ABSTRACTS – POSTERS PRESENTATIONS

P1. SELF-ASSEMBLED NANOSTRUCTURES OF PEPTIDE-AMPHIPHILES: CHARGE REGULATION BY SIZE REGULATION

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Self-assembled nanostructures of peptide amphiphiles (PAs) with molecular structures C16K2 and C16K3 (where C indicates the number of carbon atoms in the alkyl chain and K are lysines in the head group) were studied by a combination of theoretical modeling, transmission electron and atomic force microscopies and acid-base titration experiments. The supramolecular morphology of the PAs (micelles, fibers or lamellas) was dependent on the pH and ionic strength of the solution. Theoretical modeling was performed using a molecular theory that allows to determine the equilibrium morphology, the size and the charge of the soft nanoassemblies as a function of the molecular structure of the PA, and the pH and salt concentration of the solution. Theoretical predictions showed good agreement with experimental data for the pH-dependent morphology and size of the nanoassemblies and their apparent pKas. Two interesting effects associated with charge-regulation mechanisms were found: firstly, ionic strength plays a dual role in the modulation of the electrostatic interactions in the system, which leads to complex dependencies of the aggregation numbers with salt concentration; secondly, the aggregation number of the nanostructures decreases upon increasing the charge per PA. The second mechanism, charge regulation by size regulation, tunes the net charge of the assemblies in order to decrease the electrostatic repulsions. A remarkable consequence of this behavior is that adding an extra lysine residue to the charged region of the PAs can lead to an unexpected decrease in the total charge of the micelles.

P2. THE ROLE OF MOLECULAR CROWDING IN LONG-RANGE METALLOPROTEIN ELECTRON TRANSFER: DISSECTION INTO SITE- AND SCAFFOLD-SPECIFIC CONTRIBUTIONS.


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In highly crowded environments where fundamental physicochemical parameters, such as viscosity or activity coefficients, may diverge from ideality by orders of magnitude. The underlying assumptions of the usually employed Marcus semiclassical theory are not fulfilled in such context. Moreover, crowding is expected to reshape free energy landscapes of proteins and, therefore, their complex dynamics, in ways that may be determinant to their function. In this presentation I will discuss the effect of molecular crowding on the long-range ET reactions of metalloproteins. To address this elusive question, we consider two different types of one-electron copper redox proteins that share the cupredoxin fold but differ in the redox center: the type 1 (T1) mononuclear blue copper site and the purple binuclear CuA center. Besides, by means of loop engineering we developed several chimeras that incorporate different T1 centers within the CuA scaffold, as well as perturbed CuA sites, without altering the protein scaffold. The heterogeneous ET kinetics of the different protein variants adsorbed on electrodes coated with self-assembled monolayers (SAMs) alkanethiols was studied by protein film electrochemistry at variable electronic couplings and in the presence of different crowding agents.
Our results reveal a strong frictional control of the ET reactions at tunneling distances shorter than 24 Å (non-adiabatic regime), provided that reactions are performed at physiological viscosities. Moreover, we have been able to identify specific effects attributed to the protein scaffold and to the type of metal site, respectively, which account for the empirical friction parameters. These findings highlight the need of explicitly considering molecular crowding effects in protein ET reactions.

P3. MECHANISTIC INSIGHTS INTO A CHIRAL PHOSPHORIC ACID-CATALYZED ASYMMETRIC PINACOL REARRANGEMENT


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The present poster describes a Density Functional Theory investigation[1] on the first catalytic enantioselective pinacol rearrangement reaction, reported in 2010 by Antilla and co-workers. This reaction was catalyzed by a chiral phosphoric acid catalyst, and proceeded in high levels of enantioselectivity. In this work, we determined the origin of the enantioselectivity and explained the difference in reactivity between different catalysts. Two key hydrogen bonding interactions were found between the phosphate group of the catalyst and the indolyl alcohol and the indole group from the intermediate. The latter was found to be stronger in the major transition state, therefore accounting for the high levels of enantioselectivity observed. This interaction was not observed with a more bulky catalyst (TRIP), which resulted in lower levels of enantioselectivity.


P4. DESIGN OF NANO CARRIERS FOR THE IMMOBILIZATION AND CONTROLED RELEASE OF ANTIMICROBIAL PEPTIDES

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Antimicrobial peptides (AMPs) have attracted importance as new potential drugs due to the advantages that they exhibit regarding conventional antibiotics. These compounds are characterized by having a broad antimicrobial spectrum and multiple mechanisms of action, which hinders the development of resistance in microorganisms. Despite the above, the clinical use of this type of compounds is limited due to their short half-life, mainly because they are susceptible to degradation by proteases. Therefore, a proposed alternative to overcome these disadvantages is the immobilization and/or encapsulation of peptides on biocompatible carriers. Based on works described in the literature and previous experience of our group, we focused on the design of two different carrier systems: 1) rigid mesoporous silica nanoparticles (MSNPs) with or without a
chitosan shell to allow for covalent immobilization of the peptide, and 2) alginate (a natural biopolymer) nanogels (ANGs). Unlike biopolymers nanogels, MSNPs are physically and chemically stable and their physicochemical properties can be tuned to allow for a controlled release of their content and they offer the possibility of surface functionalization allowing the active targeting of different cell populations. On the other hand, for several biomedical applications such as formulations meant for intravenous route administration, the possibility of having a stable aqueous solution of ANGs is far more promising.

Taking into account the above, this work presents the design, synthesis, characterization and bioactivity of bioconjugates composed of the Ib-M6 antimicrobial peptide immobilized both on ANGs and MSNPs. This peptide has been reported as bioactive against gram-negative bacteria such as Escherichia coli O157:H7, presenting a half maximal inhibitory concentration (IC50) in the range 6-9 uM. The bioconjugates Ib-M6/ANGs were prepared by direct crosslinking of the negatively charged alginate polymer with Ca2+ cations and the Ib-M6 peptide, which exhibits a net charge +6, in aqueous medium. The MSNPs were synthesized by a sol gel process, using tetraethoxysilane as silica precursor, and then the peptide was incorporated by adsorption in aqueous media (Ib-M6/MSNPs) or the MSNPs were coated with chitosan (1% w/w in acetic acid 2% v/v) and the immobilization of Ib-M6 was carried out by the formation of an amide bond between carboxyl groups of the peptide and amine groups of chitosan. The as-prepared nanocarriers and the Ib-M6 bioconjugates were characterized by DLS, SEM, FT-IR, and SAXS. The antibacterial activity of the Ib-M6 bioconjugates was evaluated by the microdilution procedure using a synthetic aqueous sample contaminated with Escherichia coli O157:H7. The antibacterial activity of the free Ib-M6 peptide and the three different nanocarriers were also performed for comparative purposes. The results showed that it was possible to reach a high percentage of inhibition of the growth of E. coli O157:H7 after 24 h with the designed nanocarriers, which also confer protection against protease attack (trypsin).

Keywords: Bioconjugates, Co-precipitation method, Chitosan

P5. OBTAINING ENTROPIC CONTRIBUTIONS TO BIOCATALYSIS


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Since the early beginnings of chemical simulations, obtaining the activation enthalpy, entropy and free energy for biomolecular reactions has always been one of the major goals to shed light on the molecular basis of enzymatic catalysis. In the last few decades, the ever-increasing computer power allowed the development of several methodologies such as metadynamics, multiple steered molecular dynamics, and umbrella sampling for the calculation of fairly accurate free energy profiles in complex systems using multi scale QM-MM schemes. However, determining accurate activation enthalpies and entropies remained a more difficult issue. In this work we present a systematic study analyzing a methodology for the calculation of the activation parameters in both aqueous and enzymatic environments, using a DFT/Gaussian basis set QM-MM implementation for graphical processing units developed in our group. This methodology achieves the calculation of activation enthalpies by the acquisition of free energy profiles at several temperatures.
P6. DESIGN AND SYNTHESIS OF POLYHYDROXYPYRROLIDINES AS ENZYME INHIBITORS

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The increasing interest in polyhydroxypyrrolidines (PHP) relies on their potential as therapeutics for the treatment of varied diseases. The biological activity of these compounds is related to their ability to inhibit glycosidases, enzymes involved in numerous events, such as bacterial and viral infections, tumor metastasis, etc. In fact, PHP are mimetics of common sugars (iminosugars) that result from the replacement of ring oxygen atom by a nitrogen atom.

In the search of new PHP as enzyme inhibitors, we have employed the 1,3-dipolar cycloaddition of azomethine ylides and sugar enones derived from pentoses,1,2 as a key step in the synthesis of optically pure PHP, that contained an aryl substituent. These compounds were evaluated as inhibitors of the β-galactofuranosidase from Penicillium fellutanum. This enzyme, which is not commercially available, is very interesting since many pathogenic microorganisms, including mycobacteria, fungus (Aspergillus and Penicillium), and protozoa (Trypanosoma and Leishmania) display β-galactofuranosidase activity. The inhibition of enzymes involved in the metabolism of galactofuranose, which is absent in higher eukaryotes, is expected to prevent the proliferation of pathogens. Unfortunately, none of the PHP evaluated revealed a noticeable inhibitory activity of the enzyme, which is highly sensitive to steric factors. We attributed the lack of activity to the steric hindrance of the aryl group in the PHP that hampers their accommodation within the active site. Therefore, we have designed and synthesized PHP lacking of aromatic substituents attached to pyrrolidine ring. Thus, we are studying the 1,3-dipolar cycloaddition of imines, derived from 2,2-dimethoxyacetaldehyde and common amino acids, or synthetic ones derived from carbohydrates to obtain cycloadducts, even this last one entirely based on carbohydrate precursors. The products of further transformations (analogues of compounds previously synthetized) will be evaluated as inhibitors of the β-galactofuranosidase.

2-Udry, G. A. O.; Repetto, E; Vega D. R.; Varela O. J. Org. Chem, 2016, 81, 4179−4189

P7. WATER SOLUBLE IRON-NITROXYL PORPHYRIN COMPLEXES: [FEII(TPPS)HNO]4– AND [FEII(TPPS)NO]5– PKA ESTIMATION AND STABILITY STUDIES

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Interest in HNO (azanone according to IUPAC; usually nitroxyl) has increased in the last decade due to its remarkable chemical properties and increasing biological relevance.1 In addition, Fell-nitroxyl complexes are important intermediates in NO and nitrite-reducing enzymes in bacteria and fungi, which catalyze important processes related to the biogeochemical cycle of nitrogen. It has been considered that the protonated adduct is stabilized by amino acids,2 and bulky substituents.3 The stability reported for [Fe(CN)5(HNO)]3– 4 led us to consider that factors like H-bonds with water, could stabilize the Fe-HNO moiety. In this work, the heme water soluble nitroxyl complexes [FeII(TPPS)HNO]4– and [FeII(TPPS)NO]5– were obtained and characterized by UV-Vis spectroscopy. The pKa was estimated from both spectroscopic and electrochemical measurements. The protonated complex spontaneously reoxidizes to the nitrosyl species within minutes, much slower than in organic media.5 Kinetic measurements in different conditions, along with other experimental results and DFT calculations support an unimolecular reoxidation mechanism involving an homolytic rupture of the H-NO bond, via a phlorin intermediate also proposed and detected in similar systems.
The emergence of antiviral drug-resistant mutants is the most important issue in current antiviral therapy. An ideal therapeutic target to prevent drug-resistance development is represented by host factors that are crucial for the viral life cycle. Given that viruses are obligate parasites, several host factors that are crucial for viral replication also represent antiviral therapeutic targets, referred to as the “cell-based approach”. Recent efforts have focused on finding and characterizing cellular metabolic inhibitors as broad-spectrum antivirals for targeting with minimum cytotoxicity. MPA is a non-nucleoside, non-competitive inhibitor of inosine monophosphate dehydrogenase (IMPDH). It is well known by its effects as immunosuppressive and against multiplication of several viruses; this inhibition was highly reversed by exogenous guanosine addition, indicating that antiviral activity is effectively associated with GTP depletion through IMPDH blockade. Other antiviral drug is Ribavirin (RIB) is an antiviral drug which inhibits the development of several viruses. However, RIB must be administered frequently in order to maintain the therapeutic effect due to its short life time in body. The concentration of RIB in the blood often exceeds the maximum tolerable level after administration, which causes serious side effects. Poor pharmacokinetic profiles and resistance are the main two drawbacks from which currently used antiviral agents suffer, thus make them excellent targets for research, especially in the presence of viral pandemics such as DENV, ZIKV, HIV, Hepatitis. Despite the high efficiency of the human immune system, viruses are ubiquitous and versatile organisms with the potential to cause serious illnesses that require aggressive pharmacological intervention, yet existing medicines are by and large inefficient at combatting viruses, making them a target for aggressive exploration to accelerate the development of new antiviral agents.

As it is known nanocarriers can provide key advantages for the in vivo delivery of drugs or molecules with therapeutic effects, such as nucleic acids and proteins, improving their efficiency and reducing potential side and toxic effects. Biodegradable and biocompatible nanoparticles (NPs) offer the ability to protect the therapeutic molecule from early degradation (i.e. before reaching the target organ or tissue), to control the release, to bypass the biological barriers and to selectively reach the action site.
P9. MULTISCALE MODELING OF LITHIUM ION BATTERIES FROM PHYSICAL PRINCIPLES

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Argentina is geographically situated in the so-called “Lithium Triangle”, an area that gathers 54% of the world’s Lithium resources. One of humanity’s greatest goals is to migrate completely to greener alternatives for vehicular fuels. It becomes a strategic matter to capitalize our region’s natural advantage. We are developing a mathematical model capable of describing the physical and chemical phenomena that occur inside a Li-ion battery. With it, we aim to be able to predict battery performance and to propose future improvements. Battery models involve three regions: the negative electrode, the positive electrode and the electrolyte, which constitutes the separator and soaks the electrodes’ pores. Our work makes a 1D approach to these regions. Electrochemical reactions take place in the active material surface. This causes ions to (de)intercalate in the solid matrix, and create an electrical current. Newman et al. have pioneered modeling of this nature, describing ion transport within the cell.

The positive electrode’s active material is generally a Lithium-containing transition metal oxide, such as LMO. The negative electrode’s insertion material is graphite. The electrolyte is a Lithium salt, LiPF_6, which enables ionic transport in the battery upon dissolution. Li-ion batteries operate according to the “rocking chair” mechanism: ions leave one electrode’s solid lattice, move along the electrolyte and finally insert in the other electrode’s structure. This mechanism can be described with equations (Eq.1) and (Eq.2).

\[
\text{Li}_{(y+dy)} C_6 (s) = dy\text{Li}^++\text{Li}_y C_6 (s) + dye^- \quad (\text{Eq.1})
\]

\[
\text{Li}_z \text{MnO}_2 + dz\text{Li}^++dze^- = \text{Li}_{(z+dz)} \text{MnO}_2 \quad (\text{Eq.2})
\]

Our model has two scales: the solid and the electrolyte scale. The solid is modeled as active material spheres interconnected through a binding material. Material balances are solved within each particle, using the electrochemical reaction as boundary conditions. There is no convection in the electrolyte phase: transport takes place via Fick’s diffusion and via Ohm’s migration. The material source term is a boundary condition at the solid scale. The electrochemical reaction occurs at the active material’s surface, and its kinetics depend on the concentration profile inside the particle and the concentration in the surrounding electrolyte. This reaction creates an electrical potential difference across the interface. We consider that each active material particle is one spatial node in the electrolyte scale. Our goal is to solve the equations governing each scale, using our own algorithms. The main challenges of this work are to successfully couple both scales and to establish each phase’s electrical potential, a topic of much discordance in the electrochemical literature. We aim to eventually incorporate double layer effects to our model, yet not with the aid of the equivalent circuit approach but through physical principles using double layer models, Maxwell equations and material balances.
P10. MODELADO MULTIESCALA DE BATERÍAS DE ION LITIO DESDE PRINCIPIOS FÍSICOS

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Argentina se encuentra en el llamado `Triángulo del Litio', zona que concentra cerca del 54% de las reservas de litio mundiales [1]. Uno de los objetivos actuales más importantes de la humanidad es migrar a alternativas más verdes como fuentes de alimentación para el transporte vehicular. Resulta estratégico poder aprovechar esta ventaja natural de nuestra región y estar al frente del desarrollo tecnológico necesario. Estamos trabajando en un modelo para describir los fenómenos que suceden en la batería y así poder predecir su comportamiento y proponer mejoras en el funcionamiento. Los modelos de celda en general comprenden tres dominios: un electrodo positivo, uno negativo y el electrolito, que embebe los poros y compone el separador. En particular, nuestro trabajo describe dichas regiones en 1D. En la superficie del material activo de los electrodos ocurre la reacción electroquímica que originaría la corriente y a su vez daría lugar a la (des)intercalación de iones en la red. Newman y colaboradores han sido los pioneros en el desarrollo de modelos que describen el transporte de iones dentro de la batería [2,3].

El material activo del electrodo positivo suele ser un óxido de metal de transición que contenga litio, como por ejemplo el LMO, mientras que el material de inserción del electrodo negativo es un carbón tipo grafito. El electrolito es una sal de litio, LiPF6, que al ser disuelta permite el transporte iónico dentro de la batería. Las baterías de ion-litio operan según el principio de `silla mecedora': los iones se desintercalan de la estructura de uno de los electrodos para transportarse a través del electrolito e insertarse en la estructura del otro. Este mecanismo se asocia a las ecuaciones (1) y (2):

\begin{align}
\text{Liy+dyC6(s) = dy:Li+ + LiyC6(s) + dy:e-} & \quad (1) \\
\text{LizMnO2 + dz:Li+ + dz:e- = Liz+dzMO2} & \quad (2)
\end{align}

El modelo comprende dos escalas: la escala del sólido y la del electrolito. El sólido se modela como esferas de material activo conectadas eléctricamente entre sí por un binder. Dentro de cada partícula se resuelve el balance de masa para los iones litio, siendo la reacción electroquímica una condición de contorno. En la fase electrolito no hay efectos convectivos: el transporte se da por difusión siguiendo la ley de Fick (gradiente de potencial químico) y por migración siguiendo la de Ohm (gradiente de potencial eléctrico). El término fuente es la condición de contorno de la escala del sólido. La reacción electroquímica ocurre en la superficie de la partícula activa, y tiene una cinética dependiente de las concentraciones de iones tanto en la partícula como en el electrolito circundante. Además, dicha reacción genera una diferencia de potencial entre ambas fases. En la aplicación, tomamos que cada partícula esférica del sólido conforma un único nodo espacial en la escala del electrolito. El objetivo es poder resolver el sistema de manera teórica en ambas escalas, empleando algoritmos de confección propia. Dentro de los desafíos de este problema, además de acoplar satisfactoriamente dos escalas, es el correcto uso de los potenciales de cada fase, fuente de mucha discrepancia en la literatura electroquímica. Como perspectiva, se pretende incorporar los efectos de la doble capa al modelo, pero no a través del uso del concepto de circuitos equivalentes [4] usando elementos capacitivos, sino a través de principios físicos empleando modelos de doble capa, ecuaciones de Maxwell y balances de masa.

P11. DESARROLLO DE ESTRATEGIAS DE BIOSENSADO SERS BASADAS EN NANOESTRUCTURAS PLASMÓNICAS AUNS@AG@SIO2

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Las plataformas de biosensado han sido ampliamente utilizadas tanto en ámbitos científicos como comerciales, desde la detección de gonadotropina coriónica humana en pruebas caseras de embarazo como en el desarrollo de plataformas de detección patogénica temprana in situ. Si bien la estrategia bioquímica es siempre similar, la señal detectada puede cambiar para un mismo sistema. En este contexto, se busca desarrollar un sistema de detección basado en espectroscopia Raman intensificada por superficie (SERS). En particular, se desarrollaron nanoestructuras híbridas que poseen zonas que concentran densidades de campo electromagnético, o hot spots. Moléculas en estas zonas verán sus señales Raman intensificadas debido a la interacción de la radiación electromagnética con los plasmones superficiales de la superficie. Las estructuras utilizadas son nanoestrellas de oro[1] (AuNS) recubiertas por plata (AuNS@Ag)[2], las cuales son conjugadas a un reportero Raman cuyas señales se busca detectar. Luego se protege la estructura mediante un recubrimiento con sílica (AuNS@Ag@SiO2)[2]. Estas nanoarquitecturas fueron optimizadas para obtener la máxima intensificación posible en una medida SERS con un láser de 532 nm. En este trabajo se perfeccionaron estas estructuras, se eligió un reportero Raman adecuado y se optimizaron las condiciones de medida SERS. Finalmente, se exploraron las posibilidades del armado del biosensor por dos estrategias; un sistema de doble detección del tipo ELISA o fijado del antígeno a una superficie y detección simple.

P12. DETERMINATION OF KW IN NANOCONFINED WATER IN NANOdroplets

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In this work we use DFT Car-Parrinello molecular dynamics combined with the Umbrella sampling scheme to study the self dissociation constant of water (Kw) confined in nanodroplets. Three systems of different size were used to analyze the effect of confinement: aggregates of 20, 12, and 6 water molecules. We show that in the largest droplets (20 and 12 molecules) there is no difference in the value of the dissociation free energy with respect to bulk water, whereas for the hexamer we observe an increase in said energy (or equally that the Kw value drops for the smallest system). It is also shown that, for the larger droplets, the solvation shells of the hydronium and the hydroxide ions resulting from the dissociation is similar to those in the bulk but the solvation changes for the 6 molecules cluster. Thus, most of the energetics of this reaction appears to be already captured by the first hydration core, present in the two bigger clusters. The structural constraints in the hexamer, on the other hand, result in a deficient solvation of the products, which seems to be the reason as to why the free energy of dissociation becomes unfavored in this case.
P13. LIQUID-SOLID FLUIDIZED BED CFD-DEM SIMULATION AND VALIDATION BY RADIOACTIVE PARTICLE TRACKING

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Many catalytic processes and operations in the chemical and related industries are carried out in liquid-solid fluidized beds (LSFB). Information of their underlying dynamics is fundamental for proper design of the units and for implementing strategies of process intensification. Moreover, the validation of LSFB modeling to estimate their performance requires comparison with experimental results (Dudukovic & Mills, 2015). The objective of this work is to compare experimental results obtained with the Radioactive Particle Tracking (RPT) technique in a pilot scale LSFB with those predicted by a Computational Fluid Dynamics coupled with Discrete Element Method (CFD-DEM) model. For this purpose, the motion of calcium alginate spheres induced by the upward flow of water in a cylindrical column (Maestri et al., 2019) is examined. Simulation of the liquid and solid motion is solved using the CFDEM coupling software (Goniva et al., 2012). For the liquid phase, the Navier-Stokes equations are solved numerically while for the solid phase the forces acting on the particles (gravity, buoyancy, drag force, solid-solid and liquid-solid surface interactions) are calculated, according to the proposal of Wang et al. (2012). Once the model is validated, the influence of the operating conditions on the particles motion is studied by simulation. The model successfully predicts several observables measured by RPT, such as bed expansion, time averaged velocity fields (Maestri et al., 2019), Kolmogorov entropy, solid phase distribution and solid axial dispersion coefficients.

Goniva, C.; Kloss, C.; Deen, N.G.; Kuipers, J.A.M.; Pirker, S. / Particuology, 10 (2012) 582–591

P14. MULTI SCALE (QM-MM) EXPLORATION OF BIOCHEMICAL PROCESSES USING BIASED MOLECULAR DYNAMICS SIMULATIONS

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Umbrella sampling is a biased molecular dynamics based method for the calculation of one- or more-dimensional free energy profiles associated to chemical processes. In one of the versions of this method, intermediate steps between two thermodynamic states are covered by a series of windows, at each of which a biased MD simulation is performed. In chemical reactions, free energy differences between two states that differ in geometry (like reactants complex, transition state and products complex) are usually of interest since free energy barriers, for instance, can be used to calculate rate constants by means of the transition state theory. Moreover, mechanistic information can be assessed through free energy profiles calculation. In this way, in the study of chemical reactions by the umbrella sampling method, the windows are located at different values of an order parameter that is often a combination of geometric grounds that describe the progress of the process. In this context, this order parameter is generally referred to as ‘reaction coordinate’ even though it might not be the exact reaction coordinate of the system (i.e. the one-dimensional coordinate that connects reactants and products by the minimum energy pathway). In this work, we present an
improved sampling protocol for obtaining free energy profiles of biochemical reactions in solution using umbrella sampling in a quantum mechanics-molecular mechanics (QM/MM) scheme. One of the most important assumptions in umbrella sampling calculations is that the selected reaction coordinate is the only slow degree of freedom. This is usually true if all the important events of the reaction are included in the definition of the reaction coordinate. However, in QM/MM MD, time simulations longer than tens of ps are rarely computed because of their computational cost and some degrees of freedom might not be well-sampled even if they are supposed to be equilibrated. Our results suggest that solvent pattern rearrangements related to charges redistribution during the reaction are not well-sampled in the ps scale and this might lead to an overestimation of the computed free energy barriers.

P15. FUSED AND UNZIPPED CARBON NANOTUBES, ELECTROCHEMICALLY TREATED, FOR SELECTIVE DETERMINATION OF DOPAMINE AND SEROTONIN

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Glassy carbon electrodes (GC) were modified with multiwalled carbon nanotubes (MWCNT/GC) and electrochemically treated first by applying an oxidation potential and then a reduction potential. The resulting electrodes were characterized via scanning electron microscopy, Raman spectroscopy, energy dispersive spectroscopy, and electrochemical techniques, particularly cyclic voltammetry using the redox probes Fe(CN)6 3-/4- and Ru(NH3)2+/3+ and electrochemical impedance spectroscopy using Fe(CN)6 3-/4-. These modified electrodes showed an electrochemical determination selective for dopamine (DA) and serotonin (5HT) in the presence of ascorbic acid (AA) and uric acid (UA), simultaneously measured, with a high reproducibility (an RSD of 1.7% for DA and 1.6% for 5HT) and a limit of detection (LOD) of 235 nmol L-1 for DA and 460 nmol L-1 for 5HT. The GC electrodes modified with oxidized MWCNT, subsequently reduced, showed higher selectivity towards the oxidation of DA and 5HT compared with GC bare electrodes or modified with MWCNT or oxidized MWCNT.

P16. HEXA/PENTACOORDINATION TRANSITION IN THB1

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THB1 from green alga Chlamydomonas reinhardtii belongs to group 1 truncated hemoglobins (TrHB1s). It is a monomeric hemoglobin that functions as nitric oxide dioxygenase (NOD). The heme in THB1 displays two axial ligands: His77 (F8) as proximal ligand and Lys53 (E10) as distal ligand. In order to be able to bind external ligands, THB1 Fe-Lys53 bonds need to be break. The displacement of Lys53 involves a conformational change, which includes the rotation of Lys53 side chain that ends pointing outside the protein cavity. This results as well in a change of the protonation state of Lys53, which is in a neutral state when is coordinated, and is protonated when it is not attached to the heme and surrounded by water molecules outside the protein cavity. In order to clear up this mechanism, a battery of biophysical and biochemical studies were done [1]. From these experimental studies, several questions have emerged. Regarding the Lys53 opening mechanism, it is not clear if the protonation of Lys53 occurs in the heme cavity or when
Lys53 have moved to the solvent. Also, if Lys53 protonation take place inside the heme cavity, it is unknown if it is concerted with the decoordination or if the Fe-Lys cleavage and protonation occur sequentially.

In this work we have tried to shed light on the mechanism of Lys53 coordination/decoordination in THB1 by means of computer simulations. For this purpose, we performed extended molecular dynamics simulations for the wild type THB1 and selected mutants for pentacoordinated state. We have carefully observed the existence of events of Lys53 conformational changes and identified key interactions that maintain Lys53 inside the protein cavity and affect the transition. We have also observed the entrance of water molecules to the heme cavity to analyze the possibility of Lys53 protonation inside the cavity. We also analyzed the global structural movements associated with the transition, which involve the E helix and residues Lys49 and Arg52. Additionally, umbrella sampling calculations were performed to obtain the free energy profiles of the Lys53 displacement process when Lys53 is neutral and when Lys53 is protonated, in order to elucidate if Lys53 protonation happens in the heme cavity or in the solvent. To clear up if the protonation inside the cavity is concerted with the decoordination, QM-MM restrained optimizations were done. The results from this work strongly suggest that the “in” to “out” transition involves the protonation of Lys53 inside the distal cavity, which is also the driving force for Fe-Lys53 bond cleavage. Additionally, several key aminoacids have been identified as molecular determinants for the Lys53 displacement process which allow to design new mutant proteins that provide a better understanding of the molecular mechanisms governing THB1 function."

P17. CONTINUOUS HETEROGENEOUS FENTON TYPE REMOVAL OF ORANGE G USING ALUMINA SUPPORTED PRUSSIAN BLUE NANOPARTICLES

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Removal of the model azo dye Orange G via a heterogeneous Fenton type (HFT) process in a continuously operated packed bed reactor is studied. The reactor is filled with Prussian Blue nanoparticles (PBNP) supported onto γ-Al2O3 beads. The influence of oxidant concentration and molar flow rate on the dye removal efficiency is analyzed.

Methods: The catalyst used was prepared by rapid adsorption of just obtained insoluble PBNP onto 2.5 mm γ-Al2O3 beads, as described in Doumic et al. [1]. HFT experiments were carried out in a thermostated packed bed reactor. The initial dye solution concentration (0.02 mM), the mass of catalyst (20 g), the temperature (343K) and pH (3) were kept constant for all the experiments. The reactor was a 2.4 cm internal diameter glass column filled with catalyst for 8 cm length; glass beads of 2 mm diameter were packed in the entrance region to promote good dispersion. The liquid was circulated in upwards direction to ensure complete wetting of the catalyst. The reactor and a previous glass coil were immersed in a thermostatic bath regulated at the desired temperature. Inlet and outlet concentrations of dye, hydrogen peroxide and oxygen were regularly measured for each experiment for at least one hour to check that the steady state was attained. Activity of the catalyst was regularly checked against hydrogen peroxide conversion in a reference condition; no decrease in catalyst activity was observed along the whole series of preliminary experiments carried out. These preliminary results point to a combined influence of the flow rate and concentration of the oxidant. When the liquid flow rate is too low, even if the oxidant conversion increases due to a longer residence time, the improvement in OG conversion is less marked indicating a diminished efficiency. Further studies are ongoing to systematically analyze the dye conversion, leached iron and TOC conversion for assessing the influence of oxidant molar flow rate on mineralization efficiency.
P18. SYNTHEYSIS AND CHARACTERIZATION OF LUMINESCENT LA1-XEUXPO4 NANO PARTICLES THROUGH THE EPOXIDE ROUTE

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Lanthanum phosphate nanoparticles partially substituted with variable contents of Eu(III), La1-xEuxPO4, constitute promising luminescent agents with exceptional chemical stability in physiological media. Herein we introduce the preparation of these particles under mild conditions, by means of epoxide driven alkalinization [1], in order to achieve controlled size, morphology and crystalline structure. By tuning the rate of alkalinization, the solvent polarity and its viscosity, the concentration of reagents and the eventual use of capping agents, this approach offers pure phases of controlled texture and high purity. Moderate thermal treatments, that allow the massive dehydration of the parent phases, while preserving the parent nanometric texture, enhanced the luminescent properties of the resulting nanoparticles. A comprehensive screening of the effect of texture and the thermal treatment conditions over the observed luminescence is discussed in terms of the Eu(III) coordination environment. The highest quantum efficiency was obtained for the calcinated sample with x=0.1 with a value of ca. 27% (monazite phase).


P19. HIGH MOLECULAR WEIGHT CHITOSAN BASED NANO GE LS FOR RESVERATROL DELIVERY

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The retinal tissue has the highest oxygen uptake and glucose oxidation relative to any other tissue, which makes it more susceptible to oxidative stress. Constant light irradiation and atmospheric oxygen contribute to oxidative stress as the key factor for the ocular degenerative diseases. Whenever the antioxidant defense systems are depleted or not functional, vision impairment might be observed. For this reason antioxidants are fundamental agents in prophylactic forms of oxidative diseases. Nanotechnology becomes an option in antioxidant protection, stability, bioavailability, and therapeutic efficacy. Therefore, the aim of this work is to develop nanoparticles (NPs) as carriers of antioxidants for the ocular diseases prevention. Particularly, there is an increased interest in the therapeutic effects of Resveratrol (RSV). RSV is a naturally occurring polyphenolic compound, mainly found in black grapes and peanuts. Previous studies have demonstrated the various beneficial effects of RSV on human health, including its neuroprotection, anti-inflammatory action, potent antioxidant activity and anti-aging effects. On the other hand, chitosan (CHI) is an available polysaccharide extensively studied for drug delivery systems due to the biological properties such as its relative non toxicity, biocompatibility, biodegradability and mucoadhesive characteristics. CHI and the cross-linking agent tripolyphosphate-sodium (TPP) can form biocompatible micro nano-spheres that can be
efficiently employed in bioactive delivery. Hence, we designed and developed chitosan-based nanocarriers for RSV encapsulation to overcome this physicochemical and pharmacokinetic limitations. Our results included the design of colloidal NPs of CHI-TPP obtained by ionic gelation. The particle size distribution and the Z-potential were recorded by DLS. The peak of the majority population was located at 144 nm and the obtained value of the Z-potential was 21±4 mV, indicating that the suspension of the NPs is relatively stable. In addition, the protective effect of CHI against UV-induced photodegradation of RSV was determined. Also, TEM images showed spherical particles. Biological studies performed in human retinal pigment epithelial cells (ARPE-19 cells, ATCC) revealed that both free CHI and NPs were not cytotoxic. Also, uptake and intracellular incorporation was monitored through fluorescence microscopy. Finally, we obtained an 80% of loading-efficiency of the NPs, measured using absorption spectrophotometry. In conclusion, we suggest that NPs could be a potential carrier for the bioactive, opening the possibility of its application for ophthalmic uses.

P20. SYNTHESIS OF NEW FORMULATIONS FOR THE DELIVERY OF CURCUMIN AS AN ANTIVIRAL STRATEGY FOR THE TREATMENT OF INFECTIONS CAUSED BY THE ZIKA VIRUS

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Poly (D, L-lactide-co-glycolide) (PLGA) is a copolymer of great interest for medicinal applications, because it is bioregradable, biocompatible, non-toxic, and its kinetics of degradation can be modified by the copolymerization ratio of the monomers. In this work, PLGA was synthesized and characterized by thermal and spectroscopic techniques, showing a glass transition temperature of approximately 35°C, characteristics that make it suitable for controlled release of drugs. On the other hand, curcumin is a natural substance of great interest which modulates different biological activities but its low solubility represents an important drawback. Here, PLGA nanoparticles were synthesized to encapsulate curcumin and their effectiveness as antiviral molecules against Zika virus was explored through different biological tests. Our results show that the antiviral activity of PLGA-CUR formulation is at least 3 fold more effective to inhibit ZIKV in vitro infection in relation to that of free CUR.

P21. SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF A RHNO COMPLEX WITH A PCN PINCER LIGAND

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Studies of characterization and reactivity of nitrosyl complexes are of high importance to attain further understanding of nitric oxide’s role in biology. This ligand is also particularly attractive in coordination chemistry for its rich redox activity, which gives place to three limit bonding descriptions. Nevertheless, electronic delocalization is best described by Enemark-Feltham notation {MNO}n.[1] Pincer ligands, on the other hand, are also broadly studied due to their relative stability and the possibility they introduce of tuning the metallic center reactivity by changing sterical and electronic parameters. In prior works, the combination of both these types of ligands was studied in a {RhNO}8 species with a PCP ligand and activation of carbon-halogen bonds by {RhNO}9 has been reported.[2] In this work, we synthesized a {RhNO}8 complex with a PCN pincer ligand: [Rh(PCN)(NO)]+ (PHCN=N-[3-(ditert-butylphosphanylmethyl)phenyl[methyl]-N-ethylethanamine), which would be expected to favour higher oxidation states and reduce steric hindrance around the metallic center.

{RhNO}8 was obtained by a four-step synthesis, where only the first step is reported:[3]

\[
PCHN + [Rh(COE)2Cl]2 \rightarrow Rh(PCN)(H)(Cl) (1) \rightarrow Rh(PCN)(NO)Cl (2) \rightarrow [Rh(PCN)(NO)]^+ (3^+)
\]

COE=Cyclooctene

All of these compounds were characterized by 31P-NMR, 1H-NMR, FTIR and X-ray diffraction. Redox reactivity of complex (3+) and of that of its pentacoordinate derivatives, (2) and [Rh(PCN)(NO)(CH3CN)]+ (4+), was found to distinguish itself from analogous PCP complexes due to a relative stabilization of higher oxidation states. Oxidation of these three complexes was studied by FTIR spectroelectrochemistry. Reduction of complex (3+) to yield an air sensitive {RhNO}9 species [Rh(PCN)(NO)]• (3•) was also carried out. Complex (3•) was proved able to activate carbon-halogen bonds in aryl halides, in much a similar way as that of its PCP analogue.


P22. FOTOPROTECTORES EN ARMAZONES METALORGÁNICOS

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Las sustancias fotoprotectoras son moléculas que pueden absorber, reflejar o dispersar la radiación UV. Entre los agentes fotoprotectores UV más ampliamente usados en la industria están los derivados de la benzofenona, como por ejemplo la 2-hidroxi-4-metoxi-benzofenona-5-ácido sulfónico, conocida como benzofenona-4.

El uso de las benzofenonas y sus derivados es amplio y transversal a muchas áreas de la industria, por lo cual resulta de gran utilidad mejorar la fotoprotección que proporcionan para hacerlos altamente eficientes de manera de utilizar la mínima concentración eficaz. Además existen evidencias de sus efectos nocivos sobre la biota 1, de manera que se vuelve relevante el diseño de materiales soporte para su inmovilización y reducción de su dispersión en el ambiente.

Los armazones metalorgánicos o MOFs (Metal Organic Framework) son compuestos cristalinos formados por cationes metálicos y ligandos orgánicos que se caracterizan por presentar una alta porosidad y tener una elevada área específica 2, lo cual les otorga una gran capacidad de encapsulamiento de moléculas de interés 3.

En este trabajo se sintetizaron MOFs del tipo ZIF-8 (a partir de Zn2+ y 2-metil imidazol) 4 en ausencia y
presencia de benzofenona-4 y se caracterizaron por espectroscopías UV-visible e infrarroja, difracción de rayos X, y termogravimetría. Se confirmó la formación del MOF en ambos casos y la incorporación de la benzofenona al sistema. A partir de los resultados se plantearon diferentes hipótesis sobre la localización de esta molécula en el MOF. Se proponen diseños experimentales para la comprobación de cada una de ellas.


A NEW Ni(II) COMPLEXES BASED ON L-AMINO ACIDS DERIVED LIGANDS: SYNTHESIS, CHARACTERIZATION AND STUDY OF THE ROLE OF THE SUPRAMOLECULAR STRUCTURE IN THE CARBON DIOXIDE CAPTURE


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Amino acid derivatives can be considered as excellent candidates to act as ligands in the synthesis of coordination compounds due to the presence of the carboxylate and amino groups. Furthermore, the relative position of both functionalities makes them suitable as chelates[1]. Other advantage of metal coordination compounds based on amino acid ligands is related to their use as catalysts because they can be capable of transmitting chiral information during the stereoselective process[2]. Based on these features, we synthesized a new family of chiral compounds obtained from the N-derivatization reaction of L-α-amino acids with the aldehyde piperonal and a subsequent reduction. Then, the reaction of the L-tyrosine (1) and L-phenylalanine (2) derivatives with Ni(II) salts gave place to coloured solids which were assigned as the corresponding coordination compounds. For both molecules and with all the studied salts, the conditions chosen for the synthesis after a careful optimization, were two equivalents of the ligand as sodium salt, and one of the metal ion using methanol as solvent. The results obtained for ligand 1 and different Ni(II) salts (acetate, nitrate, chloride and sulphate), were very similar; in all cases large green-blue single crystals (1Ni-SC). The structure was confirmed by single crystal X-ray diffraction (XRD) experiments performed on 1Ni-SC crystals and for all Ni(II) salts it was observed a trinuclear complex with a carbonate as bridging ligand of three metal ions. The carbonate anion is derived from the CO2 present in the atmosphere and once it is spontaneously absorbed by the reaction mixture, it self-assembles into the trinuclear system. A similar synthetic procedure was followed for ligand 2, but in all cases instead of single crystals, light blue sphere-like crystalline aggregates constructed by nano and micro crystals (2Ni-CA) were obtained. Using other crystallization conditions single crystals (2Ni-SC) were obtained and XRD results showed a mononuclear octahedral Ni(II) complex bearing two molecules of 2 as chelating ligands and two water molecules occupying the remaining sites. The structural results obtained by single crystal XRD studies proved that the key factor to sustain the supramolecular structure responsible for the CO2 uptake in the L-Tyrosine derivative complex, is the OH group of the amino acid bone, which is absent in the L-Phenylalanine analogue.

Keywords: Ni(II) complex, L-α-amino acids, Crystal structure, single crystal X-ray diffraction.

The reaction of amino acids, peptides and proteins with aldoses is of interest for the understanding of a number of phenomena, which have profound relevance in several fields. It is usually studied in food chemistry as the browning reaction (Maillard), either with beneficial or detrimental outcomes. However, under mild conditions it occurs between cell constituents giving rise to aging processes. It is also involved in transport phenomena in biological fluids.

Mechanistically, the reaction takes place between a nucleophile aminoacid and an electrophile (sugar). The first step is the aldose ring opening, which is initiated by the protonation of the ring oxygen and the deprotonation of the anomeric hydroxyl function, respectively. The observed rates of mutarotation depend on the basicity of the ring oxygen and the acidity of the anomeric hydroxyl function. Thus the reaction is submitted to acid-base catalysis (Katchalsky and Sharon, 1953).

Maillard reaction cannot only be understood as amino catalyzed sugar degradation, but it is also highly dependent on general acid/base catalysis (Kaufman et al., 2018). Being such a complex, widespread reaction, understanding the influence of anions on its mechanism is helpful to control the reaction outcome. Thus, the objective of present work was to further investigate how the presence of organic anions influence the reaction acid/base catalysis.

10% β–D-glucose and 1% glycine solutions were prepared in Na2HPO4, NaHCO3, malic acid, tartaric acid and citric acid (frequently present in food, pharmaceutical and biological systems) and also borax and biphtalate in concentration 0.05M. Initial pH was adjusted at pH 7.5 ±0.2 with diluted hydro-chloric acid or diluted sodium hydroxide solutions. Different concentrations of some anions were also tested. These systems were treated at 100°C during 150 minutes and aliquots were taken at different time intervals. pH, absorbance in UV and visible ranges (294 and 420 nm, respectively) and color tristimulus values were measured.

The reactivity order was found to be: tartrate < malate < phthalate < citrate < phosphate < bicarbonate < borax. For the organic anions, a correlation between pKb and reactivity was observed. It was also found that reactivity is highly dependent on anion concentration, the more concentrated the anion, the more reactive the system. It can be concluded that organic anions may retard or accelerate the reaction according to their pKb values, and since concentration plays a role, the influence is not merely catalytic.

Katchalsky, A., Sharon, N. Biochimica et Biophysica Acta 1953, 10:290-301

The enzyme trans-sialidase (TcTs) and mucin-type glycoproteins, which are involved in the infection process. The oligosaccharides in the mucins are O-linked to the protein by a a-GlcNAc unit instead of GalNAc as in...
mammalian mucins. The O-linked oligosaccharides are derived from two cores, Galp(b1®4)-GlcNAc or Galf(b1®4)-GlcNAc which are further branched by Galf or Galp. Sialic acid is transferred from the host to the terminal b-Galp residues in the mucin oligosaccharides via TcTs. We have undertaken the chemical synthesis of these oligosaccharides, in particular those containing Galf in order to correlate their structure with the ability to act as substrates in the TcTs reaction.1,2 Additionally, these synthetic oligosaccharides could be used as tools for elucidating their biological role and for biosynthetic studies. Recently, oligosaccharides containing the motif benzyl β-D-Galp(1-6)-[β-D-Galf(1-4)]-D-GlcNAcα inhibit the binding of T. cruzi epimastigotes to the insect hindgut, a critical step leading to their differentiation into mammal-infective metacyclic forms.3

We here describe the synthesis of the pentasaccharide b-D-Galp(1®3)-b-D-Galp(1®6)-[b-D-Galf(1®2)-b-D-Galf(1®4)]-D-GlcNAc whose alditol was isolated from T. cruzi mucins by reductive b-elimination. Firstly, we performed a [3+2] convergent glycosylation strategy employing a thioglycoside or a trichloroacetimidate derivative as donors for the unit b-D-Galp(1®3)-b-D-Galp. In both cases, the pentasaccharide was successfully obtained, but with moderate overall yield. A sequential strategy was followed in order to improve the yield, using a trisaccharide b-D-Galf(1®2)-b-D-Galf(1®4)-D-GlcNAc as acceptor and a thiogalactopyranoside as donor to give the corresponding tetrasaccharide with excellent yield. Deprotection of the orthogonal Lev group gave a 3-OH free derivative that allowed the introduction of the Galp. The differences of both strategies will be discussed.


P26. PHOTOPHYSICAL PROPERTIES OF A POTENTIAL MALDI MATRIX: 3-HYDROXY-4-NITRO BENZOIC ACID

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Sample preparation for ultraviolet matrix-assisted laser desorption/ionization (UV-MALDI) mass spectrometry is based on dispersing an analyte in a large excess of a matrix (photosensitizer), both in solid state. The solid mixture is irradiated with a laser pulse and vaporized (ablated). Analyte gas ions are formed and then detected by mass spectrometry (MS). The mechanism of ionization during MALDI is still poorly understood and no adequate quantitative model for the complete process exists. The UV-MALDI technique involves both laser ablation and ionization of the matrix/analyte mixture after electronic excitation of the matrix. The knowledge of photophysical properties of UV-MALDI matrices should play a key role in understanding why some matrices lead more abundant post-source decay (decomposition) as well as in source decay of the analyte. Furthermore, it will be helpful in order to choose the proper matrix to optimize UV-MALDI-MS analysis.

Recently, 3-hydroxy-4-nitro benzoic acid was proposed as potential MALDI matrix for polypeptide analysis.1 However, photostability studies of this compound have not been reported in bibliography. In this work, absorption and emission spectra of this compound were studied, as well as the solvent effect and the effect of the presence of an amine (e.g., ethanolamine, triethylamine, butylamine) in the medium. Photostability of the compound in solution, under 366 nm light source, has been studied too.

P27. SYNTHETIC ANTIGENS BASED ON THE GLYCAN STRUCTURE OF MUCINS FROM THE INFECTIVE FORMS OF TRYPANOSOMA CRUZI

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The immunodominant glycotope α-Galp-(1→3)-β-Galp-(1→4)-GlcNAc, also known as α-Gal, expressed in the mucins of the infective trypomastigote stage of Trypanosoma cruzi has been proposed for multiple clinical applications, from xenotransplantation or cancer vaccination to serodiagnosis of Chagas disease. Regarding the latter, however, methodological limitations have precluded its consistent clinical use. It was previously shown that the trisaccharide analogue to α-Gal, with Glc in the reducing end instead of GlcNAc, was as efficient as the natural trisaccharide for recognition of antibodies to α-Gal elicited during T. cruzi infections. We describe here convenient syntheses of α-Galp-(1→3)-β-Galp and α-Galp-(1→3)-β-Galp-(1→4)-Glcp, both functionalized as the 6-aminohexyl glycosides, and their conjugation to BSA. For the synthesis of the trisaccharide a lactose derivative, which already has the β-Galp-(1→4)-β-Glcp motif, was used as starting material. For conjugation, the squarate method was chosen, which allowed the direct derivatization of the lysine amino groups of BSA by the carbohydrate moieties. The synthesized neoglycoconjugates were structurally characterized by biochemical and mass spectrometry studies and antigenically validated by conventional ELISA immunoassays. Both α-Galp-(1→3)-β-Galp-(1→4)-Glcp and α-Galp-(1→3)-β-Galp were specifically recognized by serum samples of T. cruzi-infected patients. Moreover, competition assays allowed us to map the disaccharide α-Galp-(1→3)-β-Galp as the glycotope recognized by anti-α-Gal antibodies, thereby supporting the ‘antigenic mimicry’ between α-Galp-(1→3)-β-Galp-(1→4)-Glcp and the natural α-Gal structure. The α-Galp-(1→3)-β-Galp disaccharide was next conjugated by the squarate method to immunodominant peptides present in T. cruzi recognized antigens. Further immunoassays using unconjugated peptides and 6-aminohexyl α-Galp-(1→3)-β-Galp as controls indicated that it is possible to develop bivalent serological reagents, able to display peptidic- and carbohydrate-based epitopes. Overall, these results indicate that our neo-glycoconjugates provide suitable, cost-effective and much needed tools for the improvement of currently used Chagas disease diagnostic applications.

P28. ZIKA VIRUS PERTURBS MITOCHONDRIAL MORPHODYNAMICS IN HUMAN RETINAL PIGMENT EPITHELIUM CELLS

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Introduction: Zika virus (ZIKV) is a member of the Flaviviridae family mostly transmitted by Aedes aegypti mosquitoes. Currently, there is no specific medicine or vaccine for ZIKV. A number of more serious symptoms have become associated with ZIKV infection. Notably, ocular complications due to ZIKV infection remains a major public health concern because of their ability to cause visual impairment or blindness. Most of the previous studies have shown ZIKV-induced ocular pathology in the posterior segment (i.e., retina) of the eye.

The human retinal pigment epithelium cells (RPE), the supporting tissue of the retina, consists of a monolayer of epithelial cells that contributes to the retinal-blood barrier. The permissiveness of the RPE to viral infections makes it a pertinent tissue to study host-cell interactions Mitochondria form a network distributed through the cell. These are dynamics organelles that constantly change their morphology, length
and movement along cytoskeleton. Fusion and fission are the two key events responsible for the maintenance of a proper number of functional mitochondria. An imbalance between both processes led to many pathophysiological outcomes. Objective: In the present study, we study the mitochondria dynamics and membrane potential (Δφm) in human RPE (ATCC ® CRL-2302 ™) cells infected with ZIKV virus strains from Puerto Rico (ZIKV-PR) or Argentina (ZIKV-AR). Methodology: ARPE-19 cells were infected with both ZIKV strains for 24 hours. Mitotracker Red CMXRos, a red-fluorescent probe that stains mitochondria in live cells and its accumulation is dependent upon membrane potential (Δφm). Results: ZIKV-PR reduced the population of cells with tubular mitochondria (34%; p <0.001) and increased those with fragmented morphology (207%; p <0.001). ZIKV-AR reduced tubular shapes (56%; p <0.001) in favor of the appearance of two morphological types: hyperfusion and fragmentation (37% and 200%, p <0.001, respectively). Both ZIKV strains increased the population of cells with loss of Δφm (p <0.05), an event related to the occurrence of apoptotic cell death. Conclusion: ZIKV interferes with mitochondrial physiology by generating morphology alterations in ARPE-19 cells. We hypothesized that this morphodynamics perturbation in mitochondria could contribute to a favorable replicative environment for ZIKV virus.

P29. IMPACT OF ULTRASONIC AND ENZYMATIC TREATMENT ON ARGENTINE CHITOSAN FOR USE AS A BIOACTIVE VEHICLE

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Chitosan is a biopolymer composed of the union of N-glucosamine and N-acetyl-glucosamine monomers, through β-1-4 type glycosidic bonds. Given its multiple characteristics, it has had extensive research and development in successive years. One of the main reasons is due to its ability to expose its amino groups to low pH (<5.5)(Se-Kwon, 2013). This allows it to form nanoparticles through a process known as ionic gelation, where cross-linking occurs with the polyelectrolyte and counterions. Currently, INTI-Mar del Plata produces chitosan obtained as a by-product of shrimp fishing. It lacks a commercial destination, given its amount of impurities, high molecular weight, and polydispersity. The commercial non-existence of nationally produced chitosan led to the development of the standardization of the biopolymer for its use as a nanometric scale vehicle for various drugs. This material was subjected to further purification in our laboratory, which begins with its 1% (v/v) acetic acid solubilization under stirring. Then it is precipitated with 4N sodium hydroxide. Said precipitate passes to a filtering stage where, through successive washing with double-distilled water, it is possible to eliminate a large part of water-soluble impurities. Finally, it is subjected to drying in an oven at 40 °C until it obtains a homogeneous color and constant weight. After purification, work was done to improve the intrinsic properties of the biopolymer. For this, it was necessary to apply high-intensity ultrasound (HIUS), which thanks to the cavitation that they cause in liquid interfaces, the modification of the rheological properties and even the hydrolysis of various polysaccharides and proteins can be achieved(Camino, Pérez, & Pilosof, 2009). Looking to obtain chitosan with improved functional properties for use in biomedicine from the reduction in molecular weight, and polydispersity. Another route considered is enzymatic hydrolysis. Many researchers have documented chitosan hydrolysis through various enzymes (Se-Kwon & Rajapakse, 2005). The enzymatic modification of chitosan using various enzymes was considered."
IN SITU XAS STUDY OF PR0.6SR0.4COO3-D FOR IT-SOFC CATHODE APPLICATION

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Cobaltites have been studied as cathode materials for solid oxide fuel cell (SOFC) applications. The high working temperature (900-1000ºC) requires expensive materials and reduces the device lifespan. So, there is great interest in developing new materials for intermediate temperatures (500-700ºC, IT-SOFC). In this work, we present a XAS study on Pr0.6Sr0.4CoO3-d PSC nanopowders as their possible cathode application in IT-SOFCs.

PSC was synthesized via the gelification-combustion method using Pr, Sr and Co nitrates and glycine. Nano-PSC was obtained after treatment at 700ºC for 5 h (air). In situ XAS studies were performed in the D04B-XAFS1 beamline at the LNLS, Brazil (Co K- Sr K- Pr L3-edges, 20-700ºC, different pO2). In situ XPD analysis was performed in the LNLS D10B-XPD beamline under the same conditions. Rietveld refinements (Pm3m space group, whole T range) achieved good fits, though slight distortions suggest a possible phase mixture. Crystallite size (30 nm) was calculated using Scherrer’s formula. XANES showed that Pr atoms are in +3 state, independently of T or pO2. Co is highly sensitive to T and pO2, varying the relative content of +2, +3 and +4 states. Even so, the average oxidation state of Co was invariant (+3.2), due to electronic compensation that creates Co2+-Co4+ pairs from Co3+. Co2+ induces lattice expansion and simultaneously Co4+ is small enough for O2- lattice diffusion. For comparison, micro-PSC (D>300 nm) has the same average oxidation state but with invariant Co content, with Co2+ and Co4+ significantly lower than nano-PSC.

This study shows that the electronic compensation plays an important role in the electrochemical properties of PSC. This mechanism explains the enhanced electrochemical performance of nano-PSC used as IT-SOFC cathode, along with higher SSA, due both to the local expansion generated by Co2+ and the smaller of Co4+ size that favors O2- diffusion.


1,3-DIAMINE FORMATION FROM AN INTERRUPTED HOFMANN–LÖFFLER REACTION: IODINE CATALYST TURNOVER THROUGH RITTER-TYPE AMINATION

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An iodine-catalyzed Ritter-type amination of nonactivated C–H bonds is presented enabling the formation of 1,3-α-tertiary diamines. A sulfamidyl radical serves as the promoter in a guided tertiary C–H iodination through an exclusive 1,6-HAT process. The subsequent Ritter reaction furnishes the C–N bond and establishes an unprecedented concept for catalyst turnover in iodine redox catalysis. The general robustness of the methodology, including broad functional group tolerance, was demonstrated for 24 different 1,3-diamine derivatives, which were synthesized in yields of 42%–99%.
P32. STUDY OF THE STABILITY AND STRUCTURE OF MOLECULAR INCLUSION COMPLEXES OF MYRISTIC ACID IN CYCLODEXTRINS

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β-Cyclodextrin (BCD) and 2-hydroxypropyl-β-cyclodextrin (HBCD) are cyclic oligosaccharides capable of encapsulating non-polar bioactive compounds, increasing their aqueous solubility and changing their physicochemical properties.

The objective of this work was to study the encapsulation of myristic acid (MYR) in BCD and HBCD by changing ligand-cyclodextrin (L-CD) molar ratio and stirring time. Inclusion complexes were prepared by coprecipitation and lyophilization. The stability of the complexes was studied storing the samples for 60 days at different relative humidities (RH). Encapsulation and ligand-CD supramolecular interactions were confirmed by a multianalytical approach using differential scanning calorimetry (DSC), scanning electron microscopy (SEM), small angle X-ray scattering (SAXS) and 1H-NMR spectroscopy.

The thermograms of the dried systems confirmed that the MYR was partially encapsulated (40-70%) in both cyclodextrins (CD). The encapsulation was maximized by increasing the CD proportion on the MYR-CD molar ratio and by stirring 7 hours at 25°C. After 60 days of storage at 85-95% RH, a complete encapsulation of the ligand was achieved for 1:3 MYR-BCD molar ratio. This ratio showed also the maximum modifications of the chemical shifts of the H-3 and H-5 protons of the BCD analyzed by the method of continuous variations (Job) in 1H-NMR and by the complete disappearance of the MYR scattering peaks after HBCD complexation in SAXS curves. The presence of MYR modified the water sorption isotherms of BCD and HBCD, being the amount of adsorbed water smaller in the complexes than in both cyclodextrins. The fractal contour dimension of the particles (Df) and the spectral distribution (FFT) were analyzed by the box count method from SEM images, revealing differences in the morphology and surface roughness of all the studied systems. Finally, the presence of MYR decreased the glass transition temperatures of the HBCD at all the HR tested.

The multianalytical approach allowed to conclude that the stoichiometry of the MYR-CD complexes is 1: 3, being their formation of non-covalent nature. MYR inclusion is favored in high humidity environments and involves the displacement of water molecules from the inner cavity of the CD. These data are useful for selecting storage conditions or predicting the shelf life of dehydrated food ingredients or pharmaceutical products formulated with bioactive compounds encapsulated in cyclodextrins.

P33. CASEINGLICOMACROPEPTIDE ALLOWS THE DESIGN OF SMART EMULSIONS UNDERGOING PH-DEPENDENT GELATION.

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Caseinglicomacropeptide (CMP) is a valuable peptide for its bioactive as well as for its technological properties. One of the more relevant properties of this peptide is its ability to self-assemble in solution by decreasing the pH below 4.5, leading to gel formation.

The objective of present work was to evaluate if CMP based oil/water emulsions may undergo a pH-dependent gelation, thus allowing the design of smart gelled emulsions that could protect bioactive compounds during storage and gastric transit. The properties of gelled CMP or CMP/co-emulsifier emulsions (Tween 80 (Tw), lecithin, sodium caseinate, gelatin and Arabic gum) and their effect on in vitro lipolysis were studied. The gelation of emulsions was performed by decreasing pH to 2 and 3 with the addition of 1N HCl, and the gel time was determined. After 24 hours the gelled emulsions were diluted in buffer to pH 6.5 to reverse to the liquid state. The droplet size of the emulsions was determined before and after the reversal of gelation, to evaluate the degree of flocculation or coalescence. Additionally, interfacial studies of CMP and CMP/co-emulsifier were performed to understand the emulsions behaviour.

By lowering the pH, the gelation of CMP emulsion was achieved; however, during the acidification necessary to promote gelation the emulsion partially coalesced. Among the co-emulsifiers studied, Tw proved to be the right co-emulsifier for the formation of stable gelled CMP emulsions. It was determined by DLS that the formation of a complex between CMP and Tw occurred in the bulk that would adsorb at the O/W interface leading to stable emulsions. Tw's molecules would dominate the interfacial behaviour, as determined by the interfacial drop technique. A synergistic interaction between both emulsifiers appears as the basis of this improvement in which Tw would contribute to steric stabilization of oil droplets, hindering the coalescence when decreasing pH.

The presence of Tw did not alter the free fatty acid release from CMP-Tw emulsions during an in vitro gastroduodenal digestion model, showing a high degree of lipolysis, similar to single CMP emulsions, even if Tw dominated the O/W interface. In conclusion, smart stable CMP based emulsions undergoing a reversible pH dependent sol-gel transition could be designed, allowing a high bioavailability.

**P34. HIGH MOLECULAR WEIGHT CHITOSAN AS AN ADDITIVE IN THE CULTURE OF 3T3-L1 FIBROBLASTS. EFFECTS ON CELL PROLIFERATION INDUCED BY PDGF**

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Chitosan is a polysaccharide used in nanotechnological applications due to its biocompatibility, biodegradability and its ability to protect and release drugs in a controlled manner. It is well known its capacity to collaborate in wound regeneration. In the medical field, combining chitosan and growth factors promises to normalize and accelerate the healing of complex wounds. Its physicochemical characteristics, in particular its degree of deacetylation and its molecular weight, are determining factors in the effects observed on biological systems. In this work, we study the effect of high molecular weight chitosan (HMWC) added in mouse fibroblast culture media in two aspects: a) its ability to generate changes in cell cycle and proliferation, b) its ability to enhance the effect of Platelet-Derived Growth Factors (PDGF). For this, a 3T3-L1 line was used which responds variably to recombinant PDGF-AA and PDGF-BB (two isoforms of Platelet-Derived Growth Factor) depending on their receptors, which are present on the cell surface for both types of factors. Viability and cell proliferation was analysed by MTT and Crystal violet assays. We evaluated, by means of immunocytochemistry, the expression of the nuclear protein Ki67, which accumulates only in mitotic cells. We also analysed how serum concentration at culture media may influence the in vitro effect of the chitosan application. The HMWC was absolutely innocuous when evaluating cytotoxicity at concentrations as high as 1000 µg/ml. The results show that HMWC, in the absence of fetal bovine serum, does not produce significant changes either in the proliferation or in the increase of nuclear ki67 protein, but notably enhances the effect of PDGF under those same conditions. However, the addition of serum in the culture media (greater than 2.5%) and 50 µg/ml of HMWC increase the proliferation and viability of fibroblasts significantly. The potentiating effect of HMWC on PDGF (PDGF-BB in particular) was verified at any serum concentration present in the culture media (0.1, 2.5, 5 and 10%) and to a lesser extent on PDGF-AA.
P35. NITRATE REMOVAL FROM WATER BY ADSORPTION ON ACTIVATED CARBONS DEVELOPED FROM PINUS CANARIENSIS CONES

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Pinus canariensis cones were used to prepare activated carbons (ACs) directed for the treatment of water contaminated with nitrate ions. The ACs were developed by chemical activation process applying phosphoric acid as the activating agent. The main physicochemical characteristics and nitrate adsorption capacity were determined and compared with those of a commercial AC sample recommended for anions uptake. Nitrate adsorption capacity was evaluated from determination of the adsorption isotherms and their proper description by the Langmuir model. In order to investigate the feasibility of improving its nitrate adsorption capacity, a thermal post-treatment with saturated urea solution was applied to the prepared activated carbon. The effect of post-treatment on the main chemical and textural characteristics of the AC and on their ability to remove nitrate was studied. It was found that post-treatment with urea led to a pronounced decrease in the surface area of the resulting AC, however significantly improved its nitrate adsorption capacity, even doubling that determined for the commercial sample. Enhanced nitrate adsorption onto the urea-treated AC is consistent with the development of surface basic groups and their higher contents of elemental nitrogen.

P36. EVALUATION OF THE SOLUBILIZATION OF LIPOLYSIS PRODUCTS IN DUODENAL FLUID USING A NOVEL TURBIDIMETRIC METHOD: IMPACT OF THE PRESENCE OF A FOOD EMULSIFIER

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A key step in the rate of duodenal lipolysis is the removal of lipolysis products formed at the oil-water interface that are known to inhibit lipids digestion. One of the main roles of bile salts (BS) in duodenal fluid is to solubilize different lipidic products, but predominantly fatty acids (FA), by forming mixed micelles that function as a transport vehicle to deliver FA to the apical membrane of enterocytes for their absorption. Thus, the evaluation of the capacity of duodenal fluid to solubilise fatty acids may allow to know how to regulate this step and manage emulsion composition to influence intestinal absorption. To this end a turbidimetric method was developed that was further validated by particles size analysis (DLS) and oiling off determinations. Oleic acid was used as a reference FA.

The saturation limit of the simulated duodenal fluid (0.5% wt BS) was evaluated by a steep increase of turbidity upon stepwise addition of oleic acid. At this point particles grew and excess of lipid oiled off. DLS allowed the study of the structural evolution of micelles, vesicles and droplets.

The addition of Tween80 as exogenous surfactant in the range 0.5 – 1.5 % wt, increased the oleic acid content in the aqueous duodenal phase four times. This favorable effect was due the ability to solubilize oleic acid by itself (about half the capacity of BS). Nevertheless, a negative deviation (20 – 30 %) from ideality was observed in BS-Tween80 mixtures. It can be concluded that the presence of this non ionic surfactant could strongly contribute to the removal and transport of FA.

The developed method offers a new possibility for a better understanding of the mechanisms involved in the modulation of the lipolysis that could help to rationally select the emulsifiers or stabilizers to formulate emulsions with a controlled FA uptake.
Heavy metals are common contaminants in water. These metals come from effluents from mining, metal plating (electroplating) and electronics, among others. Pollution of water sources by heavy metals represents a serious environmental problem due to their toxicity, persistence and bioaccumulation. For this reason, it is necessary to obtain information about the concentration of heavy metals in various matrices, and furthermore, to design removal processes in industrial process waters, to ensure the conditions in which they reach the environment. It is essential that the construction of the systems for this purpose has a low environmental impact.

In this work aluminum meshes are used as support, which are functionalized from cellulose acetate coatings containing magnetite@cellulose nanoparticles1. On the other hand, copper has been chosen as a cation model system because of its relevance in the electronics and electroplating industry.

Several studies suggest that many of the nanostructured metal oxides (OMNs), including nanometric ferric oxides, exhibit a very favorable adsorption of heavy metals in terms of high capacity and selectivity2,3. The size, shape and functionalization of OMNs are important factors in their adsorption performance. Aluminum meshes have been modified in different proportions (10: 2.5 and 5: 0.5)4 with cellulose acetate (30,000Da and 50,000Da) and magnetite nanoparticles, with and without cellulose coating. The resulting surfaces have been characterized by FTIR, SEM and DRX and their electrochemical behavior was analyzed. The results suggest that the interaction between copper and surface is dependent on the OMNS environment since higher cathodic currents are obtained for the system in which the nanoparticles are functionalized with cellulose. There is also an increase in the signal with a higher proportion of nanoparticles and a better reproducibility when using the polymer with the higher molecular weight. This system is a promising platform oriented to determination of metals in situ, heavy metal removal systems and treatment of industrial effluents.

Agradecimientos: OPCW, CONICET, UBA; ANPCyT, ADIMRA"
Dos ejemplos de estos sistemas son los geles supramoleculares [3] y los mesocristales, sistemas estructurados en la mesoescala. [4] Tanto el desarrollo de una red supramolecular que puede inmovilizar solvente, como el auto-ensamblado de los bloques de construcción, son vías de interacción gobernadas por la presencia de interacciones no covalentes. Por lo tanto, existe un delicado balance de factores que determinan el comportamiento tanto como agente gelante o como bloque de construcción de un cristal. En ambos casos, la química supramolecular impacta directamente en las propiedades resultantes, permitiendo controlar las características obtenidas. Los aminoácidos son excelentes candidatos para el desarrollo de nuevos materiales ecológicos de bajo costo gracias a su diversa química supramolecular, su inherente carácter quiral y su basta biodisponibilidad. Además, la presencia de los grupos funcionales amino y ácido proporciona una gran variedad de reacciones de derivatización que permiten controlar aún más sus interacciones no covalentes.

En este trabajo analizamos los factores físico-químicos implicados en la obtención de diferentes estructuras autoensambladas, como son los mesocristales y geles, obtenidas a partir de una nueva familia de pequeñas moléculas quirales basadas en los aminoácidos L-Tirosina y L-Fenilalanina. Las estructuras supramoleculares resultantes y sus propiedades fisicoquímicas fueron estudiadas empleando diferentes técnicas espectroscópicas, difracción de rayos X (DRX), microscopía de luz polarizada (POM) y microscopía electrónica de barrido (SEM). Los resultados demuestran que estos nuevos compuestos son excelentes unidades de ensamblado tanto para la formación de geles supramoleculares como para la obtención de material cristalino, donde las características del material resultante pueden ser moduladas en función de las interacciones intermoleculares dadas por los grupos funcionales presentes y las condiciones experimentales empleadas.

were evaluated by the MTT assay, which allows to determine the mitochondrial functionality of the treated cells. Caco-2 cells were seeded at a density 2.104/well in 96 well cell culture plates and pre-incubated for 24 hours (Kowapradit et al., 2010). The cells were then treated with high and low molecular (control) weight CS (50-1000 ug/ml), FA (0.05-1.5 ug/ml) and both types of matrices containing CS (250 ug/ml) with variable ratio of FA (0.05-1.5 ug / ml) in 2% FBS medium for 24 h. The results indicated that Caco-2 cells significantly increase their proliferation respect to the control when were incubated with the FA-CS treatments. These formulated matrices could be functional ingredients for FA, protecting the vitamin against light and oxygen, and favouring its bioavailability when ingested.

P40. ADSORPTION GEOMETRY OF MONO AND TETRA PHOSPHONIC ACID FUNCTIONALIZED PORPHYRIN MOLECULES ON TiO2 (110) SURFACES

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Abstract: Solar energy technologies including dye-sensitized solar cells and water-splitting photoelectrochemical cells are constructed linking chromophores to semiconductor surfaces. Promising systems are based on porphyrins bonded to TiO2 surfaces. One of the critical factors affecting device performance is the molecular adsorption geometry [1,2]. Therefore, fundamental research studying the interaction of porphyrins with TiO2 surfaces is important. Here, we studied the bonding and adsorption geometry of tetraphenyl porphyrin molecules containing one or four phosphonate groups. The investigation was carried out by means of synchrotron radiation X-ray photoelectron spectroscopy (XPS) and near edge X-ray absorption fine structure (NEXAFS) measurements. Our results show that the number of linker groups have a great influence on the adsorption geometry. Molecules with one phosphonate group adsorb with the macrocycle tilted away from the surface whereas molecules with four phosphonate groups adsorb with the macrocycle close to the surface. This is an important finding for the design of dye-sensitized solar and photoelectrochemical cells [3].


P41. RE-ABSORPTION OF CHLOROPHYLL FLUORESCENCE IN CANOPIES: A REVISED APPROACH

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Chlorophyll fluorescence is widely used as an indicator of photosynthesis and physiological state of plants. Remote acquisition of fluorescence allows the diagnosis of large field extensions, even from satellite measurements, becoming increasingly important in relation to the monitoring of plant health and Carbon Budget on the planet [1]. Nevertheless, fluorescence emerging from chloroplasts, the one directly connected to plant physiology, undergoes re-absorption processes both inside the leaf and the canopy [2]. Therefore, to draw accurate inferences about plant health, it is necessary to correct the observed canopy fluorescence taking into account these two re-absorption processes. Here we show the theoretical refinement and experimental validation of a biophysical model we developed in 2018 [3], which allows retrieving leaf fluorescence from that at top of canopy (TOC) using a correction factor which is a function of canopy and soil reflectance and canopy transmittance. We validate this model in three types of crops of agronomic interest (Pea, Rye grass and Maize) with different architecture. Our model accurately predicts leaf fluorescence spectral distribution from that measured at canopy level and also the fluorescence ratio. Furthermore, we not only eliminate artifacts affecting the spectral distribution of the emission, but we are able to calculate the quantum yield of fluorescence at leaf level from the experimental quantum yield at the canopy level. This represents an advance in the study of these systems because it allows correcting by light re-absorption, not only the fluorescence ratio but also the intensity of the observed fluorescence.


P42. INTERACTIONS BETWEEN EMULSIFIERS AND GLUTEN PROTEINS: EFFECT ON DOUGH OVERRUN AND MECHANICAL CHARACTERISTICS

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The unique viscoelastic properties of gluten proteins are the result of their hydration, unfolding, orientation and complex interchange between sulfhydryl (S-H) and disulfide (S-S) bonds. Emulsifiers with different chemical structures can be employed to improve dough performance and bakery products characteristics. The aim of this study was to evaluate the effect of different emulsifiers on gluten dough overrun and mechanical characteristics. Gluten (41% w/w) and baking powder (5% w/w) were mixed with distilled water and kneaded homogeneously with a glass rod by hand for 1 min. Four emulsifiers were tested: DATEM (diacetyl tartaric esters of monoglyceride), SSL (sodium stearoyl lactylate), Soy lecithin and Tween80. Samples containing 1% w/w emulsifiers was prepared through replacing the same content of gluten powder with the selected emulsifier and mixing well before adding distilled water into the matrix. In order to closely follow expansion and collapse of foams, samples were constituted in 100 mL graduated cylinders and kept in a water bath at 40°C during the experiment. Foam expansion was recorded during 110 min, obtaining maximum expansion at 30 min. Dough mechanical properties were tested by performing a texture profile analysis (TPA) at 25°C in a Texture Analyzer (TAXT2i Stable Microsystems) using a compression plate probe (P7/75). The overrun for pure gluten was 112% at 30 min. The addition of lecithin and Tween80 improved the foaming capacity since they showed overruns of 143%. Also, gas retention at longer times was higher in these systems. On the contrary, SSL and DATEM presented lower overruns: 93% and 99%, respectively. Texture analysis showed that dough hardness decreased (97-121 N) in those samples containing emulsifiers as compared with pure gluten (157 N). Similar results were obtained for adhesiveness and chewiness. Thus, emulsifiers increased dough softness and volume due to the ability of these molecules to interact with gluten proteins in the bulk of the viscoelastic liquid phase and also by modulating the air-water interface.
P43. SURFACE CHARACTERIZATION OF THE INTERACTION OF CU(II) WITH CARBOXYLIC AND ALCOHOL TERMINATED SAMS

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One way to achieve surfaces with controlled and adjustable properties is to modify them with well-defined molecular films. In particular, the self-assembly of thiols on gold is a method that provides a convenient and simple way to create a thin and very ordered molecular film with adapted chemical and electrical properties. On the other hand, heavy metal ions are common pollutants in water and can cause severe health damage. They are not biodegradable and can be bioaccumulated.1

In this work, the affinity of the copper (II) ion to self-assembled monolayers on bifunctional thiol on gold was studied. The thiols chosen exposed hydroxyl and carboxylic acid groups. Infrared spectroscopy of absorption reflection with Polarization modulation and X-ray photoelectronic spectroscopy was used to the physicochemical characterization of the structure and the structure-function relationship of the modified surfaces. And also their interaction with the Cu2+ ion and the influence of the alkyl chain length. PM-IRRAS gave information about the functional groups present on the surface, their environment, and how they were modified with the presence of the copper ion. Additionally, XPS provided information on the presence of copper in all tested monolayers and on the elementary relationships between S: Cu at each step of the treatment.

Results showed that all of the SAMs retained similar amounts of copper and that for short chain thiols, the copper was electrically connected to the electrode. Furthermore, upon interaction with the copper solution, most of the carboxylic acid moieties deprotonated, forming a complex with the copper cation.

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P44. LUMINESCENT MATERIALS AS SPECTRAL CONVERTERS : POWER DEPENDENT PROFILING OF SOLID NAYF4:YB3+,ER3+ UCNP AS HIGHLY EFFICIENT NIR TO UVA-BLUE EMISSION

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Upconversion (UC) refers to nonlinear optical processes in which the sequential absorption of two or more NIR photons leads to the emission of light at shorter wavelength than the excitation wavelength (NUV-Vis). The well known lanthanides based upconversion nanoparticles (UCNP) are capable to undergo such luminescent mechanisms.

From an energetic standpoint, one can take advantage from the UC photophysics to reduce the transmission losses of transmitted low-energy photons from the solar spectrum to higher-energy photons, which can then be utilized by a semiconductor in a the solar cell [2]. Conversion of low-energy photons into high-energy photons increases for example the efficiency of photovoltaic devices by converting photons with energies below a given absorption threshold into photons that can be utilized. In fact, UCNP are included as spectral converters when incorporated as upconverting layers into the solar cell increasing the short circuit current density from 16 to 17 mA cm2 [2].

The emission spectrum of the UCNP is frequently tuned by changing the composition of the material.
However, a commonly overlooked aspect is the non-linear power dependence which can influence the spectral and temporal properties of the emission. In this work, we show that under NIR (980 nm) excitation, solid NaYF4:Yb3+,Er3+ upconversion nanoparticles, well known for the green and red emission, can also emit efficiently in the UVA-blue range. We characterized their stationary and dynamic luminescence features as a function of incident power to reveal the relevant intra-band mechanisms. Our results support that the red emission at high incident power is explained by back-energy transfer. Finally, by simultaneously acquiring time resolved decays and power dependent emission slopes, we classified the spectral information to build a visual summary or fingerprint of the system as a whole.

P45. REACTIVITY OF POLYSULFIDES TOWARDS METMYOGLOBIN

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Hydrogen polysulfides, H2Sn (n>1), are gaining growing interest because some of the physiological roles formerly attributed to endogenous hydrogen sulfide, H2S, are better described as a consequence of their action.1,2 Particularly, H2Sn with n=2,3 have been demonstrated to be products of the 3-mercaptopyruvate sulfurtransferase.1,3 an enzyme of the H2S biosynthesis. Recent studies on polysulfides speciation in aqueous solution reveal that interconversion occurs, resulting on equilibria that depend on the experimental conditions.4 Also, the currently used chemicals for derivatization may cleave polysulfide chains, and hence the reliable analysis of polysulfide mixtures still represents an analytical challenge in the field. As a consequence of our studies on the reactivity of Na2S and metmyoglobin (FeIIIMb),5 we present herein a study of the kinetics of the interaction of synthetic disodium disulfane, Na2S2, with FeIIIMb at neutral pH, and the strategy to analyze the polysulfide contents of the dissolved Na2S2 preparation.

We prepared Na2S2 by the comproportionation of an equimolar mixture of disodium sulfide, Na2S, and sulfur, S8, according to described procedure.6 Although the product matches the UV-vis aqueous spectrum of a commercial vendor, the dissolution in organic solvents aided by cryptands revealed the formation of the blue trisulfide radical anion, S3.-. Derivatization of polysulfide chains of different lengths with benzyl chloride may provide the product composition in solution. Upon reaction with FeIIIMb 8 x 10-6 M, in the presence of aqueous Na2S2 (R disulfane/ Mb = 10, 20, 30; pH 6.8, anaerobic, 25ºC) the reduced hemeprotein, FeIIMb, was formed, following an exponential growth. The reaction is relevant to the understanding of the sulfide-mediated detoxification by hemeproteins,7 and to the metal centered reduction of ferric hemeproteins.

P46. LIFE-TIME STUDY FOR DERIVATIVES OF PHTHALOCYANINES VEHICULIZED IN UNILAMELLAR VESICLES OF PHOSPHATIDYLCHOLINE (UVPC) THROUGH THE LASER FLASH PHOTOLYSIS TECHNIQUE

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Phthalocyanine molecules are widely used in photodynamic therapy (PDT); however, they are highly insoluble in water [1]. It is interesting to study the associations between Zn phthalocyanine derivatives and liposomes of soybean L-α-phosphatidylcholine [2], since this would improve the efficiency of singlet oxygen quantum yield of these photosensitizers due to their aggregation in aqueous media [4]. Therefore, it is important to study variations in the properties of the proposed chromophore 2-(N, N, N-trimethylammonium) ethylthio (PC2) when incorporated into UVPC. With the purpose of detecting them, photophysical techniques such as UV-Vis spectrometry, fluorescence and laser flash photolysis were employed. Liposomes (UVPC) were characterized by the TEM, SEM and DLS techniques. The surface charge was determined by Z potential measurements.

The UV-Vis spectra showed hypsochromic shifts of the Q-band of PC2 (2X10-6M) when an organic medium as DMF was changed to a water-buffered medium at pH 7; in the latter condition, the presence of liposomes did not exhibit this shift, which only revealed the aggregation of PC2. Fluorescence measurements seemed to indicate the same result. With this, none of the techniques was able to demonstrate a possible association between PC2 and UVPC. However, laser flash photolysis studies [3] indicated the existence of a PC2-UVPC association at pH 7. The triplet excited state of phthalocyanine was detected in aqueous solutions of PC2, both in the presence and in the absence of liposomes. However, the life time of this intermediate was longer in UVPC (50 μs and 22 μs respectively).

Taking all the results obtained into account, the PC2 molecule, which has protonated amino groups and voluminous iodine counter ions, must be added in an aggregated form on the outer face (polar part) of the liposome. This way, the environment will be very hydrophilic but harder than in water, which would explain the increase in PC2 lifetime. By increasing the medium pH up to 12, two types of associations between PC2-UVPC can be observed, as there are mixtures of two life times for the PC2 triplet (one of 80 μs and another one much longer than 800 μs), band shifts in the UV-Visible from 660 nm to 703 nm, and an increase in fluorescence. The laser flash photolysis technique provides relevant information regarding phthalocyanine-liposome associations.


P47. VEHICULIZATION OF ATRAZINE IN NANOPARTICULATE SYSTEMS FOR AGRICULTURAL APPLICATIONS

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Agriculture is vitally important worldwide as a primary provider of food, as well as one of the main engines of the economy of many countries. The use of agrochemicals occupies a key role in the maximization of...
agricultural production against innumerable challenges like weeds, phytopathogens, herbivory and abiotic stress. However, its indiscriminate use can contribute to environmental pollution, putting non-target organisms at risk. Nanoherbicides possess advantages over traditional commercial formulations since they slow down the release of the herbicide (minimizes losses and therefore contamination), maintain or even increase the activity of the herbicide against weeds while being less toxic to non-target organisms. Polymer nanoparticles could be suitable as nanotransporters of agrochemicals given their biocompatibility, biodegradability and low toxicity. The use of these guarantees a more efficient interaction of the molecule under study with the species of interest.

The principal objective of this work was to design, synthesize and characterize a nanoherbicide containing atrazine to prove their effectiveness in agricultural use. Nanoherbicide (NH) consists of atrazine active ingredient included in chitosan polymeric nanoparticles (NPs). The agricultural application effectiveness was proving through a bioassay with plants. Maize (non-target) and chicory plants (target) were sprayed with 1 ml of the corresponding solution (NPs or NH). A modulated fluorometer (PAR-FluorPen FP 100-MAX-LM) was utilized to measure the variable chlorophyll fluorescence (OJIP test) of the treated leaves in vivo at 24, 48 and 72 hours after applying the treatments.

Several parameters, which provide information about health of plants, were calculated from the OJIP test: Fm/F0, Fv/F0, ABS/RC, TR0/RC, ET0/RC, Dl0/RC, among others. Chitosan NPs resulted innocuous for both type of plants, while the NH produced noxious effects only on chicory. Most of the parameters analyzed presented statistically significant differences in chicory, pointing out deleterious effects of NH on the target specie. In the case of maize, no significant differences were observed between plants treated with NPs and NH. The results of this work could confirm that the methodology used for the preparation of NPs and atrazine NH was adequate, SEM images confirmed this result.


P48. REDOX BEHAVIOUR OF {MNO}8 OF IRON AND RUTHENIUM

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The study of nitrosyl compounds is interesting because the NO ligand has three redox states: NO+, NO- and NO•, so using that ligand as an active redox ligand, it is possible to increase the oxidation state changes in a complex. The use of redox “innocent” ligands as reservoirs of electrons is an interesting approach for bond-making and bond breaking reactions at coordinatively unsaturated metals. In addition, paramagnetic nitrosyl complexes have been shown to be efficient for the activation of C-X bonds [1],[2]. Nitrosyl complexes are described by the Enemark-Feltham notation as \{(MNO)\}n [3]. In this work, complexes \{(FeNO)\}8 and \{(RuNO)\}8 were prepared, in order to obtain the \{(MNO)\}9 forms through their respective reductions.

On one hand, the complex \{[Fe(CO)2NO(PPh3)2]+\} was prepared. [4]

\([Fe(CO)3(PPh3)2]+NOBF4 \rightarrow [Fe(CO)2(NO)(PPh3)2][BF4] + CO\)

Complex 1 was characterized by 31P-NMR, 1H-NMR, FTIR and X-ray diffraction, obtaining a structure that is not reported. In addition, its redox behavior was studied by cyclic voltammetry, from which it was concluded
that the reduction is irreversible.
When performing the reduction with cobaltocene, the mixture of three diamagnetic complexes was obtained, and not the desired paramagnetic complex \{FeNO\}_9.
On the other hand, the synthesis of the complex \([\text{Ru(NO)}(\text{PPh}_3)_2\text{Cl}]\) was carried out by an alternative route to that reported [5].

\[
[\text{Ru(NO)}\text{Cl}_3(\text{PPh}_3)_2]+2\text{Co(Cp)}_2\longrightarrow[\text{Ru(NO)}(\text{PPh}_3)_2\text{Cl}] (2)
\]
Complex 2 was characterized by 31P-NMR and FTIR. Also, an attempt was made to characterize it by DRX, however, the structure \([\text{Ru(PPh}_3)_2\text{Cl}_2]\) was obtained, probably due to decomposition of 2 during the crystallization process. In turn, its redox behavior was studied by cyclic voltammetry, from which it was concluded that the reduction is irreversible. Its reduction was accomplished with \text{Co(Cp)}^+_2, which is a stronger reductant than cobaltocene and the product was characterized by 31P-NMR, 1H-NMR and FTIR. The information obtained would indicate that a paramagnetic complex \{RuNO\}_9 was obtained, however, studies are still being carried out to establish the identity of the product.


**P49. OXIDATIVE ADDITION OF AN ARYL HALIDE TO A RH(I) COMPLEX WITH A PCP PINCER LIGAND**

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Organometallic catalysts have enabled simple preparation routes for obtaining a great variety of organic compounds, which are used in different areas, such as health, technology, energy, agriculture, etc. The rupture of carbon-halogen (C-X) bonds is frequently a key step in the catalytic formation of C-C bonds. Most catalytic cycles consist in a series of elemental steps where several electrons (typically, two) are exchanged between a metallic center and its ligands, with oxidative additions (OA) and reductive eliminations being the most representative processes of this kind.

In this work, we have studied the oxidative addition reaction of an aryl halide (2-fluoroiodobenzene) with a Rh(I) complex with a pincer-type ligand: Rh(PCPt-Bu2) [1], with PCPt-Bu2 (PCP) being 1,3-bis(di-t-butylphosphinomethyl)benzene. Complex [1] was obtained by the reaction between Rh(PCP)(H)(Cl) [0] and the strong base KHMDS in an Ar atmosphere. In a N2 atmosphere, the resulting product was found to be Rh(PCP)(N2). Reduction of [0] in the presence of an aryl halide substrate led to formation of an Rh(I) intermediate which coordinates the substrate(Rh(PCN)(PhX) [2]), which slowly reacts by oxidative addition to yield a Rh(II) complex of the halide, Rh(PCN)(X) [3], as was detected by 1H NMR. The aryl radical that results from this reaction then reacts with a benzene molecule from the solvent, and the H• radical resulting from this reaction coordinates complex [3] to form Rh(PCN)(H)(X) [4]. This reactivity is unusual for Rh(I) complexes, where the normal product of OA would be the Rh(III) with both the aryl and the halide as ligands. Moreover, the coupling product that results from the aryl radical and the solvent is also relevant for organic synthesis. By adding excess substrate and base, this reactivity gives place to a catalytic cycle, where complex [4] is again reduced and reacts with excess substrate. Some preliminary studies of this cycle have been performed.
P50. STUDY OF THE REACTION BETWEEN NITRIC OXIDE AND DITHIONITE

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Sodium dithionite is the most widely used reducing agent for inorganic complexes, bioinorganic compounds and certain organic species. In most cases, the main reducing agent is the SO2- radical, which arises from the dissociation of S2O4-2. The strong reducing potential of this compound makes it very air sensitive and unstable, particularly in solution; therefore, it must be strictly manipulated in oxygen-free conditions. The principal impurity is the sulfite ion (SO3-2), which is known to react with nitric oxide giving N-nitrosohydroxylamine-N-sulfonate (NHAS), evidenced by a characteristic UV absorption band at 260nm [1]. For these reasons, commercially available sodium dithionite must be purified by recrystallization before employing it in the study of this reaction.

Evidence of the reactivity between dithionite and nitric oxide (NO) has been found during enzyme-reducing studies [2]. The kinetics of this reaction have even been followed spectrophotometrically [3], although the mechanism remains unknown. In this work, we study the reaction mechanism between dithionite and NO using UV-vis spectrophotometry, following the dithionite absorbance traces (ε315nm = 8000 M-1 cm-1), IR spectroscopy, EPR and ionic chromatography for nitrite quantification. Our results show that the studied reaction is first-order in dithionite and zero order in NO when an impure dithionite sample is used. Surprisingly, this reactivity decreases when purified dithionite was used instead.

Dithionite (impure) + NO -> Reaction
Dithionite (pure) + NO -> slow reaction

Measured EPR (electron paramagnetic resonance) spectra indicated the formation of a radical species during the experiment, which we attribute to the reaction between sulfite and NO. Accordingly, we propose that the sulfite ion traces present in the impure solid initiate the reaction with NO giving an intermediate that reacts subsequently with dithionite. The final nitrogen product is N2O, as evidenced by IR measurements.

P51. MESOPOROUS TiO2 THIN FILMS AS ANODES FOR PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION

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The need to supply the population’s high energy demands without increasing the risks of climate change make the search for cleaner energies one of the main challenges for the 21st century. Chemical fuels constitute a key energy vector in the global scheme, since it allows the energy to be easily stored and ready to use. Therefore, the production of a green and renewable fuel would be a significant advance.

Given that sunlight is the largest energy source in the world, the development of sustainable materials capable of capturing and transforming solar energy has become of great interest. One type of such materials are semiconductors, which have demonstrated their ability to split water into O2 and H2 [1], the latter being a valuable fuel, due to its high energy density and clean combustion. Titanium dioxide (TiO2) is a stable, nontoxic and abundant semiconductor, which has a suitable band gap to conduct this reaction [2].

Nanocomposites can be assembled by combination of different components, which can improve the overall properties. These nanomaterials are a starting point towards the design of integrated systems for solar fuels production.

In this work we present the synthesis of thin mesoporous TiO2 films prepared via a sol-gel approach. These films can be easily modified, which makes them an ideal support for the formation of nanocomposites. We varied the film’s thickness in order to optimize light absorption. We then modified the films with cobalt phosphate (CoPi), which is a water oxidation catalyst [3], and we studied the efficiency of the composite photoelectrodes.

The materials were characterized by means of photoelectrochemical techniques (voltammetry, chronoamperometry, impedance spectroscopy), scanning electron microscopy, X-ray diffraction and reflectometry, and UV-visible spectroscopy.

The films have proven to be highly porous and crystalline (anatase). We have found that increasing the film thickness gives rise to higher photocurrents, indicating thicker films improve light absorption, while keeping the high pore accessibility and good electrical connections. In terms of the catalyst, we have seen that the presence of CoPi is only beneficial at high overpotentials (over 400 mV).