelefraga@ua.pt

Carbonic anhydrase (CA; EC 4.2.1.1) is a metalloenzyme that catalyzes the conversion of carbon dioxide (CO_2) into bicarbonate (HCO_3^-). CA has been widely applied in various biotechnological applications, from treating gaseous effluents to developing artificial lungs. Ionic liquids (ILs) have emerged as an attractive alternative due to their physicochemical properties, biocompatibility, and high diversity, allowing enhanced interaction capacity with enzymes and promoting changes in the catalytic environment, whether favorable or not. Therefore, the aim of this study was to investigate the effect of ILs on the activity of Carbonic Anhydrase type II (CA-II) through molecular docking and evaluate the enzyme activity through colorimetric assays. For this purpose, a computational screening was performed using molecular docking. Bidding affinities were calculated, and molecular interactions identified for several IL cations and anions and CA-II. The receptor employed was bovine CA-II (PDB ID: 4CNX), and all input files were generated using AutoDockTools. The most promising ILs identified were applied to CA-II enzymatic activity assays. The docking score ranged from -4.4 kcal/mol to -3.3 kcal/mol for cations, and from -5.6 kcal/mol to -3.4 kcal/mol for anions. Electrostatic interactions, hydrogen bonds, and van der Waals interactions were identified. The IL ions binding affinity to the CA-II active site suggests a competitive inhibition mechanism, as substrates cannot access the enzyme catalytic site. Thus, the molecular docking results and enzymatic activity assays reveal that interactions of IL ions with the CA-II allosteric site generally increase enzymatic activity, whereas similar interactions involving IL ions and CA-II active site tend to promote an inhibitory effect. In conclusion, a novel approach for identifying enzymatic modulators is proposed herein, paving the way for the design of tailored ILs combinations for biotechnological applications.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI 10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC). This work was supported by the project POCI-01-0145-FEDER-031268-funded by FEDER through COMPETE2020, and by national funds (OE) through FCT/MCTES. M. M. Pereira acknowledges the financial support of FCT, Portugal, within the projects DOI:10.54499/UIDB/00102/2020 (Base funding) and DOI: 10.54499/UIDP/00102/2020 (Programmatic funding). M. Fraga acknowledges FCT for the PhD grant BD/12877/2022.

P47 Identification of deep eutectic solvents as modulators of *Yarrowia lipolytica* lipase activity using molecular docking

F.S. Buarque,[1,2] B.D. Ribeiro,[1] M.A.Z. Coelho,[1] M.G. Freire,[2] M.M. Pereira[3]

[1] *School of Chemistry, Federal University of Rio de Janeiro, Brazil.*
[2] *CICECO-Aveiro Institute of Materials, University of Aveiro, Portugal.*
[3] *University of Coimbra, CERES, Department of Chemical Engineering, Coimbra, Portugal.*
Email: filipebuarque@ua.pt

The use of deep eutectic solvents (DES) as solvents or co-solvents is an approach to be considered for controlling the biocatalytic activity of enzymes.[1,2] Thus, experimental and molecular docking studies evaluated the effect of aqueous solutions of DES composed of ammonium and fatty acids on the lipase activity of *Yarrowia lipolytica* (YlLip2). The results showed that an increase in the chain length of the ammonium-based hydrogen bond acceptor (HBA) led to improved lipolytic activity. On the other hand, there was a decrease in YlLip2 activity as the fatty acid chain length hydrogen bond donor (HBD) increased. Most of the DES studied displayed lower YlLip2 activity values than the control, except for HBA-$[N_{8881}]$Cl (individually), which exhibited a higher value than the control, whereas the DES $[N_{8881}]$Cl:hexanoic acid demonstrated similar values to the control. According to the interactions determined by molecular docking, the $[N_{8881}]^+$-HBA ion showed the highest absolute values of affinity energy with the YlLip2 structure. However, none of the HBA/HBD studied interacted with the catalytic triad amino acids. Nevertheless, they exhibited interactions with the YlLip2 allosteric sites. There were more interactions with the allosteric site amino acids in the same order as the absolute affinity energy values increased. Furthermore, $[N_{8881}]$Cl was the only one to show hydrophobic interactions with residues His49 and Phe50. Therefore, interactions with these specific amino acids of allosteric site could promote an activating effect on the catalytic activity of YlLip2 in the DES presence. Based on the results presented here, this work shows that molecular docking can be used as a new approach to identify appropriate DES for improving the catalytic activity of YlLip2 in biocatalytic reactions.

Acknowledgements: Foundation for Research Support and Technological Innovation of the State of Rio de Janeiro (FAPERJ). This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI 10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC). This work was supported by the project POCI-01-0145-FEDER-031268-funded by FEDER through COMPETE2020, and by national funds (OE) through FCT/MCTES. M. M. Pereira acknowledges the financial support of FCT, Portugal, within the projects DOI:10.54499/UIDB/00102/2020 (Base funding) and DOI: 10.54499/UIDP/00102/2020 (Programmatic funding). Buarque, F.S. acknowledge the scholarship grant from FAPERJ: E-26/204.344/2021.

References

1. M. L. Toledo, M. M. Pereira, M. G. Freire, J. P. Silva, J. A. P. Coutinho, A. P. Tavares; *ACS Sustain. Chem. Eng*. **2019**, *7*, 11806-11814.
2. P. Fickers, A. Marty, J. M. Nicaud; *Biotechnol. Adv.* **2011**, *29*, 632–644.

P48

Influence of a thiomethyl substituent on the spectroscopic characteristics of 1,4-disubstituted 1,2,3-triazoles

M.G. Vaz, A. Lampreia, J.N. Martins, A.J. Moro, C.S.B. Gomes, J.C. Lima, V. Rosa

LAQV-REQUIMTE, Department of Chemistry, NOVA School of Science and Technology (NOVA FCT), NOVA University Lisbon, 2829-516 Caparica, Portugal.

Email: mgo.vaz@campus.fct.unl.pt

Since the seminal work of Medal and Sharpless in 2001 on the synthesis of 1,4-disubstituted 1,2,3-triazoles using copper as a catalyst, an increased number of derivatives were synthetized and studied for different applications.[1,2] They have been used as precursors for ligands in coordination chemistry, as pharmaceuticals or in photochemistry. Their spectroscopic proprieties were well studied due to their ability to encompass on the same molecule, having the triazole ring as linker, donor and acceptor electron moieties. This allows to attain great quantum yields and, in some cases, large stoke shifts. Stoke shifts is an important photophysical characteristic that a molecule can present for applications in the field of medical chemistry. In this work we present the synthesis of a family of 1,4-disubstituted 1,2,3-triazoles, starting from, o-MeSphenyl and p-MeSphenyl anilines, reacted with either phenylacetylene or propargyl alcohol. Their absorption and emission spectra were acquired and studied. The contribution and influence of the thiomethyl group was analysed and compared with previously published analogues bearing methoxy substituents.

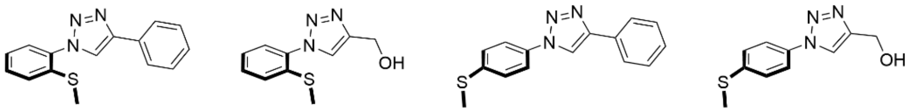


Fig. 1. 1,4-disubstituted 1,2,3-triazoles studied on this work.

Acknowledgements: This work was supported by FCT/MCTES (LA/P/0008/2020 DOI 10.54499/LA/P/0008/2020, UIDP/50006/2020 DOI 10.54499/UIDP/50006/2020 and UIDB/50006/2020 DOI 10.54499/UIDB/50006/2020) through national funds.

References

1. V. V. Fokin, K. Matyjaszewski; CuAAC: “The Quintessential Click Reaction,” in *Organic Chemistry – Breakthroughs and Perspectives (eds K. Ding and L.-X. Dai)*, Wiley, 2012, pp. 247–277.
2. M. Meldal, F. Diness; *Trends Chem.* **2020**, *2*, 569–584.

P49 Photocatalytic hydrogen production using activated carbon from tire rubber

P. C. Gomes, I. Matos, N. Lapa, J. C. Lima, S. Gago

LAQV-REQUIMTE, Department of Chemistry, NOVA School of Science and Technology, NOVA University of Lisbon, Portugal
Email: pc.gomes@campus.fct.unl.pt

The increase in world population and industrial production lead to higher electricity demand, leading to an overuse of natural resources. To overcome this problem, finding a cleaner and more efficient electricity production process is crucial. Hydrogen is the ideal candidate energy source since it can be obtained from water splitting using sunlight, biological organisms, or renewable electricity. Another advantage is that when it's converted to electricity, the major by-product is water, making the cycle free of greenhouse gases.[1]

Worn tires are another concern when it comes to sustainability, especially rubber. With the growth in demand for tires in developed countries, the number of disposed tires increases. To overcome this issue, we intend to find a way to reutilize it. Even though the valorization methods have improved and become more widespread, most disposed-of tires still end up in landfills. These materials can be converted into chars for applications such as adsorbents or as support in catalysis.[2]

In this work, we tested the hydrogen production of catalysts supported by char from rubber tires previously synthesized. For that, we measured the change of headspace volume while the solution was irradiated, using a 300 W Xe lamp. Several cycles of irradiation were performed.

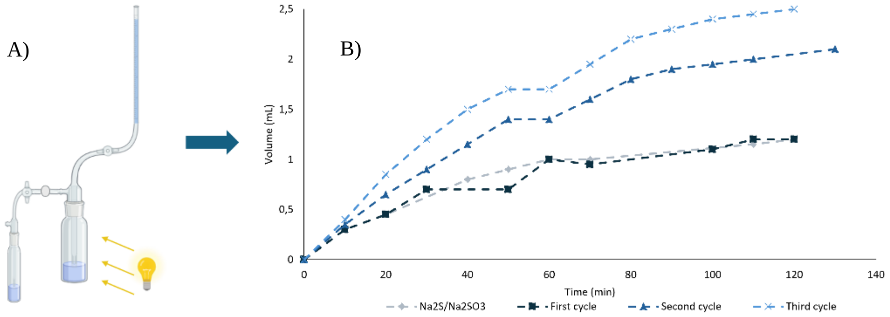


Fig. 1. A) Scheme of photocatalytic reactor used. B) Volume of hydrogen produced by the blank Na_2S/Na_2SO_3 solution used as sacrificial agent and by an activated carbon sample for 3 cycles.

Acknowledgements: This work was supported by FCT/MCTES (LA/P/0008/2020 DOI 10.54499/LA/P/0008/2020, UIDP/50006/2020 DOI 10.54499/UIDP/50006/2020 and UIDB/50006/2020 DOI10.54499/UIDB/50006/2020) through national funds and Project RObUST-Valorpneu-FCT_NOVA/23-24.

References

1. S. Kampouri, K. C. Stylianou; *ACS Catal.* **2019**, *9*, 4247–4270.
2. M. Nogueira, I. Matos, M. Bernardo, L. A. C. Tarelho, A. M. Botelho, A. M. Botelho do Rego, I. Fonseca, N. Lapa; *Waste Manag*. **2024**, *174*, 451-461.

P50 Reactivity patterns in the decomposition of indene adducts of C_{70} fullerene via retro-Diels-Alder reaction

C.S.T. Pinto, L.M.N.B.F. Santos, C.F.R.A.C. Lima

CIQUP, Institute of Molecular Sciences (IMS), Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Rua do Campo Alegre, P4169-007 Porto, Portugal
Email: up202008144@up.pt

The peculiar geometry of fullerenes (spherical shape, high symmetry, curvature of the carbon skeleton) has long fascinated chemists and physicists. With the primary focus of expanding the understanding of fullerene reactivity, this work aimed to study the kinetic and thermodynamic parameters in the solid phase of the compounds $IC_{70}MA$ (indene-C_{70}-mono-adduct), $IC_{70}BA$ (indene-C_{70}-bis-adduct), and $IC_{70}TA$ (indene-C_{70}-tris-adduct). The kinetic study involved measuring the decomposition temperatures via the Retro Diels-Alder (RDA) reaction of these adducts by thermogravimetry (TGA) and determining the respective kinetic parameters. The thermodynamic study involved determining the solid-phase heat capacities of the compounds by drop microcalorimetry and analyzing the RDA reaction by differential scanning calorimetry (DSC). It was possible to conclude from the TGA data that $IC_{70}BA$ follows a mechanism of two consecutive first-order reactions mainly involving two binding sites of indene to C_{70}. From the DSC data, it was observed that, similar to C_{60} fullerene, the decomposition temperature of the C_{70} fullerenes decreases with the increase in the number of indenes, and the process also becomes more complex due to the increase in the number of isomers. Results were analyzed to analyze the effects of the fullerene (C_{60} *vs* C_{70}) and number of indenes (1 *vs* 2 *vs* 3) in the RDA reaction.[1] To ensure that the mass loss and the final product were as expected, the resulting residues were carefully weighed and analyzed by FTIR and NMR.

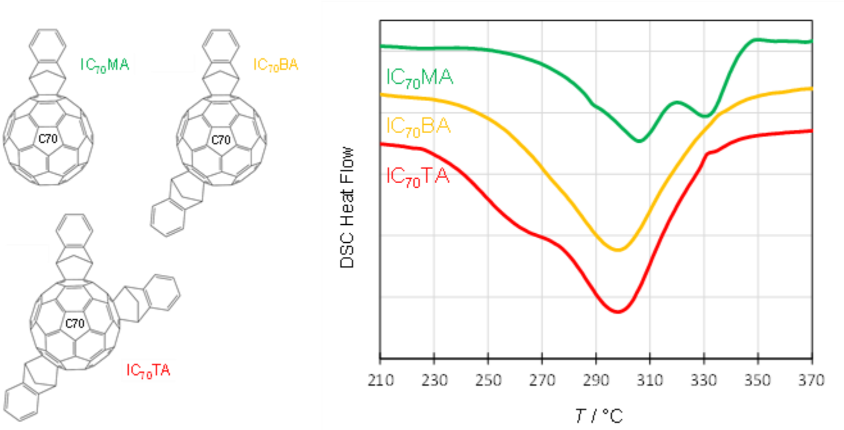


Fig. 1. Kinetic and thermodynamic study of the decomposition of C_{70} indene adducts.

References

1. D.J.L. Rodrigues, I.B.O.M. Pina, L.M.N.B.F. Santos, C.F.R.A.C. Lima; *Diam. Relat. Mater.* **2023**, *136*, 110031.

P51 Development of a novel ionic liquid-based approach for the extraction and purification of proteins from insects

E.V. Capela,[1] P. Moleiro,[1] G. Akyüz,[1] V. Vieira,[1] L.C. Branco,[2] A.P.M. Tavares,[1] M.G. Freire[1]

[1] CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[2] Associated Laboratory for Green Chemistry (LAQV) of the Network of Chemistry and Technology (REQUIMTE), Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
Email: emanuelcapela@ua.pt

Earth's population is continuously growing, and, in that scenario, the demand in for meat protein will continue to grow, with damaging impact in terms of sustainability, leading to critical environmental impacts and resources wastefulness.[1] Thus, it is imperative to identify alternative protein sources, where insects have a high potential to positively contribute to food sustainability. Insects are highly rich in proteins and other nutrients when comparing to other livestock animals and plants. The main advantage of insects over other protein sources are related with a low environmental and economic costs of production, and low carbon footprint, which becomes essential to satisfy the rise in the global protein demand.[2] Protein extraction from insects, to introduce in innovative food products is, undoubtedly, a viable way of increasing the acceptability of such rich sources of nutrients among consumers for the food industry. Based on this context, this work aimed to develop a sustainable technology for the extraction and purification of proteins from edible insect flour, using aqueous solutions of ionic liquids (ILs), envisioning their application in innovative food products. Several ILs were synthesized and characterized, followed by their application for the processing of insect flour, targeting the extraction of the protein-rich fraction. The operation conditions were optimized to improve the performance parameters of the process, and a comparison with conventional methods was performed. The proteins profile and their content were also addressed. Therefore, this work represents a steppingstone for the development of a sustainable synergy between edible insects, proteins and food products.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI 10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MEC (PIDDAC). This study was funded by the PRR - Recovery and Resilience Plan and by the NextGenerationEU funds at Universidade de Aveiro, through the scope of the Agenda for Business Innovation "InsectERA" (Project no. 20 with the application C644917393-00000032).

References

1. M. Laroche, V. Perreault, A. Marciniak, A. Gravel, J. Chamberland, A. Doyen; *Foods* **2019**, *8*, 572.
2. A. A. Shah, P. Totakul, M. Matra, A. Cherdthong, Y. Hanboonsong, M. Wanapat; *Anim. Biosci.* **2022**, *35*, 317–331.

P52 Thermodynamics of alkylsilane-based ILs with different anions

R.M.A. Silva,[1] E.Baķis,[2] A.I.M.C. Lobo Ferreira,[1] L.M.N.B.F. Santos[1]

[1] CIQUP, Institute of Molecular Sciences (IMS) – Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua Campo Alegre, 4169-007 Porto, Portugal
[2] Faculty of Chemistry, University of Latvia, Jelgavas 1, Riga, LV-1004, Latvia
Email: ana.ferreira@fc.up.pt

The insertion of silicon atoms on the alkyl chain of ionic liquids (SiILs) has been revealed to reduce the viscosity of this kind of substances. It has also been shown that the viscosity decrease can be of different magnitudes for different anions. In this work we aimed to study and understand the impact that different anions have on the thermodynamic properties of ILs composed by the [(SiCSiC)C1im] cation. The structures of the cation and the different studied anions are presented in Fig. 1.

The studied properties include the glass transition, melting point, thermal decomposition, heat capacity, and volatility. The phase behavior of the ILs was studied by differential scanning calorimetry (DSC). Thermogravimetric analysis (TGA) was used to investigate the thermal decomposition of the ILs. The heat capacity was studied through two different techniques: differential scanning microcalorimetry (in the temperature range from T = 283 K to T = 333 K), and a high-precision drop microcalorimeter (at the temperature of T = 298.15 K). The volatility of the ILs was studied by Knudsen effusion apparatus coupled with quartz crystal microbalance (KEQCM).

Glass transition was obtained for all ILs. [$N(CN)_2$] and [$C(CN)_3$]-based ILs were found to have significantly lower thermal stabilities than the other studied ILs. [$B(CN)_4$] and [OTf]-based ILs revealed lower volatility than the [NTf_2] based IL. The differences in heat capacity of alkylsilane-based ILs composed of different anions are identical to those found for conventional *n*-alkyl-based ILs.

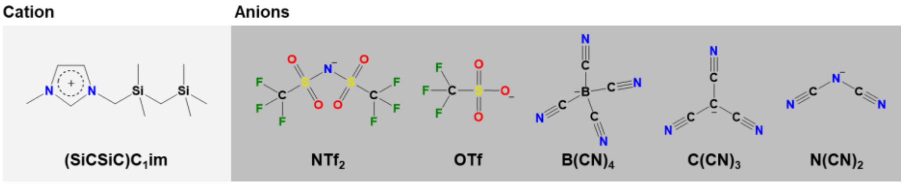


Fig. 1. Structures of cation and anions of the studied SiILs.

Acknowledgements: This work was supported by the Fundação para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020), IMS-Institute of Molecular Sciences (LA/P/0056/2020). RMAS is grateful to FCT for the award of his PhD grant (U1/BD/153093/2022). AIMCLF is also financed by national funds 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. EB acknowledges PostDoc Latvia for financial support (Grant No. 1.1.1.2/VIAA/3/19/549).

P53 Flexible host materials for energy storage

K. Bettencourt, A.S. Viana, J.P. Correia

Centro de Química Estrutural – Institute of Molecular Sciences, Faculdade de Ciencias, Universidade de Lisboa

Email: fc56587@alunos.fc.ul.pt

Lithium-ion batteries (LIBs) are well-known devices due to their good performance in electronics and mobility. Nevertheless, their increasing use has proven unsustainable due to the limited availability of lithium and the high cost of recycling. As a substitute, sodium-ion batteries (SIBs) have been considered an alternative technology because of sodium abundance, and good energy densities. However, transitioning to SIBs is challenging due to differences in ion sizes, electrochemical properties, and diffusion rates, which have a significant impact on their interaction with electrode materials. An example of this are cathode materials, which often undergo side reactions during charge/discharge cycles, reducing conductivity and causing structural collapse.[1,2]

As an emerging solution for cathode materials, polymer films have shown to be a promising flexible and easy-to-modify alternative host structures towards the development of stable and high-capacity batteries.[3] Therefore, this study aims to investigate the electropolymerization of a copolymer of dopamine (DA) and EDOT (3,4-ethylenedioxythiophene), combining the chemical functionalities of PDA with the conductive properties of PEDOT. The catechol groups in PDA grant a high coordination reversibility of sodium ions and a strong adhesion to surfaces through intermolecular interactions.[4,5]

In contrast, PEDOT is a conductive polymer widely known for its chemical stability in the oxidized state, good theoretical capacities and biological compatibility. [6,7]

In this study, the effect of the synthesis potential and monomer proportion on the growth and final physicochemical properties (e.g. redox behavior, transferred charge, thickness and wettability) of the copolymers were evaluated. Additionally, the nature and concentration of the supporting electrolyte was examined, namely on the extent of sodium uptake by the copolymer. It was found that the new materials exhibit remarkable adhesive properties and high charge transfer.

Acknowledgements: Centro de Química Estrutural is a Research Unit funded by FCT through projects UIDB/00100/2020 (https://doi.org/10.54499/UIDB/00100/2020) and UIDP/00100/2020 (https://doi.org/10.54499/UIDP/00100/2020). Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020 (https://doi.org/10.54499/LA/P/0056/2020).

References

1. P.K. Nayak *et al*.; *Angew.Chem.* **2018**, *57*, 102-120.
2. Q. Zhao *et al.; Materials* **2018**, *11*, 2567.
3. U.D. Chavan *et al.; Chem. Eng. J. Advances* **2022**, *12*, 100416.
4. L.C. Almeida *et al*; *Electrochim. Acta.* **2021**, *386*, 138515.
5. R. Cao *et al. Organic Cathode Materials for Rechargeable Batteries*. In: Z. Zhang, S. Zhang. (eds) Rechargeable Batteries. Green Energy and Technology. Springer, **2015**, 637–671.
6. D.R.C.R. Santos, Master Thesis, *Faculdade de Ciências da Universidade de Lisboa.* **2018**.
7. S. Baldanzi *et al.*; *J. Mar. Sci. Eng.* **2021**, *9*, 82.

P54 COSMO-RS as a powerful tool to characterize the polarity of ionic liquids and their mixtures

E.V. Capela, A.R.R. Teles, A.F.M. Cláudio, J.A.P. Coutinho, M.G. Freire

[1] *CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal*

Email: emanuelcapela@ua.pt

Ionic liquids (ILs) have been the focus of intensive research regarding their use as potential and alternative solvents in a wide variety of applications. Targeting their effectiveness, recent investigations have focused on their ranking in terms of polarity,[1,2] with several efforts regarding the development of predictive/extended scales essentially focused on the hydrogen bond acidity and basicity[1,2]. However, scarce efforts have been made regarding their dipolarity/polarizability. Moreover, polarity scales are mostly available for pure ILs,[3] even though it is known that mixtures of ILs can broaden their tailoring ability by properly designing their polarity. Based on this context, this work aimed to report an extended scale for the dipolarity/polarizability of ILs, and to determine the solvatochromic parameters of mixtures of ILs and adjusting their polarity. Various ILs and mixtures of ILs, at different molar ratio, were investigated by the determination of their Kamlet–Taft solvatochromic parameters, namely hydrogen-bond acidity, hydrogen-bond basicity and dipolarity/polarizability. Since experimental polarity scales only report on relative ranks because they depend on the set of probe dyes used, the COSMO-RS (COnductor-like Screening MOdel for Real Solvents) capability as an alternative tool to estimate the dipolarity/polarizability of ILs and remaining solvatochromic parameters of mixtures of ILs was further investigated. The combination of this experimental and theoretical approach allows to predict the dipolarity/polarizability of ILs and classify mixtures of ILs according to their chemical behavior, opening the possibility to pre-screen appropriate ILs or mixtures for a given task or application.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI 10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MEC (PIDDAC).

References

1. A. F. M. Cláudio, L. Swift, J. P. Hallett, T. Welton, J. A. P. Coutinho, M. G. Freire; *Phys. Chem. Chem. Phys.* **2014**, *16*, 6593-6601.
2. K. A. Kurnia, F. Lima, A. F. M. Cláudio, J. A. P. Coutinho, M. G. Freire, *Phys. Chem. Chem. Phys.* **2015**, *17*, 18980-18990.
3. S. Dreyer, U. Kragl, *Biotechnol. Bioeng.* **2008**, *99*, 1416-1424.

P55 Effect on 1,4-disubstituted 1,2,3-triazoles emission spectra when varying water content percentage

A. Lampreia, J. M. Martins, A. Moro, C.S.B. Gomes, J. C. Lima, V. Rosa

LAQV-REQUIMTE, Department of Chemistry, NOVA School of Science and Technology (NOVA FCT), NOVA University Lisbon, 2829-516 Caparica, Portugal.

Email: a.lampreia@campus.fct.unl.pt

The copper catalysed cycloaddition of azides and alkynes (CuAAC) to obtain 1,4-disubstituted 1,2,3-triazoles is one of the most useful reactions in click chemistry.[1] The regioisomers obtained by the CuAAC, present an extensive variety of features that can be applied in various scientific fields. One of its main advantages is the wide range of azide and alkyne precursors that can be used in this reaction, leading to compounds with a great diversity in electronic or steric proprieties and in a great versatility for the conception of new molecules with well-defined features. This versatility is of huge importance when designing luminescent compounds, since small changes on the molecule configuration can led to very different spectroscopic outcomes. In this work we present the synthesis of a family of 1,4-disubstituted 1,2,3-triazoles, starting from, o-MeSphenyl, p-MeSphenyl and naphthyl anilines, reacted with either phenylacetylene or propargyl alcohol. They were all characterized by spectroscopical techniques and single X- ray diffraction when possible. Their spectroscopical, absorption and emission, behaviour, when the solvent system were constituted of different percentages of water, was critically assed.

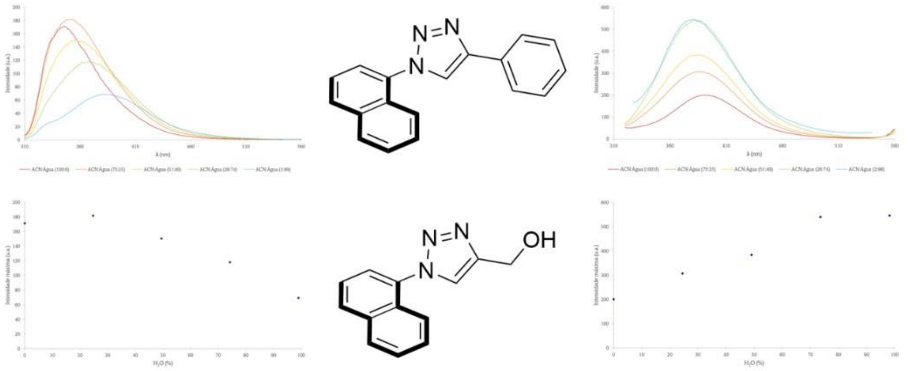


Fig. 1. Effect on two 1,4-disubstituted 1,2,3-triazoles emission spectra when varying water content percentage.

Acknowledgements: This work was supported by FCT/MCTES (LA/P/0008/2020 DOI 10.54499/LA/P/0008/2020, UIDP/50006/2020 DOI 10.54499/UIDP/50006/2020 and UIDB/50006/2020 DOI 10.54499/UIDB/50006/2020) through national funds.

References

1. V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless; *Angew. Chem. Int. Ed.* **2002**, 41, 2596–2599.

P56 A precise method to estimate the enthalpies of combustion of biodiesels

R.I.S. Rodrigues,[1] C.E.S Bernardes,[1] M.E. Minas da Piedade,[1] R.M. Borges dos Santos[1,2]

[1] Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal
[2] Centre of Marine Sciences (CCMAR/CIMAR LA), Departamento de Química e Farmácia, Faculdade de Ciências e Tecnologia, Universidade do Algarve, 8005-139 Faro, Portugal
Email: rirodrigues@ciencias.ulisboa.pt

Air pollution has, in the last decades, emerged as a significant global challenge, largely due to the excessive use of fossil fuels in the transportation sector. As a result, there is currently an urgent need of transition to more sustainable energy sources. Biodiesel is a mixture of fatty acid methyl esters (FAME) obtained by transesterification of oils from renewable sources with methanol. This is a promising alternative to conventional fuels, given the low emission of greenhouse gases[1] and the simplicity inherent to the production and use of biodiesel.[2] The combustion enthalpy, $\Delta_c H_m$, is the most important physical property of any fuel, as it allows the evaluation of its energetic efficiency. Surprisingly, literature data for $\Delta_c H_m$ of FAMEs are scarce, unreliable, or inconsistent. As its experimental determination can be demanding, there is a compelling need to develop reliable and efficient methods for the estimation of FAME's $\Delta_c H_m$. Several methods have been proposed, but they have all been found to be limited or imprecise. Benson's method[3] is one of the most rigorous group additivity methods available. It is particularly suitable to address FAMEs, given the structural simplicity of the molecules, which allows precise estimations with a very limited number of groups.
In this work, an algorithm was developed for the estimation of FAMEs $\Delta_c H_m$ based on Benson's method, and the $\Delta_c H_m$ of key FAMEs was estimated. To validate the algorithm, the enthalpy of formation, $\Delta_f H_m$, of the same molecules was determined by combining quantum chemistry calculations with well-constructed isodesmic-type reactions, from which $\Delta_c H_m$ can be easily derived. The obtained results agreed with those given by the algorithm within the so-called chemical accuracy of 4 kJ mol^{-1}.

Acknowledgements: This work was funded by FCT – Fundação para a Ciência e a Tecnologia, Portugal, through projects UIDB/00100/2020 (DOI 10.54499/UIDP/00100/2020), UIDP/00100/2020 (DOI 10.54499/UIDP/00100/ 2020), LA/P/0056/2020 (DOI 10.54499/LA/P/0056/2020), UIDB/04326/2020 (DOI:10.54499/UIDB/04326/2020), UIDP/04326/2020 (DOI:10.54499/UIDP/04326/2020), and LA/P/ 0101/2020 (DOI:10.54499/LA/P/0101/2020).

References

1. A. Bonomi, B.C. Klein, M.F. Chagas, R.D. Souza; Phase 2, Part 1: FAME and HVO/HEFA.
2. P. Kalita, B. Basumatary, P. Saikia, B. Das, S. Basumatary; *Energy Nexus* **2022**, *6*, 100087.
3. N. Cohen, S.W. Benson; *Chem. Rev.* **1993**, *93*, 2419–2438.

P57 Catechol(amine) and pyrrole-based co-polymers for (bio)sensing applications

D.M. Carneiro, J.P. Correia, A.S. Viana

Centro de Química Estrutural - Institute of Molecular Sciences, Universidade de Lisboa, Portugal
Email: dianamcarneiro@alunos.fc.ul.pt

Catechol is recognized for its chemical versatility since it can establish various types of non-covalent bonds and can also coordinate directly to a substrate through Shiff base and Michael's addition reaction. Amine groups and catechol moieties can be found in mussel byssal proteins that are known for its adhesive properties. Both functional groups are present in catecholamines species (*e.g.*, dopamine and norepinephrine) that can be reproducibly electropolymerized with controlled physicochemical properties.[1] Given its interesting bioconjugation properties, polycatecholamines have been used as biosensing platforms.[2,3] However, polycatecholamine electrochemical growth is self-limiting due to their poor conductive nature which may compromise their transduction efficiency in amperometric biosensors .[1]

To overcome that limitation, this work aims to expand polycatecholamines electrochemical applications through its combination with conductive polymers. The purpose is to take advantage of catechol and amine groups from polycatecholamines and combine them with the conductive behavior of polypyrrole (PPy), a well-known conductive polymer. Through an electro-co-polymerization process of two monomers, the intent is to develop a bi-functional co-polymer that has both adhesive and conductive properties. Such polymeric matrix can be suitable for enzymatic amperometric biosensors, since ensures the enzyme robust immobilization and transduction of the electrochemical signal.

In this study, catechol (CA), dopamine (DA), and norepinephrine (NE) species were separately electro-co-polymerized with pyrrole in different monomeric concentrations and proportions. The three co-polymeric films were extensively characterized by electrochemical, optical, spectroscopic techniques and atomic force microscopy, to assess their redox behaviour, dielectric properties, thickness, morphology, wettability, and chemical composition. It was found that the combination of the two types of monomers has a synergistic effect on the growth of a conductive co-polymer, which significantly enhanced the electron transfer of target analytes, namely phenolic compounds. Moreover, the co-polymers proved to be a suitable matrix for immobilizing enzymes – laccase and pyranose oxidase with promising catalytic activity and high sensibility for polyphenol and glucose detection, respectively.

Acknowledgements: Centro de Química Estrutural is a Research Unit funded by FCT through projects UIDB/00100/2020 (https://doi.org/10.54499/UIDB/00100/2020) and UIDP/00100/2020 (https://doi.org/10.54499/UIDP/00100/2020). Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020 (https://doi.org/10.54499/LA/P/0056/2020).

References

1. L.C. Almeida, R.D. Correia, B. Palys, J.P. Correia, A.S. Viana, *Electrochim. Acta* **2021**, *386,* 138515.
2. L.C. Almeida, R.D. Correia, A. Marta, G. Squillaci, A. Morana, F. La Cara, J.P. Correia, A.S. Viana, *Appl. Surf. Sci.* **2019**, *480*, 979-989.
3. L.C. Almeida, R.D. Correia, G. Squillaci, A. Morana, F. La Cara, J.P. Correia, A.S. Viana, *Electrochim. Acta* **2019**, *319*, 462-471.

P58 Avian immunoglobulin Y (IgY) antibodies to overcome antimicrobial resistance (AMR)

C. Almeida,[1,2] *J.A.P. Coutinho,*[1,2] *M.C. Neves,*[1,2] *M.G. Freire*[1,2]

[1] *CICECO-Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal Institution*
[2] *RYA Purification Technologies, 3830-352 Ílhavo, Portugal*
Email: ac.almeida@ua.pt

The improper use of antibiotics in the last decades has contributed to the advance of Antimicrobial Resistance (AMR). AMR is one of the most critical public health concerns worldwide, among which Methicillin-resistant *Staphylococcus aureus* (MRSA) is particularly harmful.[1] Therefore, exploring alternative therapeutic approaches beyond conventional antibiotics, such as biopharmaceuticals, is urgent. Avian Immunoglobulin Y (IgY), an antibody isolated from chicken's egg yolk, could be seen as a viable option to fight multi-resistant bacterial infections. Owing to its polyclonal feature, IgY recognizes several epitopes on an antigen, decreasing the resistance occurrence, which represents an advantage in the treatment of infections.[2] In this study, the potential role of IgY antibodies as biopharmaceuticals to fight AMR, in particular, infections caused by MRSA, was investigated. To this end, specific IgY for the Penicillin-Binding Protein 2a (PBP2a) of MRSA were recovered from the egg yolk of hyperimmunized chickens and then, purified by a 2-steps selective precipitation-based methodology using a biopolymer. Formulations comprising anti-PBP2a IgY antibodies were developed by combining them with conventional protein stabilizers, namely sugars, polyols, and amino acids, that were kept under refrigerated and freezing conditions for up to 2 months. The stability of anti-PBP2a IgY in these formulations was assessed through monitorization of their secondary structure and aggregation by Circular Dichroism (CD) spectroscopy and Size-Exclusion High-Performance Liquid Chromatography (SE-HPLC), respectively. The ability of anti-PBP2a IgY to detect the antigen was evaluated by dot-blot and Enzyme-Linked Immunosorbent Assay (ELISA). Moreover, their *in vitro* and *in vivo* toxicity were explored in human colorectal adenocarcinoma cells and rodent models. The protein stabilizers contribute to reducing the amount of anti-PBP2a IgY aggregates while maintaining their secondary structure and antigen recognition ability. These antibodies are shown to be non-toxic to either cell or animal models. These support the use of IgY in therapeutic formulations for MRSA infections, allowing to overcome AMR issues.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI 10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020) financed by national funds through the FCT/MCTES (PIDDAC). CA acknowledge FCT for the doctoral grant 2022.11570.BD. MCN acknowledge FCT for the research contract CEECIND/00383/2017/CP1459/CT0031 (DOI 10.54499/CEECIND/00383/2017/CP1459/CT0031).

References

1. M.A. Salam, M.Y. Al-Amin, M.T. Salam, J.S. Pawar, N. Akhter, A.A. Rabaan, M.A.A. Alqumber; *Healthcare (Basel).* **2023**, *11*, 1946.
2. S.A. El-Kafrawy, A.T. Abbas, C. Oelkrug, M. Tahoon, S. Ezzat, A. Zumla, E.I. Azhar; *Front. Immunol.* **2023**, *14*, 1-14.

P59

Valorization of insect flour oil using $scCO_2$ extraction

M N. José,[1] A.B. Paninho,[1,2] C.V. Esteves,[1] K. Zalewska,[1] A.I. Aguiar-Ricardo,[1] T. Casimiro,[1] A.V.M. Nunes,[1] L.C. Branco[1]

[1] LAQV, REQUIMTE, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
[2] i3N/CENIMAT, Department of Materials Science, Nova School of Science and Technology, CEMOP/UNINOVA, Campus de Caparica, Caparica, 2829-516, Portugal
Email: mn.jose@campus.fct.unl.pt

The United Nations estimates that by 2050, the global population will exceed 10 billion. While this growth can drive economic and cultural benefits, it also raises significant concerns about resource scarcity and environmental impact.[1] Edible insects have been proposed as a good and sustainable alternative to current food systems, due to their nutritional, economic and environmental value.[2] According to research, insects may be able to lessen pollution and use less water and energy during production. In addition, insects offer important elements found in human diets, such as protein (60%) and healthy fats (40%) as well as vitamins and minerals.[3]

Efficient and selective oil extraction is essential for producing high-quality food and feed oil and enabling subsequent protein separation.4 Supercritical CO_2 ($scCO_2$) extraction is gaining interest for industry as an alternative to conventional solvents due to its non-toxicity and easy separation from final products. It prevents thermal degradation and oxidation of labile compounds due to low critical temperature and the absence of oxygen during the process. Additionally, it is possible to manipulate CO_2 solvent power by adjusting temperature and pressure conditions, which allows the design of highly selective extraction processes. However, using $scCO_2$ for insect flour extraction is still relatively new.[4]

This study evaluated the influence of pressure, temperature and CO_2 flow rate on the $scCO_2$ extraction of oils from mealworm larvae (*Tenebrio molitor*) and domestic cricket (*Acheta domesticus*) flour. Key characteristics like acidity, composition, color, and thermal behavior were examined and compared to industrial techniques. Extraction yields closely matched the expected oil content. The advantages of $scCO_2$ extraction method will also be discussed.

Fig. 1. An overview of the work done focusing on $scCO^2$ extraction of insect flour oil.

Acknowledgements: This work was supported by the InsectERA – Novo sector bioindustrial Project, nºC644917393-00000032, co-financed by PRR - Recovery and Resilience Plan of the European Union (Next Generation EU). The authors also thank the support from FCT/MCTES (UIDB/50006/2020, LA/P/0008/2020 and UIDP/50006/2020 of the Associate Laboratory for Green Chemistry – LAQV).

References

1. U.N.: United Nations, Dep. Economic and Social Affairs, Population Division. Population Prospects 2019: Highlights. 10 Key Findings, 2019.
2. M. Li, C. Mao, X. Li, L. Jiang, W. Zhang, M. Li, H. Liu, Y. Fang, S. Liu, G. Yang, *et al*.; *Foods* **2023**, *12*, 4073.
3. A. Kozlu, N. Ngasakul, I. Klojdová, et al.; *Eur. Food Res. Technol*. **2024**, *250*, 1253–1267.
4. B. Purschke, T. Stegmann, M. Schreiner, H. Jäger, *Eur. J. Lipid Sci. Technol.* **2017**, *119*, 1600134.

P60 Adhesive properties of polymeric matrices made from lignin waste

A. S. Moleiro[1], *G. G. Maia*[1], *P. Ihalainen*[2], *L. Sobhana*[2], *A. S. Viana*[1]

[1] *Centro de Química Estrutural - Institute of Molecular Sciences, Universidade de Lisboa, Portugal*
[2] *MetGen, Rakentajantie 26, 20780 Kaarina, Finlândia*
Email: amoleiro@alunos.fc.ul.pt

Lignin is the second most abundant biopolymer in nature and is the main secondary product of the paper industry, predominantly used as fuel in various industrial processes.[1] The structural complexity of this highly branched macromolecule makes it challenging to study its physicochemical properties in detail (e.g. its adhesive properties). Thanks to recently developed technological processes, it is possible to fractionate lignin, for example, by enzymatic means, thus obtaining mixtures of its phenolic derivatives with a high monomeric content.[2] The main aromatic precursors are *p*-coumaryl alcohol, sinapyl alcohol and coniferyl alcohol, which may undergo oxidative polymerization reactions, enabling post-chemical conjugation and presenting electronic transfer events, due to formation of catechol moieties.[3]

The aim of this work is to electrosynthesize polymeric coatings, from impure low molecular weight lignin waste and to study their adhesive properties, which are essential in the development of biosensors. The lignin-based coatings were synthesized through potentiodynamic or potentiostatic modes, monitorized by quartz crystal microbalance technique to evaluate the mass deposition rate. The physicochemical properties of the polymers, such as adhesion, thickness and morphology, were studied using atomic force microscopy (including force-distance curves and adhesion maps) and the wettability was evaluated by contact angle goniometry. The electroactivity of the polymeric matrices confirmed the presence of catechol groups that are suitable for the physical and chemical immobilization of biomolecules. In addition, the extent of interaction between the polymeric matrices and several proteins (e.g. bovine serum albumin, lysozyme, immunoglobulin G) was successfully assessed by real-time surface plasmon resonance assays. The new platform demonstrated promising properties for future application in optical immunosensors.

Acknowledgements: Centro de Química Estrutural is a Research Unit funded by FCT through projects UIDB/00100/2020 (https://doi.org/10.54499/UIDB/00100/2020) and UIDP/00100/2020 (https://doi.org/10.54499/UIDP/00100/2020). Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020 (https://doi.org/10.54499/LA/P/0056/2020).

References

1. A. Haile, G.G. Gelebo, T. Tesfaye, W. Mengie, M. A. Mebrate, A. Abuhay, D. Y. Limeneh; *Bioresour. Bioprocess*, **2021**, *8*, 35.
2. T. Pang, G. Wang, H. Sun, et al.; *Ind. Crops Prod.* **2021**, *165*, 113442.
3. T. M. Budnyak, A. Slabon, M. H. Sipponen; *ChemSusChem*. **2020,** *13*, 4344.

P61 Quantifying the increase in electrophilic solvent assistance: 1-X-adamantane *vs*. 2-X-2-methylpropane solvolyses (X = Cl, Br, I)

L. Moreira,[1,2] A. Pinção,[1,3] R. Elvas-Leitão,[1,4] F. Martins [1,2]

[1] *Centro de Química Estrutural - Institute of Molecular Sciences, Universidade de Lisboa, Portugal*
[2] *Instituto Superior de Educação e Ciências, ISEC Lisboa, Portugal*
[3] *Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Portugal*
[4] *Departamento de Engenharia Química, Instituto Superior de Engenharia de Lisboa, IPL, Portugal*
Email: luis.moreira@iseclisboa.pt

The observed kinetic deviations for fluorinated hydroxylic solvents and their mixtures as compared to non-fluorinated aqueous media of log $k_{\text{2-X-2-methylpropane}}$ *vs*. log $k_{\text{1-X-adamantane}}$ plots (X = Cl, Br, I) have been usually ascribed as evidence of the influence of nucleophilic solvent assistance (NSA) in 2-X-2-methylpropane.[1]

Previously, we have used three multiparametric model equations,[2-4] to study solvent effects on a variety of tertiary alkyl halides and very recently we formulated a new biparametric equation that supported an alternative interpretation that pointed out to an increased electrophilic solvent assistance (ESA) in 1-X-adamantane *vs*. 2-X-2-methylpropane solvolyses.[5]

In this work, we went beyond a qualitative analysis and developed three independent but complementary methodologies that allowed us to quantify the increase of ESA in the referred solvolysis reactions. The purpose of this communication is to describe the devised methodologies and to critically analyze the results. Altogether, 27 values were collected that showed, in average, an increase of $4.7_{\pm 1.3}$ of the equation term that quantifies the sensitivity of the ESA for the 1-X-adamantane substrates.

Acknowledgements: Centro de Química Estrutural is a Research Unit funded by FCT through projects UIDB/00100/2020 (https://doi.org/10.54499/UIDB/00100/2020) and UIDP/00100/2020 (https://doi.org/ 10.54499/UIDP/00100/2020). Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020 (https://doi.org/10.54499/LA/P/0056/2020).

References

1. T.W. Bentley, G.E. Carter, *J. Am. Chem. Soc.* **1982**, *104*, 5741-5747.
2. L. Moreira, R. Elvas-Leitão, F. Martins, *J. Mol. Liquids* **2022**, *362*, 119656.
3. J. Catalán, *J. Phys. Chem. B* **2009**, *113*, 5951–5960.
4. C. Laurence, J. Legros, A. Chantzis, A. Planchat, D. Jacquemin, *J. Phys. Chem. B* **2015**, *119*, 3174–3184.
5. L. Moreira, R. Elvas-Leitão, F. Martins, *15th National Physical Chemistry Meeting* **2023**.

P62 Silica nanoparticles: a versatile avenue for stabilizing amorphous drugs

M.T. Viciosa,[1] *H.P. Diogo,*[1] *M. Dionísio,*[2] *T. Martins,*[1] *J.P. Farinha*[1]

[1] *Centro de Química Estrutural, Instituto Superior Técnico, University of Lisbon, Lisbon, Portugal.*
[2] *LAQV-REQUIMTE, Department of Chemistry, NOVA School of Science and Technology, NOVA University of Lisbon, Caparica, Portugal.*
Email: teresaviciosa@tecnico.ulisboa.pt

Since Vallet-Regí et al.[1] first proposed the use of silica matrices as drug carriers two decades ago, the number of papers published in this area has been steadily increasing. More recently, advanced control over the synthesis of these materials has made it possible to develop silica matrices on a nanometer scale. There is currently a wide variety of nanoparticles in terms of size, shape and pore dimensions and order. However, FDA-approved nanoparticle formulations are still limited to a very small number. This is partly due to the lack of in-depth knowledge of how the matrices act on the drug, or in other words, a detailed physicochemical characterization that would, for example, allow long-term properties to be predicted. In an attempt to contribute to put some light in this relationship, in this work we have prepared and started to characterize a system of non-porous silica nanoparticles with aceclofenac (ACF).

Aceclofenac (ACF), a non-steroidal anti-inflammatory drug, was chosen as a model compound, whose poor solubility in water (around 60 μg mL-1) is a limiting factor in its bioavailability (it belongs to class II in BCS). As nanocarriers, spherical silica nanoparticles of ~50 nm of diameter have been synthesized in the lab;[2] non-mesoporous particles were produced to focus initially the research in the ACF-silica relation and discarding spatial nanoconfinement effects. The physical state of the as prepared physical mixture of SiNPs and 30%wt of ACF and after heating it above the melting temperature of ACF was investigated by differential scanning calorimetry (DSC) and by dielectric relaxation spectroscopy (DRS).

Preliminary results show that ACF is amorphized after melting. The shift of the glass transition temperature when compared with bulk amorphous ACF suggests that molecular interactions with silica surface promote the stabilization in this physical state reducing or even eliminating the tendency towards recrystallisation.

The amorphization and the stability until now observed, may this nanosystem a promise option to be used in drug delivery.

Acknowledgements: This work was supported by the Associated Laboratory for Sustainable Chemistry, Clean Processes and Technologies – LAQV through national funds from Fundação para a Ciência e Tecnologia, FCT/MCTES, under project UIDB/50006/2020. A.S. also acknowledges FCT for his doctoral grant (2020.07313.BD).

References

1. M. Vallet-Regí, A. Rámila, R. P. Del Real, J. Pérez-Pariente; *Chem. Mat.* **2001**, *13*, 308–311.
2. T. Ribeiro, A.S. Rodrigues, S. Calderón, A. Fidalgo, J.L.M. Gonçalves, V. André, M.T. Duarte, P.J. Ferreira, J.P.S. Farinha, C. Baleizão; *J. Colloid Interface Sci*, **2020,** *561*, 609–619.

P63 Designing new MOF-based materials for gas separation

T.S. Dionísio, *T.O. Carvalho, T.J. Ferreira, J.M.S.S. Esperança, I.A.A.C. Esteves*

LAQV/Requimte, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa (FCT NOVA), 2829-516, Caparica, Portugal
Email: t.dionisio@campus.fct.unl.pt

Climate change and greenhouse gas (GHG) emissions are a very important issue due to the high global emissions recorded in recent years.[1] This scenario has serious consequences for our ecosystem, such as ocean acidification and loss of biodiversity. CO_2 is considered the most important gas of anthropogenic origin to be mitigated in order to control global warming, due to its long-lived nature and high concentration in the atmosphere.[2]

In this sense, new CO_2 capture/separation composites based on ionic liquids (IL) impregnated in a metal-organic framework (MOF) are being studied, in order to analyze their performance as sorbents for application in gas capture and separation. In recent years, these IL@MOF hybrid materials have shown improved properties as sorbents.

In this study, composites with two different IL, and different loadings (10%wt and 30%wt) are used, where the base MOF is UiO-66. Using a standard static gravimetric method, gas sorption-desorption measurements of N_2, CO_2 and CH_4 at 303K and 0-10 bar were performed. The influence of the anion/cation pair of the IL on the sorption capacity and on the ideal selectivity of CO_2/CH_4 and CO_2/N_2 is studied. Due to synergistic effects, the longer the alkyl chain of the IL, the higher the selectivity for CO_2.[3]The sorption capacity and CO_2/N_2 and CO_2/CH_4 ideal selectivities of these IL@UiO-66 composites is compared with their analogues IL@ZIF-8 to access their performance for CO_2 separation.

Acknowledgements: The authors thank Fundação para a Ciência e Tecnologia, FCT/MCTES (Portugal) for financial support through the doctoral grants 2021.07148.BD (T. O. C.) and SFRH/BD/139627/2018 (T. J. F.), and project PTDC/CTM-CTM/30326/2017. T. S. D. thanks Fundação Calouste Gulbenkian for the 2024 Novos Talentos Programme. This work was also supported by the Associate Laboratory for Green Chemistry-LAQV which is funded by national funds from FCT/MCTES (10.54499/LA/P/0008/2020, 10.54499/UIDP/50006/2020 and 10.54499/UIDB/50006/2020).

References

1. NOAA, "Climate Change: Atmospheric Carbon Dioxide", https://www.climate.gov/news-features/understanding-climate/climate-change-atmospheric-carbon-dioxide.
2. E-M. Ben-Salha; *Environ. Monit. Assess.* **2019**, *191*, 587.
3. T.J. Ferreira, R.P.P.L. Ribeiro, J.P.B. Mota, L.P.N. Rebelo, J.M.S.S. Esperança, I.A.A.C. Esteves; *ACS Appl. Nano Mater.* **2019**, *2*, 7933−7950.

P64 Dual role of chitosan: structuring MOF into fibers with enhanced CO_2 adsorption capacity and selectivity

T.O. Carvalho, T.J. Ferreira, J. Pais, J.M.S.S. Esperança, I.A.A.C. Esteves

LAQV/Requimte, Departamento de Química, Faculdade de Ciências e Tecnologia,
Universidade NOVA de Lisboa (FCT NOVA), 2829-516, Caparica, Portugal
Email: to.carvalho@campus.fct.unl.pt

Considering the current societal challenges and the goals set by the Paris Agreement, there is a growing interest in developing new materials for sustainable development, further refined by initiatives such as the 2030 Agenda, the European Green Deal, and Circular Economy. Carbon dioxide (CO_2) emission, primarily from the combustion of fossil fuels, is widely recognized as a critical factor in anthropogenic climate change. Controlling its atmospheric concentration is crucial, as the excessive emission of greenhouse gases is the primary source of climate change. The 21st century has seen global average temperature records consistently surpassed, with the 10 warmest years documented within the last decade.[1]

Porous materials have emerged with promising results for gas capture and separation, owing to their pore size, shape, arrangement, and composition. Efforts to control these features have led to the development of breakthrough materials such as metal-organic frameworks (MOFs), which are characterized by their high surface area and tunable porosity, making them ideal for gas storage, separation, and catalysis.[2] However, the powdery nature of MOFs presents significant challenges for practical applications, especially on an industrial scale, where shaping or incorporating them into solid structures is essential. Aerogels offer a promising solution, providing ultralight porous materials with interconnected nano-architectural-networks. Despite long-standing interest, the prominence of aerogels has notably surged in recent decades due to their potential in addressing urgent climate challenges.[3]

In this work, different MOF@chitosan composites were produced by 2 different approaches. MOFs with different loadings were chosen and impregnated into a chitosan matrix, to study the effects of the MOF structure on gas sorption properties. Using a standard static gravimetric method, gas sorption-desorption measurements of CO_2, CH_4, and N_2 were performed at 303 K and 0-30 bar. The MOF's loading and chitosan's modifications were tailored to promote synergistic effects, enhancing properties such as gas sorption capacity and selectivity performance.

Acknowledgements: The authors thank Fundação para a Ciência e Tecnologia, FCT/MCTES (Portugal) for financial support through the doctoral grants 2021.07148.BD (T. O. C.) and SFRH/BD/139627/2018 (T. J. F.), and project PTDC/CTM-CTM/30326/2017. This work was also supported by the Associate Laboratory for Green Chemistry-LAQV which is funded by national funds from FCT/MCTES (10.54499/LA/P/0008/2020, 10.54499/UIDP/50006/2020 and 10.54499/UIDB/50006/2020).

References

1. P. D. Jones, T. J. B. T.-R. M. in E. S. and E. S. Osborn, Elsevier, **2024**.
2. T.J. Ferreira, B. A. de Moura, L.M. Esteves, P. M. Reis, J. M. S. S. Esperança, I. A. A.C. Esteves; *Sustain. Mater. Technol.* **2023**, *35*, e00558.
3. A. Verma, S. Thakur, G. Goel, J. Raj, V. K. Gupta, D. Roberts, V. K. Thakur; *Curr. Res. Green Sustain. Chem.* **2020**, *3*, 100027.

P65 Hydrophobic eutectic systems as precursors of new gel electrolytes for supercapacitor applications

V. Lipskyy,[1] I. Gomes da Silva,[1] F. Montemor,[1] I. Marrucho[1]

[1]Centro de Química Estrutural, Instituto de Ciência Molecular e Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Avenida Rovisco Pais, 1049-001 Lisboa, Portugal.
Email: vitor.lipskyy@tecnico.ulisboa.pt

Supercapacitors (SC) are devices characterized by a high-power density and long cyclability. However, a significant disadvantage comes in the form of low energy density. Furthermore, available commercial SCs are based on organic electrolytes capable of reaching wider potential windows, but such electrolytes are toxic and/or flammable.[1] In this way, it is necessary to develop more sustainable electrolytes that overcome these drawbacks.

Eutectic systems (ES) are especially interesting due to the great availability of natural, non-toxic, and cheap compounds, which allow the selection and tuning of the system's properties, enabling the development of safer and more sustainable electrolytes. In the case of metallic hydrophobic ES[2], there is the added benefit since it is possible to form a gel without introducing any additional gelification agents, just by tuning the system's composition. The use of a gel electrolyte offers several advantages since it allows to mitigate not only the electrolyte leakage[3] but also the self-discharge phenomenon, thanks to the increased viscosity and resistivity of the gel when compared to liquid electrolytes.[4]

This work focuses on the study of mixtures of water and hydrophobic ES composed of fatty acids, namely hexanoic acid (C6) and octanoic acid (C8), and their respective sodium/potassium salts, analysing the compositions that present gel behaviour in order to determine their physical properties, such as ionic conductivity, viscosity and density, and electrochemical properties, by performing tests that include cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD).

Fig. 1. Preparation of gel electrolytes through the fine-tuning of the composition of the water and hydrophobic eutectic system mixture.

Acknowledgements: The authors thank the funding of Fundação para a Ciência e Tecnologia through the project PTDC/EQU-EQU/4893/202. Gomes da Silva I. thanks the financial aid of FCT/MCTES (Portugal) for the PhD scholarship 2023.00669.BD. Lipskyy, Vítor thanks the financial aid of Fundação Calouste Gulbenkian through the program "Bolsas Gulbenkian Novos Talentos".

References

1. C. Zong, Y. Deng, W. Hu, J. Qiao, J. Zhang, In Electrolytes for Electrochemical Supercapacitors; CRC Press, 2016; pp. 46–269.
2. C. Florindo, L.G. Celia-Silva, L.F.G. Martins, L.C. Branco, I.M. Marrucho; *Chem. Commun.* **2018**, *54*, 7527–7530.
3. E. Kovalska, C. Kocabas; *Mater. Today Commun.* **2016**, *7*, 155–160.
4. P. Galek, A. Slesinski, K. Fic, J.J. Menzel; *Mater. Chem. A* **2021**, *9*, 8644–8654.

List of communications

Plenary Lectures

PL1 Controlled and spontaneous symmetry breaking by means of crystallization

G. Coquerel, W.-S. Kim, B. J. Park 14

PL2 Empowering sustainable development with supercritical CO_2 technologies

A. Aguiar-Ricardo 15

PL3 Self-assembled colloids: when physical chemistry interfaces with nanomedicine and nanomaterials

E. F. Marques 16

PL4 Multiscale modeling of complex systems: from solvation to *nanoplasmonics*

C. Cappelli 17

Keynote Lectures

KL1 Ionic liquids, water and proteins: Favorable vs. competitive Interactions to design separation processes

M.G. Freire, 19

KL2 Understanding proton exchange membrane fuel cells by advanced transmission electron microscopy

M. Pereira 20

KL3 Bright and dark molecules: A photophysical journey

S. Melo 21

KL4 For nothing is secret that will not be revealed, nor anything hidden that will not be known and come to light … or when Science meets Art

A. Candeias 22

Sponsored Talk

ST1 Optimization of supercritical fluid extraction (SFE) and reaction systems

J. Carvalheira, S. Cardoso 24

Oral Communications

OC1.1 Enthalpic mapping of anthranilate and cinnamate derivatives: An experimental and computational approach

V.L.S. Freitas, C. A. O. Silva, M. D. M. C. Ribeiro da Silva 26

OC1.2 Thermodynamic study of polymorphism in the nicotinamide+adipic acid co-crystal system

I. O Feliciano, C.E.S. Bernardes, M. Fátima M. da Piedade, M.E. Minas da Piedade 27

OC1.3 For hydrophobic free energy (HFE) of linear alkylic molecules, not only size matters

J. Martins 28

OC1.4 Enhanced cancer biomarker detection in microfluidic devices using ionic liquid-based aqueous biphasic systems for serum pre-treatment

M.S.M. Mendes, V. Ch, F.A. Silva, M. G. Freire, J. P. Conde 29

OC1.5 Thermodynamics of cation-fluorinated ionic liquids

R. M. A. Silva, A.I. M.C. Lobo Ferreira, L.M.N.B.F. Santos 30

OC1.6 Thermal conductivity of ionic liquids - A reappraisal

C. A. Nieto de Castro, M.J.V. Lourenço, W.A. Wakeham 31

OC1.7 Extraction of proteins from *Tenebrio molitor* flour using deep eutectic solvents

G.Akyüz, E. V. Capela, V. Vieira, L.C. Branco, A. P. M. Tavares, M. G. Freire 32

OC1.8 Improving niraparib's solubility using a deep eutectic solvent as a drug delivery system

P. Xavier, F. Martins, N. Galamba 33

OC1.9 Varnishes? Paints? Why use toxic solvents in their formulation when there are eutectic systems?

C.C. Fernandes, A. Quirino, A. Paiva, R. Marques, A. R. C. Duarte 34

OC1.10 Chitosan and naphthaldehydes derivatives composites: adsorptive remove of tetracycline from water

J. F. M. Sousa, D. Murtinho, A. J. M. Valente, J. M. C. Marques 35

OC1.11 Sputtering of silver in thin films of long-chain imidazolium-based ionic liquids: An efficient approach to metal nanoparticle stabilization

A. C. P. M. Alves, L.M. N. B. F. Santos, J.C. S. Costa 36

OC1.12 Triazine porous organic polymers for simultaneous removal and sensing of antibiotics in water 37

P.M.C. Matias, A.C.B. Rodrigues, D. Murtinho, A.J.M. Valente 37

OC1.13 MALDI-TOF MS-based urinary peptidomics biosignature of breast cancer as a powerful approach for diagnosis

P. Sousa, J.S. Câmara, R. Perestrelo 38

OC1.14 Metrological study on a relationship between salinity and surface tension of buffered artificial seawaters

M. Serra, S. Moura, R. Quendera, O. Pellegrino 39

OC1.15 Volatilomic fingerprint of grape pomace as a sustainable approach for its valorization

T. Abreu, J.S. Câmara, J. Teixeira, R. Perestrelo 40

OC1.16 Exploring the ^{19}F NMR and photoluminescence of fluorinated dendrimers for gene delivery

L. dos Orfãos, F. Lahoz, J. Rodrigues 41

OC1.17 Exploring the kinetic and thermodynamic stability of photoresponsive cucurbituril-dithienylethene inclusion complexes

N. Basílio, A. J. Parola, P. Máximo, M. Colaço 42

OC1.18 Properties of proton and metal-ion bound to PAMAM dendrimer primary and tertiary amines

D. Fernandes, C. S. Alves, P. Pires 43

OC1.19 A new road to discover ABC transporter modulators

D. J. V. A. dos Santos, R. J. Ferreira, M. J. U. Ferreira, J.-P. Gillet, M. N. D. S. Cordeiro, C. A. Bonito 44

OC1.20 Constrained Transition State Randomization: A general transition state sampling method for bimolecular

L. P. Viegas 45

OC1.21 How cucurbit[7]urils allow the formation of a highly stable and stimuli responsive hexacationic flavylium-based quaternary rotaxane

A. Seco, N. Mcclenaghan, A. J. Parola, N. Basílio 46

OC2.1 Reactivity patterns in the decomposition of fullerene derivatives via the retro-Diels-Alder reaction

C.F.R.A.C. Lima, D.J.L. Rodrigues, C.S.T. Pinto, L.M.N.B.F. Santos 47

OC2.2 Supramolecular catalysis of diazocine isomerization

M. Colaço, J. Ewert, U. Pischel, R. Herges, N. Basílio 48

OC2.3 Assessment of the mobility and fate of halogenated substituted benzonitriles and benzaldehydes

B.D.A. Pinheiro, A.R.R.P. Almeida, M.J.S. Monte 49

OC2.4 Exploring coumarin-3-carboxamide derivatives as fluorescent metal cation detectors

L.J. Gomes, C.S.B. Gomes, A.C. Tomé , A.J. Moro 50

OC2.5 Optimizing vapor deposition of pentacene for inverted perovskite solar cells

A.F.M. Farinha, R.A.S. Pinto, L.M.N.B.F. Santos, J.C.S. Costa 51

OC2.6 Seeking new low temperature energy storage systems: *n*-alkanes as phase change materials

M.C.M. Sequeira, B.A. Nogueira, T. Nikitin, F.J.P. Caetano, H.P. Diogo, J.M.N.A. Fareleira, R. Fausto 52

OC2.7 Modeling CO_2 electrochemical reduction in porous cathodes for liquid-phase electrolyzers

I. S. Fernandes, R. Martins, M. J. Mendes, A. S. Reis-Machado 54

OC2.8 Studying the hydrogen combustion in carbon nanotubes

J. Brandão, C. Mogo, C. M. A. Rio, W. Wang, D. V. Coelho 55

OC2.9 Experimental and theoretical insight into structural, energetic and electronic properties of 4-MPy adsorption onto zinc chalcogenide-based substrates

J.S. Figueiredo, S. Fateixa, J. Lopes, A. C. Estrada, J. D. Gouveia, J. R. Gomes, T. Trindade 56

OC2.10 A robust method for property prediction via artificial neural networks: Incorporating key structural features for carbon dioxide-ionic liquid mixtures

H. Marques, J. N. Canongia Lopes, A. A. Freitas, K. Shimizu, P. S. F. Mendes 57

OC2.11 Making sense of data: Intelligible machine learning analytics for VOC vaporization enthalpy prediction

J. Ferraz-Caetano, F. Teixeira, M. N. D. S. Cordeiro 58

OC2.12 A combined structural, spectroscopic, and theoretical investigation of a water-soluble Schiff base: stability and enol-imine/keto-enamine tautomerism

H. Bouznif, L.L.G. Justino, M.I.L. Soares, T. Costa, M. L. Ramos, T. Nikitin, T.M.V.D. Pinho e Melo, N. Zouari, R. Fausto 59

OC2.13 Halogen anisotropy in solvation and membrane permeability: implications for protein-ligand binding and drug efficiency

A. Fortuna, Paulo J. Costa 60

OC2.14 Eutectic mixture formation and relaxation dynamics of co-amorphous mixtures of two antifungal imidazole drugs

W. Noor, C.D.R. Macovez, M. Romanini, J.L. Tamarit 61

OC2.15 Structural criterion for the onset of rigidity in a colloidal gel

C.S. Dias, J.C. Neves, M.M. Telo da Gama, E. Del Gado, N.A.M. Araújo 62

OC2.16 Open subsystem-based partition of molecular energies into resonance structure-resolved contributions

D.J.L. Rodrigues, E. Francisco, A.M. Pendás 63

OC2.17 Computational venom whispering to decode molecular insights of bee and snake-secreted phospholipases A_2

J.R. da Silva, J. Castro-Amorim, M.J. Ramos, P.A. Fernandes 64

OC2.18 Unveiling pesticide interactions: Insights from the *Aplysia californica* AChBP-imidacloprid complex

J.R.C. Santos, P.E. Abreu, J.M.C. Marques 65

OC2.19 HO_2* stabilization in the presence of argon

C. Mogo, J. Brandão, W. Wang, D. Coelho, C. Rio 66

OC2.20 Beyond DFT: Tackling the strong correlation problem in noble gas chemistry.

N.A.G. Bandeira, S. Oliveira, L. Maria, B.Monteiro, J.M. Carretas, J.P. Leal, J. Marçalo 67

OC2.21 Investigation of the IVR isomerization of nitrous acid

L. J. Duarte, C. M. Nunes, R. Fausto, A.A.C. Braga 68

Poster Communications

P1 Spice volatilomic pattern – A suitable approach to explore their antioxidant and anti-inflammatory properties

N. Hontman, J. Gonçalves, A. Soares, J.S. Câmara, R. Perestrelo 70

P2 Enhancing potato starch beads for effective sorption of toxic metals: the role of crosslinking degree

T.B. Costa, P.M.C. Matias, D.S. Rosa, D.M.B. Murtinho, A.J.M. Valente 71

P3 Fluorescence/phosphorescence imaging lifetime microscopy study on a ratiometric Pt(II)-chlorin oxygen sensor

T. Costa, M. Pineiro, M. Laranjo, B. Serambeque, M.F. Botelho, N.A M. Pereira, A.J.S. Alves, T.M.V. D. Pinho e Melo, J.S. Seixas de Melo 72

P4 Structural, vibrational and photochemical data of simple hydantoins – common features and substituents effects

G. O. Ildiz, B.A. Nogueira, R. Fausto 73

P5 Are Kamlet-Taft parameters sufficient to model the solution enthalpies of different APIs?

M. Chorão, N. Nunes, R. Elvas-Leitão, F. Martins 74

P6 Revolutionizing stroke diagnosis with silver nanostars and SERS analysis

C. Freitas, M. Enea, R.L. Carvalho, M. Ozório, H. Águas, E. Pereira, H.L.A. Vieira, R. Franco 75

P7 Partition of isoniazid derivatives active against tuberculosis to membrane mimetic systems: Octanol-water (log $P_{\text{oct/w}}$) *vs.* micelle-water (log K_p)

M. Reis, T. Luan, V. Leandro, M. Mendes, F. Martins, M.S.C.S. Santos 76

P8 Temperature increase in activated T-cells detected by quantum dots 655

M.F. Antunes, R.M. Almeida, H. Soares, C.E.S. Bernardes, M.E. Minas da Piedade, F. Antunes 77

P9 Hierarchical Pt/Y zeolite prepared through surfactant mediated technology: the effect of ionic strength

B. Matos, N. Nunes, A. Martins, J. Coelho, M.S. Santos, A.P. Carvalho 78

P10 Mechanochemistry: an effective method to produce metal loaded HY catalysts for HDO reaction

M. Matos, N. Nunes, R. Miguéis, M.S. Santos,A.P. Carvalho. J. Coelho, A. Martins 79

P11 Stoichiometrically diverse cocrystals of nicotinamide with dicarboxylic acids: studies of solubility behavior

A.R. Mendonça, I.O. Feliciano, M. F. M. Piedade 80

P12 Experimental and theoretical study of the crystallization process of paracetamol from solution

I. Calheiros, C.E.S. Bernardes 81

P13 Enhancing the baricitinib intrinsic dissolution rate by co-crystallization and amorphization 82

M. I. G. Silva, T. M. R. Maria, R. A. E. Castro, M. E. S. Eusébio, J. Canotilho 82

P14 Energetics and structures of borophene nanoclusters

J. M. C. Marques, F. Zergani, M. Bartolomei, F. Pirani 83

P15 Modeling preferential solvation in binary aqueous mixtures using a solvatochromic probe

A. Pinção, L. Moreira, R. Elvas-Leitão, F. Martins 84

P16 Cation effect on the viscosity and electrical conductivity of ionic liquid

C.F.P. Miranda, L.M.N.B F. Santos 85

P17 Thermodynamics of fumaric acid polymorphism

A.S. Pereira, R.G. Simões, M.F.M. Piedade, M.E. Minas da Piedade 86

P18 Metabolomic analysis of endogenous *Saccharomyces cerevisiae* strains from Madeira Island 87

F. Pereira, M. Castillo, J.S. Câmara 87

P19 Polymorphism and thermal behavior of succinic acid

P.M.S. Mateus, R.G. Simões, M F.M. Piedade, M.E. Minas da Piedade 88

P20 Synthesis of vitrimers doped with solvatochromic coumarins

T. Sousa, C.A.T. Laia, P.S. Branco, J. Sarrato, A. Pinheiro 89

P21 Diving the deep eutectic systems: The order on the water's addition

C. Sarmento, H. Monteiro, A. Santos, A. Paiva, A.R.C. Duarte 90

P22 Investigation of solid forms of sotagliflozin

R. A. E. Castro, L. Puppini, J. A. Baptista, J. Canotilho, M. E. S. Eusébio 91

P23 Novel conformational changes in ABCG2 mediated by ATP binding

P. Suzano, B. Gonçalves, M. Ferreira, D. dos Santos 92

P24 Improving the solubility of monomethyl fumarate through co-crystallization

R. Mané, M.F.M. Piedade, M.E. Minas da Piedade 93

P25 Rate constants from elementary reactions fail for combustion kinetics models

C. M. A. Rio, J. Brandão, C. Mogo, W. Wang, D.V. Coelho 94

P26 Multiprocess reaction dynamics program (MReaDy) and applications

W. Wang, J. Brandão, C. Mogo, C.M.A. Rio and D V. Coelho 95

P27 Synthesis of 6-(*N,N*-diethylamino)-flavylium salts for application in dye-sensitized solar cells

A.J. Barbosa, C.A.T. Laia, A. Jorge Parola 96

P28 Investigation of the alkyl chain length effect on the energetic properties of γ- and δ-lactones

A. L. R. Silva, G. P. León, V. Lukeš, E. Klein, M. D. M. C. Ribeiro da Silva 97

P29 [Zn(Aryl-BIAN)Cl_2] based hybrid materials for visible light driven hydrogen production from water splitting

J. Maçãs, V. Rosa, C. S. B. Gomes, I. Matos, S. Gago 98

P30 Unveiling the potential of Zr- and Zn-MOFs as photocatalysts for H_2 production from water splitting

M. Lúcio, V. Rosa, C.S B. Gomes, S. Gago 99

P31 Polymer/tubule hydrogels: structural, thermodynamic and rheological characterization

R.L. Machado, E. Loureiro, A.C. Gomes, E.F. Marques 100

P32 Research on the volatility and solubility of two methyl halogenated benzoates

G. P. León, B. D. A. Pinheiro, A. R. R. P. Almeida, M. J. S. Monte 101

P33 Sustainable technology for protein extraction from *Tenebrio molitor* flour

P. Moleiro, L.C. Branco, A.Q. Pedro, A.P. Tavares, M.G. Freire, 102

P34 Adsorption and release of NO and H_2S from a zinc BioMOF

J. Pires, M. Pinto, T. K. Tajnšek, M. Mazaj, M. Lopes, M. Batista 103

P35 Modification of carprofen palatability via formation of multicomponent solid forms

P. M. S. Inácio, J. A. Baptista, T. M. R. Maria, R. A. E. Castro, M. E. S. Eusébio, J. Canotilho 104

P36 Computational-aided evaluation of repurposing pediocin-like bacteriocins as antifungal agents against *Candida albicans*

I.R. Blanco, R.P.S. Oliveira, M.M. Pereira 105

P37 Optimizing dopamine polymerization through enzymatic pathways in aqueous biphasic systems

F.F. Magalhães, M.L. Alfier, L. Panzella, M.G. Freire, A.P.M. Tavares 106

P38 Structural, optical, and thermal properties of $BiVO_4$

B. Norte, A. C. Estrada, H. I. S. Nogueira, T. Trindade 107

P39 Thermodynamic and kinetic parameters of the crystallization of probucol and structurally related compounds from ethanol solutions

J. A. Baptista, R.A.E. Castro, J. Canotilho, M.T.S. Rosado, M.E.S. Eusébio 108

P40 Superhydrophobic Materials for Oil/Water Separation based on Supported Ionic Liquids 109

J.C.F. Nunes, M.G. Freire, A.P.M. Tavares, M.C. Neves 109

P41 Phase behavior and structural characterization of photosensitive lipid/chalcone liposomes

D. Moreira, I. S. Oliveira, N. Basílio, E. F. Marques 110

P42 The ROADMAP project – when Chemistry and Art meet for *the greater good*

C. Miguel, S. Bottura-Scardina, A.T. Caldeira, P. Flor, A. Candeias 111

P43 The curious case of $[C_8C_1im]Cl+H_2O$ system

M. Tariq, J.M.S.S. Esperança, J.N.C. Lopes, L.P.N. Rebelo 112

P44 Effect of isotopic substitution on the phase behaviour and nucleation of CO_2 hydrates

M. Tariq, M.R.C. Soromenho, M.M. Piñeiro, M. Pérez-Rodríguez, D. Kumar, A. Rodriguez, F.J. Deive, J.M.S.S. Esperança 113

P45 Experimental and computational study into the thermochemistry of furfurylamine and 5-methylfurfurylamine

L. M. P. F. Amaral, A. R. R. P. Almeida, M. A. V. Ribeiro da Silva 114

P46 Understanding the influence of ionic liquids on carbonic anhydrase activity using molecular docking

M. Fraga, M.G. Freire, M.M. Pereira 115

P47 Identification of deep eutectic solvents as modulators of *Yarrowia lipolytica* lipase activity using molecular docking

F.S. Buarque, B.D. Ribeiro, M.A.Z. Coelho, M.G. Freire, M.M. Pereira 116

P48 Influence of a thiomethyl substituent on the spectroscopic characteristics of 1,4-disubstituted 1,2,3-triazoles

M.G. Vaz, A. Lampreia, J.N. Martins, A.J. Moro, C.S.B. Gomes, J.C. Lima, V. Rosa 117

P49 Photocatalytic hydrogen production using activated carbon from tire rubber

P. C. Gomes, I. Matos, N. Lapa, J. C. Lima, S. Gago 118

P50 Reactivity patterns in the decomposition of indene adducts of C_{70} fullerene via retro-Diels-Alder reaction

C.S.T. Pinto, L.M.N.B.F. Santos, C.F.R.A.C. Lima 119

P51 Development of a novel ionic liquid-based approach for the extraction and purification of proteins from insects

E.V. Capela, P. Moleiro, G. Akyüz, V. Vieira, L.C. Branco, A.P.M. Tavares, M.G. Freire 120

P52 Thermodynamics of alkylsilane-based ILs with different anions

R.M.A. Silva, E.Baķis, A.I.M.C. Lobo Ferreira, L.M.N.B.F. Santos 121

P53 Flexible host materials for energy storage

K. Bettencourt, A.S. Viana, J.P. Correia 122

P54 COSMO-RS as a powerful tool to characterize the polarity of ionic liquids and their mixtures

E.V. Capela, A.R.R. Teles, A.F.M. Cláudio, J.A.P. Coutinho, M.G. Freire 123

P55 Effect on 1,4-disubstituted 1,2,3-triazoles emission spectra when varying water content percentage

A. Lampreia, J. M. Martins, A. Moro, C.S.B. Gomes, J. C. Lima, V. Rosa 124

P56 A precise method to estimate the enthalpies of combustion of biodiesels

R.I.S. Rodrigues, C.E.S Bernardes, M.E. Minas da Piedade, R.M. Borges dos Santos 125

P57 Catechol(amine) and pyrrole-based co-polymers for (bio)sensing applications

D.M. Carneiro, J.P. Correia, A.S. Viana 126

P58 Avian immunoglobulin Y (IgY) antibodies to overcome antimicrobial resistance (AMR)

C. Almeida, J.A.P. Coutinho, M.C. Neves, M.G. Freire 127

P59 Valorization of insect flour oil using $scCO_2$ extraction

M N. José, A.B. Paninho, C.V. Esteves, K. Zalewska, A.I. Aguiar-Ricardo, T. Casimiro, A.V.M. Nunes, L.C. Branco 128

P60 Adhesive properties of polymeric matrices made from lignin waste

A. S. Moleiro, G. G. Maia, P. Ihalainen, L. Sobhana, A. S. Viana 129

P61 Quantifying the increase in electrophilic solvent assistance: 1-X-adamantane *vs*. 2-X-2-methylpropane solvolyses (X = Cl, Br, I)

L. Moreira, A. Pinção R. Elvas-Leitão, F. Martins *130*

P62 Silica nanoparticles: a versatile avenue for stabilizing amorphous drugs

M.T. Viciosa, H.P. Diogo, M.Dionísio, T. Martins, J.P. Farinha *131*

P63 Designing new MOF-based materials for gas separation

T.S. Dionísio, T.O. Carvalho, T.J. Ferreira, J.M.S.S. Esperança, I.A.A.C. Esteves *132*

P64 Dual role of chitosan: structuring MOF into fibers with enhanced CO_2 adsorption capacity and selectivity

T.O. Carvalho, T.J. Ferreira, J. Pais, J.M.S.S. Esperança, I.A.A.C. Esteves *133*

P65 Hydrophobic eutectic systems as precursors of new gel electrolytes for supercapacitor applications

V. Lipskyy, I. Gomes da Silva, F. Montemor, I.Marrucho *134*

List of Participants

Alexandre Magalhães
Alexandre. S. Pereira
A. Jorge Parola
Ana R. R. P. Almeida Figueira
Adilson Alves de Freitas
Afonso Gonçalves
Afonso Gordo
Alejandro Ornelas
Alexandre C. P. M. Alves
Alfredo Carvalho
Ana Aguiar-Ricardo
Ana Lobo Ferreira
Ana Luísa R. Silva
Ana Paula M. Tavares
Ana Pinção
Ana Rita Mendonça
Ana Rosa
Ana S. Reis Machado
Ana S. Viana
André J. Barbosa
André Seco
André Sousa Moleiro
Andreia Fortuna
António Candeias
António Lampreia
Artur F. M. Farinha
Beatriz Matos
Bernardo Norte
Bruno D. A. Pinheiro
Cristóvão S. Dias
Carlos A. Nieto de Castro
Carlos E. S. Bernardes
Carlos F. P. Miranda
Carlos F. R. A. C. Lima
Carlos S. T. Pinto
Carolina Rio
Catarina Almeida
Catarina Campos
Catarina Miguel
Célia Sarmento
César Mogo
Chiara Cappelli
Cláudio Fernandes
Cristina Freitas
Daniel dos Santos
Diana M. Carneiro
Diogo J. L Rodrigues
Dmitriy Moreira
Duarte Fernandes
Eduardo F. Marques
Emanuel V. Capela
Filipe S. Buarque
Filomena Martins
Fraga, M
Francisco Pereira
Gastón P. León
Gérard Coquerel
Gulbahor
Gulce Ogruc Ildiz
Guliz Akyuz
Hajer Bouznif
Hermínio Diogo
Hugo Marques
Inês O. Feliciano
Iago Blanco
Inês Calheiros
Inês S. Fernandes
Isabel Marrucho
José T. Costa
Joan Ribeiro da Silva
Joana F. M. Sousa
Joana R. C. Santos
Joana S. Figueiredo
João A. Baptista
João Brandão
João Canotilho
João P. Prates Ramalho
João Paulo Leal
João Pires
Jorge Maçãs
Jorge Marques
Jorge Martins
José Ferraz-Caetano
José M. Fonseca
José Nuno Canongia Lopes
Karina Shimizu
Katherine Valentina da Silva Bettencourt
Leonardo J. Duarte
Leonor Pedrosa
Liliana J. Gomes
Luís Moreira
Luís P. Viegas
Luís Santos
Lydia dos Orfãos
M. Ermelinda S. Eusébio
M. Fatima M. Piedade
M. Serra
M. Soledade C. S. Santos
M. Teresa Viciosa
Mariana N. José

Manuel E. Minas da Piedade
Manuela M. Pereira
Mara G. Freire
Márcia C. Neves
Marco Fialho
Margarida Bastos
Maria C. M. Sequeira
Maria G. Vaz
Maria Inês Gomes da Silva
Maria João Pintassilgo
Maria Lúcio
Maria Manuela Silva
Maria S. M. Mendes
Mariana Matos
Mariana Ventura
Marina Reis
Marisa Antunes
Martim Chorão
Miriam Colaço
Mohammad Tariq
Nuno A. G. Bandeira
Nuno Basílio
Patrícia C. Gomes
Patrícia Sousa
Paulo Fialho
Pedro M. C. Matias
Pedro M. S. Mateus
Pedro Miguel Salgado Inácio
Pedro Moleiro
Pedro Suzano
Pedro Xavier
Rute I. Rodrigues
Ricardo A. E. Castro
Ricardo Franco
Ricardo G. Simões
Ricardo Mané
Rodrigo M. A. Silva
Rosa Perestrelo
Ruben Elvas-Leitão
Rui Borges
Rui Fausto
Rui L. Machado
Sérgio Seixas Melo
Talles Costa
Tatiana S. Dionísio
Telma Costa
Telma M Gomes
Teresa Abreu
Thiago O. Carvalho
Tito Trindade
Tomás Lourenço
Tomé Sousa
Vera L. S. Freitas
Vítor Lipskyy
Wahi Noor
Wenli Wang

16th National Physical Chemistry Meeting (ENQF) &
5th Computational Chemistry Symposium
Sociedade Portuguesa de Química

July 2024, Lisbon, Portugal