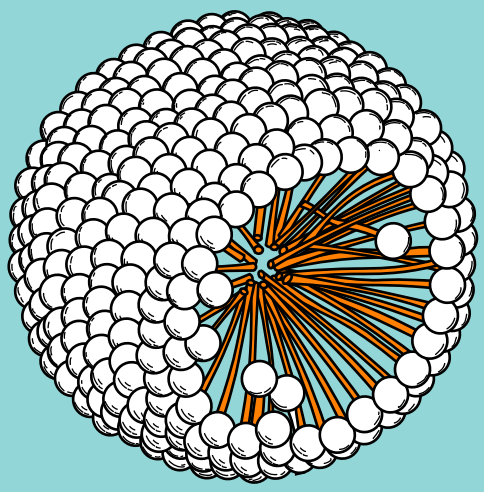
VIII Iberian Meeting on Colloids and Interfaces



Book of Abstracts

RICI8

17-19 July, 2019
Universidade de Aveiro

8ª Reunião Ibérica de Colóides e Interfaces
8ª Reunión Ibérica de Coloides e Interfases

Edited by Ana L. Daniel-da-Silva, Tito Trindade; Cover by Francisco Trindade

VIII Iberian Meeting on Colloids and Interfaces

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Bem-vindos

Bienvenidos

Welcome

2019 IYPT

http://rici8.eventos.chemistry.pt

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Welcome message

On behalf of the Scientific Committee and Organizing Committee, I warmly welcome you to the 8th Iberian Meeting on Colloids and Interfaces. RICI (Reunión Ibérica de Coloides e Interfases/Reunião Ibérica de Colóides e Interfaces) is a joint meeting promoted by the *Grupo Especializado de Coloides e Interfases* (GECI) of the Real Sociedad Española de Química (RSEQ) and the Real Sociedad Española de Física (RSEF), and the *Grupo de Colóides, Polímeros e Interfaces* of the Sociedade Portuguesa de Química (SPQ). This meeting aims to bring together the Spanish and Portuguese communities sharing interests in topics related to the Science of Colloids and Interfaces, by promoting scientific discussion and fostering cooperation at an international level. Thus, researchers from all parts of the world are welcome to contribute and to benefit from this joint event.

The eighth edition of RICI takes place in Aveiro, a city often designated by the Portuguese Venice, located in a region with a unique natural beauty shaped by *Ria de Aveiro*. This region hosts the University of Aveiro, which was founded 46 years ago and is currently one of the most dynamic universities in Portugal, belonging to the leading European consortium of innovative universities (ECIU). We are confident that this environment will also contribute for deep scientific discussion, making justice to the high-quality contributions that form the basis of the program for this conference. It is a good sign of scientific vitality of this meeting to see that many of those communications are here presented by young scientists. The scientific program includes topics that not only approach the main aspects of the Science of Colloids and Interfaces but also cross interdisciplinary areas such as advanced materials, nanoscience, energy and environmental technologies, colloidal biotechnology, medical and pharmaceutical applications, among others. In some extent, this thematic diversity also mirrors the Periodic Table of the Elements, as an essential tool to explain the diversity of matter from their basic constituents. As such, RICI8 joins the large community of citizens that are celebrating worldwide 2019 as the International Year of the Periodic Table.

It is a great pleasure to have with us reputed scientists as speakers and we thank them for their scientific contributions. Also we appreciate the contribution of the sponsors and the institutions that support this Iberian meeting. I would like to personally thank all the people involved in the implementation of RICI8, namely my colleagues of the Scientific Committee and the Organizing Committee, for all their efforts and enthusiasm.
I wish you all an enjoyable and fruitful RICI8!

Tito Trindade
RICI8 Chairman

PROGRAM

HOUR	17 July	18 July	19 July
9:00	**REGISTRATION**	**Ana Luísa Daniel-da-Silva (U. Aveiro)**: *Surface engineering of nanomaterials for water treatment*	**Maria del Puerto de Morales (IMSMadrid)**: *Design Strategies for Shape-Controlled Magnetic Iron Oxide Nanoparticles*
10:00		**Carla Vitorino (U. Coimbra)**: *Lipid nanoparticles in drug delivery: what have we learned so far?*	**Marlene Lúcio (U. Minho)**: *Colloids and interfaces studies as an approach to disease*
10:30	**OPENING SESSION**	**Alba Vázquez Arias (U. Vigo)**: *Up-converting nanoparticles as light sources for cellular activity modulation*	**Francisco Galisteo-González (U. Granada)**: *Natural triterpenoids as nanocarriers: using a drug to vehiculize another*
		Bruno Filipe Medronho (U. Algarve): *New Insights on Cellulose Gelation in Aqueous Alkali*	**José Gonçalves (IST-U. Lisboa)**: *pH-Activated Hybrid Mesoporous Nanoparticles for Controlled Release*
10:45		**Carlos Fernández Lodeiro (U. Vigo)**: *A Seeded Growth Methodology based on Iron (II) for the Synthesis of Noble Metal Nanoparticles.*	**Maria João Faria (U. Minho)**: *Liposomal hydrogels as vaginal microbicides for HIV prophylaxis*
		Rafael Muñoz-Espí (U. València): *Thermal Energy Storage in Polymer-Based Micro- and Nanocapsules*	**Verónica Morgado Serrano (ISEPorto)**: *Molecularly-imprinted histamine electrochemical sensor*
11:00	**Regine v. Klitzing (TU Darmstadt)**: *Ordering of hydrophilic and hydrophobized silica nanoparticles in thin liquid films*	**COFFEE BREAK+POSTER SESSION**	**COFFEE BREAK+POSTER SESSION**
12:00	**Ricardo Fernandes (U. Porto)**: *Debundling and colloidal stabilization of carbon nanotubes by amphiphiles*	**Ana Espinosa (IMDEA Nanociencia-Madrid)**: *Multifunctional approaches based on magnetic and photothermal nanomaterials for cancer treatment*	**Juan de Vicente (U. Granada)**: *On the mechanical behavior of directed self-assembled magnetic colloids*
12:30	**Filipe Coelho (INL)**: *Pathway-dependent effects on the formation of bioreducible polycation-DNA polyplexes in saline media*	**Ricardo Lourenço Gaspar (INL)**: *Fluorescence Cross-Correlation Spectroscopy as a Valuable Tool to Monitor Cationic Liposome-DNA Nanoparticle Assembly*	**Elisa Lenzi (CIC biomaGUNE)**: *Bioimaging of tessellated scaffold with SERS Tags*
	Fernan Berride (U. Vigo): *Disodium Cromoglycate and Guanidine: Towards unravelling the mysteries of a reversible colour change*	**Sergio Rodal Cedeira (U. Vigo)**: *Plasmonic nanocapsules as SERS tags for multiplex detection*	**Gabriela Martins (ISEPorto)**: *Biomimetic electrochemical sensor integrated in flexible polymeric devices for cancer diagnosis*
12:45	**Bárbara Abreu (U. Porto)**: *Surfactant/polymer mixtures for non-covalent functionalization of multiwalled carbon nanotubes*	**José Paulo Farinha (IST-U. Lisboa)**: *Structural color pigments based in colloidal assemblies*	**Sara Fateixa Caria (U. Aveiro)**: *Metal loaded filter membranes for extraction and SERS detection of pesticides in aqueous solutions*
	Ana Patrícia Moreira (ISEPorto): *A novel printed 3-electrode system for the electrochemical detection of sulfadiazine*	**Silvia Carneiro Soares (ISEPorto)**: *Nanotheranostics with microRNA: Application in radiotherapy*	**Raquel Lopes (U. Porto)**: *Tunable catanionic vesicles based on serine-derived surfactants: from molecular design to effective in vitro delivery of doxorubicin*
13:00	**LUNCH**	**LUNCH**	**LUNCH**
14:30	**Maria Helena Godinho (U. Nova de Lisboa)**: *Cellulose hierarchical structures: from Nature to applications*	**Pablo Taboada (U. Santiago de Compostela)**: *Self-assembly pathways and molecular species in amyloid protein fibrillation*	**Cláudia Lopes (U. Aveiro)**: *EuChemS Periodic Table and our efforts to reduce element scarcity by developing magnetic carbon-based nanocomposites*
14:45			**Bárbara Casteleiro (IST-U. Lisboa)**: *Polymer effect on Gold Nanoclusters Luminescence*
15:00			**Piero Baglioni (U. Florence)**: *Polymer hydrogel networks and complex fluid for the conservation of modern and contemporary art*
15:30	**Juan José Giner Casares (U. Córdoba)**: *Langmuir monolayers as a relevant platform in colloid and interface science*	**Nuno Araujo (U. Nova de Lisboa)**: *Designing colloidal structures with functionalized particles*	
16:00	**Diana Andreia Branco (U. Aveiro)**: *Changes in surface properties of cork upon reactive washing*	**Yuselis Castaño-Guerrero (ISEPorto)**: *SERS-based immunosensing layer for cancer biomarker detection in point-of-care*	**ENDING SESSION**
	Akmaral Suleimenova (ISEPorto): *Transparent Electrodes for Optical and Electrochemical Biosensor Applications*	**Pedro Mateus (U. Nova de Lisboa)**: *Chalcone-Based Supramolecular Amphiphiles for Light-Controlled Drug Uptake and Release*	
16:15	**Pablo Gómez Argudo (U. Córdoba)**: *Fmoc-dipeptides, air-water interface self-assembly and lipid membrane Interactions*	**Anxo Carreira Casais (U. Vigo)**: *SERS-based multiplex detection of phenol derivatives*	**PLENARY LECTURE: 50 min+10 min- Room 23.1.7**
	Celso Ferreira (INL): *Microfluidics for controlled self-assembly of cubosome nanoparticles of tunable size*	**Rita de Sousa Dias (Norwegian UST)**: *Coarse-grained Monte Carlo simulations of complexation between weak polyelectrolytes and oppositely charged nanoparticles*	**INVITED TALK: 20 min+10 min- Room 23.1.7**
16:30	**Roberto Garcia (U. Coimbra)**: *Binding cyclodextrins to a cellulosic matrix by direct etherification*	**Yizhi Zhang (CIC biomaGUNE)**: *Intracellular pH sensing and monitoring using branched SERS nanoprobes*	**ORAL COMMUNICATION: 10 min+ 5 min- Room 23.1.7**
	Carlos Abreu (IQACataluña-CSIC): *Bottom-up fabrication of organic nanofibers via ionic self-assembly*	**Sandra Cristina Nunes (U. Coimbra)**: *The role of electrostatic interactions in biological DNA-related systems: insights from Monte Carlo simulations.*	**ORAL COMMUNICATION (in parallel)- Room 23.3.4**
16:45	**Mikheil Kharbedia (U. Complutense de Madrid)**: *Turning surface wave turbulence into coherent hydrodynamic structures*	**Daniel García Lojo (U. Vigo)**: *Microfluidic-induced Supercrystals for ultrasensitive SERS detection*	
	Ana Margarida Cerqueira (ISEPorto): *Label-free quantum dot conjugates for human protein IL-2 based on molecularly imprinted polymer*	**Tânia Firmino da Cova (U. Coimbra)**: *Unveiling the effect of structural flexibility and cavity space filling on the molecular recognition of cyclodextrins by free energy calculations*	**SESSIONS CHAIRMANS**
17:00	**COFFEE BREAK**	**MUSEU VISTA ALEGRE VISIT**	**Francisco Monroy (U. Complut. Madrid):** 17 July, 11:00-13:00, 23.1.7
17:30	**Ana Cristina Estrada (U. Aveiro)**: *Photodegradation of adsorbable organic halides (AOX) from pulp and paper industry wastewater using TiO2 nanomaterials*		**Bruno Silva (INL)**: 17 July, 12:30-13:00, 23.3.4
	Monisha Elumalai (INL): *Optical devices for DNA detection and quantification for food & Environmental Applications*		**José Paulo Farinha (IST-U. Lisboa)**, 17 July, 14:30-17:00, 23.1.7
17:45	**João Pedro Vareda (U. Coimbra)**: *Heavy metal uptake with silica aerogels and xerogels modified with amines*		**Jordi Esquena (IQACataluña-CSIC),** 17 July, 16:00-17:00, 23.3.4
	Liliana Truta (ISEPorto): *Glass-based biosensing device for monitoring CA15-3 cancer biomarker*		**Helena Nogueira (U. Aveiro)**, 17 Juy, 17:30-19:00, 23.1.7
18:00	**Manuel Cano Luna (U. Córdoba)**: *Effect of the Capping Ligand on the Electrocatalytic Performance of Gold Nanoparticles for Fuel Cell- and Water Splitting-Cathodes*		**Nuno Basílio (UNLisboa)**, 17 July, 17:30-19:00, 23.3.4
	Vítor Gaspar (U. Aveiro): *Bioinspired Polydopamine Nanocolloid-Stem Cell Combinations for Targeted Chemo-Phototherapy in 3D Microtumor Models*		**Artur Valente (U. Coimbra)**, 18 July, 9:00-11:00, 23.1.7
18:15	**Jussara Alves Penido (U. Coimbra)**: *How does surfactant act to separate different dyes using an aqueous two-phase system?*		**Goreti Sales (ISEPorto)**, 18 July, 10:30-11:00, 23.3.4
	Raquel Vaz (ISEPorto): *Biopolymeric photonic sensing of cancer protein biomarkers*		**María José Ruiz (U. Granada)**, 18 July, 12:00-13:00, 23.1.7
18:30	**Tiago Martins (IST-U. Lisboa)**: *Polymer nanoparticles with reversible crosslinking for coatings*		**Alberto Canelas Pais (U. Coimbra)**, 18 July, 12:30-13:00, 23.3.4
	Natalia Sánchez Arribas (U. Complutense de Madrid): *Cationic lipids containing amino acid residues as siRNA nanovectors for gene therapy*		**Tito Trindade (U. Aveiro)**, 18 July, 14:30-17:00, 23.1.7
			Juan Ruso (U. Santiago de Compostela), 18 July, 16:00-17:00, 23.3.4
			Mercedes V. Salicio (U. Salamanca), 19 July, 9:00-11:00, 23.1.7
			Maria Elisabete Oliveira (U. Minho), 19 July, 10:30-11:00, 23.3.4
			Pablo Taboada (U. Sant. Compostela), 19 July, 12:00-13:00, 23.1.7
			Ana Luísa Daniel-da-Silva (U. Aveiro), 19 July, 12:30-13:00, 23.3.4
			Eduardo Marques (U. Porto), 19 July, 14:30-17:00, 23.1.7
19:00	**WELCOME RECEPTION**	**CONFERENCE DINER**	

Scientific Topics

- Colloids, Biocolloids, Nanoparticles and Colloidal Nanoscience
- Surfaces, Interfaces and Films
- Polymers, Foams, Emulsions, Liquid Crystals and Gels
- Surfactant Science and Technology
- Advanced Materials and their Characterization
- Theory and Modeling Applied to Soft Matter
- Colloidal Biotechnology, Medical, Pharmaceutical and Food Applications
- Experimental Methods in Colloidal and Interface Science
- Colloids and Surfaces in Energy and Environmental Technologies

Plenary lecturers

- Piero Baglioni, University of Florence, Italy
- Regine von Klitzing, TU Darmstadt, Germany
- Maria del Puerto de Morales, Institute of Materials Science of Madrid, Spain
- Maria Helena Godinho, Universidade Nova de Lisboa, Portugal
- Pablo Taboada, Universidade de Santiago de Compostela, Spain
- Ana Luísa Daniel-da-Silva, Universidade de Aveiro, Portugal

Invited speakers

- Ana Espinosa, IMDEA Nanociencia-Madrid, Spain
- Carla Vitorino, Universidade de Coimbra, Portugal
- Juan José Giner Casares, Universidad de Córdoba, Spain
- Juan de Vicente, Universidad de Granada, Spain
- Marlene Lúcio, Universidade do Minho, Portugal
- Nuno Araújo, Universidade de Lisboa, Portugal
- Ricardo Fernandes, Universidade do Porto, Portugal

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INVITED LECTURES

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OC2 SURFACTANT/POLYMER MIXTURES FOR NON-COVALENT FUNCTIONALIZATION OF MULTIWALLED CARBON NANOTUBES

OC17 POLYMER NANOPARTICLES WITH REVERSIBLE CROSSLINKING FOR COATINGS

OC22 CATIONIC LIPIDS CONTAINING AMINO ACID RESIDUES AS SIRNA NANOVECTORS FOR GENE THERAPY

OC23 UP-CONVERTING NANOPARTICLES AS LIGHT SOURCES FOR CELLULAR ACTIVITY MODULATION

OC24 A SEEDED GROWTH METHODOLOGY BASED ON IRON (II) FOR THE SYNTHESIS OF NOBLE METAL NANOPARTICLES

OC28 STRUCTURAL COLOR PIGMENTS BASE IN COLLOIDAL ASSEMBLIES

OC29 PLASMONIC NANOCAPSULES AS SERS TAGS FOR MULTIPLEX DETECTION

OC30 NANOTHERANOSTICS WITH MICRORNA: APPLICATION IN RADIOTHERAPY

OC34 MICROFLUIDIC-INDUCED SUPERCRYSTALS FOR ULTRASENSITIVE SERS DETECTION

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OC31 SERS-BASED IMMUNOSENSING LAYER FOR CANCER BIOMARKER DETECTION IN POINT-OF-CARE

OC32 SERS-BASED MULTIPLEX DETECTION OF PHENOL DERIVATIVES

OC35 CHALCONE-BASED SUPRAMOLECULAR AMPHIPHILES FOR LIGHT-CONTROLLED DRUG UPTAKE AND RELEASE

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OC40 LIPOSOMAL HYDROGELS AS VAGINAL MICROBICIDES FOR HIV PROPHYLAXIS

OC41 PH-ACTIVATED HYBRID MESOPOROUS NANOPARTICLES FOR CONTROLLED RELEASE

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OC46 TUNABLE CATANIONIC VESICLES BASED ON SERINE-DERIVED SURFACTANTS: FROM MOLECULAR DESIGN TO EFFECTIVE IN VITRO DELIVERY OF DOXORUBICIN

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OC7 BINDING CYCLODEXTRINS TO A CELLULOSIC MATRIX BY DIRECT ETHERIFICATION

OC8 TURNING SURFACE WAVE TURBULENCE INTO COHERENT HYDRODYNAMIC STRUCTURES

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OC11 BOTTOM-UP FABRICATION OF ORGANIC NANOFIBERS VIA IONIC SELF-ASSEMBLY

OC12 LABEL-FREE QUANTUM DOT CONJUGATES FOR HUMAN PROTEIN IL-2 BASED ON MOLECULARLY IMPRINTED POLYMER

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OC19 GLASS-BASED BIOSENSING DEVICE FOR MONITORING CA15-3 CANCER BIOMARKER

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P7 DETECTION OF C-REACTIVE PROTEIN USING APTAMER-CONJUGATED GOLD NANOPARTICLES

P9 HYBRID NANOPLATAFORMS FOR CANCER THERANOSTICS

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PLENARY LECTURES

PL1

Ordering of hydrophilic and hydrophobized Silica nanoparticles in thin liquid films

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The presentation addresses ordering phenomena of Silica nanoparticles (NP) confined in thin films: 1) either pristine (hydrophilic) NP dispersed in thin aqueous films or 2) partially hydrophobized NP adsorbed at the air/water interface of foam films.
In the first part suspensions of pristine Silica NP are confined in a Colloidal Probe AFM (CP-AFM) between two solid surfaces. Oscillatory forces occur and the wavelength λ scales with the particle number density as $\lambda=\rho^{-1/3}$. An extrapolation towards high volume fractions shows that the $\rho^{-1/3}$ scaling law for λ ends up into a cubic lattice found for one-component systems like organic solvents, where λ=d (d: diameter of molecules, particles etc.). A deviation from the exponentially decaying cosine function was found and can be described by an additional repulsion term [2,3] which will be discussed. Furthermore, it will be shown how oscillatory forces can be switched on and off by external stimuli [4].
Partially hydrophobized Silica NP order laterally at the interfaces of a free-standing film. Depending on the NP concentration they can form single aggregates or even percolation networks. The latter seem to stabilize foam films and even foams, *i.e.* so called Pickering foams [5,6].

Acknowledgements: We thank the deutsche Forschungsgemeinschaft (DFG) for financial support.

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PL2

Cellulose hierarchical structures: from Nature to applications

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Cellulose nano rods extracted from the cell wall of the tissues of Plants were found to generate lyotropic liquid crystals that are at the origin of solid cholesteric-like arrangements[1-3]. The nematic chiral phase organization assures not only the mechanical properties of the Plant but it is also responsible for the structural colors displayed by some fruits, leaves and flowers[4-6]. Quite fascinating is to transform the white cotton flower into a pallet of vivid cellulose-based structural colors, which goes from violet to red. In this work, we will focus on liquid crystalline structures, obtained from cellulose-based colloidal solutions, and the production of solid photonic films. We will show how small perturbations in the colloidal solutions induce a huge effect on the photonic characteristics of the solid films produced. The intricate hierarchical structures produced by plants are difficult to mimic. However, the solid architectures obtained from cellulosic liquid crystalline structures are a source of inspiration for the manufacture of functional and interactive materials, from the most abundant polymer on our planet.

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PL3

Surface engineering of nanomaterials for water treatment

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Clean water is of crucial importance for global health and economic development. A wide range of emerging pollutants are frequently detected in drinking water sources, treatment plant effluents and natural waters at levels that may jeopardize public or ecosystem health.[1] These pollutants include pesticides and contaminants of emerging concern such as pharmaceuticals and personal care products that disrupt endocrine systems or cause other effects. These facts highlight the need for technological innovation in the development of effective water treatments

Nanotechnology has provided a novel technology platform, which can address critical environmental problems and enable new opportunities.[2,3] Nanomaterials possess increased specific surface area and unique surface properties such as surface chemisttry and wettability, that are of relevance for water treatment and contaminate site remediation.[4] Herein novel chemical strategies for the surface modification of nanoparticles are discussed, through several examples of systems developed for specific applications in water remediation. Focus will be given to the rational design of the surface of magnetic nanomaterials, aiming the development of advanced nanosorbents with high adsorptive performance and reusability.[5,6]

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PL4

Unreaveling protein oligomerization and fibrillation pathways as a therapeutic tool against neurodegenerative-associated diseases.

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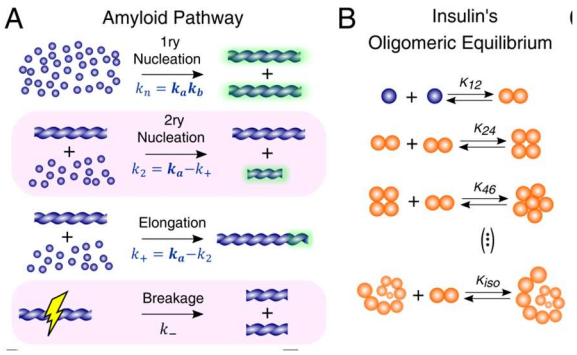
Some of the most prevalent neurodegenerative diseases are characterized by the accumulation of amyloid fibrils in organs and tissues [1]. Fibrillation is not exclusive of these disease-related proteins, and an important number of non-disease associated proteins have also been already found to form ordered cytotoxic aggregates and amyloid-like fibrils *in vitro* [2], which enable to gain important knowledge on the biophysical and biochemical mechanisms involved in fibrillation phenomena. In this regard, some of the main aspects concerning the origin and possible mechanisms by which proteins fibrillate will be exposed, with a special emphasis on the factors that originate and influence this process.

Although the pathogenic role of protein amyloid fibrils has not been completely established yet, increasing evidences suggest other aggregation pathways producing smaller, hard-to-detect soluble oligomers as the main reason for cell toxicity and cell-to-cell transmissibility [3]. Then, it would be highlighted how the monitoring of the amyloid fibrillation kinetics can be used to unveil the protein oligomerization states from on/off- pathways and their relative importance regarding amyloid fibrillation using simple, high-throughput compatible, biophysical assays based on experimental and numerical simulation methods [4]. This approach can be of great importance since diffusible oligomers have emerged as promising targets affecting downstream pathogenic processes, and molecules that attenuate the magnitude and extent of oligomerization states might be considered as promising on/off-pathway drug inhibitors, opening new potential therapeutic options to classic strategies trying to prevent the nucleation and spread of amyloid fibrils.

To conclude, the exceptional physical characteristics of the amyloidal protein state as its stability, mechanical strength and resistance to degradation implies that this type of structures possess a range of potential technological applications in biotechnology and materials science, then, some interesting examples of such potential applications will be briefly discussed.



Scheme 1: Aggregation pathways of a model protein (human insulin) investigated through amyloid fibrillation kinetics. (**A**) Reaction steps participating in the amyloid pathway. Green glows represent an increase in the mass of fibrils. (B) Oligomeric equilibrium of insulin.

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PL5

Design Strategies for Shape-Controlled Magnetic Iron Oxide Nanoparticles

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The improvement of the performance of magnetic iron oxide nanoparticles in their different applications requires the design of more complex synthetic nanostructures, uniform in size and with morphologies different from the spherical one (Fig. 1), leading to enhanced properties, i.e. high magnetic anisotropy, larger specific surface area, and arising new ones like vortex magnetic domains structures or magnetomechanical properties [1]. Those properties are very advantageous not only in theranostic applications (MRI and magnetic hyperthermia) but also in others like environmental remediation. Although there are a vast number of synthetic routes leading to anisometric magnetic iron oxide nanoparticles showing a great performance in biomedicine, there is room for improvement to control how these materials are produced in a more robust, reproducible and scalable way [2,3].

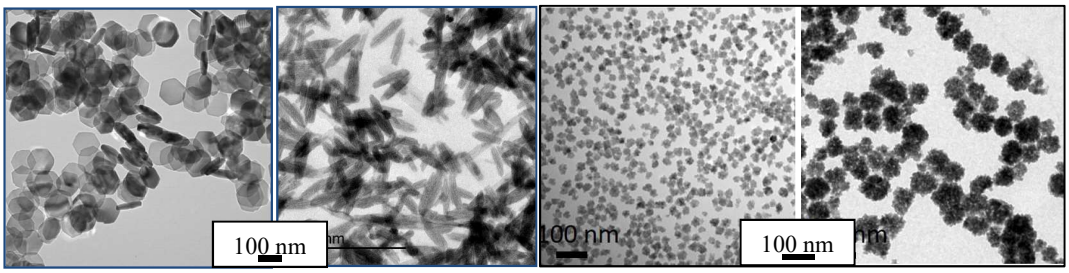

Figure 1: Magnetic iron oxide nanoparticles with different morphologies.

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PL6

Polymer hydrogel networks and complex fluid for the conservation of modern and contemporary art

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We pioneered one of the most exotic application of soft matter and materials science to conservation of cultural heritage. Art Conservation poses a formidable and exciting challenge to soft matter scientists in two respects. First, the majority of the most performing and environmentally safe cleaning and consolidation agents for artworks are soft matter systems. Second, the interaction of these agents with the artifact involves an exceptionally complicated range of interfacial interactions. Recently we proposed innovative cleaning system, namely a semi-interpenetrated polymer network (SIPN), where a covalently cross-linked poly(hydroxyethyl methacrylate), pHEMA, or Poly(vinylalchohol), PVA, network is interpenetrated by linear chains of poly(vinylpyrrolidone), PVP. The chemical gels, simply loaded with water, were designed to safely remove surface dirt/grime from water-sensitive artifacts. Modified SIPN can be designed to confine complex cleaning fluids, able to remove aged varnishes. These fluids are 4 or 5-components water-based nanostructured systems, where solvents are partially dispersed as nano-sized droplets in a continuous aqueous phase, with the help of surfactants. The mechanical behavior of the gel was optimized by varying both the cross-linking density and the polymer concentration. In this lecture, I will review the most meaningful achievements in this field, focusing on the application of micelles and o/w microemulsions confined into semi-interpenetrated hydrogels. The structure and dynamics of these complex systems was mainly investigated by Small Angle scattering (SANS and SAXS), quasielastic neutron scattering (QENS) and Fluorescence Correlation Spectroscopy (FCS). These systems mark a paradigm shift in modern conservation and have been used on modern and contemporary artifacts as Picasso, Lichtenstein, Pollock, de Chirico, etc.. Finally, I will summarize the main perspectives that this field can disclose for Chemists and Conservators communities.

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INVITED LECTURES

IL1

Debundling and colloidal stabilization of carbon nanotubes by amphiphiles

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Carbon nanotubes (CNTs) are a relatively new nanomaterial with a plethora of potential applications, such as reinforcement in composites, catalysis, drug delivery and energy storage. However, pristine CNTs are prone to bundle due to the strong intertube van der Waals interactions. This is a drawback because most applications require individual and aligned nanotubes. Thus, several methods have been devised to debundle and exfoliate CNTs in water, where non-covalent dispersing methods are one of the most common. In this process, dispersant molecules (e.g. surfactants and polymers) adsorb on CNT surface through hydrophobic interactions while their polar headgroups provide colloidal stabilization of CNTs via electrostatic and/or steric repulsions. Understanding the equilibrium and kinetics features of the interactions between the nanotubes and the dispersants (such as the fraction of dispersant adsorbed, residence time on CNT surface, binding strength, surface coverage) are important aspects to design better dispersants in order to get more stable CNTs aqueous dispersions [1,2].

In this lecture molecular aspects on CNT dispersibility, such as the binding dynamics and dispersibility of low and high molecular-weight dispersants are presented. A rigorous protocol to evaluate the CNT dispersion efficiency of different surfactants resulted in well-defined sigmoidal dispersion curves, which reflect the molecular features of the dispersants (different polar head groups and tail length) [2]. It was also found that kinetic reasons are behind the need for dispersant concentrations required to reach a substantial SWNT concentration [3].

The binding dynamics, such as the fraction adsorbed, the residence time and the lateral diffusion, of high molecular-weight dispersants on single walled carbon nanotubes (SWNTs), assessed by ^{1}H NMR diffusion studies will also be discussed.[3] Additionally, the competitive binding between a block copolymer (F127), a protein (BSA) and several surfactants will be presented [4].

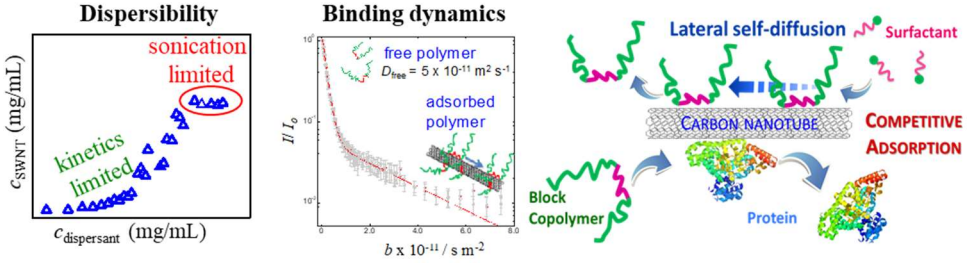

Figure 1: Sigmoidal dispersibility curve of suspended SWNTs vs surfactant conc. (left). Biexponential signal decay observed for block copolymer (F127) by ^{1}H NMR diffusometry (center). Dynamic processes studied on CNT surfaces obtained from NMR diffusometry data (right).

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IL2

Langmuir monolayers as a relevant platform in Colloid and Interface Science

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The Langmuir monolayer technique is a well-established experimental methodology for conducting basic studies at the air/liquid interface.[1] With the advent of new in situ probing techniques, the scope and applications of the Langmuir technique have been greatly increased, reaching organic/inorganic hybrid composites, complex biomolecules and functional nanoparticles, among others.[2]

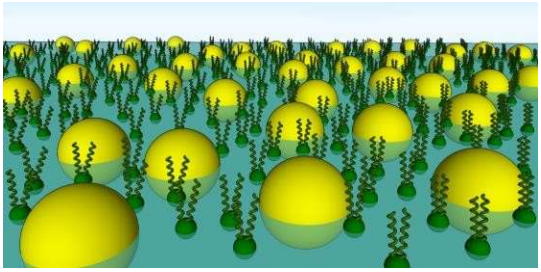
The possibility of finely tuning the available surface area per molecule combined with the detailed experimental information that can be attained makes the Langmuir technique a relevant platform to obtain unique insights in Colloid and Interface Science.

Mechanosensation, i. e., conversion of applied pressure to defined modification in molecular arrangements was explored. Gold nanoparticles were hybridized with a purposefully designed self-assembling molecule based on non-covalent intermolecular interactions. The air/liquid interface served in this case for assembling supramolecular structures that mimic biological behaviour.[3]

With the viewpoint on nanoscience, the self-assembly of a set of Fmoc-dipeptides at fluid interfaces was assessed. The impact of the amino acid sequence on the resulting supramolecular structures were evaluated in detail by the Langmuir technique. The partition coefficient appears as a relevant and easily calculated molecular parameter providing an immediate guide for predicting the self-assembly behaviour. This idea was extrapolated to the interaction of the Fmoc-dipeptide derivatives with a model cell membrane.[4]

Langmuir monolayers for mimicking biological surfaces are highly versatile and offered stimulating insights on the internalization mechanism of fluorinated quantum dots that could be related with in vitro experiments.[5]

In summary, despite been established on the classical Colloid and Interface Science, Langmuir technique is still contributing with remarkable ideas, techniques and results. Much more fascinating research is certainly yet to come.



Langmuir monolayers might include different nano-entities beyond classical surfactants.

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IL3

Lipid nanoparticles in drug delivery: what have we learned so far?

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Lipid nanoparticles, in particular solid lipid nanoparticles (SLNs) and nanostructured lipid carriers (NLCs), are colloidal carriers, with sizes typically ranging from 100 to 300 nm. They are derived from o/w emulsions, in which the liquid lipid (oil) is replaced by biodegradable and biocompatible solid lipids, i.e., lipids that are in the solid state at both room and body temperatures (in case of SLN), or blends of liquid and solid lipids (in case of NLCs), and stabilized by an aqueous emulsifier(s) solution. Solid lipids can vary from pure lipids or a mixture of lipid compounds, encompassing triglycerides, partial glycerides, fatty acids, and waxes. On the other hand, the emulsifiers, including a large variety of non-ionic and ionic surfactants, are chosen depending on the administration route, being often used in association, in order to prevent particle agglomeration more efficiently[1].

Their biocompatible and biodegradable nature, physicochemical stability, control over drug release, cost-effectiveness and easy scaling-up are some of the advantages that have positioned them as a promising alternative drug delivery system when compared with the conventional colloidal carriers[2].

In this work, design considerations of solid lipid based nanoparticles will be extensively displayed, with focus on the optimization of formulation/production methods aiming at addressing a diversity of unmet medical needs. This includes the development of innovative solid dosage forms for oral administration, based on (i) oral films, and (ii) tableted NLC coated with conventional synthetic[3] or natural polymer agents[4], (iii) hydrogels[5], and (iv) monolithic drug-in-NLC-in-adhesive patches for transdermal delivery[6], and more recently, surface modified ultra-small NLC to prompt site-specific drug delivery for the treatment of glioblastoma multiforme[7].

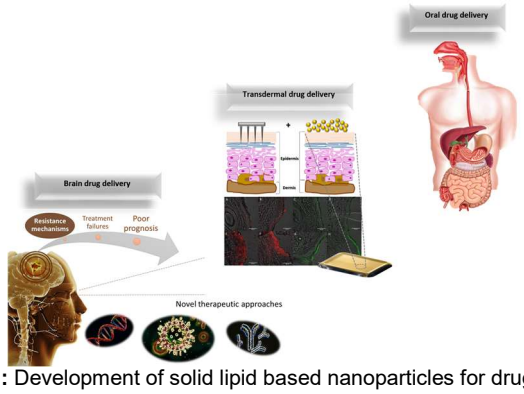

Figure 1: Development of solid lipid based nanoparticles for drug delivery.

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IL4

Multifunctional approaches based on magnetic and photothermal nanomaterials for cancer treatment

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Nano-based thermal treatments as magnetic hyperthermia (MHT) and photothermal therapy (PTT) are two promising emergent treatments and *non-invasive* approaches for tumor ablation, where localized heat generation is mediated by magnetic and photo-activatable nanomaterials.[1, 2] Until very recently, these thermal nanotherapies, have been developed separately: MHT is mainly focused on the use of magnetic iron oxide nanoparticles due to their excellent biodegradability[3], while metallic nanoparticles such as gold nanomaterials are often preferred due to their strong absorption cross sections. They have recently begun to intersect due to the recent discovery and use of photothermal properties of iron oxide nanostructures[4] or to the use of magneto-photothermal hybrids[5], which efficiently combine both heating features in one-single object.

A comprehensive comparison of the heating efficiency of magneto- versus photo-thermal effect is presented, where different magnetic nanoparticles have been confronted with different metallic nanoparticles in aqueous, cellular, and tumoral environment.[6] Intracellular processing markedly impacted MHT, while endosomal sequestration could have a positive effect for PTT. In the search for the most therapeutically viable modality, the effect of nanoparticle concentration and the experimental exposure parameters (magnetic field strengths/frequencies and laser power densities) have been investigated. The intracellular biotransformations of these nanomaterials in the biological environment has also been explored through the study of their physical and chemical modifications at the nanoscale over the time. [7]

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IL5

Designing colloidal structures with functionalized particles

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Colloidal particles are considered ideal building blocks to produce materials with enhanced physical properties. The state-of-the-art techniques for synthesizing these particles provide control over shape, size, and directionality of the interactions. In spite of these advances, there is still a huge gap between the synthesis of individual components and the management of their spontaneous organization towards the desired structures. The main challenge is the control over the dynamics of self-organization. In their kinetic route towards thermodynamically stable structures, colloidal particles self-organize into intermediate structures that are much larger than the individual particles and become the relevant units for the dynamics. To follow the dynamics and identify kinetically trapped structures, one needs to develop new theoretical and numerical tools. In this seminar, we will discuss the self-organization of functionalized colloidal particles with limited valence [1,2,3,4].

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IL6

Colloids and interfaces studies as an approach to disease

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Colloids and interfaces studies using lipid model systems have been successfully applied to medicine and pharmaceutical development and nowadays also support the development of nanotherapies (NTs). One of the main challenges of nanomedicine is the development of methods that allow, using simple mimetic models as membrane models, to predict the biological behavior of NTs[1]. *In vitro* biophysical assays may be interesting solutions in response to this challenge, since they allow the understanding of drugs or NT properties at the molecular level. Furthermore, under controlled conditions, the mimetic models of biological interfaces can help to rationalize and predict drugs and NT behaviors and their interactions *in vivo*[1].

This communication aims to present some routines developed in our research group (Figure 1) with a view to predicting aspects related to the physiological barriers presented to drugs or NT that can condition their therapeutic and toxic effects. The interactions of drugs with membrane model systems are used to determine their membrane/water distriution coefficient, which is a predictor of drug affinity to the membranes as well as drug permeability and absorption, giving also important information regarding the most appropriate nanocarrier for drug loading. Further information about the membrane permeation and biophysical impairment by drugs can be also gained through in depth-dependent fluorescence quenching experiments (steady-state and time-resolved) and small and wide angle x-ray scattering studies which can suggest drug membrane toxicity. These studies will also help to understand if the drug released from a lipid nanosystem will be immediate or more controlled. In addition, it is possible to evaluate the influence of the drugs changing the cooperativity and the main phase transition temperature of lipid assembled nanocarriers giving a prevision of NTs stability. The drug bioacummulation by extensive binding to serum proteins and the stealth properties of NTs can be further monitored by binding studies to human serum albumin based in fluorescence quenching of intrinsic protein fluorophores. Finally, prediction of cellular uptake studied can be studied by bio tracking of the drug using fluorescence lifetime imaging microscopy.

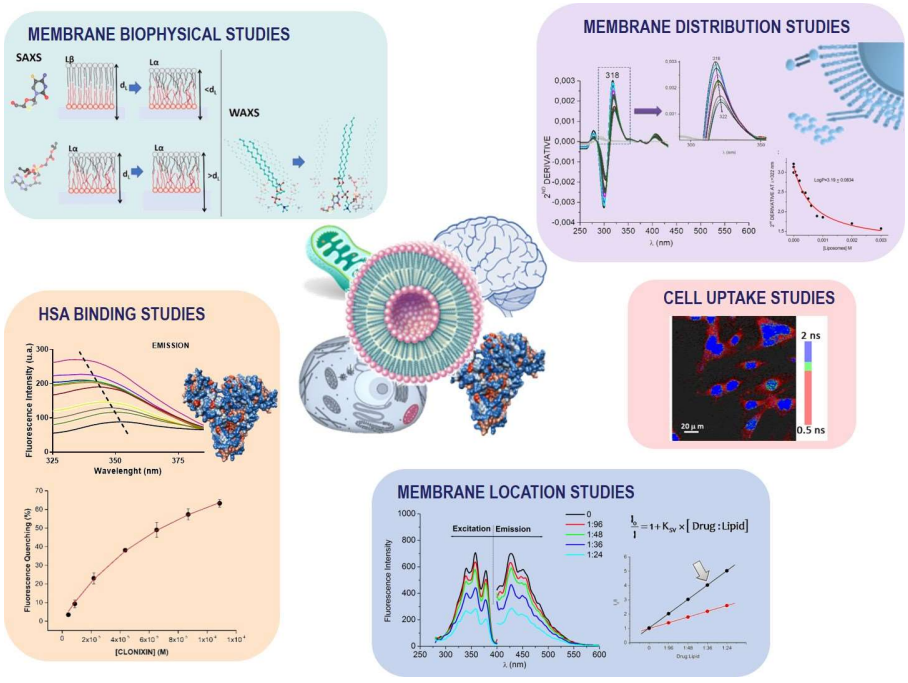

Figure 1: Colloidal dispersions and biointerfaces combined with biophysical studies for prediction of drugs/NTs performance.

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IL7

On the Mechanical behavior of Directed Self-assembled Magnetic Colloids

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Magnetorheological (MR) fluids are colloidal systems prepared by dispersion of magnetisable particles in (non-magnetic) liquid carriers. Interestingly, they exhibit a remarkable rheological change (so-called MR effect) upon the application of a magnetic field. The reason for this is the magnetic field-guided colloidal assembly of the dispersed magnetisable particles. The self-assembly can be controlled through the field configuration (DC, AC or combinations) and the strongest MR effect is achieved in saturating fields [1].

In the first part of this communication we propose a new setup to measure the rheological properties of MR fluids under homogeneous magnetic fields in saturation. First, the device optimization is carried out using magnetostatic Finite Element Method simulations. Next, Computational Fluid Dynamics simulations are performed and validated against experiments and theoretical calculations for Newtonian liquids. Finally, yield stress fluids are addressed and in particular MR fluids [2].

In the second part of this communication we show our most recent advances towards the understanding of magnetorheology under non-stationary magnetic fields. For this purpose a triaxial magnetic field generator is constructed and preliminary experimental data are reported on the directed self-assembly and rheological evaluation of MR fluids. In particular, we subject MR fluids to carefully controlled intervals of uniaxial DC fields and precession fields in the velocity gradient direction. With this, bigger aggregates are formed and the MR effect is subsequently enhanced as demonstrated in both steady shear and small-amplitude dynamic oscillatory shear tests, which documented larger viscosities and G' values, respectively, for an array of precession field configurations. Experimental results are found to be in good qualitative agreement with particle-level simulations and videomicroscopy observations.

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ORAL COMMUNICATIONS

OC1

Pathway-dependent effects on the formation of bioreducible polycation-DNA polyplexes in saline media

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The delivery of genes for therapeutic applications requires advanced nanocarriers that can package and protect DNA, and then deliver it to ill cells or tissues. Polyplexes – soft nanoparticles resulting from the complexation of DNA with cationic polymers – are promising vehicles to achieve these goals, but further advances in the technology are needed to achieve the desired efficiency for use in gene therapy applications1. One promising approach to enhance the gene delivery efficiency of these particles makes use of polycations with disulfide bonds along their backbone that degrade in the reducing potential of the cytosol. This leads to an enhanced release of genes inside cells, and lowers the toxicity of the polymer2. In this work, we investigate the role of adding salt to the polyplex systems under different methodological order, up to physiological concentrations, on the structure, size and charge of conventional and bioreducible poly-L-lysine polyplexes. As a general trend, polyplexes assembled in water and transferred to physiological buffer afterwards display smaller sizes and enhanced colloidal stability when compared to polyplexes assembled in physiological buffer from start (figure 1). Since these parameters are key to the pharmacokinetics of nanocarriers, this approach can be used as a new tool to manipulate the properties of gene nanocarriers and enhance their transfection efficiency. Current live-cell imaging and transfection efficiency studies are focused on elucidating how these two methods of preparation influence cellular uptake and transfection efficiency.

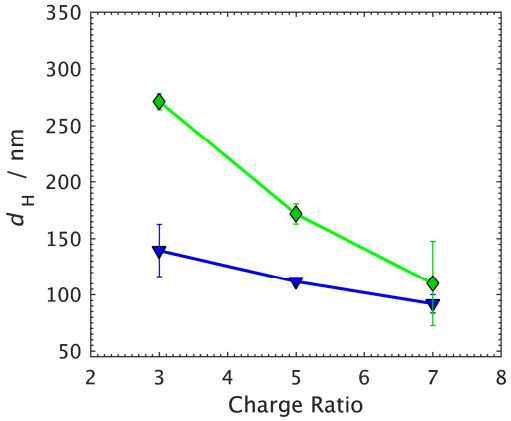

Figure 1: Influence of the order of salt addition (100 mM) on the size of polyplexes. As can be seen, polyplexes prepared in water and transferred to saline media after (▼) have a smaller size than polyplexes prepared in saline media from start (♦). The tendency is observed for the entire range of positive-to-negative charge ratios investigated.

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OC2

Surfactant/polymer mixtures for non-covalent functionalization of multiwalled carbon nanotubes

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Carbon nanotubes (CNTs) have become important and exciting nanomaterials for a wide range of applications.[1] Because of CNT insolubility in aqueous media, surfactants or surface-active polymers are often used to functionalize and stabilize the exfoliated material, owing to the electrostatic or steric repulsions provided by the adsorbed amphiphile.[2-4] Although surfactant/polymer systems have been extensively investigated[5], studies regarding their use for non-covalent functionalization of CNTs are scarce. Yet, surfactant/polymer association could greatly enhance the dispersibility and applicability of the CNTs.[1]

Herein, we have explored a methodology to exfoliate highly entangled powders of multi-walled carbon nanotubes (MWNTs), under stringently controlled conditions, in aqueous surfactant/polymer mixtures combining (i) non-ionic surfactant with ionic polymers and (ii) ionic surfactants with non-ionic polymer. From the profile of the dispersibility curves, several quantitative parameters were extracted, which altogether permit reliable comparisons between the different systems investigated. Strong surfactant/polymer synergistic effects were found, with the maximum MWNT dispersibility being attained at much lower dispersant concentration when compared to the individual components. SEM imaging further shows a significant degree of MWNT debundling in the as-obtained dispersions (Fig. 1). These studies are of great interest for the choice of optimal conditions and dispersants to obtain non-covalently funcionalized MWNTs, which can then be applied as building blocks for novel composite materials and nanostructured coatings.

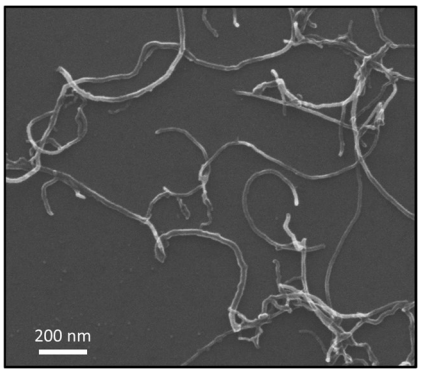

Figure 1: SEM micrograph of MWNTs invidually dispersed by a CTAB/PVP mixture.

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OC3

Disodium Cromoglycate and Guanidine: Towards unravelling the mysteries of a reversible colour change

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Disodium Cromoglycate (DSCG, Figure 1A) behaves as a Lyotropic Chromonic Liquid Crystal (LCLC) in water.[1] In silico studies[2] show the stacks on the LCLC are formed due to H-bonding between water and DSCG, favouring the establishment of π-π interactions between chromene moieties. Moreover, low ordered phases such as the nematic phase of DSCG can be distorted due to dopant addition, particularly when using ionic salts these distortions can induce (de)stabilization of the ordered phases.[3]

Here, we present the effects of doping a DSCG nematic phase with various chiral molecules, such as N-Methyl Codeine (NMC, Figure 1B),[4] L-Alanine (L-Ala, Figure 1C) and L-Arginine Hydrochloride. This doping renders a high pitch chiral anisotropic phase, as confirmed through the observation of aligned tactoids under POM (Figure 2).

Curiously, in the case of DSCG samples doped with guanidine containing molecules, such as L-Arginine and Tetra Methyl Guanidine (L-Arg and TMG, Figure 1D and E), a colour change is observed: an aqueous colourless solution of DSCG 9wt% + 0.3M NaCl with 0.4wt% of either L-Arg or TMG turns yellow upon standing for several hours at 25 °C and it changes to pink when heated above clearing temperature (T_c), being the last colour change reversible with temperature (Figure 3).

To rationalize these colour changes, charge transfer and salt bridge effects between guanidine/guanidinium and carboxylate groups (Figure 4) has been explored by experimental and computational studies.

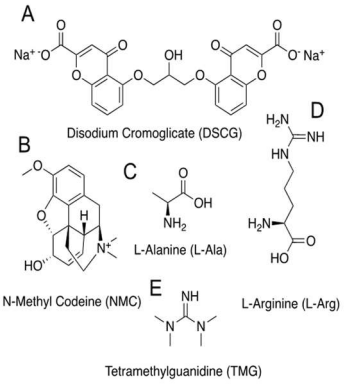

Figure 1: Molecules used throughout this work.

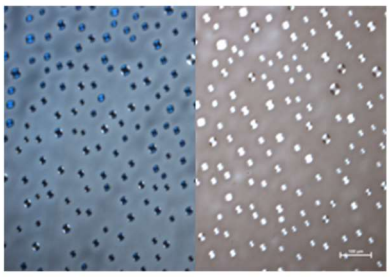

Figure 2: Tactoids aligned under POM for a DSCG/L-Arginine sample.

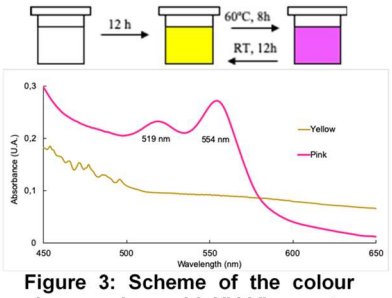

Figure 3: Scheme of the colour change, along with UV-Vis spectra of a 9 wt% DSCG 0.4 wt% L-Arg in H_2O + NaCl 0.3M.

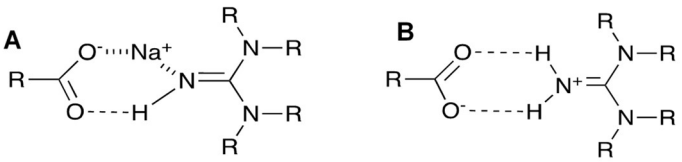

Figure 4: Schemes depicting A: possible structure of a sodium mediated strong charge transfer between carboxylate and guanidine and B: possible structure of a salt bridge effect between carboxylate and guanidinium.

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OC4

A novel printed 3-electrode system for the electrochemical detection of sulfadiazine

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Electrochemical biosensors played an important role in advancing point-of-care (POC) detection systems, being well established for many years in analytical research. However, most of the devices consist on screen printed electrodes (SPEs) designed by printing suitable inks on different supports, mostly plastic, as PET or PVC, or ceramics. But an extended worldwide use of such SPE with synthetic and non-biodegradable support materials pose environmental concerns. A novel support is proposed herein to replace such non-eco-friendly materials, consisting on a natural compound that confers the required electrical and mechanical stability features to the final POC device.

As proof-of-concept, sulfadiazine (SDZ) was selected herein as target compound. SDZ is an antibiotic employed in fish health to improve production efficiency in aquaculture operations. The molecule recognition element used in this work is assembled by molecular imprinting technology by electropolymerizing Pyrrol in the presence of SDZ, on top a conductive layer of poly(3,4-ethylenedioxythiophene) (Figure 1). Electropolymerization was conducted by cyclic voltammetry and the template was removed by an alkaline solution.

The electrochemical performance of the resulting biomimetic sensor was evaluated by the direct detection of SDZ, in differential pulse voltammetry measurements. The results showed that the current signals increased for increasing concentrations of SDZ, revealing a good electroactive behaviour of this compound and the ability of the biomimetic film to recognize it. Moreover, the new devices displayed linear responses over from 8.0 to 152.0 µM, with good reproducibility and accurate readings. For comparison purposes, the same biomimetic element was assembled on commercial carbon SPEs of ceramic support prepared with the same PEDOT layer, and tested in parallel. In general, the sensitivity of biomimetic sensors prepared on the naturally-based substrates were better than commercial SPEs, yielding a higher sensitivity and a 10× lower limit of detection.

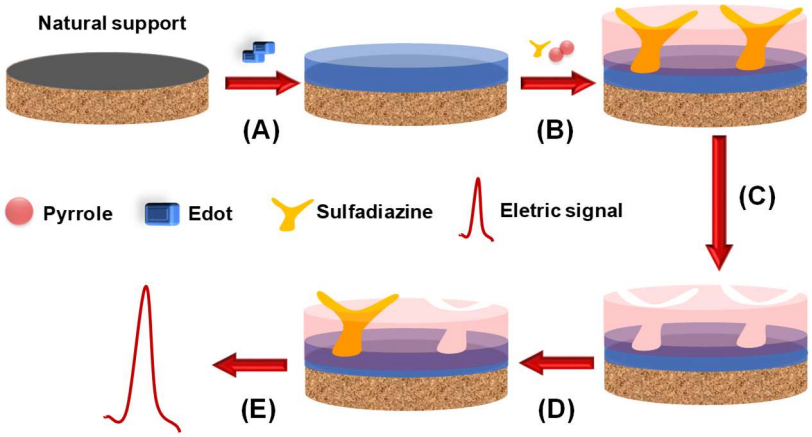

Figure 1: Synthesis of biomimetic sensor for detection Sulfadiazine. (A) Electropolymerizing EDOT; (B) Electropolymerizing Pyrrole in presence of template; (C) Template removal; (D) Rebinding the molecule to the biomimetic sensor; and (E) Electrical signal generated by the sensor in the molecule recognition process.

Acknowledgements: We thank the financial support of 3C´s – Cellulose and Cork in the Control of antibiotics in aquaculture (PTDC/AAG-TEC/5400/2014 and POCI-01-0145-FEDER-016637), to FEDER, through COMPETE2020, POCI, and FCT (Fundação para a Ciência e a Tecnologia I.P.).

OC5

Changes in surface properties of cork upon reactive washing

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Cork materials are widely used in food and composite industries due to their unique physical properties. Natural and composite stoppers for wine bottles occupy the major market segment among cork products (ca 70%) furnishing unique properties such as resistance to compression, elasticity and relaxation properties, controlled permeation and diffusion of liquids and gases [1], [2]. In the process of transforming the oak bark into the cork stopper, this material has to pass through several industrial steps, where reactive washing (RW) plays an important role in disinfection and appearance (colour homogeneity and whiteness). RW consists in the treatment of stoppers with H_2O_2 under strong alkaline conditions and increased temperature. This causes changes in the surface of the cork material, which may affect the receptivity to the coating agents (silicone / paraffin and polymer formulations) and sealing in bottles of alcoholic beverages. This study aimed to relate the RW with changes in surface composition and surface energy of cork material and with affinity of stoppers towards spirit drinks with different degrees of alcohol. The surface composition was assessed by FTIR-ATR and confocal Raman spectroscopy and the surface energy through the measurement of contact angles using the sessile drop method with probe liquids according to the OWRK method. The surface morphology was assessed by optic microscopy, SEM and AFM.

The natural cork stoppers showed changes in the surface composition upon RW. Thus, FTIR-ATR and confocal Raman analyses revealed partial degradation of suberin layer on the cork surface and increased exposure of hydrophilic polymers (e.g. cellulose and hemicelluloses). Accordingly, the contact angles (CA) of stoppers with water decreased substantially, especially at the lateral surface of stoppers. The latter fact was explained by the greater exposure of the cork cells to the reagents in the radial cut (lateral) than in the tangential cut (top) of the stoppers obtained by drilling the oak bark planks. This was also confirmed by the image analyses (SEM and AFM). The surface energy (SFE) of the stoppers processed by RW revealed almost a 3-fold polar component and a 30% decrease in CA regarding the dispersive component of SFE on the top and side surfaces of the stoppers, comparing to non-washed natural cork stopper. At the same time, the absolute values of SFE changed insignificantly. The observed surface features imply changes in the sealing capacity towards alcoholic beverages such as wine and spirits over a wide range of ethanol contents, as revealed by modelling studies using a wetting envelope created when the OWRK model is solved for the case of contact angles of 0-90° (Figure). In the wetting envelope the area bounded by the axes and the curve is less than 90° (lyophilic) and that outside this boundary is greater than 90° (lyophobic). In fact, the wettability of the lateral side of the stoppers inversed from nonwettable to wettable after the RW, being the most critical for the high percentage ethanol solutions.

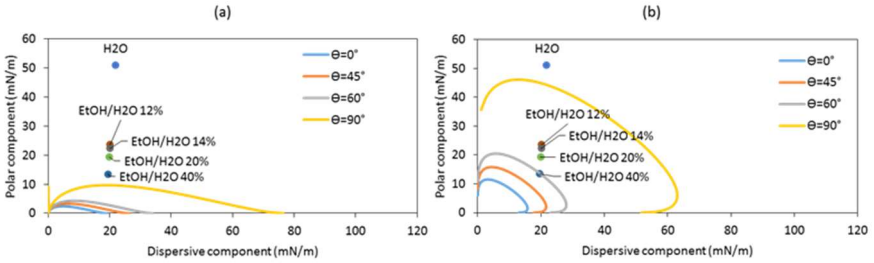

Figure-The wetting envelope for the lateral stopper surface with distinct ethanol solutions before (a) and after of RW (b).

The results of this work highlight the importance to develop novel strategies alternative to RW with new conditions and, probably, with other reagents and may explain the difficulties with stopper´s coating using conventional polymeric formulations. The modeling of the wetting envelope allows predicting how the surface of the stoppers behaves in the presence of ethanol solutions after being modified by the reactive washing process in use.

Acknowledgements: This work was developed within the scope of the project NEWASHCORK (POCI-01-0247-FEDER-034048) financed by ANI and co-financed by FEDER and supported by CICECO-Aveiro Institute of Materials, FCT Ref. UID/CTM/50011/2019, financed by national funds through the FCT/MCTES.

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OC6

Fmoc-dipeptides, air-water interface self-assembly and lipid membrane Interactions

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Fmoc-dipeptides appear as a highly relevant building block in smart hydrogels and nanovehicles for biological applications. The interactions of the Fmoc-dipeptides with the cell membrane determine the efficiency of the nanomaterials based on the Fmoc-dipeptides, as the internalization of nanovehicles for drug delivery. Here we aim at the understanding of the interplay of the interactions between the Fmoc-dipeptides and a phospholipid surface as a function of the aminoacid sequence.

The DMPA (1,2-dimyristoyl-sn-glycero-3-phosphate) phospholipid in Langmuir monolayers was used as a model cell surface. A set of seven derivatives of Fmoc-dipeptides with a broad range of hydrophobicity were included. Mixed monolayers composed by DMPA:Fmoc-dipeptide in equimolar ratio were built and characterized in situ at the air/water interface. Surface pressure-molecular area isotherms (π-A), Brewster Angle Microscopy (BAM) and UV-vis reflection spectroscopy (ΔR) were combined to provide a holistic picture on the interactions of the Fmoc-dipeptide with the phospholipid molecules. An increase in the hydrophobicity led to an enhanced interaction of the Fmoc-dipeptide and DMPA molecules. The compression of the mixed monolayer could displace a significant fraction of the Fmoc-dipeptide from the monolayer. A high hydrophobicity promoted self-assembly of the Fmoc-dipeptides over interaction with the phospholipid surface. The interplay of these two phenomena was analyzed as a function of the aminoacid sequence of the Fmoc-dipeptides. The results suggest that the adjustment of the hydrophobicity of the Fmoc-dipeptides within a defined range might optimize their efficiency for the interaction with the lipid membranes.

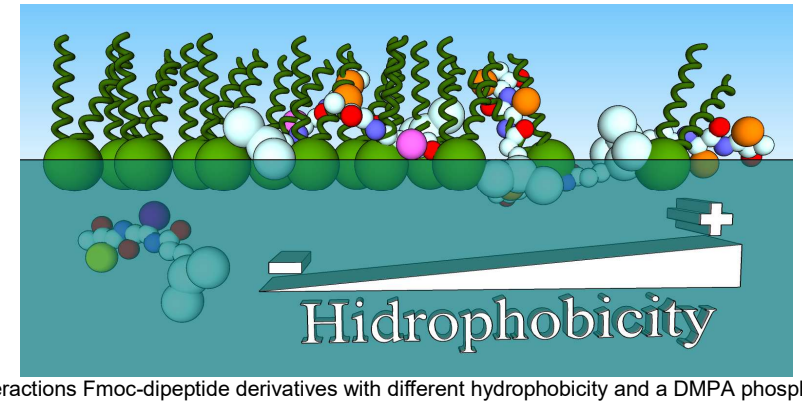

Figure 1: Interactions Fmoc-dipeptide derivatives with different hydrophobicity and a DMPA phospholipid surface.

Acknowledgements: Support from the Ministry of Economy and Competitiveness of Spain through the MANA project CTQ2017-83961-R is acknowledged. FIS2017-85954-R (Agencia Estatal de Investigación, AEI, Spain, co-funded by Fondo Europeo de Desarrollo Regional, ERDF, European Union). J.J.G.-C. acknowledges the Ministry of Economy and Competitiveness for a “Ramon y Cajal” contract (RyC-2014-14956).

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OC7

Binding cyclodextrins to a cellulosic matrix by direct etherification

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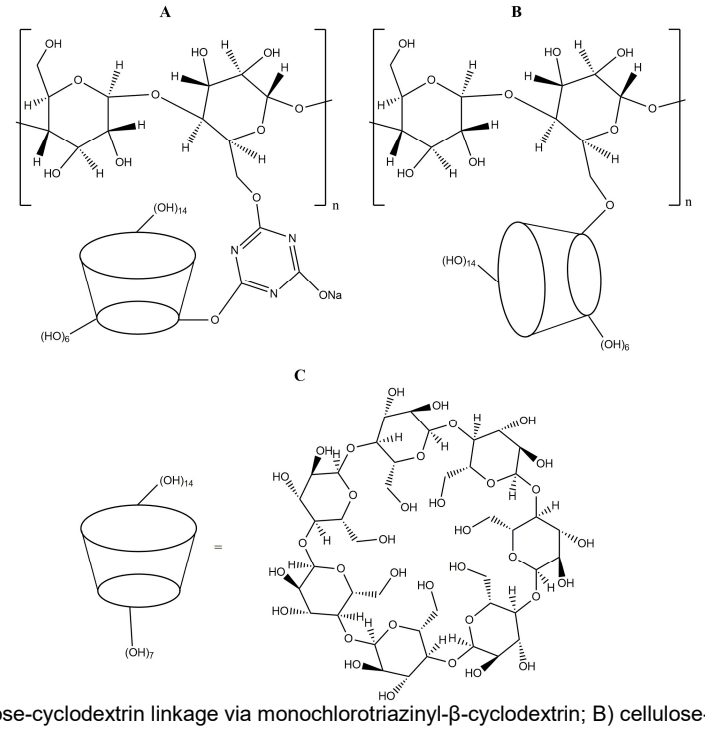
Cellulose surfaces such as paper sheets, cotton fabrics or nanocellulose films can benefit from having cyclodextrin molecules covalently linked to the polymer chains. Applications include the controlled release of fragrances, the removal of undesired species and the protection of active compounds from degradation. Those chemical bonds are usually attained by means of crosslinkers, namely citric acid, epichlorohydrin, or butanetetracarboxylic acid (BTCA).[1] Alternatively, the cyclodextrin is previously modified with a monochlorotriazinyl functional (Scheme 1A) group or with *N*-methylolacrylamide,[2] which are highly reactive towards nucleophilic substitution and condensation, respectively. Nonetheless, either way, a moiety remains in the final compound, between the cellulose chain and the macrocycle.
In this work, an approach without crosslinkers is suggested with the aim of attaching β-cyclodextrin to a cellulosic matrix, neither keeping nitrogen atoms nor labile ester bonds in the end product (Scheme 1B). The binding of β-cyclodextrin (Scheme 1C) on α-cellulose was carried out by reacting tosylated cyclodextrin with sodium cellulosate in an aprotic solvent. β-cyclodextrin was first reacted with tosyl imidazole, according to the procedure proposed by Tan *et al*.[3] α-cellulose was alkalized in a non-aqueous medium. Then, direct etherification occured via a S_N2 mechanism. The percentage of available sites for inclusion was measured by gravimetry (weight gain), by spectrophotometry with phenolphthalein and by acid-base titration following inclusion of cyclohexylamine. Solid-state grafting with BTCA was performed for comparison purposes. While the attachment of cyclodextrin to cellulose by direct etherification yielded poorer results, it stands as one of the few ways to have a cellulose-cyclodextrin derivative without the presence of moieties from other chemicals in the molecular structure.



Scheme 1: A) Cellulose-cyclodextrin linkage via monochlorotriazinyl-β-cyclodextrin; B) cellulose-cyclodextrin ether via monotosyl-β-cyclodextrin; C) structure of β-cyclodextrin.

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OC8

Turning surface wave turbulence into coherent hydrodynamic structures

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Hydrodynamic turbulence is involved in a wide diversity of phenomena which include stellar plasma, ocean waves, atmospheric currents, magnetic waves in solids and so on; It is based on energy transition from large to small scales and vice versa by a nonlinear interaction among the fundamental constituents of the system, as waves, particles, spin moments or fluid masses[1]. The particular scenario of the wave turbulence on the surface of viscoelastic material under the action of external force, which is sustained against the viscous dissipation, leads to the possibility of creating patterns and consequently, liquid templates in order to be able to exercise control over fluid motion[2]. Here, we expose a study carried out with distinct type of soft matter as colloidal suspensions, polymeric solutions and surfactants, where, by changing surface physical and chemical properties, we transform chaotic wave motion into coherent structures (Figure 1). These metafluids develop a great variety of behaviours like collective assemble in polyhedrons or parametric waves ordered in solid lattices. With our result we demonstrate a paradigm for creating a novel type of material that is far from physical equilibrium and simultaneously allows a direct control on the surface propagating waves.

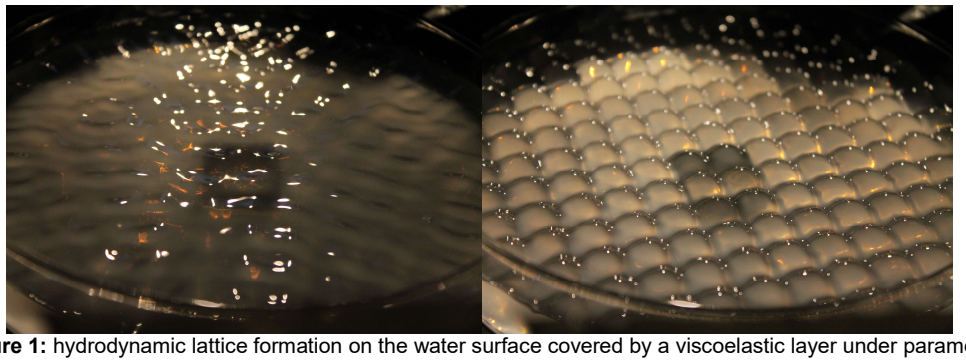

Figure 1: hydrodynamic lattice formation on the water surface covered by a viscoelastic layer under parametric excitation. The amplitude of vertical agitation increases from left to right while the chaotic waves are ordered in dynamic crystal

Acknowledgements: This work was supported by MINECO (FIs2015-70339-C2-1-R).

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OC9

Transparent Electrodes for Optical and Electrochemical Biosensor Applications

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Biosensing technology keeps rapidly evolving thus, offering better answers for the high demands of point-of-care devices. Nowadays, biosensors should be low-cost, disposable, of quick response, portable, as well as display outstanding sensitivity and reliability of results. New approaches based on combined responses and bioinspired materials show great promise for the required improved sensitivity and accuracy of biosensors. Herein, a novel design relying on combination of optical and electrical functionalities applied to detect cancer biomarkers is presented.

Molecular imprinting tecnique was used as main strategy for the selective recognition of a protein cancer biomarker, the carcinoembryonic antigen (CEA). The sensing layer consisted of a highly ordered colloidal array of nanoparticles that was assembled with the molecular imprinted polymer. Polypyrrole embedded the synthetic nanocavities as complementary recognition sites for CEA. The sensor was constructed on glass transparent conductive electrodes prepared by laser direct writing. The analytical features were assessed both by electrochemical and optical measurements upon biomarker recognition.

The developed sensor displays significant advantages as a label-free, simple, and low-cost solution that may be used for point-of-care detection of cancer related biomarkers. Moreover, the dual detection method demonstrates sensitivity and stability properties very promising to improve the diagnosis of cancer diseases.

Acknowledgements: We thank the Fundação para a Ciência e a Tecnologia for PhD grants PD/BD/142776/2018 and SFRH/BD/115173/2016. The project IBEROS (INTERREG POCTEP/0245_IBEROS_1_E) is gratefully acknowledged for financial support.

OC10

Microfluidics for controlled self-assembly of cubosome nanoparticles of tunable size

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Cubosomes are nano-sized dispersions of bicontinuous cubic liquid-crystalline phases. Typically they are composed of lipid and water and stabilized with a hydrophilic polymer. Compared to liposomes, these particles have a nanostructured interior with a higher fraction of lipid, being ideal to deliver bioactive hydrophobic molecules in health and food applications[1]. Cubosomes are typically prepared either by fragmenting the cubic liquid crystal in excess water using high energy input (e.g. ultra-sonication), or using solvent-shifting approaches, in which the lipid is first dissolved in a water-miscible solvent (typically ethanol), and later mixed with water and polymer stabilizer[2]. In both cases, poor experimental control at the micron- and nanoscales (e.g. poor control on concentration and heat gradients), limits the fine tuning of the particle properties and results in cubosomes with broad size distributions. In this work, we employ the solvent-exchange method using a microfluidic device[3], achieving rapid and controlled mixing at the micron-scale and obtaining cubosomes of tunable size and low polydispersity. The micron-sized channels in microfluidics lead to laminar flow regimes and enhanced experimental control. In this regime, hydrodynamic focusing can be used to decrease the mixing time between the different components, by decreasing the distances that molecules must travel for total mixing. An ethanol-lipid solution is flowed in a central inlet, which is squeezed by two side streams of water with stabilizer. As the lipid-ethanol solution narrows, ethanol and water are mixed in a controlled way by diffusion, leading to formation of cubosomes (figure 1). By manipulating the flow rate ratio (Q_R) between the two solutions we manipulate the width in which the hydrodynamic focusing occurs, influencing the assembly time in a homogeneous way. This way, by manipulating the Q_R, we are able to tune the size of the cubosome nanoparticles. Nanoparticle size is a key parameter in drug delivery, and being able to control it is therefore a relevant step towards the design of new and more efficient formulations.

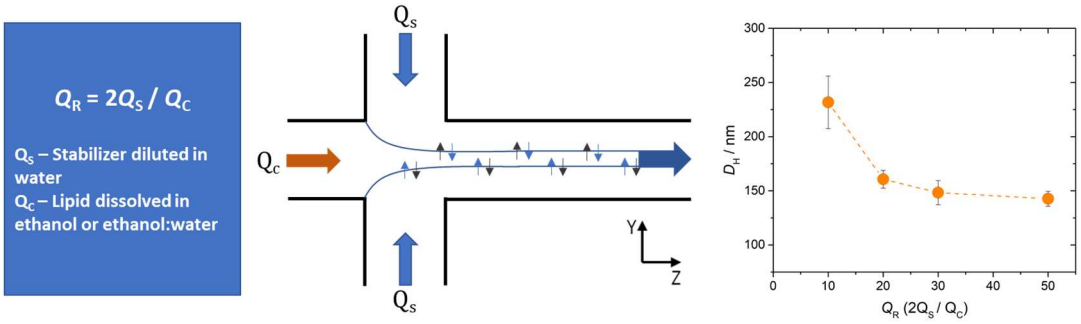

Figure 1: Schematic representation of the experiment setup. The calculated Q_R is used to manipulate the ratio in which the side solutions (Q_S) and centre solution (Q_C) are injected inside the microfluidic device. As the Q_R is changed inside the device, the centre solution has its width decreased which results in a shorter mixing time between the solvents. The change in time is translated in different particle sizes. The obtained samples from the device are later characterized using Dynamic Light Scattering (DLS).

Acknowledgements: This research is supported by Microfluidic Layer-by-layer Assembly of Cationic Liposome - Nucleic Acid Nanoparticles for Gene Delivery project (032520) co-funded by FCT and the ERDF through COMPETE2020.

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OC11

Bottom-up fabrication of organic nanofibers via ionic self-assembly

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Self-assembly is versatile strategy for the synthesis of nanomaterials with a low energy penalty[1]. Several non-convalent interactions can be tuned to obtain specific structures at various length scales. Herein, using dyes as charged planar building blocks, we explore the potential of ionic self-assembly for the construction of organic nanofibers. Specifically, we have selected chromonic dye molecules, i.e. molecules with a polyaromatic core and peripheral ionic groups that form long and oriented molecular stacks in water as a result of $\pi-\pi$ stacking interactions[2,3]. By using oppositely charged chromonics, the structure of the stacks can be fixed and insoluble nanofibers precipitate from the solution. The obtained nanofibers have been characterized by several experimental techniques such as Transmission (TEM) and Scanning Electron Microscopy (SEM), X-ray difraction and spectroscopy, among others. The obtained organic nanofibers can have very high aspect ratio and are crystalline. Moreover, they show aggregation and solvent dependent optical properties. Carbon nanofibers can also be obtained by carbonization of the organic nanofibers that give a high carbon yield. The materials show potential for applications in sensing and supercapacitors.

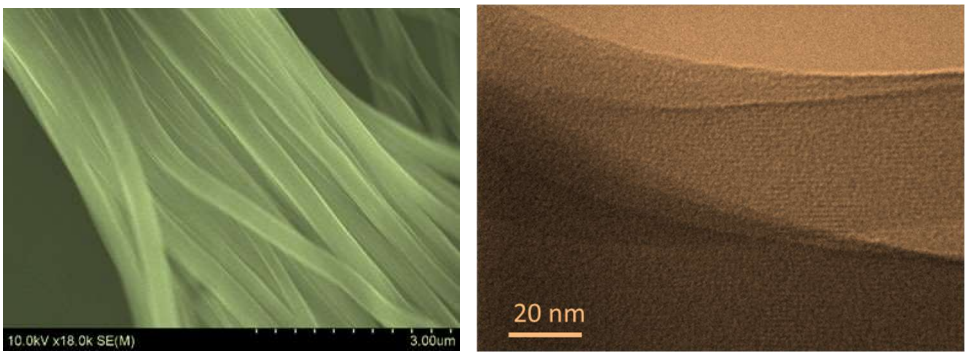

Figure 1: SEM (left) and TEM (right) images of organic nanofibers obtained by ionic self-assembly

Acknowledgements: Financial support from the Ministry of Science, Innovation and Universities of Spain (grant CTQ2017-84998-P) and CSIC (I-LINK1188) is gratefully acknowledged.

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OC12

Label-free quantum dot conjugates for human protein IL-2 based on molecularly imprinted polymer

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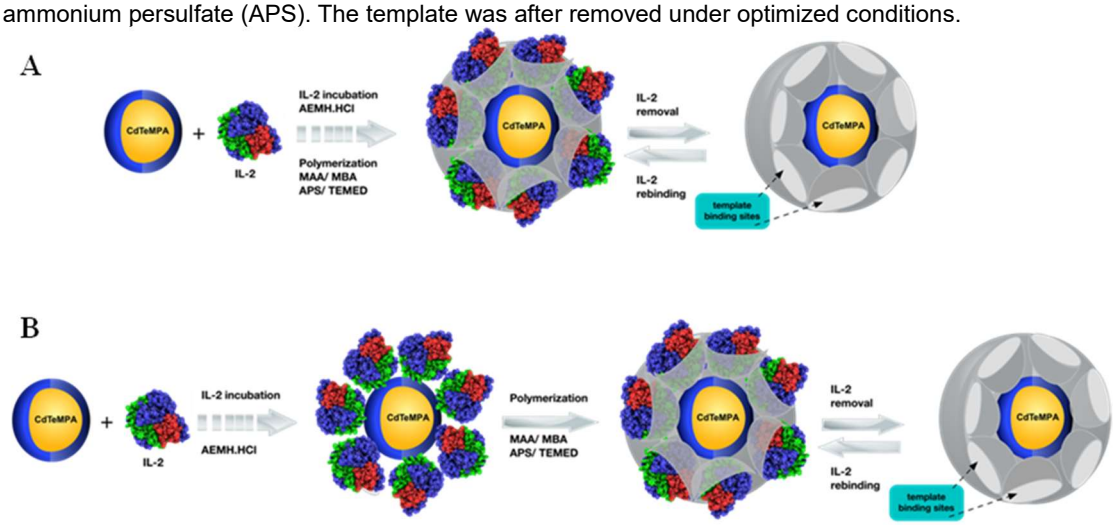
The development of a fluorescent-based sensor by combining quantum dots (QDs) with molecularly-imprinted technology (MIP), intensively optimized to generate exceptional operating features is presented. This sensor is designed to target human interleukin-2 (IL-2) in synthetic human serum. IL-2 is a regulatory protein released as a triggered response from the immune system towards an inflammation[1].
For this purpose, cadmium telluride (CdTe) QDs are prepared with 3-mercaptopropionic acid (MPA) and modified afterwards to produce an IL-2 imprinted polymer. This was made by first incubating IL-2 in PBS with aminoethyl methacrylate hydrochloride (AEMH), and polymerizing after with methacrylic acid (MAA) and *N,N´*-methylenebis(acrylamide) (MBA), upon initiation with tetramethylethylenediamine (TEMED) and ammonium persulfate (APS). The template was after removed under optimized conditions.



Scheme 1: (**A**) Bulk imprinting strategy for the preparation of the conjugated-QDs; (**B**) Surface imprinting strategy for the preparation of the conjugated-QDs.

During IL-2 rebinding, the fluorescence intensity of CdTe-MPA QDs is quenched in a concentration dependent manner (Scheme 1). Optimal fluorescence signals yielded a linear response versus logarithm of IL-2 concentration from 35 fg/mL to 39 pg/mL, in a 1000-fold diluted synthetic human serum. The limit of detection obtained is 5.91 fg/mL, lying below the concentration levels of clinical interest[2].
Overall, the method presented herein is a demonstration that the combination of MIP and QDs for protein detection constitutes a powerful tool in clinical analysis, providing low cost, sensitive and quick responses. The same concept may be further extended to other proteins of interest.

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OC13

Photodegradation of adsorbable organic halides (AOX) from pulp and paper industry wastewater using TiO2 nanomaterials

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Adsorbable organic halides (AOX) generated in the pulp and paper industry during the bleaching process are majority recalcitrant and have long half-life periods producing noxious effects to the surroundings and human health if released on the environment. In order to meet increasingly stringent discharge limits, pulp mills are forced to adopt technologically advanced treatment systems. Several industrial wastewater treatments have been developed[1], but are still non-destructive for recalcitrant material, such as AOX. Advanced Oxidation Processes (AOP) emerged as powerful alternatives for organic pollutants not treatable by conventional techniques, due to the high chemical stability and/or low biodegradability. These processes are based on the generation of highly reactive hydroxyl radicals which mineralize organic matter efficiently in the presence of oxidants whose activity is enhanced by UV light. Among the various AOP, semiconductor photocatalysis is an attractive process because it causes extensive mineralization of a wide range of organics with minimal environmental impact.[2] Titanium dioxide (TiO_2) has been the most used semiconductor photocatalyst for effluent treatment because it is relatively inexpensive, photo-stable over a wide range of pH and the photogenerated holes-electrons are efficient in producing highly reactive oxygen species.[3] This makes TiO_2 an efficient photocatalyst to decrease AOX concentration in cellulose bleaching effluent, in the presence of UV radiation and under suitable conditions.[4] However, the recycling of this photocatalysts is a major drawback. Thus, new industrial solutions for the sustainable reuse of the starting materials, avoiding costly and time consuming processes in their reuse or disposal are needed.

This work is motivated by the need to produce TiO_2 photocatalysts with high photocatalytic efficiency and that can be easily recovered from the effluent after treatment. Herein magnetic nano-TiO_2 particles have been investigated. The photocatalytic activity of these materials on the degradation of AOX from bleaching stream of Kraft pulp making process, as well as, the reuse of photocatalysts in consecutive phodegradation assays was studied and will be discussed.

Acknowledgements: This work is financed by Portugal 2020 through European Regional Development Fund (ERDF) in the frame of Operational Competitiveness and Internationalization Programme (POCI) in the scope of the project PROTEUS - POCI-01-0247-FEDER-017729. This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, FCT Ref. UID/CTM/50011/2019, financed by national funds through the FCT/MCTES. Ana C. Estrada also acknowledges the costs resulting from the FCT hirings funded by national funds (OE), through FCT – Fundação para a Ciência e a Tecnologia, I.P., in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19. A.L Daniel-da Silva acknowledges FCT for the IF-2014 FCT Investigator Programme.

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OC14

Heavy metal uptake with silica aerogels and xerogels modified with amines

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Aerogels are nanostructured, lightweight materials of outstanding properties, such as high surface area and small pore sizes[1]. Sol-gel chemistry enables the manipulation of the surface chemistry, whose modification with appropriate functional groups, allows aerogels to be tailored for specific applications. One of the most recent applications is their use as adsorbents, with particular emphasis for heavy metals [2]. In this work, silica gels were modified with different amine-containing groups to obtain non-selective adsorbents for heavy metals removal from wastewaters. Because the amine groups act as Lewis bases and the metal cations as Lewis acids, the adsorbent and adsorbate phases interact strongly, in agreement with the HSAB theory [3]. The gels were dried using two distinct approaches, one to obtain aerogels that feature no structural changes during drying, and the other to prepare xerogels, which shrink during solvent evaporation. These changes allow the synthesis of materials with the same chemical composition but significantly different physical properties (*e.g.*, surface area and porosity). The adsorptive performance of each counterpart is compared and used as criterion for the selection of the best drying approach. It is found that, in most cases, very similar results are obtained. The best performing materials were studied through batch equilibria and kinetic tests, with copper, lead, cadmium and nickel. In single-metal solutions, very high uptakes are obtained even at pollutant concentrations up to 100 mg/L. With higher amounts of adsorbent, more than 70% of the metal is removed in one batch from a starting concentration of 500 mg/L. The adsorptive process is fast, with the majority of metal ions being removed in less than 1 hour for the best cases. Insights on the sorption mechanisms reveal that the removal is due not only to complexation, but also to other mechanisms such as precipitation at the surface of the adsorbent.

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OC15

Effect of the Capping Ligand on the Electrocatalytic Performance of Gold Nanoparticles for Fuel Cell- and Water Splitting-Cathodes

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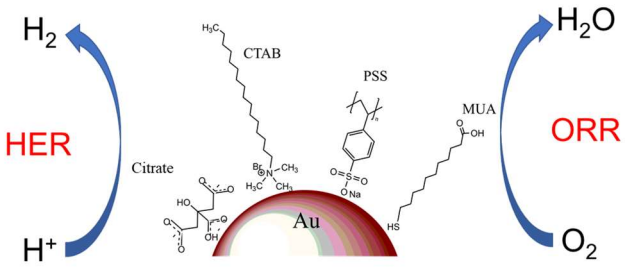
Oxygen reduction (ORR) and hydrogen evolution (HER) reactions are the most important cathodic processes involved on fuel cell and water splitting technologies, respectively.[1-3] The development of bifunctional electrocatalysts materials unambiguously plays a key role on the rapid advance of these renewable energy sources. For the first time ever, this work proposes 15 nm citrate-stabilized gold nanoparticles (AuNPs) as bifunctional electrocatalysts for ORR and HER, and also reports the drastic influence of the capping ligand on their resulting electrocatalytic performance (Scheme). For this, a simple ligand exchange method based on concentration gradient was optimized and its successful was demonstrated using several characterization techniques. In addition, the surface structure of the different ligand-stabilized AuNPs was inferred by lead underpotential deposition. Static and dynamic electrochemical studies for both ORR and HER were performed using different ligand-stabilized AuNPs as electrocatalysts, demonstrating that, among the proposed capping agents, citrate ligand confers the best performance. This procedure can be useful to explore other capping ligand types, which could enhance the electrocatalytic performance of bifunctional Au-cores. Furthermore, the reported approach can be extrapolated to other metal based nanocatalysts.



Scheme: The different ligand-stabilized AuNPs proposed as bifunctional electrocatalysts.

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OC16

How does surfactant act to separate different dyes using an aqueous two-phase system?

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Aqueous two-phase systems (ATPS) are formed mainly by water and other two components (e.g., a polymer and a salt), and they have been extensively used as a green alternative to remove compounds such as metal ions, dyes, nanomaterials or biomolecules from aqueous matrices[1]. Recently, we have investigated the use of the cationic surfactant hexadecyltrimethylammonium bromide (C_{16}TAB) as an additive to separate two oppositely charged dyes, remazol yellow (RY) and methylene blue (MB), by the different phases of an ATPS. Despite of the efficiency of this separation process, its mechanism was not yet fully understood. The description of this mechanism is important to extend the separation process to other types of molecules in similar systems. In this work we investigated how C_{16}TAB affects the RY and MB partition in ATPSs formed by poly(ethylene oxide) (PEG) and sulfate salts, at different surfactant concentrations. For understanding the ability of the surfactant in the selective modification of the RY partition in ATPS, we have also investigated the effect of the surfactant alkyl chain length on the interaction surfactant-dye. For that, we have used the following cationic surfactants: dodecyl, tetradecyl, and hexadecyltrimethylammonium bromide (C_{12}TAB, C_{14}TAB, and C_{16}TAB) in water and in aqueous solutions of PEG and sulfate salts. The different solutions were characterized by conductometry, tensiometry (Figure 1-a), isothermal titration calorimetry (Figure 1-b), and NMR spectroscopy techniques. It has been found that the partition of the RY is highly dependent on the C_{16}TAB concentration. That is, in the absence of C_{16}TAB, both dyes are concentrated at the top phase of the system; however, by increasing the C_{16}TAB concentration, the concentration of RY at the bottom phase increases. In the limit, the partition coefficient of RY between the top and bottom phases reaches a value lower than 1, whilst MB is only slightly affected (Figure 1-c). This behavior was favored in ATPS formed by high molecular weight PEG or magnesium sulfate. The RY was found to interact with C_nTAB surfactants forming different structures: small soluble aggregates, insoluble aggregates, pre-micelles, and mixed micelles. It can be seen that the occurrence of C_nTAB-RY interactions is dependent on the alkyl chain length, suggesting that the formation of aggregates are dependent on both electrostatic and hydrophobic interactions. Besides, the C_nTAB-RY molar ratios at which phase transitions is occurring are also dependent on the temperature.

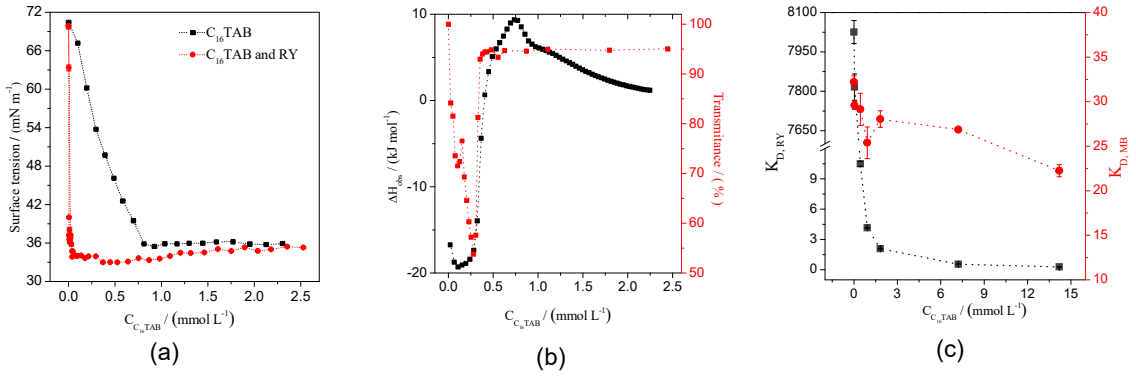

Figure 1. Effect of C_{16}TAB on the surface tension **(a)**, and enthalpy and turbidity **(b)** of RY (0.025 mmol L^{-1}) aqueous solutions, at 25ºC. **(c)** Effect of the C_{16}TAB concentration on the distribution coefficients ($K_{(D,dye)}$) for RY and MB in the ATPS formed by PEG 1500 + $(NH_4)_2SO_4$ + water at 25ºC.

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OC17

Polymer nanoparticles with reversible crosslinking for coatings

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Water-borne polymer nanoparticles have proven their value as nanomaterials for coating applications with reduced environmental impact and mechanical high-performance. [1,2] On the other hand, synthetic self-healing materials are a class of new emerging smart materials with the ability to self-repair physical damage. [3,4]. Here, we combine both approaches by developing water dispersions of polymer nanoparticles that form films by polymer diffusion and dynamic covalent chemistry. The low glass transition temperature of poly(butyl methacrylate) (PBMA) provides high mobility of the macromolecules and allow simultaneous actuation of reversible imine crosslinking. [4] The mobility of the polymer chains during film formation depends on the temperature, chain length and degree of cross-linking, and can be assessed by fluorescence methods. [5]
We developed aqueous dispersions of monodisperse polymer nanoparticles, either functionalized with aldehyde or with amine groups (Figure 1). In films cast from a mixture of both dispersions, interdiffusion of the polymer chains promotes the contact between the two functional groups (aldehyde/amine), originating the crosslinking reaction. The imine bond is reversible in the presence of water, allowing the healing of damage to the films.

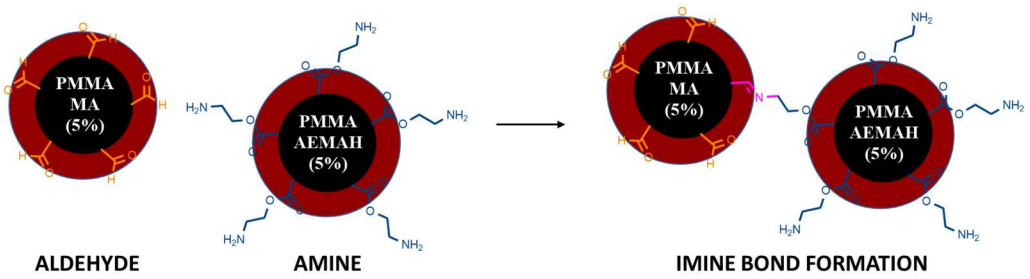

Figure 1: Reversible crosslinking: imine bond formation.

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OC18

Optical devices for DNA detection and quantification for food & Environmental Applications

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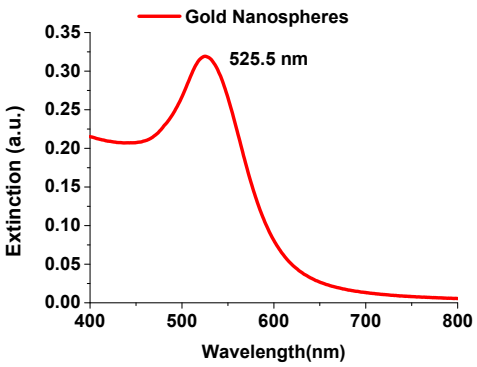
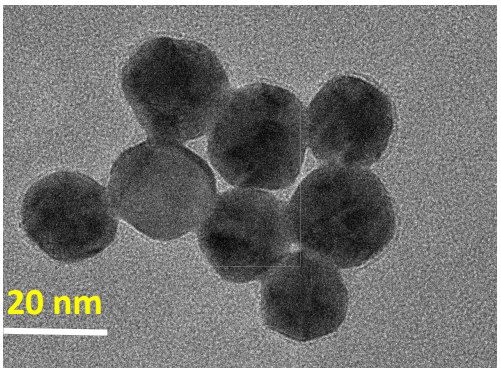
This work involves development of an optical sensing platform based on the colorimetric response of the gold nanospheres interfaced with oligonucleotides for the detection of environmental DNA(edna) from invasive species. Zebra Mussel (ZM),*Dreissena polymorpha* are invasive species that causes severe damages economically as well as environmentally.Early detection of Zebra mussels eDNA is significant to avoid their rapid increase in the enviroment. Gold nanoparticles, due to their unique optical properties will be functionalized with DNA probes able to capture the complementary target resulting in hybridization events.

The method involves Gold nanoparticle synthesis done by citrate reduction method, and their characterization by Uv vis spectroscopy where in, the maximum peak position of gold nanospheres is found to be around 525.5 nm and Size of the gold nanoparticles are found to be 23.3 ± 1.6 nm per 300 Nanoparticles. Loading DNA probes around the nanoparticles is done by salt ageing[1]/ Low pH method[2]. The method that has maximum loading is compared. The Loading of DNA around Nanoparticles is confirmed by Dynamic light scattering measurements and the number of DNA around nanoparticles is approximately measured through oligreen test using micro platter. Hybridization tests are carried out based on the principle that, the Single strand DNA (ssDNA) targets and the DNA probes on the gold nanoparticle surface forming a complex decreasing the interparticle distance and causing aggregation[3]. Finally, this detection system is implemented in a portable optical sensing device. This portable, simple and rapid optical sensing device is not only useful in Environmental applications but also in other fields such as food analysis or health.



(1)



(2)

Figure 1: Maximum peak position of gold nanoparticles by UV-vis spectroscopy
Figure 2: Size of the gold nanoparticles by Transmission electron Microscopy

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OC19

Glass-based biosensing device for monitoring CA15-3 cancer biomarker

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Cancer is a leading cause of death worldwide, being breast cancer amongst the most common forms of the disease. Advances in health-related practices have anticipated the detection of breast cancer and allowed establishing appropriate follow-up procedures. Monitoring circulating biomarkers as CA15-3 is amongst the several tools used to this end. Thus, there is great interest in developing new biosensors for CA15-3 that are suitable for a point-of-care (POC) use.

This work describes the application of an eco-friendly substrate to assembly a new sensor for CA15-3 detection in POC. It consists in the development of an artificial antibody based on molecularly imprinted polymer (MIP) technology and electropolymerization of *o*-phenylenediamine (*o*-PD). The polymer was tailored on a glass microscope slide hand-coated with a commercial conductive carbon inks based on screen-printed electrodes technique (C-glass SPEs). Afterwards, the surface was modified with platinum nanoparticles (Pt NPs), followed by a bottom-up assembly of the artificial antibody for CA15-3 detection.

The analytical performance of the resulting devices was performed through square wave voltammetry (SWV) and electrochemical impedance spectroscopy (EIS), showing sensitive readings for CA15-3 concentrations ranging between 1.0 mU/mL and 100.0 U/mL in phosphate buffer (PB) pH7.50, with limit of detection (LOD) below 1.4 mU/mL. Chemical modifications of the surface were characterized using a confocal Raman-AFM spectroscopy and Scanning Electronic Microscopy (SEM). In general, the CA15-3 artificial antibody was successfully applied in spiked fetal bovine serum (FBS) samples, demonstrating linear responses below to the normal physiological levels (30.0 U/mL). Therefore, the developed sensing material may be a simple, selective and a promising tool to monitor this cancer biomarker in a clinical context.

***Keywords*:** Cancer, CA15-3 biomarker, Protein surface imprinting, Glass substrate, Homemade screen-printed electrodes (C-glass SPEs).

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OC20

Bioinspired Polydopamine Nanocolloid-Stem Cell Combinations for Targeted Chemo-Phototherapy in 3D Microtumor Models

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The use of bioinspired, colloidal polydopamine nanoparticles for biomedical applications has received a growing interest in the past decade due to their inherent bioadhesivenes, high drug-loading capacity and bioimaging capabilities [1]. The potential of polydopamine (PDA) nanoparticles for multimodal cancer therapy has also been very atractive due to the possibility to explore synergistic chemo-phototherapy in cancer due to PDA inherent photothermal response under near infra-red (NIR) light [1]. Despite various advantages, PDA nanoparticles selectivity to cancer cells is poorly specific, thus limiting the realistic applicability of these colloids. In this context, trojan horse inspired therapies using nanoparticles internalized in stem cells [2], such as human bone marrow derived mesenchymal stem cells (MSCs), provides a promising alternative to increase the bioavailability of drug delivery systems in inflammation or tumor sites due to the natural tropism of MSCs to these unique microenvironments *in vivo* [3]. Herein, we formulated Doxorubicin-ICG dual loaded bioinspired PDA nanocolloids for stem cell-based delivery to improve particles bioavailability in cancer cells. PDA nanoparticles exhibited an average diameter of (94.05 ± 0.76 nm), negative surface charge (Figure 1A) and a high drug loading capacity ~99%. These particles were highly stable in complete cell culture medium and were readily internalized by hBM-MSCs (Figure 1B). Interestingly, PDA nanocolloid-stem cell trojan horse combinations were able to be incorporated in dense 3D *in vitro* tumor models comprised by metastatic MDA-MB-231 breast cancer cells (Figure 1C). Moreover, following irradiation with NIR light (808 nm) 3D microtumors presented higher cellular death in comparison to non-irradiated controls. Overall, the explored PDA-stem cell trojan horse approach has demonstrated potential to be used for multimodal chemo-photothermal therapy of solid tumors in a foreseable future.

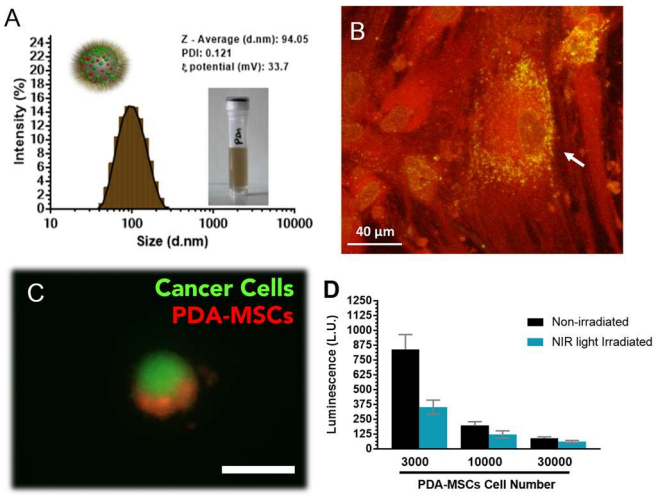

Figure 1: A) DLS analysis of PDA nanocolloids. B) Confocal micrographs of PDA Nanoparticles uptake in hBM-MSCs. (Green channel – PDA; Red channel – cell membrane). C) PDA-stem cell attachment to breast cancer solid 3D *in vitro* tumor models. D) ATP analysis of 3D *in vitro* tumor models incubated with PDA-MSCs and irradiated with NIR light.

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OC21

Biopolymeric photonic sensing of cancer protein biomarkers

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Determining cancer disease indicators such as proteins in biofluids demands selective and accurate methods, which are not currently available or entail high costs. Biosensors based on molecularly imprinted polymers (MIPs) are a promising tool for low cost, fast and selective detection of biomarkers.

MIPs are polymeric matrices with a predetermined selectivity and specificity for a given analyte, thus being able to mimic natural recognition molecules, as antibodies and cell receptors. Therefore, it is possible to use MIPs to recognize proteins, amino acids, peptides or nucleotides, as well as synthetic chemicals. Furthermore, they are stable and resistant to a wide range of temperature, pressure, solvents and pH conditions[1]. Therefore, our aim is to develop a MIP for the specific recognition of a protein cancer biomarker (e.g., carbohydrate antigen 15-3, CA15-3), to overcome the limitations of the current diagnostic methods.

Herein, the sensor is constructed on a biopolymer matrix to meet the requirements of an eco-friendly disposable device, and it is based on a photonic crystal assembled within the imprinted polymer. After removal of the biomarker molecule, specific recognition cavities assure the selective recognition of the biomarker. Since the photonic crystal is constituted by periodic arrangements of regularly shaped colloidal nanoparticles[2], their optical properties depend on the type of material, shape, size of the particles and space between them.

A label-free detection is thus envisioned and the sensor performance is evaluated by changes in the optical properties when the protein cancer biomarker is present. The aim is to obtain a sensor with a low detection limit, fast response, high selectivity, repeatability and reproducibility.

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OC22

Cationic lipids containing amino acid residues as siRNA nanovectors for gene therapy

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The discovery of RNA interface therapy has allowed the study of broad genetic diseases from a different point of view than through classical transfection. Thus, while plasmid DNA replace the wrong sequence that is causing celullar damage, small interfering RNAs (siRNAs) present the ability of silencing specific target genes. However, unprotected RNA is susceptible to degradation by nucleases present in the bloodstream while its negative charge prevents it from crossing the also negatively charged cellular membrane. Therefore, the use of a delivery strategy to introduce siRNAs in cells is necessary. Lipid vector-assisted delivery is an attractive option, specially with cationic lipids (CLs). The electrostatic interaction with double strains RNA stabilises the formation of complexes (lipoplexes), which are able to protect, transport and deliver silencing siRNAs into cells. Earlier studies[1] have demostrated that liposomal gene carriers based on gemini cationic lipid are efficient silencing vectors. Following this strategy, and with the aim to obtain higher circulation times and low immune adverse effects, gene nanovectors based on amino acid components within a cationic type lipid are presented. The silencing efficiency of lipoplexes formed by an anti-GFP siRNA and a mixed lipid composed of a helper neutral lipid (MOG) and a cationic lipid containing arginine or histidine residues, have been evaluated. Lipoplexes were physicochemically characterized by zeta potential, agarose electrophoresis, cryo-transmission electron microscopy and small-angle X-ray scattering. The gene-silencing activity was evaluated in EGFP expressing in HeLa cells through flow cytometry and fluorescence microscopy in presence of human serum. Cytotoxicity of lipoplexes has been studied by CCK8 experiments, while nano liquid chromatography tandem mass spectrometry (LC-MS/MS) experiments have been performed to examine the proteomic profile surrounding the lipoplex when it is incubated in human serum. Together, these *in vitro* studies have determined the silencing activity of these amino acid containing nanocarriers and represent the first steps for using them in future gene therapy applications.

Acknowledgements: This work was supported by projects CTQ2015-65972-R and CTQ2015-64425-C2-2-R.

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OC23

Up-converting nanoparticles as light sources for cellular activity modulation

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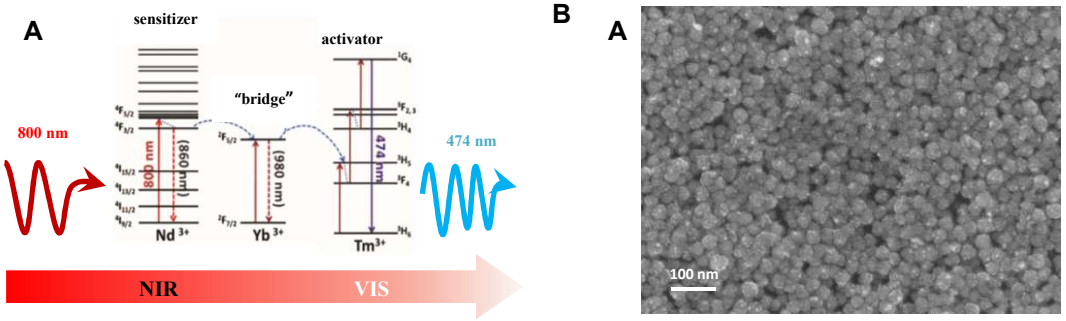
Light-triggered control of photochemical processes has emerged as a potential alternative therapy where light offers high spatiotemporal precision manipulation of live cell functioning [1]. In recent years, near-infrared light (NIR, 700-1000nm) with deep tissue penetrability and minimal invasiveness, has been successfully applied for imaging and therapy *in vivo*. Nevertheless, the vast majority of photoactuators available in living cells are efficient just under blue light [2]. Hence, it is necessary to find an approach that can effectively convert NIR light to visible light. Rare-earth up-converting nanoparticles (UC-NPs) can transform NIR light to visible light (Figure A) and can act then as nanotransducers for optical control of cellular activity mediated by photosensitive proteins.

Herein, we explore the potential application of UC-NPs as bio-activators for reversible oligomerization of modified *Arabidopsis thaliana* photoreceptor cryptochrome 2 (CRY2olig) optogenetic module in response to blue light. This photosensitive protein CRY2olig is fused to mCherry fluorescent protein (CRY2olig-mCherry) which acts as reporter to visualize and record the process by epi-fluorescence microscopy.

In this study, we report the fabrication of a nanostructured substrate based on UC-NPs assembly through layer-by-layer (LBL) technique (Figure B). Our preliminary studies show that HeLa cells grow successfully on the UC-NPs substrate and express CRY2olig-mCherry, which exhibits reversible oligomerization in response to blue light. Ongoing work aims to exploit this UC-NPs based system for optical control of photosensitive proteins, tool that will expand the growing arsenal of optogenetic strategies.



(A) Upconversion process of tri-dopants based UC-NPs. **(B)** Scanning electron microscopy (SEM) characterization of UC-NPs substrate.

Acknowledgements: A. Vazquez-Arias acknowledges the Ramon Areces Foundation for its financial support.

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OC24

A Seeded Growth Methodology based on Iron (II) for the Synthesis of Noble Metal Nanoparticles

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Metallic nanoparticles (NPs) have nowadays many applications from sensing or catalysis to biomedical approaches.[1] The huge versatility of these materials is mainly based on their optical properties which can be tuned controlling their size, shape and composition. In any case the synthesis of noble metal nanoparticles with narrow size distribution is still quite challenging. Spherical nanoparticles of different metals are an example of this. For instance, the synthetic procedure to obtain monodisperse gold nanoparticles needs tight temperature control, several synthetic steps and/or the use of different surfactants and polymers.[2]
This work opens up a new synthetic route to obtain spherical nanoparticles with different composition (Au, Au@Ag and Au@Pd) with narrow size distributions based on a seeded growth and using Fe(II) as mild reducing agent (**Figure 1**).
Taking advantage of the well-known seeded growth methodology[3] and the controlled addition of reagents through syringe pumps, different metal nanoparticles were synthesized. Small gold NPs were used as seeds and the overgrown with gold, silver or palladium has been done due to the ability of iron (II) to reduce[4] their corresponding metal salts precursors. Through the careful control of the Au seed to metal salt concentrations ratio it is possible to nicely tune the final particle size.
Interestingly, the proposed methodology give rise to particles stabilized by citrate ions which can be easily exchanged with different molecules (such as proteins or thiolated molecules) expanding the potential applicability of the particles in a number of fields.
In summary, we propose a new methodology that enables fast synthesis of different metal nanospheres, at room temperature, with size control in aqueous media.

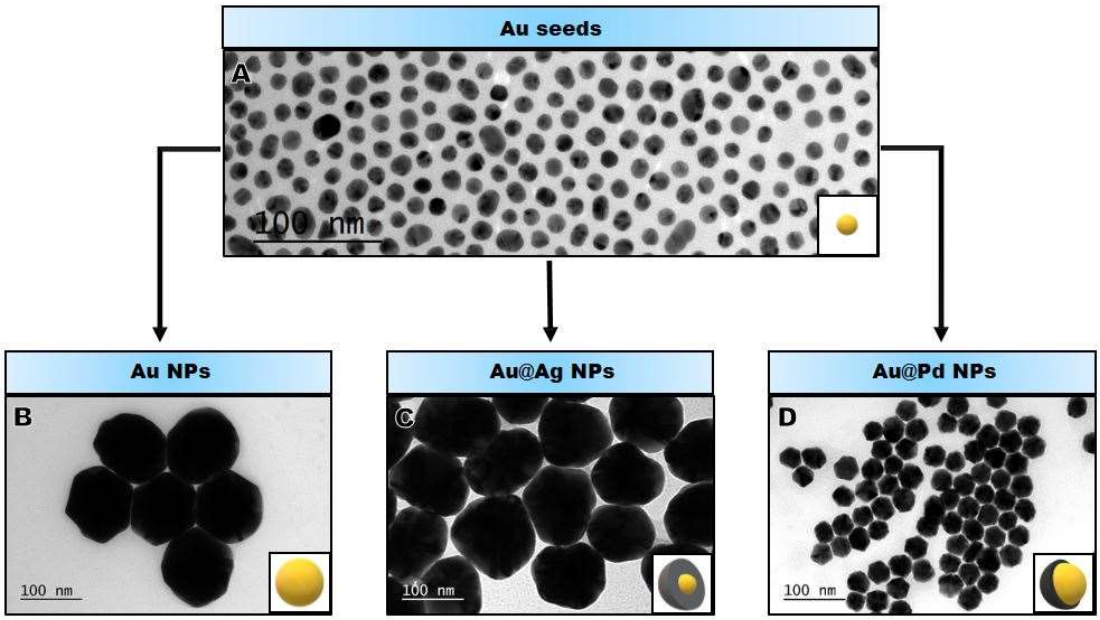

Figure 1: Schematic representation of different synthesized NPs: (A) Au Seeds, (B) Au NPs, (C) Au@Ag NPs and (D) Au@Pd NPs.

Acknowledgements: We thank the Spanish Ministerio de Economía y Competitividad (MAT 2016-15374) and Centro de Investigaciones Biomedicas, CINBIO (ED431G-02)

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OC25

New Insights on Cellulose Gelation in Aqueous Alkali

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Cellulose processing for new advanced materials is a rather challenging issue since dissolution is often an initial required step but far from being trivial. [1] The list of efficient solvent systems is limited, and current discussion is still not unanimous on the relevant solvent key features or interactions that drive dissolution. [2] Nevertheless, once dissolved, the cellulose solutions are typically metastable and thus sensitive to aging or pH and temperature changes, which may induce gelation-regeneration of the cellulose dopes. [3] Such gelation-regeneration phenomenon is still a poorly understood process but of major importance for the development of, for instance, cellulose-based films or fibers. [4] Among the solvent systems available, aqueous NaOH is a common solvent for cellulose dissolution particularly due to the fact that it is inexpensive and considered of low toxicity. [5] In this communication, cellulose gelation in aqueous NaOH will be explored using an unusual set of characterization methods for cellulose solutions, such as cryo-transmission electronic microscopy, polarization transfer solid-state nuclear magnetic resonance, diffusion wave spectroscopy and wide angle X-ray diffraction. [6] Moreover, the role of additives, such a urea, will be discussed.

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OC26

Thermal Energy Storage in Polymer-Based Micro- and Nanocapsules

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Energy storage systems are necessary to face the chronological mismatch between production and demand that renewable energies constantly suffer from. A promising contribution, object of current investigation, is the use of solid–liquid phase-change materials (PCMs), which store thermal energy in form of latent heat during the melting process and recover it during recrystallization [1]. PCMs are usually encapsulated to ensure the cyclability of the process, to avoid leakage, and to protect the surrounding media from negative effects, such as corrosion [2].

In this work, we present the encapsulation of both hydrophilic and hydrophobic PCMs in polymer or polymer/metal oxide hybrid capsules prepared by different colloidal techniques, all of them involving emulsification processes.

In the first part of the work, hydrated inorganic salts were encapsulated in polyurethane systems prepared by polyaddition in inverse miniemulsions, estabilized by so-called Pickering stabilization with magnetite, cerium oxide(IV), and/or titanium oxide(IV) nanoparticles. The inorganic nanoparticles, commercially purchased or synthesized in our laboratory, were first functionalized with octadecyl trimethoxysilane (ODTMS) following a procedure previously reported [3]. Capsules obtained by this procedure are typically in the micrometer/submicrometer range (Figure 1). The mean size of the capsules and the dispersity in the size distribution decreased very significantly in the presence of the hydrated salt, which acts as an osmotic pressure agent that contributes to the colloidal stability of the system during polymerization. As a remarkable aspect, we investigated the combination of more than one hydrated salt in the same material, which would result in PCM application at different temperatures.

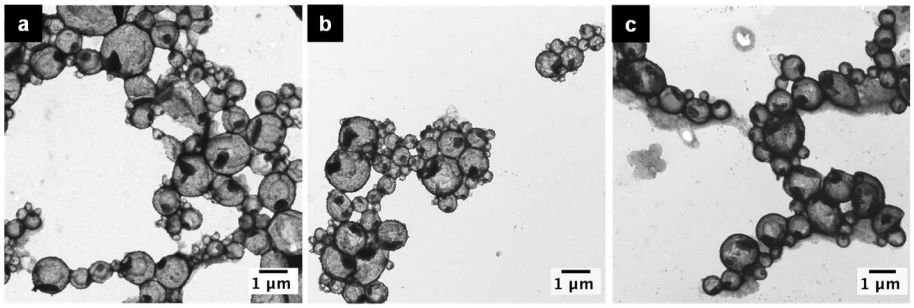

Figure 1: TEM micrographs of polyurethane capsules prepared by Pickering stabilization with (a) magnetite, (b) magnetite–titania (b), and (c) magnetite–ceria nanoparticles, encapsulating the hydrate salt $Na_2SO_4 \cdot 10H_2O$.

In the second part of the work, alkanes and fatty acids were encapsulated in polystyrene or poly(methyl methacrylate) systems prepared by two techniques: either by free radical polymerization in direct miniemulsion or by emulsion–solvent evaporation. As in the previous case, the combination of more than one PCM simultaneously was investigated. The resulting capsules have typical sizes below 200 nm.

The ability to store thermal energy of the different systems prepared was studied by differential scanning calorimetry (DSC). Supercooling problems (i.e., crystallization at significantly lower temperature than the melting point), common in PCMs, were corrected by the co-encapsulation of small amounts of a nucleating agent. The storage of thermal energy is efficient and reproducible after a large number of cycles.

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OC27

Fluorescence Cross-Correlation Spectroscopy as a Valuable Tool to Monitor Cationic Liposome-DNA Nanoparticle Assembly

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Cationic liposome–DNA (CL-DNA) nanoparticles consist of anionic DNA complexed with oppositely charged cationic liposomes (CLs). These nanoparticles are among the most promising non-viral vectors in gene delivery due to attractive advantages that include low immunogenicity, potential for large-scale production and high flexibility of functionalization. Albeit low transfection efficacy when compared to their viral analogues, there is still considerable room for improvement of these nanoparticles by introducing clever strategies tailored to overcome specific cellular barriers and immune defense mechanisms innate with systemic gene delivery. The main driving force for CL-DNA complex formation comes from the entropic gain resultant from counterion release when both components, CLs and DNA, neutralize each other[1]. However, the actual mechanism leading to the final compact state of such nanoparticles is complex and depends on the route of assembly[2]. It has been convincingly shown that manipulating colloidal interactions between DNA and CLs by varying parameters, such as, the amount of PEG, lipid membrane charge density and salt concentration, deeply impacts the number of lamellar layers and stability of the PEGylated CL-DNA nanoparticles formed[2]. This aspect can be explored to further tailor the structure and size of CL-DNA nanoparticles as a means of optimizing their interactions with biological systems and improve their therapeutic efficiency. In this work, we demonstrate how Fluorescence Cross-Correlation Spectroscopy (FCCS) can be used as a valuable characterization tool to monitor the assembly of CL-DNA nanoparticles. FCCS is able to measure the individual and correlated dynamics and motions of two different fluorescence dyes. Hence it provides a quantitative measure of the amount of colocalization between the dyes and their diffusion coefficients. By labeling cationic liposomes and DNA with different fluorescent probes we design novel experiments that reveal the intricate modes of complexation between CLs and DNA. In particular, by labeling liposomes with two different colors we propose a new method to evaluate the number of lamellar layers per CL-DNA nanoparticle.

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OC28

Structural color pigments base in colloidal assemblies

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Colloidal photonic crystals are widely found in nature. Their shining structural color arises from the modulation of the electromagnetic waves by Bragg reflection from photonic stop bands, originated from the periodic arrangement of nanoparticles that leads to selective reflectance of incident light. [1] Since no absorption of light is involved, materials with structural color show no photobleaching and can generate a wide range of colors in non-toxic and environmentally friendly ways. Synthetic non-iridescent structural color materials (with color that do not depend on the angle of observation) can be obtained from quasi-ordered colloidal arrangements (photonic glass), structures that possess only short-range order. [2] These find a wide range of potential applications including reflective displays, colorimetric sensors, textiles, etc. In this study we fabricated novel polymeric non-iridescent colloidal photonic pigments by two self-assembling approaches. One based on concentrated polymer microgels, [3] and the other on microspheres composed by polymer nanoparticles assembled by microfluidic droplet technology. To break long-range order, we added small amounts of black polydopamine nanoparticles that also act as incoherent light scattering absorbers, originating very bright and non-iridescent photonic pigments (**Figure 1**).

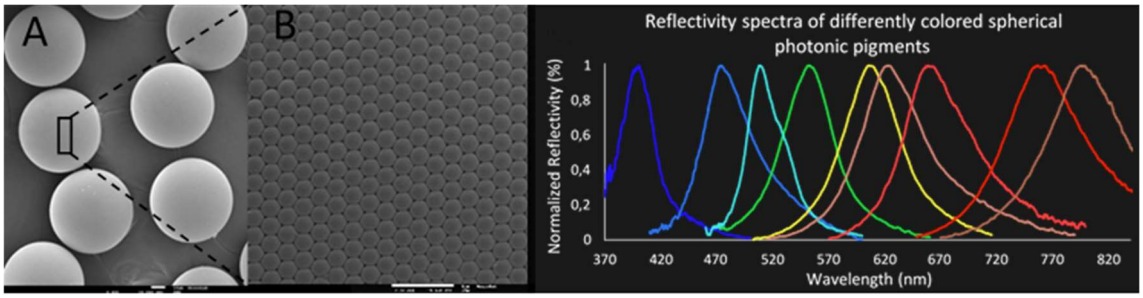

Figure 1: A) Highly monodisperse spherical photonic pigments of 55µm in diameter, obtained upon temperature induced self-assembling of polymeric nanoparticles inside emulsion droplets; B) Hexagonal closed packed arrangement of polymeric nanoparticles, 290 nm in diameter, at the spherical photonic pigment surface; C) Reflectance spectra of spherical photonic pigments with structural color, composed of differently sized polymeric nanoparticles (from 170 to 330 nm in diameter).

Acknowledgements: This work was supported by PhD grant PD/BD/113533/2015 and FCT-Portugal and COMPETE (FEDER) within projects PTDC/CTM-POL/3698/2014 and UID/NAN/50024/2013.

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OC29

Plasmonic nanocapsules as SERS tags for multiplex detection

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The unique optical properties of noble metal nanoparticles, NPs, arise from the so-called localized surface plasmon resonances (LSPRs). LSPRs are strongly dependent of NPs shape, size or composition. A wide range of methods based on wet chemistry have been developed to synthesize NPs with tailored optical properties. Recently our group has developed a strategy involving galvanic replacement reaction coupled seeded growth to fabricate Au/Ag nanorattles[1]. This work opens new venues towards the shape control of multimetallic hollowed nanostructures beyond the morphology of sacrificial templates.

Surface-enhanced Raman scattering (SERS) is an ultrasensitive technique which relies on the enhancement of the Raman scattering signals of a certain molecule when is close to a plasmonic nanostructure. This technique also allows the indirect identification of target molecules through the use of SERS tags, Raman encoded NPs, which comprises a specific Raman reporter attached to metallic NPs and often surrounded by a protected shell[2].

Herein we propose a new synthetic route to fabricate a SERS tag based on a room-temperature galvanic reaction coupled seeded growth method using Ag nanospheres (NSs) as sacrificial templates. During the process different Raman reporters could be trapped inside the resulting hollow Ag@Au NSs. The SERS tags NPs have been characterized by TEM revealing that the morphology of the sacrificial template remained after the reaction (Fig 1.A and B). Besides, we have analysed the SERS performance of the tags (Fig 1.C). This approach allowed us to codify the plasmonic particles with a library of Raman active molecules leading to the formation ultrasensitive SERS-encoded nanoparticles.

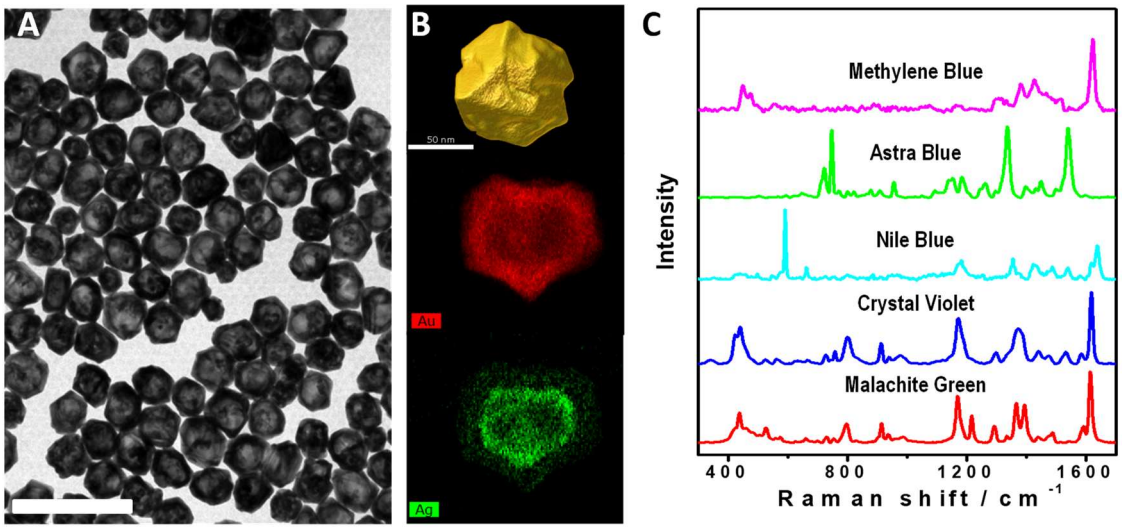

Figure 1: (A).Representative TEM image of the closed Au nanorattles. Scale bar is 200nm (B) 3D visualization of the tomographic reconstruction of Au nanorattle and EDX mapping showing the Ag and Au distribution. (C) SERS spectra of different Au nanorattles encoded with several Raman reporters as indicated.

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OC30

Nanotheranostics with microRNA: Application in radiotherapy

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Radiotherapy is one of the most widely approaches used for treating patients with prostate cancer (Pca).[1] There are two major limitations of this technique: the difficulty in delineating the contours of tumor volume for planning and problems associated with radioresistant mechanisms of tumor cells, resulting from mutations and disorders of gene expression.[2] One of the major regulatory mechanisms of gene expression occurs in the post-transcriptional stage by degradation of messenger RNA, where microRNAs play an important role in the pathogenesis of PCa.[3]

Therefore, this work proposes the development of a nanosystem based on gold nanoparticles (AuNP) with miRNA to improve diagnosis by computed tomography in the planning phase of the treatment and, simultaneously, increase the sensitivity of the cancer cells to radiotherapy. Radiosensitization tests shall be made in PC3 and LNCaP cells. The AuNPs are further modified with molecularly imprinted polymers (MIP), to enhance the affinity of the nanosystem to the therapeutic target and consequently contribute to reduce colateral damage in healthy tissues (Figure 1).

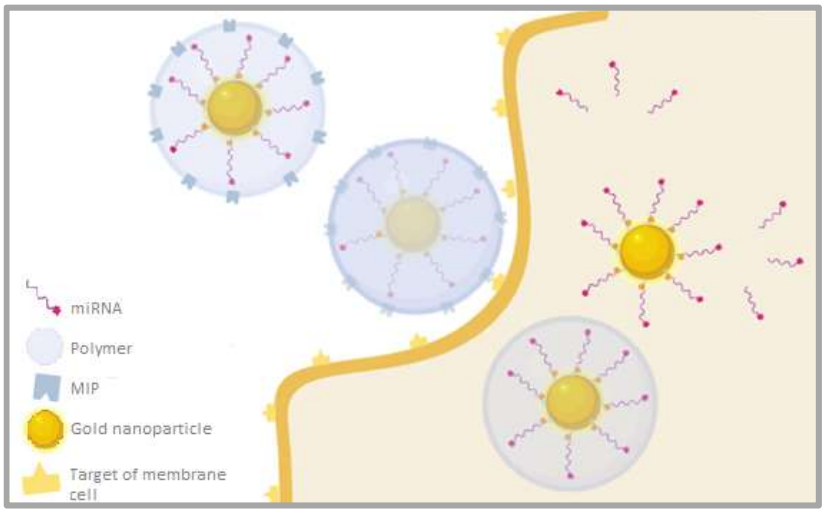

Figure 1: Gold nanoparticle with miRNA coating with polymer

Acknowledgements: The authors acknowledge the funding of project IBEROS, Instituto de Bioingeniería en Red para el Envejecimiento Saludable, POCTEP/0245-BEROS-1-E, PROGRAMA INTERREG 2014-2020, to FEDER within the cooperation region of Galiza/Spain and North of Portugal. SS is grateful for the financial support of Fundação para a Ciência e Tecnologia (grant reference: SFRH/BD/138271/2018).

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OC31

SERS-based immunosensing layer for cancer biomarker detection in point-of-care

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With the increasing incidence of cancer, its prevention becomes a major public challenge[1]. An earlier identification of the disease may result in a higher probability of survival, and a more effective and less expensive treatment. In this context, screening specific markers offer the additional advantages of allowing a non-invasive and relatively inexpensive process to detect cancer[2]. The early detection of these biochemical indicators can be helpful for cancer detection at an early stage, in people who have no symptoms of the disease[3].

Conventional methods in cancer detection are are reliable and accurate, but require long time and laborious work to reach results. In contrast, electrochemical immunosensors are widely used in the detection of cancer biomarkers because these methods are rapid and robust, while having an excellent sensitivity and specificity. These are quite competitive, in terms of cost, when compared with existing technologies, which will also develop to allow miniaturization and integration within other systems. At present, detection by electrochemical immunosensors has attracted considerable interest because responses are readily quantifiable[4].

Traditionally, fluorescence-based detection systems have been widely used as diagnostic tools for immunoassays; however, these systems have several drawbacks, including a poor limit-of-detection and photobleaching. A relatively novel readout strategy is Surface-Enhanced Raman Scattering (SERS), which seems to be very effective at overcoming the above limitations[5].

In this work we are presenting an immunosensor that combines the specificity of antigen-antibody binding with the novel detection capacity of the SERs technique, which has shown highly promising features for CEA detecion. The sensor showed linear range within 0.25 and 250 ng/mL.

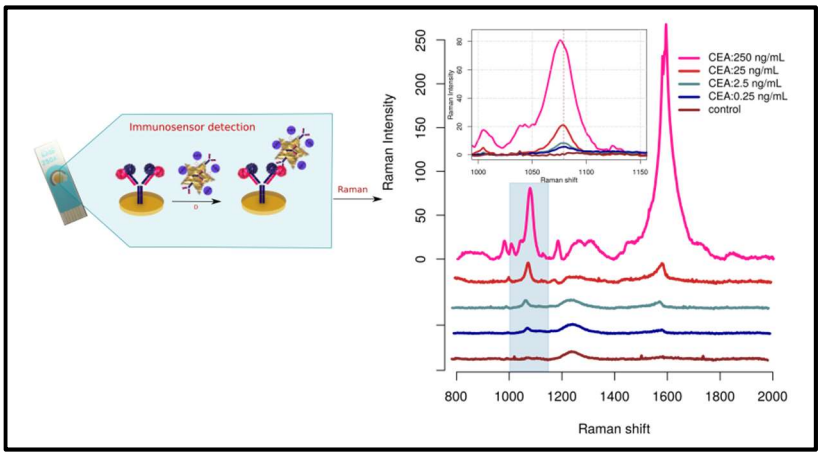

Figure 1: *Scheme for building of the CEA Raman probe detection. Linear range 0.25 ng/ml to 250 ng/ml.*

Acknowledgements: The authors acknowledge RamSERS, Development of a portable Raman Spectrometer for cancer biomarker detection, NORTE-01-0247-FEDER-017834 (call 33/SI/2015), supported by Norte2020, FEDER, COMPETE 2020.

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OC32

SERS-based multiplex detection of phenol derivatives

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Phenol and its derivatives are common pollutants in food and fresh water. Their presence could cause acute effects on human health and also long-term effects. The most common detection methods are chromatographic and colorimetric methods[1]. Typically, these methods involve complicated processes and sometimes expensive reagents. The detection of phenol derivatives in foods is interesting since they are considered as contaminants[2]. For instance, o-cresol is an analyte used in the detection of exposure to toluene, which can be measured in blood or urine[3]. In addition, the presence of 1-naphthol in urine samples may indicate that exposure to broad spectrum of insecticides such as carbaryl and naphthalene[4]. Therefore, the simultaneous detection of several phenol derivatives is very important and highly desirable.

Surface Enhanced Raman Spectroscopy (SERS) is a powerful technique that is gaining increase attention in last years in sensing field due to its very high sensitivity and selectivity with almost no need of sample preparation[5]. In this context, we propose a SERS-based sensor for the multiplex detection of phenol and different phenol derivatives. The proposed method is based on the SERS-based detection of the product resulting from the chromogenic reaction between phenol or its derivatives with the Gibbs reagent, 2,6-dichloroquinone-4-chloroimide, in basic medium to form coloured indophenols or indophenolates.
Although the chromogenic reaction allows the detection of phenol and its derivatives down to the microMolar limit. Unfortunately, this methodology does not allow the simultaneous detection of different phenol derivatives due the overlapping of the broad bands observed in the absorption spectrum. Alternatively, each phenol derivative could be unambiguously identified through its characteristic and well-defined SERS spectrum. Figure 1A shows the SERS spectra obtained after the chromogenic reaction with three different phenols, namely phenol, 1-naphthol and o-cresol. The analysis by principal component analysis (PCA) allows the differentiation of the different phenol derivatives (see Figure 1B). Furthermore, by analysing the variation of PC2 with the phenol concentration allowed the quantitative detection of phenol (see Figure 1C). Additionally, the well-defined characteristic SERS spectra of each derivative allows their semi-quantitative determination in binary and tertiary samples.

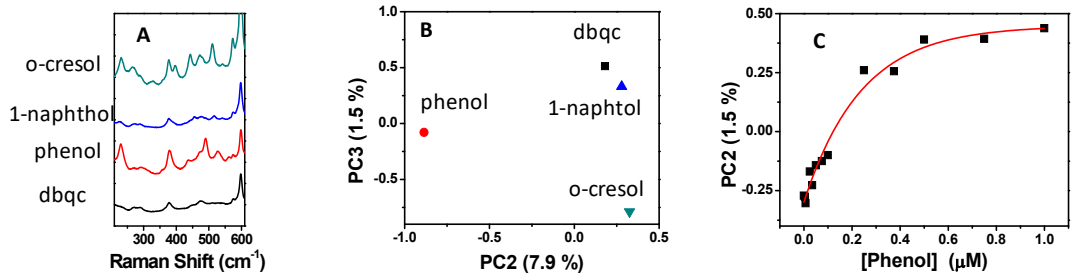

Figure 1: A. SERS spectra of 2.6-dichloroquinone-4-chloroimide (dbqc) used as blank, and the three phenol derivatives after the reaction with the Gibbs reagent (phenol, 1-napthol and o-cresol) at 2.5 μM concentration. Laser line 633 nm. **B**. PCA 2D representation of the principal components 2 and 3 of the phenol, 1-naphthol, o-cresol and dbqc. **C**. Calibration for the phenol concentration using a Hill - Langmuir fitting.

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Acknowledgements: Anxo Carreira-Casais thanks the Ministerio de Clencia, Innovación y Universidades for his FPU fellowship.

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OC33

Intracellular pH sensing and monitoring using branched SERS nanoprobes

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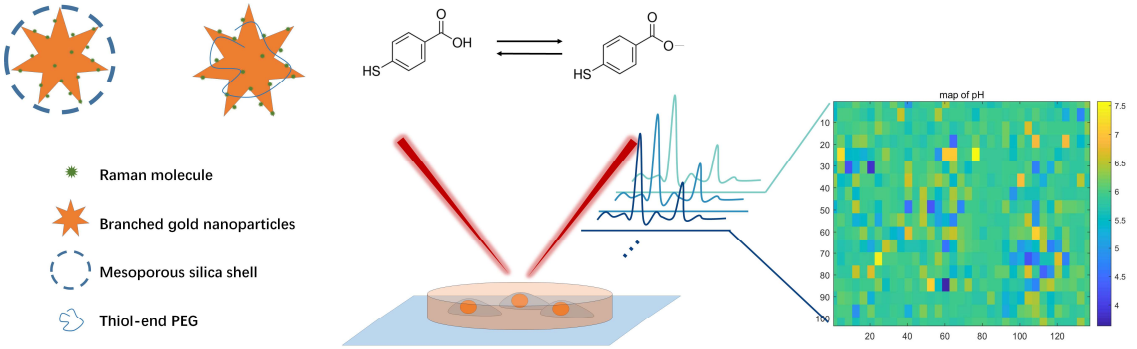
Intracellular pH value is an important physiological parameter that is strictly regulated inside the cell. Abnomal pH variation could cause the dysfunction of cells and influence the cellular microenviroment, which is associated with many diseases including cancer.[1] Sensing and dynamically monitoring the intracellular pH could assist researchers in understanding the biological function of cells such as cell proliferation and metabolism etc., as well as provide valuable information on cancer progression and metastasis.

Surface enhanced Raman spectroscopy (SERS), as an alternative optical technique to fluorescence, shows great potential in long-term monitoring the cellular pH due to its high photostability and sensitivity. However, a problem of the exsting SERS based pH sensors is that proteins or maromolecules in cell media could influence the sensor by adsorbing on the nanoprobes or interacting with the Raman molecules.[2] In our work, we synthesized branched gold nanoparticles, functionalized with 4-mercaptobenzoic acid (4-MBA), a pH sensitive Raman molecule, to exploit intracellular pH monitoring using SERS (Scheme 1). Two types of nanostructures, PEG stabilized gold nanostars and in situ grown gold nanostars with mesoporous slilca[3], have been used and compared in the pH sensing procedure. Their detection sensitivity and stability in the pH buffer and complete cell culture media have been discussed. Then, a breast cancer cell line was used as a model to visualize the localized intracellular pH using SERS, and monitored the pH variation during long-term incubation.



Scheme 1: Illustration of intracellular pH sensing using branched SERS nanoprobes.

Acknowledgements: We thank the European Research Council (ERC Advanced Grant 4DBioSERS) for financial support, and the China Scholarship Council (CSC) for supporting a stay of Yizhi at CIC biomaGUNE.

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OC34

Microfluidic-induced Supercrystals for ultrasensitive SERS detection

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Microfluidic platforms allow generating a highly-ordered assembly of uniform gold nanoparticles inside their microchannels through the pervaporation of the solvent (Figure 1A-B).[1] Furthermore, the microfluidic approach enables the fabrication of uniform assemblies of any dimension or morphology. The resulting plasmonic devices could be used for the detection of analytes, even without affinity for gold nanoparticles. Surface-enhanced Raman spectroscopy, SERS, is an advanced analytical technique that can be used for the ultrasensible detection of analytes since it offers orders of magnitude increases in Raman signals. It occurs at the surface of a plasmon surface mainly due to the presence of strong electromagnetic fields generated after the plasmon excitation. Moreover, this effect could be more intense in the case of hierarchical nanoparticles assemblies due to an antenna effect as demonstrated by recent simulations.[2]

While the plasmonic substrates made by drop-casting show poor uniformity that limits their potential plasmonic applications, the microfluidic approach gives rise to platforms with highly uniform and intense SERS activity (being both key parameters to achieve quantitative analysis and low detection limits (LOD). Herein, we will show the fabrication and characterization of plasmonic platforms fabricated using Au octahedra synthesized through a wet chemical method. Besides, the sensing capabilities of the platforms will be analysed by investigating the SERS efficiency using different Raman active analytes. For instance, experiment performed with Crystal Violet showed a great LOD, lower than 100zM, which is several orders of magnitude lower than those found in the literature

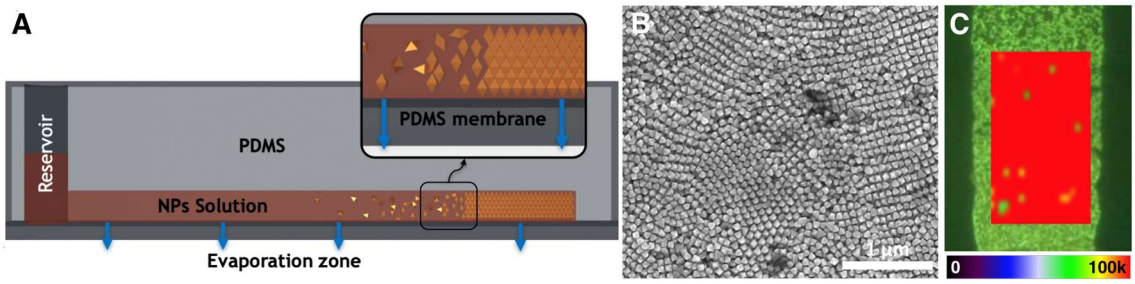

Figure 1. (A) Schematic illustration of the evaporation-based microfluidic cell used for controlled assembly of Au nanoparticles. **(B)** SEM images of the hierarchical nanoparticles assembly **(C)** Raman optical image and SERS mapping at 1617 cm-1 in the presence of 100 zM of Crystal Violet.

Acknowledgements: We thank the Ministerio de Economía y Competividad (MAT2016-77809-R) for financial support through the "FPI" fellowship.

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OC35

Chalcone-Based Supramolecular Amphiphiles for Light-Controlled Drug Uptake and Release

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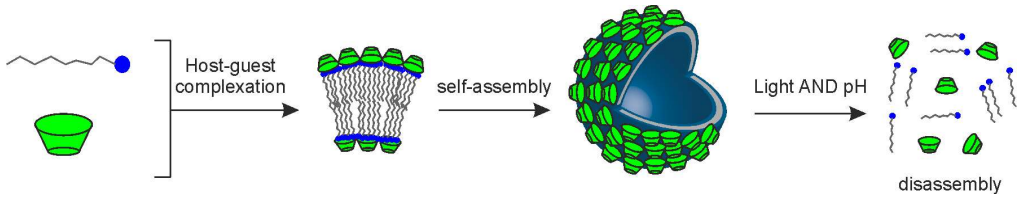
The encapsulation of pharmaceutical compounds in drug delivery vehicles provides a viable strategy to enhance bioavailability by improving factors such as low solubility, stability, toxicity, inability to cross membranes, etc. Furthermore, the controlled release of cargo drugs in their active form is of crucial importance to increase efficiency and reduce toxicity.[1]
Supramolecular amphiphiles, i.e., amphiphilic species that upon interaction with a host molecule forms a supramolecular complex which promotes self-assembly into aggregates of nanometric dimensions such as micelles and vesicles, show great promisse as drug delivery vehicles.[2] The dynamic and reversible nature of the noncovalent interactions endows the resultant aggregates with excellent stimuli-responsive features.
In this work we have synthetised an amphiphilic trans-chalcone that was shown to form complexes with p-sulfonatocalix[4]arene. The host-guest complexation promotes self-assembly into nanoaggregates which dissociate upon light exposure as a result of flavylium formation.



Scheme 1: Supramolecular amphiphile assembly and disassembly.

Acknowledgements: We thank the Fundação para a Ciência e a Tecnologia for financial support under project PTDC/QUI-COL/32351/2017.

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OC36

Coarse-grained Monte Carlo simulations of complexation between weak polyelectrolytes and oppositely charged nanoparticles

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Systems comprising of nanoparticles and oppositely charged polyelectrolytes have a great technological interest, being major components in formulations used in pharmaceutical, food, cosmetics, detergents, and paint industries. The stability of colloidal suspensions and the interaction of its constituents are important issues in formulations, and a large effort has been made to understand how the properties of each individual component affect the overall characteristics of the formulations.
Of special interest are weak, or annealed, polyelectrolytes. Contrary to strong (quenched) polyelectrolytes, the ionization of annealed polyelectrolytes is pH dependent. This allows for fine-tuning of the properties of the polyelectrolyte and the resulting complexes they form with other macroions. In addition, annealed polyelectrolytes exhibit charge mobility, where protons are mobile along the chain, giving rise to non-uniform charge profiles[1]
Using Monte Carlo simulations, we have studied the complexation between charged nanoparticles and oppositely charged, annealed, polyelectrolytes. In particular, systems consisting of a single nanoparticle with multiple polyelectrolyte chains, and systems of two nanoparticles and a polyelectrolyte chain were considered. We have found that the titration behavior is dependent on the mixing ratio between nanoparticles and polyelectrolytes, and varies mildly with its chain length. Furthermore, the mobility of charges in the polyelectrolyte allows for a maximization of the electrostatic interactions between nanoparticle and polyelectrolytes by concentrating the charge in the adsorbed chains, which coexist with nearly neutral and non-adsorbed chains.[2]
The influence of chain ionization on bridging between nanoparticles has also been looked into. We found that its ability to bridge both nanoparticles changes with pH. Furthermore, for intermediate polyelectrolyte charge fractions and with increasing nanoparticle separation distances, the annealed PE is able to link nanoparticles at larger distances as compared to the quenched one.[3]

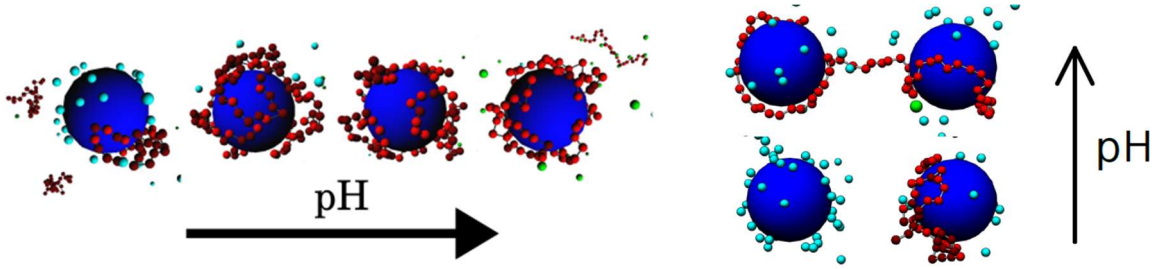

Figure 1: Representative snapshots showing the evolution of nanoparticle-weak polyelectrolyte systems with pH.

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OC37

The role of electrostatic interactions in biological DNA-related systems: insights from Monte Carlo simulations

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Electrostatic interactions have been recognized as an important factor in diverse aspects of DNA based systems, from DNA compaction and condensation, to the respective interaction with different biological components. These include membranes and surfaces, proteins and other relevant biomolecules. Electrostatics is also relevant in the design and assembly of DNA complex nanostructures and nanotechnology based gene delivery systems. DNA–DNA interactions are dominated by long-range electrostatic forces due to the highly charged nature of these polyelectrolyte systems. In some cases the overall behaviour is dictated by electrostatic interactions, in others electrostatics play an indirect, although critical role.
Despite of the complexity of these systems, the essential aspects of charge effects in biological DNA-related systems can be characterized resorting to Monte Carlo simulations employing coarse-grained models.

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OC38

Unveiling the effect of structural flexibility and cavity space filling on the molecular recognition of cyclodextrins by free energy calculations

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Cyclodextrin (Cd)-guest interactions have been extensively explored for developing supramolecular smart materials to improve solubilization, transport and targeting of therapeutic agents.[1,2] This work deals with the question whether (and how) the accessible cavity volume for guest molecules of different natures and sizes determines the intimate conformations and stability of the Cd-complexes. Is the effect comparable to that observed with guest size and structural complexity? Novelty consists in the ability to explain, at the molecular level, the critical role of Cd deformation, which is an often neglected phenomenon, in the interaction and stability of larger cavity Cd-based systems.[1-3] The structural and thermodynamic rationale for the impact of the Cd flexibility and the accessible cavity volume for guest molecules of different nature, on the intimate conformations and stability of the complexes, is still missing. The combination of the MD/PMF-based approach[1] and DFT calculations, for β- and γ-Cds allows predicting the energy penalty for Cd deformation and the respective impact on complex stability. Also, different contact patterns are presented, which allows identifying individual atom contributions in the formation of inclusion complexes.
Specifically, the interaction patterns and the leading factors affecting the thermodynamic signatures and stability of inclusion complexes between Cds and different model guests are detailed, combining our previously designed MD/PMF-based procedure[1,2] and the analysis of the electronic charge density of the binding partners and the respective gradients, which allows visualizing and quantifying regions of stabilizing/destabilizing noncovalent interactions.[2,3] Naphthalene (Np), adamantane (Ad) and lycorine derivatives are used as models of drug-leading structures.
Guest size affects Cd-guest contact and the inclusion degree, inducing Cd deformation, which opposes inclusion. Complexation depends on the available Cd cavity volume, as guest fitting variations and the enthalpy penalty from Cd deformation impact on the binding constants (promoting a reduction of up to 10^4).[3] Cd deformation plays an important role in the interaction behavior of larger cavity Cd-based systems, being crucial in carbohydrate-mediated recognition phenomena. It corresponds to an increase in energy of ca. 90 kJ mol^{-1} in the simpler analyzed model system.[3] The complexes of γ-Cd are less stable than the β-Cd complexes. The stability of complexes with Np and Ad derivatives are determined and compared with that of the single Np and Ad molecules. It is shown that β-Cd is, in general, more effective than γ-Cd in encapsulating Np, Ad and anhydrolycorine, and that the Cd cavity size difference plays a more important role than the guest size in the stability of the inclusion complexes. The binding constants of β-Cd-based complexes increase monotonically as the size of the guest increases, while those of γ-Cd show higher stability with decreasing degree of substitution. Solvation patterns suggest that the improved stability of the β-Cd complexes as compared with γ-Cd is also due to the higher desolvation degree in both host cavity and guest backbone. The cavity size and propensity to deform has a significant effect on the strength of the interactions, and a series of different findings prove that this phenomenon is the basis for the stability of different Cd-based complexes.
The estimate of the inclusion thermodynamic signatures and binding constants must be complemented with information on the enthalpy penalty associated to collapsed host structures, in order to obtain a reliable description of the binding process.

Acknowledgements: The Coimbra Chemistry Centre is supported by the Fundação para a Ciência e a Tecnologia (FCT), Portuguese Agency for Scientific Research, through the Project UID/QUI/00313/2019.

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OC39

Natural triterpenoids as nanocarriers: using a drug to vehiculize another

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Triterpenoids, natural substances present in many plants in nature, are used in conventional medicine due to their anti-inflammatory, hepatoprotective, analgesic, anti-microbial, virostatic, anti-cancer, and anti-HIV effects. Maslinic acid (MA) belongs to these kinds of natural products with remarkable biological properties, together with other triterpene acids (e.g. oleanolic, ursolic and betulinic acids). They are widely found in nature and are present at high concentrations in olive-pomace oil, being the main component of the protective wax-like coating of the olive skin. MA, for example, shows anti-tumoral effects in many cancer cell lines, including Caco-2, HT29, astrocytoma, non-small lung, ovary and melanoma[1]. However, the main difficulty to get benefit of their properties is the extremely low solubility in aqueous media. With nanoparticle technology we have found a good solution to this issue, increasing water solubility in a factor of 10^7, from 4 μg/l to 40 g/l. Moreover, these nanoparticles may serve as carriers for other hydrophobic drugs, opening the possibilities to synergistic actions. Properties of these novel systems, as well as first applications assayed will be discussed.

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OC40

Liposomal hydrogels as vaginal microbicides for HIV prophylaxis

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Approximately 36.9 million people worldwide are living with the human immunodeficiency virus (HIV) and the female population accounts for more than half of these infections.[1] Although considerable progress has been made, HIV stands as an increasing global health concern and new prevention strategies to prematurely fight and control the virus dissemination are critical. Thereby, and bearing in mind that women acquire HIV mainly through sexual intercourse, vaginal microbicides seem to be a promising approach for topical pre-exposure prophylaxis (PrEP).[2]

In this study, liposomes loaded with tenofovir disoproxil fumarate (TDF) were incorporated in hydrogels (HG) containing emtricitabine (FTC) for vaginal administration (Figure 1). In order to attain optimal mucoadhesive properties, liposomes with different surface charges (positive, negative and neutral) were evaluated regarding their size, polydispersity index (PDI), zeta potential and rheology before and after incubation with a mucin suspension. Furthermore, the quenching effect of the different liposomal systems was evaluated on mucin's intrinsic fluorescence and zwitterionic formulations were selected for the following studies. Initially, a detailed characterization of drugs biophysical impact on these nanosystems was conducted, validating our vehicle choices for TDF and FTC.

The performance of these formulations was evaluated by the in vitro study of drugs release profile, permeation kinetics, cytotoxicity and rheological behaviour after incorporation in the HG. Both liposomes and HG allowed sustaining release of the drugs (33.9 ± 5.7 % and 48.5 ± 7.5 % of TDF and FTC released within 2 h versus 51.4 ± 3.6 % and 72.9 ± 3.1 % when in their free form); TDF encapsulation enhanced the drug permeation (49.6 % versus 14.7 % at 6 h); zwitterionic formulations did not exhibit significant cytotoxicity and HG maintained suitable pseudoplastic profiles adequate for administration after nanosystems incorporation. The data obtained support that the proposed liposomal hydrogels may constitute a promising approach for the vaginal administration of TDF and FTC, in the context of topical PrEP.

Figure 1: Schematic representation of the rational design process to develop mucoadhesive liposomal gel formulations containing TDF and FTC.

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OC41

pH-Activated Hybrid Mesoporous Nanoparticles for Controlled Release

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Implementation of Controlled-Release Systems (CRSs) requires the use of materials that are susceptible to specific physical/chemical stimuli and a vehicle to prevent premature interactions between the environment and the loaded cargo[1,2]. Among a variety of inorganic-based nanomaterials, mesoporous silica particles (MSNs) have several attractive features for application as a delivery system, due to their high specific surface areas, large pore volumes, high mechanical stability, and a great diversity of surface functionalization options[3,4]. We developed novel hybrid MSNs composed of a mesoporous silica nanostructure core and a pH-responsive polymer shell[5]. The polymer shell was prepared by RAFT polymerization of 2-(diisopropylamino)ethyl methacrylate (DPAEM) (pKa ~6.5), using a hybrid grafting approach. The nanoparticles have diameters of ca. 100 nm at pH < 6.5 and ca. 60 nm at pH > 6.5. An excellent control of cargo release is achieved by the combined effect of electrostatic interaction of the cargo with the charged silica and the extended cationic polymer chains at low pH, and the reduction of electrostatic attraction with a simultaneous collapse of the polymer chains to a globular conformation at higher pH (Figure 1). The system presents a very low (almost null) release rate at acidic pH values and a large release rate at basic pH, resulting from the squeezing-out effect of the coil-to-globule transition in the polymer shell.

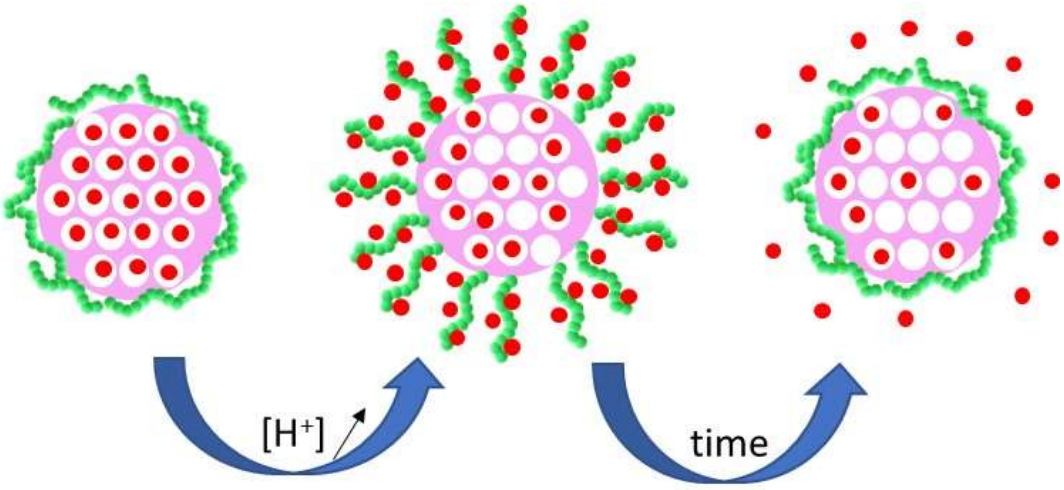

Figure 1: Representative scheme of the behaviour of SRB-loaded MSN-pDPAEM.

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

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OC42

Molecularly-imprinted histamine electrochemical sensor

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Histamine (HIS) is a relevant biogenic amine that mediates local hypersensitivity, but it may be also ingested from different sources, including fish[1]. The levels of HIS in fishery products have therefore legal limits. Several analytical methods have been developed for the determination of Histamine (HIS) including High Performance Liquid Chromatography (HPLC), Liquid Chromatography (LC), capillary electrophoresis (CE), gas chromatography–mass spectrometry (GC–MS), and gas chromatography (GC)[2]. These methods are not suitable for local analysis of HIS and have some disadvantages, such as large material consumption, a long analysis time and expensive equipment.

Biosensors using molecularly imprinted polymers (MIPs) are considered a suitable alternative or complementary analytical tool in the detection of many biomolecules, due to their high selectivity, rapid detection, and *in-situ* application feasibility. Thus, this work describes a novel electrochemical sensor for HIS by tailoring a a MIP sensing material on a suitable working electrode on a printed 3-electrode system. The polymeric film was generated *in-situ* by electropolymerization of a conductive polymer.

The device was optimized by evaluating the changes in the electron transfer properties of a standard redox probe ($K_3[Fe(CN)_6]$)/($K_4[Fe(CN)_6]$) by cyclic voltammetry and electrochemical impedance spectroscopy. The results obtained so far revealed that modifications made on the sensing element were successful and that the resulting sensor may detect as low as 1.0×10^{-7} mol/L of HIS. Studies are progressing and focus additional optimization steps and a full characterization of the device.

Acknowledgements:

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OC43

Bioimaging of tessellated scaffold with SERS Tags

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Surface Enhanced Raman Scattering (SERS) imaging is an interesting bio-imaging technique to study mammalian cells in real-time. Developments in SERS probe fabrication related to Nano Particle (NP) properties and the discovery of new Raman encoding molecules have opened up their use as tools to monitor complex 3D cellular systems. In particular, such SERS probes can be actively or passively targeted to cells to follow the movement and viability of cells over time. By coupling such interactions with confocal Raman microscopy, a more detailed overview of cells in 4D (namely three dimensional and temporal information) can be achieved.

In this project, we used a scaffold (*Figure 1A*) composed of Poly(lactic-co-glycolic) Acid (PLGA) and printed using electrohydrodynamic co-jetting technology [1]. In order to monitor the evolution of the mammalian cells growing inside the scaffold over time, we labeled the scaffold and the cells with two different SERS probes. We employed gold-nanostars (AuNSs) synthetized following a seed-mediated growth method (Figure 1B) and encoded with two different Raman Reporter (RaRs) molecules, 2-naphthalenethiol (2NAT) and 4-biphenylthiol (BPT) as our SERS tags. Gold nanoparticles enhance the Raman scattering effect of the molecules that are close to their surface. Furthermore, AuNSs sharp edges and tips provide high sensitivity to local changes in the dielectric environment, as well as larger enhancements of the electric field around the nanoparticles [2]. In order to add RaRs to AuNSs, a phase-transfer method was used which exploited the hydrophobicity of the RaRs to link them directly onto NPs´ surface via thiol interactions. Finally, to obtain hydrophilic and biocompatible SERS probes, an outer layer of amphiphilic polymer that effectively enwrapped the RaR and AuNS together was included[3].
In order to monitor the growth and progression of the scaffold-encapsulated cellular sample, 3D SERS imaging was conducted using a NIR laser (785nm) over various days.
The SERS maps collected were analyzed with multivariate analysis: Principal Component Analysis (PCA) was used to check the number of components that account for most part of the sample variance, and Multiple Linear Regression was used to discover the occurrence of the two different SERS tags inside the structure. *Figure C* shows an example of the SERS signal derived from the two SERS probes after 25 days; it is clearly possible to distinguish the presence of both 2NAT (top image, labelling the cells) and BPT (bottom image, labelling the scaffold). These preliminary results suggest that AuNSs are suitable SERS probes for 4D SERS imaging as they offer clear Raman signals that remain stable over time, in very different environments (intracellular and inside the PLGA scaffold).

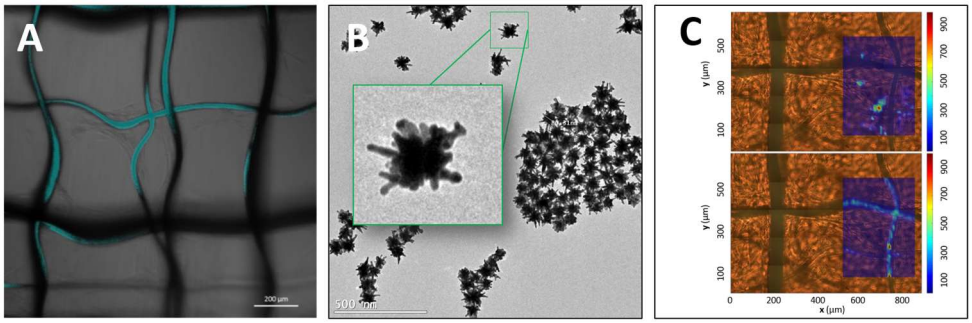

Figure 1: A) The blue fluorophore confocal images of the scaffold with superimpose the BF image; B) TEM images of the AuNSs, before encoding; C) Overlapping of optical image taken with 40x immersion objective and spectral maps analyzed with multiple linear regression using 2NAT (top image) and BPT (bottom image) as reference spectra.

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OC44

Metal Loaded Filter Membranes for Extraction and SERS Detection of Pesticides in Aqueous Solutions

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Organic pesticides have been widely used for crop protection, preventing food deterioration during storage or transport and also to inhibit proliferation of harmful pests. Their exhaustive use in the agriculture has raised serious concerns due to contamination of soils and water sources, with impact in aquatic organisms as well as animals and humans [1]. On site water quality monitoring might diminish pernicious effects, but there is need of sensitive/simple and easy to handle analytical methods for the detection of these pollutants. Spectroscopic methods based on surface-enhanced Raman scattering (SERS) have been exploited in recent years for the detection of pesticides in effluent waters. These methods are foreseen with great utility namely when associated to the use of analytical kits and portable equipment [2,3]. Moreover, conventional substrates based on rigid solid substrates or metal hydrosols are not suitable for sample extraction, limiting their application in water quality monitoring [4]. T

The fabrication of SERS platforms that allows fast collection and analysis of vestigial analytes is quite challenging but desirable. This communication describes the development of flexible platforms (Ag/LCP) based on liquid-crystal polymer (LCP) textile fibers decorated with Ag nanoparticles (NPs) for the extraction and SERS detection of pesticides in water samples spiked with pesticides (e.g. thiram) [5]. Firstly, we will demonstrate that SERS coupled with confocal Raman microscopy can be explored as a tool to map the local distribution of chemisorbed thiram molecules over the Ag/LCP substrates. Then, thiram spiked water samples, such as Aveiro Estuary water and fruit juices, have been analysed using the SERS substrates that have shown best analytical performance. In addition, SERS active membranes were also prepared by using the as prepared Ag/LCP composites supported on polyamide (PA) filters. It will be demonstrated that these composites can be used for the extraction of thiram dissolved in aqueous solutions and subsequent SERS detection, thus providing new active filter membranes for water analysis.

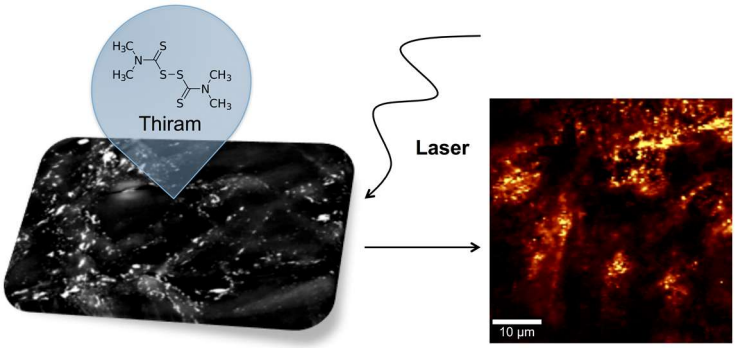

Figure 1: Scheme illustrating the use of Ag/LCP filter membranes in the extraction of pesticides from water for subsequent SERS imaging.

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OC45

Biomimetic electrochemical sensor integrated in flexible polymeric devices for cancer diagnosis

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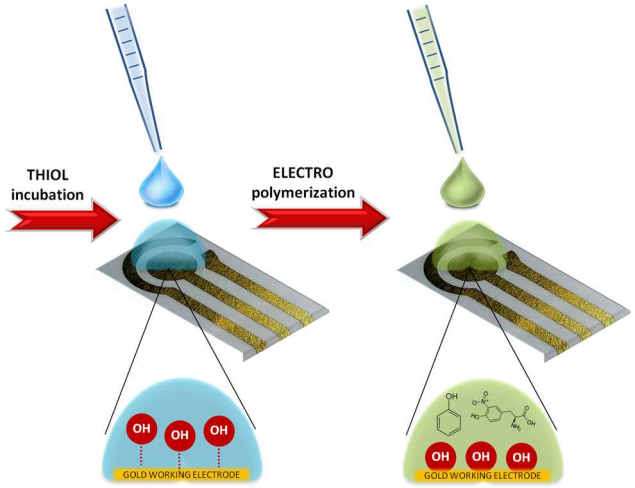
Early diagnosis of cancer biomarkers has currently been pointed out as a crucial tool to improve the therapeutic strategies and, subsequently, to increase the survival rates. Particularly, various studies have suggested a strong link between oxidative stress (OS) biomarkers and diverse aging-associated degenerative diseases including cancer[1,2]. In this context, the development of simple, affordable and easy-to-use diagnostic assays are of great valuable to be use in *point-of-care* (POC) testing.
Herein, we have developed highly sensitive electrochemical sensors by applying a single (gold) conducting layer on the top of flexible, transparent polymeric substrates. Different parameters, such as, adherence, roughness and gold thickness were carefully investigated and the electrochemical performance of these electrodes was assessed by cyclic voltammetry (CV). As a proof-of-concept, the electrodes were coated with a molecular imprinted polymer (MIP) designed for sensitive electrochemical detection of 3-nitrotyrosine (3-NT), a known OS biomarker[3]. This biomimetic material was produced by electropolymerization of the phenol monomer (*see* ***scheme 1***) and several experimental parameters, such as, number of cycles, range of potential applied, monomer and template concentrations were optimized in order to finely tailor the characteristics of the imprinted molecular cavities. Finally, the analytical performance of the (bio)sensor device was assessed by performing calibration curves in phosphate buffer solution near physiological pH. Under optimal conditions, the developed sensor showed good sensitivity and limits of detection down to picoMolar level.
Overall, the described low-cost flexible electrodes hold the potential to become a quick, disposable sensing device for *in-situ* detection of 3-NT. Besides the mentioned attributes, when compared to previous methods, the proposed technology showed one of the best limits of detection found in literature.



Scheme 1: Schematic representation of the assembly of the gold-modified biomimetic sensor.

Acknowledgements: The authors gratefully acknowledge to the project IBEROS, Instituto de Bioingeniería en Red para el Envejecimiento Saludable, PROGRAMA INTERREG 2014-2020, reference POCTEP/0245_IBEROS_1_E and the financial support to CANCER Project through Norte 2020 – Programa Operacional Regional do Norte, reference NORTE-01-0145-FEDER-000029.

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OC46

Tunable catanionic vesicles based on serine-derived surfactants: from molecular design to effective *in vitro* delivery of doxorubicin

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Amino acid-based cationic/anionic surfactant vesicles show promising features to perform as effective drug nanocarriers. We have recently developed catanionic vesicles based on cationic (16Ser) and anionic (8-8Ser) serine-based surfactants. Both net negatively charged— *x*(16Ser)=0.20, where x(16Ser) is the cationic surfactant molar fraction—and positively charged—*x*(16Ser)=0.58—vesicles are available, hence providing a surface charge-tunable system (Fig. 1, top).[1] The *in vitro* performance of these vesicles was evaluated for the delivery of the anticancer drug doxorubicin (DOX) using a cancer cell model (A549).[2] The neat surfactants and both vesicle formulations present low toxicity, with high cell viability for concentrations below 32 micromolar. DOX is successfully encapsulated in the vesicles, resulting in a surface charge switch to negative for the 0.58 system, making both the 0.20 and 0.58 DOX-loaded vesicles highly interesting for systemic administration. Cell uptake studies using flow cytometry and confocal microscopy showed drug accumulation near nuclear regions (Fig. 1, bottom) and an increase of cell uptake up to 250% and 200% for the 0.20 and 0.58 vesicles, respectively, compared to the free DOX. The *in vitro* cytotoxicity studies show that DOX-loaded vesicles induce cell death, confirming the therapeutic potential of the formulations.[2] Altogether both vesicle formulations are efficient drug nanocarriers with potential for phased delivery, an advantage for prolonged treatment periods or even on-demand release.

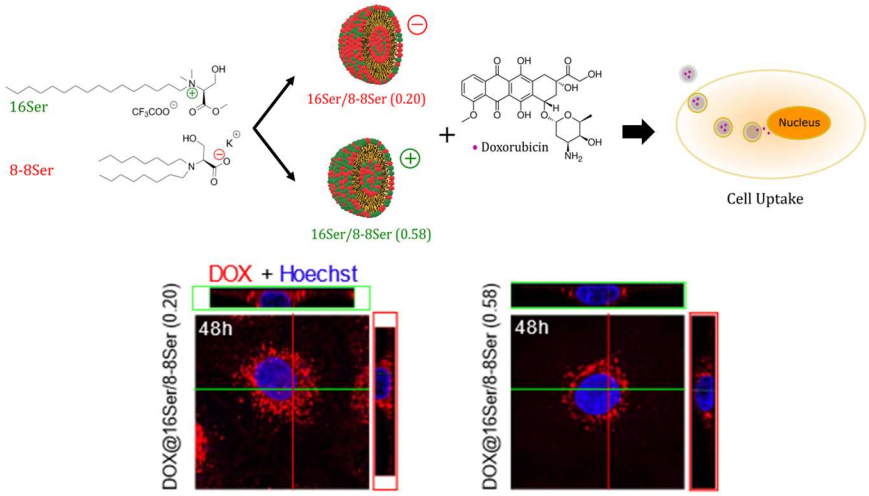

Figure 1: Top, assembling catanionic vesicles based on the serine-derived surfactants 16Ser and 8-8Ser for the delivery of doxorubicin (DOX) to cancer cells; bottom, confocal microscopy images of the DOX-loaded catanionic vesicles showing DOX (red) accumulation around nuclear regions (blue).

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OC47

EuChemS Periodic Table and our efforts to reduce element scarcity by developing magnetic carbon-based nanocomposites

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At the begining of the year, the European Chemical Society (EuChemS) launched the EuChemS Periodic Table, a new version of the Mendeleev Table of Elements, which depicts the element scarcity.
Element scarcity is intrinsically linked with several issues including Circular Economy, more efficient recycling practices, consumer behavior and innovative alternatives. For instance, we know now that our phones are made up of more than 30 elements (Figure 1) – over half of which may give cause for concern in the years to come because of increasing scarcity. More, is estimated that every month around 10 million smartphones are discarded or replaced, only in the European Union1, and unless solutions are provided in the next years, we risk seeing many of the natural elements that make up the world around us run out or become unusable, due to facts such as limited supplies, location in conflict areas, or our incapacity to fully recycle them1. This fact alerts us that serious actions are needed to tackle these challenges ahead.

In this context, a new line of research has emerged in recent years that seeks to find new sources for the elements considered in risk (Technological Critical Elements - TCE). In our research group we particularly interested in the development of efficient processes for the recovery and recycling of TCE elements from electronic waste, by preparing and applying some nano magnetic adsorbents in the recovery and recycling of some of these critical elements. One of these examples is a magnetic composite prepared with magnetite nanoparticles and exfoliated graphite, which has the ability to remove lanthanides (La, Eu and Tb) from aqueous solutions at low concentrations. This adsorbent had a removal efficiency greater than 80% after 15 minutes of contact (pH ca. 8), using only 50 mg / L of material.

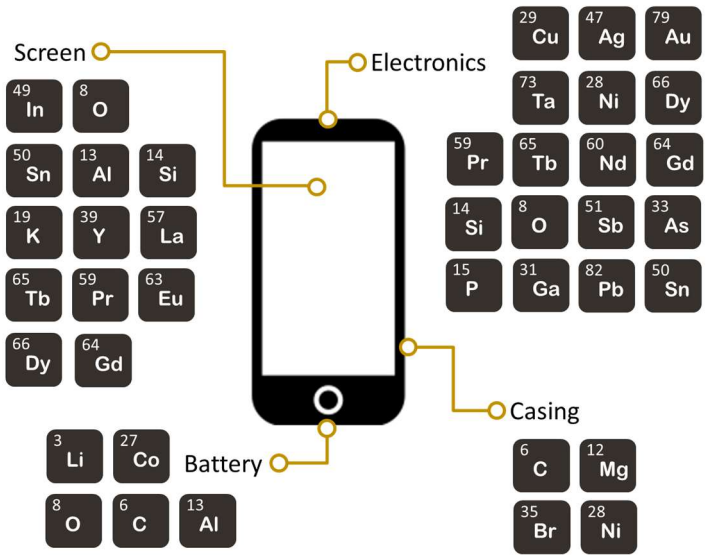

Figure 1: Chemical composition of a smartphone (adapted from http://www.eurare.eu).

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OC48

Polymer effect on Gold Nanoclusters Luminescence

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Gold Nanoclusters (AuNCs) are nanostructures with a few gold atoms and dimensions below 2 nm. They have been increasingly studied due to their unique properties, such as size-dependent luminescence, very high photostability, catalytic activity, low toxicity and biocompatibility. [1] Applications across different fields, from medicine and biology to physics and chemistry, include catalysis, sensing, imaging and theranostics.[2]
We are mainly interested in the application of AuNCs as labels for advanced optical imaging and sensing. Our aim is to explore the AuNCs optical properties when these are incorporated in nanomaterials to increase their stability. One of our strategies is to prepare polymer nanoparticles containing a very large number of AuNCs, using miniemulsion polymerization. [3] This allow us to maintain the AuNCs optical properties (NIR fluorescence emission) for imaging and optical targeting.
Polymer-AuNCs hybrid nanoparticles were prepared trough photo-miniemulsion polymerization of methacrylate monomers, resulting in monodisperse nanoparticles with diameters around 50 nm (Figure 1A), high colloidal stability and optimized optical properties. The materials further show emission enhancement in the NIR region upon formation of plasmonic gold nanoparticles (AuNPs) that interact with the AuNCs, [4] resulting in an increase brightness of the nanoparticles (Figure 1B).

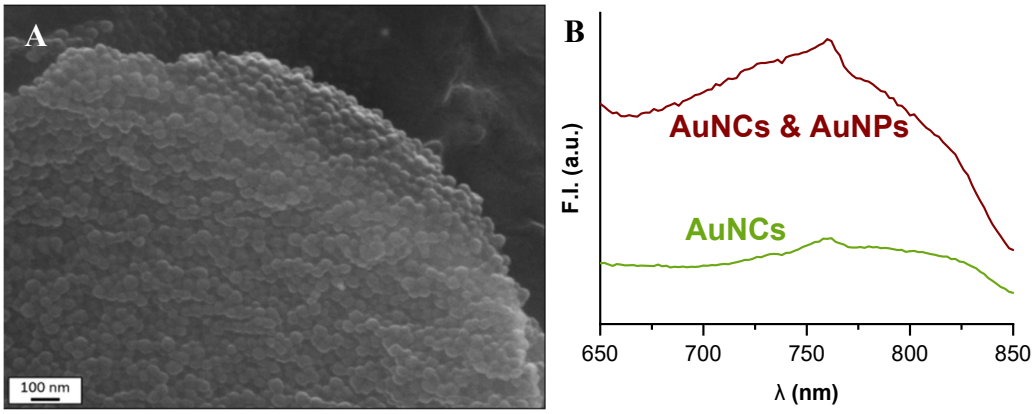

Figure 1: *A) SEM image of polymer nanoparticles containing AuNCs. B) Fluorescence emission spectrum of polymer-AuNCs nanoparticles containing AuNPs (λ_{exc}=550 nm)*

Acknowledgements: This work was partially supported by Fundação para a Ciência e a Tecnologia (FCT-Portugal) and COMPETE (FEDER), projects UID/NAN/50024/2013 and PTDC/CTM-POL/3698/2014. B. C. thanks FCT for PhD grant PD/BD/137511/2018.

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POSTER COMMUNICATIONS

P1

Giant lipid vesicles loaded with biopolymers and magnetic microparticles

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In this work, we have studied giant vesicles loaded with biopolymers and magnetic microparticles.[1] In a first attempt to characterize the system, we have evaluated the differences between the diffusion of the superparamagnetic beads when the inner aqueous medium contains different concentrations of glucose and hyaluronic. In the second part of the work, we have applied rotating fields to transport these hybrid capsules on a solid substrate.[2] In the next future, we want to assess the effect of some cations in the mechanical properties of the confined gel through the diffusion measurements, and how the induced variations in the mechanical properties may determine the translational mechanism.

Acknowledgements: This work was supported in part by MINECO under the grant CTQ2016-78895-R. F.M.-P. and A.M.-M acknowledge support from MINECO (Grant No. RYC-2015-18495).

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P2

Ligand-Regulated Photothermal Performance of Bipyramidal Gold Nanoparticles

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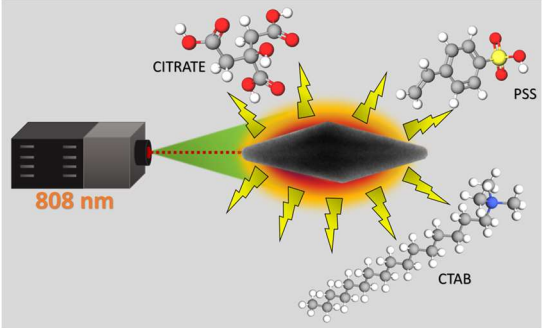
Selective killing of tumor cells is a worldwide challenge. Hyperthemia is a highly atractive alternative to the targeted drug delivery systems, especialy because it is a non-dependent treatment of cancer phenotypes. Among the different hyperthermia technologies, near-infrared (NIR) laser-induced tissue photothermal therapy mediated by gold nanoparticles (AuNPs) displays multiple advantages, such as simple instrumentation, tunable performances and minimum tissue damage. Optimization of photothermal yield and long-term stability of the required anisotropic AuNPs with sharp tips is desirable for the translation of this novel cancer therapy.

Herein, bypiramidal AuNPs were synthesized using a mild thermal treatment of conventional Au seeds.[1] The resulting Cetyltrimethylammonium Bromide (CTAB) capped AuNPs were successfully ligand-exchanged with polystyrene sulfonate (PSS) and, subsequently, with citrate ligand.[2] The successful ligand exchange process was exhaustively characterized by transmission electron microscopy, zeta-potential, Fourier-transform infrared and X-ray photoelectron spectroscopies. The degradation process of the different ligand-stabilibized bypiramidal AuNPs was monitored for two month by measuring the wavelength of the longitudinal localized surface plasmon resonance peak. PSS ligand was found to confer the best stabilizing coating. Furthermore, the photothermal performance was also evaluated usind a NIR laser irradiation (at 808 nm), showing that citrate ligand provides the higher kinetic rate. This work pays the way for searching new capping ligands that could confer longer stability times and higher photothermal performance of anisotropic plasmonic nanoparticles.



Scheme: The different ligand-stabilized bipyramidal AuNPs tested in this work.

Acknowledgements: FQM-204 Research group; CTQ2017-83961-R project.

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P3

Effects of hydrodynamic interactions on diffusion in gels

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The diffusion of nanoparticles in porous materials is relevant for many different processes, such as the motion of biomolecules in crowded biological environments, filtration techniques, drug delivery and transport in gels. The nanoparticle diffussivity in these kind of systems depends on the structural proporties of the environment (e.g. on the pore connectivity) and the available void which, in turn, depends on the size of diffusive particles.[1] Excluded volumem, potential forces (dispersion, DLVO, etc) and hydrodynamic friction[2] are the most important types of interactions between the gel and the tracer particles. We have numerically investigated the diffusion of inert tracer particles (i.e. with just excluded volume) in different types of fixed gels. We analyse and compare the diffusion coefficient of these tracers when hydrodynamic interactions (HI) are considered which reveal far-from-trivial dependence on the time-dependent diffusion coefficient and the gel structure (Figure 1). HI modify the dynamics of mobile tracers (which move through the whole system through the “infinte” percolating pore). Close to the percolation threshold (where few mobile tracers are restricted to move along singular fractal pathways[3]) the introduction of HI interactions slow-down their diffusion at short times and modify the critical sub-diffusion exponent.[4]

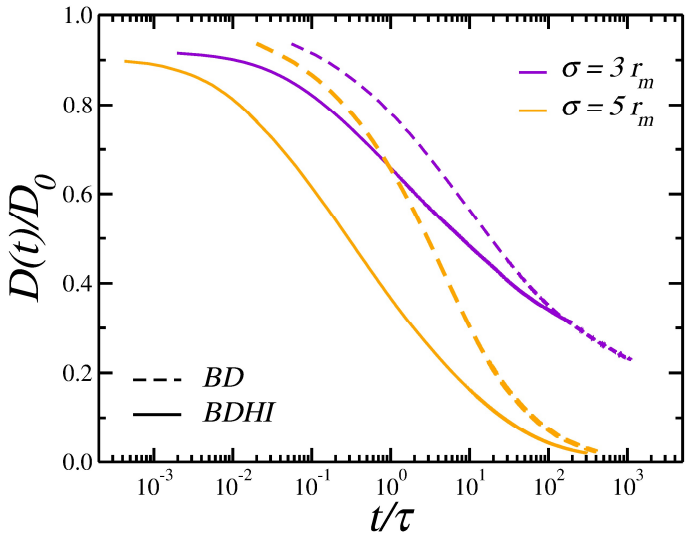

Figure 1: Time-dependent diffusion coefficient of inert mobile tracers of different sizes when hydrodynamic interactions between tracer and gel particles are considered or not.

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P4

Spinel ferrite nanoparticles for the uptake of chromium from water

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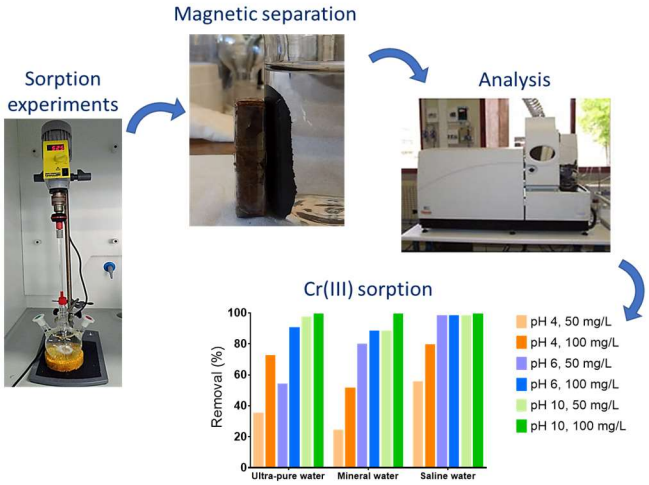
Current environmental policies aim to eliminate potential toxic species in aquatic ecosystems and to promote the water reuse after adequate treatment of wastewaters. Chromium is among the most toxic trace elements present in liquid effluents of various industries[1] whose levels in wastewaters should be reduced. Magnetic nanoparticles (NPs) have proved its efficiency as sorbents for the uptake of various contaminants from waters by using magnetic separation technologies[2,3]. Our own interest in this field led us to an overview on the work reported in the literature for the specific case of chromium contamination. As such, it was found that most studies on the application of adsorption technologies for the removal of chromium have focus on mono-elemental spiked ultra-pure water and using unrealistic concentrations of chromium. This led us to explore the application of magnetic nanosorbents in this context by using distinct operational parameters in the sorption process.

The research communicated here concerns the Cr(III) uptake from aqueous systems with distinct composition and using variable amounts of nanosorbent for subsequent magnetic separation. Spinel type ferrite nanoparticles (NPs: Fe_3O_4, $MnFe_2O_4$ and $CoFe_2O_4$) have been synthesised and then fully characterized by a plethora of techniques. Subsequently, the ferrite NPs were evaluated for their sorption characteristics of chromium present in water samples using the general approach illustrated in Scheme 1. These experiments were performed by varying the amount of sorbent, pH and ionic strength of the medium, and also the presence of organic matter. The results presented here show that both manganese and cobalt ferrite NPs are efficient nanosorbents for the removal of aqueous Cr(III). In particular, $CoFe_2O_4$ NPs have shown 95% chromium removal from saline water and saline water with dissolved organic matter at pH 6, and a similar percentage removal was found when using ultra-pure, mineral, saline water and saline water with dissolved organic matter, at pH 10. The application of nanosorbents based on $CoFe_2O_4$ will be put in perspective by considering their efficiency and limitations for the treatment of wastewaters and industrial effluents.



Scheme 1 – Representation of sorption process of Cr(III) using magnetic nanoparticles.

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P5

Colloidal Gels Controlled Delivery of Anti-inflammatory/Anti-cancer Pharmaceutics in *In vitro* Disease-mimicking Models

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Colloidal gels, consisting of oppositely charged nanoparticles, are being increasingly explored as controlled release depots for focal delivery[1] in numerous tissue engineering and biomedical applications[2] due to their unique physicochemical properties[3,4]. Herein, through a bottom-up approach, we present a biodegradable multicomponent colloidal gel which self-assembles from nano-sized blocks into a macroscale construct via electrostatic complexation. To fabricate the colloidal gels, a nanoprecipitation-based technique was optimized to enable the production of spherical and highly monodisperse anionic Zein-Hyaluronan (Zein-HA) and cationic poly(lactic-co-glycolic acid)-Polyethylenimine (PLGA-PEI) nanocarriers, that constituted the oppositely charged building blocks. The polyelectrolyte nanocarriers self-assembly was performed, under mild physiological conditions and confirmed by the formation of dense nanoparticle-nanoparticle networks. The formulated colloidal gels demonstrated moldability and fit-to-shape properties, indicating their potential to be used as bioactive tissue fillers, presenting a significant potential to be applied in tissue engineering applications. Additionally, successful colloidal gels application as focal drug delivery depots were confirmed by their significant Quercetin encapsulation efficiency (94%) and long-term controlled release, up to 3 weeks. Furthermore, upon contact with LPS-activated Raw 264.7 macrophages, flavonoid-loaded colloidal gels reduced the production of nitric oxide and increased arginase activity over that of the free drug, indicating the successful development of biocompatible colloidal gels for long-term focal delivery of anti-inflammatory therapeutics. Moreover, this colloidal gel could be applied for anti-cancer therapies by using this system as anti-cancer drugs delivery system and also as a scaffold for 3D cancer models that can be used as platforms for drug screening.

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P6

Effect of temperature and water content on the solubility of kraft lignin in deep eutectic solvents

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The growth in resources consumption combined with the huge challenges of climate change and feedstock scarcity will rapidly increase the demand for products manufactured from renewable and sustainable sources. In this respect, agroflorestal residues are expected to play a crucial role in the future soon. Due to numerous advantages of lignin and tannins, a great interest in developing added value products for various applications based on these natural polyphenols is emerging. However, the added value uses are still poor mainly due to scarce separation techniques available which, in most of the cases, result in low extraction yields, extensive degradation or even undesired chemical modifications.
The present work intends to study the solubility of kraft lignin in deep eutectic solvents (DES) based on lactic and propionic acids combined with urea, choline chloride and betaine. DES present several advantages over other classic dissolution systems such as lower environmental impact and the possibility of recovering and reuse [1].
Lignin solubility was observed to be enhanced at higher temperatures for all the studied systems. Moreover, the addition of water led to a decrease in solubility power of the lactic acid based systems, being this effect less pronounced in the propionic acid based system. Nevertheless, the later system keeps a good dissolution performance until a water content of ca. 50%, being an economically and environmentally interesting system to dissolve kraft lignin.

Acknowledgements: This work was financially supported by the Portuguese Foundation for Science and Technology, FCT, via the projects PTDC/AGR-TEC/4814/2014 and "ReFloRest" ref.: 30619 (02/SAICT/2017) and researcher grant IF/01005/2014. Elodie Melro acknowledges FCT for the PhD grant (SFRH/BD/132835/2017). The CQC is supported by FCT through the programmes PEstOE/QUI/UI0313/2013 and COMPETE. This work was supported by the Associate Laboratory for Green Chemistry LAQV which is 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). A. Paiva acknowledges the finantial support from project IF/01146/2015 attributed within the 2015 FCT researcher program.
This project has received funding from the European Union's Horizon 2020 (European Research Council) under grant agreement No ERC-2016-CoG 725034

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P7

Detection of C-reactive protein using aptamer-conjugated gold nanoparticles

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C-reactive protein (CRP) is the most well-known biomarker of inflammation in cardiovascular diseases, being used for standard clinical practice. Gold nanoparticles (Au NPs) have been used for CRP detection due to their facility to conjugate with biomolecules and exceptional electrical and optical properties. However, current assays for CRP detection involve the preparation of complex materials using antibodies and frequently require costly equipment for detection that leads to expensive assays [1].

In the present work, a simple strategy for CRP detection using AuNPs functionalized with an aptamer (Au_NPs@ssDNA) was investigated (figure 1). AuNPs@ssDNA were prepared, characterized and tested against CRP. Spherical Au NPs 13 nm average size were synthesized using the Turkevich method. After synthesis and surface modification the materials were characterized using UV-vis spectroscopy, zeta potential and DLS measurements and TEM. The aptamer and CRP were characterized using circular dichroism. Au NPs@ssDNA were tested for CRP detection in solutions of known concentration. The detection of CRP was performed using UV-vis spectroscopy by monitoring the aggregation ratio of Au NPs (A_{670}/A_{LSPR}) along time, i.e. the ratio between the absorbance at 670 nm and the absorbance of the LSPR band.

The aptamer-conjugated Au NPs successfully detected the CRP. It was found a linear correlation between A_{670}/A_{LSPR} ratio and CRP concentration, within the concentration range 0 – 17.5 nM, either with or without addition of NaCl. The system demonstrated specificity to CRP without interference of albumin (up to albumin concentrations of 6.6 mg/L). These are preliminary but promising results that suggest that this optimized system can be envisage for rapid (< 10 min), simple and inexpensive colorimetric detection of CRP.

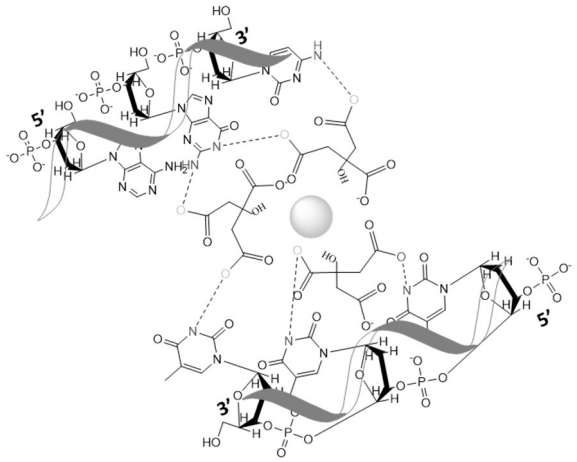

Figure 1: Scheme of possible interaction between the aptamer and citrate coated AuNPs.

Acknowledgements: This work was developed within the scope of the project IF/00405/2014/CP1222/CT007, the project CICECO-Aveiro Institute of Materials, Ref. UID/CTM/50011/2019, financed by National funds through the FCT/MCTES and iBiMED (UID/BIM/04501/ 2013). A. L. D.-d.-S. acknowledges FCT for the contract (IF/00405/2014). M. A. thanks FCT for the PhD grant SFRH/BD/13688/2018

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P8

Micellization characterization of aqueous solution of salt-free catanionic surfactants

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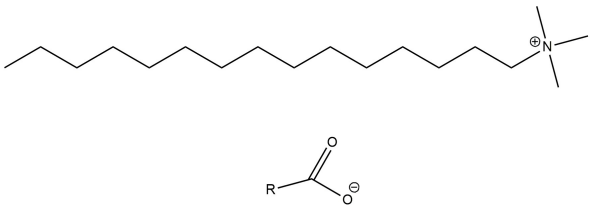
In this communication we discuss the effect of counterion in the micellization properties of a series of hexadecyl-*N,N,N* trimethylammonium surfactants, in aqueous solutions, at 25 ºC. The counterions used are *n*-alkyl carboxylates (*n* = 1, 2, 4, 6, 8, 10 carbon atoms). The characterization of these aqueous systems have been carried out by conductometry and isothermal titration calorimetry. The critical micelle concentration (*cmc*), degree of dissociation of counterions, and the corresponding thermodynamic micellization parameters were estimated. It has been found that the *cmc* decreases by increasing the counterion chain length; an exception has been found to the formate counter ion surfactant. Such behaviour can be related with the occurrence of hydrolysis and consequent release of hydrogen ions. This has been supported by pH measurements. On the other hand, for the *n*-decyl carboxylate, the ITC measurement shows an intriguing trend, which was corroborated by DLS analysis. In the latter, it has been suggested that larger aggregates are found. Even so, it can be concluded, for all surfactants, that the micellization process is entropy-driven.



Scheme 1: Molecular structure of salt-free based catanionic surfactants. R = H, CH_3, $CH_3(CH_2)_n$ (*n*=2, 4, 6, 8).

Acknowledgements: This work has been partially funded by the ''The Coimbra Chemistry Centre" which is supported by the Fundação para a Ciência e a Tecnologia (FCT), Portuguese Agency for Scientific Research, through the projects UID/QUI/UI0313/2013 and COMPETE Programme (Operational Programme for Competitiveness).

P9

Hybrid nanoplatforms for cancer theranostics

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Most diagnostic and therapeutic systems used for detection and treatment of cancer do not take advantage of the physiological abnormalities of cancer cells, and they cause adverse side effects that limit their effectiveness. In addition, the stages of diagnosis and therapy are carried out independently, which implies delays in the application of the treatment and, thus, subsequent risks to the patients´ health.[2] To overcome these drawbacks, we developed a nanoplatform capable of targeting the therapeutic action and monitoring the response to therapy simultaneously. Hence, we designed a hybrid nanosystem able to simultaneously combine its potential as a photodynamic (PDT) and plasmonic photothermal (PPTT) therapeutic agent in order to kill malignant cells was developed. To do that, gold nanorods (GNRs) were functionalized by means of the layer-by- layer (LbL) assembly technique using alternating layers of polyelectrolytes (PEs) poly(styrene sulfonate) (PSS) and poly-L-lysine (PLL) as anionically and cationically charged polymeric layers, and an outer layer of hyaluronic acid (HA) to provide the hybrid particles with sufficient colloidal stability and targeting ability. In order to provide the nanoplaform with PDT capabilities, the photosensitizer (PS) indocyanine green (ICG) was previously grafted to the PLL polymer and assembled on the PE surface coating. In this manner, PSS/PLL@ICG/HAcoated GNR hybrid particles were obtained, in which the therapeutic PDT activity of the dye ICG and the photothermal properties of the metal NPs can be simultaneously be applied for efficient cancer therapeutics. It was demonstrated that PSS/PLL@ICG/HA-coated GNR displayed high photo- and chemical stability. Since ICG can also absorb near infrared (NIR) light and transform it by internal conversion into heat, the heating profiles provided by the present hybrid nanoparticles (NPs) and the potential interference between the different components was analysed. Also, the single oxygen (1O2) production under NIR light excitation by the hybrid nanosystem was evaluated at several power intensities in vitro by means of fluorescence and absorbance spectroscopies, and fluorescence microscopy.

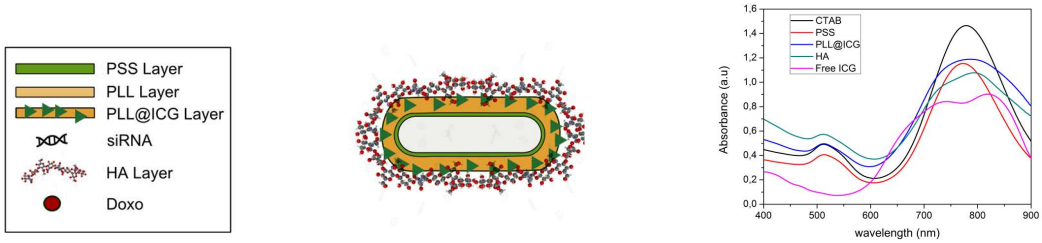

Figure 1: Scheme of the nanoplatform, and confirmation of the assembly process by UV-Vis spectroscopy

Acknowledgements: This work was supported by Agencia Estatal de Investigación (AEI) through Project MAT2016-80266-R, and Xunta de Galicia (Grupo de Referencia Competitiva ED431C 2018/26; Agrupación Estratégica en Materiales-AEMAT ED431E 2018/08). FEDER funds are also acknowledged.

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P10

Relationship between surface properties of eucalyptus kraft pulps and their absorption capacity

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Absorption capacity is a key characteristic for cellulosic pulps used for non-papermaking needs.[1] The surface properties of six defiberized in a hammermill eucalyptus bleached kraft pulps, obtained at different cooking and bleaching conditions, were studied employing sorption isotherms and contact angles in order to determine a relationship between them and the absorption capacity of pulps. The sorption isotherms were obtained at three temperatures (25ºC, 30ºC and 35ºC) for relative pressure between 0,05-0,95 using the Dynamic Vapor Sorption Resolution instrumentation (DVS). The experimental sorption data of all samples were fitted to the GAB model and the parameters of this sorption model (monolayer capacity and surface area) were estimated from the experimental results using the nonlinear regression analysis. The contact angles were measured in the OCA contact angle system using the sessile drop method. The specific volume and absorption capacity of pre-formed pulp fibre pads were determined according to a Scandinavian absorbency testing procedure (Scan-C33:80). The pulps were analysed on the neutral sugars as alditol acetates and the fibre morphology assessed using a Kajaani FS300 fibre analyser.

The sorption isotherms showed, as expected, that an increase in temperature results in a decreasing at the equilibrium moisture content. This result can be explained by the increment of the molecules excitation state resulting in the increase between their mutual distances and, consequently, in the decrease of the binding energy between molecules becoming less stable and breaking away from the water binding site of the pulp's surface.[2] The contacts angles of pulps varied between 17º and 27º thus demonstrating their strong wettability, when the solid-liquid attraction prevailed over the liquid-liquid one.[1]

The results of the sorption isotherms, contact angles, specific volume/porosity of pre-formed pulp pads and their absorption capacity demonstrated that an easier formation of the monolayer and multilayer didn´t correlate directly to a better absorption as predicted by Kelvin or Washburn equations.[1] Based on the analysis of the sorption isotherms and the contact angles, it was concluded that the higher monolayer capacity of the pulp fibres is related to the lower contact angles of the pulps (easier wetting). These surface properties did not correlate directly with the content of hemicelluloses and with the content of knots in defiberized pulps, but with the morphology of the fibres (curl and kink index) and their packing in the pads. In turn, the absorption capacity correlated positively to the porosity of pads and to the content of carboxylic groups, which are enable to form strong hydrogen bonds with water molecules thus increasing the water retention capacity. The knots affected negatively the absorption capacity of pulps. Similarly, it was found that the absorption rates correlated positively to the porosity of fibres network in pads (e.g. higher porosity corresponds to lower absorption time) and that the knot content affects negatively the absorption time. Concluding, the absorption properties of studied pulps, such as absorption capacity and absorption time, are related to not only the chemical composition or accessibility but also to the morphology (e.g. coarseness, curl and kink) of pulp fibres and their air-laid fibre network organization (e.g. porosity and binding mode).

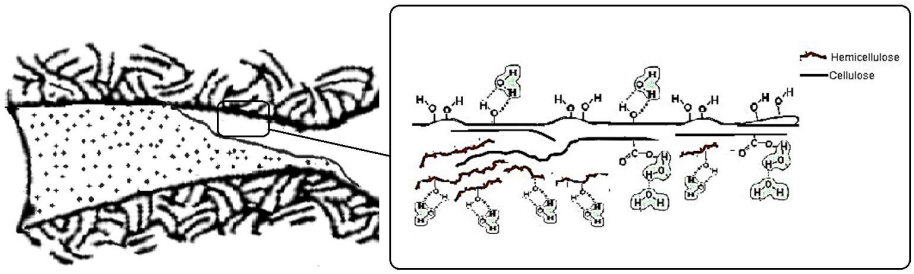

Figure - Schematic representation of the hydrogen bounding between water molecules and hydrophilic groups present at the fiber surface and the capillary structure on the inter-fiber space filled partially with condensed water.

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P11

Molecular Recognition at Interfaces: Exploring the Host-Guest Chemistry of an Amphiphilic Calix[4]arene

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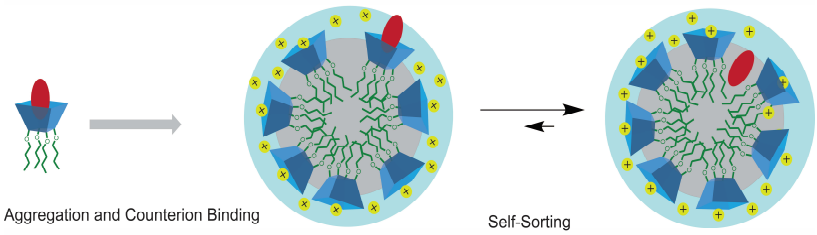
Molecular recognition of small molecules and ions by artificial receptors embedded or confined in micelles or vesicles is believed to provide better models of biological systems in comparison with bulk solutions. In this work[1] we have investigated the complexation of a fluorescent probe (*trans*-4-[4-(dimethylamino)styryl]-1-methylpyri- dinium iodide (DMSI)) with amphiphilic calixarene receptor. Below the critical micelle concentration (CMC), the probe forms a host–guest complex with the calixarene behaving like a traditional system operating in bulk solution. Above the CMC, multiple equilibrium processes are established, and the probe can exchange between the cavity of the calixarene in the monomeric state, micellized state and/or the micellar hydrophobic core (Scheme 1). Detailed analysis of the results obtained from fluorescence and NMR experiments allowed us to propose a quantitative model to describe the system. The increment of the local concentration of Na^+ counterions at the Stern layer displace the dye to the micelle core through competitive binding of Na^+ in the cavity of the receptor and is decisive for the observed self-sorting behavior.



Scheme 1: Counterion-controlled self-sorting phenomenon at the interface of a micelle formed from amphiphilic calix[4]arene.

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P12

Dendrimer mediated core-satellite nanostructures for SERS sensing

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Surface enhanced Raman scattering spectroscopy (SERS) is a ultra-sensitive technique that enables the detection of Raman active molecules even at single molecule level[1]. SERS is based on the enhancement of the Raman scattering signal of a certain analyte when is in contact or close to a plasmonic nanostructure. A further Raman enhancement could be achieved if the molecule is located at the intersticial gaps (called hot-spots) between nanoparticles. The narrower interparticle gaps, the higher is the enhancement. Different strategies have been recently developed to create plasmonic nanostructures with controlled hot-spots such as self-assembly, layer-by-layer[2].

Herein, we propose a strategy based on the combination of AuNPs and dendrimers to form core-satellite nanostructures and obtain control hot-spots for SERS sensing. To fabricate the core-satellite nanostrutures, citrate stabilized Au nanospheres (AuNSs, acting as satellite) were attached through electrostatic forces to the surface of dendrimer functionalized gold nanorods (AuNRs, acting as core) (Fig.1A). The dendrimers used were $C_{1242}H_{2289}Br_{81}N_{120}O_{399}$ (3G3) and $C_{260}H_{486}Br_{18}N_{26}O_{82}$ (2G2).

In this particular case, the dendrimers 3G3 and 2G2 will play different important roles: (1) to provide positive charge to the AuNRs, since these dendrimers present quaternary amines as functional groups; (2) to determine the interparticle gap (which can be modulated by selecting 3G3 or 2G2 dendrimer) in the core-satellite nanostructure; (3) to capture molecules without affinity for AuNPs since they present a internal hydrophobic cavity, and therefore allowing their detection by means of SERS.

In this work, first we analyse by SERS the ability of 3G3 or 2G2 stabilized AuNRs to capture and detect pyrene (see Fig. 1B) and also the improvement of SERS capabilities when they form core-satellite nanostructures by combination with Au nanospheres. As shown in Fig.1C, the SERS intensity strongly depends on the ratio satellites/core, increasing the SERS intensity with AuNSs:AuNRs ratio. Besides, we also study the influence of the dendrimer dimension in the SERS sensitivity of the core-satellite nanostructures. Thus the smaller the dendrimer dimension is, the higher SERS intensity is observed. It could be explained in terms of smaller intersticial gaps between the nanoparticles (core and satellites) and therefore leading to more intense hot-spots.

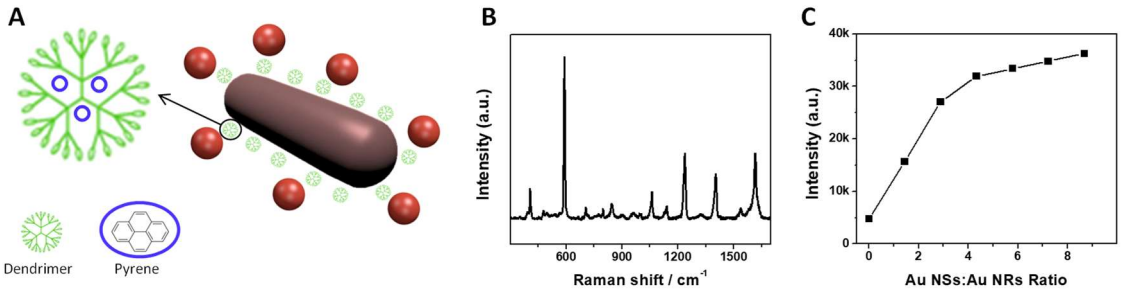

Figure 1. A) Scheme of a core-satellite nanostructure fabricated by combination of a dendrimer stabilized Au nanorod with citrate stabilized Au nanospheres. B) Characteristic SERS spectrum of pyrene detected using core-satellite nanostructures. C) SERS intensity of pyrene at 590 cm^{-1} as a function of AuNSs:AuNRs ratio forming the core-satellite nanostructures. Laser excitation line is 785 nm.

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P13

Disposable Electrochemical Biosensor for Protein Interaction Studies

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The interaction of proteins with other molecules may be established by conventional optical methods, but alternative approaches on a small flat support may be of interest to many applications. Many different devices could be established for this purpose, but electrochemical-based supports shall display highly sensitive and quick readings.
Thus, an electrochemical biosensor that can simulate a protein surface on a biological system is first developed herein. To this end, two different proteins were immobilized on a commercial screen-printed electrode (SPE) based on a gold working electrode that was previously amined. Interaction studies were made by adding a given target compound to the surface, for a given time, and by monitoring afterwards the electrochemical features of the resulting surface by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry studies.
The analytical features for the electrochemical protein interaction sensor were studied, for each protein, by calibrations with a target compound to which the interactions were being followed. The analytical data collected for this purpose was mostly generated by EIS. The effect of pH and time of interaction were also tested herein. In terms of the linear range of detection, the system was responding to the target compound with a limit of detection in the range of ~0.5 µM, depending of the protein. Linear response was observed against concentration or log(concentration), also depending on the protein underlying on the Au-SPE support.
Overall, this biosensor is able to monitor rapidly protein-target compound interactions, being easy to use and inexpensive. In principle, the approach described herein may be adapted to other proteins or target compounds, making it very interesting when compared to the conventional systems in the literature used to study such interactions.

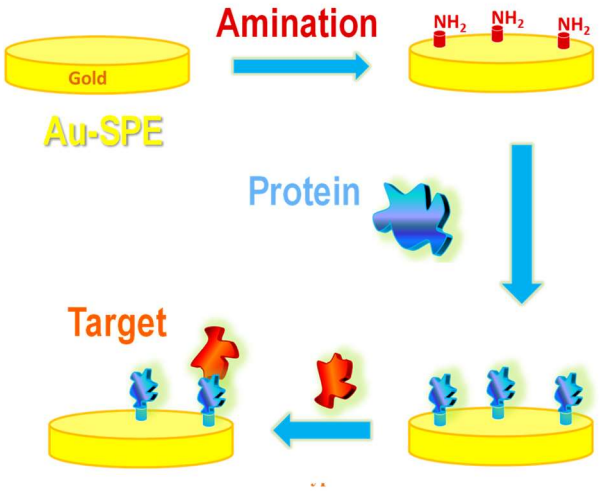

Figure 1: Schematic representation of SPE assembly, using a gold SPE (Au-SPE) that was amined and after modified with the protein for subsequent interaction with the target compound.

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P14

Encapsulation of Water-in-Water (W/W) Emulsions

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Water-in-Water (W/W) emulsions are dispersions of one aqueous phase (dispersed phase) into another aqueous phase (continuous phase) [1,2]. These emulsions can be prepared in Aqueous Two-Phase Systems (ATPS), where phase segregation occurs because of thermodynamic incompatibility between the two hydrophilic components, induced by differences in hydration between the two water-soluble components [3]. W/W emulsions can be formed in aqueous biphasic systems, without oil and without surfactant, by applying agitation. It is known that Water-in-Water emulsions can be stabilized by particles [4,5] able to adsorb at the W/W interface, forming Pickering emulsions. These fat-free dispersions can be highly interesting for food and drug delivery applications.

In the present work, Water-in-water (W/W) emulsions have been introduced in the interior of capsules. W/W emulsions have been prepared using a highly charged anionic polyelectrolyte (sodium alginate, NaAlg or sodium carboxymethyl cellulose, NaCMC), which has been mixed in aqueous solutions with a globular protein (bovine serum albumin, BSA). These two combinations of macromolecules showed phase separation, forming ATPS, and their phase behaviour was studied. BSA-in-alginate and BSA-in-NaCMC water-in-water emulsions were formed and characterized. These emulsions showed to be relatively stable, which was attributed to the high viscosity of either alginate or NaCMC. The emulsions were introduced into capsules, by dropping to Ca^{2+} or Fe^{3+} aqueous solutions (illustrative example in Fig. 1).

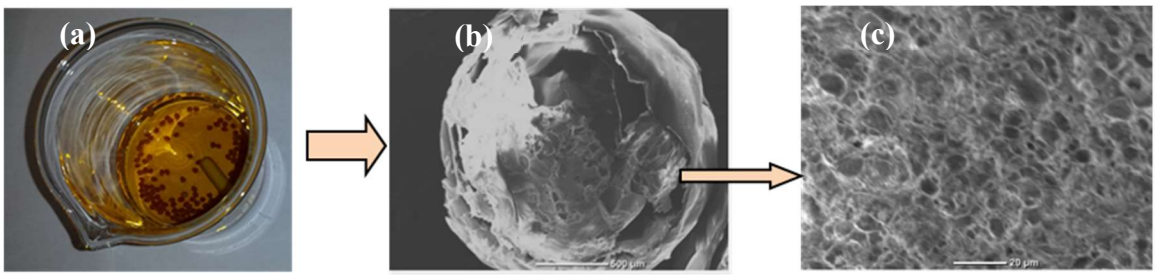

Fig. 1. Example of capsules and the macroporous interior of a freeze-dried capsule.

Both alginate and NaCMC formed ionic complexes with Ca^{2+} or Fe^{3+}, obtaining capsules that contained emulsions in the interior. Fig. 1a shows an illustrative of example of capsules formed with Fe^{3+}. Freeze-drying was used as a gentle method to remove water, obtaining dried capsules. These capsules might have a smooth surface (made of polyelectrolyte-Cation complexes) and a highly porous interior (formed by the presence of W/W emulsion droplets). Fig. 1b and 1c show an example of a capsule and its porous interior. These porous capsules might have interesting applications in encapsulation of active components (drugs, fragances, etc.) and the various possibilities are being evaluated.

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P15

Hybrid inorganic-organic core-shell nanoparticles with plasmon-like properties

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Plasmonic fields can be defined as quantized waves in a collection of mobile electrons which are disturbed from their equilibrium positions by light[1]. These light-matter interactions are extremely interesting due the high local field obtained at nanoscale. Nanostructured noble metals have been the most widely studied materials in plasmonics due to their optical properties within the UV-vis-NIR spectrum[2]. However, plasmonic properties have been recently observed in other non-metallic materials such as organic thin films based on J-aggregates[3]. Now, the main objective of this work is to go further demonstrating that it is possible to synthesize an inorganic-organic hybrid nanostructure which exhibits plasmon-like properties.

In this work, we have synthesized and analized colloidal dispersions of excitonic core-shell nanoparticles formed by a core of silica and densely packed J-aggregates shell. The role of the silica nanoparticles is being the inorganic scaffold or template for molecular J-aggregates whom will bring the plasmon-like properties to the colloids. In order to achieve that, first silica nanoparticles with size control have been obtained following the method proposed by Bogush et al.[4] Then, J-aggregates are deposited through electrostatics on the silica surface using the Layer-by-Layer technique. TDBC (1,1′-disulfobutyl-3,3′-diethyl-5,5′,6,6′-tetrachlorobenzimidazolyl-carbo-cyanine) has been chosen as organic molecule to form J-aggregates. The optical response of the hybrid nanoparticles was studied as a function of the number of J-aggregate depositions on the silica surface. The hybrids have been characterized by Transmission Electron Microscopy (TEM), Zeta potential, fluorescence spectroscopy and UV-vis spectroscopy. As the loading of J-aggregates increases, a new excitonic resonance appears which can be only justified by a plasmon-like resonance. These experimental results has been confirmed by numerical simulations revealing the potential use of J-aggregate materials as an excitonic alternative to plasmonics. Finally, we discuss how this new colloidal synthetic route of hybrid excitonic core-shell nanoparticles can push forward the development a new organic route for nanophotonics.

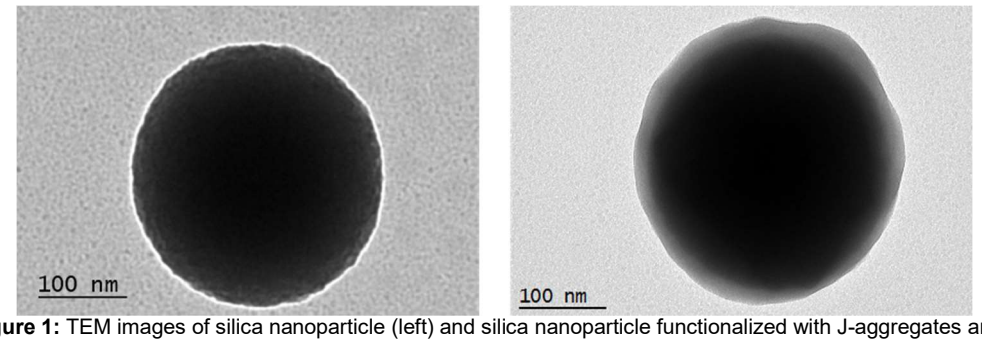

Figure 1: TEM images of silica nanoparticle (left) and silica nanoparticle functionalized with J-aggregates and a polyelectrolyte (right)

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P16

Polyelectrolyte functionalized frameworks for security applications

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Nowadays numerous techniques used to guarantee the security and authenticity of branded products, objects, important documents, etc, namely watermarks, holograms, and markers are already known. However, despite those techniques not being expensive and being easy to perform, they do not allow a quick and unambiguous authentication. So, to overcome this disadvantage, efforts are being made in using luminescent materials as an alternative to the common security techniques.

Materials with lanthanides in their composition have been considered very important for security purposes, since they present optimal physical and optical properties, varying luminescence from UV-Vis to NIR. They are also advantageous because they are stable and soluble, present sharp emission bands with high intensity, can be easily mass produced and can be excited in a significative range of wavelengths (UV-Vis to NIR).[1–4]

Luminescent security tags that emit radiation when excited by using UV radiation are presently the most commonly used security elements to assure the originality of a document, object or currency. Generically, a taggant is a material that can be dispersed in a matrix in ppm concentrations, without provoking changes in its structure, allowing that way a clear identification and minimizing its risk of being counterfeit. All of these materials reveal to be very important for security documents, since they also are resistant to photobleaching.[5]

So, in this project two luminescent coordination complexes based on a polyelectrolyte (PE) were obtained, by mixing lanthanide ions (europium – Eu and terbium – Tb) with PE and low molecular weight organic ligands. The complexes with Eu and Tb were colourless to the naked eye, but when UV excited presented high red and green luminescence, respectively.

The interaction between the coordination complexes and different metal solutions (nitrates) was tested and changes in the intensity of the luminescence were evaluated. Both lanthanide-containing frameworks show a significant quenching in the presence of Cu^{2+} and Ni^{2+} ions. In the presence of other ions the quenching is not so significant (e.g., Ag^{+} and Cr^{3+}) or present even a slightly enhancement of the luminescence intensity (Ca^{2+}, Na^{+}, K^{+} and Mg^{2+}). The effect of the type of anion on the luminescence intensity of the complexes was also assessed. By using different sodium salts it can be concluded that no luminescence quenching was observed, neither significative changes in luminescence intensity.

This suggests that luminescent materials can be of great interest for security application, based on their excellent optical properties and on their selectivity to copper and nickel ions.

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P17

Enhance of water absorption by crosslink cellulose

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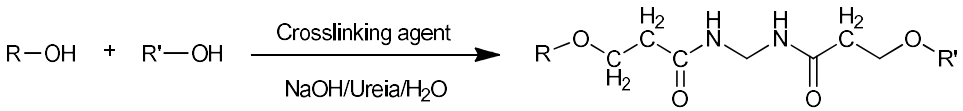
Hydrogels are 3D crosslinked polymers able to sorve large amounts of water used in many applications, including diapers, napkins, soil additives for agriculture and drug delivery systems. Our aim is to improve the water sorption ability of cellulose and cellulose-containing materials. Cellulose and cellulose derivatives are natural and abundant polymers with applications in a vast range of industries.[1,2] Cellulose hydrogels can be prepared using several methodologies namely pre-irradiation grafting, chemical or physical crosslinking, esterification, radical polymerization, graft polymerization, among others.[3,4] Chemical crosslinkers such as citric acid, epichlorohydrin, butanetetracarboxylic acid or *N*,*N*'-methylenebisacrylamide have been widely used to prepare hydrogels.[1–4] The strategy used in this work for the preparation of hydrogels consisted in the crosslinking of cellulose or cellulose/poly(vinyl alcohol) mixtures with methylenebisacrylamide. Poly(vinyl alcohol) (PVA) shows ability to form hydrogels and additionally, is non-toxic, non-carcinogenic, shows bioadhesive characteristics and is easily processed. PVA hydrogels exhibit a high degree of swelling in water, a rubbery and elastic nature and have demonstrated a great potential to act as a matrix for many applications, including drug delivery, wound dressing and sensors. Thus, the effect of crosslinking on the structure and properties of α-cellulose and α-cellulose/polyvinyl alcohol (PVA) gels was evaluated. The used procedure was based on another previous described by *H.Geng*[3]. In summary, first both polymers were dissolved separately: α-cellulose needed a pre-cooled solution of urea/NaOH, whilst PVA was dissolved in water, at 80 ºC under reflux conditions. The crosslinked blends of α-cellulose/PVA, with different concentrations of crosslinker, were characterized by spectroscopic and microscopic analysis. Besides the equilibrium and kinetics of water sorption was also studied. The water uptake studies showed that crosslinking had an impact in the capacity of water absorption of α-cellulose. The crosslinking reaction was carried out between the hydroxyl groups of α-cellulose and PVA with *N*,*N*'- methylenebisacrylamide, as described in Scheme 1.



Scheme 1: Generic reaction of reticulation between two polymers, using a crosslinking agent.

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P18

A biophysical insight of Camptothecin interaction with biomembrane models based in colloidal interfaces

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Camptothecin (CPT) has been described as a chemotherapeutic agent with a mechanism of action targeting the nuclear enzyme topoisomerase I[1]. Considering, the CPT intracellular target it is inevitable the drug interaction and penetration of the cell membranes. Evidences of changes in membrane lipids composition have been described for a number of pathologies, including cancer. In fact, cancer cells present diverse chemical, structural and biophysical characteristics that are different from normal cells. These lipid alterations can, for example, promote resistance of cancer cells to chemotherapeutics, a major clinical problem that leads to therapy failure. In this context, understanding the interactions of chemotherapeutic compounds with biological membranes is crucial, since it is directly associated with therapeutic activity [2]. Moreover, the knowledge acquired with biophysical studies play a significant role in the design of new drugs and in the development of delivery systems[3,4].

Due to cell membrane complexity, biomimetic model systems and biophysical techniques have been developed and applied in the drug-membrane interaction studies. In the present study, several colloidal interfaces were considered as biomimetic models: single-lipid liposomal membrane models composed by DMPC or DOPC and lipid mixture liposomal membrane models mimetic of breast cancer cell membrane (DOPC:CHOL:EPC:DOPS:DOPE:CL:SM) and mimetic of cell membrane (DOPC:DOPE:DOPS:CHOL:SM). The distributon coefficient (*Log D*) of CPT between membrane and aqueous buffered solution (mimicking the pH environment for breast cancer cell membrane – pH 5.8 – and for cell membrane – pH 7.4) was performed by derivative spectroscopy[4].

The ability of CPT to partition into lipid bilayer of the studied biomimetic models was demonstrated and results showed that CPT has higher affinity for more fluid lipid bilayers, such as the ones of cancer cell membranes (*Log D*=3.06±0.12), than for cell membrane (*Log D* =2.71±0.11).

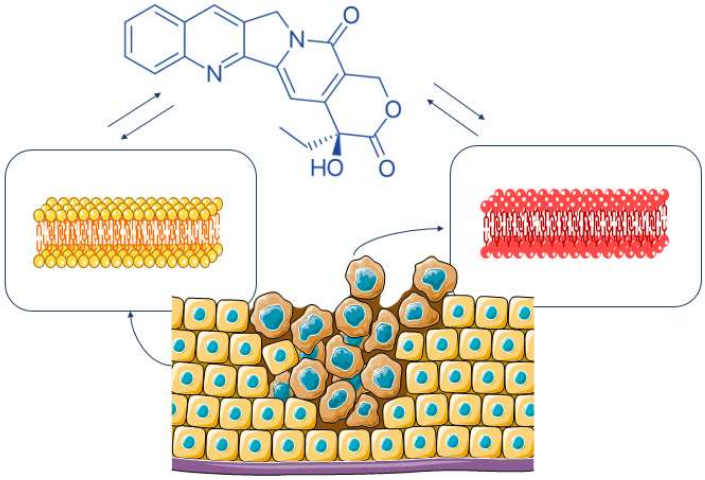

Figure 1: Representative summary image of the research developed.

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P19

Novel liposomes for Alzheimer's disease treatment

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Alzheimer's disease is one of the most debilitating neurological diseases, afflicting an ever-increasing number of a majorly elderly population worldwide[1]. Curcumin is a phytochemical which has been described to aid in the neuroprotection of the brain against oxidative stress insults and to reduce amyloid-β accumulation in the brain afflicted by Alzheimer's disease[2]. However, its solubility in human blood and its pharmacokinetics is very unfavorable, leading to rapid elimination from the blood stream. Moreover, it is poorly absorbed by the intestines, limiting oral administration.
The use of liposomes to encapsulate and carry curcumin to the brain is already being proposed for therapy. We developed a novel type of liposomes, with a unique mixture of phospholipids mimicking cellular components, that can encapsulate curcumin in a highly efficient manner. These liposomes have an adequate size to cross the human blood brain barrier and are not cytotoxic to fibroblast and neural cell lines. Moreover, curcumin is incorporated in these cells and has a neuroprotective effect [3], reducing ROS production and increasing cell viability upon incubation with an oxidative stress inducer. Furthermore, these liposomes do not show any *in vivo* toxicity in a zebrafish embryotoxicity model, with curcumin being incorporated without side effects. The functionality of zebrafish blood brain barrier (BBB), which is similar in structure to the human one, is fully obtained 3 days after fertilization, and provides valuable information[4]. With this system we can diminuish the production of ROS, and presumably slow the progression and alleviate the symptoms of Alzheimer's disease.

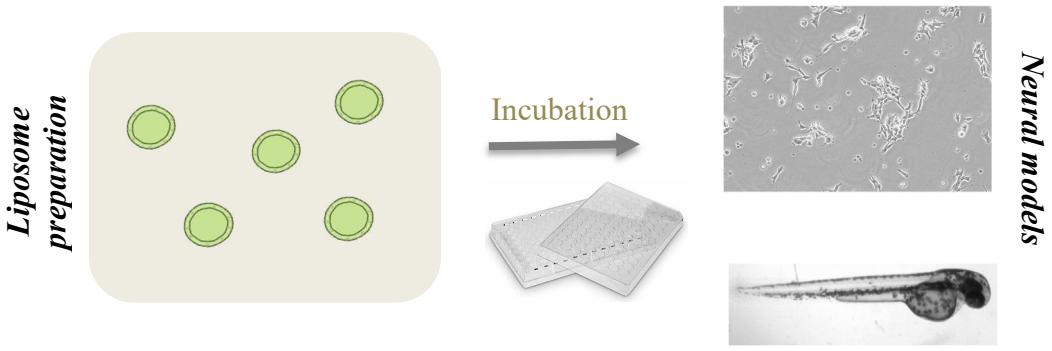

Figure 1: Schematic overview of the production and validation of the novel mimetic liposomes in models of neural oxidative insult.

Acknowledgements: This work was supported by the strategic programme UID/BIA/04050/2019, funded by national funds through the FCT IP, and project FUN2CYT: Harnessing the potential for biomedical applications of pleiotropic cytokines LIF and oncostatin M (PTDC/BTM-MAT/30568/2017, POCI-01-0145-FEDER-030568) supported by POCI through FEDER and FCT IP.

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P20

Dendrimer-based plasmonic systems for the SERS detection of pesticides in water

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Dendrimers are useful multifunctional materials given their well-defined architecture and tunable chemistry. Herein, the chemistry of poly(amido)amine (PAMAM) dendrimers of variable functional groups and generations is explored to produce a variety of plasmonic systems based on colloidal Au/Ag nanoparticles. The resulting colloidal systems have been investigated as sensitive platforms for surface-enhanced Raman scattering (SERS) studies. Noteworthy, metal coated nanoparticles of tunable size, surface chemistry and shape were achieved by varying the dendrimers' chemistry. In addition, by taking advantage of the surface chemistry of PAMAM dendrimers, assemblies of multiple plasmonic nanoparticles were obtained, improving the SERS efficiency of these materials. The resulting colloids were then used to monitor selectively the presence of pesticides in water samples (*e.g.* diethyldithiocarbamate, thiram and paraquat), in certain situations reaching detection limits down to 10 nM in the target analyte. Moreover, the use of PAMAM dendrimers to prepare nanometal coated colloids offers practical advantages for SERS trace analysis, such as improved colloidal stability under variable experimental conditions (*e.g.* pH, ionic strength).

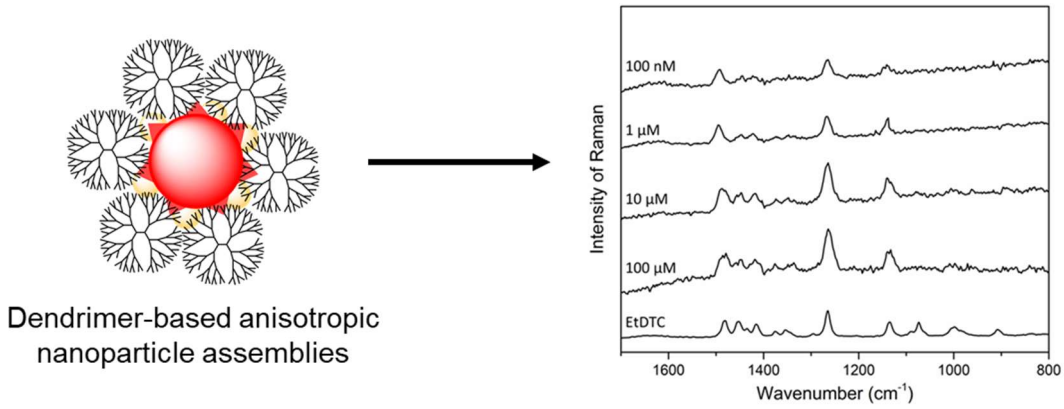

Figure 1: *PAMAM/Au assemblies as colloidal substrates for SERS detection of diethyldithiocarbamate.*

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Interaction of a model anticancer drug with models of healthy and cancerous cell membranes

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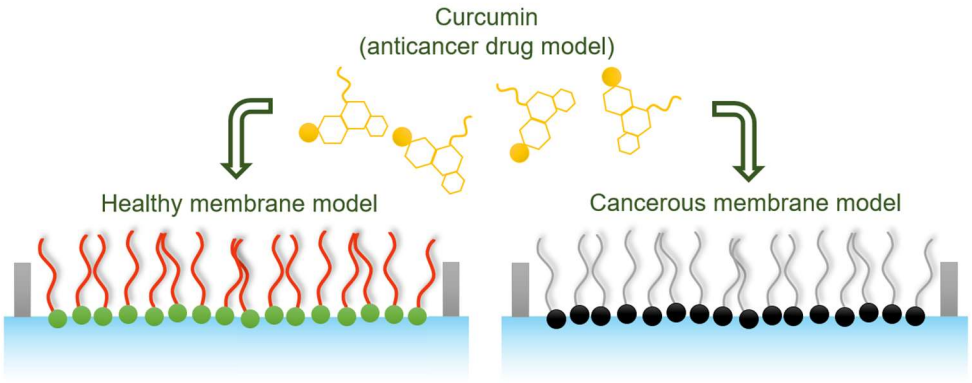
Development of anticancer treatments is a multidisciplinary challenge which involves many researchers from different scientific areas. The current challenge is to accomplish advanced, personalized and efficient therapies that kill cancerous cells preventing the development of tumor, but reducing the undesirable side effects of conventional chemotherapy on patients. To achieve this, one of the most important strategies is the development of novel anticancer drugs. The therapeutic process involves entering through the cancer cell membranes and delivering the drug inside them while leaving the healthy ones unaltered. For this reason, it is important to study the viability of anticancer drugs against healthy and cancerous cells. In this work, we address the interaction of a model anticancer drug, curcumin, with healthy and cancerous models of cell membrane by Langmuir monolayer technique. Langmuir monolayers at the air-water interface have been widely used to mimic cell membranes in attempts to determine the mechanisms involved in their interaction with bioactive molecules as this technique allows fine control over the composition and packing of the membrane model[1].

There are important differences in lipid composition and membrane function of tumor cells compared to healthy cells such as a lower amount of cholesterol and the presence on unsaturated lipids in tumor cell membranes[2,3]. These, make cancer cells more fluid than healthy cells, possibly affecting their interaction with bioactive compounds. The molar ratio of cholesterol:phospholipids as well as lipid composition may differ depending on the kind of the cell and degree of malignancy, leading to the possibility of designing a huge amount of different artificial systems.

In this research work, we model the healthy cell membrane by a mixed monolayer of DPPC phospholipid and cholesterol (Chol) in a molar ratio Chol:DPPC= 0.67 at the air-water interface and the cancerous cell membrane by unsaturated sphingomyelin (Sph) and a lower proportion of Chol (Chol:Sph=0.25). First, we characterize these model membranes in terms of their surface pressure-area monolayers and Gibbs elasticity. Then we study the effect of curcumin on the monolayers and the thermodynamic stability of both model membrane models (see scheme 1). Our results show that the interaction of curcumin with cancerous cell membranes is favored hence, causing its thermodynamic stabilization. This result demonstrates the potential of curcumin as a drug candidate against cancer development in future studies. It also demonstrates the importance of the combination of lipids in membrane models in the design of targeted strategies in cancer treatment.



Scheme 1: Mixed monolayers formed by curcumin and lipids modeling healthy and cancerous cell membranes

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P22

Green synthesis of gold nanoparticles led by algae *Cystoseira tamariscifolia* and evaluation of their biological activity

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In recent years, the development of efficient green chemistry methods for synthesis of metal nanoparticles has emerged as an eco-friendly alternative for the production of well-characterized nanoparticles [1]. Gold nanoparticles are presently under intensive study due to their attractive physicochemical and biological properties as well as their potential applications in the development of new technologies for nanomedicine, both in theraphy and diagnosis [2,3]. Seaweed phytochemicals, including hydroxyl, carboxyl, and amino functional groups, can serve both as effective metal-reducing agents and as capping agents to provide a robust coating on metal nanoparticles in a single step [4].

In this study, we tested if *Cystoseira tamariscifolia (CT)* is a potential agent involved in the reducing and stabilizing processes for the green synthesis of gold nanoparticles. An aqueous extract of this macroalga was prepared and used to produce spherical, stable, polycrystalline nanoparticles with a mean diameter of 7.6 ± 2.2 nm for Au@CT (gold nanoparticles produced in CT extracts), as demonstrated by UV–vis spectroscopy, TEM, HRTEM, STEM and zeta potential measurements. Moreover, the biomolecules present in the extract and nanoparticles were characterized by Fourier Transformed Infrared Spectroscopy (FTIR). *In vitro* antioxidant activity assays also showed that CT extract has a high reducing power, phenolic content and DPPH scavenging activity.

Effects of Au@CT and CT extract alone on cellular metabolism were evaluated by tetrazolium-based colorimetric cellular assay (MTT), and on cell membrane integrity by lactate dehydrogenase activity (LDH) assay. Wound-healing assay revealed impacts on cell proliferation and migration capacity. These assays were performed to investigate whether Au@CT and CT extract alone affect cell viability in mouse (L929 cell line) and human (BJ5-ta cell line) fibroblast cells as *in vitro* models. Lower concentrations of the alga extract and derived nanoparticles did not cause any cytotoxicity. This, together with the wound-healing assay, indicates a potential positive role in cell regeneration.

The zebrafish embryotoxicity (ZET) assay, recomended by OECD to evaluate acute toxicity, was performed to obtain a correlation between *in vitro* and *in vivo* toxicity. These embryos are translucent, allowing direct, real time observation and the evaluation of whole organism responses, from mortality to more specific parameters such as neurotoxicity. The results show that toxicity is evident only at very high concentrations

These results reveal that green synthesis in CT extracts of non-toxic, bioactive nanoparticles have very desirable features with potential applications in biomedicine.

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P23

Topical formulation containing omega-3 and/or resveratrol encapsulated in lipid colloidal dispersions for psoriasis

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Among inflammatory and autoimmune skin diseases, psoriasis stands out with an incidence of 2% of the world's population. Psoriasis is a chronic inflammatory disease that manifests mainly in sensitive friction areas (e.g. knees, elbows, navel and lower back) in the form of typical erythematous squamous plaques and papules, which may be pruritic or even painful. Despite the main goal of therapy is to improve the life quality of patients, the conventional therapies have a series of clinical limitations, therefore the research for alternative strategies relatively to drugs and/or bioactive compounds delivery mechanisms that increase the therapeutic efficacy and reduce the adverse effects is considered an added value in the dermatological area. Several studies reported that bioactive compounds, such as resveratrol or fish oils rich in omega-3 fatty acids, have anti-inflammatory and immunomodulatory effects, which justifies their use in inflammatory and/or immunological diseases, such as psoriasis[1,2]. Lipid colloidal dispersions, such as lipid nanoparticles or liposomes, have been investigated for therapeutic applications in skin diseases, with the aim to improve the therapeutic efficacy. Concerning the topical application, these nanosystems present various advantages[3,4], namely improvement of cutaneous penetration; reducing skin irritation by preventing bioactive components from being in direct contact with the skin; and the possibility of improvement cutaneous hydration, either by an occlusive effect or by the replacement of the hydrolipidic film as a consequence of the lipid composition of the nanosystems. However, the lipid colloidal dispersions have a reduced viscosity, which is one of the limitations for the direct topical application. For this reason, and to improve the stability and rheological properties, some authors have incorporated these formulations into classic semisolid bases, such as creams or hydrogels[5,6]. Taking these consideration, the objective of the present work was to develop and optimize a topical semisolid formulation containing fish oils rich in omega-3 encapsulated in lipid nanosystems (lipid nanoparticles and liposomes) for possible application in psoriatic or inflammatory skin lesions. Moreover, an well known anti-inflammatory bioactive compund, resveratrol (RSV), encapsulated only in liposomes was used. Ultrasound and hydration of the lipid film techniques were applied to develop the nanostructured lipid vectors (NLC) and liposomes, respectively. After their development, the formulations were characterized for stability and accelerated stability, to select the ones that would be more promising. Subsequently, assays were performed to predict therapeutic performance and to evaluate the anti-inflammatory effect. Finally, the selected formulations were incorporated into a semi-solid base (hydrogel) and subjected to rheology, occlusion and permeation assays. Regarding the mean size and polydispersion index (PDI), both the liposomes and the NLC presented acceptable values, considering that the intended application is a cutaneous topical application in psoriatic skin that is damaged, inflamed and more permeable. As for the zeta potential, all formulations presented values below ± 30 mV allowing prediction of lipid nanosystem instability, which is not ideal in a storage context, but it could be beneficial for cutaneous penetration, since the deformable systems are the most able to cross the barriers of the stratum corneum. ATR-FTIR analysis for liposomal formulations with and without the co-encapsulation of bioactive compounds proved the establishment of hydrogen bonds between the RSV and the polar heads of liposome phospholipids and electrostatic interaction with omega-3. The lipid nanosystems demonstrated to be stable in the long term. Therapeutic performance studies (i.e. bioactive relase profile, permeation studies and anti-inflammatory and antioxidant assays) have highlighted therapeutic properties relevant to the psoriasis treatment (e.g. anti-inflammatory features, COX-1 inhibition and nitic oxide production and antioxidant capabilities). In order to allow better topical applicability, the formulations were incorporated into a semi-solid base (hydrogel), which exhibited a pseudoplastic behaviour, favourable for the intentional administration.

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P24

Hybrid nanomaterials of graphene oxide and copper sulfide for the photodegradation of sulfamethoxazole in water

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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] We have been interested in preparing carbon nanostructures (e.g. graphene oxide) decorated with semiconductor nanophases, as new photocatalysts for water treatment technologies.[3] In particular, copper sulfide has been investigated as the semiconducting material due to the ability to harvest photons efficiently in the visible spectral region, exhibiting a band-gap at 1.2-2.2 eV, which is dependent on the crystalline phase present.[4] Furthermore, it will be described that the combination of magnetic nanoparticles to such photocatalysts allows the magnetic separation of the photocatalysts for subsequent reuse. Herein, the optimisation of diverse chemical routes aiming to develop efficient and reusable GO supported photocatalysts (Figure 1) was assessed by performing experiments using a visible light photoreactor for the degradation of sulfamethoxazole.

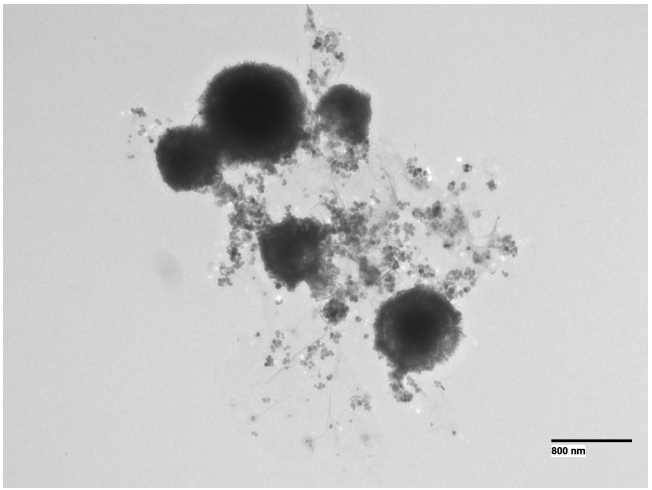

Figure 1: TEM image of Cus@Fe_3O_4/GO hybrid material.

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P25

Encapsulation and release of lisozyme by temperature/pH-responsive tubule-based hydrogels

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Stimuli-responsive colloidal assemblies based on amino acid-based surfactants are rather promising systems for drug delivery [1], because of their versatility and enhanced human biocompatibility. In addition to forming micelles and liposomes, some amino acid-based amphiphiles can self-organize into other complex supramolecular structures, such as fibers, twisted ribbons, helical tapes and nanotubes [2-4].

In this work, we have focused on the structural characterization of hydrogels formed by double-chained lysine-based amphiphiles, *n*Lys*m*, that self-assemble into tubular structures, and on their ability to encapsulate and release a model biomolecule, lysozyme (LZM). To obtain structural insight on the tubular assemblies, microscopic techniques such as video-enhanced light microscopy (VELM), scanning electron microscopy (SEM), cryogenic scanning electron microscopy (cryo-SEM), cryogenic transmission electron microscopy (cryo-TEM) and atomic force microscopy (AFM) were used (figure 1). Interactions of the tubules with the protein lysozyme, under varying experimental conditions, was investigated by DSC microcalorimetry and UV/VIS spectroscopy, with the main goal of assessing the efficiency of the tubules as pH- and temperature-sensitive nanocarriers. Results on the toxicity of the tubules *per se* and the tubule/LZM aggregates in human cells will also be presented.

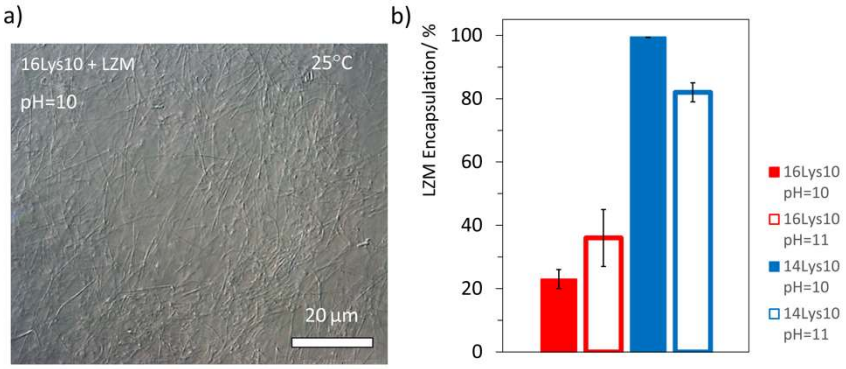

Figure 1: (a) Light micrograph of 16Lys10/LZM supramolecular structures, in a buffer solution at pH = 10; (b) percentage of LZM encapsulation by the lysine-based hydrogels (b).

Acknowledgements: We thank Fundação para a Ciência e Tecnologia, FEDER/COMPETE and P2020|COMPETE for financial support through grants POCI-01-0145-FEDER-032351 (PhotoSAN), UID/QUI/00081/2013, POCI-01-0145-FEDER-006980, NORTE-01-0145-FEDER-000028, and UID/QUI/50006/2013. I.S. Oliveira is also grateful to FCT for support through the PhD grant SFRH/BD/108629/2015.

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P26

Developmental neurotoxic effect of nanoparticles: towards real-time assessment using zebrafish embryos as vertebrate model

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Exposure to neurotoxic agents during embryonic development can cause irreparable short- and long-term damage to vertebrates, including for humans, as it may affect the central nervous system (CNS) and the blood brain barrier (BBB)[1]. The reported CNS susceptibility during embryogenesis suggests that there may be a critical window of exposure during brain development. Nowadays, therapies using nanoparticles are an important alternative for most of the diseases, since they allow, for example, more effective and localized delivery of drugs and higher success in treatments [2]. However, the exposure to them at an embryonic stage can cause neurotoxic damages.
In this study, the putative toxicity of two different nanoparticle formulations was evaluated, namely gold nanoparticles, which were produced by Green synthesis, and liposomal nanoparticles. Both have known and interesting bioactivities, such as anti-inflammatory, antioxidant, antifungal and antibacterial[3][4].
Thus, the capacity of the neuroprotective effect of the nanoparticles in contact with toxins was tested, the evaluation was done through the ZET assay, with the endpoits shown in the figure and following parameters, mortality, epiboly, malformation, heart beat, spotaneus movements, hedd-trunk angle, hatching and free-swimming.
2D cell models are easy to reproduce, however they fail to mimic real conditions. Animal models are better than 2D models, however many ethical problems are involved. Zebrafish embryos compose a low-cost and highly informative non- animal alternative to evaluate early developmental responses associated with neurotoxicity[5][6]. As model has multiple advantages for its use in toxicity tests including *ex-utero* fertilization, transparency of the embryos which allow observations at real time, rapid development and high fecundity[5][6]. Zebrafish embryos possess neural development characteristics similar to the vertebrate ones, which makes them ideal to assess embryo neurotoxicity *in vivo*.
Obtained results show that zebrafish is a profitable and reliable model organism for neurotoxicity tests. Nevertheless, there is a need to continue these neurotoxic tests in more complex models, so that these nanoparticles can become an alternative therapy.

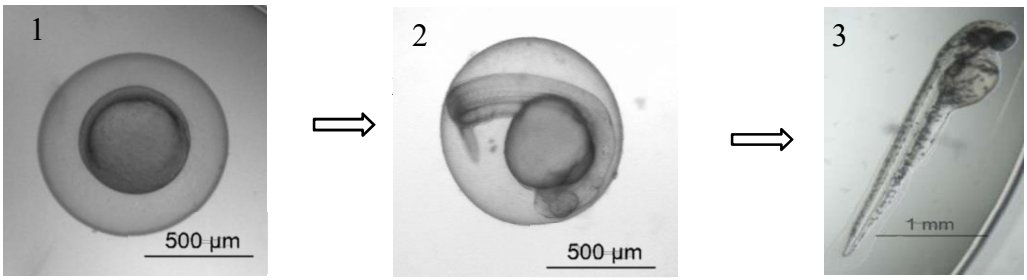

Figure 1: Different endpoints of zebrafish development at 1-8 h_{pf}, 2- 32 h_{pf} and 3- 56 h_{pf} *h_{pf}- hours post fertilization.

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P27

Synthesis and characterization of Cobalt(II)/Nickel(II)-Imidazolate Nanoparticles

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Energy production and storage and environmental pollution removal constitute some of the main priorities of modern society nowadays. Metal Organic Frameworks (MOFs) are ideal candidates to find more efficient nanosystems to construct devices based on such nanomaterials for these applications. MOFs are characterized by their large specific surface, ultrahigh porosity, tunable pore size distribution and structural tailorability. These characteristics will determine their properties and as a cnsequence their performance.

Recently, zeolitic structures based on imidazolates (ZIFs) have appeared as an important subfamily of MOFs, which have been used to derive, for example, crystalline hybrid hollow metal oxides. In this work, we followed a previously developed synthetic with some modifciations for the fabrication of nanoporous metallic crystalline networks composed of Co^{2+}/Ni^{2+} and 2-methylimidazole, nanoZIFs, at different proportions of the constituents. This methodology is very simple, carried out in aqueous medium and at room temperature and allows the fine-tuning of the morphology, crystallinity and compositon of the resulting porous nanoparticles (NPs). The obtained NPs were structurally and physico-chemically characterized by determining their size distributios, morphology, heat degradability, and structure. In addition, their colloidal stability and the associated size/morphological and compositonal changes of the porous NPs in several solvents of different polarities were investigated in detail, as well as the influence of the stabilizing surfactant (CTAB) used during the synthetic process.

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P28

Synthesis and functionalization of novel multifunctional nanoparticles for multimodal therapy of melanoma

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Upconversion nanoparticles (UCNPs) have the ability to generate UV or visible emissions under continuous wave near infrared excitations. These nanomaterials are attracting increasing attention due to their unique properties, as for instance narrow emission bands, high penetration depth into tissues, low background signals, large Stokes shifts, high resistance to photobleaching, photostability, and long luminescence lifetimes. [1] These characteristics allow their use in several biomedical applications, including targeted drug delivery, photodynamic therapy (PDT), photothermal therapy (PTT). [1, 2, 3, 4]
Consequently, UCNPs are currently emerging as a new class of theranostic agents in biomedicine, as they can provide completely new platforms for both detection and treatment of cancer. Melanoma is the most aggressive form of skin cancer and one of the most challenging malignancies to treat with a steeply rising incidence and a poor prognosis in advanced stages. [5] Conventional clinical treatment of melanoma often fails in tumour complete eradication, due to the low response rates to single therapies, side effects and recalcitrance to traditional chemotherapy and radiotherapy [6].
Therefore, in HOTsPOT project we aim the development of multimodal nanoplatforms for the treatment of melanoma skin cancer. Our approach is based on the development of NIR excitable upconversion nanoplatforms that combine in a single platform, targeted generation of i) hyperthermia, ii) reactive oxygen species and iii) antitumor drug delivery, respectively in a context of photothermal therapy (PTT), photodynamic therapy (PDT) and chemotherapy. For that purpose, SrF_2:Yb/Er UCNPs and $NaYF_4$:Yb/Er UCNPs were synthesized and coated with a mesoporous silica shell to allow the incorporation of the tumor targeting molecule, the photosensitizer, and the antitumor drug. Preliminary characterization results regarding particle size and morphology (TEM) and chemical composition (EDS and FTIR) are presented and discussed.

Acknowledgements: This work was supported by the project HOTsPOT [PTDC/BTM-MAT/31794/2017 (POCI-01-0145-FEDER-031794)] funded by FEDER, through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (OE), through FCT/MCTES. Thanks are also due for the financial support to CESAM (UID/AMB/5001772019) and CICECO (UID/CTM/50011/2019), to FCT/MCTES through national funds.

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P29

Viral mimetic assemblies: novel nanostructures for drug delivery

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Recently, the design of versatile tools to improve cell targeting and drug delivery in medicine is taking upmost relevance in nanobiotechnology. Biological and inorganic nanocarrier drug delivery systems have their advantages and disadvantages in terms of cell targeting and specificity, cell internalization, efficient payload delivery, and safety profiles[1,2]. Herein, we present two different nanostructures that present relevant characteristics as drug delivery systems. Both nanohybrids are composed by mesoporous silica nanoparticles (MSNP), although the organic coating over the silica surface that make them advantageous is different. One of them is covered by multi-walled carbon nanotubes (MWNT), named MWNT@MSNP, while the other nanohybrid is covered with a biological coating, Tobacco Mosaic Virus (TMV) nanoparticles, named TMV@MSNP. MWNT@MSNP are capable of escape from endosomes after 72 h, by mimicking the spike-shape from animal virus[3]. On the other hand, TMV@MSNP, a wool ball-like nanostructure, showed a higher cell uptake than bare MSNP due to the TMV biological coating[4]. These outstanding features, together with the high loading capacity of MSNP, make them ideal candidates as drug delivery systems.

Acknowledgements: We thank the Economy and Competitiviness Ministry of Spanish Government

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P30

Thermotropic ionic liquid crystals from lysine-based amphiphiles: structure-property relationships

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Thermotropic liquid crystals (TLCs) are intermediate structures between crystals and liquids, which often respond to external stimuli such as mechanical stress or electrical fields, thereby changing their optical properties (e.g. birefringence and color) [1,2]. They have had a great impact in technology, playing a crucial role in the development of displays, sensors and optoelectronic devices [2]. Fundamental studies, on the other hand, have focused on the development and characterization of novel mesogenic molecules and structure-function relationships, which may foster the expansion of applications. In the last two decades, ionic liquid crystals which are liquid crystalline phases containing cations and anions have also been subject to intense research and growing interest, due to the combination of properties of conventional uncharged TLCs and those of ionic liquids [3,4].

In this work, we have investigated the thermal phase behavior of lysine-based amphiphiles (sodium salts) with two asymmetric tails lengths and a pseudo-gemini structure, generally designated as *m*Lys*n,* where *n* and *m* represent the number of carbon atoms in alkyl tails. Probing techniques used include DSC, TGA, polarized light microscopy and XRD. As will be shown, structural isomerism (*m/n* vs. *n*/*m*) and total chain length (*n* + *m*) of the compounds have a significant impact on the ionic TLCs formed and their optical properties, highlighting the importance of chemistry and molecular design on the development of functional materials. The PLM results show that when the charge is located on the same side of the longer chain, the phase behavior of the surfactants is much more complex than for the respective isomers. Furthermore, the lysine surfactants phase behavior is dominated by high temperature smectic phases, characterize by focal conics textures (figure 1).

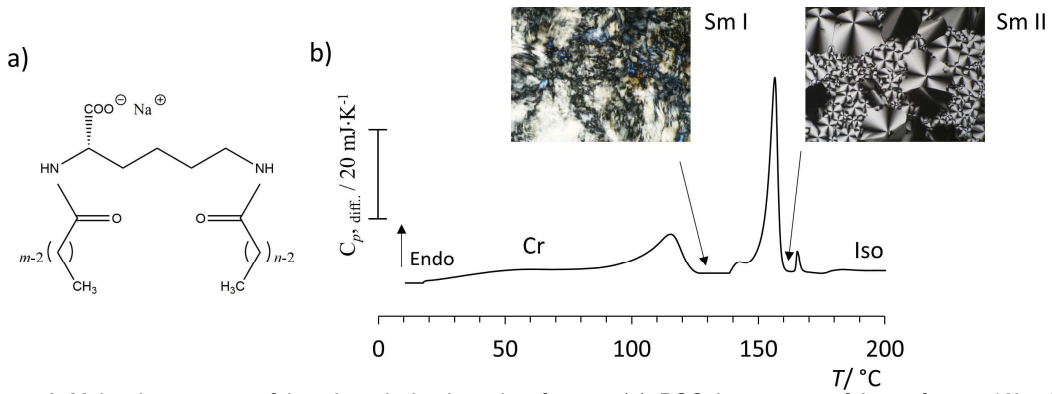

Figure 1: Molecular structure of the *m*Lys*n* lysine-based surfactants (a). DSC thermogram of the surfactant 12Lys8 and micrographs of the birefringent smectic phase textures (Sm I and Sm II) obtained by polarized light microscopy.

Acknowledgements: We thank Fundação para a Ciência e Tecnologia, FEDER/COMPETE and P2020|COMPETE for financial support through grants POCI-01-0145-FEDER-032351 (PhotoSAN), UID/QUI/00081/2013, POCI-01-0145- FEDER-006980, NORTE-01-0145-FEDER-000028, and UID/QUI/50006/2013. I.S. Oliveira is also grateful to FCT for support through the PhD grant SFRH/BD/108629/2015.

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P31

Mono-substituted Mn(II) Keggin-type polyoxometalate: integration in graphene nanocomposites and application in photocatalysis

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Organic dyes are a group of environmentally hazardous materials that due to their high toxicity and carcinogenicity are responsible for a massive pollution. Several wastewater treatments have been developed, however their degradation is not complete. Thus, various oxidative advanced methods have been adopted for water treatment. In particular, photocatalysis emerged as a powerful alternative for organic pollutants degradation not treatable by conventional techniques, preferentially using solar light irradiation.

Polyoxometalates (POMs) show many advantages as photocatalysts, namely the possibility of multi-electron photo-reduction, followed by reversible electron exchange with a substrate and the possibility of heterogenization without loss of properties. The incorporation of transition metals can modify the photochemical reactivity of POMs, changing the photo-oxidative activity/selectivity and the clusters visible light absorption. POM based nanocomposites have been studied in several contexts[1] and will be tested as photocatalysts in this work, using graphene oxide as the POM support.

This research aims to prepare nanostructured hybrid materials based on manganese(II)-substituted Keggin type anions[2] supported in graphene oxide (Figure 1) for the photocatalytic degradation of organic pollutants. We have been interested in exploiting synergetic effects that may result from the combination of POMs and graphene oxide envisaging the photocatalytic degradation of water pollutants. The resulting materials were full characterized before and after application in the photocatalytic experiments. The materials were tested as photocatalysts in the degradation of aqueous solutions of rhodamine B, as a model dye, using a visible light reactor. Their catalytic activity will be presented and discussed.

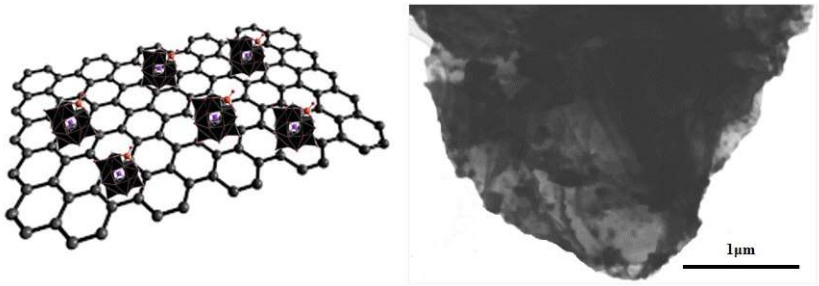

Figure 1: Scheme of a hybrid nanomaterial based on the mono-substituted Mn(II) Keggin-type polyoxometalate, $[PW_{11}Mn(H_2O)O_{39}]^{5-}$, supported in graphene oxide and the STEM image of the corresponding material prepared in this work.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, FCT Ref. UID/CTM/50011/2019, financed by national funds through the FCT/MCTES. Maria J. Martins thanks the Fundação para a Ciência e Tecnologia (FCT) for the PhD grant SFRH/BD/131433/2017. Ana C. Estrada also acknowledges the costs resulting from the FCT hirings funded by national funds (OE), through FCT – Fundação para a Ciência e a Tecnologia, I.P., in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19.

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P32

ZnO NPs loaded alginate beads for controlled release of zinc in acidic agricultural soils

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Nanoengineered materials have been investigated in agricultural production in order to mitigate environmental problems caused by conventional fertilization.[1] Due to a lack of synchronization between the release of minerals from bulk ionic fertilizers and the uptake by plants, only a small part of the fertilizers applied to the soils are actually used by plants, with the remaining portion removed by leaching or run-off thus causing negative environmental impacts.[2] Nanoengineered materials can be used to control the release of nutrients according to specific soil biochemical conditions allowing a reduction of nutrients loss and of fertilizers application rates.[2-3]

Biopolymers such as cellulose, alginate or chitosan are adequate for the development of ecofriendly nanocomposite fertilizers and, as such, good substrates for the immobilization of nutrient-containing nanoparticles because they are natural, low-cost and biodegradable polymers. Although there are reports in the literature concerning the use of biopolymers for controlled release of nutrients, the majority of the research has been directed to the release of macronutrients in aqueous solutions.[4]

In the present work, ZnO NPs loaded alginate beads were prepared and their potential as materials for the controlled release of cationic Zn in acidic agricultural soils was investigated. The materials were added to soils with distinct pH and organic matter content. The amount of labile Zn^{2+} dissolved from ZnO NPs added to soil along time was studied using a soil 0.01 M $CaCl_2$ extraction and the rate of cationic Zn release was correlated with the morphology of the particulates and the characteristics of the soils. The alginate beads showed lower Zn release in acidic soils as compared to the use of the salt $ZnCl_2$. For the same amount of Zn added to agricultural soil LUFA 2.2 (100 mg Zn kg^{-1} soil dry weight) and a period of incubation of 30 days, the extractability of Zn from soil amended with ZnO NPs loaded alginate beads was two times lower than the extractability of Zn from the soil amended with $ZnCl_2$. The release of Zn^{2+} from alginate beads was obtained in a controlled manner. In fact, for 1-2 days of incubation, a small increase of extractable Zn^{2+} was observed for soils amended with ZnONPs/alginate beads and after 7-10 days the concentration of extractable Zn^{2+} reached a plateau. The results presented here will be discussed having in perspective the potential of these nanoengineered materials for the controlled release of micronutrients in acidic soils.

Acknowledgements: Thanks are due for the financial support to CESAM (UID/AMB/50017 - POCI-01-0145-FEDER-007638), to Portuguese FCT/MCTES through national funds (PIDDAC), and the co-funding by the FEDER, within the PT2020 Partnership Agreement and Compete 2020, under project NanoFertil (references: POCI-01-0145-FEDER-016749 and PTDC/AGR-PRO/6262/2014). S. M. Rodrigues also acknowledges the financial support from FCT (Project IF/01637/2013). T. Trindade and N. Martins thank the CICECO-Aveiro Institute of Materials (Ref. FCT UID /CTM /50011/2013), financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. N. Martins is funded by National funds (OE), through FCT- Fundação para a Ciência e Tecnologia, I.P., in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by the law 57/2017, of July 19.

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P33

Surface modification of ZnS and ZnS:Mn colloidal quantum dots using tetrapyrrolic macrocycles

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Quantum dots (QDs) are semiconductor nanoparticles that show quantum size effects and exhibit a unique set of optical properties, including large absorption coefficients, size-tunable band structure, high fluorescent quantum yields and photochemical robustness.[1] As such, these colloidal systems have been explored in several applications, such as in optoelectronic devices and nanomedicine. An important class of colloidal QDs comprise nanocrystals of II-IV semiconducting compounds. Although cadmium based semiconductors have been largely explored, there is great interest in exploring alternative fluorescent QDs namely by applying novel post-synthesis strategies of chemical surface modification.[1,2]

In this context, we will present here our research on the synthesis of ZnS and Mn doped ZnS colloidal QDs and their surface functionalization using tetrapyrrolic compounds. The synthesis of ZnS and ZnS:Mn QDs was performed using the liquid phase thermolysis of single-molecule precursors type Zn(II) dialkyldithiocarbamate in oleylamine.[3] The conjugation of selected key tetrapyrrolic macrocycles and the synthesized QDs has been carried out by self-assembly processes, using different reactional conditions (e.g. solvent, concentration ratio). The optical properties of the conjugates (optical absorption and fluorescence emission) and their characterization by powder X-ray diffraction (XRD), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FT-IR) will be presented and discussed in detail.

Acknowledgements: Thanks are due to FCT/MCTES for the financial support to CESAM (UID/AMB/50017/2019) and CICECO-Aveiro Institute of Materials (UID/CTM/50011/2019) through national funds, to the University of Aveiro and FCT/MCT for the financial support for the QOPNA research Unit (UID/QUI/00062/2019) through national founds and, where applicable, co-financed by the FEDER, within the PT2020 Partnership Agreement, and to the Portuguese NMR Network. This work was supported by the project [Corlutna (POCI-01-0145-031523)] funded by FEDER, through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI), and by national funds (OE), through FCT/MCTES.

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P34

Dissolution of kraft lignin in alkaline solutions

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Lignin is a highly abundant complex biopolymer that constitutes a large portion of cell walls of vascular plants[1,2]. It has a highly branched aromatic structure which is believed to bind cellulose and hemicellulose in the fibrils via strong hydrogen bonding and ester linkages[3,4]. About 85% of the total world lignin production is obtained by kraft pulping process[5], which employs harsh conditions such as high pHs and considerable large amounts of aqueous sodium hydroxide and sodium sulfide solutions[6]. The resulting material, so called Kraft lignin, in mainly hydrophobic[7]. Dissolution of kraft lignin, as an often required first step for several production processes and applications, is typically not straightforward. Nevertheless, a wide variety of solvents for lignin have already been developed and, among them, organic solvents, ionic liquids and deep eutectic solvents are particularly relevant[8]. Strong aqueous alkaline systems are often cited in literature as suitable systems for dissolving kraft lignin but surprisingly the solubility of lignin in these systems is not reported. Therefore, in this work several alkaline solutions, such as lithium, sodium, potassium, cuprammonium, tetrabutylammonium and tetrapropylammonium hydroxide were used for the dissolution of kraft lignin. In these systems, the cation of the hydroxide was found to play an important role since the solubility of lignin decreases with the cation radius in the order of LiOH > NaOH > KOH > CuAOH > TPAOH > TBAOH. Overall, LiOH is the most efficient hydroxide to dissolve kraft lignin, but the poor solubility of LiOH in water is a limitation regarding the dissolution of large amounts of lignin. A good alternative is NaOH, where a solution with 6 wt%, can dissolve up to 40 wt% of kraft lignin. The differences in the soluble and insoluble fractions, were analyzed by infrared spectroscopy, elemental analysis, thermogravimetry and gas chromatography accoupled with mass spectroscopy. The combination of these techniques suggests that this type of alkaline system dissolves preferentially lignin fragments with sulfur and small fragments, while can also degrade larger lignin molecules.

Acknowledgements: This work was supported by funding from the Portuguese Foundation for Science and Technology (FCT) through the projects PTDC/AGR-TEC/4814/2014 and “ReFloRest” ref.: 30619 (02/SAICT/2017) and researcher grant IF/01005/2014. Elodie Melro acknowledges FCT for the PhD grant (SFRH/BD/132835/2017). The CQC is supported by FCT through the project PEstOE/QUI/UI0313/2013.

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P35

Development of an electrochemical biosensor for Machado-Joseph disease biomarker detection

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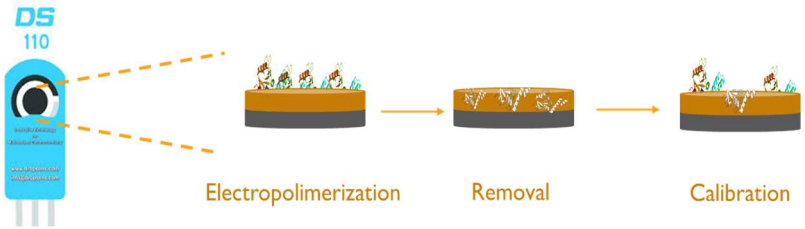
Machado-Joseph disease (MJD) or spinocerebellar ataxia type 3 (SCA3) is a neurodegenerative disease with an autosomal dominant inheritance pattern. Nowadays, it is the most common form of spinocerebellar ataxia and an incurable disorder, which leads to death[1].

MJD is caused by the expansion of CAG trinucleotide repeat in the coding region of the gene ATXN3 and the aggregation of the resulting product. This polyQ expansion is thought to be the key of the disease, in which the length of this polyQ extension is linked to earlier and more severe symptons[2]. This mutant protein disturbs the normal neuronal function and leads to its degeneration, with subsequent formation of neuronal intranuclear inclusions. Although there is no treatment available, a more accurate diagnosis of MJD may lead to relieved symptoms[2]. Research activities targeting such possibility include the identification of biomarkers in several biological fluids that may turn out an important means to early diagnosis or even potential therapy biomarkers within future[3,4].

Thus, this work develops novel and low cost electrochemical (bio)sensing devices to detect ataxin 3 protein (atx3), comprising a molecularly-imprinted polymer as biorecognition element. This element was obtained as an electrochemically synthesised molecularly-imprinted polymer (MIP) that was tyramine-based. The tyramine monomer was mixed with atx3, on a carbon screen-printed electrode (SPE), and assembled as shown in scheme 1. The surface modification and the ability of the material to rebind the atx 3 oligomers was measured by electrochemical techniques, namely electrochemical impedance spectroscopy, square wave voltammetry and cyclic voltammetry.

The biorecognition element was successful constructed on the SPE. The control of the surface modification was evaluated electrochemically. Further tests are progressing to obtain a specific and sensitive biosensor for the detection of the target biomolecule.



Scheme 2: Schematic representation of the construction steps of the biosensor, from electropolymerization with tyramine in conjunction with the biomarker (atx3 oligomers), to rebinding of atx3 that leads to the calibration, made with increasing concentrations atx3.

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P36

Tuning the Photoluminescence Properties of Carbon Nanoparticles

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Carbon nanoparticles (CNPs) have aroused a great interest due to its strong blue fluorescence emission. However, the blue fluorescence limits its applications in several cases; therefore, the synthesis of CNPs with multicolor emissions becomes mandatory. A widely used strategy of modulation of CNP photoluminescence is doping the carbon network with nitrogen atoms. Despite the great number of works carried out with N-doped CNPs, some contradictory experimental observations have been reported. These contradictions seem to be due to structural differences resulting of the different synthesis routes. Therefore, it is difficult to correlate the photoluminescence properties with the nanoparticle structure. To address this issue, we have developed an easy methodology of synthesizing different carbon nanoparticles using an acidic treatment previously reported and five distinct starting materials as precursors. The chemical and morphological characterizations were carried out by XPS, FTIR, TEM and Nanoparticle Tracking Analysis (NTA).

Results demonstrated that the chemical composition and nanoparticle diameter depend on the precursor employed in the synthesis. Using this methodology, it is possible to modify the chemical composition without reducer agents that often incorporate oxidized species on the basal plane, which can modify the photoluminescence properties of carbon nanoparticles. Besides it was possible to modify the nanoparticle diameter from 10 to 96 nm. We have analyzed PL dependence of both, the nanoparticle size and the chemical composition. Results allow us to assign four emissive center ascribed to: $\pi \rightarrow \pi^*$ transition for aromatic domains in zigzag configuration (400 nm), $\pi \rightarrow \pi^*$ transition for aromatic domains in armchair configuration (450 nm), $\pi \rightarrow \pi^*$ charge-transfer transition (500 nm) and $n \rightarrow \pi^*$ transition (550 nm). Our results also proved that bands corresponding to $\pi \rightarrow \pi^*$ exhibit a marked quantum confinement effect. Besides, the relative emission intensity of the band attributed to $n \rightarrow \pi^*$ transition, linearly increases with the fraction of C-N groups attached at the basal plane of nanoparticles, this fact allows concluding that the emission can be mainly due to $n \rightarrow \pi^*$ transition of nonbonding orbital of N-groups to the π^* orbital of the Csp^2 domains. In addition, the band assigned to charge-transfer $\pi \rightarrow \pi^*$ transition is quenched by the carbonyl groups attached to the basal plane of carbon nanoparticles. Summarizing, our results allow correlating for the first time, the relative intensity of the emission bands assigned to functional groups of carbon nanoparticles with the fractions of carbonyl or C-N bonds of attached at its basal plane. We think that these correlations are helpful to interpret some contradictory observations previously observed and can be of broad interest to the community doing research in the field of bioimaging, optical sensing or light-emitting devices.

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P37

Photocytotoxicity of porphyrin@GO hybrids against cancer cells

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Photodynamic therapy (PDT) is a minimally invasive medical technology which promotes cytotoxicity activity towards tumoral malignant cells.[1] Porphyrins assume leading roles as photosensitizers for PDT, due to their remarkable light absorption characteristics, minimal dark toxicity and good ability to generate singlet oxygen.[1] In order to improve their physiological solubility and selectivity, porphyrins have been functionalized with several types of carrier molecules, as graphene oxide (GO).[2] Throughout this research work, different tetracationic porphyrins were non-covalently conjugated to GO: i) the 5,10,15,20-tetrakis(1-methylpyridinium-4-yl)porphyrin (TMPyP), ii) ZnTMPyP and iii) a dibenzoporphyrin analogue of TMPyP (P1-C5). The formation of such hybrids was monitored through UV-Vis and spectrofluorimetric titrations and further studied by confocal Raman microscopy and electron microscopy.[3] The photocytotoxicity of the non-immobilized porphyrins, of GO and of hybrid systems on T24 human bladder cancer cells was evaluated through PDT assays (Figure 1) under irradiation with blue (BL; 417 nm, 2.5 J/cm^2) or red light (RL; 630 nm, 25 J/cm^2). The most cytotoxic non-immobilized porphyrin under BL was ZnTMPyP and under RL was P1-C5. GO did not show any toxicity upon BL or RL irradiation. The as-developed hybrids displayed light toxicity, but no remarkable synergistic effects were observed by the presence of both GO and porphyrin. Still, the on-going research suggests that it is possible to increase the antitumoral activity of the hybrids by increasing their content of porphyrin. The results obtained so far aim to contribute to improve the porphyrin@GO properties for PDT.

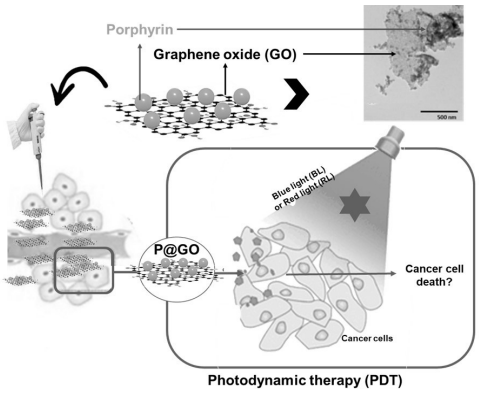

Figure 1: Porphyrin@GO hybrids as potential PDT agents.

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P38

Developing photosensitive catanionic vesicles based on a flavylium derivative for controlled drug delivery

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Over the last decades, there has been a rising interest on drug delivery systems due to their potential in improving drug efficiency. This improvement is attained by protecting drug degradation from metabolism, site-directing the drug to reduce its side effects, improving bioavailability in the target and increasing the circulation time of the drug [1]. Vesicles, which are colloidal aggregates made of surfactant bilayers, are among the most promising drug delivery systems. If stimuli- responsive functional groups are added to the surfactants [2,3], the controlled release of the drug may be significantly improved. The responsive groups can be sensitive to physiological stimuli, like the low pH observed in tumors, or external stimuli such as light.

In this work, our goal has been to develop mixed cationic/anionic aggregates that are sensitive to both light and pH using a newly synthesized flavylium derivative as the responsive compound. Various mixed systems were explored using different cationic quaternary ammonium surfactants, namely single-chained, double-chained and gemini surfactants, varying the total surfactant concentration and the cationic/anionic mixing ratio. Special focus on formation and characterization of catanionic vesicles was given using dynamic light scattering, ζ-potential determination, light microscopy, differential scanning microcalorimetry and UV-Vis absorption spectroscopy [4]. In general, results showed that vesicles were more prone to form vesicles, and comparatively more stable ones, when using bulky cationic surfactants, namely gemini surfactants. The vesicles presented more significant changes in morphology upon both pH lowering and light irradiation rather than light irradiation alone. The combination of both stimuli results in the formation of a phenylchromenylium group from a trans chalcone moiety, while light causes the isomerization from trans to cis form of the chalcone moiety [5].

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P39

Micelar ionic liquid-based micellar systems in an integrated platform for the removal of Indigo Carmin

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The textile industry is one of the manufacturing industries that contributes most to water and soil pollution[1]. Wastewaters containing synthetic dyes, namely indigo carmine (IC), represents a serious problem for human health and for the ecosystem and most of the conventional effluent treatments are not totally effective, being, in some cases strongly difficult and expensive approaches[2]. So, it is urgent the development of alternative and effective strategies for the treatment of aqueous wastes and bioremediation a valid alternative[3]. Oxidative enzymes such as laccases, peroxidases and tyrosinases exhibit a great potential in the oxidation of persistent environmental pollutants. In this work an alternative and integrated platform for the removal of IC from simulated aqueous effluents using laccase and surfactant-based ionic liquids (ILs) was evaluated, allowing the treatment and reuse of wastewater from textile industry.

In a first step the activity of laccase was evaluated in aqueous solutions of three families of ILs, 1-alkyl-3-methylimidazolium chloride ([C$_n$mim]Cl]), 1-alkyl-trimethylammonium bromide ([N$_{n111}$]Br]) (both acting as cationic surfactants), and cholinium carboxylate ([Ch][C$_n$O$_2$]) (acting as anionic surfactants). A high activity of laccase is attained (90% of residual activity) with the aqueous solutions (100 mM) of [N10111]Br and [C$_{10}$mim]Cl. After, the effect of the IL-based surfactants ([N$_{10111}$]Br and [C$_{10}$mim]Cl) in the degradation of IC by laccase was studied. The results demonstrated a higher and faster degradation efficiency of IC using aqueous solutions of [N$_{10111}$]Br (~82% in 30 min), whereas without IL only 14% of IC was degraded. After 24 h, almost a complete degradation (>90%) of IC was achieved (Figure 1).

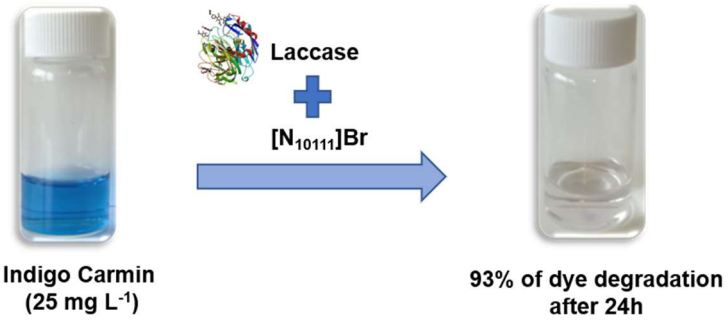

Figure 1: Images of indigo carmine decolorization by laccase in the presence of [N$_{10111}$]Br at room temperature.

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P40

Hybrid Nanomaterials of Graphene Oxide/Polysaccharide for Water Softening

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Hard waters are characterized by high concentrations of calcium and magnesium ions, which have a detrimental effect on water infrastructures and may cause the failure of household electrical appliances due to metal carbonate deposition. Several methods have been applied in the removal of such divalent ions aiming water softening including chemical precipitation, ion exchange process and capacitive deionization.[1,2] Commercial ion exchange resins are currently employed for water hardness removal, but present several shortcomings such as the need of high amount of a salt for resin regeneration, with impact on the salinity of municipality waters and the inherent workload for the domestic consumer.

Herein, hybrid materials comprising graphene oxide (GO) modified with a polysaccharide (e.g. κ-carrageenan) were prepared and tested for the removal of Ca^{2+} from water. The κ-carrageenan was chemically modified with an alkoxysilane[3] and then grafted to the GO surface. The covalent linkage of the κ-carrageenan macromolecules onto GO was demonstrated by FTIR spectroscopy, elemental microanalysis and zeta potential measurements. Noteworthy, the surface charge of the resulting GO/κCRG material was negative along a broad pH range, which is in principle an advantage for the removal of aqueous cations via electrostatic interactions.

The water softening performance of GO/κCRG was assessed by batch adsorption experiments, performed in synthetic hard water, at variable sorbent dosage (Figure 1). The results indicate the great potential of this class of composites for application in sustainable water softening treatment, and open an avenue for their use in other water treatments, such as heavy metal ions removal.

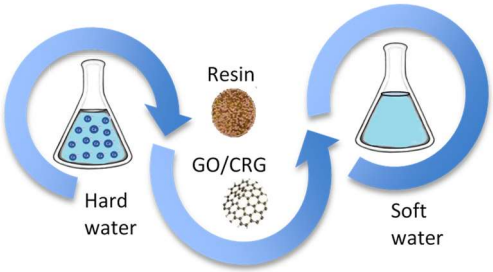

Figure 1: Schematics of water softening adsorption experiments.

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P41

Lysine- and threonine-based catanionic vesicles: structural characterization and biological activity

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Over the last two decades, several nanostructured vehicles that protect and deliver biomolecules effectively to target cells have been developed and optimized, from liposomes, polymers and dendrimers to nanotubes and nanoparticles. In this context, surfactants are a class of compounds widely used in the pharmaceutical industry due to their high surface activity and self-assembling versatility. Amphiphiles with low cytotoxicity are of special interest for the design of effective drug and gene delivery formulations. Cationic/anionic systems built from amino acid-based surfactants present higher levels of biocompatibility and biodegradability, with good interfacial performance and multifaceted self-assembly, from elongated micelles to vesicles, liquid crystalline nanoparticles and tubular structures.[1]

In this work, the vesicle-forming ability of different catanionic systems based on surfactants derived from two amino acids, threonine and lysine, were explored. The threonine derivatives have simple monomeric configuration and different alkyl chain length, and are designated by *n*ThrNa, where *n* is the number of carbon atoms in the hydrocarbon chain, ranging from 8 to 16. The lysine-derived surfactants are anionic and double-chained, with a variable degree of chain length mismatch, comprising compounds 8Lys*n* and *m*Lys8, and 10Lys*n* and *m*Lys10, with *n*, *m* = 12, 14 and 16, where numbers represent the number of C atoms in each alkyl chain.[2] Phase behavior studies and microstructural characterization of several aqueous mixtures based on 12ThrNa and *m*Lys8 as the anionic surfactant, and on gemini serine-based and gemini conventional surfactants as the cationic surfactants have been carried out. Detailed results from high-resolution light microscopy, cryo-SEM, DLS and zeta potential measurements are presented and discussed. The toxicological profile of the vesicles was evaluated in animal cell lines. Biomolecule encapsulation and release studies were performed, testing the effectiveness of the selected vesicle systems in conditions close to physiological ones.

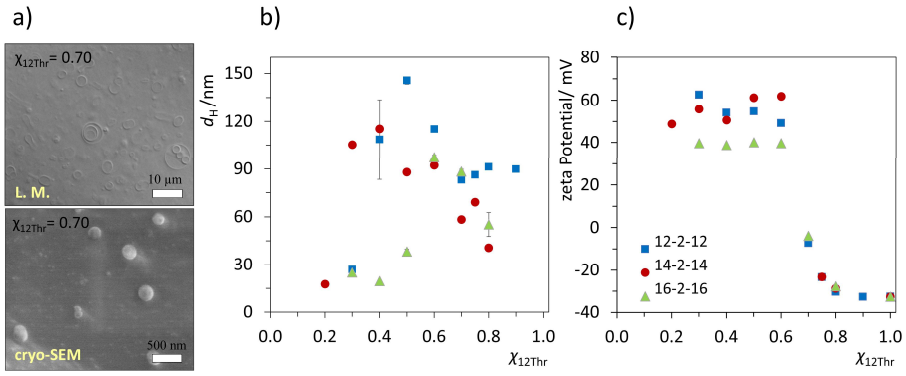

Figure 1: Light microscopy, a) top, and cryo-SEM, a) bottom, imaging of 12ThrNa:12-2-12 catanionic vesicles. Mean hydrodynamic diameter, b), and zeta potential, c), of 12ThrNa/gemini catanionic vesicles, for varying molar ratio of the amino acid surfactant, at 25 ºC.

Acknowledgements: We thank Fundação para a Ciência e Tecnologia and FEDER/COMPETE for financial support through grants UID/QUI/00081/2013, POCI-01-0145-FEDER-006980, NORTE-01-0145-FEDER-000028, and UID/QUI/50006/2013. I.S. Oliveira is also grateful to FCT for support through the PhD grant SFRH/BD/108629/2015.

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P42

PVA-NLC films for transdermal drug delivery

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Transdermal drug administration claims significant advantages over conventional routes, including the maintenance of constant drug plasma levels for prolonged periods of time and circumvention of liver first pass. These allows improving drug bioavailability, avoiding gastric irritation, and preventing drug degradation from the harsh conditions of gastrointestinal tract. Moreover, it provides a practical, painless and non-invasive way to self-administer medications, with the ability of stoppering the drug input when no longer desirable, by simply patch removal.[1] However, the main challenge in the transdermal administration of drugs is to overcome the skin barrier imposed by the stratum corneum (SC). A strategy to improve the penetration of drug molecules through the SC relies on the use of lipid nanosystems, in particular nanostructured lipid carriers (NLC), due to their peculiar features.[2] NLC are colloidal systems (40 nm -1000 nm) composed of a lipid matrix consisting of a mixture of biocompatible and biodegradable solid lipids (i.e., lipids that are solid at both room temperature and body temperature) and liquid lipids (oils) dispersed in an aqueous solution of surfactant.[3] Upon skin application, these carriers form an oclusive layer, that leads to an increaded skin hydration and decreased corneocyte packing, enhancing drug penetration.[4]

This work aims at designing an innovative polyvinyl alcohol (PVA) adhesive patch containing NLC loaded with olanzapine (OL) and simvastatin (SV), for the treatment of psichiatric disorders. NLC were prepared using the hot high pressure homogenization, as described elsewhere.[1] Several PVA patches were further developed following a 3^2 factorial planning. The PVA concentration and the lipid content were considered as key formulation variables. Mechanical properties, adhesion, release and permeation are the critical quality attributes evaluated. NLC formulations exhibited an average size of 178 ± 3 nm with a polydispersity index of 0.226 and a zeta potential of -21.0 ± 0.1 mV. Release studies showed that the PVA-NLC patches enables a controlled drug release and that it depends on the concentration of PVA used. The formulation containing 12% (w/w) of PVA and 15% of NLC provided the best permeation rate along with adequate adhesiveness and resistance, being considered a promising therapeutic approach for further pre-clinical studies.

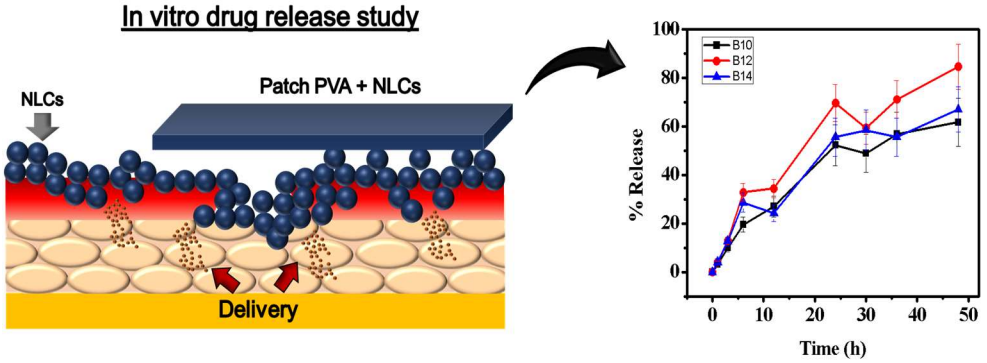

Figure 1: Solid lipid-based nanoparticles release scheme for drugs transdermal administration

Acknowledgments: The authors acknowledge Fundação para a Ciência e a Tecnologia (FCT), Portuguese Agency for Scientific Research, for financial support through the Research Project no. 016648 (Ref. POCI-01-0145-FEDER-016648), the project Pest UID/NEU/04539/2013, COMPETE (Ref. POCI-01-0145-FEDER-007440), and Project UID/QUI/00313/2019.

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P43

DODAB:MO versus novel liposomes for protein delivery: comparing toxicity and encapsulation efficiency

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Nanotechnological solutions for biomedicine underlie the need to carefully validate biocompatibility of the developed technology and eventual exposure risk [1].
Many lipids have been used to produce liposomes, which mimic cell membranes and are very interesting in terms of interaction with cells, tissues and organs. The features of liposomal formulations are dependent on the lipid characteristics, such amphiphile shape, electrical charge and constitution of the lipid mixture [2]. Our group developed a Dimethyldioctadecylammoniumbromide (DODAB) and monoolein (MO) formulation that was validated for delivery of different biomolecules [3] and is now being optimized for protein delivery. These liposomes were compared with a novel liposomal formulation, which consists in a mixture of 5 different lipids similarly to vesicles produced by human cells.
The purpose of this comparative study was to identify the most suitable formulation for efficient delivery of proteins, specifically of bioactive cytokines, to human cells with the minimal toxicity.
Both types of formulations were characterized in terms of size (DLS), surface charge (zeta potential) and stability. Using small quantities of model protein bovine albumin serum (BSA), we optimized the sensitivity of the quantification by the Bradford method, to calculate encapsulation efficiency in both systems. Toxicity was evaluated using *in vitro* animal cell models (MTT assay), hemolysis assessment (spectroscopy).
The balance between efficiency in cargo loading and delivery, and toxicity assessment, is crucial to better adjust the formulation according to the intended application.
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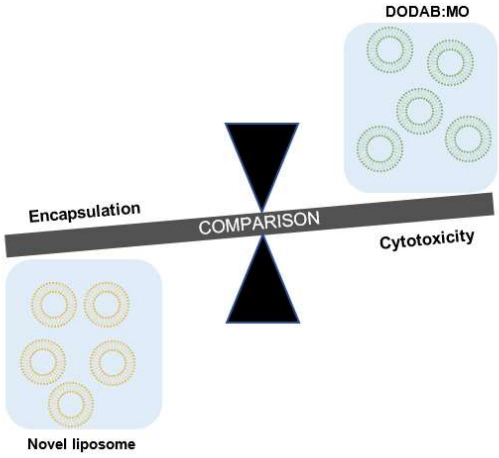

Figure 1 Comparison between encapsulation and cytotoxicity parameters regarding novel liposomes and DODAB:MO formulation.

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P44

Characterizing Biointerfaces formed by Supported Vesicle Layer (SVL) on Polyelectrolytes Multilayers (PEMs). Drug Release and Cell Interaction.

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The use of biointerfaces remains to be crucial in biomaterials applications, biosensors or tissue engineering[1]. The first step to understanding cell-cell/biomolecule and cell-surface interactions or to create models to mimic the function of the extracellular matrix (ECM) pass by the functionalization of surfaces with bioactive substances. Liposomes are the most common delivery vesicles. However, their adsorption on solid surfaces usually results in their spontaneous reorganization and formation of a supported lipid bilayer[2,3]. We hypothesize that polyelectrolyte multilayers (PEMs) supports would allow an intact adsorption of liposomes (SVL) avoiding their disruption, given us a potentially useful tool in biofunctionalization surfaces.

Gold-coated quartz crystals were modified with 3 bilayers of cationic poly-L-lysine (PLL) and anionic hyaluronic acid (HA). A top layer of cationic liposomes loaded with Nile Red (d=120 nm, ζ-potential=10 mV) was added, followed by 2 HA/PLL bilayers. The assembly was monitored by quartz crystal microbalance with dissipation (QCM-D). The encapsulation efficiency (*EE*) and release to NaCl 0.15 M were quantified by fluorescence spectroscopy. Inverted Confocal Microscopy was used to observe the cell interaction with synthesized biofilms at different time-points. Likewise, the internalization of liposomes was studied varying the coating of SVL.

The QCM-D data allowed us to observe the adsorption of intact spherical liposomes on the PEMs deposition (Figure 1). The release studies was carried out substituting the gold-coated quartz crystals by coverglasses. We determined average encapsulation efficiency at two differents temperatures (37ºC and 20ºC) using Nile Red. Further coating of the constructed SVL with HA/PLL bilayers did not compromise their stability and increased the diffusion barrier. This result showcases that the release can be controlled by additional top layers but also the protective efficiency of this coating as compared to Nile Red release of free liposomes in aqueous suspension (95% at 1 h). The incubation with MDA-MB-231 breast cancer cells at different time-points (1, 3 and 6 hours) varying the coating of SVL showed a higher internalization of liposomes by endosomes in the case of SVL that than whith SVL coated by 1 HA/PLL layer. The microscopy results showed the adhesion and sticking of cells favorable in these biofilms.

SVLs onto PEMs show a powerful tool to growth of efficient biofilms to explore the cell-cell/biomolecules and cell-surface interactions to promote the development of biomaterials applications, biosensors or tissue engineering.

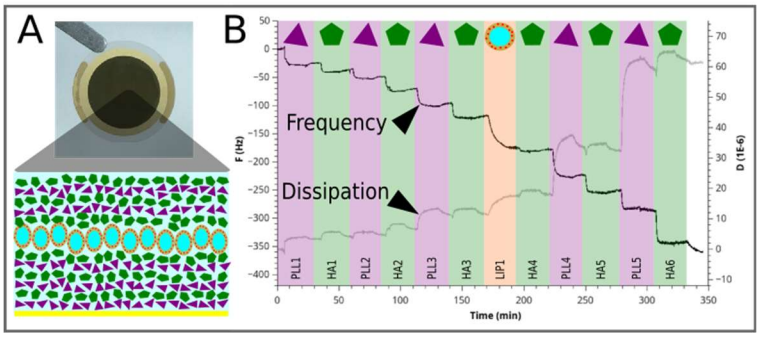

Figure 1: (A) LbL film architecture on gold surfaces. (B) Δf and ΔD variations in QCM-D.

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P45

Nanostructured scaffolds for bone regeneration

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Small materials, within the meso or nano scale, have been involved in a revolution both form the scientific point of view as industrial. Within this type of materials, the bioceramics have been gaining strength, little by little. The reason for this development lies in its advantages, are based on natural components, they are biocompatible and bioactive, they are cheap and their production on a large scale is easy to implement.

Here we have focused on the study of hydroxyapatite nanoparticles. Synthetic hydroxyapatite (HAp, Ca10(PO4)6(OH)) has a chemical similarity to the inorganic component of bone matrix and exhibits strong affinity to host hard tissues. It is of great importance to develop new nano-HAp synthesis methods focused on the precise control of particle size morphology and chemical composition[1]. For this purpose, we have developed different manufacturing of nanoparticles that allow a controllable and accurate control of the most important characteristics: size, shape and crystallinity. Besides, a further step was taken toward the construction of synthetic materials that resemble calcified tissues, and for this reason we explored the magnesium ion (Mg^{2+}) substitution. The control of Mg^{2+} incorporation into HA nanorods gave rise to a tailored crystallinity degree, cell parameters, morphology, surface hydration and solubility[2] .

Also, we have developed mechanically robust scaffolds, exhibiting a highly interconnected fiber mesh structure, by optimizing the distribution of HA nano-rods within hydrogels composed by collagen and structural agents. Samples showed a definite degree of roughness in the pore wall surface, a quality required to attain a suitable host tissue acceptance. The presence of nano-HA particles, also induce an enhanced scaffold mineralization, achieving a crystal growth of the shape, composition and orientation equivalent to that presented by the mineral phase of calcified tissues[3].

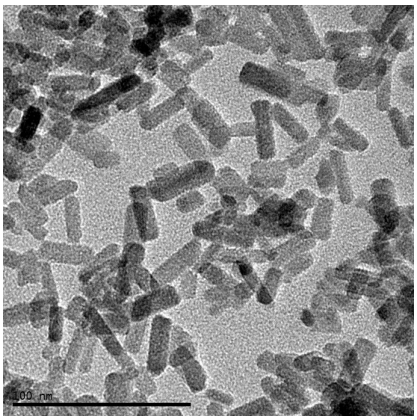

Figure 1. TEM and H-TEM microphotographs of HAp nano-rods samples.

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P46

Molecularly-imprinted polymer on cork for selective antibiotic adsorption in aquaculture environment

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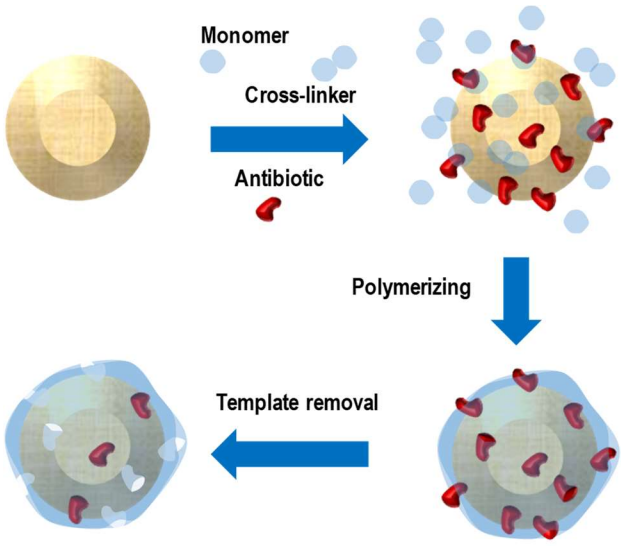
Antibiotics are naturally occurring, semi-synthetic and synthetic compounds with antibacterial activity employed for improving human and animal health and growth. Antibiotics play today a major role in modern agriculture and livestock industries and their use has risen in many developed nations, promoting their release into natural ecosystems.

One of the increasing risks of antibiotic release into the water environment is the emergence of antibiotic resistance in human pathogens. This is of great concern to public health, not only for hindering the successful treatment of infectious diseases, but also for obstructing the combat to other pathologies in which antibiotic prophylaxis is needed for avoiding associated infections.

Removing the antibiotics from the water environment may be one of the solutions to this problem. Cork is a very nice support to this end, for several reasons. It is hydrophobic, has low cost, and allows chemical modification. The affinity of these materials to antibiotics may also be enhanced by modifying the surface of granular cork with biomimetic materials (or plastic antibody). As proof-of-concept, amoxicillin was selected as target antibiotic.

Thus, this work described the modification of granulated cork with a polymeric layer of a molecularly-imprinted polymer for an antibiotic (Scheme 1). In this, the cork was washed in alkaline media and modified with an amine layer and acrylic acid. This surface was then incubated in a mixture of acrylic acid, ethylene glycol dimethylacrylate, and antibiotic. The polymerization was initiated by benzoyl peroxide. After polymerization, the template was removed by suitable washing in aqueous environment.

The ability of the modified work to adsorb amoxicillin was tested by incubating a specific amount of this material in the antibiotic solution, at different concentrations of antibiotic and different timings. The amount of antibiotic remaining in the solution was monitored by HPLC, following a conventional procedure described in the literature. The optimization of all variables is undergoing to reach a clear difference between the molecularly-imprinted and the control materials.



Scheme 1: *Schematic representation of the cork modification by tailoring a molecularly-imprinted polymeric layer on it.*

Acknowledgements: We thank the financial support of 3C´s – Cellulose and Cork in the Control of antibiotics in aquaculture (PTDC/AAG-TEC/5400/2014 and POCI-01-0145-FEDER-016637), to FEDER, through COMPETE2020, POCI, and FCT (Fundação para a Ciência e a Tecnologia I.P.).

P47

Stimuli-responsive liposome-polycation-DNA systems (lipopolyplexes) for gene therapy: selecting optimal formulations through fluorescence cross-correlation spectroscopy

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The poor delivery of nanoparticles to their target cancer cells hinders nanooncology success in the clinical setting. This "delivery problem" is due to the large number of biological barriers that the nanosystem has to overcome to reach the target cells. This is particularly important for gene therapy, since the cargo must be released within the target cell to perform its function. In this work, a dual sequential stimuli-responsive lipopolyplex formulation has been designed and prepared to address this issue (Figure 1). The lipopolyplexes include a targeting agent that is exposed by the cleavage of the pH-responsive PEGylated lipid in the slightly acidic pH of tumors and favors cell uptake. Then, the cationic lipids in the formulation will provoke endosomal escape, while the reducing environment in the cytosol will break disulfide bonds within the polymeric core, releasing the cargo DNA. The pH-responsive PEGylated lipid was synthesized following an established procedure[1]. Then, polymer-DNA complexes (polyplex) with different Polymer N/DNA P ratios (1-3) were prepared by mixing polylysine (or bioreducible, disulfide bond-containing polylysine) and plasmid DNA in different proportions in water. Finally, PEGylated and non-PEGylated cationic liposomes were added to the prepared polyplexes to try to obtain different lipopolyplex formulations, studying a range of lipid N/ DNA P between 0.5 and 2. The obtained particles were characterized by Dynamic Light Scattering, Z Potential, Transmission Electron Microscopy (TEM) and Fluorescence Cross-Correlation Spectroscopy (FCCS, employing an Atto 488-labeled polymer and a Texas Red-labeled lipid). The obtained formulations had a range of hydrodynamic diameters between 70 nm and 12 µm, depending on their composition. A clear trend towards smaller particles was obtained when increasing the amount of cationic liposomes added to polyplexes with a low N/P ratio (0.5-1), while the opposite was true for an N/P ratio=3. As expected, the Z Potential values obtained were dependent on the surface charge of the starting polyplex as well as the amount of cationic liposomes added. The co-localization of the polymeric and lipid components determined by FCCS varied greatly between samples, observing similar trends in PEGylated and non-PEGylated lipopolyplexes, but with larger cross-correlation percentages for non-PEGylated nanoparticles. Overall, an extensive set of conditions to prepare dual-responsive lipopoliplexes for gene therapy in the context of cancer has been evaluated. The formulations that fulfill the initial requirements for the target application regarding their size and presence of all desired components will be later tested for their different functionalities *in vitro*.

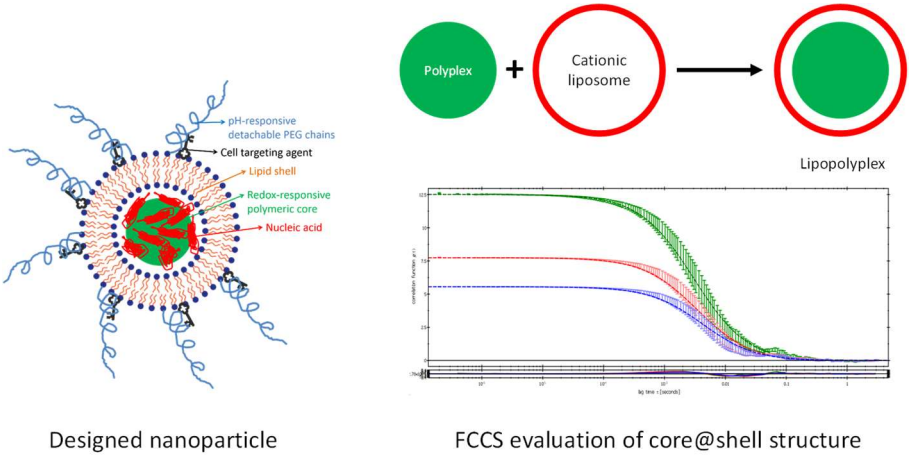

Figure 1: Schematic representation of the designed nanosystem (left), FCCS auto- and cross-correlation curves corresponding to one of the samples prepared in the present work (right).

Acknowledgements: This research is supported by Microfluidic Layer-by-layer Assembly of Cationic Liposome - Nucleic Acid Nanoparticles for Gene Delivery project (032520) co-funded by FCT and the ERDF through COMPETE2020. JLP is supported by a post-doctoral fellowship from the *Ramón Areces* Foundation.

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P48

Fabrication of novel gelatin-siloxane-based hybrid magnetic particles using alkoxysilane coupling agents

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Hybrid materials with organic-inorganic character are attracting increasing interest due to their remarkable properties and multifunctional nature, with prospects for many new applications in diverse fields. The diverse range of hybrid materials compositions and properties are ascribed, in part, to the intimate mixing of organic and inorganic phases and interactions at nanoscale that are promoted by covalent bonds between both components. The covalent bonds are formed by reaction of the organic component with organosilanes such as 3-isocyanatopropyltriethoxysilane (ICPTES) and 3-glycidoxypropyltrimethoxysilane (GPTMS). The use of alkoxysilane coupling agents is crucial to obtain homogeneous mixtures between both phases. The use of biopolymers as the organic component has experienced remarkable growth due to their attractive properties such as biocompatibility, biodegradability, low cost and availability.[1] Having these advantages in mind, gelatin was selected as the organic component of the prepared systems.
Herein, we report a non-emulsion method for preparing spherical gelatin-siloxane-based hybrid particles. The gelatin was firstly derivatized with two alkoxysilanes (ICPTES and GPTMS). Then, the resulting compounds were reacted with tetraethyl orthosilicate to yield spherical hybrid particles via hydrolysis/condensation reaction.[2] The same approach was used to coat magnetic nanoparticles with a shell of hybrid composition to obtain core@shell hybrid materials (Figure 1) with magnetic properties. The relevant properties of the resulting materials were studied using electron microscopy, solid state NMR, thermogravimetric analysis, FTIR spectroscopy and elemental analysis.

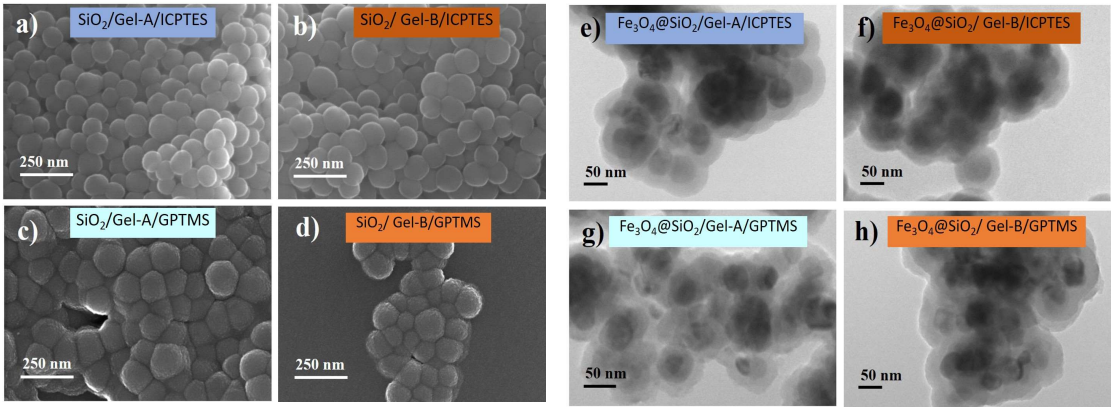

Figure 1: *SEM images of silica/gelatin-siloxane hybrids (a, b, c and d) and TEM images of core@shell gelatin-siloxane-based hybrid magnetic particles (e, f, g and h).*

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, FCT Ref. UID/CTM/50011/2019, financed by national funds through the FCT/MCTES. The authors thank the RNME (National Electronic Microscopy Network) for microscopy facilities. S. F. Soares thanks the Fundação para a Ciência e Tecnologia (FCT) for the PhD grant SFRH/BD/121366/2016. A. L. D.-d.-S. acknowledges FCT for the research contract under the Program 'Investigador FCT' 2014.

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P49

Lipid-based nanosystems loaded with curcumin as a promising strategy for cancer therapy

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Cancer remains a leading cause of death worldwide, and the latest WorldCancerReport has estimated 20 million new cancer cases yearly by 2025 [1]. Indeed, despite classical therapy has shown significant benefits in cancer treatment, the majority of cancer therapies remain unsuccessful. This ineffective action occurs mainly due to drug-induced toxicity and adverse reactions, low target specificity of single anti-cancer drugs and above all, due to drug resistance during cancer progression. Consequently, to overcome such limitations, researchers have shifted focus onto new strategies for the prevention of cancer multidrug resistance (MDR), having natural compounds, such as plant polyphenols, emerged as an exciting solution, mainly due to their chemosensitizer activity [2]. Moreover, within polyphenols sources, the *Curcuma* genus has acquired great importance mainly due to the presence of curcumin, a compound with anti-inflammatory and antioxidant properties, recognised as valuable for cancer treatment. Furthermore, Curcumin is known to inhibit cyclooxygenase that plays an important role in carcinogenesis [3].

In the first step of this study, using derivative spectroscopy; quenching of intrinsic fluorescence of human serum albumin; dynamic and electrophoretic light scattering, differential scanning calorimetry and small and wide angle x-ray diffraction, curcumin revealed a weak pharmacokinetic profile with low bioavailability and solubility, bioaccumulation, high affinity to human serum albumin, as well as a tendency to induce membrane biophysical changes, highlighting the need of encapsulating curcumin extracts using nanocarriers.

Following this rationale, this research focused on encapsulating: (i) curcumin; (ii) extract of *C. longa* (the biggest source of curcuminoids) and extract of *C. aromatic* (known for its medical relevance) in cubosomal core-filled vesicles (CCFV) of Dimethyldioctadecylammonium bromide:Monoolein (1:2). The nanocarriers, obtained by ethanolic injection, showed an encapsulation efficiency of approximately 100%, exhibited sizes lower than 200 nm and high stability when stored up to 4 months and a positive surface charge. Moreover, an *in vitro* biphasic controlled release, a high affinity of curcumin and curcumin extracts when encapsulated into PEGylated liposomes, as well as the ability to prevent interactions with plasma proteins, was also observed. As final remark, by using: (i) fluorescence decay of a lipophilic probe (DPH-PA) under the action of a peroxyl radical generator (AAPH); (ii) COX inhibition by fluorescence; and (iii) inhibition of lipid peroxidation by Fourier transform infrared spectroscopy (FTIR spectroscopy), the formulations developed herein, confirmed the antioxidant activity of the encapsulated natural compounds and consequently their potential in cancer therapy.

Acknowledgements:

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P50

Porphyrin-containing SPEEK composite membranes for fuel cells

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In the last decade, research on fuel cells has increased, aiming at developing commercially viable cells that can provide a cleaner and more efficient source of energy.[1] Proton exchange membranes (PEM) are some of the most important components influencing performance, durability and cost of fuel cells. PEMs function as electrolytes for transferring protons from the anode to the cathode, as well as providing a barrier to the passage of electrons and gas cross-leaks between the electrodes.[2] The PEM most used in fuel cells is Nafion, which possesses a high chemical stability and excellent proton conductivity. However, its high cost, loss of conductivity at high temperatures and low humidity have restricted its commercialization. Consequently, many efforts have be made to find a PEM that is a good alternative to Nafion.[3]

Poly ether ether ketone (PEEK) is a chemically and thermally stable aromatic polymer that has been employed as the backbone for proton-conducting polymer electrolytes. As previously described, the hydrophilicity of PEEK can be increased by the introduction of charged groups (using sulfuric acid) to the polymer, see Figure 1.[4] Moreover, research has been performed with sulfonated poly ether ether ketone (SPEEK) membranes, due to its high chemical and thermal stability, relatively high proton conductivity and low cost.[5]

SPEEK is a good candidate for porphyrin composite membranes due to the ability of its sulfonated groups to interact with the protonated central core of the porphyrin macrocycle (TPPy). Composite membranes based on SPEEK and different porphyrins, 5,10,15,20-tetra(4-methylpyridyl)porphyrin (TPPy) and Cu(II)-5,10,15,20-tetra(4-methylpyridyl)porphyrinate (CuTPPy), were prepared for portable applications. SPEEK membranes with a sulfonation degree of 63% and different porphyrin loadings [porphyrin/SPEEK weight percentages (WT%): 0.1%; 0.2% and 0.3%], were used. Steady-state and time-resolved studies in solution and in the solid state (UV-Vis, fluorescence emission, transient absorption spectroscopy and singlet oxygen sensitization quantum yields), together with water uptake, structural and morphological analyses were carried out. The composite membranes with porphyrins (TPPy) and (CuTPPy) show a better thermal degradation performance compared to the the Nafion membrane. The decrease in the fluorescence quantum yield and the bathochromic shift of the absorption maximum going from solution to the membranes together with the triexponential fitting of the fluorescence decays give support for the formation of J-aggregates in the membranes. Moreover, from the overall photophysical data it was concluded that, in general, the radiationless deactivation channels (internal conversion and singlet to triplet intersystem crossing) are the main excited state deactivation pathways.

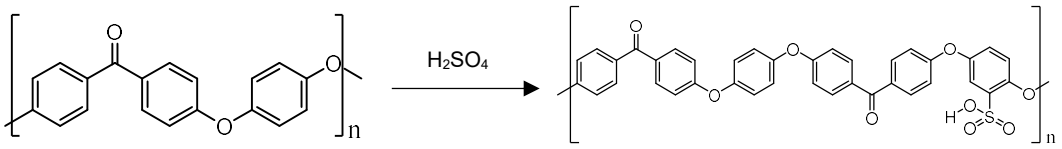

Figure 1: Schematic representation of sulfonation of poly ether ether ketone (SPEEK).

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P51

Characterization of TiO_2 and CeO_2 engineered nanomaterials for cytotoxicity assessment at environmental relevant concentrations

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Nanoparticle (NP) research is an area of intense scientific interest and fast growth, due to its multidisciplinary applications and economic importance. NPs can be found in everyday products[1]; consequently, humans are inevitably and constantly exposed to them. Despite their versatile application and benefits, the effect and impact of NPs on the environment and public health is uncertain[2]. Titanium dioxide nanoparticles (TiO_2NP) are among the most abundantly used NPs[3]. However, evidence shows they cause oxidative stress on brain cells, increased micronucleus formation, DNA breakage in blood lymphocytes and lymphoblast cells, and generation of reactive oxygen species (ROS)[3]. Cerium oxide nanoparticles (CeO_2NP) have been receiving more attention in nanomedicine, increasing the likelihood of human exposure. Concern over the adverse effects of CeO_2NP has been expressed, since data on the ecotoxicological effects is scarce and contradictory[4]. While being highly biocompatible, exerting a cytoprotective effect, exposure to CeO_2NP has otherwise been proven to have adverse effects on lungs, spleen, liver and kidneys[5].

Project NanoLegaTox aims at explore the toxicological effects on human lungs, brain and liver of titanium dioxide and cerium oxide nanoparticles, when in presence of legacy environmental contaminants arsenic and mercury, at environmental realistic concentrations. Therefore, nanoparticle characterization is key to the project's success as it plays an important role to understand their interaction with the metals and the biological behaviour of these nanomaterials. Size and shape were given particular attention, as these parameters have been shown to alter cellular uptake, protein adsorption, accumulation in organelles and distribution throughout the body. Due to the analytical challenges associated with characterisation in culture media and during exposure, a first thorough characterisation of the engineered nanomaterials (ENMs) was performed in its native state, i.e. commercially available sample of TiO_2NP and CeO_2NP, and include particle size distribution, shape and agglomeration/aggregation state by Transmission Electron Microscopy (TEM) and Scanning Electron Microscope (SEM); crystal structure by X-ray powder diffraction (XRD); zeta potential by Laser Doppler Micro-electrophoresis; surface composition by FT-IR and Elemental Analyser. The actual size and shape of any agglomerations formed upon addition of the ENMs to cell culture media with added fetal bovine serum was also investigated to clearly identify the true size and shape effect during nanotoxicity in vitro assessment. It was observed that the solution properties (e.g. as ionic strength; pH; high protein content) did alter the NMs physicochemical characteristics.

Based on these results, it is clear that in order to be able to make adequate assumptions about the toxicity of nanoparticles in *in vitro* experiments, it is important to characterize the nanoparticle stock suspension but also the particles under relevant experimental conditions, despite the challenges associated with performing the characterization of the ENMs in cell culture media, particularly at low concentrations.

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P52

Photocatalytic Assessment of the Toxicity of TiO_2 Nanoparticles

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Titanium dioxide nanoparticles (TiO_2 NPs) are one of the most manufactured semiconductors worldwide. This extensive use has given rise to an increasing release of these materials into the environment which may constitute a risk from an ecological point of view. Along these lines, the formation of reactive oxygen species (ROS) as a result of the irradiation of TiO_2 NPs by UV light, may harm individual organisms through mechanisms of oxidative stress resulting in various toxicity effects.[1] For that reason, the implementation of methods capable of determining the adverse effects of these materials is of utmost importance. In this study, we aim at determining the influence that dosage as well as different morphological features (crystallinity, surface/mass ratio, etc.) of TiO_2 NPs exerts on their toxicity in aqueous media. To this end, the photocatalytic degradation of an organic dye in the presence of different TiO_2 nanoparticles have been performed.

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P53

Sorption of imidacloprid and cymoxanyl onto poly-β-ciclodextrin gels

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Pesticides play an important role in agricultural, household and forestry areas by preventing or controlling pests and so increasing crop yields. In the European Union, agrochemicals annual sales reach almost 400,000 tons with ca. five hundred approved active substances (Figure 1) [1]. However, their persistence, toxicity, bio-accumulation and non-specificity as well as the capacity to permeate the soil, pollute surface and ground waters after leaching, run-off and volatilize made them an issue of increasing concern [2].
The active ingredients, metabolites, inert ingredients and degradation products in commercial formulations represent a class of substances with high interest in environmental field because of their toxicity and persistence [3]. In the last decade, with the purpose of prevent and control the contaminant levels different technologies have been developed to remove or decrease the concentration of pollutants in soil, water and air. The predominantly used methods for contaminant removal include chlorination, ozonisation and advanced oxidation processes [4, 5]. A different approach involves the application of adsorbent and super-adsorbent materials for environmental remediation [6]. Among them activated carbon is, in general, the most effective one [7]. However, its reuse is difficult and expensive.
In this communication, we report the synthesis and characterization of composite gels of poly(β-cyclodextrin) with activated carbon, at low percentages, for the removal of two different phytopharmaceutical compounds: cymoxanil and imidacloprid. The removal efficiency of the composite gel was compared with activated carbon and poly(β-cyclodextrin). The sorption isotherms and sorption kinetics were also evaluated. It has been found that the incorporation of a small amount of activated carbon on the gel matrix leads to a significant improve in the removal efficiency of both pesticides. The use of these gel matrices was also assessed.

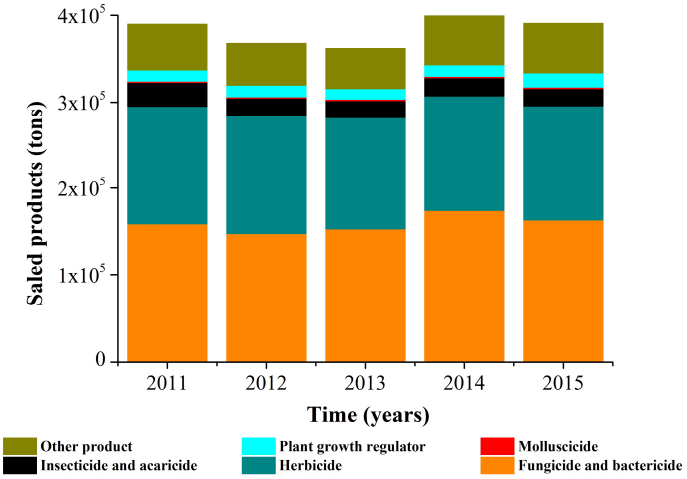

Figure 1. Representation of the agro-pharmaceuticals sales progress between 2011 and 2015. Data source: Eurostat [1].

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P54

Aqueous copper(II) luminescent probes based on Eu(III)-containing coordination gel composites

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Metal ions plays a key role in a variety of chemical, biochemical and environmental processes. Copper is an essential trace metal in human nutrition; however, as it general happens, an excess of copper in human diet can be dangerous to health [1, 2]. Thus, methods for the quantitative detection and quantification of Cu(II) ions, in aqueous solutions, are relevant and has gained considerable attention in recent years. In particular, fluorescent sensors have been developed as a consequence of their simplicity [3, 4].
This communication reports the synthesis of a new coordination gel composite composed by Europium(III) chloride and poly(sodium acrylate) (PSA). The Eu(III)/PSA gel composite shows excellent luminescent emission and visible luminescent colors; consequently, they arise as good candidates for acting as luminescent sensing materials. To investigate the ability of these gels to detect different cations, a series of mono-, di- and trivalent cations have been tested (Figure 1). It can be seen that the emission intensity of luminescence (at 616 nm) of the gel composite changes by changing the metal ion. In general, in the presence of different metals, the color of the fluorescent gel composite changes from red to light red. However, in the presence of Cu(II) a significant luminescence quenching is observed: This observation suggests that the Eu(III)/PSA gel composite can be developed for detection of Cu(II) ions. The selectivity of Eu(III)/PSA gels towards different anions was also checked; from all anions studied, no anion demonstrated significant change in luminescence. The interference of other competing metal ions toward Cu(II), in aqueous solution, was further ascertained by using solutions containing more than one metal ion. The interaction between Cu(II) and the gels does not seem to be affected by any competing mechanism. Indeed, we have good evidences that Eu(III)/PSA gel can be used to detect, in a selective and precise way, the presence of copper ions, even in the presence of the other metal ions and therefore, is a promising material to act as Cu(II) sensor. The possible mechanism of luminescence quenching is discussed and further complemented with the analysis of SEM, UV-Vis and EDX mapping data.

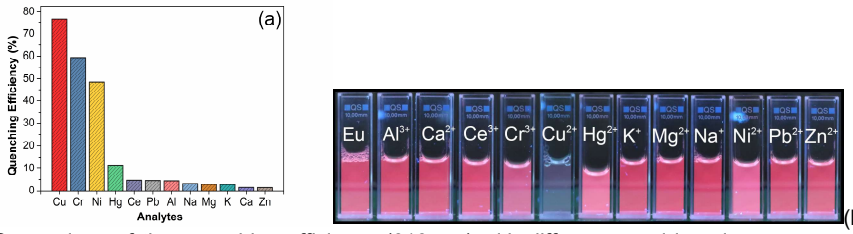

Figure 1. (a) Comparison of the quenching efficiency (616 nm) with different metal ions in aqueous solution and (b) fluorescence photographs changes of Eu(III)/PSA (red) in the presence of 3.33 mM of metal ions under UV light (365 nm) in aqueous solution.

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P55

Development of polymeric gels for their application in regenerative medicine

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Neurodegenerative diseases as, for example, Parkinson´s (PD), Alzheimer´s (AD) and Huntington´s (HD), are responsible of around 9.4 million global death[1] and are the consequence of neurogenesis alterations that cause irreparable loss of brain nerve tissue. Hydrogels based on natural biopolymers are a feasible strategy to imitate the complex 3D brain tissue environment by virtue of their excellent biocompatibilities, low immunological responses and similarity with the extracellular matrix (ECM).[2] The ECM serves as a physical scaffold and it is composed by relatively small amounts of fibrous and high available laminin proteins and polysaccharides such as hyaluronic acid (HA).[3] In this sense, HA is a linear polysaccharide that influences the tissue formation, inflammation processes and morphohenesis and it could be used to mimic ECM due to its biocompatibity and biodegradability. However, HA hydrogels lack the specific biochemical signals to perform the tissue regeneration.

Thus, by menad of the methacrylation of HA (HAMA) through carboxyl and hydroxyl groups we can produce polymeric scaffolds with elastic moduli similar to the brain tissue (100-1000 Pa).[4] HA hydrogels were cross-linked through methacrylation under UV light and further swelled in water to determine the rheological behavior previous to in vitro experiments in order to confirm their suitability to adhere, host and faacilitate proliferation and differentiation of mesenchemical stem cells (MSCs). We could confirm that these novel biopolymer hydrogels can potentially act as a replacement for damaged neuronal tissue caused by neurodegenerative diseases.

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P56

Carbon particles and lipids at fluid interfaces: a simple model for preliminary toxicity assessments of inhaled particles

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Particles are ubiquitous in science and technology that makes necessary the development of methodologies for evaluating their potential toxicity for human and environmental health. Focusing the interest to the human health, the most usual route for particles entrance in human organism is the inhalation of suspended particles and powders combined as an aerosol with other chemical compounds. Nanosized particles can go through the respiratory tract to the alveolar region where they can be incorporated into the lung surfactant layer compromising the normal physiological respiratory function.

Lung surfactant is a complex mixture formed by different lipids (around 90 wt%) and proteins overlaying the internal wall of the alveoli in such a way that can be considered like an insoluble monolayer at the water/vapor interface. This monolayer allows maintaining the mechanical equilibrium in the lung during the respiration, avoiding the alveolar collapse due to their role in the reduction of the surface tension until quasi-null value upon compression. Therefore, the incorporation of any chemical affecting the mechanical performance of lung surfactant layers may modify the normal physiological function. However, the evaluation of the effects of inhaled compounds in real systems is difficult, which makes necessary to use model systems for making preliminary toxicity assessments of inhaled particles. Langmuir monolayers of some of the constituent of the lung surfactant, in most cases only the lipid fraction, can be accounted as the most extended model systems for performing a preliminary evaluation of the potential toxicity of inhaled particles.[1,2]

This work is focused in our recent efforts for understanding the effect of the incorporation of carbon-based particles into Langmuir monolayers of lung surfactant models. For this purpose, the interfacial behavior of different monolayers combining different types of carbonaceous particles and 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) has been studied by a pool of surface-sensitive techniques. The used lipids was chosen because it is the main component of the lung surfactant and present a decisive role in the mechanical performance of lung surfactant layers, even the role of the proteins cannot be neglected for a deep understanding of the real toxicity of particles.

The obtained results have evidenced that the incorporation of carbonaceous particles, namely carbon nanosheets, combustion particles and different combustion particles, within the lung surfactant layers presents effects that result in a worsening of the mechanical properties of the monolayer. The first effect is associated with the impoverishment of the lung surfactant composition as result of the formation of lipid-particles complexes that favors the dispersion of particles into the water subphase, modifying the interfacial composition and consequently compromising the monolayer stability. The second effect is associated with the hindering of the molecular packing due to the steric hindrance associated with particles incorporation, which results in a premature collapse of the interface and consequently, in a weaken of the mechanical properties of the lung surfactant. The here presented results have shown that particles negatively affect the interfacial behavior of lipids which can impact in the physiological function of the respiratory cycle

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P57

Effect of sodium salts on the diffusion of poly(vinyl alcohol) in aqueous solutions

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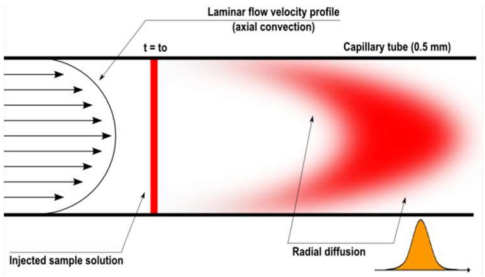
The Taylor dispersion technique[1,2] has been used of measuring the tracer diffusion coefficients, D^0_T, for poly(vinyl alcohol) (PVA) in aqueous systems containing two specific electrolytes (i.e., NaCl and Na_2SO_4) at three concentrations (0.020, 0.050 and 0.100 mol dm^{-3}), and at 25 ºC. The selection of these salts has been based on the Hofmeister series of cations and anions[3], which order the ions with respect to the behaviour of some macroscopic properties (as, for example, surface tension) and that can be interpreted as a salting-out or salting-in effect, depending on whether the target ions are strongly (kosmotropic) or weakly hydrated (chaotropic). In this work, we have measured the mass transport of PVA in the presence of salts composed by kosmostrope (Na_2SO_4) and chaotrope (NaCl) anions.
These data, complemented by NMR measurements, make possible to have a better understanding of the effect of these sodium salts on transport and thermodynamic behaviour of PVA.



Scheme 1: Representation of the diffusing compound flow as seen by the Taylor dispersion technique.

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3D mesoporous plasmonic structures for SERS imaging and sensing

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Surface Enhanced Raman Spectroscopy (SERS) is expected to provide further insight in the detection of molecules in complex systems, as the obtained signal is specific for each chemical nature, which opens the window for the detection of a large range of analytes.[1] However; this technique requires the molecules to be located in close proximity to the surface of metal nanoparticles for amplification of their Raman scattering signal. We propose herein the preparation of a 3D mesoporous plasmonic structure, not only to create specific interactions between the desired analyte with the plasmonic surface, but also to work as a filter to avoid possible interferences originated by the rest of components in the complex system. This kind of substrate may find relevant applications in fields such as cell cultures, as it would open the possibility to *in vitro* studies of biological systems in a 3D environment, rather than using common 2D strategies.

The porous system is composed of different levels of porosity, ranging from few nm up to μm. For the plasmonic structure, gold nanospheres are coated with mesoporous silica shells (AuNp@mSiO_2) through silica condensation from tetraethyl orthosilicate (TEOS) and using cetyl-trimethylammonium bromide (CTAB) as a surfactant to template the nanosized porosity.[2] Bigger cavities are obtained by coating polystyrene particles with the AuNp@mSiO_2. This composite material is synthetized by initially coating the polymer particles with charged polyelectrolytes, thus taking profit of the negative charge of the mesoporous silica shells for surface attachment. In a latter step, hardening and creation of hollow spaces are finally achieved by calcination and subsequent removal of the polymeric templates.

In summary, this work is focused in the synthesis of nanocomposites using different approaches to create mesoporous-plasmonic structures, with a great potential for 3D sensing by using SERS.

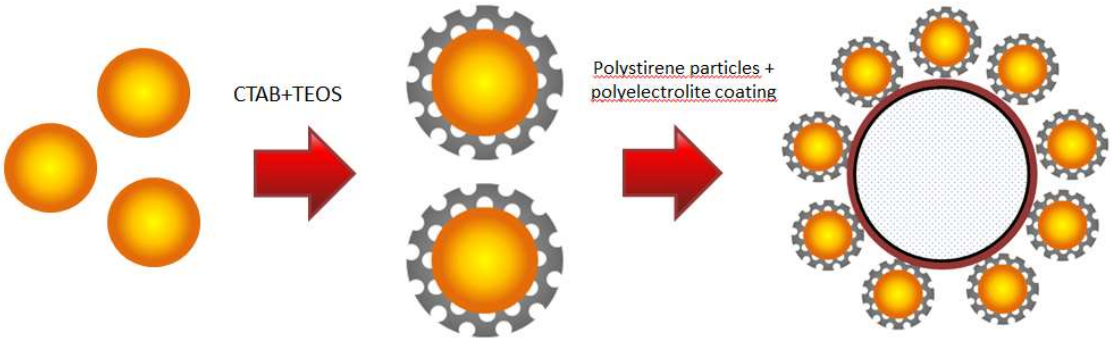

Figure 3. Synthesis of the mesoporous plasmonic structure for SERS analysis

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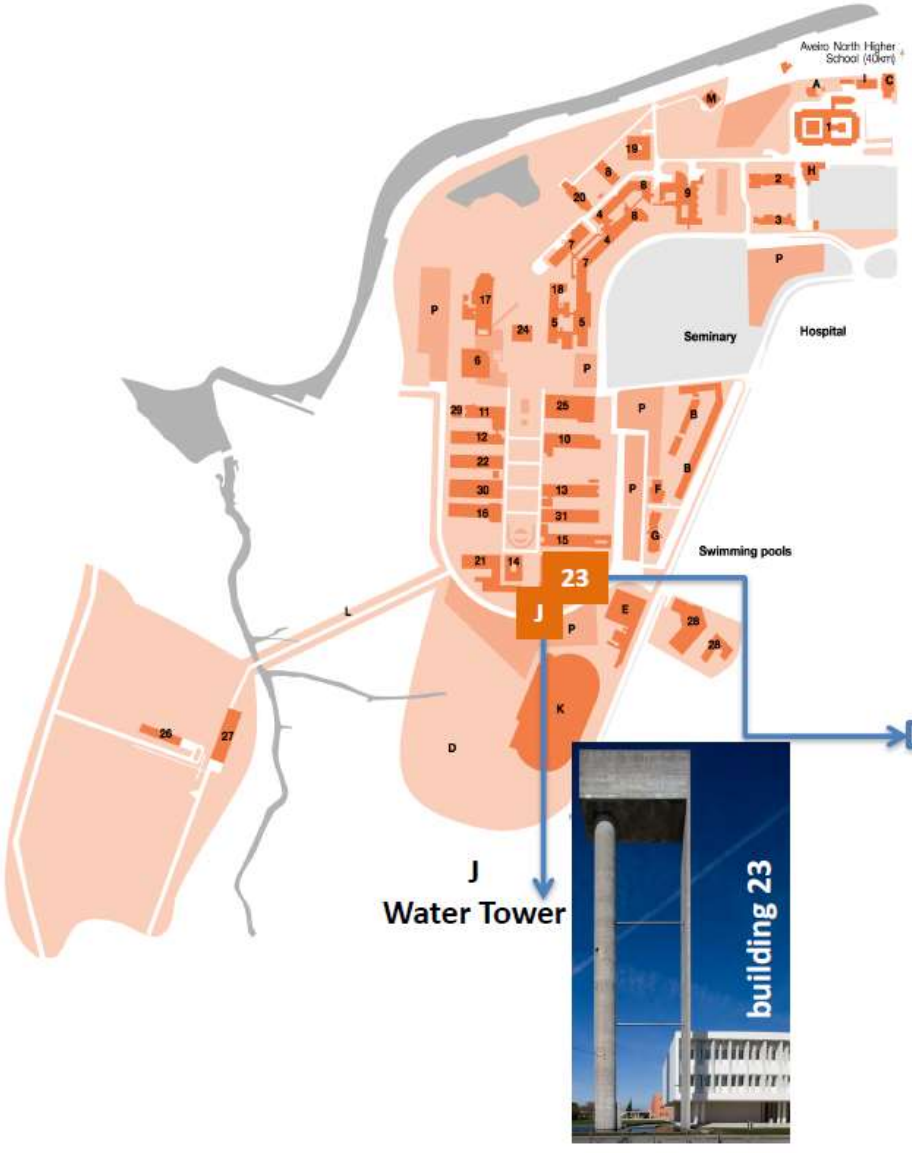

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