

th

PYCHEM

Portuguese Young Chemists Meeting



Book of Abstracts



SOCIEDADE PORTUGUESA DE QUÍMICA

SPQ – Sociedade Portuguesa de Química

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6PYChem – 6th Portuguese Young Chemists Meeting

15th to 18th May 2018,

Avenida Luísa Todi 61-67

2900-459 Setúbal, Portugal

6pychem@chemistry.pt

Book of Abstracts of the 6th Portuguese Young Chemists Meeting



Institutional Support



FUNDAÇÃO
ORIENTE

Sponsors



WILEY-VCH



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Welcome Message



On behalf of the Portuguese Young Chemists group from the Portuguese Society of Chemistry (SPQ), we kindly welcome you to join us at the 6th Portuguese Young Chemists Meeting (6th PYCheM), set in the beautiful city of Setúbal, from May 15th to 18th 2018.

This biennial conference, dating back to 2008, is dedicated to gather young researchers from all subfields of Chemistry, as well as other related scientific areas of Research.

Young chemists and researchers from any nationality are particularly encouraged to share their scientific highlights amongst their peers from chemical sciences, expand their international research network and attend lectures from recognized experts in various fields of Chemistry.

This event will count with 3 plenary lectures, 11 invited lectures, 30 oral communications and 2 poster sessions with over 95 posters.

The Portuguese Young Chemists Award (PYCA) attributed by The Young Chemists Group (GQJ) from SPQ aims to promote excellence in Chemistry developed by young researchers, with particular focus on the scientific impact on the Society. Moreover, GQJ is pleased to announce that the European Young Chemists' Network (EYCN), in collaboration with Evonik Industries, will kindly sponsor the EYCN best poster award presented at the 6th PYCheM by a young researcher.

The beautiful and historical city of Setúbal is located south of Lisbon on the northern bank of the Sado River estuary. It is possible to observe nature conservation areas such as Sado Estuary Nature Reserve and Arrábida Natural Park, with a unique natural beauty and also dolphins in the wild. We hope you will find these four days to be an informative, stimulating and pleasant time in this conference.

Welcome to Setúbal,

The 6th Portuguese Young Chemists Meeting Organizing Committee



Committees

SCIENTIFIC COMMITTEE

João Mano (PT, Univ. Aveiro)
Isabel Ferreira (PT, IPB)
Maria de Lurdes Cristiano (PT, Univ. Algarve)
Eduardo Marques (PT, Univ. Porto)
Laura Rodriguez (ES, Univ. Barcelona)
Helder Santos (FI, Univ. Helsinquia)
Carlos Baleizão (PT, Univ. Lisboa - IST)
Nuno Maulide (AT, Univ. Viena)
Susana Costa (PT, Univ. Minho)
Maria Manuel Marques (PT, Univ. NOVA de Lisboa - FCT)
Beatriz Royo (PT, Univ. NOVA de Lisboa - ITQB)
Filipe Paz (PT, Univ. Aveiro)
Anthony J. Burke (PT, Univ. Évora)
Uwe Pischel (ES, Univ. Huelva)
Sérgio Seixas de Melo (PT, Univ. Coimbra)

ORGANIZING COMMITTEE

Artur J. Moro (Univ. NOVA de Lisboa - FCT)
Nuno Basílio (Univ. NOVA de Lisboa - FCT)
Ana Lúcia Pinto (Univ. NOVA de Lisboa - FCT)
Miguel Santos (Univ. NOVA de Lisboa - FCT)
João Avó (Univ. Lisboa - IST)
Carina Crucho (Univ. Lisboa - IST)
Tatiana Vitorino (Univ. NOVA de Lisboa - FCT)
Noémi Jordão (Univ. NOVA de Lisboa - FCT)
Tiago Moreira (Univ. NOVA de Lisboa - FCT)
Hugo Cruz (Univ. NOVA de Lisboa - FCT)
Andreia Forte (Univ. NOVA de Lisboa - FCT)
André Seco (Univ. NOVA de Lisboa - FCT)
Vânia Pais (Univ. NOVA de Lisboa - FCT)
Jessica Machado (Univ. NOVA de Lisboa - FCT)

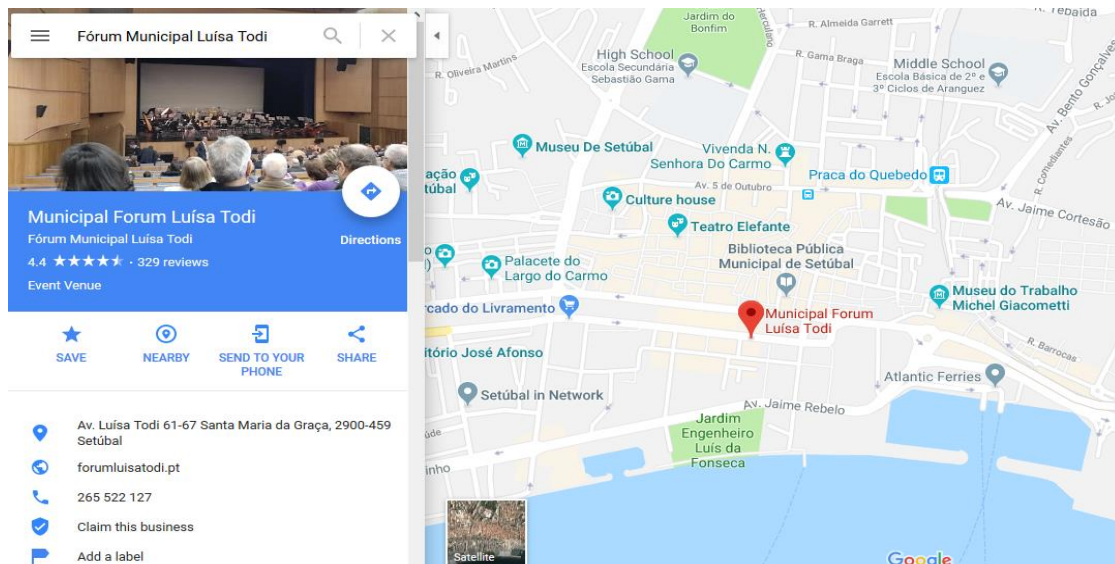
SPQ SECRETARIAT

Leonardo Mendes
Cristina Campos

Maps and Guidelines


MEETING VENUE

The conference venue will be held at Fórum Luísa Todi, located in the center of Setúbal, very close to the river, from May 15th to 18th 2018.



Address

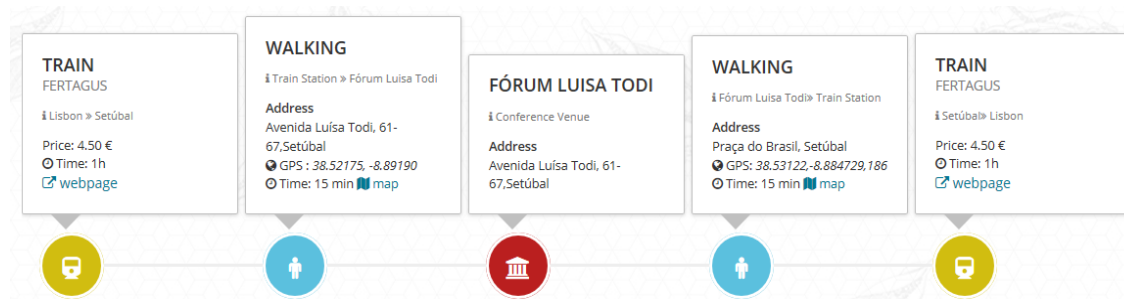
Avenida Luísa Todi 61-67, 2900-459 Setúbal – Portugal

 GPS coordinates: 38.5217546, -8.8919008

HOW TO ARRIVE

Coming from Lisbon the best choice to get to the venue is to take the train Fertagus in one of the following stations: *Roma-Areeiro*, *Entrecampos*, *Sete Rios* or *Campolide*.

NOTE: Beware that not all Fertagus trains departing from these stations are headed to Setúbal. Some (most) will stop half-way at Coima. The trip to Setúbal by train takes nearly an hour, and then is about 15 minutes' walk from the venue.



COFFEE BREAK

The coffee break in the conference venue will be held at Galeria Municipal do 11 (antigo Quartel do 11) near by the Fórum Luísa Todi, from May 16th to 17th 2018, and in the Fórum Luísa Todi (@Foyer) at May 18th, 2018.

Address

Galeria Municipal do Onze (antigo Quartel do 11)

Avenida Luísa Todi, Baluarte do Cais, nº5

2900-461 Setúbal, Portugal

REGISTRATION

The registration should be performed on May 15th from 17:00 to 20:00 at the main hall of Fórum Luísa Todi.

ACCESS TO INTERNET

In the building it is possible to access the wireless network using the following credentials:

Wireless credentials - User Name: CMSetubal_Publico

LANGUAGE

English is the official language of the congress.

VOLTAGE

In Portugal the line voltage is 220V.

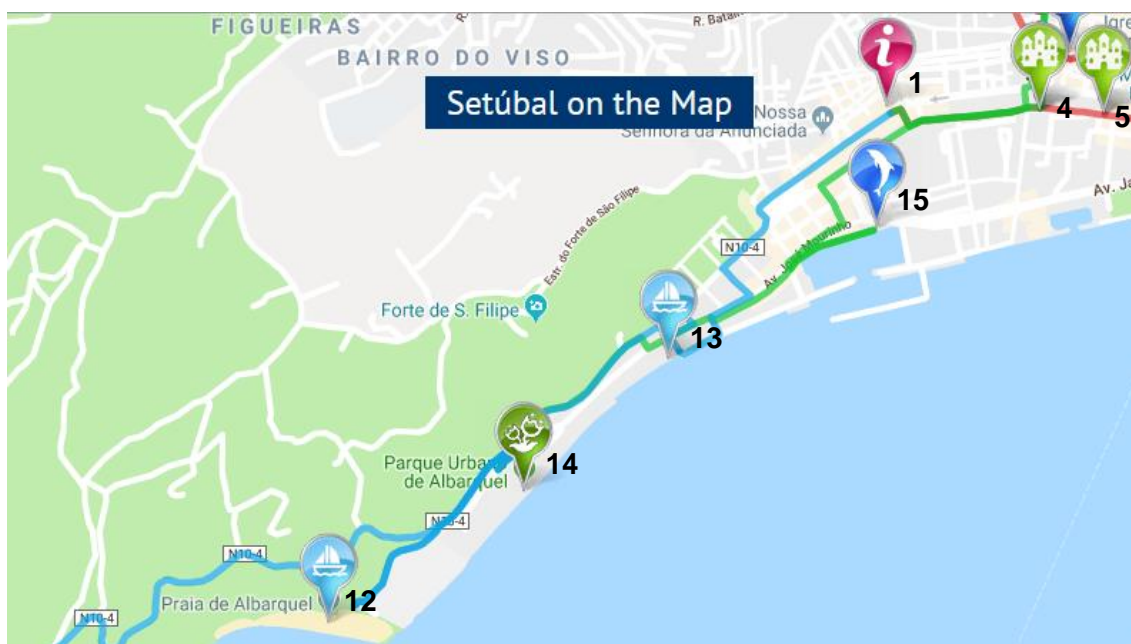
INSURANCE

Participants are responsible for arranging their own health and accident insurance.

BANKING

Several banks and ATMs are located within 8 minutes' walk distance from the venue.

POINTS OF INTEREST



- 1 – Casa da Baía: Tourism Promotion Center
- 2 – Casa da Cultura/Culture House
- 3 – Fórum Luísa Todi
- 4 – Livramento Market
- 5 – Municipal Gallery of the Old Bank of Portugal
- 6 – Michel Giacometti Museum
- 7 – Bocage
- 8 – Casa do Corpo Santo/Baroque Museum

- 9 – Jesus Convent (Church)
- 10 – Jesus Convent (Museum)
- 11 – Parque do Bonfim
- 12 – Albarquel Beach
- 13 – Saúde Beach
- 14 – Albarquel Urban Park
- 15 – Dolphin boat watching

WHERE TO EAT

Restaurant	Typical dishes	Average price
Leo do Petisco	fried cuttlefish	€
Casa Santiago (Rei do Choco-Frito)	fried cuttlefish	€€
Novo 10	fish and fresh seafood	€€
O Batareo	grilled fish and fresh seafood	€€
O Ramila	fish and fresh seafood	€
Poço das Fontainhas	fresh fish	€€
Ribeirinha do Sado	roasted fish, fried cuttlefish or the specialty: rich fish pasta - fish soup	€€
Âncora Azul	fish casserole (the value already includes drink, dessert and coffee)	€
Tasquinha do Rio	fish and meat dishes, snacks	€
Retiro da Algodeia	grilled fish and meat dishes	€€
Rockalot Acqua Bay	pizzas in a wood-fired oven, sushi, pasta with cuttlefish or black pork cheeks with truffle and pear puree	€
Pérola da Mourisca	snacks	€€
Burguesa – Burger & Gin	hamburgers	€

SOME BARS TO VISIT IN THE DAY OR NIGHT

- Tucanos
- Get in
- Laranja
- Álibi
- Taifa

Social Program

WELCOME COCKTAIL

The welcome cocktail will be held in the venue in the bar lounge Roof61, in the first day of congress (May 15th) at 17:00.

TASTING & CONFERENCE DINNER

The Conference dinner of PYCheM (which is included in the registration price) will take place at Casa Ermelinda Freitas, one of the top-ranked wine producers in Portugal, during the evening of May 17th. The dinner will be preceded by a visit to the vineyards and wine production facilities, followed by a tasting session with 5 of their wines, served with traditional, locally-sourced products. The tour takes around an hour and a quarter. Bus Transportation to Casa Ermelinda Freitas from Fórum Luísa Todi (and back) is included.



Scientific information

ORAL COMMUNICATIONS

The oral communications are divided in:

PL| Plenary sessions (45 minutes for presentation, plus 5 minutes for Q&A).

IL| Invited Oral Communications (20 minutes for presentation, plus 5 minutes for Q&A).

OC| Oral Communications (10 minutes for presentation, plus 5 minutes for Q&A).

NOTE: To all participants presenting oral communications, it is kindly asked to contact one organization member **24 hours in advance at the reception desk** to deliver your PowerPoint presentation.

POSTER COMMUNICATIONS

Two poster sessions will be held in the congress, giving the opportunity for exchange of ideas and networking between all participants.

Poster Session 1: odd numbered (10:35-11:25 and 15:30-16:20, **May 16th**)

Poster Session 2: even numbered (10:30-11:25 and 15:15-16:05, **May 17th**)

NOTE: The maximum size for the posters is **A0** in portrait orientation (**0.84 x 1.19 m**).

The posters should be placed before 10:00 of the corresponding day and should be removed until 19:00.

Awards

PORTUGUESE YOUNG CHEMISTS AWARD – PYCA 2018

The Portuguese Young Chemists Award (PYCA) attributed by GQJ/SPQ aims since 2010, to promote excellence in Chemistry developed by young researchers, with particular focus on the scientific impact on the Society. The prize is awarded every two years, to recent doctors with less than 35 years and laureates the investigation performed during their PhD. It is opened to Portuguese or foreigner young researchers that received his/her PhD degree in any field of the chemical sciences from a Portuguese University between January 2016 and December 2017.

This award comprises a monetary prize and a certificate, kindly sponsored by ChemPubSoc Europe (Wiley-VCH), and a scientific book, kindly sponsored by Gradiva Editora and will be delivered to the winner at the 6th PYChem, where he/she might talk about his/her work.



WILEY-VCH



BEST POSTER AWARD AT THE 6TH PYCHEM

The Young Chemists Group (GQJ) of the Portuguese Chemical Society (SPQ) is pleased to announce that the European Young Chemists' Network (EYCN), in collaboration with Evonik Industries, will kindly sponsor the EYCN best poster award presented at the 6th Portuguese Young Chemists Meeting (6th PYChem) by a young researcher. The award comprises a monetary prize and a certificate and will be delivered at the 6th PYChem.



Schedule

	Tuesday May 15 th	Wednesday May 16 th	Thursday May 17 th	Friday May 18 th	
09:00		Opening Ceremony			09:00
09:20		PL1 Chihaya Adachi	PL2 Luisa de Cola	PL3 Jonathan Clayden	09:20
09:50			IL5 Zita Martins		09:50
10:10		IL1 Márcia Vilarigues	OC12 Ana Rita Neves	IL9 Célia Fonseca-Guerra	10:10
10:15					10:15
10:30					10:30
10:35		Coffee Break and Poster Session I	Coffee Break and Poster Session II	OC22 José Pereira	10:35
10:50				Coffee Break @ Foyer	10:50
11:25		IL2 Javier Montenegro	IL6 Nuno Mateus	IL10 Nathan McClenaghan	11:25
11:50		OC1 Massimo Tosolini	OC13 Carla Pereira	OC23 Veronica Tona	11:50
12:05		OC2 Fausto Queda	OC14 Joana Oliveira	OC24 Cláudia D. Alves	12:05
12:20		OC3 Ángel Vidal-Vidal	OC15 José Pinela	OC25 João Ravasco	12:20
12:35		OC4 João F. Borges	OC16 Joana Azevedo	OC26 Luca Pisciottoni	12:35
12:50		OC5 João António	OC17 Catarina Pinto	OC27 M. Inês P. S. Leitão	12:50
13:05		Lunch	Lunch	Lunch	13:05
14:20		IL3 Filipe Paz	IL7 Pol Besenius	IL11 Ana Rita Duarte	14:20
14:45		OC6 Márcia Ribeiro	OC18 Tiago Moreira	OC28 Micael Silva	14:45
15:00		OC7 Sílvia Quaresma	OC19 Noémi Jordão	OC29 Eduarda S. Morais	15:00
15:15		OC8 Bárbara L. Oliveira		OC30 Sofia Domingos	15:15
15:30		Coffee Break and Poster Session I	Coffee Break and Poster Session II	Coffee Break @ Foyer	15:30
16:05			IL8 Eurico Cabrita	EYCN João Borges	16:05
16:20		IL4 Tiago Rodrigues			16:20
16:30			OC20 Bruno Medronho	NEQ/AAC Márcia Campos	16:30
16:45		OC9 Miguel M. Santos	OC21 Ana S. D. Ferreira	PYCA award	16:45
17:00	Welcome Cocktail and Registration	OC10 Telma B. Soares			17:00
17:10		OC11 Rita C. Acúrcio		Best Poster Award	17:10
17:15					17:15
17:25				Closing ceremony	17:25
17:30					17:30
17:45		GQJ Assembly	Conference dinner (until 23:00)		17:45

PL - Plenary Lecture; IL - Invited Lecture; OC - Oral Communication; EYCN - European Young Chemists Network; PYCA - Portuguese Young Chemists Award

Detailed Schedule

Wednesday, May 16th 2018

09:00-09:20 Opening Ceremony

Session 1 | Chairman: Artur Moro (LAQV@REQUIMTE - Univ. NOVA de Lisboa - FCT) | Auditorium

09:20 | **PL1** | Chihaya Adachi (OPERA - Organic Photonics and Electronics Research, Japan)
Control of excitonic processes in organic semiconductors aimed for high performance light emitting devices

10:10 | **IL1** | Márcia Vilarigues (Univ. NOVA de Lisboa - FCT, Portugal)
Painting with light – a study on historical recipes

10:35-11:25 Coffee break and Poster Session I (Galeria Municipal do 11)

Session 2 | Chairman: Beatriz Royo (Univ. NOVA de Lisboa – ITQB) | Auditorium

11:25 | **IL2** | Javier Montenegro (CIQUS - University of Santiago de Compostela, Spain)
Supramolecular Tools in Cell Delivery and Synthetic Biology

11:50 | **OC1** | Massimo Tosolini (University of Trieste, Italy)
Metal Complexes as Anion Transporters

12:05 | **OC2** | Fausto Queda (LAQV@REQUIMTE - Univ. NOVA de Lisboa - FCT, Portugal)
Bacterial Cell Wall Surrogates from Chitosan: a new molecular recognition system

12:20 | **OC3** | Angel Vidal-Vidal (University of Vigo, Spain)
High Efficient Capture and Sensing of Quat Herbicides Using Ring-Shaped Nanostructures as Host Systems

12:35 | **OC4** | João Filipe Borges (University of Aveiro, Portugal)
Engineering Marine Polysaccharides-based Hollow Multilayered Microcapsules for Enhanced Cellular Uptake

12:50 | **OC5** | João Pedro Marante António (iMed.U LISBOA - Faculty of Pharmacy, Portugal)
Diazaborines: Boronic acids under disguise for selective inhibition of Human Neutrophil Elastase

13:05-14:20 Lunch

Session 3 | Chairman: Sandra Gago (LAQV@REQUIMTE – Univ. NOVA de Lisboa - FCT) | Auditorium

- 14:20 | **IL3** | Filipe Alexandre Almeida Paz (University of Aveiro, Portugal)
Chemistry Architecture: Building Functional Metal-Organic Frameworks
- 14:45 | **OC6** | Márcia Almeida Ribeiro (IST - University of Lisbon, Portugal)
New photoactive pillared MOFs assembled by mechanochemistry for energy applications
- 15:00 | **OC7** | Sílvia Quaresma (IST – University of Lisbon, Portugal)
BioMOFS: potential systems for biomedical applications
- 15:15 | **OC8** | Bárbara Luís de Oliveira (University of Lisbon, Portugal)
Sensors Based on Customly Designed Iron(II) Coordination Polymers

15:30-16:20 Coffee Break and Poster Session I (Galeria Municipal do 11)

Session 4 | Chairman: Javier Montenegro (CIQUS - University of Santiago de Compostela, Spain) | Auditorium

- 16:20 | **IL4** | Tiago Rodrigues (Instituto de Medicina Molecular, Portugal)
Using artificial intelligence to understand the pharmacology of natural products
- 16:45 | **OC9** | Miguel Santos (LAQV@REQUIMTE – Univ. NOVA de Lisboa - FCT)
New perspective on osteosarcoma using bisphosphonate-based Ionic Liquids
- 17:00 | **OC10** | Telma Bezerra Soares (CF-UM-UP – University of Minho, Portugal)
Fluorescent graphene oxide quantum dots as traceable, pH sensitive nanocarriers for an anticancer drug
- 17:15 | **OC11** | Ana Rita Acúrcio (iMed.U LISBOA - Faculty of Pharmacy, Portugal)
New small-molecule immune system modulators towards cancer immunotherapy

17:45-19:00 GQJ Assembly (Fórum Luísa Todí)

Thursday, May 17th 2018

Session 5 | Chairman: Nathan McClenaghan (Institut des Sciences Moléculaires, France) | Auditorium

- 09:00 | **PL2** | Luisa de Cola (University of Strasbourg, France)
Stimulus responsive and self-assembled materials
- 09:50 | **IL5** | Zita Martins (IST – University of Lisbon, Portugal)
Abiotic formation of the building blocks of life – implications to the origin of life on Earth and elsewhere
- 10:15 | **OC12** | Ana Rita Neves (Faculty of Pharmacy, Portugal)
From the Sea to... the Sea! Antifouling Marine-Inspired Synthetic Steroid Derivatives

10:30-11:25 Coffee break and Poster Session II (Galeria Municipal do 11)

Session 6 | Chairman: Nuno Basílio (LAQV@REQUIMTE – Univ. NOVA de Lisboa - FCT) | Auditorium

- 11:25 | **IL6** | Nuno Mateus (ICETA/REQUIMTE – University of Porto, Portugal)
ANTHO4SKIN – Recycling anthocyanins from food wastes for cosmetic applications
- 11:50 | **OC13** | Carla Pereira (CIMO - Instituto Politécnico de Bragança, Portugal)
Recovery of Anthocyanins from Sweet Cherry Wastes: Process Modeling and Optimization Using Response Surface Methodology
- 12:05 | **OC14** | Joana Oliveira (ICETA/REQUIMTE – University of Porto, Portugal)
Colour modulation of blue anthocyanin-derivatives. Lignosulfonates as a tool to improve the water solubility of natural blue dyes
- 12:20 | **OC15** | José Pinela (CIMO - Instituto Politécnico de Bragança, Portugal)
Ultra-high Pressure-assisted Extraction of Phenolic Compounds from Watercress: Characterization and Process Optimization
- 12:35 | **OC16** | Joana Azevedo (ICETA/REQUIMTE - University of Porto, Portugal)
Reactivity of cork extracts with (+)-catechin in wine model solutions: Identification of a new family of ellagitannin-derived compounds (corklins)
- 12:50 | **OC17** | Catarina Pinto (CQC - University of Coimbra, Portugal)
The molecules of color in Portuguese postage stamps

13:05-14:20 Lunch

Session 7 | Chairman: Eurico Cabrita (UCBIO/REQUIMTE – Univ. NOVA de Lisboa - FCT, Portugal) | Auditorium

- 14:20 | **IL7** | Pol Besenius (Institute of Organic Chemistry, Germany)
Regulated Assembly of Functional Multicomponent Supramolecular Polymers
- 14:45 | **OC18** | Tiago Moreira (LAQV@REQUIMTE – Univ. NOVA de Lisboa - FCT, Portugal)
Highly Transparent, Conductive and Flexible Electrodes for Electrochromic Devices Using a “Green” Hybrid Copper-Nanowire-Reduced-Graphene-Oxide Coating
- 15:00 | **OC19** | Noémi Jordão (LAQV@REQUIMTE – Univ. NOVA de Lisboa - FCT, Portugal)
Innovative Electrochromic and Photochromic Ionic Liquids

15:15-16:05 Coffee Break and Poster Session II (Galeria Municipal do 11)

Session 8 | Chairman: João Filipe Borges (University of Aveiro, Portugal) | Auditorium

- 16:05 | **IL8** | Eurico Cabrita (UCBIO/REQUIMTE – Univ. NOVA de Lisboa - FCT, Portugal)
Rationalizing CO₂ capture with ionic liquids using high pressure NMR spectroscopy
- 16:30 | **OC20** | Bruno Medronho (University of Algarve, Portugal)
Advances in cellulose dissolution and regeneration: From scattering and rheology to a new NMR approach
- 16:45 | **OC21** | Ana Ferreira (UCBIO/REQUIMTE – Univ. NOVA de Lisboa - FCT, Portugal)
Looking inside a pore: Probing sol-gel microenvironment by PFGSE HRMAS NMR

17:30-23:00 Conference Dinner (Casa Ermelinda Freitas)

Friday, May 18th 2018

Session 9 | Chairman: Uwe Pischel (CIQSO - University of Huelva, Spain) | Auditorium

- 09:20 | **PL3** | Jonathan Clayden (School of Chemistry, University of Bristol, UK)
Exploiting Conformational Control: Reactivity, Relays and Receptors
- 10:10 | **IL9** | Célia Fonseca-Guerra (Vrije Universiteit Amsterdam, The Netherlands)
Attractive and repulsive orbital interactions in hydrogen bonding and aurophilic interactions
- 10:35 | **OC22** | José Pereira (CICECO and CESAM – University of Aveiro, Portugal)
Computational optimization of bioadsorbents for the removal of pharmaceuticals from water

10:50-11:25 Coffee break

(Fórum Luísa Todi @Foyer)

Session 10 | Chairman: Jonathan Clayden (University of Bristol, UK) | Auditorium

- 11:25 | **IL10** | Nathan McClenaghan (Institut des Sciences Moléculaires, France)
From Foldaxanes to Explosomes: Photoactive Supramolecular Systems
- 11:50 | **OC23** | Veronica Tona (Institute of Organic Chemistry - University of Vienna, Austria)
Chemoselective Aminations via Electrophilic Activation of Amides
- 12:05 | **OC24** | Cláudia Daniela Alves (University of Coimbra, Portugal)
Asymmetric Neber Reaction in the Synthesis of 2-(Tetrazol-5-yl)-2H-Azirines
- 12:20 | **OC25** | João Manuel Ravasco (iMed.Ulisboa - Faculty of Pharmacy, Portugal)
Bifunctional trans- cyclooctenes (BITCO's) for enhanced spatial and temporal resolution study of biological systems
- 12:35 | **OC26** | Luca Pisciotani (CNRS - University of Bordeaux, France)
Synthesis of electroactive subcomponents for molecular machines
- 12:50 | **OC27** | Maria Inês Paiva da Silva Leitão (ITQB - Univ. NOVA de Lisboa)
Guanosine Derived N-Heterocyclic Carbenes: synthesis and applications

13:05-14:20 Lunch

Session 11 | Chairman: Miguel Santos (LAQV@REQUIMTE – Univ. NOVA de Lisboa - FCT, Portugal) | Auditorium

- 14:20 | **IL11** | A. Rita Duarte (LAQV@REQUIMTE – Univ. NOVA de Lisboa - FCT, Portugal)
Green chemistry and deep eutectic systems in life science applications
- 14:45 | **OC28** | Micael Silva (UCBIO/REQUIMTE – Univ. NOVA de Lisboa - FCT, Portugal)
ILs as tunable modulators for protein stability
- 15:00 | **OC29** | Eduarda Serra Morais (CICECO - University of Aveiro, Portugal)
Anti-inflammatory and antioxidant nanostructured cellulose membranes loaded with phenolic-based ionic liquids for cutaneous application
- 15:15 | **OC30** | Sofia Domingos (iMed.Ulisboa - Faculty of Pharmacy, Portugal)
Novel chemical tools to explore Parkin activation

15:30-16:05 Coffee Break

(Fórum Luísa Todi @Foyer)

Session 12 | Chairman: Carina Crucho (IST - University of Lisbon, Portugal) | Auditorium

16:05-16:30 EYCN - João Borges

15:30-16:45 NEQ/AAC - Márcia Campos

16:45-17:10 PYCA Award

17:10-17:25 Best Poster Award

17:25-17:45 Closing Ceremony

List of Communications

PLENARY LECTURES

PL1| *Control of excitonic processes in organic semiconductors aimed for high performance light emitting devices*

Chihaya Adachi

PL2| *Stimulus responsive and self-assembled materials*

Luisa de Cola

PL3| *Exploiting Conformational Control: Reactivity, Relays and Receptors*

Jonathan Clayden

INVITED LECTURES

IL1| *Painting with light - a study on historical recipes*

Márcia Vilarigues

IL2| *Supramolecular Tools in Cell Delivery and Synthetic Biology.*

Javier Montenegro

IL3| *Chemistry Architecture: Building Functional Metal-Organic Frameworks*

Filipe Alexandre Almeida Paz

IL4| *Using artificial intelligence to understand the pharmacology of natural products*

Tiago Rodrigues

IL5| *Abiotic formation of the building blocks of life – implications to the origin of life on Earth and elsewhere*

Zita Martins

IL6| *ANTHO4SKIN – Recycling anthocyanins from food wastes for cosmetic applications*

Nuno Mateus

IL7| *Regulated Assembly of Functional Multicomponent Supramolecular Polymers*

Pol Besenius

IL8| *Rationalizing CO₂ capture with ionic liquids using high pressure NMR spectroscopy*

Eurico Cabrita

IL9| *Attractive and repulsive orbital interactions in hydrogen bonding and aurophilic interactions*

Célia Fonseca Guerra

IL10| *From Foldaxanes to Explosomes: Photoactive Supramolecular Systems*

Nathan McClenaghan

IL11| *Green chemistry and deep eutectic systems in life science applications*

Ana Rita Duarte

IL - EYCN| *EYCN – The European Young Chemists' Network – Promoting Chemistry and Connecting Young Chemists in Europe and Beyond*

João Borges

ORAL COMMUNICATIONS

OC1| *Metal Complexes as Anion Transporters*

Massimo Tosolini

OC2| *Bacterial Cell Wall Surrogates from Chitosan: a new molecular recognition system*

Fausto Daniel dos Santos Queda

OC3| *High Efficient Capture and Sensing of Quat Herbicides Using Ring-Shaped Nanostructures as Host Systems*

Angel Vidal Vidal

OC4| *Engineering Marine Polysaccharides-based Hollow Multilayered Microcapsules for Enhanced Cellular Uptake*

João Filipe Borges

OC5| *Diazaborines: Boronic acids under disguise for selective inhibition of Human Neutrophil Elastase*

João Pedro Marante António

OC6| *New photoactive pillared MOFs assembled by mechanochemistry for energy applications*

Márcia Almeida Ribeiro

OC7| *BioMOFS: potential systems for biomedical applications*

Sílvia Andreia Almeida Quaresma

OC8| *Sensors Based on Customly Designed Iron(II) Coordination Polymers*

Bárbara Luís de Oliveira

OC9| *New perspective on osteosarcoma using bisphosphonate-based Ionic Liquids*

Miguel Maurício Machado dos Santos

OC10| *Fluorescent graphene oxide quantum dots as traceable, pH sensitive nanocarriers for an anticancer drug*

Telma Bezerra Soares

OC11| *New small-molecule immune system modulators towards cancer immunotherapy*

Ana Rita de Carvalho Acúrcio

OC12| *From the Sea to... the Sea! Antifouling Marine-Inspired Synthetic Steroid Derivatives*

Ana Rita da Conceição Neves

OC13| *Recovery of Anthocyanins from Sweet Cherry Wastes: Process Modeling and Optimization Using Response Surface Methodology*

Carla Susana Correia Pereira

OC14| *Colour modulation of blue anthocyanin-derivatives. Lignosulfonates as a tool to improve the water solubility of natural blue dyes.*

Joana Alexandra da Silva Oliveira Pinto da Silva

OC15| *Ultra-high Pressure-assisted Extraction of Phenolic Compounds from Watercress: Characterization and Process Optimization*

José Virgílio Santulhão Pinela

OC16| *Reactivity of cork extracts with (+)-catechin in wine model solutions: Identification of a new family of ellagitannin-derived compounds (corklins)*

Joana Filomena da Costa Azevedo

OC17| *The molecules of color in Portuguese postage stamps*

Catarina Monteiro Pinto

OC18| *Highly Transparent, Conductive and Flexible Electrodes for Electrochromic Devices Using a "Green" Hybrid Copper-Nanowire-Reduced-Graphene-Oxide Coating*

Tiago André Semedo Moreira

OC19| *Innovative Electrochromic and Photochromic Ionic Liquids*

Noémi Tamar do Carmo Jordão

OC20| *Advances in cellulose dissolution and regeneration: From scattering and rheology to a new NMR approach*

Bruno Filipe Figueiras Medronho

OC21| *Looking inside a pore: Probing sol-gel microenvironment by PFGSE HRMAS NMR*

Ana Sofia Diogo Ferreira

OC22| *Computational optimization of bioadsorbents for the removal of pharmaceuticals from water*

José Manuel Santos Pereira

OC23| *Chemoselective Aminations via Electrophilic Activation of Amides*

Veronica Tona

OC24| *Asymmetric Neber Reaction in the Synthesis of 2-(Tetrazol-5-yl)-2H-Azirines*

Cláudia Daniela Da Cruz Alves

OC25| *Bifunctional trans- cyclooctenes (BITCO's) for enhanced spatial and temporal resolution study of biological systems*

João Manuel Janeiro Martins Ravasco

OC26| *Synthesis of electroactive subcomponents for molecular machines*

Luca Pisciotani

OC27| *Guanosine Derived N-Heterocyclic Carbenes: synthesis and applications*

Maria Inês Paiva da Silva Leitão

OC28| *ILs as tunable modulators for protein stability*

Micael Simões Silva

OC29| *Anti-inflammatory and antioxidant nanostructured cellulose membranes loaded with phenolic-based ionic liquids for cutaneous application*

Eduarda Serra Morais

OC30| *Novel chemical tools to explore Parkin activation*

Sofia Leonor Afonso Domingos

NEQ/AAC| *Synthesis and characterization of promising theranostic agents for cancer*

Márcia Campos

POSTER COMMUNICATIONS

PC1| *Thermodynamic Stability of Flavylium Salts as a Valuable Tool to Predict its Reactivity Against π -Nucleophiles*

Alfonso Alejo Armijo

PC2| *Synthesis and characterization of pyridinechalcones*

Ambrósio Luis Gandala Camuenho

PC3| *One-pot Azaindole synthesis from substituted aminopyridines*

Ana Cristina da Costa Mortinho

PC4| *Preparation of copper-based chalcogenides by electrospinning technique*

Ana Cristina Gomes Ferreira

PC5| *From red wine to energy: Pyranoanthocyanins as light-harvesters in Dye-Sensitized Solar Cells*

Ana Lúcia Moreira Pinto

PC6| *Pectic Polysaccharides: from agro-food wastes towards advanced applications in food industry*

Ana Luísa Mosqueira Alves Pires Fernandes

PC7| *Metabolic adaptation of human osteoblasts to growth on non-poled and poled-PLLA films*

Ana Rita Araújo Silva

PC8| *Sustainable synthesis of heterocyclic compounds on a soluble polymer support*

Ana Sofia Brancos dos Santos

PC9| *Cytotoxic Impact of Platinum- and Palladium-based Drugs on MG-63 Cells*

Ana Sofia da Costa Martins

PC10| *Magnetic-responsive double layer cell sheets using internalizable magnetite nanoparticles: new prospects for bone regeneration*

Ana Sofia Matias da Silva

PC11| *Intriguing properties of a copper(I)-tin(II) ABX₃ type mixture*

André Miguel Lopes Seco

PC12| *Preparation of copper-based chalcogenides by electrospinning tec Synthesis of bis-functionalized furanose derivatives towards new types of nucleoside and nucleotide analogs*

Andreia Jesus Lopes Fortuna

PC13| *Development of Magnetic and Luminescent Functional Ionic Liquids*

Andreia Sofia de Almeida Baptista Forte

PC14| *Screening of GSR in skin by microscopy FTIR-ATR imaging*

Angela Lizeth Alvarez Jimenez

PC15| *Combining Gold Nanoclusters and Polymer as Probes*

Bárbara Augusta Pereira Casteleiro

PC16| *Manganese N-Heterocyclic Carbene Complexes in Catalytic Reductions*

Beatriz Royo

PC17| *Valorisation of spent coffee grounds using subcritical water*

Bruno Miguel da Silva Pedras

PC18| *Diffusion coefficients of metal acetylacetonates in liquid ethanol and supercritical CO₂*

Bruno Miguel Martins Zêzere

PC19| *A Novel Polysaccharide-based Approach for Cryopreservation*

Bruno Miguel Soares Guerreiro

PC20| *A new generation of photoluminescent transparent glasses*

Carina Alexandra Félix Figueiredo

PC21| *Solid-state investigation of zeolite acidity using trimethylphosphine oxide probe molecules*

Carlos Manuel Pereira Bornes

PC22| *Complete study of protein GB1 encapsulated in a reverse micelle system by nuclear magnetic resonance*

Carmen Alicia Moreno Montoya

PC23| *Multifunctional laminarin microparticles for cell adhesion and expansion*

Catarina de Almeida Custódio

PC24| *Photoluminescent species present in artificial 'hackmanite'*

Catarina Sofia Miranda Viola

PC25| *Ultra-concentrated surfactant systems to produce highly efficient eco-friendly detergents. Control of solutions properties.*

Cátia Sofia Mateus Esteves

PC26| *Ligand and spin state effects in Mn(III) single molecule magnets*

César Augusto Pifre Reis

PC27| *Dry Powder Formulations for Antibiotic Pulmonary Delivery*

Clarinda Isabel da Silva e Costa

PC28| *Antimicrobial and antifungal activities of a coloring extract rich in betacyanins obtained from the flowers of Gomphrena globosa L*

Custódio Miguel Lobo de Freitas Roriz

PC29| *Novel AZT-Triazoles for HIV Resistant Strains*

Daniel Augusto Machado de Alencar

PC30| *A comprehensive investigation of tryptanthrin, an alkaloid from indigo and isatin*

Daniela Ribeiro Pinheiro

PC31| *Impact of preterm birth on newborn urinary metabolic profile: a preliminary study*

Daniela Sofia Bandeira Gomes Duarte

PC32| *Novel Hypervalent Iodine reagents for Sulfonyl-transfer reactions*

Diogo Lopes Poeira

PC33| *Silica Glyconanoparticles for Liver Cancer Targeting*

Edgar Ângelo Jacinto Castanheira

PC34| *Removal of Methomyl by Adsorption on activated Carbon From Aqueous Solution*

Emílio Figueira Tchikuala

PC35| *3D Structures from Cross-linked Nanocellulose*

Frone Adriana Nicoleta

PC36| *Deep Eutectic Solvents as promising electrolytes and electrochromic materials*

Hugo Gonçalo da Silva Cruz

PC37| *Synthesis of novel pincer Pd borohydride complex and its alcoholysis*

Igor E. Golub

PC38| *Highly soluble salts of adamantylamine anti-Parkinsonian drug*

Inês Catarina Batista Martins

PC39| *The separation of betulinic and oleanolic acids by simulated moving bed chromatography: Experimental and modeling studies*

Ivo Samuel Caniceiro Azenha

PC40| *Synthesis of naphthalene/anthracene based chromenes for application to electrochromic devices.*

Jack Fletcher-Charles

PC41| *Solar photodegradation of formalin using visible light-active composites*

Joana Ferreira Leal

PC42| *Gamma radiation induces degradation of phenolic acids*

Joana Filipa de Paiva dos Santos Madureira

PC43| *Children's saliva metabolome in dental caries research*

Joana Leonor Sousa Almeida Pereira

PC44| *Hybrid carbon nanostructures aiming at photocatalytic applications*

Joana Lúcia Marto dos Santos Lopes

PC45| *Fluoresceins with Delayed Fluorescence as probes for Fluorescence Microscopy*

Joana Mafalda Nunes Paulo Silva Martins

PC46| *A new generation of ring-fused chlorins as promising PDT agents*

João Carlos Salgueiro Simões

PC47| *A recyclable benziodoxole-based reagent: a new group transfer agent immobilized on a soluble polymer support*

João Cristóvão Santos Silva Macara

PC48| *Chemical Modification of Laminarin for Biomedical Applications*

João Manuel Marques Rodrigues

PC49| *Effect of Caffeic Acid Polyacylations in Color Stability of Heavenly Blue Anthocyanin: A thermodynamic and Kinetic study.*

Johan Mendoza Chacón

PC50| *Magnetic skyrmion phase in the topological chiral magnet Cu_2OSeO_3*

José Francisco Rodrigues Malta

PC51| *Oleocanthal Isolated from Olive Oil by Countercurrent Chromatography Reduces Breast Cancer Cell Migration*

Juan Ortega Vidal

PC52| *Application of Proteins for organocatalysis*

Karolina Zalewska Patrício

PC53| *Synthesis of a cyclopentenone family and evaluation of their anti-proliferative activity in human cancer cells*

Késsia Hapuque Santos de Andrade

PC54| *Enzymatic Kinetic Resolution of (+/-)-Menthol in Deep Eutectic Solvents*

Liane Pereira de Meneses

PC55| *Extending the blue color stabilization of anthocyanin derivatives*

Luis Cruz

PC56| *Synthesis, Crystal Structure, And DFT Calculations Of Two New Dinuclear Cu(I) Complexes Bearing Ar-BIAN Ligands Functionalized By NO₂ Group*

Mani Hosseinzadeh

PC57| *Synthesis and characterization of promising theranostic agents for cancer*

Márcia Alexandra de Campos Aguiar

PC58| *Theoretical Study of an Efficient Hybrid Adsorbent Based on Silica-Supported Amino Penta-Carboxylic Acid for Water Purification.*

Marcos André Pinto de Carvalho

PC59| *Donor/Acceptor Hofmann Clathrates*

Marcos António Martins Bento

PC60| *Oxazol-5-(4H)-ones-based RIPK1 inhibitors as potential modulators of necroptosis*

Maria Beatriz Tomaz Ferreira

PC61| *Cardoon (Cynara cardunculus L.) flowers as sources of phenolic compounds with high biological potential*

Maria Inês Moreira Figueiredo Dias

PC62| *Polyoxometalate/graphene nanocomposites for the photocatalytic degradation of water pollutants*

Maria João da Costa Martins

PC63| *Design of thiophene-based polymers for electrochromic applications*

Mariana Sofia dos Santos Antunes

PC64| *Synthesis and studies of new building blocks for rotaxane-based molecular machines*

Maxime Douarre

PC65| *One-pot reaction: A sustainable and green approach for drug modification*

Miguel Alexandre Gomes Mateus

PC66| *Light-induced release of bio-relevant cargo from 4-sulfocalix[4]arene in water*

Miguel Angel Romero Carrasco

PC67| *Nanobioconjugation of Toxicodendron vernicifluum Laccase and Gold Nanoparticles for Enzymatic Activity Enhancement*

Miguel Peixoto de Almeida

PC68| *Flow assisted synthesis of possible bioactive carbocycles from pyridinium salts*

Milene Andreia Gamito Fortunato

PC69| *Adsorption and Release Kinetics of Polyelectrolyte Microcapsules doped with Porphyrins: A Fluorescence Study.*

Nuno Guilherme Branco Neto

PC70| *Structural elucidation and molecular dynamics applied to the understanding and characterization of HIV surface glycoproteins*

Patrícia Filipa Alves Serra

PC71| *Synthesis and in vitro antileishmanial activity of selected tetraoxanes against Leishmania donovani*

Patricia Sofia Menalha Amado

PC72| *Hybrid materials functionalised by gamma irradiation for the conservation of Roman mosaics*

Paula Alexandra Pinto Rodrigues

PC73| *Supramolecular Assemblies Based on Diarylethenes Derivatives*

Pedro Miguel Mendonça Ferreira

PC74| *Exploiting the Structural and Conformational Profile of the 20S native human proteasome*

Pedro Miguel Pinto Fernandes

PC75| *Exploring the Stenhouse Chemistry: Formation and mechanistic insights of new Stenhouse/Cyclopentenone systems*

Rafael F. A. Gomes

PC76| *Magnetic studies on symmetric and asymmetric binuclear hydrazide metal complexes*

Rafaela Farelo Silva Tenera Marques

PC77| *Gels for cleaning artworks: An NMR approach*

Raquel Alexandra Valadares Barrulas

PC78| *New polymer for wine protein removal*

Ricardo Alexandre Ventura das Chagas

PC79| *Water soluble acridones for Redox Flow Batteries*

Ricardo Daniel Costa Pereira

PC80| *Catalyst-dependent Selectivity in Sulfonium Ylide Cycloisomerisation Reactions*

Rik Oost

PC81| *Caged amino acids for controlled release of bioactive compounds with light*

Rita João Pereira Fernandes

PC82| *Fibre membranes with deep eutectic solvents and enzymes for CO₂ solubilisation and transformation*

Rita Paula Paiva Craveiro

PC83| *New anthracene based 1,3-diamine structures*

Rita Rodrigues Fernandes de Jesus

PC84| *Irradiation and storage time effects on chemical parameters of Agaricus bisporus Portobello*

Rossana Veviana Centeio Cardoso

PC85| *Nanomaterials based on polyoxomolybdate as sustainable catalysts for oxidative desulfurization of fuels*

Sandra Maria Nunes Gago

PC86| *Metal-doped hybrid siliceous materials prepared by a sol-gel method*

Sofia Farias Soares

PC87| *Sustainable Separation Plataforms based on Aqueous Biphasic Systems formed by Ionic Liquid and Carbohydrates*

Sónia Isabel Neto Pedro

PC88| *Metabolic profiling of pancreatitis and KRAS-induced pancreatic cancer in a mouse model*

Tatiana João Ribeiro Gonçalves Carneiro

PC89| *A linear trinuclear oxidodiperoxido-molybdenum(VI) complex with single triazole bridges*

Tatiana Ribau Amarante

PC90| *Silica-based hybrid nanoparticles for high performance coatings*

Tiago Dourado Martins

PC91| *Novel enantiopure tryptophan-derived oxazoloisindolinones: from synthesis to in vitro stability profile studies of promising anticancer small molecules*

Valentina Barcherini

PC92| *Synthesis of (Triazolyl)methyl Amide-linked Pseudodisaccharide Nucleosides as Potential Inhibitors of Glycosyltransferases*

Vítor José Inácio Martins

PC93| *NMR study of [Bmim][BF₄]-water mixtures*

Wagner Menezes da Silva

PC94| *Antimicrobial Ionic Liquids: synthesis and anti-bacterial activities*

Zeljko Petrovski

PC95| *N-heterocyclic carbenes derived from 7-methylguanosine*

Zuzanna Filipiak

PYCA AWARD

Catalytic valorization of lignocellulosic biomass

Lucília S. Ribeiro

Plenary Lectures

Control of excitonic processes in organic semiconductors aimed for high performance light emitting devices

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Through almost 30 years' research and development, organic light emitting diodes (OLEDs) finally realized the ultimate electroluminescence efficiency, i.e., nearly 100% electron to photon conversion. The strong demands for ideal OLED emitters pushed the development of novel light emitting molecules from fluorescence into room temperature-phosphorescence and thermally activated delayed fluorescence (TADF). In particular, the recent sophisticated molecular design allowed a wide variety of aromatic compounds for TADF emitters. In this talk, we introduce our recent attempts of novel organic light emitting materials aimed for high performance TADF, singlet-fission, and lasers.

Stimulus responsive and self-assembled materials

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Despite the substantial progress that has been made in biomaterials synthesis and functionalization, the challenge of delivery in vivo in desired organs biomolecules or drugs and to mimic the ECM with implants that are able to reduce immunoresponse is still unmet.

Towards this aim, we reported a novel biocompatible hydrogel with the ability to release a migration-inducing factor, for the recruitment of stem cells [1]. The hydrogel is a composite made of breakable container –type materials able to respond to an external stimulus. In particular in the last 5 years we devoted much effort in the creation of “containers’ able to break in small fragments (<5 nm) by a redox reaction, [2] enzymatic degradation, [3] and pH. They can also be capsules in which large biomolecules such as enzymes and proteins can be entrapped and release on demand [4]. The hydrogels that contain such containers are formed in physiological conditions, without any catalyst and at room or at body temperature. They are perfectly biocompatible and can be made degradable. Cells are able to populate and proliferate in the matrices and even stem cells are able to grow and differentiate. Interestingly these soft materials can be injected as liquid and are able to solidify in few seconds or even in milliseconds in different tissues and organs.

Finally, I wish to close my talk showing novel capsules that can be realized using a unique approach to template virus proteins to reconstruct virus-like particles. We use luminescent Pt(II)-complex amphiphiles, able to form supramolecular structures in water solutions, that can act as templates of viruses capsid proteins. The platinum assemblies can have different morphologies and extremely high emission of which the color depends on the assembly. Interestingly we are able to change the size and shape of the particles even though we use the same natural proteins. The obtained virus-like particles can be visualized by their intense emission at room temperature, generated by the self-assembly of the Pt(II)-complexes inside the capsid [5].

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Exploiting Conformational Control: Reactivity, Relays and Receptors

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Nature uses ingenious mechanisms to solve challenges of molecular reactivity and molecular communication, many of them making use of exquisite control of molecular conformation. The lecture will explore the use of synthetic molecules with well-defined conformations to solve problems in synthesis (for example, the metal-free arylation and vinylation of enolates^[1,2] or amines^[3], and the synthesis of medium rings^[4,5]) and function (the design and construction of artificial membrane-bound receptors^[6,7]).

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Invited Lectures

***Painting with light* - a study on historical recipes**

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Stained glass is part of our tangible cultural heritage, present in diverse cultural and creative expressions. A less known part of this heritage are the paints used for their production.

We propose to deconstruct and reconstruct historical recipes for production of paints to be applied on glass, aiming at a clearer understanding of the accomplishments of craftsman in their time.

The tools provided by the fields of technical art history and experimental archaeology are being used to establish a methodology for the production of historically accurate reconstructions of paints that will act as references for further studies of historic stained-glass. Representative recipes of paints, such as grisailles, yellow silver stain, enamels and sanguine red, are being selected from treatises and recipe books dated from the 12th century to the 19th century and reproduced in laboratory. These allows the characterization of this paint material with analytical techniques such as Optical Microscopy, Particle Induced X-ray Emission, X-Ray Diffraction, Scanning Electron Microscopy, UV-Vis spectroscopy and Colorimetry.

This methodology is being used for the production of samples for corrosion studies, and to test conservation procedures and products.

Furthermore, the results of the research are correlated with historical paints applied on stained-glass aiming to understand how this historical written information represents the practices at the stained-glass workshops.

Supramolecular Tools in Cell Delivery and Synthetic Biology

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Supramolecular Chemistry is the discipline that allows us to study and understand the weak and fundamental interactions that regulate the complex processes accomplished by living organisms.^{1,2}

For instance, the transport of macromolecules across the membrane of the cells is of fundamental importance in chemical biology, medicine and beyond.² The supramolecular conjugation between cationic amphiphiles and anionic biomacromolecules constitutes one of the most widely applied strategies for intracellular delivery of nucleotides and proteins.² Our research group is interested in the application of hydrazone bond formation to modify the properties of polymers and peptides and trigger the membrane transport and delivery of macromolecules with biological relevance.^{3,4} The synthetic potential of this methodology has allowed the efficient delivery of different nucleotides (siRNA and DNA) as well as functional proteins including Cas9 for gene editing by the CRISPR/Cas9 system.^{3,4}

We have also recently started a research program to implement the lessons learned in supramolecular chemistry in the fabrication of artificial tubular networks as cytoskeleton mimics. We believe that the controlled self-assembly of robust peptide structures in confined spaces constitute an excellent synthetic tool for the development of bottom up approaches for minimal cell-like entities in synthetic biology.

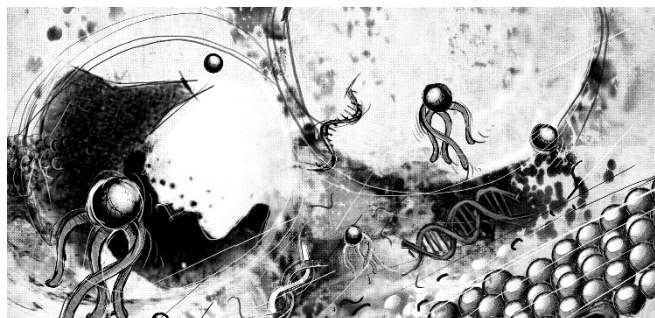


Figure 1. Conceptual drawing of amphiphilic vehicles and nucleotide cargos for membrane translocation and cell delivery.

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Acknowledgments

We acknowledge the support from MINECO (CTQ2014-59646-R, SAF2017-89890-R) and the Xunta de Galicia (ED431G/09, ED431C 2017/25 and 2016-AD031), the ERDF, the ERC Starting Grant (DYNAP-677786) and the Human Frontier Science Research Program (RGY0066/2017).

Chemistry Architecture: Building Functional Metal-Organic Frameworks

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The quest for novel zeo-type compounds remains intensive research area in Materials Science due to their role as a large slice in the global chemical economy. Though Metal-Organic Frameworks (MOFs) have been known for decades, it was Omar Yaghi's vision [1] that showed that these crystalline compounds could sustain permanent porosity and being used as functional materials. Countless new MOFs are found on a daily basis. However, scientific reports are usually based on slow, time-consuming methods, using hazardous solvents, with MOFs exhibiting poor thermal and mechanical stabilities, which also hinders their use in applications.

We have over a decade of experience in MOF chemistry and applications, with focus on the use of phosphonate-based linkers (-PO₃) connected to lanthanides (Ln), yielding functional lanthanide-polyphosphonate MOFs (LnMOFs): while tetrahedral -PO₃ linkers mimic the connectivity found in zeolites, promoting structural robustness and thermal stability, Ln cations induce photoluminescence (PL) boosted by the linkers (*i.e.*, antenna effect) [2]. In addition, the presence of various phosphonic acid groups lining the surface of the crystallites confers to the materials the great ability to catalyse a number of reactions of industrial interest. This communication will summarize some of our key achievements in the design of such functional materials [3] while also showing their great potential concerning structural flexibility [4].

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Using artificial intelligence to understand natural products the pharmacology of natural products

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Disease modulators are the centerpiece of drug discovery. Natural products have traditionally served as a privileged source of inspiration for molecular design, given the pre-validation of their frameworks as protein-binding motifs [1, 2]. While supplying development pipelines with adequate amounts of natural products is being tackled by total syntheses, unveiling the molecular targets of natural products remains arguably the biggest challenge in pre-clinical studies [3]. In this regard, laborious chemoproteomics approaches remain the gold-standard method to discover pharmacology of bioactive matter. These, however, suffer from numerous drawbacks, including the need for chemical modification of the original compounds, which can have significant impact on binding affinities. In opposition, *in silico* tools offer a viable means for generating research hypotheses in a cost-effective fashion [1].

Herein, I provide a brief overview of machine learning methods that have been employed by us to unravel pharmacology networks of bioactive natural products [1, 4]. Specifically, I will focus on the discovery of (-)-englerin A as a Ca_v1.2 channel ligand [5], and beta-lapachone as a 5-lipoxygenase inhibitor [6]. In the latter case, we correlate inhibition of 5-lipoxygenase with the already known anticancer effects.

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Acknowledgments

T.R. is a Marie-Sklodowska Curie Fellow.

Abiotic formation of the building blocks of life – implications to the origin of life on Earth and elsewhere

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The exogenous delivery of organic molecules to our young planet between 4.56 to 3.8 billion years ago may have played a crucial role in the origin of life. Space missions to comets and asteroids, as well as laboratory analysis of micrometeorites, interplanetary dust particles (IDPs) and meteorites have detected several indigenous organic molecules, some of which are the main components of the cell, the basic unit of life. Micrometeorites and IDPs contain ketones, aliphatic and aromatic hydrocarbons, while carbonaceous meteorites, which are 4.568 billion years old (i.e. as old as the solar system) contain a variety of extra-terrestrial organic compounds. These include carboxylic acids, amino and diamino acids, sulfonic and phosphonic acids, purines and pyrimidines, sugar-related compounds, and hydrocarbons, among others. Space missions have visited comets, including comet Wild-2, which contains glycine, and comet 67P/Churyumov-Gerasimenko, which has alcohols, carbonyls, amines, nitriles, amides, isocyanates, the polymer polyoxymethylene, phosphorus and glycine. All this organic inventory contributed to the origin of life in our planet and possibly elsewhere. Indeed, other places of our solar system that have habitability conditions (i.e. water, nutrients and a source of energy) for life to emerge include Mars and the moons Europa and Enceladus. In this talk I will discuss the exogenous sources of the building blocks of life, how to distinguish between terrestrial and extra-terrestrial organic molecules, and potential locations in our solar system where life may exist.

ANTHO4SKIN – Recycling anthocyanins from food wastes for cosmetic applications

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There is a growing market demand for the incorporation of plant-derived ingredients in new products of the cosmetic industry. Anthocyanins are polyphenols arising from plant secondary metabolism that have been shown to display many bioactive properties such as free radical scavenging, metal-chelating, antimicrobial, wound healing and chemopreventive activities. The ability to prevent oxidative damages has led to the incorporation of natural bioactives in lotions and facial creams to prevent skin diseases and premature ageing, therefore the biological activities of anthocyanins make them novel potential compounds for cosmetic formulations. However, native anthocyanins present a low solubility in lipophilic media, which compromises their effective application.

In this project, anthocyanins from industrial wastes are recycled and used in their genuine forms. Enzymatic lipophilization is performed by addition of selected chain fatty acids to improve their solubility in lipophilic systems. Their biological activities are then assessed by developing a new skin barrier model using keratocytes living cells. Assays on the absorption of these bioactives at the skin level are performed and compared to native anthocyanins absorption. The behavior of the cells incubated with the lipophilized anthocyanins is also monitored continuously with a microelectrode-based biosensor device (Electric Cell-Substrate Impedance Sensing – ECIS). This new system allows a simple, fast and reliable screening of the capacity of the new lipophilized anthocyanins in comparison with the native ones to cross the skin barrier and at the same time to monitor cell morphology and perform cell-based assays including wound healing assays, all from a skin care standpoint.

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Regulated Assembly of Functional Multicomponent Supramolecular Polymers

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Aqueous self-assembly of molecular building blocks into ordered architectures, polymers and materials opens exciting avenues for fundamental developments in nanoscience and applications in biomedical technologies, optoelectronics and catalysis. I will present my group's recent efforts in controlling peptide and glycopeptide supramolecular polymerisations in solution and on surfaces,[1] as well as recent efforts on self-assembled Au(I)-metallopeptides.[2]

Inspired by protein functionality in their biological setting, we have produced electrostatic- and redox-regulated supramolecular polymerisations in water.[3] The synthons are based on β -sheet encoded anionic and cationic peptides that form anisotropic supramolecular copolymers with a nanorod-like morphology. The materials are designed for on-off polymerization in response to pH-, as well as redox-triggers. The pH-triggered monomer-polymer transition is simply tuned via thermodynamically controlled comonomer affinities, whereas kinetically controlled assemblies are achieved only by coupling multiple equilibria through enzyme catalysed redox-processes, leading to temporal resolution in aqueous supramolecular polymerisations (Fig. 1).[4]

Balancing out positive non-covalent interactions with repulsive forces produces well-defined peptidic nanorods.[5] In view of recent reports that anisotropic shapes in the design of biomedical carrier materials outperform conventional isotropic structures, we are particularly interested in the development of supramolecular multifunctional glycopeptide materials and their biomedical applications.

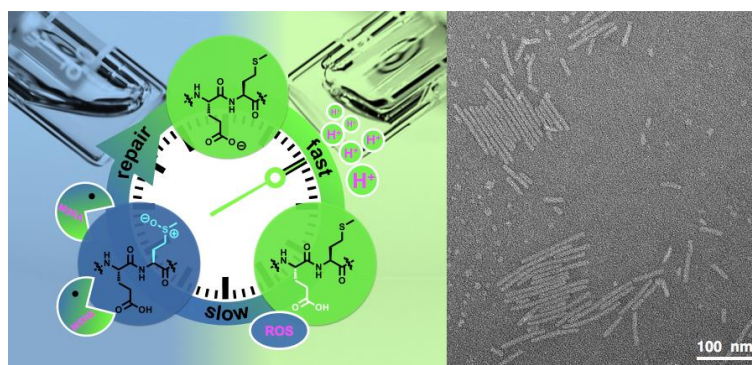


Figure 1. Transient Hydrogels Mediated by Redox-Responsive Supramolecular Polymerisation.[4]

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Rationalizing CO₂ capture with ionic liquids using high pressure NMR spectroscopy

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In recent years the use of Ionic Liquids (ILs) as a new type of non-aqueous solvents for many chemical or biochemical processes has attracted considerable attention. One of the main advantages of these solvents lies on the possibility of designing “task-specific” ILs as a result of the numerous cation-anion possibilities, opening fascinating possibilities to alter their solvent properties over wide ranges. Since it is impossible to experimentally investigate even a small fraction of the potential cation-anion combinations, a molecular-based understanding of their properties is crucial. Due to their high selectivity for CO₂ absorption, one potential field of application of ILs is in climate change mitigation efforts, as alternative materials for CO₂ capture. To develop an understanding of the real potential of ILs as an effective media for CO₂ capture, we developed a High Pressure NMR (HPNMR) based methodology for measuring not only CO₂ solubility in ILs, but also the strength of the interactions between CO₂ and ILs.

Application of our NMR based methodology allowed us to study the mechanism of CO₂ solvation in ILs and optimize their structure to maximize CO₂ absorption [1, 2]. Using HPNMR we were able to determine directly the CO₂ molar fraction in different ILs. Nuclear Overhauser effect based experiments were used to determine relative cation/anion orientations in the IL before and after CO₂ absorption and multinuclear diffusion NMR experiments, using the PGSE techniques, allowed a relative quantification of the strength of the ion pair interaction for different combinations of cation/anion [1]. This methodology gives an insight to the nature of cation/anion/CO₂ relationship, establishing a procedure for a molecular based interpretation for the solvation mechanism in different conditions [1, 3]. The disclosed molecular interactions between CO₂ and the ILs enabled the rationalization of the underlying characteristics for developing better ILs for CO₂ capture [2].

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Attractive and repulsive orbital interactions in hydrogen bonding and aurophilic interactions

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Hydrogen bonds and metallophilic interactions are of utmost importance in the supramolecular chemistry. Understanding the bonding mechanism of these weak interactions enables chemists to tune them for manufacturing new materials. A computational study on the hydrogen bonding of the mismatched DNA base pairs CC and GG (C=cytosine, G=guanine) and on metallophilic interaction in atomic dimers ($M^+ \cdots M^+$) and molecular perpendicular $[H_3P-M-X]_2$ (where M = Cu, Ag, Au and X = F, Cl, Br, I) will be presented. The importance of the Pauli (steric) repulsion in the mechanism of hydrogen bonding and aurophilic interactions will be revealed based on quantitative molecular orbital analysis and energy decomposition.

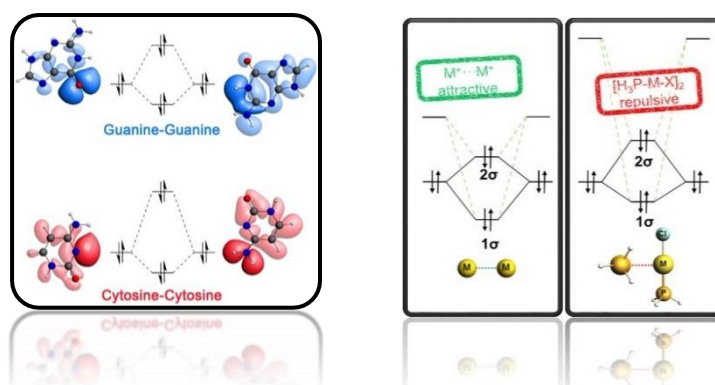


Figure 1. Repulsive orbital interactions in hydrogen bonding (left) and aurophilic interactions (right).

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Acknowledgments

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From Foldaxanes to Explosomes: Photoactive Supramolecular Systems

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On-going work on imparting photoactivity to micrometric polymersome host capsules will be presented. Due to the low membrane permeability of the polymer membrane to water (permeability being $P \sim 3.1 \pm 1.6 \mu\text{m}\cdot\text{s}^{-1}$ for poly(butadiene)-b-poly(ethylene glycol) PB-b-PEG and $P \sim 30 \mu\text{m}\cdot\text{s}^{-1}$ for POPC phospholipid vesicles), a significant osmotic pressure imbalance can in principle be induced inside the polymersome. We demonstrate that fast osmotic pressure imbalance can be easily photo-induced leading to micro-explosions, taking advantage of specific photo-cleavable dyes, such as coumarin derivatives, but also of more standard ones such as calcein and methylene blue in specific conditions. Snapshots of real-time polymersome explosion under irradiation is shown in the Figure. This process has been shown to be efficient and selective in space, time and wavelength.[1] Other types of supramolecular architecture that will be considered include helix/foldamer-on-thread “foldaxane”. [2]

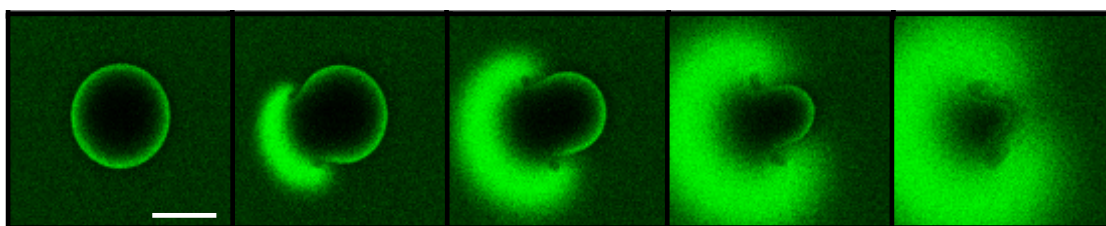


Figure 1. Snapshots of a calcein-loaded polymersome explosion under irradiation at 488 nm under confocal observation (each frame is separated by 70 ms; scale bar is 10 μm).

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Acknowledgments

Financial support from the French Agence National de la Recherche (projects NOSynthCell, FOSET & PETIMIT) is gratefully acknowledged.

Green chemistry and deep eutectic systems in life science applications

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Natural Deep Eutectic Solvents are mixtures of naturally occurring metabolites such as sugars, aminoacids or organic acids which are typically solids at room temperature but when combined at a particular composition become liquid at room temperature. In this communication we highlight the existence of these systems in animals and their role in the survival of animals to environments with extreme temperature differences between winter and summer [1]. The presence of these new class of liquids in plants has been reported in 2003 as the missing link in understanding cellular metabolism and physiology. Future developments are envisaged on the application of these systems in a biomimetic perspective in the field of cryopreservation through vitrification. The tolerance of living beings to these systems and the understanding of the biological mechanisms behind these provides valuable cues towards the development of natural cryopreservants based on natural deep eutectic solvents with inherent low toxicity. Herein, we present the possibility to use NADES based on trehalose (Treh) and glycerol (Gly) in cryopreservation, as cryoprotective agents (CPA). The evaluation of the thermal behaviour of these eutectic systems, showed that NADES have a strong effect on the water crystallization/freezing and melting process, being able to reduce the number of ice crystals and hence ice crystal damage in cells, which is a crucial parameter for their survival. Using this NADES as CPA, it was possible to achieve similar or even better cellular performance when compared with the gold standard for cryopreservation dimethyl sulfoxide (DMSO). In this sense, this work relates the physical properties of the systems with their biological performance in cryopreservation. Our strategy results in the demonstration of NADES as a promising nontoxic green alternative to the conventional CPA's used in cryopreservation methods. Gathering knowledge from different fields of science, this work is intended to be the starting point to a new approach that can be followed to solve major problems of our society such as cryopreservation of cells and tissues, but ultimately organ storage, increasing their shelf-life and allowing more time between harvest and transplantation, saving thousands of lifes.

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The research leading to these results has received funding provided from the European Union Horizon 2020 program, granted through the project Des.solve (ERC consolidator), ERC-2016-COG 725034.

EYCN – The European Young Chemists’ Network – Promoting Chemistry and Connecting Young Chemists in Europe and Beyond

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The European Young Chemists’ Network (EYCN), the young member’s division of EuChemS, is a highly motivated team of young scientists from 24 European countries.

The EYCN spent the last years working towards promoting the exchange of knowledge, experience, new ideas and projects among young chemists linked to academia and industry. It also aims to improve the visibility of chemistry, bring it closer to a wider audience and include new people from outside the research field – such as industry, business and management. The EYCN supports young chemists at the beginning of their careers with awards and activities focused on developing soft-skills and expanding their career perspectives. Every two years, the EYCN announces the European Young Chemist Award (EYCA) in collaboration with the Italian Chemical Society. The EYCN organizes career days and, since 2011, it promotes the Young Chemists Crossing Borders exchange program (YCCB) in collaboration with the Younger Chemists Committee of the American Chemical Society (ACS YCC) [1]. In April 2016, the EYCN hosted its 1st European Young Chemists’ Meeting (EYChem) in Guimarães (Portugal) and its 2nd edition is coming in 2019. Our network is actively working towards a mentoring program for prospective Marie Curie fellowship and ERC starting grant applicants.

If you wish to get in touch with us, please visit our website at www.eycn.eu, or contact us using our social media profiles on Facebook (@EYCN), Twitter (@YoungChemists) or LinkedIn (@EYCN).

We look forward to collaborating with you!



Figure 1. EYCN Delegates that attended the 12th EYCN Delegates Assembly in Heraklion, Greece, in May 2017.

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Oral Communications

Transition Metal Complexes as Anion Transporters

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There is a growing interest in the potential biological activity of synthetic trans-membrane anion transporters¹ mainly related to the fact that defects in anion-transport proteins can lead to a number of diseases known as “channelopathies”, the best known being cystic fibrosis (CF), a severe illness caused by impairment of chloride transport through the CFTR anion channel in epithelial cell membranes. It has been proposed that synthetic anion carriers may supply to the deficient chloride transport in ill cells and some experimental evidences have started to appear in the literature.² We have recently reported that a simple Pd(II)-diphosphine complex (**1a**) is able to efficiently transport chloride anions across a phospholipid bilayer acting with a carrier mechanism in which the metal complex resides in the membrane and shuttles the ions across the membrane, by exchanging chloride with OH⁻ (**Fig. 1a**)³ with high selectivity against oxygenated anions (NO₃⁻, ClO₄⁻). With the aim to better understand the mechanism of action and to optimize the transport efficiency of this new class of anion transporters we are now exploring several mutations of the diphosphine ancillary ligand using electron withdrawing or donating groups or alkyl chains in order to tune the affinity for the anions and the lipophilicity of the ligand (**Fig. 1b**). The anion transporting ability have been studied using phospholipid liposomes as model membranes and fluorescent pH or anion sensitive probes. The results show a significant effect of the lipophilicity of the ligand on the transport ability of the complex, and a less important effect of the electronic properties of the ligand substituents. The results of these studies as well as preliminary experiments aimed to open new directions and exploring the use of different metal ion and ligands will be presented and discussed.

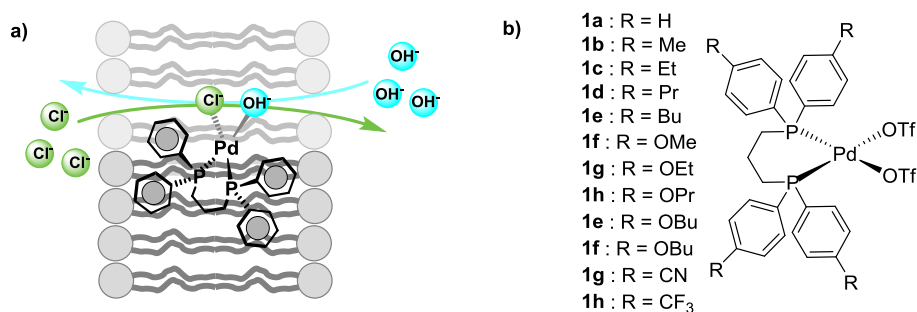


Figure 1.

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Bacterial Cell Wall Surrogates from Chitosan: a new molecular recognition system

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Peptidoglycan (PGN) is the major component of the bacterial cell wall, and is composed of alternating β - [1,4] linked N-acetylglucosamine (NAG) and N-acetylmuramic acid (NAM) residues, cross-linked by short peptide bridges (Figure 1). PGN is recognized by invertebrate and vertebrate innate immune system (IIS) and is capable of inducing an innate immune response.[1] Due to the biological relevance of PGN several research groups have contributed to the development of mucopeptide synthesis. Our research group have been dedicated to the preparation of glucosamine building blocks and NAG-NAM disaccharides.[2-3] During our research on PGN recognition by molecular patterns on IIS, we came across with the structural similarity of chitin/chitosan and the carbohydrate skeleton of bacterial PGN, murein.[2] Thus we have embarked on the synthesis of PGN of different molecular weight from chitosan, taking advantage of its β - [1,4] glycosidic linkage, through selective chemical modifications of the naturally abundant biopolymer. Herein we will present our recent developments on the quest for an artificial bacterial PGN, starting with commercial chitosan through chemoselective modifications and enzymatic recognition.[4]

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Acknowledgments

We thank the Fundação para a Ciência e Tecnologia for financial support for the projects PTDC/SAU-IMU/111806/2009 and PTDC/QEQ-QOR/2132/2012. The Associate Laboratory Research Unit for Green Chemistry - Technologies and Processes Clean - LAQV financed by national funds from FCT/MEC (UID/QUI/50006/2013) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145- FEDER - 007265) is acknowledged. The NMR spectrometers are part of The National NMR Facility, supported by FC&T(RECI/BBB-BQB/0230/2012). iNOVA4 Health Research Unit (LISBOA-01-0145-FEDER-007344), which is co-funded by FC&T/Ministério da Ciência e do Ensino Superior, and by FEDER under the PT2020 Partnership Agreement, is acknowledged. The LC-MS/MS equipment is part of The National MS Facility, supported by FC&T (REDE/1518/REM/2005).

High Efficient Capture and Sensing of Quat Herbicides Using Ring-Shaped Nanostructures as Host Systems

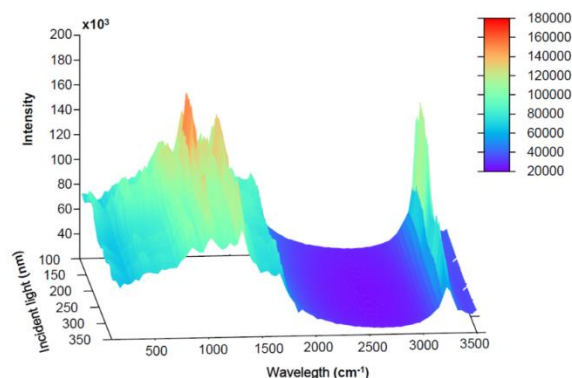
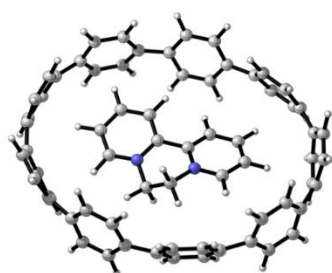
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Weed killers are phytosanitary substances used to control and remove unwanted weed species leaving the desired crop unharmed [1]. Through history, herbicides have played a key role in order to avoid large losses in crops and to obtain sufficient food for the growing world population. Despite of the great advantages that they bring to agriculture negligent applications together with the excessive dose that is usually added to treat various pests generates serious environmental problems due to contamination of soils and water. Since the biological activity of cationic quaternary ammonium pesticides (quats) was discovered in the 1950s they have been used widely in the management of crops, but nowadays many of them are banned in many parts of the world due to the potential environmental harmful and toxic effects.

In this work we have used novel ring-shaped nanostructures aimed to both capture and sense quaternary ammonium herbicides. The hosts, chemically known as $[n]$ Cycloparaphenylenes, possess a unique rigid architecture composed of n -benzene rings linked at *para* positions to form a fully conjugated cylindrical structure [2,3] that enhances the capture ability of this supramolecular structure for different quat guests [4]. Complexation thermodynamics and different spectroscopical studies have been carried out on the supramolecular complexes formed between different quat herbicides and the nanorings using highly accurate computational calculations. The sensing applications are explored using 3D-Pre-Resonance-Raman spectroscopy to selectively amplify selected vibrational modes to facilitate the identification of the desired molecules.



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Engineering Marine Polysaccharides-based Hollow Multilayered Microcapsules for Enhanced Cellular Uptake

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Over the last few decades, there has been a tremendous interest on the design of nano- and micro-sized carriers with the aim of enhancing the loading, protection, delivery and targeting efficacy of therapeutics for addressing biomedical, biotechnological and pharmaceutical applications [1]. Among them, hollow microcapsules prepared by resorting to inorganic sacrificial templates, natural biopolymers and the bottom-up Layer-by-Layer assembly technology have attracted considerable attention since their physicochemical and mechanical properties can be precisely tuned at the nanometer scale. However, they have shown a great tendency to aggregate, which represents a major hurdle when aiming for cellular internalization.

Herein, we report the preparation of well-dispersed marine polysaccharide-based hollow multilayered microcapsules through the alternate deposition of aqueous solutions of oppositely charged chitosan (CHT) and alginate (ALG) biopolymers onto porous CaCO₃ sacrificial microcores, followed by core template dissolution [2]. CHT and ALG were chosen as the cationic and anionic biopolymers, respectively, due to their proven biocompatibility, non-cytotoxicity, non-immunogenic properties, and structural similarity to the native biological systems. The successful preparation and morphological properties of the hollow multilayered microcapsules were assessed by scanning electron microscopy, transmission electron microscopy, fluorescence microscopy and confocal laser scanning microscopy, thus revealing the fabrication of well-dispersed spherical microcapsules with ~5 μm. The non-aggregated CHT/ALG microcapsules showed an enhanced cellular uptake by fibroblasts, being of key importance for cellular internalization. The engineered microcapsules hold great promise for being used as micro-reservoirs for the encapsulation, protection and on-demand controlled release of bioactive molecules, thus opening new perspectives in drug/gene delivery, intracellular trafficking and advanced tissue engineering strategies.

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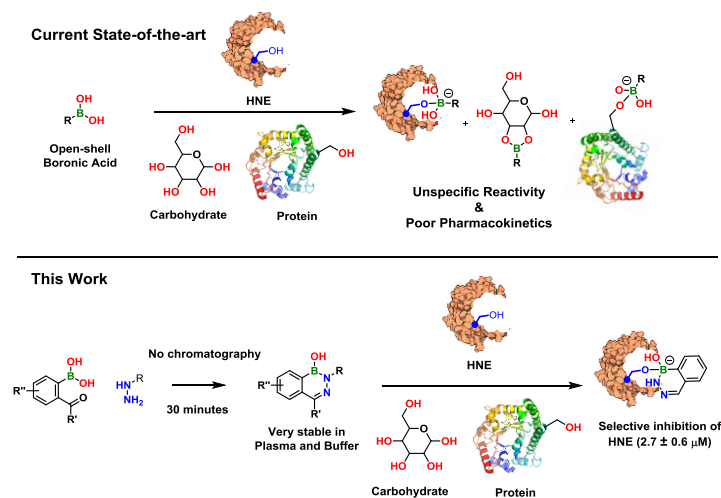
Diazaborines: Boronic acids under disguise for selective inhibition of Human Neutrophil Elastase

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Boronic Acids (BAs) are a preeminent functionality extensively used to design biologically active compounds and functional biomaterials. Due to boron's open shell, this class of inhibitors also exhibits unspecific reactivity with endogenous nucleophiles that often increases their off target toxicity. Here diazaborines are presented as a new class of boron based warheads for serine proteases inhibition, in which the boron functionality is stabilized in the form of an aromatic BN heterocycle. In this study, diazaborines were readily synthesized in a single step in yields up to 96%, without any chromatographic operation and were shown to selectively inhibit Human Neutrophil Elastase (HNE) serine protease with IC₅₀ values in the low μM range. Synthetic and theoretical studies performed on this system suggest that, like BAs, the reaction mechanism involves the formation of a reversible covalent bond between the diazaborine boron center and the catalytic serine oxygen. Finally and differently from BA, diazaborines were shown very stable in different biocompatible conditions like buffer and human plasma. These results demonstrate that diazaborines can effectively shield the boronic acid moiety from unspecific reactivity while retaining selective activity against HNE, paving the way for the development of the next generation of serine proteases.



Acknowledgments

Support for this work was provided by FCT through UID/MULTI/00612/2013, PEst-OE/QUI/UI0612/2013, PTDC/QEQMED/5512/2014, PTDC/QEQ-QOR/1434/2014, PTDC/BBB-BEP/2463/2014, PD/BD/128239/2016 and UID/DTP/04138/2013.

New photoactive pillared MOFs assembled by mechanochemistry for energy applications

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In this communication we are presenting a new approach for the preparation of photoactive MOFs, as active material in electroluminescence and solar cells. This strategy relies on the synthetic versatility of MOFs and the properties of the ligands. The novelty of this project is to combine the semiconductor behavior of the MOFs with the light harvesting capability of the photoactive ligands in a 3D-MOF structure, assembled by mechanochemistry.

MOFs are hybrid materials displaying exceptional properties, depending on the careful selection of metal clusters and multi-functional linkers. Experimental and theoretical studies have supported MOFs behavior as conductive crystalline structures [1]. Here, we will focus on the preparation and structural characterization of new MOF frameworks, using larger functional ligands with improved light harvesting properties (diphenylanthracene-DPA or perylenediimides-PDI derivatives). For the assembly of 3D MOF structures using these new functional ligands, we will use as template a 1-D MOF framework already known (CSD code: DIKQET and FALGEG), and the new ligands will act as pillars with axial coordination to the metal clusters [2]. The standard methodology to prepare MOFs relies on solvothermal techniques, however in our case the challenge is to overcome the extremely low solubility of the new ligands. Mechanochemistry seems to be the most promising synthetic technique to be used, due to the fast and selective reactions, that occur without solvents, neat grinding, or, if needed, a catalytic amount of solvent.

The new and unexplored frameworks obtained during this project are to be used as active materials in electroluminescence and solar cells, with obvious advantages over traditional organic devices: easy to prepare, precise characterization of the active layer and stable over time.

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BioMOFs: potential systems for biomedical applications

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In the last decade, Metal Organic Frameworks (MOFs) have emerged as potential systems for biomedical applications, in particular for the controlled delivery of active pharmaceutical ingredients (APIs).[1,2] The APIs can be incorporated either within the MOF porosity or as a constitutive part of the framework (called BioMOF). We are particularly interested in obtaining BioMOFs using APIs and safe and/or bioactive metals as building blocks. When compared to MOFs, BioMOFs, present additional benefits: 1) Porosity is no longer required as the release of the API is achieved through the degradation of the solid; 2) The API is part of the matrix, avoiding multistep procedures to prepare the loaded material, 3) The metal can also be bioactive promoting a synergetic effect and 4) The use of porous BioMOFs presents enhanced applications, as it can lead to the co-delivery of others APIs adsorbed in the pores.[3]

Here, we present several novel BioMOF structures synthesized using biocompatible and/or bioactive cations (Na, K, Mg, Ag, Zn, Ca) and azelaic acid, an API commonly used to treat skin disorders (e.g. acne), and dipyrindamole, a coronary vasodilator and antiplatelet agent, used to prevent thrombosis. These novel compounds were structurally characterized (Figure 1) and their thermal and chemical stability is being explored. For azelaic acid, antimicrobial tests were already performed showing some antibacterial activity.

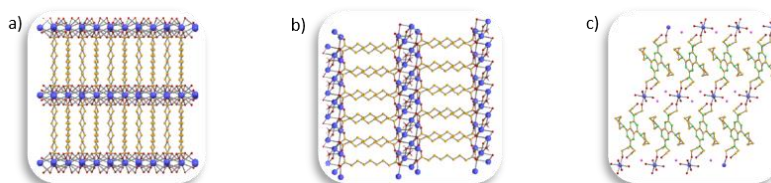


Figure 1. Molecular diagrams for azelaic acid with Na a) and K b) and dipyrindamole with Mg c)

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Sensors Based on Customly Designed Iron(II) Coordination Polymers

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Spin crossover (SCO) complexes show magnetic responses to subtle external stimuli, e.g., temperature, light, pressure and guest molecules, involving simultaneously changes in colour, dielectric constant or electrical resistance. These characteristics make them potential candidates for the detection of different organic and inorganic compounds, working as sensors. Hofmann clathrates, a class of metal-organic frameworks (MOFs) and their analogues are among the most known and well-studied for practical applications as SCO compounds, as well as other coordination polymers.[1,2] These solids have more flexibility and ways of modifying porosity than inorganic porous compounds, allowing desorption and adsorption of guest molecules and, consequently, leading to the perturbation of various physical and chemical properties of the framework affecting also its SCO behaviour. These metallocyanate compounds have the rigidity required to promote the strong cooperativity between the SCO active centres. Due to the importance of chirality in biological processes there was an increase in the development of chiral zeolites and related porous solids over the past few decades. There are numerous examples of porous metal-organic coordination networks reported in recent years, but chiral MOFs synthesized from chiral components are much less explored. Herein we present the synthesis and characterisation of Hoffmann clathrates amongst other coordination polymers and our attempts to introduce chirality in their structure. The study of the magnetic properties of these materials using SQUID is also explored. Using different ligands with distinct characteristics such as polarity, size and chirality we can compare the properties of the structures formed and debate about their application in the fields of pharmaceuticals, biology, chemistry and engineering.

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We thank Fundação para a Ciência e Tecnologia and the MOLSPIN cost action for financial support.

New perspective on osteosarcoma using bisphosphonate-based Ionic Liquids

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Bisphosphonates (BPs) are a class of drugs directed for the treatment of osteoclast-mediated bone loss disorders. Their structural similarity with inorganic pyrophosphate renders them very high affinity for bone tissue.¹ In addition, recently they have been also considered as potential antitumor agents.

However, BPs suffer from several drawbacks such as polymorphic structures and low bioavailability which are in some way related with the common side effects (e.g. muscle, joint and bone pain, muscle spasms, numbness) associated with these drugs. Thus, there is a need to develop new ways to increase the oral bioavailability of BPs while reducing the associated systemic toxicity.

Synthesis of Ionic Liquids from Active Principle Ingredients has been one of the focus of our group over the last years.² The combination of drugs as anions or cations with appropriate organic counter ions has proven to be an innovative approach to tackle the polymorphism behavior of several drugs as well as to improve their water solubility, permeability and corresponding bioavailability and biological activity.³

In this communication we report the preparation of Ionic Liquids from the bisphosphonates etidronic, alendronic and zoledronic acids (BP-ILs, Figure 1) as anions by combination with biocompatible organic cations in quantitative yields. The polymorphic profile of the prepared BP-ILs and their solubility in water and biological fluids, as well as toxicity towards human healthy and cancer cell lines will be discussed.

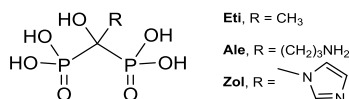


Figure 1. Structure of Etidronic (Eti), Alendronic (Ale) and Zoledronic (Zol) acids.

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Fluorescent graphene oxide quantum dots as traceable, pH sensitive nanocarriers for an anticancer drug

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Similarly to what happens in other European countries, in Portugal, 24.3% of all mortality cases are due to cancer, which makes this disease the second cause of death only surpassed by circulatory and cardiac diseases [1]. In the treatment of cancer, doxorubicin (DOX) has shown great treatment potential, being regarded as one of the most potent of the Food and Drug Administration (FDA) approved chemotherapeutic drugs although presenting some limitations that include drug resistance and high toxicity [2]. So, the development of suitable carrier systems for DOX local delivery in cancer tissues is necessary.

In the proposed work, the optical properties of GO-Dots and the advantages of these emerging luminescent nanomaterials were explored, namely their abundant surface carboxylic groups that enable the conjugation with a large diversity of functional groups. Further advantages comprise excellent biocompatibility, high surface-to-volume ratio and its inherent fluorescent property that allows monitoring the cellular uptake of systems [2]. GO-Dots were synthesized by acidic chemical oxidation of carbon black according to a reported method [2]. GO-Dots pH dependence (due to ionization of its surface groups) was characterized by fluorescence and electrophoretic light scattering. After establishing the GO-Dots behavior according to the surface ionization groups, conjugates of DOX and GO-Dots (GO@DOX) were prepared at different pH values. *In silico* predictions indicated that, at the physiological pH of blood circulation and healthy tissues, drug and dots possess opposite charges being able to establish electrostatic interactions while at acidic pH values characteristic of cancer tissues, a trigger effect will cause the release of the drug, since GO-Dots are protonated and uncharged. The GO@DOX conjugates were studied by fluorescence and UV-Vis absorbance spectroscopy, confocal Raman scattering and ATR-FTIR. Finally, since GO@DOX conjugates are too small, and cannot be administrated without being rapidly eliminated by kidneys, their encapsulation in lipid nanosystems is a future goal. Therefore the incorporation of GO@DOX into liposomes was studied. Liposomes were labelled with two fluorescent probes (n-(9-anthroyloxy)-stearic acid probes (n = 3 or 12)) which were capable of respectively reporting a location near the polar head groups and deeper localization at the acyl lipid chains level. In both cases it was possible to detect quenching of the probes fluorescence, indicative of the GO@DOX insertion into the lipid membrane.

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New small-molecule immune system modulators towards cancer immunotherapy

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Modulation of immune checkpoint receptors is currently a powerful strategy in cancer therapy [1]. To date, several immune checkpoint receptors have been identified and used as therapeutics in oncology, as programmed cell death protein 1 (PD-1). When engaged by one of its ligands, PD ligand 1 (PD-L1) or PD ligand 2, PD-1 limits autoimmunity. PD-1 ligands are upregulated in many human cancers and their blockade lead to activation of T cells and therefore enforce tumor recognition. Presently, PD-1/PD-L1 pathway is one of the most successful pathways in the context of clinical cancer immunotherapy with several approved drugs. The most successful therapies rely on the use of antibodies. However, despite their outstanding success, they still have numerous disadvantages.

Small-molecule modulators have emerged as safer therapeutic alternative [2]. Our study focused the discovery of small-molecule inhibitors targeting PD-L1 to disrupt PD-1/PD-L1 interaction. Limited structural information of PD-L1 led us to a detailed structural characterization based on *in silico* studies (molecular docking). After assessing structural features (e.g. binding pocket), we followed a structure based virtual screening campaign. Potential PD-L1 inhibitors were selected and their activity tested by Homogeneous Time Resolved Fluorescence (HTRF) assay. We were able to identify PD-L1 inhibitors. Therefore, immune checkpoint blockade using small molecules represent a step forward in cancer immunotherapy.

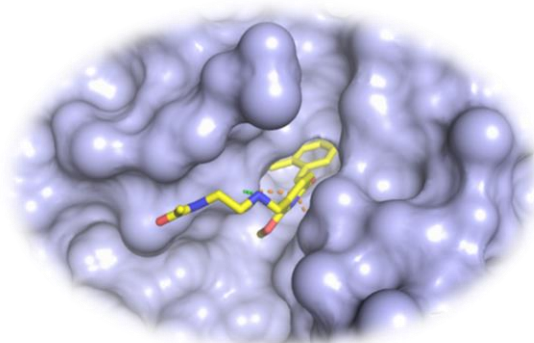


Figure 1. PD-L1 binding pocket.

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From the Sea to... the Sea! Antifouling Marine-Inspired Synthetic Steroid Derivatives

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Marine organisms produce biological active compounds that inhibit the growth of fouling organisms or the settling of their larval forms [1]. Therefore, to combat biofouling on man-made submerged surfaces the synthesis of marine-inspired compounds is worth to explore as an eco-friendly and sustainable option as an alternative to the exhaustibly extraction of biological active compounds from marine organisms [2]. In this work, a series of bioinspired marine steroid derivatives with different lipophilicities was synthesized to evaluate the antifouling (AF) activity and understand its structure-activity relationship. Seven steroid derivatives were successfully synthesized in moderate to high yields (40-97%). The structures of the obtained derivatives were confirmed through spectroscopic methods, namely infrared spectroscopy (IR) and nuclear magnetic resonance (¹H and ¹³C NMR, HMBC, and HSQC), as well as high-resolution mass spectrometry (HRMS). Anti-macrofouling activity was evaluated using an *in vivo* anti-settlement test with *Mytilus galloprovincialis* larvae and anti-microfouling activity was evaluated against five biofilm-forming marine bacteria [3]. In the presence of five steroid derivatives, the settlement of mussel's larvae was lower than 40% (at 50 μM) and antifouling effectiveness vs toxicity studies revealed for the most potent compound a LC₅₀/EC₅₀ ratio >50 (LC₅₀ > 200 μM and EC₅₀ = 3.7 μM). Four steroid derivatives showed the ability to inhibit different species of marine bacteria biofilm at 12.5 μM (40-80%). Overall, in this work, a promising antifouling profile was disclosed combining anti-macrofouling and anti-microfouling activities for synthetic steroids.

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Support for this work was provided by the Strategic Funding UID/Multi/04423/2013 through national funds provided by FCT – Foundation for Science and Technology and European Regional Development Fund (ERDF), in the framework of the programme PT2020 and partially supported by Structured Program of R&D&I INNOVMAR - Innovation and Sustainability in the Management and Exploitation of Marine Resources, reference NORTE-01-0145-FEDER-000035, Research Line NOVELMAR and the project PTDC/AAG-TEC/0739/2014 - COMPETE (POCI-01-0145-FEDER-016793) - RIDTI (Project 9471). ARN and JRA also acknowledge FCT for the PhD scholarship (SFRH/BD/114856/2016) and postdoctoral scholarship (SFRH/BPD/87416/2012), respectively.



Recovery of Anthocyanins from Sweet Cherry Wastes: Process Modeling and Optimization Using Response Surface Methodology

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Sweet cherries (*P. avium* L.) are widely consumed fruits appreciated for their sweet taste and appealing appearance. Their colour vary with the maturation stage, being an excellent indicator of the optimal harvest time. When ripen, these fruits acquire a dark red coloration that is mainly influenced by the anthocyanin concentration in the fruit peel and pulp [1]. These compounds are present in several natural matrices and their colour can vary from blue to violet and red depending on the surrounding medium conditions (pH, temperature, humidity, salinity, stress and storage conditions, etc.) [2]. Beyond bioactive properties, these compounds also possess a great coloring capacity, which justify their increasing exploitation for food industry application, especially for cherry wastes recovery, given the fact that bird bitten and fallen fruits are not suitable for sale nor consumption and represent a significant part of the production.

Thus, the aim of the present work was to optimize the extraction of these compounds from sweet cherry wastes, by studying the conditions that maximize the maceration extraction yield. For that purpose, a response surface methodology was applied using five levels for each of the independent variables (time, temperature, and solvent concentration). The quantification of anthocyanins present in the extracts was performed by high performance liquid chromatography coupled to a diode array detector (HPLC-DAD). For the model application, the anthocyanin concentration and the extraction yield were used as responses.

Through this extraction method, it was possible to obtain a yield of 1.86 ± 0.41 mg/g of cherry dry weight, in the optimal conditions of: 63.0 ± 3.2 min; $61.7 \pm 1.3^\circ\text{C}$ and $53.1 \pm 1.4\%$ of ethanol. The obtained residue represented 87% of the total cherry dry weight and the anthocyanin content was of 3.05 ± 0.41 mg/g of dry residue. The results obtained in this study demonstrate the potential application of sweet cherries as sources of anthocyanins.

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Colour modulation of blue anthocyanin-derivatives. Lignosulfonates as a tool to improve the water solubility of natural blue dyes

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The impact of a lignosulfonate (calcium) (L) on the chromatic features of two anthocyanin-derived bluish dyes (portisin, P and pyranoanthocyanin dimer, PD) was evaluated in aqueous solutions using UV-Visible spectroscopy. It was demonstrated that the interaction between each dye and this macromolecule at pH 1 occurs by two mechanisms, association and copigmentation that are dependent on L concentration. For instances, at low concentrations of L (up to 0.27 μM) it is observed the association of dyes promoted by their complexation with lignin (different molecules of dye are bound to the same binding sites of L). At higher concentrations of L (25 μM), the aggregation of dyes decreases and each molecule is bound to a different site of L resulting in the formation of a charge-transfer complex (copigmentation). Moreover, the titration of both dyes (P and PD) in the presence of L (19 μM) showed a strong stabilization of their pyranoflavylum cation forms revealed by the considerably higher $\text{pK}_{\text{a}1}$ (6.6 ± 0.1 and 6.2 ± 0.1 for P and PD, respectively) in the presence of this macromolecule when compared to the values obtained in the absence ($\text{pK}_{\text{a}1} = 4.61 \pm 0.03$ and 4.93 ± 0.04).

In addition, the water solubility of the dyes in the absence and presence of L was also evaluated by turbidimetry and the results showed that the water soluble lignosulfonate improved the solubility of the dyes over time.

Acknowledgments

This work received financial support from FEDER funds through COMPETE, POPH/FSE, QREN and FCT (Fundação para a Ciência e Tecnologia) by two post-doctoral scholarships (SFRH/BPD/112465/2015, SFRH/BPD/84805/2012), an investigator contract (IF/00225/2015) and grants PTDC/AGR-TEC/2789/2014 COMPETE POCI-01-0145-FEDER-016616, REDE/1517/RMN/2005. This work also received financial support (UID/QUI/50006/2013 - POCI/01/0145/FEDER/007265) from FCT/MEC through national funds and co-financed by FEDER, under the Partnership Agreement PT2020 and FEDER-Interreg Espanha-Portugal Programme (Project ref. 0377_IBERPHENOL_6_E).

Ultra-high Pressure-assisted Extraction of Phenolic Compounds from Watercress: Characterization and Process Optimization

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Ultra-high pressure (UHP), usually in the range from 100 to 800 MPa, is a novel technology increasingly used in the food industry as a cold pasteurizing method. UHP has also been reported as a good alternative to the conventional methods of extraction of high added-value compounds from plant materials, as it avoids the degradation of thermosensitive molecules and can improve the process efficiency [1-2]. Therefore, this study was carried out to characterize the phenolic profile of watercress (*Nasturtium officinale* R. Br., a fast-growing semiaquatic plant with medicinal properties) [3] and optimize the UHP-assisted extraction of these compounds using the response surface methodology. For this, freeze-dried watercress samples were processed according to a five-level full factorial design combining the independent variables: processing time (t , 1.5–33.5 min), pressure (P , 0.1–600 MPa) and solvent (S , 0–100% ethanol, v/v). The individual and grouped phenolic compounds (analysed by HPLC-DAD-ESI/MS) and the extraction yield were used as response variables. The chromatographic analysis revealed that the phenolic profile was constituted mainly by flavonoids, namely quercetin and isorhamnetin glycoside derivatives, whereas phenolic acids were less abundant. In addition, four kaempferol glycoside derivatives were identified for the first time in this species [5]. The developed theoretical models were successfully fitted to the experimental data and used for extraction optimization. The UHP conditions that maximized the extraction yield (crude extract) and the recovery of phenolic compounds were as follows: $t= 34$ min, $P= 531$ MPa, $S= 26\%$ and $t= 3$ min, $P= 600$ MPa, $S= 100\%$, respectively [2]. In conclusion, the developed extraction process promoted the selective extraction of phenolic compounds from watercress using a green solvent and reduced extraction times.

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Reactivity of cork extracts with (+)-catechin in wine model solutions: Identification of a new family of ellagitannin-derived compounds (corklins)

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Cork stoppers are traditionally employed in wine bottles to seal and protect the wine allowing at the same time for a proper wine ageing. Different polyphenols have been found to migrate from different cork stoppers into bottled wine model solutions [3], being ellagitannins the most relevant ones. The aim of this study was to identify and characterize new ellagitannin-derived compounds in cork and to evaluate the reactivity of these compounds in model solutions with a major wine component, (+)-catechin. This reactivity yields to the formation and identification of several ellagitannin-catechin-derived compounds with a more complex structure. These newly-formed compounds may have an impact on the resulting wine sensorial properties. One of these new classes of ellagitannin-catechin-derived compounds are the corklins.

Furthermore, the work has been evolving towards the detection of corklins in commercial wines and may eventually be used as cork wine markers.

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Acknowledgments

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The molecules of color in Portuguese postage stamps

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The color of Portuguese postage stamps has remained unknown until nowadays. It is known from a previous analysis that we have done to some postage stamps of the United Kingdom that carminic acid, cochineal, (for reds) and the iconic mauveine (for lilacs / purple) were used in UK postage stamps in the period ranging from 1847 to 1901[1]. Regarding the Portuguese postage stamps coloring materials, little is known with the exception that at the 23th April, 1853, a box with printing inks from England arrived to Portugal [2,3]. In this work we will present a study, based on an analysis involving different techniques (X-Ray Fluorescence, UV-VIS spectroscopy, HPLC-DAD-MS, steady and time resolved fluorescence) of a selected number of Portuguese postage stamps from the period 1857-1909 with red, rose, purple and orange colors.

Amongst others, the inorganic pigments cinnabar (HgS), lead oxides (Pb₃O₄) and chromates (PbCrO₄), lead sulphides (PbS), see Figure 1, and the organic compounds carminic acid and eosin y were found in the analysed postage stamps. The use of these molecules of color [4], in particular the inorganics, contrasts with those used in the printing of United Kingdom postage stamps [1]. In addition, a non-destructive analysis method for identification of some of the molecules of colour present in the analyzed postage stamps, involving XRF (for cinnabar, lead oxide, lead chromate, lead sulfide), UV-Vis (for Carminic Acid and Eosin Y) and fluorescence spectra, combined with quantum yields and lifetimes (for Eosin Y), has been developed [5].



Figure 1. Mapping of 150_1898_Rep2 postage stamp for Pb [5].

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Acknowledgements: Acknowledgments are due to the Center of Coimbra, supported by the Foundation for Science and Technology (FCT) through Project PEst-OE / QUI / UI0313 / 2014, to the ERDF, to COMPETE and to the "Coimbra Trace Analysis and Imaging Laboratory". We also thank the Eng. J. Miranda da Mota for providing us with of some of the postage stamps investigated.

Highly Transparent, Conductive and Flexible Electrodes for Electrochromic Devices Using a “Green” Hybrid Copper-Nanowire-Reduced-Graphene-Oxide Coating

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This work reports the use of novel transparent electrodes employing copper-nanowires/reduced-graphene-oxide hybrid coatings using green synthetic methods for electrochromic displays. Those electrodes are robust and combine sheet resistances lower than $30\Omega\cdot\text{sq}^{-1}$ and transmittances higher than 70%. These properties make these electrodes suitable for flexible electronic applications when coated on flexible substrates as polyethylene terephthalate (PET).

As proof-of-concept, this work evidences the successful use of these substrates to produce high-performance electrochromic devices. The produced substrates were coated with PEDOT (Poly(3,4-ethylenedioxythiophene)) by spray-coating, assembled with the *know-how* of Ynvisible®, giving rise to high color contrasts, high coloration efficiencies, fast switching times and a long durability.

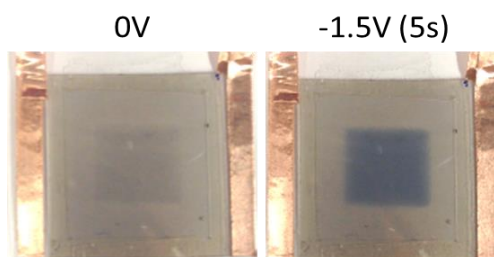


Figure 1. Electrochromic device produced with PEDOT spray-coated on the CuNWs/GO substrates.

Acknowledgements

EC (project NMP4-SL2012-310651 under FP7-NMP-2012-SMALL-6) and Portuguese FCT-MCTES (UID/QUI/50006/2013) co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER – 007265) are acknowledged for financial support.

Innovative Electrochromic and Photochromic Ionic Liquids

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In the last decades, stimuli-responsive materials gained much attention due to their ability to respond an external stimuli (e.g. light, electron-transfer) by changing their properties (e.g. solubility, optical properties) [1]. In our group, different electrochromic ionic liquids (ILs) based on bipyridinium derivatives (di- and tetra-substituted) have been prepared and then tested as liquid or solid electrochromic devices [2-5]. Reversible and efficient electrochromic devices based on functionalized bipyridinium ILs can be applied for electrochemical windows and car mirrors. Recently, photochromic ionic liquids based on diarylethene derivatives have been firstly developed and their photochromic properties will be evaluated.

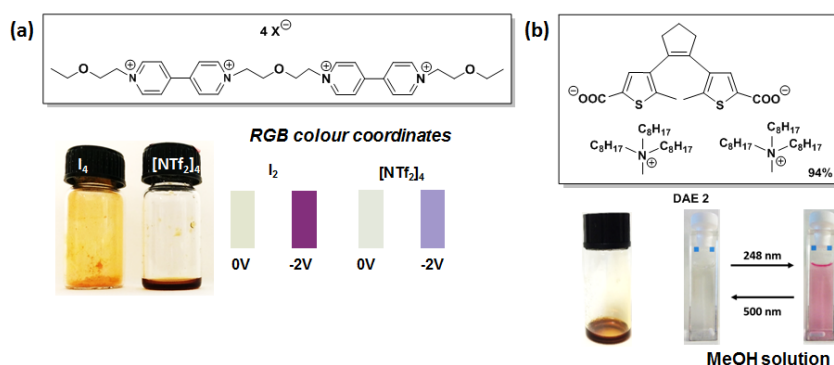


Figure 1. Examples of (a) an electrochromic ILs based on 4,4'-bipyridinium derivatives and their incorporation in device; (b) a photochromic ILs based on diarylethene derivatives.

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This work was supported by the following projects POCI-01- 0145-FEDER- 016387 (ERDFCOMPETE2020), PTDC/QEQ-QFI/1971/2014 and IF/0041/2013 (from FCT-MCTES) and the post-doctoral grant SFRH/BPD/102705/2014.

Advances in cellulose dissolution and regeneration: From scattering and rheology to a new NMR approach

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As the major carbohydrate produced by plant biosynthesis, cellulose occupies a prominent place as a 'green' polymer for the production of innovative and sustainable materials. Unlike other polymers, cellulose is not meltable and therefore most of its applications rely on an efficient dissolution step followed by shaping processes. Cellulose is insoluble in water but can be dissolved in acidic or alkaline conditions, given the proper conditions. However, work in developing new solvents for cellulose has been following a "trial and error" empirical character. It is clear that a better understanding of the dissolution of cellulose has deep implications, not least for industrial developments. In the first part of this talk some basic fundamentals will be reviewed together with current perspectives. We will see that hydrogen bonding mechanism alone cannot explain the low aqueous solubility. Our recent work rather emphasizes the role of cellulose charge and the concomitant ion entropy effects, as well as hydrophobic interactions [1, 2]. In the second part, a new NMR methodology is introduced as a promising technique regarding an efficient and robust characterization of the solution state of cellulose [3]. With this method it is possible to identify the liquid and solid fractions of cellulose, the degradation products, cellulose polymorphs, etc [4, 5]. Finally, combining static light and small angle X-ray scattering we will also probe the effect of cellulose aggregation on solution rheology [6].

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Acknowledgments

This work was supported by the Portuguese Foundation for Science Technology (FCT) through project PTDC/AGR-TEC/4814/2014 and researcher grant IF/01005/2014.

Looking inside a pore: Probing sol-gel microenvironment by PFGSE HRMAS NMR

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Sol-gel materials have been extensively studied for carrying out organic reactions inside the porous material, creating a prolific transversal field of research that combines chemistry, material science, biology, biotechnology and medicine [1]. However, a deeper understanding of the nature of the matrix, particularly of the intrapore environment, is lacking in the literature.

Following our previous work [2-3], we probed the chemical environment of sol-gel matrices used to encapsulate enzymes for biocatalysis (TMOS/MTMS, TMOS/PTMS, TMOS/ETMS and TMOS/BTMS) by studying the self-diffusion behaviour of three solvents, namely, 1-pentanol, acetonitrile and n-hexane by Pulsed Gradient Spin Echo diffusion with high-resolution magic angle spinning NMR.

The spin echo attenuation of all the solvents showed the presence of two diffusion domains: one with almost liquid like diffusion coefficient (D_{fast}) and a second with slower diffusion coefficient (D_{slow}). The data was also analysed in terms of molecular exchange model between the two diffusion domains, and the physical parameters were obtained.

The diffusion behaviour of probe molecules in sol-gel systems obtained by this NMR methodology provided information on the translational mobility of molecules, which can be used to obtain useful information concerning the intraparticle and interparticle chemical environment, and how this can be relevant for dynamic processes in many applications, like biocatalysis.

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Acknowledgments

This work has been supported by (FCT/MEC) through projects/grants SFRH/BPD/88144/2012 (ASDF) and PTDC/QUI/64744/2006; UCIBIO and LAQV that are financed by national funds from FCT/MEC (UID/Multi/04378/2013 and UID/QUI/50006/2013) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER-007728 and POCI-01-0145-FEDER – 007265). The NMR spectrometers are part of the National NMR Network (RNRMN) and are funded by FCT/MEC Infrastructure Project N° 022161.

Computational optimization of bioadsorbents for the removal of pharmaceuticals from water

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Pharmaceutically active ingredients are amongst the most persistent contaminants, resisting to wastewater treatment plants conventional processes and pose serious threats to organisms and the environment. Adsorption by activated carbons is one promising methodology for the removal of pharmaceuticals from water due to its versatility and high removal efficiency. However, activated carbons are expensive. Primary sludge from paper mills has been appointed as a potential cheap and renewable source of carbon for activated carbon production (1). Computational chemistry may help shed some light unto the molecular mechanisms underlying the adsorption of pharmaceuticals in activated carbons.

In this work, it is proposed the usage of primary paper mill sludge for the production of activated carbons. The different materials were characterized by a set of techniques and the gathered data used in the formulation of a valid molecular model to reproduce the elemental composition, functional group variability and porosity. The developed model was used to collect relevant information through molecular dynamics/Monte Carlo techniques, enabling the future improvement of the initial material.

The obtained data from Monte Carlo simulations suggest that activated carbons with higher oxygen levels have higher surface area, and consequently superior maximum capacity values for pharmaceutical adsorption. Moreover, the presence of positive ions in the adsorption medium acts as a cooperative factor, given the formation of complexes and the stabilization of open configurations.

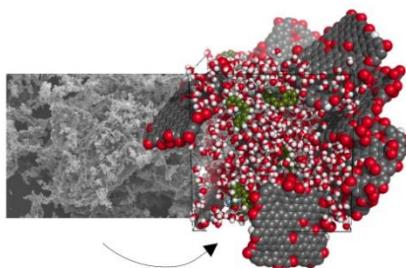


Figure 1. From experimental material to computational model.

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Acknowledgments

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, POCI-01-0145FEDER-007679 (FCT Ref. UID/CTM/50011/2013 and in the scope of the research project PTDC/AAGTEC/1762/2014.

Chemoselective Aminations via Electrophilic Activation of Amides

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The amide functional group is typically considered the most robust among carboxylic acid derivatives. Nevertheless, electrophilic amide activation is an emerging tool for the chemoselective functionalization of carboxamides under mild conditions. In this presentation, we will detail two conceptually related strategies for amination via electrophilic amide activation and transient formation of a keteniminium intermediate (Figure 1). In the first approach (path a), the use of an azide as reaction partner enables a stereoselective and modular α -amination of amides, with release of nitrogen gas as a byproduct. [1] In the second transformation (path b), interception of the keteniminium intermediate with a hydroxamic acid results in a formal (ortho-amino)arylation after sigmatropic rearrangement. [2] The scope and limitations of these methodologies will be presented and discussed.

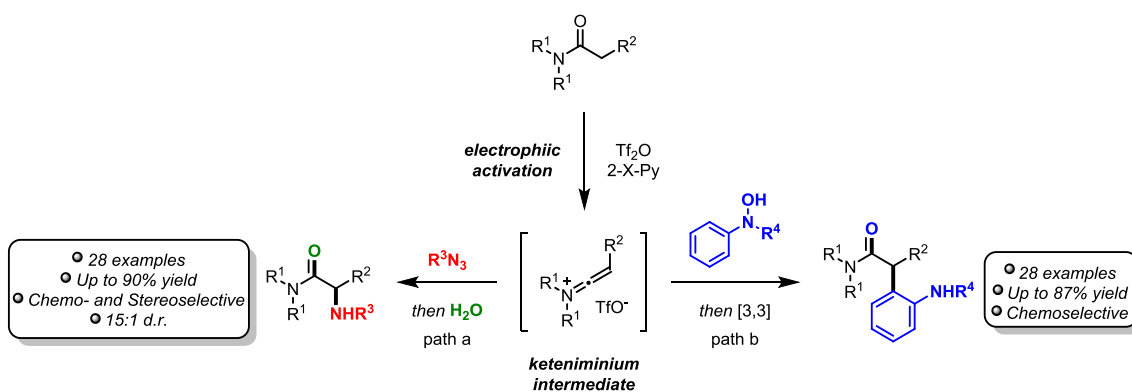


Figure 1. Chemoselective aminations via electrophilic amide activation.

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Acknowledgments

We are grateful to the University of Vienna for continued support of our research program. Financial support for this work was generously provided by the ERC (StG FLATOUT and CoG VINCAT) and the DFG (Grants MA-4861/4-1 and 4-2).

Asymmetric Neber Reaction in the Synthesis of 2-(Tetrazol-5-yl)-2*H*-Azirines

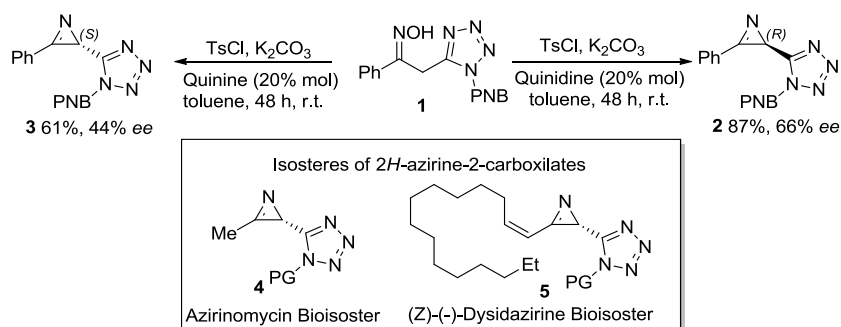
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We have previously described the synthesis of novel 2-(tetrazol-5-yl)-2*H*-azirines via the Neber reaction of β -ketoxime tetrazoles.¹ We set out to develop an asymmetric version of this synthetic methodology which could be applied to the synthesis of bioisosteres of naturally occurring biological active 2*H*-azirine-2-carboxylates² (tetrazolyl derivatives **4** and **5**). Preliminary studies with ketoxime tosylates already demonstrated that the alkaloid-mediated reaction allows the asymmetric synthesis of 2-(tetrazol-5-yl)-2*H*-azirines.¹

We decided to explore an one pot procedure by carrying out the *in situ* tosylation of β -ketoxime tetrazoles followed by the Neber reaction in presence of chiral organocatalysts. We selected the conversion of β -ketoxime **1** into the corresponding 2*H*-azirines as our model reaction. To our delight, this methodology led to higher yields and higher enantioselectivity. Within the organocatalysts already studied, quinidine is still the most efficient allowing the isolation of chiral 2*H*-azirine **2** with 87% yield and 66% ee. The enantiomeric 2*H*-azirine **3** could also be obtained selectively using quinine as organocatalyst. Nevertheless, some of the new organocatalysts have demonstrated promising results. In this communication, further details of this study will be disclosed.



Scheme 1. Asymmetric Synthesis of 2-(Tetrazol-5-yl)-2*H*-Azirines with Quinidine and Quinine as Organocatalysts.

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Acknowledgments

Thanks are due to Coimbra Chemistry Center (CQC) supported by the Portuguese Agency for Scientific Research, Fundação para a Ciência e a Tecnologia (FCT) through project POCI-01-0145-FEDER-007630 co-funded by COMPETE2020-UE for financial support and for the strategic project UID/QUI/0619/2016 attributed to CQE-UE. We acknowledge the UC-NMR facility for the NMR spectroscopic data.

Bifunctional *trans*-cyclooctenes (BITCO's) for enhanced spatial and temporal resolution study of biological systems

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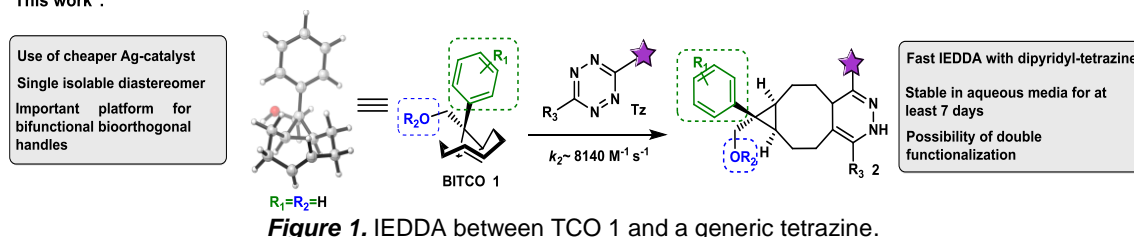
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Amongst the bioorthogonal toolbox, inverse electron demand Diels–Alder (IEDDA) reactions stand out from the others by its unmatched kinetics, excellent orthogonality and biocompatibility for probing and spatial and temporal controlling biomolecule functions *in vitro* and in living systems.¹ The gold bioorthogonal standard *trans*-cyclooctene (TCO) is known to react highly efficiently in aqueous solution ($2000 \text{ M}^{-1} \text{ s}^{-1}$)² Despite 8-member ring modifications can enhance the kinetics (*cis*-cyclopropane fusion), increase its stability (dioxolane-fused), or induce a click-to-release mechanism, the scaffold is highly sensitive to modification, prone to degradation and tolerates only the appendage of a single payload.^{3,4}

We envisioned a double functionalization of the TCO scaffold with minimal impact on reactivity and stability, via diastereoselective cheap silver-catalysed method, to potentially enhance spatial and temporal resolution and double attachment of therapeutic and/or fluorogenic payloads.

This work⁴:



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Synthesis of electroactive subcomponents for molecular machines

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Molecular machine development represents an important topic in supramolecular chemistry, being the subject of the 2016 Nobel Prize in Chemistry. Molecular ring-on-thread rotaxane structures are one major class of molecular machines and are widely applied as molecular shuttles¹ and molecular switches.² In the interest of building functional molecular machines, three cyclic electro-active hydrogen-bonding receptors have been synthesized: two of them present a ferrocene moiety, while the third one is a triarylamine-bearing macrocycle (**Fig.1**).

X-ray structure was obtained and the interactions of macrocycles with commercially available barbital as prototypical guest were studied by UV-visible and ¹H NMR spectroscopies.

A model rotaxane has also been achieved and its synthesis has reported.

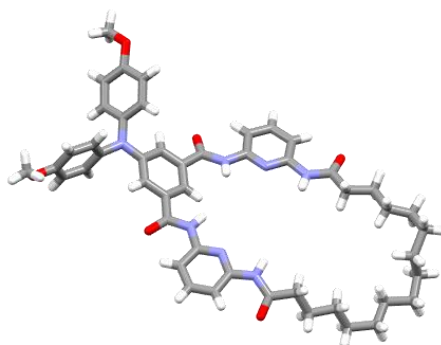


Figure.1. X-ray structure of triarylamine-containing macrocycle.

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Financial support from French ministry of higher education and research for Ph. D. grant is gratefully acknowledged, as well as ANR support (project "PETIMIT").

Guanosine Derived N-Heterocyclic Carbenes: synthesis and applications

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The methylation of nucleic acids occurs naturally in our cells forming DNA adducts.^[1] These are precursors of N-heterocyclic carbenes showing an enhanced reactivity. Although they can lead to mutagenic lesions, they are also involved in the synthesis of nucleic acids among other processes.^[2] For purine based NHCs, when stabilized by a transition metals, all the sites involved in base-pairing are kept intact (Figure 1), allowing to use hydrogen bonding properties as a recognition tool. Specifically, we hypothesize that these metal complexes can be used as highly selective anticancer agents, due to their ability to interact with DNA via base pairing. Herein, we present the synthesis of guanosine derivatives and the evaluation of their cytotoxic activity against several human cell lines, as well as a comparative study with cisplatin^[3]. Our compounds show selectivity against the glioma cell line U251, with the highest activity being displayed by the palladium NHCs.

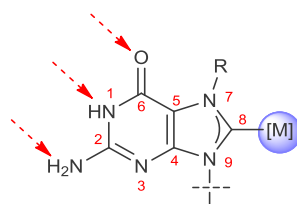


Figure 1. Schematic representation of a guanine derived metal-NHC and its base-pairing sites (red arrows).

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ILs as tunable modulators for protein stability

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Over the past years, the use of Ionic Liquids (ILs) as co-solvents to control protein stability has been extremely explored.^[1] Due to their tunable properties, a consequence of the large number of combinations of cations and anions, ILs can act as protein stabilizers or destabilizers, or even modulate folding events.

In our previous studies with imidazolium-based ionic liquids (IL), we disclosed the effects of specific P-IL interactions on protein stability.^[2,3] These studies revealed that the interaction with the anion dictates the overall protein stability, yet cation still plays a role, and we observed that the imidazolium hydrophobic chain length has a denaturing character which is correlated with its size. With these evidences, we have been studying the interactions of the destabilizing IL [C₄mim][dca], which combines the imidazolium-cation [C₄mim]⁺ with a strong denaturing anion (dicyanamide – [dca]⁻), with domain B1 of the protein G (GB1), a globular and highly stable protein.^[4] We have also been studying the effect of the IL [Ch][Glu], that results from the combination of choline cation [Ch]⁺ with glutamate anion [Glu]⁻ in a 1:1 ratio, on GB1 stability. This novel biocompatible IL is inspired in the combination of two of the most highly concentrated organic charged metabolites found in cells and acts as a protein stabiliser.

In this communication, combining different NMR techniques with the determination of protein stability by fluorescence and calorimetric studies, we will present results concerning the mechanism of the opposite effects of two different ILs in the stability of the same protein. We will show that charged metabolites found in cell milieu can form ILs with the potential to modulate protein stability/folding landscape.

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Anti-inflammatory and antioxidant nanostructured cellulose membranes loaded with phenolic-based ionic liquids for cutaneous application

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Excessive human exposure to sun and to endogenous and environmental pro-oxidant agents are the main factors that contribute to premature skin aging, and cancer [1,2]. Studies have shown that UV-induced skin damage is in part caused by the formation of noxious reactive oxidant species (ROS) [2], leading to a wide variety of pathological effects [3,4]. Consequentially, the demand for skin healthcare materials able to deliver anti-inflammatory and antioxidant compounds, as well as cosmetics with anti-aging and ultraviolet protection properties has increased considerably. In recent years, the utilization of natural compounds, such as phenolic acids, and biopolymers in this domain is gaining increasing attention [5,6].

In this study, bacterial cellulose (BC) membranes were loaded with ionic liquids (ILs) based on phenolic acids. The obtained BC-ILs membranes were homogeneous, conformable and their swelling ability agreed with the solubility of each IL. The membranes revealed controlled ILs dissolution rate in the wet state and high antioxidant activity. *In vitro* assays revealed that these new BC-ILs membranes are non-cytotoxic and present relevant anti-inflammatory properties. Permeation studies showed a prolonged release profile of the bioactive ILs. Thus, this work, successfully demonstrates the potential of BC-ILs membranes with antioxidant and anti-inflammatory properties with high potential for skin treatment.

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Novel chemical tools to explore Parkin activation

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Parkinson's disease (PD) is the second most prevalent neurodegenerative disease worldwide, affecting approximately 1.5% of the population above 60 years of age and 4% of the population at the age of 80 [1].

Although PD is primarily a sporadic disorder of unclear aetiology, it is now clear that genetic factors contribute to the pathogenesis of the disease. For example, mutations in the *parkin* gene, which encodes Parkin protein, are a relatively frequent cause of autosomal recessive early-onset forms of PD [1].

Parkin is a ring-in-between-ring (RBR) E3 ubiquitin ligase, composed by six distinct domains. The catalytic module of PARKIN has a multidomain architecture consisting of RING1, IBR and RING2 domains (the latter harbouring the catalytic cysteine), and is responsible for the ubiquitination and consecutive proteasome degradation of a number of protein substrates [2].

The ubiquitination-proteasome system is fundamental to several cellular events and its malfunction is thought to be a key to the pathogenesis of neurodegenerative diseases. However, medicinal chemistry approaches to regulate this pathway have always been hindered by the lack of suitable robust methodologies for screening endeavours [2].

To address this challenge, a series of activity-based probes for profiling Parkin activity is being developed. Concurrently, a yeast-based phenotypic assay [3] is being implemented and the biological activity of selected probes evaluated.

These novel chemical tools hold promise as innovative biomarkers for Parkin activation, providing the bases for Parkin high-throughput screening campaigns.

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Synthesis and characterization of promising theranostic agents for cancer

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We recently developed a new type of photochemically stable platinum (II) chlorins, which are remarkable photosensitizers that can be used in photodynamic therapy (PDT), due to its therapeutic capacity. Simultaneously, due to its highly luminescence properties, in the biological relevant 650-850 nm red and near infrared spectral region, they may be used for biological imaging [1,2]. In this communication, the synthesis, photochemical and photophysical characterization of a novel series of compounds with different degrees of hydrophilicity will be disclosed. In addition, their photocytotoxic effect was evaluated against three cell lines, the HT1376 line of bladder carcinoma, the A375 line of melanocytic melanoma and the OE19 line of oesophageal carcinoma, demonstrating potential therapeutic effect as PDT agents. Furthermore, photophysical studies indicate that they may be used as ratiometric oxygen sensors.

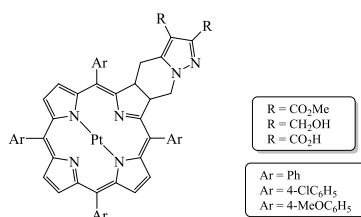


Figure 1. Overview of studied compounds.

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Acknowledgments

This work was funded by *Fundação para a Ciência e a Tecnologia* (FCT), co-funded by FEDER through COMPETE 2020 within project POCI-01-0145-FEDER-PTDC/QEQ-MED/0262/2014, and through PT 2020/CENTRO 2020 within project CENTRO-01-0145-FEDER-000014/MATIS. The Coimbra Chemistry Centre (CQC) and CNC.IBILI are supported through projects POCI-01-0145-FEDER-007630 and POCI-01-0145-FEDER-007440, respectively.

Poster Communications

Thermodynamic Stability of Flavylium Salts as a Valuable Tool to Predict its Reactivity Against π -Nucleophiles

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A-type proanthocyanidins (PACs) are natural products widely distributed in nature with many biological properties. Our research group has synthesized some analogues to PACs following a procedure based on flavylium chemistry [1] and recently reported the antimicrobial and antibiofilm activities of some of those analogues [2]. Flavylium salts are involved in a complex network of chemical equilibria involving several species [3]. The stability, relative energy of each of the chemical species (thermodynamics), and their rates of interconversion (kinetics) are very dependent on flavylium substituents. The overall thermodynamic stability of a flavylium cation may be measured by the apparent acidity constant K_a that characterizes all equilibria among a given flavylium and all the other species and it depends primarily on its hydration reaction [3]. We envisioned this thermodynamic stability of flavylium salts could be a simple and valuable tool to predict the reactivity of those against other nucleophiles (not only water), such as π -nucleophiles. Thus, the aim of this work was to establish a relationship between the pK_a of flavylium salts and the yields obtained in their reactions with several π -nucleophilic units (i.e., catechin and phloroglucinol).

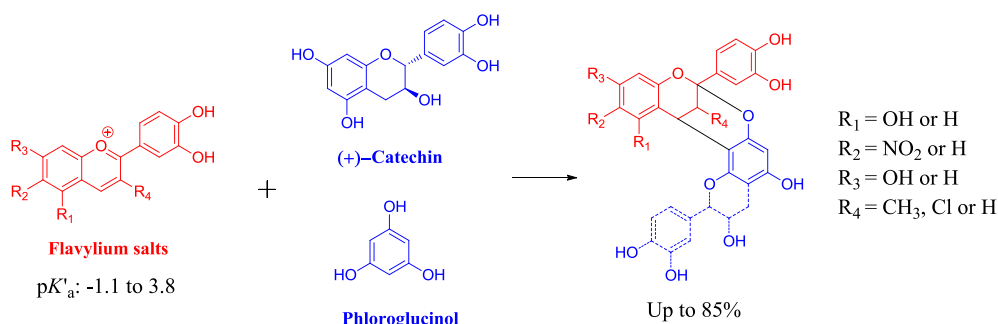


Figure 1. Reaction of several flavylium salts with a selection of π -nucleophiles.

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Acknowledgments

We wish to thank Universidad de Jaén for pre- and post-doctoral fellowships granted to the presenting author.

Synthesis and characterization of pyridinechalcones

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Substitution by pyridine of the phenyl ring linked to the carbonyl group in chalcones gives rise to derivatives that may be designated as pyridinechalcones.[1], These compounds show a pH-dependent equilibrium network similar to those of 2-hydroxychalcones.[2] Following the initial work with 4-pyridinechalcone [1], three new pyridinechalcones are herein presented. Structural elucidation of the synthesized compounds was done by ¹H- and ¹³C-NMR, elemental analysis, ESI-MS and by X-ray crystallography. UV-Vis and ¹H NMR were used to follow the species in solution as a function of pH and UV irradiation. Photochromism was observed upon irradiation of the pyridinechalcones to give the hemiketal as major species in the photostationary state; Fig. 1a illustrates the thermal reversion in 2-pyridinechalcone. This compound contains an ortho-carboxypyridine moiety that was exploited in the complexation of metal ions, such as Cu(II), Fig. 1b.

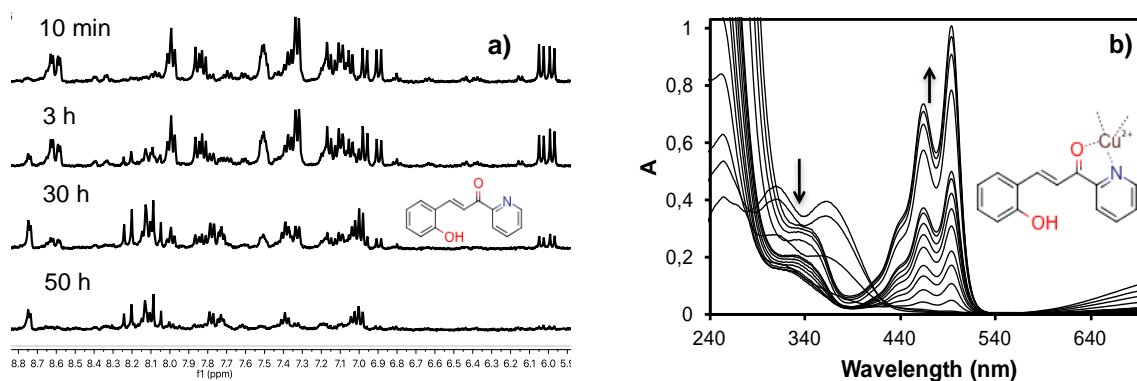


Figure 1. **a)** Thermal recovery (in the dark), followed by ¹H NMR of 17 mM Py2 in CD₃OD/D₂O (1:1 v/v) at pD=5.6 after irradiation at 365 nm; **b)** Spectral variations of 4.4×10⁻⁵M Py2 upon addition of 0–4 mM Cu²⁺ at pH 5.4 in MeOH:H₂O 1:1; solutions equilibrated in the dark (3 days, 294 ± 2 K).

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Acknowledgments

This work was supported by the Associate Laboratory for Green Chemistry- LAQV which is financed by national funds from FCT/MCTES (UID/QUI/50006/2013) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER – 00726).

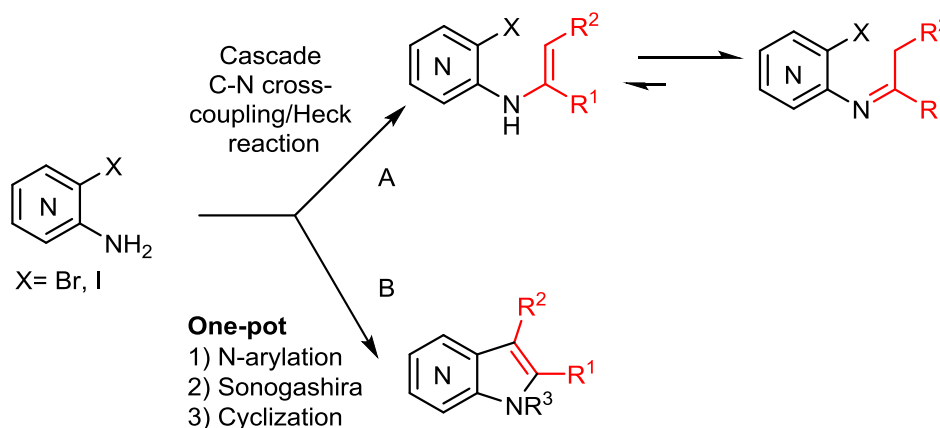
One-pot Azaindole synthesis from substituted aminopyridines

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Azaindoles have attracted the interest of the scientific community due to their privileged properties that make them potential targets for medicinal chemistry.^[1] The common synthetic strategies rely on the use of aminopyridines, followed by building up the pyrrole ring. Since the pyridine ring is electron-deficient, it makes these structures difficult to obtain, in particular by metal-catalysed reactions.^[2] Our group has been focused on metal-catalysed cross-coupling reactions for the preparation of bioactive heterocycles, including azaindoles, from amino-halopyridines (Scheme 1).^[3] The follow-up of our research led us to a new synthetic route, consisting on a direct synthesis from inexpensive aminopyridines.^[4] Herein we will present our approach based on a one-pot manner to obtain azaindoles substituted in the pyridine ring thus exhibiting selectivity to one isomer.



Scheme 1. Previously reported work, Route A: Cascade reaction using C-N cross-coupling followed by Heck reaction and Route B: One-pot N-arylation followed by Sonogashira coupling and cyclization.

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Preparation of copper-based chalcogenides by electrospinning technique

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Copper-based chalcogenides have received great attention due of their intrinsic proprieties, low toxicity and earth-abundant compositions. These compounds can be used in many applications e.g. supercapacitors, photovoltaic cells, photocatalysis, sensors, battery electrodes and biomedicine [1,2].

Electrospinning is a low-cost technique for the production of nanometer scale fibers with tunable surface properties and extremely high surface area, very high porosity, high permeability, low basic weight, the ability to retain electrostatic charges, among others properties [4].

The purpose of this work is to apply electrospinning to the preparation of nanofibers of copper thermoelectric compounds. Moreover, the expected high surface area and low dimensionality can bring benefits to their thermoelectric properties, which will be the aim of future studies. Preliminary results showed that nanofibers of some compounds, e.g. CuS/PVP and CuSbS/PVP, can be successfully produced by this technique, which, to our knowledge, happens for the first time. Examples of representative SEM images of the nanofibers are presented in Figure 1.

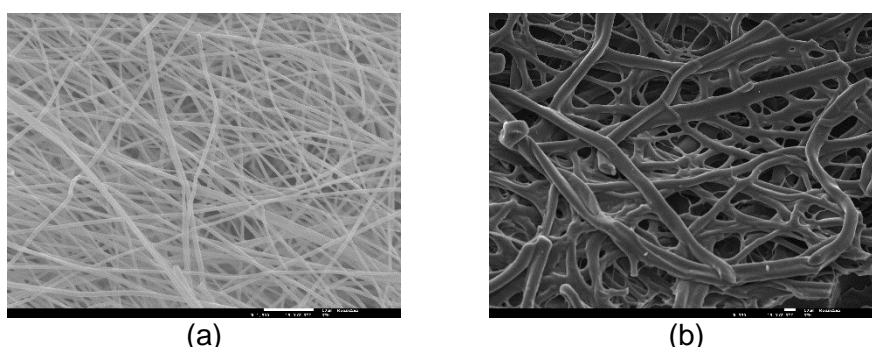


Figure 1. SEM images of nanofibers (a) Cu-S-PVP as spun; (b)Cu-S-PVP 450 °C under nitrogen.

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Acknowledgments

The authors gratefully acknowledge the FCT support through the UID/Multi/04349/2013, POCI-01-0145-FEDER-016674 and M-ERA-NET2/0010/2016 projects.

From red wine to energy: Pyranoanthocyanins as light-harvesters in Dye-Sensitized Solar Cells

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Following the work of Grätzel in Dye-Sensitized Solar Cells (DSSCs)¹, several types of pigments such as the original ruthenium,² and organic dyes, have been used as light absorbers.³ Anthocyanins are the main polyphenolic pigments found in young red wines, which can be transformed into more stable structures such as pyranoanthocyanins, during wine ageing and maturation. They have been shown to display higher color intensity and stability over a wide pH range comparatively to their anthocyanin precursors.⁴ Herein, a series of pyranoanthocyanin derivatives (Figure 1) were synthesized and applied as dye sensitizers in DSSCs. The spectral response and current vs. potential properties of photoanodes using these dyes were measured. A relation was established between dye structure and cell efficiency.

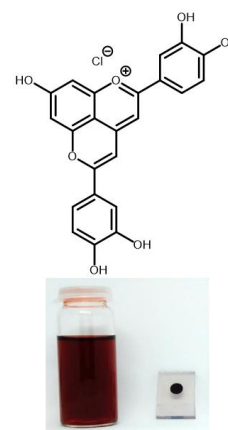


Figure 1. -
Pyranoluteolinidin-catechol⁴
solution (left) and
photoanode (right).

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Pectic Polysaccharides: from agro-food wastes towards advanced applications in food industry

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In the last years, recycling and valorization of waste materials became a priority target for many industries for lowering waste production, for solving ecological issues and for obtaining high-value by-products [1]. The waste materials generated by agro-food industry are promising and an abundant source of bioactive substances such as polyphenols, pectic polysaccharides and proteins. Pectic polysaccharides have been used in the food industry as thickeners, stabilizers, emulsifiers and gelling agents [2]. Besides these usual applications, these polysaccharides have also been shown to interact with other food components, such as polyphenols, raising the hypothesis of their use for the development of highly innovative food systems.

Polyphenols are an are widely recognized due to their health properties and consequently, consumption of polyphenols rich food products have been promoted [3]. However, upon food processing polyphenols usually lose their stability, biological properties, confer unpleasant tastes [4] or lose their genuine colour, which causes lower consumer acceptability together with losses and technical limitations to food processors. The aim of the present work is to explore the potential of pectic polysaccharides fractions obtained from agro-food wastes to modulate food organoleptic properties, such as colour and taste modulation of polyphenols.

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Metabolic adaptation of human osteoblasts to growth on non-poled and poled-PLLA films

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Poly (L-lactic) acid (PLLA) has shown great potential for bone tissue engineering because of its high biocompatibility and biodegradability. Furthermore, PLLA exhibits piezoelectric properties, at a comparable scale as the bone natural polymer, collagen, and believed to be able to modify cell behavior [1-2]. The analysis of the metabolome of biological systems provides substantial information on metabolic changes triggered by key cellular events during cell/biomaterial interaction. To our knowledge, this the first NMR-based metabolomic study regarding the metabolic adaptation of human osteoblast cell line (HOb) in contact with non-poled and negatively-poled PLLA films.

An untargeted metabolomic strategy was employed to characterize the metabolome of lysed HOb cells and cell extracts in the presence of non-poled or negatively poled PLLA, compared to the absence of polymer. Multivariate analysis unveiled that PLLA-grown cells are subjected to enhanced oxidative stress and activate energy metabolism at the cost of storage lipids and glucose. Some evidence of changes in protein and nucleic acid metabolisms was also noted, as was enhanced membrane biosynthesis. Analysis of aqueous extracts NMR spectra demonstrated that, compared to plastic, PLLA-exposed cells showed enhanced use of choline compounds, creatine, glutamate and hypoxanthine, with more marked variations for non-poled PLLA than for negatively poled-PLLA. Regarding lipophilic extracts, only a decrease in fatty acid methyls was noted, with no further changes in other lipid environments or average FA chain length and unsaturation degree. These results enabled small but clear metabolic effects of the presence of PLLA (either non-poled or negatively-poled) on HOb cells to be identified and suggest that poled PLLA is more efficient in sustaining cell growth than non-poled PLLA.

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Sustainable synthesis of heterocyclic compounds on a soluble polymer support

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Heterocyclic compounds are important scaffolds that are present in bio-active compounds^[1], so there is an increasing need of new and more selective synthetic methodologies that allow access to these scaffolds and simultaneously its diverse functionalization. We have been focusing on synthetic routes involving cross-coupling reactions to attain heterocyclic compounds.^[2]

Our group has been exploring novel synthetic routes towards the challenging azaindoles (indole bioisosteres), via a cascade reaction involving C-N cross coupling/Heck reaction.^[6] Recently, we have been improving the access to highly functionalized azaindoles using PEG as support. Indole synthesis using polyethylene glycol (PEG) has been previously reported.^[3,4,5]

Additionally, Pd-catalyzed reactions such as the Sonogashira reaction using anilines and aryl halides have also been investigated by us, using a soluble polymeric support, in order to reduce side products, to simplify purifications and to improve product yield (**Figure 1**).

Moreover, we have also been investigating novel approaches relying on palladium-catalyzed cross-coupling reactions to attain azaindoles derivatives as a sustainable and versatile new route. The most recent results will be presented in this communication.

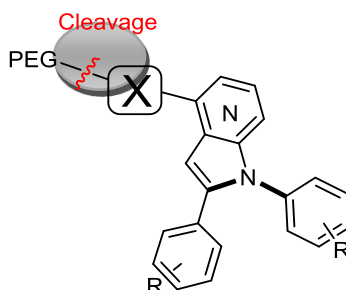


Figure 1. Heterocyclic compounds immobilized in a soluble polymeric support.

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Cytotoxic Impact of Platinum- and Palladium-based Drugs on MG-63 Cells

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The search for improved anticancer drugs has been a matter of growing interest and the accidental discovery of the antitumor activity of Cisplatin triggered the search for other potential antineoplastic metal-based complexes. Platinum (II) complexes such as Cisplatin, Carboplatin and Oxaliplatin are among the most efficient chemotherapeutic drugs presently used in the clinic, however, their deleterious side effects (systemic toxicity and acquired resistance) have justified research on potential new platinum compounds and other metal complexes, such as palladium (II) compounds. The Pd₂Spermine (Spm) and the Pt₂Spm complexes have shown promising cytotoxic behavior in breast cancer [1], ovarian carcinoma [2] and squamous tongue epithelioma [3] cell lines, and their testing on osteosarcoma (MG-63) is here reported. These novel complexes were tested in comparison with Cisplatin and Oxaliplatin, and their cytotoxicity on MG-63 cells was characterized by three distinct methods: MTT and Alamar Blue cell proliferation assays, and the SRB cell density assay. Although, in single administration, Pd₂Spm has shown higher cytotoxicity against MG-63 cells (ten times lower IC₅₀), Pt₂Spm induces higher cytotoxicity on MG-63 cells when combined with Doxorubicin (Dox), acting more similarly to conventional drugs. Interestingly, further addition of Methotrexate (Mtx) to each of the novel complexes or conventional drugs does not seem to enhance the cytotoxic effects of the drug cocktails. The enhanced synergism of this new metal-based complexes, particularly Pt₂Spm when combined with Dox, supports the interest of exploring potential new drugs both in single administration and in combination protocols.

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Magnetic-responsive double layer cell sheets using internalizable magnetite nanoparticles: new prospects for bone regeneration

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One of the major challenges in tissue engineering is to produce functional 3D tissue models able to recapitulate the complex and physiological structure of natural tissues. Current artificial tissue-substitutes have restricted clinical applications due to unmatched complex combination of cells and extracellular matrix as seen in native tissues. [1] In an attempt to develop hierarchical cellular 3D constructs, we herein propose the construction of magnetic responsive double layer cell sheets able to be harvest as a whole by applying a magnetic force, thus, without requiring any enzymatic treatment. For the purpose, rhodamine B-labeled supermagnetic iron oxide nanoparticles (10 nm) were synthesized by the co-precipitation method and characterized by FTIR and TEM. Nanoparticles stability in culture medium was also investigated for 21 days.

The developed nanoparticles were then incubated with an osteoblastic cell line (MC3T3-E1) and human adipose derived stem cells (hASCs), allowing the developed of magnetic cell sheet monolayers. The presence of alignment F-actin filaments were confirmed in both cell monolayers. Additionally, in the osteoblastic cell sheet, a collagen type I enriched matrix was evidenced. Afterwards, a magnetic double layer cell sheet using both phenotypes was engineered. MC3T3-E1 were stained with DIO as hASCs were stained with DID priori to cell sheet formation. The developed double layer cell-sheets were co-cultured in culture medium with and without osteogenic differentiation factors. After 21 days of incubation, the microtissues could be macroscopically visualized and easily detached by applying a magnetic-force. Mitochondrial activity, cell proliferation and calcium quantification were all accessed, and the osteogenic potential of the double cell-sheet layers was investigated. An enhanced osteogenesis was evidenced in the presence of differentiation factors. Such findings were supported by an increased ALP activity, matrix mineralization and an osteopontin intensified detection. With this system we intend to demonstrate the possibility to create a plethora of cell phenotype combinations as well as evidence the ability of the developed technology to easily create complex 3D functional tissues.

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The authors acknowledge the financial support by the European Research Council grant agreement ERC-2014-ADG-669858 for project "ATLAS". The work was developed within the scope of the project CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID /CTM /50011/2013), financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement.

Intriguing properties of a copper(I)-tin(II) ABX₃ type mixture

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Inspired by the typical perovskite ABX₃ structure, in which “A” and “B” stand for mono and di-cations, respectively, and “X” for halogens [1], a mixture of tin (II) dichloride and copper (I) iodide was prepared by manual grinding. The result was a pale-yellow powder that exhibited photoluminescent behavior with a red luminescence (figure 1). The optical properties of this compound were studied using both diffuse reflectance and emission spectroscopy. 2D luminescence maps were created and quantum yields were measured, reaching as high as ca. 13%. The lifetime analysis showed that the system exhibits a single-exponential fast first-order kinetics followed by a slower second order kinetics. This behavior agrees with a excitonic recombination of semiconductors like perovskites [2].



Figure 1. Red luminescence exhibited by the compound.

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Synthesis of bis-functionalized furanose derivatives towards new types of nucleoside and nucleotide analogs

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Nucleoside and nucleotide analogues are important groups of molecules in medicinal chemistry, due to their ability to display a variety of biological effects, such as anticancer [1], antiviral [1] and cholinesterase inhibitory properties [2]. Such molecules are capable to mimic their natural counterparts, acting by inhibition of nucleotide-dependent enzymes, interfering with nucleic acid synthesis and cell cycle progress [1].

Hence, we were motivated to explore the synthesis of structurally innovative and previously unreported isonucleotides, comprising a phosphate group and an N-heteroaromatic moiety linked to a position other than C-1 of the sugar ring, and nucleosides having a guanidine moiety as a mimetic of a purine nucleobase, *via* 3,5-bis functionalization of furanose scaffolds. Also, chemically and enzymatically stable isostere moieties for a phosphate group were included in the structures, which may turn them resistant to nucleotidases. The synthetic strategies for the access to the target molecules included azide-alkyne 1,3- dipolar cycloaddition, sugar azidation, guanidinylation, phosphorylation or Arbuzov-type reaction. In this communication, the synthetic work will be presented and discussed.

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'Fundação para a Ciência e Tecnologia' (FCT) is acknowledged for funding (project IF/01488/2013, IF/00069/2014 and CQB strategic projects UID/MULTI/00612/2013).

Development of Magnetic and Luminescent Functional Ionic Liquids

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Ionic Liquids (ILs) as tuneable organic salts possessing peculiar properties have been applied in many research fields including material science and pharmaceuticals, among others.^[1] Nowadays, a recent class of these salts, the magnetic ionic liquids (MILs), has gained greater attention. These compounds have the advantage of combining ionic liquids properties as well as magnetic materials. This combination allows these organic salts to respond to a strong magnetic field.^[2] Specifically, they have been used in electrochemical and chemical engineering applications including extraction and separation processes and also in medical applications.^[3,4] Herein, we have developed biocompatible magnetic and luminescent ionic liquids or organic salts based on the combination between choline derivative cations and Mn(II), Gd(III) and Tb(III) anion complexes (Figure 1A). All prepared compounds were completely characterized by spectroscopy (NMR, FTIR, UV-Vis, Emission); magnetic susceptibility; and thermal properties. In parallel, to improve their physical-chemical as well as biological properties, some of these systems were trapped in Mesoporous Silica Nanoparticles (MSNs), Figure 1B and then detailed characterized.

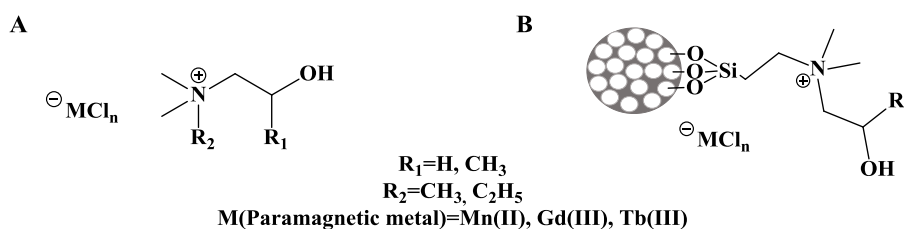


Figure 1. (a) magnetic organic salts based on choline derivatives; (b) Mesoporous silica nanoparticles (MSNs).

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Acknowledgments

The authors would like to thanks to FCT-MCTES (PTDC/CTM-NAN/120658/2010, IF/0041/2013/CP1161/CT005 and PD/BD/109625/2015 projects).

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Combining Gold Nanoclusters and Polymer as Probes

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Gold Nanoclusters (AuNCs) are a new type of gold particles that have been developed in the last decades. They are studied for applications in different fields – from medicine to chemistry and physics. With dimensions below 2 nm, low toxicity, biocompatibility, fluorescence emission and high photostability, AuNCs are considered a link between molecules and atoms [1]. We are interested in the application of AuNCs as labels for advanced imaging applications, being our goal is to develop novel materials containing AuNCs, improving AuNCs stability and resistance to different environments. Our approach is to incorporate AuNCs in polymer nanoparticles, so that they maintain their optical properties. Different polymerization techniques have been used: miniemulsion polymerization and polymerization induced self-assembly (PISA). While the first technique is a robust system for polymer particles production [2], the second allows the production of highly functionalized polymer particles [3]. We have already produced polymer nanoparticles, by both polymerization techniques, with diameter from 20 nm to 60 nm.

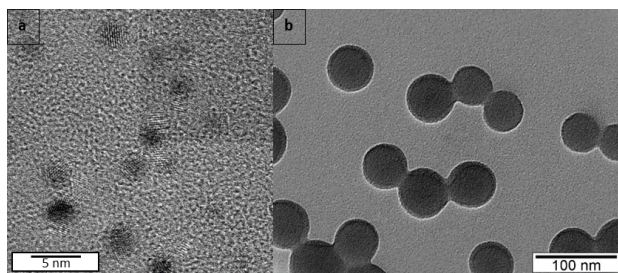


Figure 1. a) HR TEM of Au₂₅(MHA)₁₈. b) TEM of polymer nanoparticles produced by miniemulsion polymerization.

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Manganese N-Heterocyclic Carbene Complexes in Catalytic Reductions

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In recent years, the development of catalysts based on first-row transition metals has become a central topic in catalysis. Among 3d metals, manganese is a particularly attractive candidate for catalysis due to their natural abundance and their unique features of being non-toxic and a biocompatible metal. So far, the majority of the Mn-based catalysts described in the literature are coordination compounds bearing N-, O-, and P- ligands; pure organometallic Mn-based catalysts are scarce. In this work, we have explored the reduction of carbonyl functionalities, aldehydes and ketones, with silanes using manganese(I) compounds bearing bis-N-heterocyclic carbenes (**1**, **2**) (NHCs), mixed NHC-pyridyl (**3**), and bipyridyl (**4**) ligands, Figure 1. Excellent ketone conversions were achieved for complexes **1-3** bearing NHC ligands.[1] Interestingly, the replacement of pyridine rings with the strong donating NHCs improves the catalytic efficiency of the Mn catalysts. The scope of the reaction and the mechanistic details will be discussed. In addition, we have studied the electrocatalytic reduction of CO₂ mediated by **1**. Experimental data showed that **1** is a highly active catalyst for the selective reduction of CO₂ to CO in the absence of acids. Combined UV-Vis and IR spectroelectrochemical experiments help us to provide mechanistic insights of the reductive process.[2]

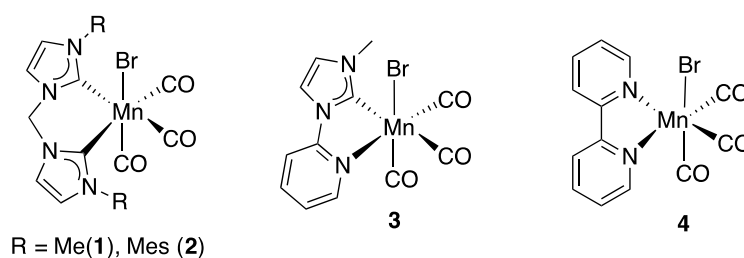


Figure 1. Manganese(I) complexes explored in the reduction of carbonyl groups

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Acknowledgments

Provide information such as for UDI/Multi/04551/2013, RECI/BBB-BQB/0230/2012 (NMR facilities), PD/BD/105994/2014 (M.P.) and IF/00346/2013 (B.R.); the European Commission for CARISMA, COST ACTION CM1205 and the ERC-CG-2014-648304 (J.LI.-F.) project, and from ICIQ Foundation and CELLEX and other financial support.

Valorisation of spent coffee grounds using subcritical water

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Spent coffee grounds (SCG) is the by-product obtained in the preparation of instant coffee. Every year 6 million tons of this residue are generated worldwide and most of it is still discarded as waste. SCG is a rich source of phenolic compounds (Machado et al. 2012) and carbohydrates, which are present in a complex lignocellulosic matrix (Mussatto et al. 2011). Phenolic compounds and carbohydrates from lignocellulose are recovered, mostly using organic solvents and acidic solutions. Subcritical water (SBW) is an environmental friendly alternative to these conventional solvents. SBW is liquid water at high temperatures and above its vapor pressure, which has a lower dielectric constant, increasing the solubility of less polar molecules, such as phenolics, and also a higher ionic product, which makes SBW a more reactive medium for the hydrolysis of lignocellulosic matrices (Brunner 2009).

Before the experiments with SBW, the chemical characterization of SCG was performed for carbohydrates (50%), proteins (13.4%), lipids (12.3%), lignin (12.8%), ash (1%) and phenolics (2.3%).

Several assays were performed with SBW at different temperatures (150, 180, 200, 220 °C). The increase in temperature led to an increase in the yield of phenolic compounds and carbohydrates recovered, up to 200 °C, leading to around 34 g of carbohydrates /100g SCG and 4 g of phenolics/100g dry SCG. These results represent a recovery of 65% of the total amount of carbohydrates, and a higher recovery of phenolic compounds when compared with the conventional extraction method used. The extracts collected at lower temperatures, until 150 °C, had a higher content in phenolic compounds, around 150 mg/g of dry extract, while the samples collected at higher temperatures were richer in carbohydrates. The antioxidant activity of the extracts was higher for the extracts richer in phenolic compounds and the antimicrobial activity was also evaluated for the different extracts.

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Diffusion coefficients of metal acetylacetonates in liquid ethanol and supercritical CO₂

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The knowledge of transport properties like diffusion coefficients (D_{12}) is of chief importance for modeling, design and optimization of rate-controlled processes. However, due to the lack of a reliable and rigorous theory for D_{12} estimation, the experimental measurement of such coefficients is necessary [1].

Metal acetylacetonates, $\text{Me}(\text{acac})_n$, are organometallic complexes consisting of anions and metal cations. These compounds exhibit a high stability and solubility in organic liquids, making them ideal for numerous industrial applications such as catalysts in organic reactions, additives in rubber and polymers formulations, and in extraction and other separation processes of metals [2-4].

In this work, D_{12} of five metal acetylacetonates - chromium(III) acetylacetonate, palladium(II) acetylacetonate, nickel(II) acetylacetonate, vanadyl(II) acetylacetonate, and titanium(IV) oxyacetylacetonate - were measured in liquid ethanol using the chromatographic peak broadening method (CPB) [5]. The measurements were performed at atmospheric pressure and in the temperature range 303.15-333.15 K. Overall, the obtained diffusivities scored 0.789×10^{-4} to $2.002 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$. The results were compared with the diffusivities of $\text{Me}(\text{acac})_n$ in supercritical carbon dioxide.

The experimental data of both liquid and supercritical systems were subsequently modeled using well-known predictive and correlation models from the literature, achieving relative deviations from 0.32 to 34.71 %.

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This work was developed in the scope of: Project CICECO-Aveiro Institute of Materials (Ref. FCT UID/CTM/50011/2013), financed by national funds through the FCT/MEC and when applicable co-financed by FEDER under the PT2020 Partnership Agreement.

A Novel Polysaccharide-based Approach for Cryopreservation

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Cryopreservation of biological tissue has had a big spotlight in the field of medicine, as it aims for long-term storage of whole organs for transplantation and constant improvement of biobanking methodologies. However, current procedures still struggle with cryoprotectant cytotoxicity, optimal freeze-thaw rates and efficient carrier formulas [1]. The constant need for tailoring the conditions for each individual sample therefore becomes a strenuous approach in ensuring the highest functional viability.

In this work we implemented a fully biodegradable, bio-based, fucose-rich heteropolysaccharide of bacterial origin in cryoprotective formulas. So far, it has been shown to have potential use in food, pharmaceutical, oil drilling and bioremediation applications. In this work, the biopolymer was shown to have antioxidant activity and an antifreeze activity similar to that of antifreeze proteins. When included in cryoprotective commercial formulas, it retained its rheological properties while also securing outstanding colloidal stability of all electrolyte-rich media. Cryogenic studies on microplate-adhered mammalian cells showed that the biopolymer has great promise for implementation in cryoprotective formulas: it shows no significant cytotoxicity, its inherent viscosity does not hinder nutrient diffusion and is able to preserve both the morphological and functional integrity of cells by protecting them against cryoinjury and osmotic shock at an extracellular level.

The ability to freely tailor the biopolymer's properties either for perfusion or immersion solutions and a multitude of beneficial properties renders it as a valuable asset in novel formulations, reducing their cost. The demonstration, for the first time, of its performance in cryobiology is comparable to currently used commercial synthetic polymers, which adds considerably to its value and further drives industrial implementation stemming from bio-production.

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This project was financially supported by UCIBIO, LAQV and CENIMAT/I3N which are financed by national funds from FCT/MCTES (UID/Multi/04378/2013, UID/QUI/50006/2013 and UID/CTM/50025, respectively) and co-financed by the ERDF, under the PT2020 Partnership Agreement (POCI-01-0145-FEDER-007728, POCI-01-0145-FEDER-007265 and POCI-01-0145-FEDER-007688, respectively), and exploratory project grant IF/00589/2015 attributed within the 2015 FCT Researcher Program.

A new generation of photoluminescent transparent glasses

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Nowadays, due to the unavailability of rare-earths, the greatest technological concern is to find raw materials that are more accessible and that can be applied in large scale at affordable prices. The use of common and inexpensive raw materials is the key for future sustainable applications such as lasers, optical amplifiers, white light emitting diodes (white-LEDs) and solar concentrators ^[1]. Recently, transparent glasses doped with different metals have received special attention due to their stability and luminescent optical properties. Copper, silver and gold clusters entrapped in zeolite ^[2] or glassy ^[3] frameworks have been probed depicting promising luminescent properties. Manganese is also a low-cost and environmental-friendly candidate to obtain luminescent materials with high External Quantum Efficiency and high Stokes shifts. The tetrahedrally coordinated Mn^{2+} typically presents a green emission, while the octahedrally coordinated Mn^{2+} displays orange to red emission, due to the forbidden d–d transition ${}^4T_1(G) \rightarrow {}^6A_1$, suitable for UV-to-Visible light down-conversion applications ^[4]. In this project, borosilicate glasses were selected as a host matrix for manganese since it possesses excellent chemical durability, mechanical strength and high thermal shock resistance ^[5]. Multicomponent base glasses were produced using Si and B as network formers, and Na and K as network modifiers which act as counter ions for negatively charged defects. Considering this, borosilicate glasses embedding photoluminescent manganese by co-precipitation method were synthesized. This strategy of synthesis of glasses with different ratios of network formers and the changing of the network modifiers allowed us to improve the quantum efficiency of glasses up to 40% with room-temperature photoluminescence at 640 nm. Furthermore, phosphorescence decays, quantum efficiencies and structure analyses will also be presented highlighting the effect of glass composition on the optical properties.

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Solid-state investigation of zeolite acidity using trimethylphosphine oxide probe molecules

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Over the past decades, the acidic properties of zeolites were extensively investigated and found major industrial applications, namely as catalysts in petrochemical industry processes. Several spectroscopic and analytical techniques were employed to investigate these properties, and most contributions found in the literature are controversial. Solid-state NMR is among the most used spectroscopic techniques to investigate zeolite acidity. Combined with the adsorption of molecular probes, accurate information about acid sites can be obtained. Trimethylphosphine oxide (TMPO) has been used in the last few years to investigate both solid and liquid acids [1]. The broad chemical shift range and high natural abundance of the NMR active nucleus (³¹P) and its smaller size, compared with other widely used phosphorous-containing probes, makes TMPO a very attractive probe to investigate zeolites acidity.

This project aims at performing a comprehensive study of acid sites in several related zeolites, prepared with subtle modifications to obtain materials with distinct acidic properties, namely the type, strength, amount of both Lewis and Brønsted acid sites. Site-selective information can be obtained combining multinuclear 1D and 2D solid-state NMR experiments with computational calculations. In this work we introduce a new method to TMPO adsorption that avoids the large amount of crystalline probe obtained using the conventional method. Preliminary results showed that TMPO is a powerful probe to obtain structural information on the pore surface, allowing not only the differentiation between Brønsted and Lewis acidity but also accessing the acid strength of these sites. We anticipate using 1D and 2D homonuclear and heteronuclear correlation techniques, such as ¹H-X HETCOR MAS NMR (X=²⁹Si, ³¹P, ¹⁷O), DQ-SQ correlation spectroscopy and double/triple resonance recoupling methods (*e.g.*, RESPDOR, REAPDOR, TRAPDOR) using conventional and DNP surface-enhanced SSNMR methods.

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This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID/CTM/50011/2013), financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement.

Complete study of protein GB1 encapsulated in a reverse micelle system by nuclear magnetic resonance

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Protein encapsulation into reverse micelles water cores tumbling in a low viscous solvent has emerged as a powerful tool in NMR for the determination of biologically relevant protein structures [1]. Water cores inside reverse micelles provide a protective environment for proteins. In this non-bulk water environment, intrinsic to biologic systems, the dynamics of water are distinctly different from those of water in pure liquid [2], allowing to study the interaction of biological macromolecules with water, which are fundamental to understand their structure, dynamics and function [3].

In this work the globular domain B1 of the protein G (GB1) was successfully encapsulated in a reverse micelle formed by the anionic surfactant AOT, water, and the low viscosity solvent isooctane. A completed structural and dynamic study of the system was performed by NMR. Comprehensive structural and dynamic information of the protein encapsulated was obtained for different sizes of reverse micelle nucleus cores. Distinct types of interactions between non-bulk water molecules inside the cores and the surface of the protein were characterized and the clustering of different hydration-dynamics over the protein structure was mapped.

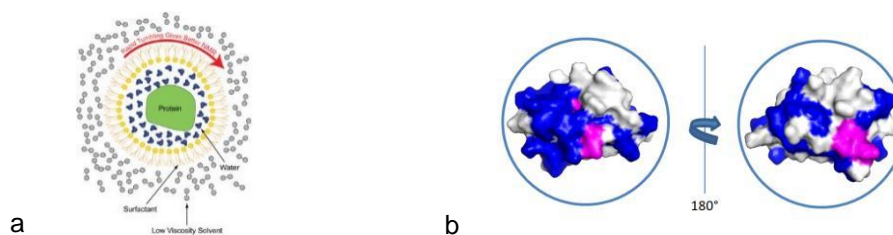


Figure 1. Protein encapsulated in a reverse micelle tumbling in a low viscosity solvent (a) [3]. Mapping of different water- protein interactions inside an AOT reverse micelle water core (b).

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Multifunctional laminarin microparticles for cell adhesion and expansion

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Microfabrication technologies have been widely explored to produce microgels that can be assembled in functional constructs for tissue engineering and regenerative medicine applications. Here, we propose microfluidics coupled to a source of UV light to produce monodisperse multifunctional methacrylated laminarin microparticles using photopolymerization. Laminarin is a natural polymer obtained from brown algae with low molecular weight and low viscosity [1]. These properties make this polymer particularly appealing to be processed using microfabrication techniques. Photopolymerizable hydrogels from methacrylated laminarin (MeLam) have recently been proposed as an enabling platform to encapsulate human stem cells that remain fully viable for several days [2]. In this work, we report a simple and efficient microfluidic approach to produce monodisperse MeLam microparticles with encapsulated platelet lysates (PL). PL loaded scaffolds and microparticles have been successfully used to improve the biological performance of biomaterials. PL supplementation of cell culture media is also gaining an increasing interest as animal serum substitutes, especially for cells that need to be implanted in the patient [3,4]. Herein, the encapsulation of PL was used for the improvement of cell attachment and expansion in MeLam microparticles. The methacrylate groups present on the photopolymerizable laminarin backbone could act also as anchoring sites for the immobilization of thiolated molecules. In the present work, the microparticles were functionalized with thiol-biotin molecules for the subsequent binding of biotinylated RGD molecules in an attempt to accelerate and enhance cell adhesion.

Overall, our findings demonstrate that multifunctional methacrylated laminarin microparticles provide an effective support for cell attachment and cell expansion. Moreover, expanded cells provide the link for microparticles aggregation resulting in robust 3D structures. This suggests the potential for using the methacrylated laminarin microplatforms to rapidly produce large tissue engineered constructs.

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Acknowledgments

The work was developed within the scope of the project CICECO - Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID/CTM/50011/2013), financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. This work was also supported by the European Research Council grant agreement ERC-2014-ADG-669858 for project ATLAS. C.A.C. acknowledges funding support from the Portuguese Foundation for Science and Technology (FCT) (fellowship SFRH/BPD/100594/2014).

Photoluminescent species present in artificial ‘hackmanite’

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Sodalite is a zeolite-type mineral, with the general composition of $\text{Na}_8[\text{SiAlO}_4]_6\text{Cl}_2$. ‘Hackmanite’ is a natural sodalite mineral with sulfur in its composition^[1]. It is well known by its photochromic properties^[2], where a pink colour is obtained when irradiated with 254 nm^[1], due to the presence of S_2^{2-} clusters. The photoluminescence, which is given by other sulfur specie, S_2^- , can also be found in ‘hackmanite’^[2]. These photoluminescent sulfur sodalite-type have high Stokes-shifts^[3], ca. 250 nm, high external quantum efficiency (EQE) and stability at high temperatures.

High sulfur concentrations can induce self-quenching in luminescence^[1]. To better understand this effect three samples of sodalite were made, based on the following stoichiometry: $\text{Na}_8[\text{SiAlO}_4]_6\text{S}_x\text{Cl}_{2-2x}$, using different sulfur concentrations ($x=0.2, 0.3$ and 0.8).

Since it is also possible to incorporate other halogens in the sodalite structure, several sodalites with different halogens, like bromide and iodide, were also synthesized using the same stoichiometry. In this way, it is possible to understand if the presence of different halogens affects the sodalite structure and if they lead to the formation of new species.

To achieve all of these luminescent compounds, three reagents were mixed: NaX ($X=\text{Cl}, \text{Br}$ or I), Na_2SO_4 and 4A LTA zeolite, considering the desired stoichiometry. All reagents were ball-milled together during 1h, and afterwards mixed using a shaker powder mixer, for 3h. The mixture was heated in an electric furnace, at 900°C during 1h, in a reductive atmosphere of 5% H_2 , 95% Ar (v/v).

In chloride and bromide sodalites, S^{2-} clusters were found at low concentrations of sulfur ($x=0.2$ and 0.3).

At higher concentrations ($x=0.8$), a different type of clusters was found (tentatively S_4^{2-} species). This last type of clusters were also found on iodine sodalites.

Chloride sodalite was deposited on a glass surface, at a temperature of 750°C, and it remained luminescent, and for this reason, are a suitable candidate for application in solar cells and as luminescent solar concentrators.

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Ultra-concentrated surfactant systems to produce highly efficient eco-friendly detergents. Control of solutions properties.

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Ultra concentrated surfactant systems can be used to produce highly efficient detergents able to be applied in very low dosage, constituting an excellent way to reduce the waste of plastics and the transportation costs. The role of co-solvents, as non-aqueous polar molecules, glycols or other alcohols, in mixed surfactant systems has been studied due to their ability to change the performance of surfactants [1]. Co-solvents can reduce the viscosity and the surface tension of surfactants solutions [2] and are usually economically beneficial and environmental friendly.

The presence of glycols and alcohols in mixed concentrated surfactant systems, acting as solvents, were evaluated in order to obtain systems with improved properties, with addition of very low water amount. The rheology of these systems, as well as their critical micelle concentration and surface tension, were evaluated.

In a system containing 52% of active surfactant, the use of both dipropylene glycol n-butyl ether (DPnB) in combination with an water soluble alcohol, like ethyl diglycol (EDG), ethanol, isopropyl alcohol (IPA), propylene glycol methyl ether (PM) or dipropylene glycol monomethyl ether (DPM), results in a clear and stable mixture and a viscosity under 1.00 Pa.s, which means easy solution handling. The effect of DPnB in reducing viscosity is more pronounced when compared with the other alcohols. All other solvents only show some visible effect when used in combination with DPnB, otherwise the system presents a very high viscosity.

The synergistic effect between mixed surfactants systems and solvents results in formulations with low critical micellar concentration and surface tension.

Our results show that the presence of alcohols as solvents of mixed surfactant systems can lead to efficient and eco-friendly high concentrated cleaning products.

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Acknowledgments

The authors are thankful to P2020 Program (Project SUGARDWASH) for financing the project.

Ligand and spin state effects in Mn(III) single molecule magnets

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Mn(III) Schiff-base complexes have been widely developed because of their promising applications. These compounds have been reported as displaying single molecule magnet behaviour or spin-crossover phenomena, which can be used in storage devices and quantum computing.[1]

When displaying single molecule magnet behaviour, the most important properties are both the magnetization relaxation (τ_0) and barrier (U_{eff}). The former should be as low as possible and the latter as high as possible to avoid the loss of information. This magnetization barrier can be enhanced if there is an axial distortion ($D < 0$) on the d_z^2 orbitals providing a zero-field splitting that can be observed in Mn(III) high spin state ($S=2$) due to the permanent Jahn-Teller effect.

When displaying spin-crossover behaviour a switch between the d -electrons on the Mn(III) orbitals can occur and this can be promoted by temperature changes, light induction, etc.[2]

We report a series of Mn(III) complexes with N_4O_2 donor atoms and study their magnetic behaviour. The ligands were obtained by reacting three different amines with four different aldehydes to form both hexadentate and tridentate Schiff-base ligands.

The Mn(III) complexes were formed reacting $MnCl_2 \cdot 4H_2O$, NH_4BF_4 and the different ligands in air. All compounds were characterized by FTIR, UV-vis, NMR, cyclic voltammetry, elemental analysis and X-ray crystallography. Magnetic measurements on all compounds were also performed by SQUID magnetometry.

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Acknowledgments

We thank FCT for the financial support.

Dry Powder Formulations for Antibiotic Pulmonary Delivery

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Chronic obstructive pulmonary disease (COPD), asthma and cystic fibrosis (CF) are the most common chronic neutrophilic inflammatory lung diseases [1,2]. In 2015, COPD led the fourth leading cause of mortality worldwide, claiming 3.2 million lives. Despite the high costs related with treatment and patient hospitalization, these diseases represent a worldwide public health challenge [2]. Therefore, anti-inflammatory therapies, such as corticosteroids, have awakened a particular interest for chronic lung diseases treatment. However, severe inflammatory diseases require high doses of anti-inflammatory drugs what a long-term systemic therapy can have some adverse effects such as osteoporosis, adrenal suppression, diabetes, and cardiovascular diseases [1]. Dry powder formulations are promising issues in the pharmaceutical landscape due to increased storage stability, minimize infection risk enabling an easier availability and higher patient compliance. However, the pharmacokinetic profile for inhaled agents may vary due to poor aqueous solubility of bioactive agent or specific physico-chemical properties of the formulations, posing delivery challenges. Thus, to help to achieve the requirements for an effective drug delivery in lungs, in this work, dry powder formulations of trehalose containing pegylated- and poxylated-fusidic acid were performed by supercritical CO₂-assisted spray-drying (SASD) [3]. Fusidic acid is an antimicrobial agent with a bacteriostatic action in bacterial conjunctivitis, colitis, cystic fibrosis and respiratory infections [4]. The conjugation of fusidic acid with poly(ethylene glycol) and poly(2-ethyl-2-oxazoline) were performed in an one pot reaction, preventing reaction wastes and reducing the reaction and purification steps. The physical, chemical and microbial characteristics of formulations were studied by diverse techniques as NMR, Karl-Fisher, FTIR-ATR, Andersen Cascade Impactor and Morphologi G3 and minimum inhibitory concentration (MIC) assays.

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Antimicrobial and antifungal activities of a coloring extract rich in betacyanins obtained from the flowers of *Gomphrena globosa* L

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There is a huge diversity of pigments from natural origin that can be exploited as colorants in the food industry. Nonetheless, they can additionally provide several bioactive properties, which represent an added-value for food products. Carotenoids, chlorophylls, anthocyanins and betalains are some of the most studied plant-based pigments. Betalains, can be subdivided according to their chemical structure into betacyanins and betaxanthins [1]. Although less exploited than *Beta vulgaris* L., *Gomphrena globosa* L. is an important source of betacyanins [2], with antimicrobial and antifungal activity [3]. Thus, the aim of this study was to obtain a pigmented extract from *G. globosa* with a high antimicrobial and antifungal activity. This objective was implemented by the application of the response surface methodology (RSM), a robust optimization technique that allows to study jointly the effects of several variables and responses, namely in extraction procedures (in this case ultrasound assisted extraction (UAE)). To evaluate the antimicrobial and antifungal properties, the responses were the minimum inhibitory (MIC), minimum bactericidal (MBC) and minimum fungicidal (MFC) concentrations. The optimized UAE conditions were: 10.8 min, 410.5 W, 57.8% ethanol content (ethanol-water mixtures were used) and 5 g/L as solid-liquid ratio, providing the following responses: 1) antibacterial activity: MIC of ~0.15-0.35 g/L) and MBC of ~0.30-0.65 g/L; and 2) antifungal activity: MIC of ~0.20-0.30 g/L and MFC of ~0.40-0.65 g/L. In conclusion, the obtained results evidenced the potential application of the extracts from *G. globosa* as sources of betacyanins (natural colorants), but also as important antimicrobial and antifungal agents.

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Novel AZT-Triazoles for HIV Resistant Strains

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The emergence of cross resistant strains towards HIV-1, side effects associated with extended use of drugs and poor bioavailability, as well as high cost of antiretroviral treatment have led to an urgent need for the development of new efficient drugs that are cost-effective with fewer side effects and higher bioavailability.

AZT was the first approved drug for the treatment of HIV¹, and is now a fundamental component to control the replication of the virus. However, its poor bioavailability and extended use cause many side effects such as cardio myopathy and anaemia², in addition to the emergence of resistant strains. Therefore, appropriate modification of AZT can lead to increased efficiency and introduces additional tools to maximize its range of activity. Our group has developed methodologies to introduce triazole groups, which are known to have antiviral activity³, via click chemistry catalysed by ruthenium and copper. This modification involved variation the substituents in the triazole wingtip groups (R^1 and R^2) in terms of steric as polarity. These compounds were characterised by NMR and MS, and were tested for HIV strains. These results will be discussed in this communication.

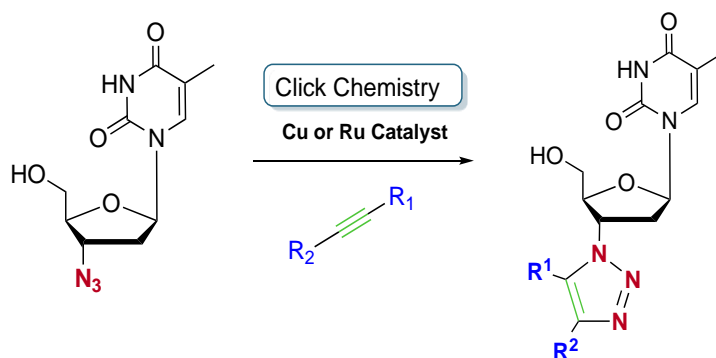


Figure 2. - Reaction of AZT Triazole derivative.

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A comprehensive investigation of tryptanthrin, an alkaloid from indigo and isatin.

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Tryptanthrin (indolo[2,1-b]quinazoline-6,12-dione) is an indoloquinazoline alkaloid isolated from several natural sources, including indigo plants, fruits and mammals (urine of Asian elephant) [1]. Tryptanthrin is also an oxidation product of indigo, displaying antipathogenic, anticancer, antioxidant and anti-inflammatory activity [2]. Due to the increase relevance several synthetic methodologies have been developed for the synthesis Tryptanthrin. These include oxidation of indigo and the cyclization of isatin and isatoic anhydride [1,3].

In this work, the one-pot one-step approach to synthesize tryptanthrin from indigo was developed. The reaction proceeds under microwave irradiation without the presence of a strong oxidizing agent (Figure 1).

Further, the results of a detailed study of the photochemical and photophysical properties, in various solvents, via steady state and time-resolved fluorescence techniques are reported.

A comprehensive electronic spectral and photophysical properties of tryptanthrin was undertaken in solvents of different polarity and further compared with indigo. A significant higher Stokes Shift have been found in polar protic solvents relative to nonprotic solvents. From time-resolved fluorescence and fs-TA absorption, this is further interpreted on the basis of the existence of a charge transfer state.

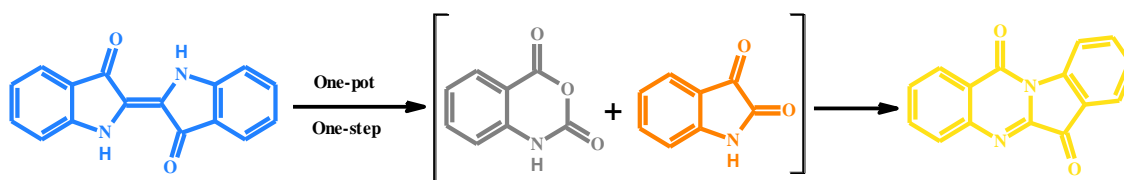


Figure 1. Schematic MW-assisted synthesis of tryptanthrin.

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Impact of preterm birth on newborn urinary metabolic profile: a preliminary study

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Preterm birth (PTB) is defined as birth before 37 gestational weeks. It is the leading cause of neonatal deaths and the second cause of infant death under 5 years (after pneumonia), causing ca. 3.1 million infant deaths per year [1]. Presently, US medical costs associated with PTB infants in year 1 are 10 times greater compared to term infants [2]. In Portugal, a PTB incidence of 5% was reported for 2013 [3]. Metabolomics is defined as the qualitative and quantitative analysis of metabolites present within organism, cell, or tissue [4]. So, it can aid in the detection and possible identification of biomarkers in this condition. The present work aimed to evaluate the impact of PTB on urine metabolic profile of newborns and, concomitantly, establish a metabolic trajectory of PTB newborns until theoretical term time, the first one, to our knowledge.

Newborn urine samples were collected at the Maternity Bissaya Barreto, University Hospital Center of Coimbra (CHUC), with parental informed consents obtained for each infant. Samples were analyzed by Nuclear Magnetic Resonance (NMR) spectroscopy on a Bruker Avance III spectrometer, operating at 500 MHz.

Here, multivariate analysis was applied to the ¹H-NMR urine spectra in order to discriminate preterm (n=36) and term newborns (n=46) in the first days of life. Preterm newborns were also followed over time during internment and a preliminary analysis was made so we could identify putative markers of deviant behaviors indicative of some health complications during that period.

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Silica Glyconanoparticles for Liver Cancer Targeting

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Hepatic cancer was declared the second deadliest cancer worldwide by the world health organization in 2015, and therefore there is a large interest on the development of a platform for targeting.

In this communication we will present the development of glyconanoparticles that may be recognized by the asialoglycoprotein receptor in human hepatocellular carcinomas. To achieve this objective, we develop silica nanoparticles (SiNPs) with diameter under 100 nm coated with a glycopolymer using a “grafting from” methodology by controlled radical polymerization. In addition, incorporation of a highly bright dye in the silica structure will allow a live track of the nanoparticles using optical imaging techniques^[1]. We selected a galactose-based polymer, to target tumorous hepatic cells due to the presence of hepatic asialoglycoprotein receptor, a type C-lectin that binds reversibly and specifically to galactose and *N*-acetylgalactosamine^[2].

Mesoporous nanoparticles (MSNs) with controlled pore structure and small size offer several advantages, including high loading capacity and the ability to protect guest molecules in the systemic circulation, giving the possibility to include stimuli-responsive polymers for theranostic.

This platform will be a promising approach to diagnose various tumors by changing the sugar recognition moiety. In the future we intend to create a copolymer shell of a pH-responsive inner block and a glycopolymer outer block to achieve controlled release with site-specific delivery of drugs.

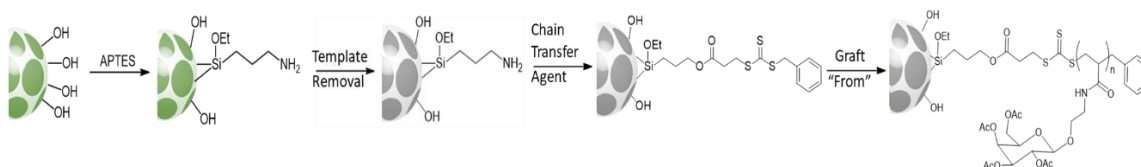


Figure 1. Synthesis of MSNs coated with galactose-based polymer.

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Removal of Methomyl by Adsorption on activated Carbon From Aqueous Solution

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The search of new and less expensive precursors, namely natural or industrial wastes, for the activated carbon (AC) production and its use for the wastewater treatment is an important area in environmental sciences. Methomyl, due to its vast use and solubility in water is a potential contaminant of groundwater

Residues of wood and seed of baobab from Benguela region (Angola), were crushed into fragments up to 3mm before the prewash step with an aqueous solution of 20% in H₂SO₄ by period of 24h. The solution was filtered and the remainder was washed with distilled water and then oven dried at 110 ° C.

The Acs' production was done in a horizontal tubular furnace. The precursors were impregnated with H₃PO₄ and KOH and the activation done at 400 ° C under nitrogen flow. After activation, the samples were cooled to room temperature in an inert atmosphere and then removed from the oven and then washed and oven dried. The carbon material has been removed to remove excess chemical agent and other residual substances such as ash.

The precursors were characterized by thermogravimetric analysis and helium pycnometry. The content of cellulose and lignin was done by Agroleico (Porto Salvo, Portugal), using the Portuguese Standards NP2029 and ME-414, respectively. The Acs' samples were characterized by nitrogen adsorption at 77K, FTIR, CHNS-O elemental analysis and determination of the point of zero charge (pzc).

The adsorption of methomyl from liquid phase was performed at 25 ° C under an acidic medium, pH ~ 3. After the 24-hour contact time, the Acs' suspensions were filtered and a residual pollutant concentration determined by UV / Visible spectrophotometry using a PerkinElmer Lambda 850 spectrophotometer at 233nm [1].

The activated carbon samples show apparent surface area between 167 and 395m²/g, pore volume from 0.17 to 0.65cm³/g and mean pore width around 1.08nm. The adsorption of methomyl, a hazardous and problematic pollutant, from aqueous solutions reached the maximum adsorption capacity of 243mg/g at an equilibrium concentration of 1mg/L [2,3].

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Os autores agradecem à Fundação para a Ciência e a Tecnologia (FCT, Portugal) o financiamento concedido no âmbito do projeto PEst-OE/QUI/UI0619/2014. Tchikuala, E.F., agradece a bolsa de estudo concedida pelo governo da República de Angola; Fundação Calouste Gulbenkian (Doutoral Grant nº146128 "Bolsas de apoio à investigação para estudantes de doutoramento dos PALOP"). Centro de Química de Évora e Departamento de Química da Universidade de Évora.

3D Structures from Cross-linked Nanocellulose

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Regenerative medicine, as an area of modern medicine, can offer life expectancy in serious cases of loss or dysfunction of a tissue or organ. A key element in tissue engineering is the three dimensional (3D) structure of biomaterials that provides structural support for cell attachment, proliferation, and differentiation [1]. These 3D structures should be biocompatible, non-toxic, with good mechanical properties and high enough porosity and interconnected pores to allow cell adhesion, support cell growth and regeneration of the extracellular matrix. For better results, the porosity consisting of both mesopores and macropores, must exceed 80% [2].

In this work, 3D structures were obtained from bacterial cellulose (BC) nanofibers by surface treatment in mild conditions. BC nanofibers were obtained by the mechanical treatment of the biosynthesised membranes [3]. To ensure the stability of the 3D structures, surface treated BC nanofibers were cross-linked. For this purpose, two natural, inexpensive and non-toxic cross-linkers (a phenolic aldehyde and a monosaccharide) were tested. Further, thermal cross-linking combined with freeze-drying technique was used to prepare 3D structures as potential scaffolds for tissue engineering.

The effects of the chemical grafting and cross-linking on the properties of BC 3D structures were investigated by thermogravimetric analysis (TGA), scanning electron microscopy (SEM), Fourier transform infrared spectrum (FT-IR) and dynamic mechanical analysis – compression tests (DMA). SEM images showed clear differences between the 3D structures obtained from surface treated compared to untreated BC. For example, a 3D structure with high porosity and well aligned and interconnected pores was obtained from surface treated and monosaccharide cross-linked BC compared to that containing non-functionalized BC. Differences in the thermal stability and mechanical behavior were induced by the surface functionalization and cross-linking as noticed in the results of the TGA and DMA analyses. The better results obtained after cross-linking were explained by the three dimensional network structures formed via a Maillard reaction in the case of the monosaccharide cross-linker or a Schiff reaction in the case of the phenolic aldehyde.

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This work was supported by two grants of Ministry of Research and Innovation, CNCS–UEFISCDI, project PN-III-P4-ID-PCE-2016-0431, Contract no. 148/2017 (CELL-3D) and project PN-III-P2-2.1-PED-2016-0287 (CELLAB-SLP), Contract no. 122/2017.

Deep Eutectic Solvents as promising electrolytes and electrochromic materials

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Deep Eutectic Solvents (DES) have attracted much attention due to the possibility to use as a greener alternative solvent [1]. They can be prepared by the complexation between suitable hydrogen bond acceptors (HBA) and hydrogen bond donors (HBD).

Reversible electrochromic devices incorporating DES as alternative electrolyte and bipyridinium electrochromic probes ($[(\text{CH}_3)_2\text{bpy}]\text{Cl}_2$ and $[\text{C}_5\text{O}_2]2\text{bpy}]_2$) have been tested and compared to conventional systems [2,3]. Two different configuration cells based on 3-electrode and 2-electrode (figure 1) systems have been tested as electrochromic device (ECD).

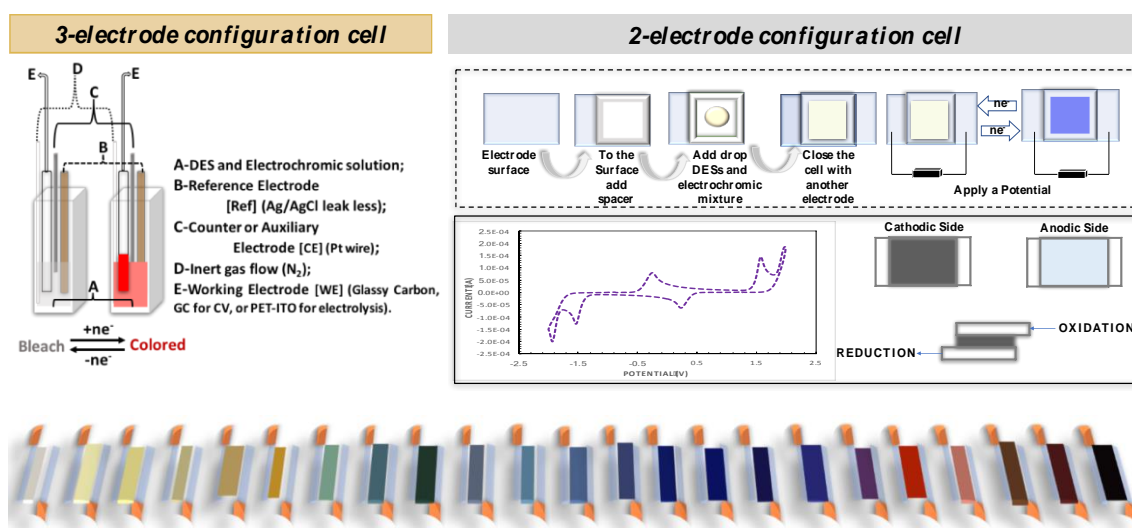


Figure 1. 3- and 2-electrode configuration cells and coloration profile of electrochromic devices.

The most promissory DES based on viologen salt derivatives can act simultaneously as electrolyte and electrochromic. The coloration efficiency and reversibility can be tuned changing only the alcohol counterpart and/or the side chains and anion of the viologen derivatives. DES can be explored as functional and efficient multi-colored ECDs. These innovative materials can open attractive applications for material science and energy devices.

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Synthesis of novel pincer Pd borohydride complex and its alcoholysis

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Herein we present synthesis and experimental (XRD, FTIR, NMR) and theoretical (DFT, NBO, AIM) characterization a novel pincer Pd borohydride $[(C_6H_5)Ru\{2,5-((tBu)_2PCH_2)_2C_5H_3\}]Pd(\eta^1-BH_4)$, which at the excess of proton donors transforms into binuclear Pd borohydride cluster with $\mu, \eta^1: \eta^1-BH_4$ unique type of coordination. Similar products previously were observed at alcoholysis reactions with participation of transition metals (Cu, Ru) tetrahydroborate complexes [1-2].

The non-covalent intra- and intermolecular interactions (e.g. (di)hydrogen bonds) are known to have a great impact on reactivity of boron hydrides in reactions with proton transfer and hydrogen evolution. The first proton transfer reaction, whis is going *via* preliminary dihydrogen-bonded complexes formation is rate-limiting stage of overall alcoholysis process, further acceleration of reaction rate related to increasing hydride donor ability in alcoxyboron hydrides [3].

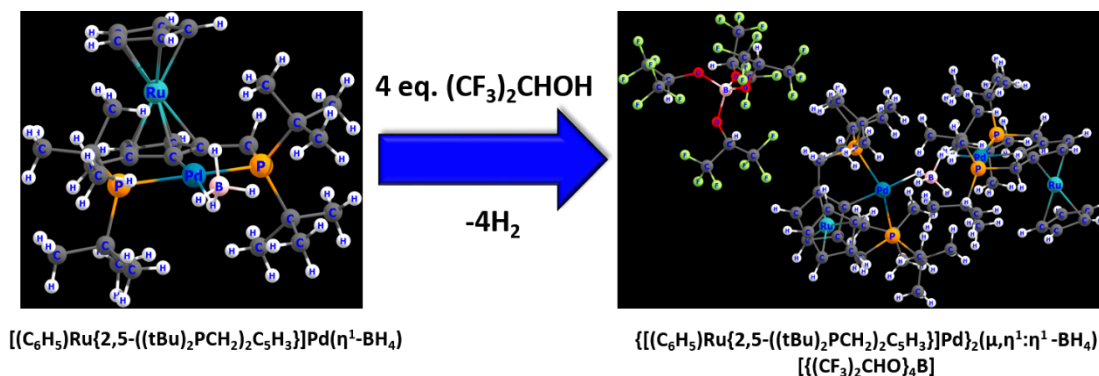


Figure 1. Transformation pincer Pd borohydride under alcoholysis.

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Acknowledgments

This publication was prepared with the support of the "RUDN University Program 5-100" and funded by the Russian Foundation for Basic Research (RFBR) projects 16-03-00324 and 17-03-01128.

Highly soluble salts of adamantylamine anti-Parkinsonian drug

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Approximately 40% of the approved Active Pharmaceutical Ingredients (APIs) face numerous problems, such as poor aqueous solubility, dissolution rate and low bioavailability, that can compromise their effectiveness.[1] Among several strategies, salt formation is considered to be one of the most promising approach as allows improving API physicochemical properties without compromise their biological behaviors.[2] The anti-Parkinsonian drug Adamantylamine (ADA) exhibits a very low aqueous solubility (1.03 mg/mL) and is administrated as an hydrochloride salt.[3] In this form, high concentration levels are attained in the blood, causing some toxic effects in the central nervous system, such as hallucinations and nervousness.[4] Considering this limitation, we report herein the synthesis and characterization of new salts with remarkable improved ADA physicochemical properties (solubility and thermal stability) - Figure 1 shows an example. Structure-property relationships will be also presented and discussed.

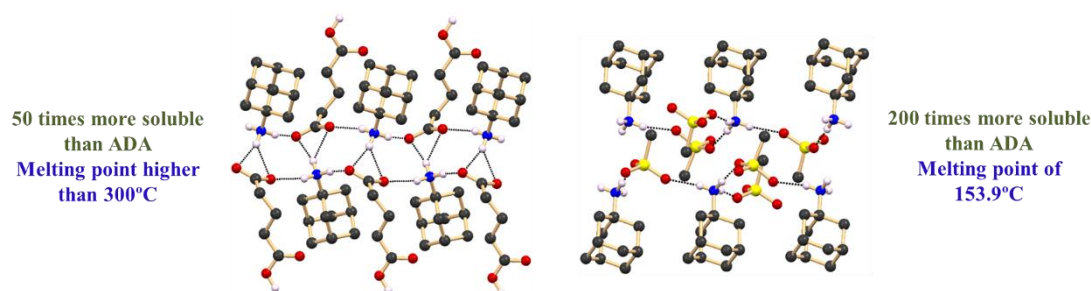


Figure 1. Crystal structure of ADA:glutarate (left) and ADA:mesylate (right) with higher solubility and stability properties.

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The separation of betulinic and oleanolic acids by simulated moving bed chromatography: Experimental and modeling studies

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Betulinic and oleanolic acids are two triterpenoids known to exhibit key pharmacological activities (e.g., antioxidant, anti-inflammatory, hepatoprotective, and anti-tumor) and occur naturally in *Eucalyptus globulus* bark [1]. Their extraction from this biomass residue has been reported in the literature [2] and represents an opportunity to obtain high value products as the price of each compound greatly increases with purity. The challenge, however, arises with their separation since they occur simultaneously in this natural matrix and are isomers. In this way, the simulated moving bed chromatography technique (SMB) is a promising approach for such separations, because its cyclic countercurrent mode of operation enables the isolation of compounds with low chromatographic selectivities, which is the case of isomers and particularly enantiomers [3].

In this work, a SMB unit was designed for the separation of betulinic and oleanolic acids. HPLC pulse experiments revealed that their isolation can be efficiently accomplished with an Apollo C18 column and 50/50 (% v/v) acetonitrile/methanol mixture as mobile phase. Pure equilibrium and mass transport parameters were determined through breakthrough experiments, and then validated with the simulation of a breakthrough assay of a multicomponent mixture. The rigorous phenomenological simulation results showed that the designed SMB unit successfully separates the betulinic and oleanolic acids with purities above 99 wt.% from a representative natural extract of *Eucalyptus globulus* bark.

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Ivo S. Azenha thanks Fundação para a Ciência e a Tecnologia (FCT) for the PhD grant SFRH/BD/126509/2016.

Synthesis of naphthalene/anthracene based chromenes for application to electrochromic devices

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The world of organic electronics is an ever-evolving and developing area with exciting advancements taking place every day. It is believed that these advancements can lead to a future with low-cost, large-scale, low energy, flexible devices which may replace those currently in use. Electrochromic devices are considered by some as an avenue to this future due to their 'optical memory'(1) and low switching potentials.(2) Our work aims to synthesize, characterise, and fabricate electrochromic devices using O-doped polycyclic aromatic hydrocarbons.

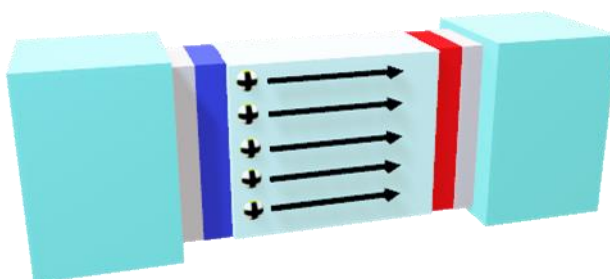


Figure 1. Three-dimensional diagram of a typical ECD used in smart windows. In this case the substrate layer on which the device is built is glass, and both electrodes must be transparent. Similar to that seen in a review from Granqvist et al.(3)

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Acknowledgments

The authors greatly thank Dr Antoine Stopin for his input and help with the project thus far. We also thank the European Project Rise:INFUSION for financial support.

Solar photodegradation of formalin using visible light-active composites

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Formalin (aqueous solution of formaldehyde) is one of the most common disinfectants applied in aquaculture. After its use, it is commonly diluted and released into aquatic environment, without a specific treatment [1]. It does not undergo direct photodegradation [2], whereby its removal from water is sometimes achieved using photocatalysts with UV light. However, UV radiation is harmful for human beings (skin exposure to germicidal wavelengths of UV light causes skin burns) and additionally another potential danger is the UV production of ozone, which can be also harmful to health. Thus, one of the goals of this work was to evaluate the efficiency of two visible light active TiO₂ catalysts (TiO₂-Tetra-phenyl-porphyrin (TPP) and TiO₂-Graphene oxide (GO)) on photocatalytic solar degradation of formaldehyde in water.

Composites were synthesized and their optical properties assessed. Water samples (synthetic and from aquaculture) containing formaldehyde were irradiated under simulated sunlight and analysed by UV-Vis, through a derivatization reaction. The dissolved organic carbon was also determined after the irradiation experiments to evaluate if mineralization occurred.

The photocatalyst TiO₂-GO proved to be more effective in removing formaldehyde from water than TiO₂-TPP, increasing the photo-degradation reaction rate and promoting some mineralization. Although the degradation efficiency using the photocatalysts was lower in aquaculture's water than in synthetic aqueous solutions, the results are promising.

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Gamma radiation induces degradation of phenolic acids

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The aim of this work was to study the degradation by gamma radiation of four phenolic acids (gallic acid, protocatechuic acid, vanillic acid and syringic acid) that are recalcitrant pollutants present in cork wastewaters [1]. The irradiations were carried out at room temperature using a Co-60 experimental equipment, under different pH (natural, 3, 7 and 10) and atmospheres (aerated, N₂O and O₂) for isolated and aqueous mixture phenolic acids' solutions. The applied absorbed doses were 5-20 kGy at a dose rate of 1.5 kGy/h. The degradation of phenolic acids was analyzed by HPLC-DAD and the identification of radiolytic products was carried out by LC-DAD-ESI/MS. The obtained results indicated that the degradation of the compounds was higher in isolated than in the mixture solutions suggesting a protective effect in the quaternary mixture solution. The N₂O saturation promoted the highest degradation rates in the mixture, at natural pH, however in aerated conditions it was achieved degradation efficiencies >50% for a treatment dose of 20 kGy. Concerning the identification of the radiolytic products two different compounds were identified (trihydroxybenzoic acid, [M-H]⁻ at m/z 169, and methyl gallate, [M-H]⁻ at m/z 183) as radiolytic products of the studied phenolic acids (Figure 1).



Figure 1. MS fragmentation spectra of a) 2,3,4-trihydroxybenzoic acid and b) methyl gallate.

The degradation mechanisms of the studied phenolic acids was proposed. The results highlighted that ionizing radiation could be used as clean technology for pollutants degradation using doses of 20 kGy.

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The authors are grateful to the FCT support: C2TN (UID/Multi/04349/2013, RECI/AAG-TEC/0400/2012), CIMO (UID/AGR/00690/2013), L. Barros contract; FEDER-Interreg España-Portugal programme (0377_Iberphenol_6_E).

Children's saliva metabolome in dental caries research

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Background: Nuclear Magnetic Resonance (NMR) metabolomics of saliva, a relevant fluid in oral cavity integrity maintenance, has enabled the identification of oral cancer and periodontal disease biomarkers [1]. Although recognized as a potentially useful tool in caries research, saliva metabolomics has not yet been thoroughly explored in children [2]. **Objectives:** This work describes a ¹H-NMR study of children saliva to probe metabolic changes underlying: 1) dental caries (caries-afflicted [CA], n=15 vs. caries-free [CF], n=23); 2) saliva stimulation pattern (stimulated saliva [SS], n=30 vs. unstimulated saliva [USS], n=38); 3) USS collection methods (passive drool [PD], n=5 vs. SalivaBio's Children's Swab[®], Salimetrics, State College, PA, USA [SCS], n=5) and 4) dentition stage (primary + mixed, n=25 vs. permanent, n=13) and 5) gender (males, n=22 vs. females, n=16). **Methods:** Whole saliva from healthy children (4-16 years old) was collected under standardized conditions. USS samples were obtained through PD and SCS and SS collection involved paraffin-wax chewing. 1D ¹H-NMR spectra were recorded for all samples on a 500 MHz Bruker Avance III spectrometer. **Results:** Multivariate analysis of saliva ¹H-NMR spectra unveiled a separation between CA and CF groups (predictive power of $Q^2=0.39$ for Partial Least Squares-Discriminant Analysis, PLS-DA, model). Differences in the levels of alanine, glutamine, isoleucine, leucine, proline, butyrate, fucose, glucose, choline, dimethylsulfone, methanol, uracil and 5 still unassigned metabolites were found to explain such separation. Whereas PLS-DA showed no differences between SS and USS samples, a clear separation was observed between PD and SCS samples ($Q^2=0.80$). It appears that the SCS device releases a particular compound, still unknown, in large quantities, and also tends to retain other compounds. Regarding dentition stage and gender, no significant differences were found between saliva samples. **Conclusions:** NMR of saliva revealed important metabolic changes associated to dental caries in the saliva metabolome. Distinct profile changes were also detected when SCS was used, in comparison to PD, suggesting that SCS may not be a suitable device for saliva collection in metabolomic studies.

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This project was developed within the scope of the project CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID /CTM /50011/2013), financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. We also acknowledge the Portuguese National NMR Network (RNRMN), supported by FCT funds, and DD acknowledges FCT grant SFRH/BD/119509/2016. JLP is also grateful to Tatiana Carneiro and Rita Silva for aid in NMR analysis of saliva samples.

Hybrid carbon nanostructures aiming at photocatalytic applications

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Heterogeneous photocatalysis is an important process for multiple applications, namely in the field of water purification. [1] This growing interest is rooted in the possibility of employing sunlight to promote the oxidation of organic pollutants dissolved in water via reactions that occur at the surfaces of suspended particulates that act as photocatalysts. [2] The growth of inorganic phases on carbon nanostructures has been an important route to produce such photocatalysts.[3]

We have been particularly interested in developing carbon nanostructures decorated with semiconductor nanophases as photocatalysts for water treatment technologies.[4,5] For example, graphene oxide (GO) can act as an heterogenous substrate for the growth of semiconductor nanocrystals, thus developing visible-light photocatalysts that are relatively inexpensive and environmentally friendly. In this communication, we report a new synthesis for hybrid graphene oxide-based materials that also comprise metal chalcogenide nanophases. This chemical route is extensive to a range of semiconductor compounds, some of them with great potential for the photo-oxidation of organic pollutants present in aqueous solutions. Illustrative examples of this photocatalytic process will be presented and the main challenges that need further research foreseen practical applications will be discussed.

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Fluoresceins with Delayed Fluorescence as probes for Fluorescence Microscopy

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Fluorescein derivatives are reported to have Thermally Activated Delayed Fluorescence (TADF), which can be useful in fluorescence imaging applications and time-resolved fluorescence microscopy, due to their long emission lifetime[1]. To ascertain its viability for these techniques, a fluorescein derivative (figure 1) was characterized towards its photophysical properties, as well as the characteristics of its complexation with relevant proteins. The compound exhibits a high molar absorptivity and good stability in most solvents, similarly to other fluorescein derivatives. The prompt fluorescence quantum yield (Φ_{PF}) was found to be very sensitive to solvent polarity (24% in ethanol and 6% in water). To confirm the formation of a triplet state through intersystem crossing (ISC), studies were made in the absence and presence of O_2 using time-resolved and steady state spectroscopy techniques. The triplet formation quantum yield, determined by laser-flash photolysis, was remarkably high (ca. 0.60) and the lowest triplet state (T_1) was found to be close in energy to the lowest excited singlet state (S_1), with $\Delta E_{ST} = 116.7$ meV, which is low enough to enable an efficient reverse intersystem crossing and the occurrence of TADF. This TADF emission is sensitive to oxygen and medium polarity and rigidity. Interestingly, this compound also showed significant singlet-oxygen enhanced fluorescence. These results indicate that the compound is applicable in confocal FLIM as a possible O_2 probe, studies which are still ongoing.

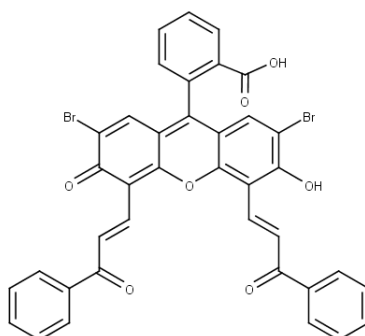


Figure 1. Chemical structure of the fluorescein derivative in study.

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This work was supported by the Associate Laboratory for Green Chemistry- LAQV which is financed by national funds from FCT/MCTES (UID/QUI/50006/2013) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER - 007265).

A new generation of ring-fused chlorins as promising PDT agents

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Photodynamic therapy (PDT) presents several advantages over the classic anticancer therapies, from the high selectivity of photosensitizers to solid tumors, to the generation of cytotoxic reactive oxygen species (ROS) near the target which minimize the side effects usually observed. Here we describe the development of new tetrahydropyrazolo[1,5-a]pyridine fused chlorins that not only show enhanced chemical and structure stability, but also increased hydrophilicity. These characteristics in association with a rich pattern of absorption bands within the phototherapeutic window (600 and 800 nm), which balances deeper penetration of tissues with providing enough energy to excite the oxygen to its singlet state (most effective wavelengths inferior to 800 nm), make these compounds very active photodynamic agents. Synthetic details, structural characterization, and cytotoxicity evaluation of these very promising compounds will be disclosed in this communication.

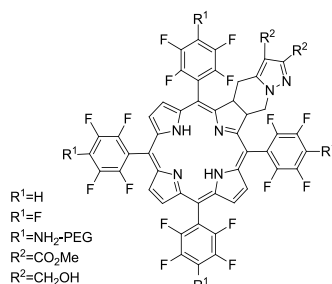


Figure 1. Overview of synthesized photosensitizers.

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This work was funded by Fundação para a Ciência e a Tecnologia (FCT), co-funded by FEDER through COMPETE 2020 within project POCI-01-0145-FEDER-PTDC/QEQ-MED/0262/2014, and through PT 2020/CENTRO 2020 within project CENTRO-01-0145-FEDER-000014/MATIS. The Coimbra Chemistry Centre (CQC) and CNC.IBILI are supported through projects POCI-01-0145-FEDER-007630 and POCI-01-0145-FEDER-007440, respectively.

A recyclable benziodoxole-based reagent: a new group transfer agent immobilized on a soluble polymer support

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The use of hypervalent iodine reagents in organic synthesis is a topic of interest in modern organic chemistry. This iodine based compounds were traditionally used as oxidizing reagents but, in the last decade, its potential as a transfer agent of numerous groups has arose.¹ Nowadays, benziodoxole-based compounds are used not only as oxidizing reagent but also as reagents to transfer trifluoromethyl group, alkynes, among many other functional groups.² In this work, we describe the use of an iodine(III) benziodoxole-based compound as an SO₂-surrogate.

The SO₂ group is present in a wide variety of compounds, from polymers to drugs or pesticides. Unfortunately, most methods to prepare these compounds involve the use of metals, high amounts of additives, hazardous compounds and conditions.³ So, it is of utmost importance to discover cheaper and greener sulfonylation integration methods. In this presentation, the synthetic efforts to create an SO₂R transfer reagent immobilized on a polymer support and its application will be presented.

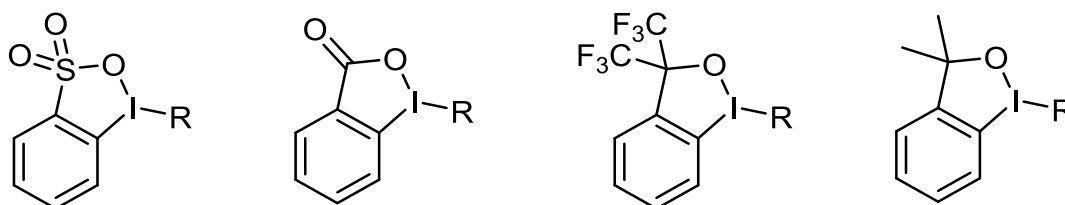


Figure 3. Benziodoxole-based compounds.

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Chemical Modification of Laminarin for Biomedical Applications

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Chemical modification of natural polysaccharides provides a simple and powerful way to increase the development of new biomaterials with different and desired properties such as biocompatibility, biodegradability, biological resistance, flexibility, rigidity, particular physical responses, among others. The use of natural polymers for biomedical applications is attractive because they are economical, readily available and non-cytotoxic. One of the major drawbacks when working with polymers is the lack of control on further chemical modifications [1].

Laminarin, also called laminaran, is a natural polysaccharide and an active component found in many macro-algae. Laminarins are of increasing current interest because some of their derivatives have been shown to have interesting biological activities such as antitumoral, anti-inflammatory and anticoagulant, but the most well-known are antioxidant and antimicrobial activities [2-4].

There are few reported studies with chemical modifications in laminarin structure [5]. Thus, this work will focus on the development of simple and selective chemical methodologies in laminarin polysaccharide that allow the conjugation of this natural polysaccharide with different small molecules. Hydroxyl groups are ubiquitous in polysaccharides structure and are involved in most of the chemical modifications. The most useful functionalities are ester, ether, amide, amine and alkyl groups.

In this communication, we report different chemical modification steps, characterization and properties of different laminarin derivatives. Insertion of allyl, amine, acid carboxylic and dopamine groups will be reported. Derivatives will be characterized by ¹H NMR, UV-Vis and FTIR spectroscopy techniques and the final properties will be discussed.

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Acknowledgments

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Effect of Caffeic Acid Polyacylations in Color Stability of Heavenly Blue Anthocyanin: A thermodynamic and Kinetic study

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Anthocyanins are molecules that confer red and blue hues to most flowers, leaves and fruits, respectively through the flavylum cation, AH^+ , and quinoidal base, A (and/or ionized quinoidal base, A^-).^[1] In common anthocyanins AH^+ is stable only at very low pH values, whereas the blue quinoidal base is stable at slightly acidic media but with a small molar fraction. In order to stabilize the blue colors in anthocyanins, two main strategies have been described: metalloanthocyanins^[2,3] and intermolecular sandwich type staking (ISTS) of polyacylated anthocyanins.^[2,4] The last, based on self-aggregation and co-pigmentation that protect the AH^+ against the water attack and formation of hemiketal (B) and other uncolored species.^[2,5,6] The Heavenly Blue Anthocyanin (HBA1), in the morning glory flower, has the particularity to confer reddish color to the buds and blue color to the petals.^[7] *In vitro*, the blue colors are stable on basified media, but there is not kinetic and thermodynamic information to allow a quantitative explanation to this behavior. Therefore, the equilibrium and rate constants of HBA1 and their derivatives with two (HBA2) and none (HBA3) acylated units, that permit obtain the mole fractions of all the species along the pH scale, were calculated. The ISTS on HBA1 retards 40-fold the hydration reaction (k_h) and increases 100-fold the dehydration (k_{-h}), when compared with HBA3. These results demonstrate that A is thermodynamically more stable than B in HBA1. The energy level of B increases with the number of acylated units, but the inversion of energies between B and A takes place only in HBA1, achieving the stability of A and its deprotonated forms (A^- and A^{2-}).

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Magnetic skyrmion phase in the topological chiral magnet Cu_2OSeO_3

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Topological spin textures are one of the most interesting ordered phases in condensed matter. A representative example of such spin textures is the magnetic skyrmion in chiral magnets - a swirling spin structure carrying a topological quantum number. Skyrmions were observed in Cu_2OSeO_3 [1], a chiral antiferromagnet ($T_N \sim 60$ K) that can be synthesized as single crystals by reacting CuO and SeO_2 in a chemical vapour transport reaction. In nanocrystalline form, it can be produced by oxidation of CuSeO_3 during annealing in air at ~ 400 °C. As skyrmion lattices may find use in nanotechnological devices, such as data storage systems and in other applications [2], the effect on the magnetic properties of size reduction to nanoscale deserves to be investigated. Our studies on the synthesis, structural characterization and low-temperature magnetic properties, featuring the skyrmionic phase, of nanostructured Cu_2OSeO_3 will be presented and discussed.

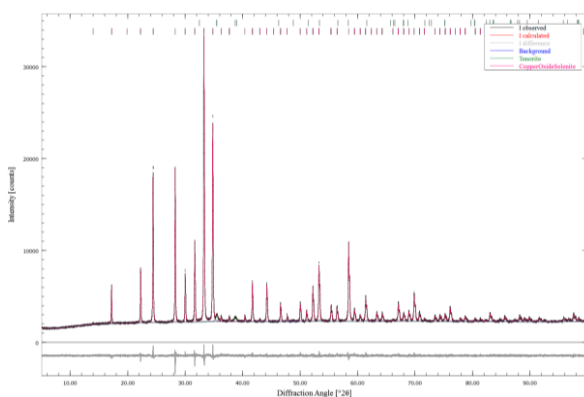


Figure 1. XRD pattern of Cu_2OSeO_3 .

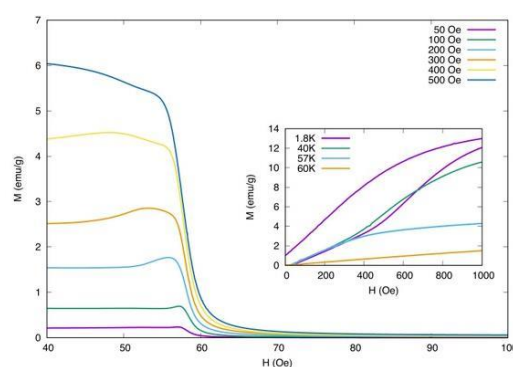


Figure 2. $M(T)$ and $M(H)$ (insert) curves of the synthesized Cu_2OSeO_3 nanostructured polycrystalline compound.

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Oleocanthal Isolated from Olive Oil by Countercurrent Chromatography Reduces Breast Cancer Cell Migration

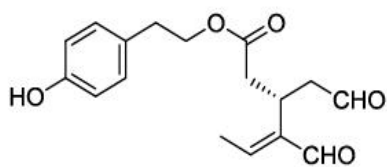
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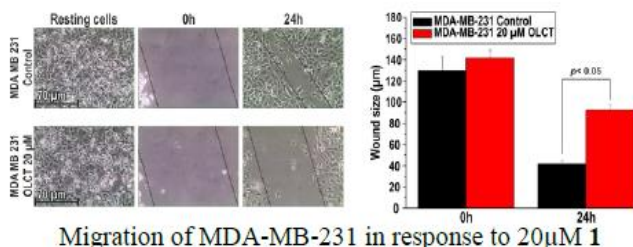
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Extra-virgin olive oil (EVOO) is unique among vegetable oils due to its high level of monounsaturated fatty acids and the presence of active components in the unsaponifiable fraction, such as the phenolic compounds. One of these phenolics is the so-called oleocanthal (OLCT) (**1**), which has received much attention for its potential in the prevention and/or treatment of various diseases [1].

The aim of this collaborative work was to isolate **1** from EVOO by an innovative technique and to investigate its active antitumoral role in breast cancer cells migration. Thus, an olive oil sample was extracted with a mixture of methanol/water. The resulting phenolic extract was subjected to fast centrifugal partition chromatography (FCPC) using a biphasic solvent system composed of hexane, ethyl acetate, ethanol and water. The fractions containing OLCT were re-purified by semipreparative HPLC to give pure **1** (>98%), whose structure was confirmed by NMR and MS [2]. Cells from the triple negative human breast cancer line, MDA-MB-231, were seeded in a 6 well (35 mm) Petri dish and grown to 70-80% confluence. Next, cells were incubated with DMSO (as vehicle) or 20 μ M **1**. After 24 h the wound healing assay was performed [3]. Using a yellow tip, we scratched the monolayer resulting in a wound of \sim 120 μ m. Cells treated with 20 μ M **1** showed a significant impairment of migration, a sign of the possible antitumoral role of **1** in breast cancer cells.



Oleocanthal (**1**)



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Acknowledgments

Authors wish to thank the University of Jaén and MINECO (BFU-74932-C2-1-P) for general financial support.

Application of Proteins for organocatalysis

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Proteins are one of the most important biomacromolecules of living organisms containing large spectra of properties and applications [1]. It is particularly relevant the application of proteins in biochemistry, pharmaceutical and food industries [2, 3]. Many laboratories have explored simple organic molecules, including amino acids (L-proline) and synthetic peptides, as catalysts for asymmetric organocatalytic reactions [4]. Effective peptide-based catalysts possess features that are difficult to achieve with common catalysts, such as high catalytic performances and enantioselectivities. Over the past decade numerous functionalized peptides have been reported as effective asymmetric catalysts for a range of synthetically useful reactions: acylation, oxidation, ester hydrolysis, aldol reactions, among others [5,6]. Despite the molecular diversity of proteins they share the common trait of being only marginally stable. Ionic Liquids (ILs), low-melting organic salts, can stabilize some proteins over a wide range of temperatures and according to the cation and anion structures from IL [7]. Recently, ILs have successfully been reported as efficient solvent media for enzymatic reactions and some specific applications with proteins [8]. C-C bond forming reactions catalyzed by L-proline and peptides upraised, many research groups have been focused on development of more selective catalytic systems derived from natural sources for this functional transformation. In this context, we tested the pancreatic casein hydrolysate as new organocatalysts for the Michael addition between cyclohexanone to trans-nitrostyrene as model reaction. The preliminary studies showed that it is possible to obtain the desired pure Michael product in moderate to high conversions. Further studies using several nitroalkanes in the presence of cyclohexanone or acetone have been performed. The asymmetric version has been also tested and compared with conventional system (L-proline). The use of proteins, in particular casein, seems to be very promising for Michael reaction as well as to extend to other catalytic reactions.

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We thank the Fundação para a Ciência e Tecnologia for financial support (IF/0041/2013/CP1161/CT005); Programa Operacional MAR2020 Ref. 16-02-01-FMP-0042) and Solchemar Company.

Synthesis of a cyclopentenone family and evaluation of their anti-proliferative activity in human cancer cells

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Functionalized cyclopentenones (CP) are an important class of molecules that can be viewed as a highly versatile intermediate for the synthesis of many natural and synthetic biologically active compounds¹. The reason for this biological activity is mostly due to the electrophilic character of the CP ring. The α,β -unsaturated carbonyl group can function as a Michael acceptor resulting in the alkylation of critical biomacromolecules of the cells. This being a plausible mechanism of cytotoxic activity. It has been described the formation of a highly electrophilic intermediary upon 1,4-addition by glutathione acting on a cell detoxification mechanism². Our group have been involved in the preparation of novel CP³ and in this work we have synthesized a library of CP derivatives with lateral substituents in position 2 and position 4 and evaluated their biologic activity on human cancer cells in an attempt to elucidate the structure activity relationship (SAR)⁴.

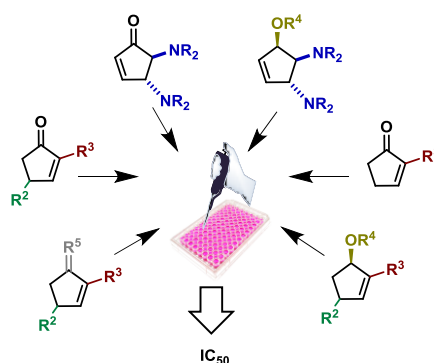


Figure 1. Biological evaluation of cyclopentenones.

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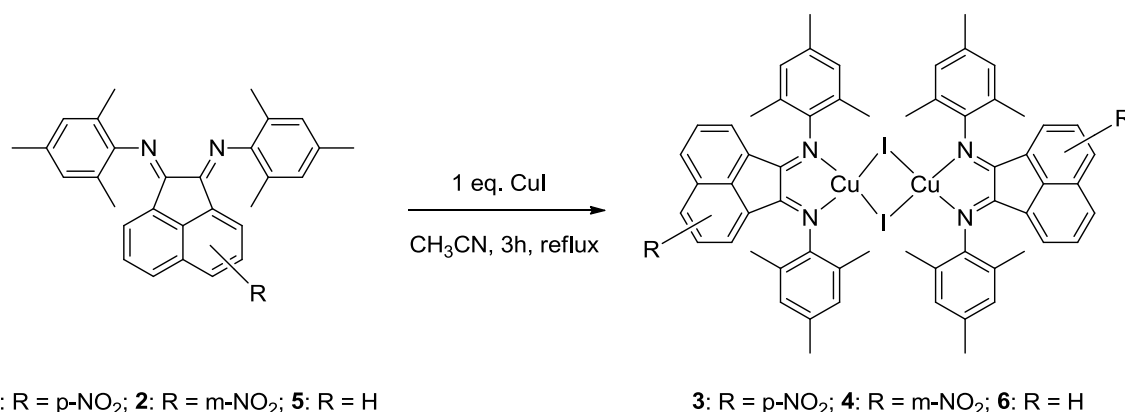
Synthesis, Crystal Structure, And DFT Calculations Of Two New Dinuclear Cu(I) Complexes Bearing Ar-BIAN Ligands Functionalized By NO₂ Group

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Two new bis(aryl-imino)-acenaphthene, Ar-BIAN (Ar = Mes = 2,4,6-trimethylphenyl) ligands, bearing the NO₂ group in the naphthalene moiety at *para* (**1**) and *meta* (**2**) positions, and their respective dinuclear halide bridge Cu(I) complexes [Cu₂(μ-I)₂(Mes-BIAN-p-NO₂)₂] (**3**) and [Cu₂(μ-I)₂(Mes-BIAN-m-NO₂)₂] (**4**) were synthesized. Single X-ray structure of **3** and **4**, as well as the previously reported [Cu₂(μ-I)₂(Mes-BIAN)₂] (**6**) [1], exhibit typical distortion from 109° of a C_{2v} geometry around Cu(I) nuclei due to reduced bite angle N-Cu-N of Ar-BIAN ligands (~80°). This distortion however is more accentuated in **3** and **4** than in **6** owing to the introduction in *meta* and *para* positions of the electron withdrawing NO₂ group which promotes the enhancement of a more red-shifted MLCT studied by UV-Vis spectroscopy and interpreted with the help of TD-DFT calculations.



Scheme 1. Synthetic pathway of complexes **3**, **4** and **6**.

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Acknowledgments

This work was supported by the Associate Laboratory for Green Chemistry-LAQV which is financed by national funds from FCT/MCTES (UID/QUI/50006/2013) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER - 007265). We also thank UID/MULTI/00612/2013 for funding.

Synthesis and characterization of promising theranostic agents for cancer

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We recently developed a new type of photochemically stable platinum (II) chlorins, which are remarkable photosensitizers that can be used in photodynamic therapy (PDT), due to its therapeutic capacity. Simultaneously, due to its highly luminescence proprieties, in the biological relevant 650-850 nm red and near infrared spectral region, they may be used for biological imaging [1,2]. In this communication, the synthesis, photochemical and photophysical characterization of a novel series of compounds with different degrees of hydrophilicity will be disclosed. In addition, their photocytotoxic effect was evaluated against three cell lines, the HT1376 line of bladder carcinoma, the A375 line of melanocytic melanoma and the OE19 line of oesophageal carcinoma, demonstrating potential therapeutic effect as PDT agents. Furthermore, photophysical studies indicate that they may be used as ratiometric oxygen sensors.

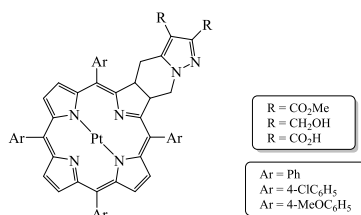


Figure 1. Overview of studied compounds.

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Acknowledgments

This work was funded by *Fundação para a Ciência e a Tecnologia* (FCT), co-funded by FEDER through COMPETE 2020 within project POCI-01-0145-FEDER-PTDC/QEQ-MED/0262/2014, and through PT 2020/CENTRO 2020 within project CENTRO-01-0145-FEDER-000014/MATIS. The Coimbra Chemistry Centre (CQC) and CNC.IBILI are supported through projects POCI-01-0145-FEDER-007630 and POCI-01-0145-FEDER-007440, respectively.

Theoretical Study of an Efficient Hybrid Adsorbent Based on Silica-Supported Amino Penta-Carboxylic Acid for Water Purification

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All-atom molecular dynamics (MD) simulations were performed to gain insight into the molecular-level phenomena governing the recognition of several cations by the chemically modified silica with diethylenetriaminepentaacetic acid (SiDTPA). Three different anchoring configurations were assembled differing in the distance between anchoring sites to a silica surface that had deprotonated silanol groups to simulate a pH of 5. For each cation [Pb(II), Zn(II), Cd(II) and Cu(II)] two MD simulations of 50 ns were performed with each of these systems: one having the cation explicitly placed inside the recognition site and another with the cations in bulk solvent. Bearing in mind that the cations might establish different interactions with both the SiDTPA moiety and silica surface, thermodynamic integration simulations were performed with the purpose of estimating the relative association free energies of M^{2+} to the different configurations of SiDTPA. The obtained results suggest that the structure with the longest distance between anchoring sites is the most favourable configuration for binding Cu(II) cations, because the approach of the carbonyl groups towards the silica surface is more favorable, thus creating a smaller binding pocket that can more easily accommodate smaller cations.

The theoretical results obtained for metal cations removal agree with the experimental analysis that were performed. These studies suggest that the new material could be used as a promising effective, reusable and low-cost adsorbent for an efficient removal of heavy metal cations, namely Cu(II), from aqueous solutions containing competing ions.

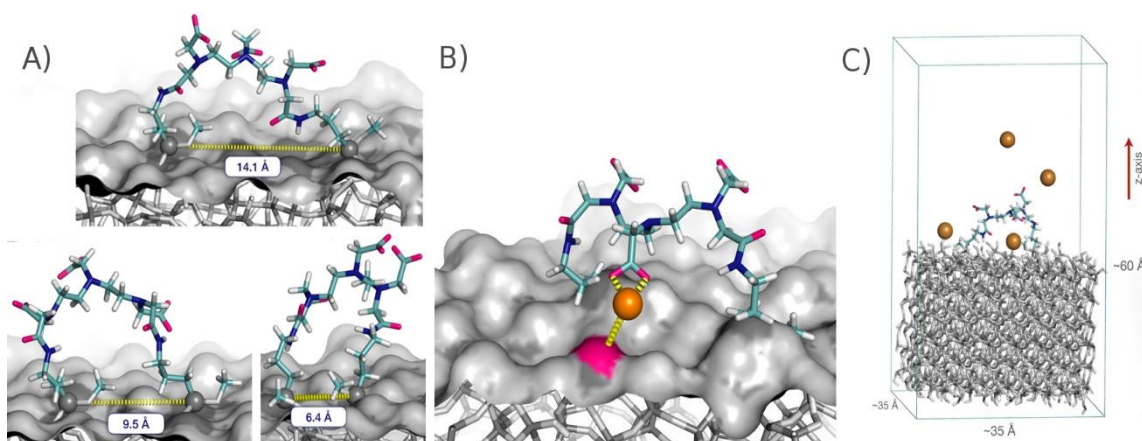


Figure 1. A) Different anchor points of the DTPA moiety into the silica surface; B) Interaction of Cu^{2+} with a single COO^- site of SiDTPA, and the interaction with one Si-O^- group (pink surface patch) of the silica surface; C) General aspect of the SiDTPA simulation box, comprising the silica substrate (grey scale), DTPA (blue/pink), cations (orange).

Theoretical Study of an Efficient Hybrid Adsorbent Based on Silica-Donor/Acceptor Hofmann Clathrates

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Hofmann clathrates are bimetallic three-dimensional (3D) and two-dimensional (2D) coordination frameworks constituted by Fe(II) ions that are coordinated with cyanometallic anions $[M(CN)_x]^{y-}$ (where M = Ni, Pd, Pt, Cu, Ag, Au, Nb) and *N*-donor heterocyclic ligands.[1] These pillared structures are appealing for potential chemical sensing applications since they can adjust their porosity.[2] Hoffman structures are commonly composed of units that make the bond in the crystal tridimensional structure are made by nitrogen atoms included in ligand that do the coordination to the metal centre, this structures have a big application in materials area because of their properties.

Spin crossover (SCO) complexes show magnetic responses to subtle external stimuli, e.g., temperature, light, pressure and guest molecules, involving simultaneously changes in colour, dielectric constant or electrical resistance.[3] These characteristics make them potential candidates for the detection of different organic and inorganic compounds. Hofmann clathrates, a class of metal-organic frameworks (MOFs) and their analogues are among the most known and well-studied for practical applications as SCO compounds. Our strategy on Hofmann clathrates consisted in inserting a photoactive unit (Figure 1) that has both acceptor and donor capabilities promoting the electronic and optic properties of the 3D structure envisaging a material with applications in photocatalysis, solar cells, LEDs and OFETs. Here we present the synthesis and characterization of Hofmann clathrates with thiazole-derived spacers and the magnetic and optical properties are also discussed.

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Acknowledgments

The authors thank FCT for financial support.

Oxazol-5-(4H)-ones-based RIPK1 inhibitors as potential modulators of necroptosis

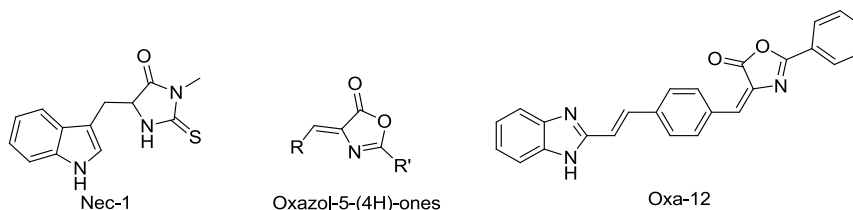
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Necroptosis is a form of caspase-independent form of regulated necrosis that occurs when apoptosis is inhibited. Receptor-interacting protein kinase 1 RIPK1 and RIPK3 mediate necrosome formation and are activated in a variety of pathologies that currently lack effective therapies such as stroke, myocardial infarction, septic shock, and acute pancreatitis. Necrostatin-1 was the first reported necroptosis inhibitor, acting by inhibiting RIPK1 activity. However, it is not only modestly potent, so therapeutically relevant *in vitro* doses may lead to off-target effects, its metabolic stability sub-optimal, resulting in a short *in vivo* half-life.¹

Herein, based on our experience with oxazolones (OXA)² we present the development of new OXA-based RIPK1 inhibitors as potent necroptosis inhibitors (**Scheme 1**)³ where preliminary screening of oxazol-5-(4H)-ones derivatives in cell lines (BV-2 microglia and L929 fibrosarcoma) showed a lead compound with an inhibition activity similar to Nec-1.



Scheme 1. Structures of the necrosis inhibitors Nec-1, general structure of oxazol-5-(4H)-ones and structure of OXA-12.

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Cardoon (*Cynara cardunculus* L.) flowers as sources of phenolic compounds with high biological potential

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Cardoon (*Cynara cardunculus* L.) belongs to Asteraceae Dumortier family and its flower aqueous extracts have been used for centuries as coagulants in the production of traditional ewes' milk cheeses, obtaining specific characteristics of textures and flavour [1]. The use of cardoon flowers (*Cynara* spp.) as a coagulant is obligatory for many Portuguese and Spanish cheeses due to their high content of aspartic proteases and high milk-clotting activity [1,2]. Cardoon flowers from specific genetic resources distributed in *Serra da Estrela* region have been studied and approved for the application as cheese coagulant in order to obtain cheeses with higher quality and confirming the authenticity of cheeses, simultaneously [3], with consequently increase of the bioactive properties of these products. Therefore, it is very important to know the phenolic composition and the bioactive properties of *C. cardunculus*. Three different cardoon genotypes from *Serra da Estrela* region were used to prepare hydromethanolic extracts that were further characterized in terms of phenolic compounds and bioactivities. Genotype, components of the flowers and harvesting time proved to have a great influence in the content of phenolic compounds (the major compounds found were apigenin and caffeoylquinic acid derivatives). For the antioxidant activity, the stigma and the fibrous white inner presented the lowest EC₅₀ values. Regarding antibacterial assays, all the samples presented activity against Gram-positive bacteria, mainly *Listeria monocytogenes*. The presence of phenolic acids and non-anthocyanin flavonoids showed high correlations with antioxidant/antibacterial activities. Besides its proteolytic action for milk clotting process, cardoon inflorescences show the potential to be sources of bioactive compounds in PDO cheeses. To obtain simultaneously proteolytic action, high phenolic content and high biological activity, these results could help defining the best combination of harvesting procedure time of conservation and processing of cardoon flowers.

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Polyoxometalate/graphene nanocomposites for the photocatalytic degradation of water pollutants

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Several water treatment technologies have been developed to address the clean water shortage and to assure water supply for future generations. Among these technologies, those based on photocatalysis have shown great potential as low cost and environmentally friendly processes [1]. In particular, there has been interest to develop new materials that act as catalysts for the photo-oxidation of organic pollutants, namely under solar light irradiation conditions [2].

This research aims to prepare new nanostructured hybrid materials based on polyoxometalate (POM) clusters supported in graphene oxide [3] for the photocatalytic degradation of water pollutants. POMs show multi-advantages for application as photocatalysts, namely their switchability by visible light, the possibility of multi-electronic photo-reduction, followed by reversible electron exchange with a substrate, the possibility of heterogenization without loss of properties and finally their relative low cost [4]. On the other hand, graphene oxide substrates contain oxygen moieties that allows chemical functionalization and have shown interesting properties as adsorbents [5]. Furthermore, we have been interested in exploiting synergetic effects that result from the combination of POMs and graphene oxide envisaging the photocatalytic degradation of water pollutants of pharmaceutical origin. Our preliminary results that result from the above approach will be presented, together with a full characterization of the hybrid nanomaterials before and after have been employed in the photocatalytic experiments.

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Design of thiophene-based polymers for electrochromic applications

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Since the discovery and rationalization of the properties of polyacetylene, semi-conductor polymers emerged as important materials for the design of (opto)electronic devices, including several applications based on their electrochromic properties.[1] The present work presents two different families of conjugated polymers that were synthesized in order to be used in electrochromic devices. One group focus on copolymers with electron-donating and electron-withdrawing units,[2] like the polymer represented in Figure 1. The other group is constituted by homopolymers with a thiophene moiety. The polymers will be compared to check the impact of slight structural changes in their optical and electrical properties.

The polymers were characterized by Nuclear Magnetic Resonance spectroscopy (NMR), Gel Permeation Chromatography (GPC), Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). The polymers were also studied in solution through UV-Vis absorption and photoluminescence spectroscopy. The electrochromic devices were constructed using the polymer as electrochromic layers. So, initially the polymer was deposited by spray-coating in a substrate of Polyethylene Terephthalate/Indium Tin Oxide (PET/ITO), then the electrolyte was added and finally the device was closed. The devices were then analysed through spectroelectrochemistry and chronoamperometry, highlighting the subtle effects of the structural changes in the electrochromic performances.

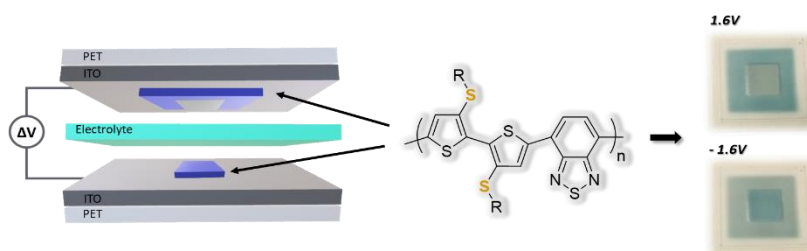


Figure 1. Architecture of electrochromic devices and one device with the copolymer illustrated in the figure (R=2-ethylhexyl).[2]

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Synthesis and studies of new building blocks for rotaxane-based molecular machines

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The idea of nanotechnology emerged in 1959 during a lecture given by Richard Feynman entitled "There's Plenty of Room at the Bottom". Even though this talk went unnoticed at the time, the concept of machines on a molecular scale grew over the following years. It entered pop-culture in 1966 with the movie "Fantastic Voyage" and it reached its apogee in 2016 when Professors Sauvage, Fraser Stoddart and Feringa received the Nobel Prize in Chemistry for their work on "the design and synthesis of molecular machines". There are now examples of complex and functional interlocked structures in the literature. [1]

The purpose of our research is to synthesize modular functional and autonomous molecular machines and to study the shuttling of a macrocycle along the thread of a [2]-rotaxane. So far, we successfully developed a range of electro-active macrocycles along with hydrosoluble stopper-like structures.

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Financial support from ANR (project "PETIMIT").

One-pot reaction: A sustainable and green approach for drug modification

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Polymer drug conjugates are important formulation enhancers. One of the most popular methods, is conjugation with polyethylene glycol (PEG). PEGylation has been demonstrated as highly efficient strategy to extend the half-life of drugs, thus enabling the reduction of the frequency of administration. Yet, long term exposure to PEG can cause immunogenic reactions. In response to this fact, other alternative polymers have been investigated for drug conjugation. Among all, oxazoline-based polymers (POxs) are recognized as the most promising PEG substitutes, in particular, poly(2-methyl-2-oxazoline) and poly(2-ethyl-2-oxazoline) because of their demonstrated low toxicity and immunogenicity [1,2]. Recently, it was reported that oligo-oxazolines synthesized in scCO₂ could be conjugated to improve the performance of drug nanocarriers [3]. The synthesis of POxs occurs efficiently in scCO₂, via living cationic ring-opening polymerization, using boron trifluoride etherate (BF₃.OEt₂) as initiator. Low molecular weight polymers are obtained in high yield and low polydispersity [4]. In this work, fusidic acid (FA) was activated and further conjugated with PEG or POX in a one-pot reaction, following a friendly and clean environmental reaction strategy. The final product was then characterized by NMR, FT-IR, ESI. Additionally, minimum inhibitory concentration assays for three strains of *S. aureus* were performed to investigate the antimicrobial activity of POxylated and PEGylated fusidic acid, comparing to the non-conjugated active chemical entity.

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Light-induced release of bio-relevant cargo from 4-sulfocalix[4]arene in water

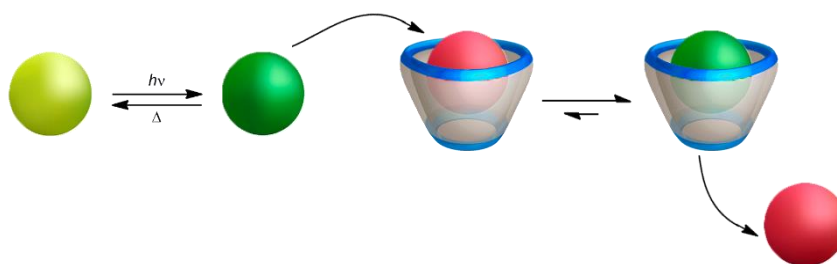
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Calix[*n*]arenes are synthetic hosts with the capacity to recognize molecules with ammonium groups.[1] Such species have great interest as guests for being frequently involved in biological processes.[2] Light as stimulus enables the spatiotemporal release of functional guests from supramolecular assemblies, and thus, recently we have employed a photoswitchable chalcone/flavylium system to control guest delivery from a cucurbituril complex.[3] Herein we expand this approach towards water-soluble complexes of acetylcholine and amino acids (lysine and arginine) with the 4-sulfocalix[4]arene host.

The supramolecular interaction between these bio-relevant guests and the calixarene host[4] was consolidated and the working conditions of the chalcone/flavylium photoswitch were optimized to achieve maximum cargo release. Furthermore, the reversibility of the system in a thermally activated process was demonstrated. The results, based on fluorescence and NMR spectroscopy, will be discussed.



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The work was supported by the Spanish MINECO (CTQ2017-89832-P), ERDF, and the Junta de Andalucía (P12-FQM-2140 and pre-doctoral contract for M.A.R.). The NMR equipment is part of The National NMR Facility, supported by the Portuguese FCT (RECI/BBB-BQB/0230/2012). N.B. acknowledges a postdoctoral grant from FCT/MEC (SFRH/BPD/84805/2012).

Nanobioconjugation of *Toxicodendron vernicifluum* Laccase and Gold Nanoparticles for Enzymatic Activity Enhancement

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The combined use of nanoparticles and enzymes is a resource often used to modulate the enzymatic activity and to incorporate the enzymes in biochemical sensors. [1] This modulation can be focused either in improving the activity or extending the useful range of enzyme activity (e.g. pH). [2] In this work, we produced nanobioconjugates (NBC) using spherical gold nanoparticles (AuNP) capped with a peptide and a plant-derived laccase isolated from *Toxicodendron vernicifluum*, an oxidase with known biotechnological applications. Dynamic light scattering, electrophoretic light scattering, and gel electrophoresis, confirmed the formation of stable NBC, with a log *K* in the range 6.8–8.9. The catalytic activity of these NBC was found to be ca. 9 times higher than the free enzyme. We propose a geometric model revealing that the NBC-adsorbed enzyme is the main contributor for this activity increase. These active NBC were also tested in a pH range around the enzyme optimal pH, and we observed a significant enzymatic activity increase for acidic and close to neutral pH values, a feature that expands the useful pH range of the enzyme. Our results are useful not only for a better understanding of enzyme-AuNP interactions, but also the NBC can be used as building blocks for more complex bionanotechnology systems, namely in electrodes and biocathodes.

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The authors are grateful to Fundação para a Ciência e a Tecnologia (MCTES funds) and European Union (European Social Fund and European Regional Development Fund), for financial support through projects UID/QUI/50006/2013–POCI-01-0145-FEDER-007265 (LAQV), UID/Multi/04378/2013–POCI-01-0145-FEDER-007728 (UCIBIO) and UID/CEC/04516/2013 (NOVA LINCS), in the context of the COMPETE program from QREN, project NORTE-01-0145-FEDER-000011, in the context of the NORTE 2020 program, and fellowships SFRH/BD/95983/2013 (MPdA), SFRH/BPD/84018/2012 (PQ), SFRH/BPD/103788/2014 (SS) and SFRH/BPD/63850/2009 (IG), in the context of the POCH program, both from Portugal 2020 partnership agreement.

Flow assisted synthesis of possible bioactive carbocycles from pyridinium salts

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The discovery of potent biological properties of aminocyclopentitols and the promise that such effects might be exploited as an advantage in medicine have encouraged their synthesis [1]. An attractive approach for the synthesis of these compounds is the photochemical transformation of pyridinium salts to bicyclic-aziridines followed by aziridine ring-opening to afford aminocyclopentene derivatives [2]. However, the reported productivity for this photoreaction under batch conditions is low 0.003 - 1.33 gL⁻¹h⁻¹ and 0.01- 0.36 gL⁻¹h⁻¹, using water and methanol as nucleophile/solvent, respectively, which constrains the subsequent synthetic pathways [2]. To overcome this productivity problem, we developed three home-made continuous-flow reactors, a fluorinated ethylene propylene tube (FEP) reactor (internal diameter of 0.4 cm) and two parallel quartz reactors containing two different internal diameters (0.4 and 0.2 cm). Herein is reported the synthesis of bicyclic vinyl aziridines by photochemical transformation of pyridinium salts under continuous-flow conditions, followed by nucleophilic ring-opening usually under physiological conditions (Figure 1), with a variety of nucleophiles such as azides and thiols (aryl and alkyl, mercaptomethyl tetrazole as well as cysteine), resulting in aminocyclopentitols with potential biological activity.

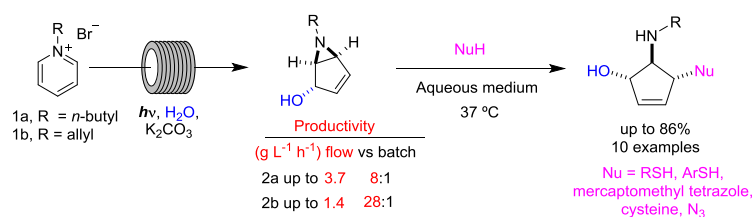


Figure 1. Flow assisted photochemical transformations of pyridinium salts to bicyclic vinyl aziridines, followed by nucleophilic ring-opening reaction usually under physiological conditions.

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Adsorption and Release Kinetics of Polyelectrolyte Microcapsules doped with Porphyrins: A Fluorescence Study

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Polyelectrolyte microcapsules (PECs) are engineered colloids usually obtained by Layer-by-Layer (LbL) methodologies. They have been employed in various field such as pharmacy, food industry, agriculture and medicine due to their controllable size, composition, porosity, stability and easy surface functionalization [1]. In this study, PECs made of poly(styrenesulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) were obtained using conventional LbL. These systems were doped with a 5,10,15,20-tetrakis-(4-sulfonatophenyl) porphyrin (TSPP, negatively charged) or 5,10,15,20-tetrakis-(N-methyl-4-pyridinium-yl) porphyrin (TMPyP, positively charged). The adsorption and release profiles were followed using spectroscopy (UV-Vis, Steady-state and Time-resolved fluorescence) and microscopy (FLIM) in controlled environments that mimics different parts of the human body (gastric and intestinal conditions). The experimental data were fitted accordingly to zero-order, Ritger-Peppas, Higuchi and Peppas-Sahlin mathematical models. (PAH/PSS)₂PAH PECs with a CaCO₃ core showed the best release efficiency (60%, five hours) in gastric conditions. All the experimental details will be presented and fully discussed.

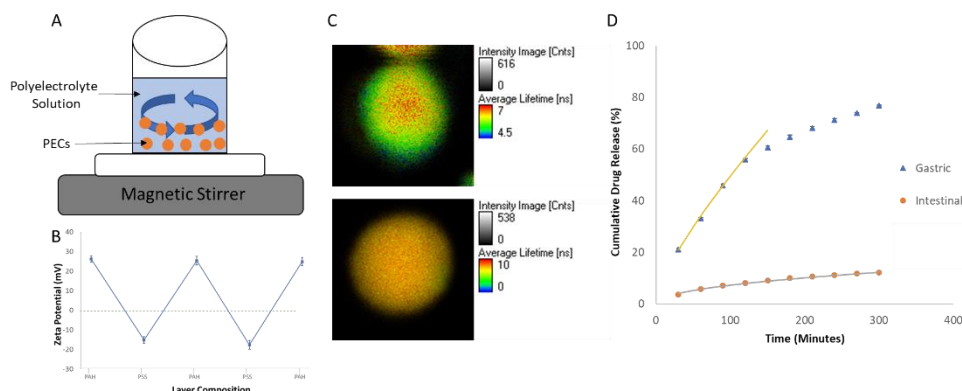


Figure 1. A) PECs preparation; B) Zeta-potential; C) Fluorescence Lifetime Image of TSPP (Top) and TMPyP (Bottom) doped PECs; D) Cumulative Drug Release (%) of TMPyP doped PECs in gastric and intestinal conditions.

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The authors gratefully acknowledge financial support from FCT through Projects REEQ/115/QUI/2005 and Pest-OE/QUI/UI0100/2013/2014. V.V.S. acknowledges postdoctoral grant SFRH/BPD/7420/2010.

This abstract was deleted due to absence of presenting author(s).

Synthesis and *in vitro* antileishmanial activity of selected tetraoxanes against *Leishmania donovani*

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Leishmaniasis, one of the most neglected tropical diseases in terms of drug development, is caused by protozoan parasites belonging to the genus *Leishmania*, transmitted via the bite of plebotomine sand flies. It remains a serious disease in tropical and subtropical areas of the world.¹

Currently, the available drugs for treatment of leishmaniasis (e.g. paromomycin, liposomal amphotericin B and miltefosine) are expensive, show toxicity to the host and low efficacy, mainly due to increasing selection of resistance.² Thus, there is a urgent need to develop effective, safe and affordable antileishmanial drugs.

Earlier studies on the biological activity of synthetic trioxolanes against promastigote forms of *Leishmania infantum* indicated that endoperoxides could provide new leads for anti-leishmanial therapy.³ We then evaluated the activity of a representative library of new synthetic 1,2,4,5-tetraoxanes, easily obtained by synthesis, against intramacrophage amastigote forms of *Leishmania donovani*, demonstrating the potential of the tetraoxane pharmacophore for antileishmanial chemotherapy. The tetraoxanes tested exhibited similar IC₅₀ values to miltefosine, while showing much lower toxicity. Our results also indicated that the nature of the substituents linked to the endoperoxide moiety has a relatively modest effect on activity. From the library selected, we selected 3 tetraoxanes as the most promising candidates.

Our results provide a relevant starting point for the development of tetraoxanes as effective, safe and cheap drugs against Leishmaniasis.

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The authors gratefully acknowledge Fundação para a Ciência e a Tecnologia (FCT), and FEDER/COMPETE 2020-UE, through projects UID/Multi/ 04326/2013 (Centre of Marine Sciences - CCMAR) and PTDC/MAR-BIO/4132/2014. Patrícia Amado thanks FCT for financial support through grant SFRH/BD/130407/2017.

Hybrid materials functionalised by gamma irradiation for the conservation of Roman mosaics

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Radiation processing techniques are based on the physical interaction of radiation with matter, being the first capable of promoting specific chemical reactions. Particularly, gamma irradiation, a clean and environmental-friendly technology — no need for solvents, initiators, high temperatures nor final purifying operations, since the process is almost absent of chemical residues besides water vapour — has been successfully applied over the years in the preparation and the modification of macromolecular materials [1].

This project intends to prepare and functionalize PDMS based hybrid materials with biocide activity by gamma irradiation techniques [2]. The main goal is to produce a material, which can work simultaneously as consolidant and as biodeterioration preventer, and that can be used as an additive to existing composite materials used in Roman mosaics conservation or in a standalone presentation. The final product should conjugate several important properties such as transparency, flexibility, robustness, water-repellence, anti-reflexive properties and resistance to environmental factors.

By adjusting experimental conditions like reactants' concentration, irradiation method and atmosphere, dose rate and samples' absorbed dose, etc., it is possible to functionalise polymeric based materials, therefore tailoring its properties and making them suitable to different applications. This functionalisation occurs mainly through polymerization, scission, crosslinking and grafting reactions [1, 3]. A dedicated method of preparation/functionalisation of hybrid materials, with PDMS as the principal precursor, has been under optimisation, leading to a new group of very stable materials, foreseeing good compatibility with native supports such as stone or binding mortars and biostatic/biocide activity against potential microbial deterioration agents of cultural heritage.

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Supramolecular Assemblies Based on Diarylethenes Derivatives

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The design and construction of functional systems from self-assembly and molecular recognition processes are recognized as topics of current interest that can lead to new classes of materials, devices, and technologies, such as self-healing, shape-memory, among others.[1] Contrary to conventional synthetic strategies, where the formation and rupture of covalent bonds often occur under kinetic control, the supramolecular approach is based on thermodynamically controlled noncovalent interactions and dynamic covalent bonds.[1] Systems under thermodynamic equilibrium, such as supramolecular polymers, are highly reversible by their nature, since their components are continuously interconverting.[2] In this work, supramolecular assemblies based on host-guest interactions in aqueous media using diarylethene derivatives as light-responsive units and cucurbit[n]urils as host macrocycles were developed and characterized by different techniques. Large assemblies of supramolecular polymers were detected using ESI-MS, UV-Vis and NMR spectroscopy.

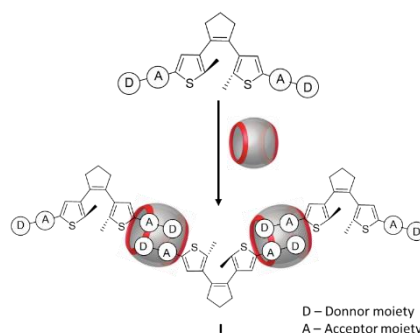


Figure 1. Scheme of Supramolecular Polymerization, using Diarylethene derivatives and cucurbit[n]urils.

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Acknowledgments

This work has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 734834 INFUSION.

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Magnetic studies on symmetric and asymmetric binuclear hydrazide metal complexes

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In the last few years, the need to produce smaller information devices increased and has attracted a large number of research groups from across Europe to tackle this need. Their effort led to the production of materials that store information at the molecular level with increased capacity. A promising phenomenon for information storage is spin crossover (SCO). SCO candidate compounds can be found among a limited group of $3d^4$ – $3d^7$ transition metal ions, the most common being Fe(II), Fe(III) and Co(II). Fe(III), with its advantageous redox stability, is a good candidate for fabrication of SCO materials, an area towards which research has been moving. [1]

Among the ligands known to have the right ligand field strength to promote SCO, hydrazide derivatives are a class of versatile candidates. These compounds are easy to synthesise and have the option of ligand derivatization, thus allowing to fine-tune the SCO properties.

Here we report the synthesis and characterization of both symmetric and asymmetric hydrazides ligands with different halogen substituents on the phenolate ring. These ligands were reacted with Fe(III) and Co(II) to form binuclear complexes with different aromatic environments. The magnetic profiles of the new compounds were determined by Mössbauer spectroscopy and SQUID magnetometry and the ligand effect studied.

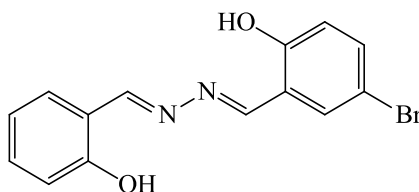


Figure 1. Molecular structure for an example of the ligands.

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Acknowledgments

The authors thank Fundação para a Ciência e Tecnologia for financial support.

Gels for cleaning artworks: An NMR approach

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Ionic liquids (IL) have been proposed for several applications from CO₂ capture to catalysis and electrochemistry.[1] Recently these fascinating materials have also been suggested for the cleaning of artworks.[2] In this field, the methodologies should simultaneously be non-toxic, environmentally friendly and easy to apply.[3] Many of the contaminants are phenol and polyphenol derivatives.[4] Agar gels are a practical solution already in use, however the molecular details of the cleaning process are still undisclosed.

Herein we present our latest results towards the development of improved agarose-IL gels for cleaning of paper artworks. Our approach relies on a nuclear magnetic resonance (NMR) protocol that screens molecular interactions in the presence of phenol-like model compounds. The results obtained initially in IL solutions, are later on validated against agarose-IL gels. Diffusion NMR studies in combination with Nuclear Overhauser Effect experiments allow us to identify preferential sites of interaction as well as to characterize the strength and nature of the molecular interactions.

The NMR results provided crucial data to understand the molecular behavior of agarose gels and further improve the efficacy of the cleaning methodology. This work delivers valuable insights for the development of gel materials to be used in cleaning of artworks.

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New polymer for wine protein removal

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With increased growing-season temperatures in some countries, grapes have the potential to reach maturity quicker. Riper grapes have also higher quantities of unstable proteins¹. This emphasizes the need for a deeper knowledge of the mechanism responsible for white wine protein haze formation and the development of new methods to its remediation. Recently, an update to the protein haze mechanism was proposed. This was based on the identification of sulfur dioxide as a major modulating factor inducing wine thaumatins aggregation upon heating².

Since lowering the sulfur dioxide concentration to values where it does not interact with proteins is industrially challenging (due to its antiseptic and antioxidant properties), removing the heat unstable proteins by fining with bentonite is still the most practical option to avoid protein haze formation in white wines. To surpass the several drawbacks of bentonite fining, we developed a polymer that acts as a processing aid which can remove heat-unstable proteins from white wines. The polymer was tested in a buffer solution for the removal of cytochrome C and isolated wine protein from model wine solution (pH 3.2, 12% ethanol, 5 g/L tartaric acid) with satisfactory results. Performing isothermal protein adsorption assays it was registered a maximum adsorption capacity of the polymer of 345 ± 15 mg protein/g polymer after 24 hr at 25 °C for isolated wine proteins.

Synthesis scale-up with the aim of testing the polymer in real winery conditions and assess its performance in industrial scale are currently being developed.

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Water soluble acridones for Redox Flow Batteries

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Acridone (**1**) is known to be highly fluorescent with more than 50% of the quant loss made through the radiative channel [1] and an emission (color) that is sensitive to its environment, which are both desirable attributes relevant to designing media-sensitive chromophores for biolabeling purposes. In fact, acridone derivatives have been used as fluorescent markers [2] and colorimetric sensors[3].

In our effort to obtain new electrolytes presenting long-term stability for Redox-Flow Batteries we synthesized chlorosulfonated and sulfonated acridone (**2**) together with their *N*-alkylated (methyl (**3**), pentyl (**4**)) derivatives, Figure 1, and study of their spectroscopic, photophysical and electrochemical properties in solution at different pH and at RT. The study includes absorption and emission spectra together with quantitative measurements of the deactivation of the first excited singlet state, from which the rate constants for all the decay processes has been obtained. The results of our studies and mechanism of disulfonated acridone oxidation will be discussed.

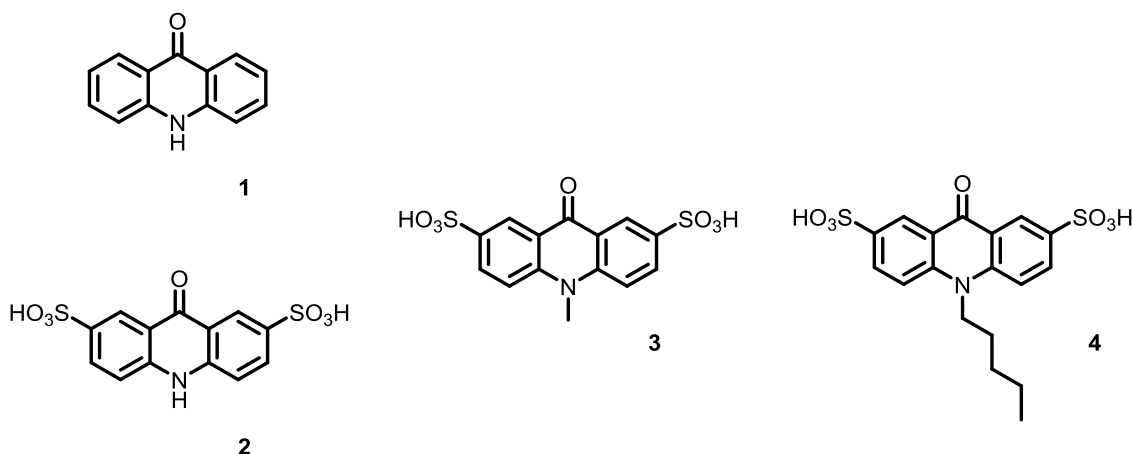


Figure 1

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Catalyst-dependent Selectivity in Sulfonium Ylide Cycloisomerisation Reactions

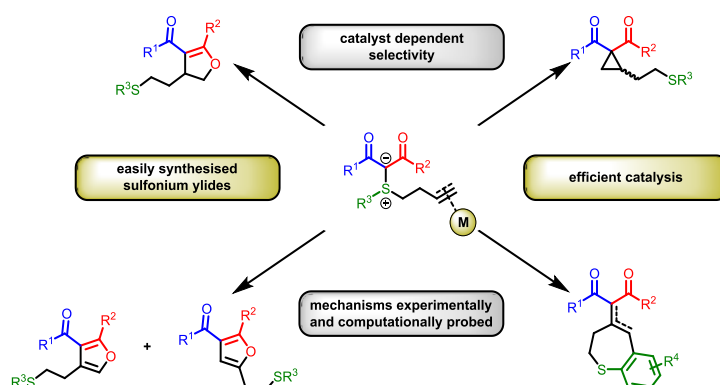
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Sulfonium ylides have long occupied a privileged position in organic synthesis due to their use as synthetic reagents in such ubiquitous reactions as the Stevens rearrangement and the Corey-Chaykovsky reaction.[1] In recent years, the application of stabilised sulfonium ylides has been expanded to previously unreactive substrates though transition-metal-mediated activation.[2] Prior work in the Maulide group focussed on the synthesis of cyclopropanes[3] and furans[4], through Au-catalysed cyclisation reactions of allyl ester- and propargyl ester-substituted sulfonium ylides respectively.

Herein, we present an unusual case of catalyst-dependent selectivity in cycloisomerisation reactions of unsaturated, sulfur-tethered sulfonium ylides. Mechanisms for each transformation have been proposed, with support from computational calculations and mechanistic experiments.



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Caged amino acids for controlled release of bioactive compounds with light

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The use of conditional trigger signals (temperature, pH, pressure, etc.) presents advantages such as temporal and spatial control over molecules, which is especially interesting for controlling drug release events. Light is an ideal external trigger signal, given the multitude of light sources available to exert that trigger. To make a light-responsive active compound it is usual to use the introduction of a photoremovable protecting group that makes it inactive until light action (caging). [1]

Macrocycles are one of the major known systems for carrying and releasing active compounds, mainly due to their increased solubility, bioavailability and stability. [2] The cucurbit[n]uril family is currently used for this purpose. These synthetic receptors are particularly attractive owing to their high affinity towards positively charged amphiphilic molecules which are the main characteristics of many drugs. [3] Furthermore, the high binding affinities for these macrocycles can surpass the bench-mark high affinity binding pair in nature: biotin-avidin. [4]

The objective of the present work is to develop a series of caged amino acids (due to their biocompatibility) for the selective release of relevant active compounds from cucurbit[n]uril capsules. These can be used as a “proof-of-concept” for development of new drug release systems based on light triggers.

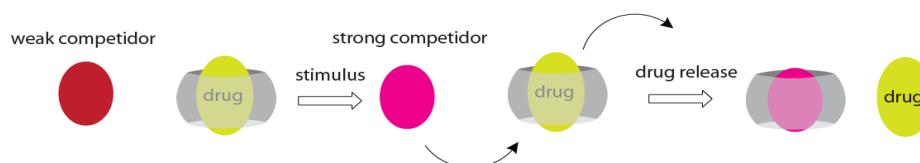


Figure 1. Drug release from a molecular capsule by specific external stimulus.

Techniques such as absorption UV-Vis, Fluorescence, NMR and ITC were used to characterize the caged amino acids and to follow the displacement event from irradiated samples. Thus far, caged tyrosine appears to hold the most promising results.

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Fibre membranes with deep eutectic solvents and enzymes for CO₂ solubilisation and transformation

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In this work, a three-dimensional material able to solubilize atmospheric CO₂, will be developed. The material will be a fibre membrane, produced via electrospinning, composed of poly(vinyl alcohol) (PVA). The membrane will additionally encapsulate deep eutectic solvent (DES), which will allow the CO₂ solubilisation and its capture and/or transformation [1]. The enzyme carbonic anhydrase will also be added to this material, to achieve the transformation from CO₂ to bicarbonate.

DES composed of choline chloride (ChCl), ethyleneglycol and urea in different molar ratios- ChCl:uea (1:2) and ChCl:ethyleneglycol (1:8)- were prepared as previously described[2]. A PVA solution of 9 wt% was prepared with the 0.5 and 2 wt% of DES. The electrospinning parameters such as temperature, humidity, distance and pumping rate were optimized. When carbonic anhydrase was added, its activity in DES was assessed through a pH assay and a colorimetric assay [3].

It was possible to obtain fibre membranes without defects, and to observe that the presence of DES alters fibre viscosity and mechanical performance. Enzyme activity is altered in the presence of DES, although not compromised. Solubility studies of CO₂ in the DES and in the fibres containing DES are promising, and will be compared to the ones obtained with traditional technologies.

This work joins sustainable and greener materials and technologies that can further be used to reduce CO₂ emissions, as well as the use of CO₂ as a valuable starting material.

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Acknowledgments

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New anthracene based 1,3-diamine structures

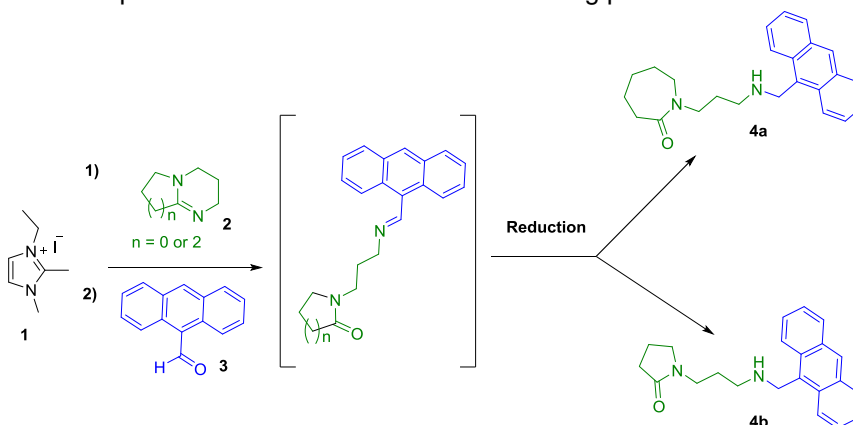
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The 1,3-diamines core is found in many natural products and pharmaceuticals. In particular, chiral 1,3-diamines are substructures of natural products and biologically active compound such as marine batzelladines alkaloids and the bromopyrrole alkaloid manzacidin A [1].

We have previously observed that 1,2-dimethyl-3-ethylimidazolium iodide (1) catalysis the reaction of DBU or DBN and an aldehyde, resulting in the ring opening of the superbase to a caprolactam-based 1,3-diamine structure that can be further reduced to 1,3-diamines [2]. Since polycyclic aromatic ring are able to intercalate between the DNA bases as is the case of the anticancer agents Doxorubicin and Daunomycin [3] we here present new anthracene based 1,3-diamine structures (**4a** and **4b**) from reaction of DBU and DBN with the aldehyde (**3**) (Scheme 1). Evaluation of compounds **4** as DNA intercalators are being pursuit.



Scheme 1

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Irradiation and storage time effects on chemical parameters of *Agaricus bisporus* Portobello

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Mushrooms are one of the most perishable products and tend to lose quality right after harvest. The short shelf-life of mushrooms (1-3 days at room temperature) is an impediment to the distribution and marketing of the fresh product. Treatment by irradiation emerges as a possible conservation technique that has been tested successfully in several food products and increases the extractability of some bioactive compounds [1,2]. The present work reports the effects of gamma radiation and storage period (0, 4 and 8 days) on the chemical composition of one the most widely cultivated mushrooms, *Agaricus bisporus* Portobello; specifically, free sugars, ergosterol and organic acids. The irradiations were performed in an experimental ⁶⁰Co equipment at the doses of 1, 2 and 5 kGy and a dose rate of 1.4 kGy/h. Free sugars and ergosterol were determined using high performance liquid chromatography coupled to a refraction index and UV detector, respectively, while organic acids were determined using ultrafast liquid chromatography coupled to a diode array detector. The results shown that storage period had a higher effect on all the evaluated parameters than the tested radiation doses. It was possible to observe preservation of the fructose, mannitol and trehalose contents in the irradiated samples, along storage time. A higher ergosterol level was found by applying the doses of 1 kGy. All the applied doses also preserved the total organic acids (oxalic, quinic and malic acids) in relation to the control sample. These results indicated the potential of using gamma rays in order to increase the extraction of specific compounds also suggesting to be a feasible alternative process to ensure the quality and prolong the shelf life of mushrooms, since the effects on the tested parameters were less significant than that caused by the storage time.

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Nanomaterials based on polyoxomolybdate as sustainable catalysts for oxidative desulfurization of fuels

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There is a strong global environmental concern regarding the issue of emission of greenhouses gases, namely the hazardous emission of sulfur oxides that has led to the implementation of strict regulations limiting the sulfur content in fuels. These restrictions have motivated the development of sustainable methods as complements to the hydrodesulfurization (currently in use in refineries), which is efficient in removing an important series of sulfur compounds but not effective for benzothiophene derivatives. Oxidative desulfurization (ODS) arises as one of the most promising technology that can remove this type of compounds under mild operation conditions, without the need of hydrogen and using green oxidants. [1]. In this work, new sustainable heterogeneous catalysts based on polyoxomolybdate and ionic liquids (POMs-ILs) supported on mesoporous silica nanoparticles (MSNs-POM-ILs) have been prepared (Figure 1). Their analogous homogeneous compounds (POM-ILs) were also prepared for comparison. All materials were full characterized by several techniques. The new materials were tested as heterogeneous catalysts in ODS process of a multicomponent model diesel and their desulfurization performance was compared with the homogeneous catalysts. Their reusability and stability were also studied for consecutive catalytic cycles.

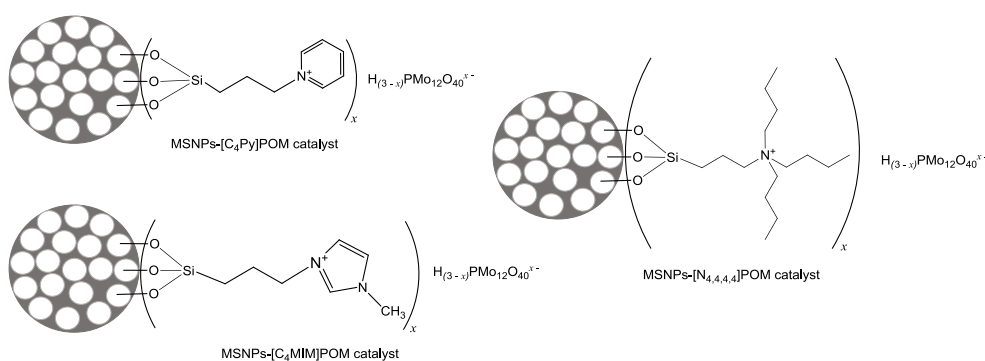


Figure 1. Heterogeneous Catalysts MSNs-POM-ILs (ILs = pyridinium, methylimidazolium, ammonium; POM = $[H_xPMo_{12}O_{40}]^x$).

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Metal-doped hybrid siliceous materials prepared by a sol-gel method

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Considering the numerous concerns regarding the extensive use of synthetic polymers, biopolymers have earned special attention due to their biocompatibility and biodegradability properties, low-cost and high availability from renewable sources. Among the forms of use, biopolymer–silica hybrids have drawn attention as promising materials owing to their unique properties and potential applications in distinct fields. These materials benefit from the flexibility and reactivity of polymer functional groups and the structural robustness and chemical inertness of the inorganic moiety [1]. Due to the reactive groups along the polymer chains, metal ions can easily interact with biopolymers [2]. Hence metal-doped hybrid siliceous materials with innovative optical, electrochemical and magnetic properties might be expected, owing to metal ions incorporation.

Herein, we report a non-emulsion method for preparing metal-doped biopolymer–silica hybrid particles. The biopolymer was firstly treated with an alkoxy silane that contains isocyanate groups. Then, the resulting compound was mixed with a silica precursor in the presence of aqueous solutions of selected metal transition ions and the mixture underwent hydrolysis and condensation under alcoholic basic conditions to yield spheroidal hybrid particles via a sol-gel method. The resulting materials were extensively characterized using electron microscopy (Figure 1), solid state NMR, thermogravimetric analysis, FTIR spectroscopy and elemental analysis. EDX analysis indicated that metal ions are homogeneously distributed along the hybrid material. We anticipate that the materials described here will have impact on the application of metal-doped biohybrids, namely in heterogeneous catalysis.

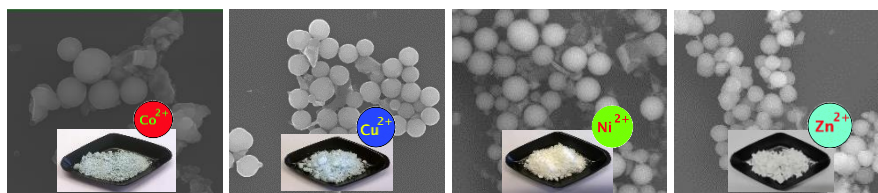


Figure 1. Scanning electron microscopy (SEM) images of metal-doped hybrid siliceous materials.

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Sustainable Separation Platforms based on Aqueous Biphasic Systems formed by Ionic Liquid and Carbohydrates

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Ionic-liquid-based aqueous biphasic systems (IL-based ABS) represent an appealing alternative to the current separation and purification processes, in which an exponential increase of research has been observed in the past years [1]. In this field, imidazolium-based ILs and inorganic salts have been largely considered as phase-forming components. Nevertheless, these systems display some biodegradability and toxicity concerns, boosting the research on ILs derived from natural sources. These bio-based alternatives are especially promising when considered for the purification of biologically active compounds with interest to the food and pharmaceutical industries [2]. Aiming at establishing effective and sustainable separation processes, in this work, carbohydrates were combined with tetralkylphosphonium-based and tetralkylammonium-based ILs, including glycine-betaine analogues, to form ABS. To evaluate their ability to form two-phase systems and infer its applicability, the systems were tested for the separation of antioxidants (vanillic, syringic and gallic acids), at different temperatures and pH conditions. The novel systems developed are sustainable competitive separation platforms when compared to ABS formed by less biocompatible ILs and salts. Finally, it was shown that these systems can be efficiently recovered and reused.

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Metabolic profiling of pancreatitis and KRAS-induced pancreatic cancer in a mouse model

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Pancreatic cancer (PC) is the fourth leading cause of cancer death. The prognosis for individuals with PC has evolved slowly in the past decades due to limited progress in methods for early diagnosis and therapy. PC is genetically heterogeneous and mutated KRAS is known to be one of the drivers of the disease [1]. Transgenic KRAS mouse models have, therefore, been used to investigate the disease development. In this context, metabolomics can contribute to the identification of metabolic deviations associated with this type of cancer. This work aimed at characterizing the metabolic changes in mouse pancreatic tissue due to the benign condition of pancreatitis and PC progression in KRAS-mice, from low-grade to high-grade PC, using ¹H-Nuclear Magnetic Resonance (NMR)-based metabolomics. Pancreatic extracts were obtained from healthy wild-type (WT, C57BL/6) mice (controls, n=7), WT mice with pancreatitis, induced by caerulein injections (n=6), LSL-Kras^{G12D/+}-p48^{Cre/+} mice with PanIN lesions (low-grade, n=5, and high-grade, n=7) and LSL-Kras^{G12D/+};LSL-Tpr53^{R172H/+};Pdx-1-Cre mice with spontaneous PC (adenocarcinoma, n=6, and sarcomatoid, n=9) [1]. Pancreatitis induced a pancreatic metabolite profile that was distinct from both normal tissue and low-grade PC, with changed levels in some amino acids, organic acids and nucleotides. In addition, progression of pancreatic carcinogenesis was characterized by decreased levels of glutamine, 2-phosphoglycerate, phosphocholine, phosphoethanolamine, glycerophosphocholine and UDP-glucose or -glucuronate, and increased levels of 3-HBA, ascorbate, lactate, niacinamide, glucose and sucrose. No significant metabolic differences were observed between the two adenocarcinoma and sarcomatoid tumors. Given the considerable heterogeneity of pancreatic tissue, normalization of metabolite levels by cell number enabled the determination of metabolic deviations from those simply due to differences in cell numbers/distribution in pancreatic tissue. In conclusion, metabolomics may be useful to help define metabolic biomarkers of pancreatitis and of PC onset and progression.

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A linear trinuclear oxidodiperoxido-molybdenum(VI) complex with single triazole bridges

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Triazoles (1,2,3-triazole and 1,2,4-triazole) are especially interesting since they combine the coordinative abilities of both pyrazoles and imidazoles.[1] They are effective ligands for bridging Mo^{VI} centers that are also linked by μ -O²⁻ groups.[2] We have been studying triazolylmolybdenum(VI) oxide hybrids as (pre)catalysts for the oxidation of olefins (epoxidation), sulfides, alcohols, and aldehydes.[3-5] The use of 1,2,4-triazole leads to [MoO₃(trz)_{0.5}] consisting of layers of corner-sharing {MoO₅N} octahedra with the organic subunits projecting into the interlamellar regions.[2, 3] The compound displayed a truly unique reaction-induced self-separating (RISS) catalytic behavior when used with aqueous H₂O₂ as oxidant.[3] It reacts with the oxidant to form a soluble active species and exhaustion of the oxidant leads to spontaneous reassembly of the 2D structure of [MoO₃(trz)_{0.5}]. Finally the compound precipitates, allowing straightforward recovery and reuse. This was, to our knowledge, the first report of a self-precipitating catalyst with an extended 1D, 2D or 3D crystalline structure. To better understand the behavior of [MoO₃(trz)_{0.5}] as a RISS catalyst, it was necessary to ascertain the nature of the active species formed in solution. To this end we have studied the reaction of MoO₃ with H₂O₂ in the presence of 1,2,4-triazole, and after isolation obtained the trinuclear oxidoperoxido complex (Htrz)₂[Mo₃O₆(O₂)₄(trz)₂].H₂O. The trinuclear species is the first example of a discrete Mo^{VI} complex bearing 1,2,4-triazole ligands, and a rare case of a discrete metal-triazole complex that contains only single [M–(N–N)–M] bridges. The compound was explored in olefin epoxidation with hydroperoxides, epoxide alcoholysis, and aldehyde acetalization.

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Silica-based hybrid nanoparticles for high performance coatings

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The use of hybrid nanoparticles is a very promising approach for coating applications, encompassing in a single vehicle the properties of the nanofillers (e.g., silica nanoparticles) and of the polymer. [1] Here we describe the development of materials for tunable photonic wide-angle color displays based on water-borne hybrid nanoparticle. The inorganic/organic material prepared shall provide the mechanical strength from monodisperse silica nanoparticles and flexibility, transparency and hydrophobicity from the polymer shell. [2] The polymer chain-ends will be decorated with groups that react reversibly in aqueous dispersions of the nanoparticles (dynamic covalent chemistry), allowing error-correction during self-assembling, but crosslink the nanoparticles in the dried film.

The silica nanoparticles were prepared by adaptation of the Stober method [3] and characterized by dynamic light scattering (DLS) and transmission electron microscopy (TEM), confirming diameters of 253 nm with a low polydispersity. The surface modified with amine-alkoxysilane and latter modified by addition of the chain transfer agent (CTA) allowing the controlled polymerization of BMA by reversible addition-fragmentation chain transfer (RAFT). [4] The surface modification was quantified by ¹H NMR and UV spectra and the presence of a polymer shell was confirmed by zeta potential.

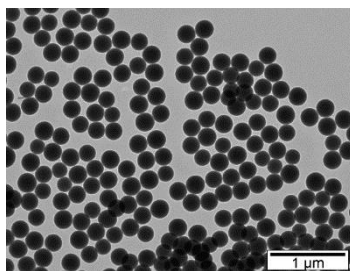


Figure 1. TEM images of nanoparticles with ca. 253 nm of diameter.

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This work was partially supported by Fundação para a Ciência e a Tecnologia (FCT-Portugal) and COMPETE (FEDER), projects SFRH/BD/132486/2017, UID/NAN/50024/2013 and PTDC/CTM-POL/3698/2014.

Novel enantiopure tryptophan-derived oxazoloisoindolinones: from synthesis to *in vitro* stability profile studies of promising anticancer small molecules

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The tumor suppressor p53 has been studied deeply in the last 40 years. It is a key protein expressed in all types of human cancers, that is involved in the identification and regulation of oncogenic events in cancer cells. p53 is generally inactivated by its transcriptional targets, MDM2 and MDMX or by genetic mutation. Considering the importance of p53 in cancer therapy, reactivation of this protein represents a promising anticancer strategy¹. Recently, two tryptophan-derived oxazoloisoindolinones SLMP53-1² and DIMP53-1³ emerged as reactivators of wild-type and mutant-type p53 from a screening of a chemical library of tryptophan derivatives. In this communication, we will present our optimization efforts on SLMP53-1, as well as the stability studies with these promising anticancer small molecules in microsomes, plasma and PBS. A detailed identification of the Phase I metabolites will be also given.



Figure 1. Enantiopure tryptophan-derived oxazoloisoindolinones.

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This work was supported by FCT (Fundação para a Ciência e a Tecnologia) through iMed.U LISBOA (UID/DTP/04138/2013), fellowship PD/BI/135334/2017 (V. Barcherini), SFRH/BD/117931/2016 (Margarida Espadinha), grant IF/00732/2013 (M.M.M. Santos), grant IF/01091/2013 (A.M.M. Antunes) and also by the European Union and National Funds under the project PTDC/DTP-FTO/1981/2014-POCI-01-0145-FEDER-01658.

Synthesis of (Triazolyl)methyl Amide-linked Pseudodisaccharide Nucleosides as Potential Inhibitors of Glycosyltransferases

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Glycosyltransferases are enzymes responsible for the glycosylation of biomolecules such as oligosaccharides, proteins and lipids, leading to the formation of glycans and other glycoconjugates. The later molecules are involved in several important biological processes, such as cell adhesion and signalling. Aberrant glycosylation patterns in glycoproteins and other glycoforms is considered a hallmark of cancer. [1] Therefore, inhibition of glycosyltransferases is a potential therapeutic strategy for anticancer. [2]

In this work, analogues of sugar diphosphate nucleosides, which are natural substrates of glycosyltransferases, comprising a (triazolyl)methyl amide moiety as a neutral and potential enzymatical/hydrolytical stable bioisostere of the diphosphate moiety, were synthesized. [3] The synthetic strategy for their access was based on a convergent approach involving the synthesis of N-propargyl glucuronamide-containing nucleosides and azido sugar precursors and their further coupling through a “click” azide-alkyne 1,3-dipolar cycloaddition reaction. [3] Variations on the regiochemistry of the N-glycosidic bond (N9- or N7-linked nucleosides) as well as on nucleoside ring system A (i.e. furanose and pyranose motifs) were made (Figure 1).

In this communication, the synthetic work will be disclosed and discussed.

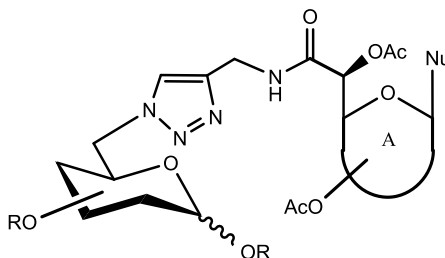


Figure 1. General structure of the synthesized compounds.

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NMR study of [Bmim][BF₄]-water mixtures

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Ionic liquids (ILs) have wide range of applicability as a solvent for inorganic and organic synthesis, catalysts, electrolytes for batteries and supercapacitors, membrane fuels cells, drug delivery, gas capture and storage and many other which arise all days [1]. The presence of water in ionic liquids is very common due to the remaining of the synthetic route or its hygroscopic character. The mixtures of water/ionic liquids may reveal different and useful physicochemical properties [2].

In this work, 1-butyl-3-methylimidazolium tetrafluoroborate/water mixtures were analysed over the whole water composition (x_w) in order to study the rotational and translational behaviour of the ions. We employed a multinuclear NMR approach to determine anion/cation/water diffusion coefficients and longitudinal relaxation rates at different water content.

In neat IL, the cation diffuses faster than the anion, and at low x_w , anions and cations share almost the same diffusion coefficient, but above a critical water concentration, the anion begins to diffuse faster than the cation. We identified this composition as approximately 10% x_w where the ions share the same diffusion coefficient. We found that the water at this composition seems to have a much more dramatic effect in the rotational diffusion of the anion that decreases substantially and approaches that of the anion in the diluted IL [3].

Translational and rotational dynamics of the ions suggest that water is first incorporated in pockets in the nanostructure of the IL allowing the ions to maintain most of the cation/anion interactions present in neat IL but already disrupting some anion/cation interactions due to preferential interaction with the anion. HOESY and NOESY data show that water displays contacts both with the cation and the anion in a positive NOE regime in contrary to the negative regime found for the cation/anion and cation/cation cross-relaxation. This is in accordance with the high relative diffusion coefficient of water and suggests that water molecules can exchange between preferential location sites that allow water to maintain contacts both with the anion and cation [3].

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Acknowledgments

This work has been supported by CNPq-Brazil through grant 201863/2014-6 (W. Silva). The NMR spectrometers are part of the National NMR Network (PTNMR) and are partially supported by Infrastructure Project No 022161 (co-financed by FEDER through COMPETE 2020, POCI and PORL and FCT through PIDDAC).

Antimicrobial Ionic Liquids: synthesis and anti-bacterial activities

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Ionic Liquids (ILs) containing active pharmaceutical ingredients (IL-APIs) recently proved as good drug delivery tool for active pharmaceutical ingredients and drug modulations [1-3]. Our group already described the suitable combination of pharmaceutical drugs and counter-ions as innovative approach to improve the original bioavailability, avoiding polymorphism as well as effective therapeutic behavior [1,2]. Herein, the synthesis of some antimicrobial IL-APIs containing chemically labile antimicrobial compounds such as ampicillin, amoxicillin, penicillin and amphotericin B and its physical-chemical characterization is described [1]. Also, an antimicrobial activity studies is discussed in details by comparison to original pharmaceutical drugs.

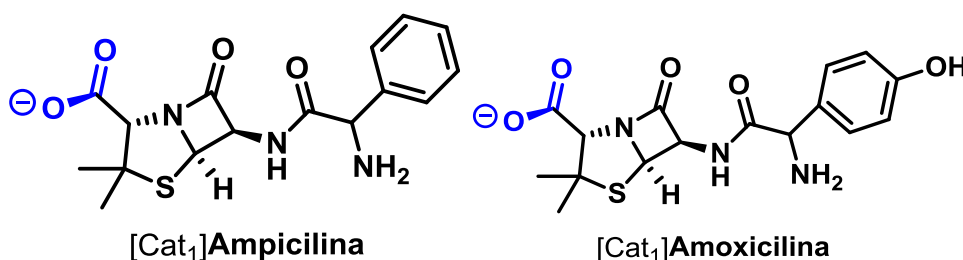


Figure 1. Structure of Ampicilin and Amoxicilin based Ionic Liquids.

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Acknowledgments:

The authors thank the FCT funding and LAQV facilities. L. C. Branco thanks one contract under Investigador FCT and Z. Petrovski thanks to FCT for grant funding SFRH/BPD/111262/2015.

N-Heterocyclic carbenes derived from 7-methylguanosine

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7-methylguanosine is a purine nucleoside derivative known to be a relevant component of mRNA involved transcription [1]. The methyl group at N-7 induces a higher acidity for the C-H bond of the imidazole ring and becomes, from an organometallic perspective, an N-heterocyclic carbene (NHC) precursor. This lability was reported by Tomasz [2] more than forty-five years ago and has allowed for the use of 7-methylguanine nucleosides as biomarkers. Our research group has recently developed methodologies for synthesis of NHCs derived from 7-methylguanosine stabilized by transition metals. The synthesis involves an oxidative addition of a C-H bond to a platinum (0) precursor, yielding a stable NHC platinum hydride. The isolation of such compound contrasts with previous reports from Cavell and McGuinness [3] for imidazolium salts, in which NHC formation is observed only marginally. To shed the light on the mechanistic pathway for this reaction, we have studied the C-H oxidative addition to platinum (0) precursors. Thus, we have examined the formation of NHCs derived from caffeine, guanine and benzimidazole, and evaluated their stability by 1H NMR. The results of our work will be reported in this communication.

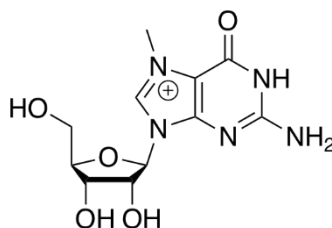


Figure 1. Structure of 7-methylguanosine.

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Acknowledgments

I would like to thank the Erasmus+ programme for the scholarship during my stay at ITQB-NOVA.

Catalytic valorization of lignocellulosic biomass

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The selective conversion of lignocellulosic biomass is of great industrial importance in order to contribute to the replacement of fossil fuels and the sustainable production of high added value products [1]. On the other hand, the conversion of cellulose is extremely difficult due to its strong crystalline structure. In this work, ball-milling of cellulose has shown to be an efficient and sustainable pretreatment method (unlike the usual use of acids) capable of considerably reducing its crystallinity degree and, therefore, facilitating its conversion [2]. Different metal catalysts supported on various carbon materials were then efficiently synthesized for the direct conversion of cellulose and hemicelluloses (xylan) by hydrolytic hydrogenation. The best catalytic system enabled reaching sorbitol and xylitol yields close to 80 % [3]. These results are among the best ever obtained for cellulose and xylan catalytic conversion by an environmentally friendly process for the production of those compounds of high practical interest. Sorbitol and xylitol are two of the most important sugar alcohols, both being on the TOP-12 of high added-value products that can be obtained from biomass [4, 5]. In addition, considerable yields of sorbitol (50 %) were also attained from the direct conversion of cellulosic materials that are generally considered as residues (e.g. cotton and paper). The methodology used is innovative and very promising because it allows the intensification of the process, reducing costs, minimizing waste generated and energy expenditure and maximizing productivity.

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Acknowledgments

This work is a result of project "AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020", with the reference NORTE-01-0145-FEDER-000006, supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF) and of Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by ERDF through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia. L.S. Ribeiro acknowledges her supervisors Dr. Manuel Fernando R. Pereira and Dr. José J. Melo Órfão, and her Ph.D. scholarship (SFRH/BD/86580/2012) from FCT.

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