Bichromophoric systems: Design variables and applications

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Functional bichromophoric compounds are designed to operate through the interplay of different light-interacting units joined covalently in the same molecule. These systems are being considered for applications that include single molecule localization microscopy and intracellular polarity sensing. The present contribution includes the design, synthesis, and characterization of bichromophoric compounds for two-photon photochemical control of molecular release and group deprotection. Specifically, we have recently demonstrated a new biphotonic scheme for photo-release control which produces a spatial localization of a chemical specie within a volume the order of a femtoliter. The systems consist of a non-linear optical absorbing section bonded to a second chromophoric moiety which undergoes dissociation after indirect excitation through energy transfer. The antenna section consists of a cyanine type dye, and the releasable section consists of a derivatized anthracenic chromophore, bonded to the cyanine through an etheric-meso-carbon bond. The long-lived upper excited states of the two-photon absorbing antenna chromophore are involved in the photorelease process.

Discovery and characterisation of novel glycoenzymes for glycoside synthesis and antigen removal using metagenomic screens

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Gaining access to enzymes that are able to degrade or synthesise specific glycosides, especially those containing modified sugars, can be very challenging. Mother Nature has already supplied an enormous diversity of biocatalysts, each of which could serve as a starting point for directed evolution studies. The problem can be in accessing this diversity in a reasonably efficient manner. Here I shall describe two ways in which we have approached this problem. One of these is through synthesis of libraries of genes from within
promising glycoside hydrolase families, selected to represent phylogenetically distinct sub-families of genes. In the other approach we have used activity-based, or functional metagenomics to generate a library of over 600 expressed glycosidases. These libraries have been subjected to “first-pass” high-throughput characterisation for substrate specificity, thermal stability, pH profile and mechanism. This sub-library has then been screened to identify preferred catalysts for cleavage of specific unnaturally modified sugars (e.g. azido sugars). Once candidate enzymes are identified they are then mutated to “glycosynthase” versions that can be used to “tag” glycans. In parallel we have screened the human gut metagenomic libraries for enzymes that can be used to remove the Gal or GalNAc residues that function as the antigenic determinants from A and B type red blood cells, thereby generating “universal” O type blood. Such libraries can also be used to select the optimal candidate for further improvements through directed evolution. High-throughput screening of metagenomic libraries for glycoside phosphorylases will also be discussed.
Carbamoylimidazoles as novel cruzain inhibitors having in vitro and in vivo activity against Trypanosoma cruzi

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Chagas disease is one of the main causes of heart failure and morbidity in Latin America. Chemotherapy for this neglected tropical disease features several limitations, among which poor efficacy and high toxicity are the major drawbacks. Drug discovery in Chagas disease has relied on selected Trypanosoma cruzi enzymes, among which cruzain is a chemically and genetically validated pharmacological target. Herein, a structure-based virtual screening (SBVS) is reported, which resulted in the discovery of a potent noncovalent cruzain inhibitor (K_i = 100 nM) having in vitro activity against T. cruzi. This compound provided a suitable starting point for molecular optimization efforts, which led to the design of a series of carbamoylimidazole derivatives as novel cruzain inhibitors. Among this series, a substituted imidazole demonstrated to be a potent cruzain inhibitor (K_i = 20 nM) featuring in vitro activity against whole cell parasites (IC_{50} = 7.5 µM). Additionally, these compounds showed promising ability to reduce parasite burden in mouse models of Chagas disease and no toxicity at 100 mg/kg. In view of the current paucity of novel, potent and reversible cruzain inhibitors, the carbamoylimidazole derivatives reported herein consist of promising lead compounds to be explored as drug candidates for Chagas disease therapy.

ABCChem 4

Withdrawn

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Exploration of molecular recognition processes

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Docking (posing) calculations coupled with binding free energy estimates (scoring) are a mainstay of structure-based drug design. Docking and scoring methods have steadily improved over the years, but remain challenging because of the extensive sampling that is required, the need for accurate scoring functions and challenges encountered in accurately estimating entropy effects. To address these issues we have been developing a number of novel strategies in our laboratory. In particular, in this presentation, we will describe the Movable Type sampling (MTS) method developed in our laboratory that estimates binding free energies, entropies and enthalpies. The utility of MTS will be explored through a series of examples that involve rigid or flexible (See Scheme 1) protein-ligand docking, protein-protein docking and entropy estimation. We will show that MTS allows us to compute thermodynamic quantities associated with myriad biological processes rapidly, accurately and yields structural information at a minimal computational cost relative to currently available methods.

**ABCChem 6**

**Neurotransmitter sensing via aptamer-field-effect transistors**

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Measurements of neurochemicals in the extracellular space are limited by combinations of poor chemical, spatial, and temporal resolution. Brain chemistries, therefore, are unable to be investigated dynamically, particularly at the level of neural circuits and across numerous signaling molecules. To understand neural signaling at scales pertinent to encoded information, micro-to nanoscale sensors are needed for multiplexed, highly selective readouts of extracellular neurotransmitter concentrations with sub-second response times. We have designed, developed, and tested sensors that are approaching these critical attributes. Neurotransmitter recognition is by oligonucleotide receptors (aptamers) linked to field-effect transistor (FET) arrays for electronic transduction of reversible binding events via conductance changes. For example, using aptamer-FETs, we have selectively detected serotonin and dopamine over five orders of magnitude with fM detection limits in artificial cerebrospinal fluid. Serotonin was measured in brain tissue at physiological concentrations. Currently, we are investigating and tuning temporal resolution of aptamer-
functionalized FETs using microfluidics. We are investigating the impact of different surfaces chemistries on sensitivity and biofouling. We are also lithographically fabricating FETs on silicon microprobes for in vivo testing. Beyond serotonin and dopamine, we are developing sensors for a broad array of monoamine, amino acid, and peptide neurotransmitters.

**ABCChem 7**

**One-pot synthesis of pyrrolo[3,4-b]pyridin-5-ones by MCR: Diversity oriented synthesis approach**

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The rapid generation of molecular complexity and diversity from simple and readily accessible starting materials is a contemporary research theme in the practice of modern organic synthesis. The combination of a multicomponent reaction with an efficient post-transformation, typically a ring-forming process, has been proven to be a powerful tool for the synthesis of highly functionalized heterocyclic compounds. A variety of reactions including condensation, ring-closure metathesis, cycloaddition, macrolactonization, intramolecular SNAr reaction, etc. have been combined with an isonitrile based multicomponent reaction (I-MCR) for the construction of cyclic scaffolds. This presentation will summarize some of our recent contributions in this area. Several strategies with a great atomic economy to the synthesis of highly functionalized polyheterocyclic compounds will be discussed.

**ABCChem 8**

**Selective hydrofunctionalization of alkynes promoted by rhodium-N-heterocyclic carbene catalysts**

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The homogeneous catalytic activity of a set of rhodium complexes with N-heterocyclic carbene (NHC) ligands in two specific atom-economy reactions, alkyne hydrothiolation and alkyne hydrophosphination, has been studied. The high steric hindrance and powerful electron-donor capacity of the bulky NHC
used, along with ancillary donor ligands, seems to be determinant to get selective transformations and to facilitate valuable information about the mechanism of the mentioned reactions. Following our studies on rhodium(III)-NHC derivatives, we report now on our recent studies on the catalytic activity of a set of rhodium complexes with N-heterocyclic carbene (NHC) ligands on alkyne hydrothiolation. Rhodium(I) compounds of formula \([\text{Rh(μ-X)(IPr)(η}^2\text{-olefin)}]_2 \ (X = \text{Cl, OH}), \text{RhCl(IPr)(py)(η}^2\text{-olefin)} \) and \(\text{Rh(oq)(IPr)(η}^2\text{-olefin)} \) (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-carbene, py = pyridine, oq = quinolinolinate) are very active catalysts for alkyne hydrothiolation under mild conditions, presenting high selectivity towards α-vinyl sulphides. Several intermediates relevant for the catalytic process have been detected. Most of the studied rhodium carbene catalysts have in common a mechanism that proceed via oxidative addition of the S-H bond to rhodium(I) intermediates and successive alkyne insertion into the Rh-S, or Rh-H, bond followed by reductive elimination steps. In particular the \([\text{Rh(μ-Cl)(IPr)(η}^2\text{-cyclooctene)}]_2 \) complex has resulted to be an efficient catalyst precursor for the addition of diphenylphosphine to terminal alkynes. Interestingly this complex is able to catalyze the regioselective double hydrophosphination of a wide range of terminal aromatic or aliphatic alkynes including substrates containing heteroatoms or a sensitive moiety as cyclopropane. The distinctive stereoelectronic properties of the NHC ligand prevent the catalyst poisoning by diphosphine coordination thereby allowing for the closing of a productive catalytic cycle. The process seems to be initiated by ligand exchange between diphenylphosphine and cyclooctene and cleavage of the chlorido bridges to give a mononuclear phosphine complex, followed by oxidative addition of the P-H bond to generate terminal phosphido Rh(III) hydride species.

**ABCChem 9**

**Chelating azolylidene and Ru II complexes: Effect of pendant arm and co-ligands in catalytic transfer hydrogenation**

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The incorporation of hemilabile coordinating moieties into the ligand scaffold is a fundamental approach for the synthesis of efficient catalysts, as this type of
units can coordinate/de-coordinate during the catalytic cycle facilitating the transformations. Thus, a large variety of hemilabile motifs have been incorporated into N-heterocyclic carbene (NHC) scaffolds in order to exploit the unique mesoionic and donating properties of these privileged ligands. In this work, we have synthesised a series of imidazolyl- and triazolyl-idene RuII complexes containing a potentially hemilabile pendant arm (pyridine, picolyl or allyl) and varying the co-ligands around the metal centre, p-cymene, acetonitrile and butadienesulfonyl (Figure 1), namely, [Ru(ImPyMe)(h1-\text{SO}_2\text{CHCHCH}_2)(\text{CH}_3\text{CN})_3]\text{PF}_6 (\text{ImPyMe} = 1\text{-}(2\text{-pyridil})\text{-}3\text{-methylimidazolyl}-2\text{-idine}), [(p\text{-cymene})\text{Ru(TzAllylMe)}\text{Cl}]\text{PF}_6, [(p\text{-cymene})\text{RuII(TzPyMe)}\text{Cl}]\text{OTf}, [\text{Ru(TzAllylMe)}(\text{CH}_3\text{CN})_4]\text{PF}_6, [\text{Ru(TzPyMe)}(\text{CH}_3\text{CN})_4]\text{OTf}_2 and [\text{Ru(TzPyMe)}(h1-\text{SO}_2\text{CHCHCHCH}_2)(\text{CH}_3\text{CN})_3]\text{OTf}, \text{TzRMe} = 1\text{-}R\text{-}4\text{-butyl}-1,2,3\text{-triazolylidene} (R = \text{allyl} or 2\text{-picolyl}, \text{TzAllylMe} or \text{TzPyMe respectively}). Catalytic transfer hydrogenation of benzophenone to diphenylmethanol has been used to evaluate the effect of the NHC, pendant arm and co-ligands on the metal centre. As expected, the best catalytic systems contain p-cymene and triazolylidene ligands, as the latter is a better σ-donating ligand than its imidazolylidene analogue.

Figure 1.

**ABCChem 10**

Recent advances in sustainable methods for fluorination and fluoroalkylation
Fluorine is the 13th most abundant element in the Earth’s crust, and yet, despite its relatively high abundance, organo-fluorine compounds are scarce in nature. However, previous research has shown how fluorine impacts the structure, reactivity, and function of fluorine-containing molecules. As a result, organo-fluorine compounds have been of immense interest in materials science, agrochemical development and medicinal chemistry. For example, in medicinal chemistry, fluorination is now applied routinely in lead optimization stage to tune metabolic stability, lipophilicity, among other factors that frequently impact the bioavailability and/or binding affinity of drugs. As such, over 20% of pharmaceuticals and approximately 40% of newly registered agrochemicals possess one or more fluorine atoms.

On the other hand, enamides represent a versatile class of intermediates in organic chemistry, that find use in many valuable synthetic transformations. Herein, we present our recent developments on novel and sustainable synthetic methods to introduce fluorine (-F) and fluoroalkyl (-Rf) groups into organic molecules. Emphasis is placed on several C–H bond functionalizations such as hydroxyfluorination, gem-difluorination-hydroxylation, trifluorination, C(sp²)–H fluorination and C(sp²)–H trifluoromethylation reactions of enamides. These methodologies have enabled us to prepare a series of fluorinated heterocyclic frameworks of pharmaceutical interest, using readily available and inexpensive reagents, via a direct C(sp²)–H bond functionalization. Accordingly, the enamide motif is thus established as a pluripotent scaffold to afford a wide variety of fluorine-containing small molecules and heterocycles in a sustainable fashion.
Enamide as a pluripotent scaffold for direct fluoro-functionalizations

ABCChem 11

Eco-friendly route to functionalized amines and suzuki cross-coupling reactions

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Amine synthesis is an important reaction in drug discovery; especially secondary and tertiary amines constitute an important class of chemical compounds that has promising potential for industrial, pharmaceutical and agrochemical applications. One classical approach to the synthesis of functionalized amine derivatives is based on reductive amination with an appropriate carbonyl compound such as aldehydes and ketones over a period of 12-24 hrs using conventional heating. In the current research an efficient methodology for the reductive alkylation of amines is being developed using a new environmental friendly catalyst, titanium (IV) isopropoxide/sodium borohydride. Special focus is placed on greener synthesis strategies employing microwave radiation to perform the synthesis. The microwave reaction protocol involves solvent-free conditions with shorter reaction times and is expected to contribute significantly
towards green synthesis of functionalized amines. The scope and limitations of the reactions were assessed using a structurally diverse set of aldehydes, ketones and amines. In the second project we are examining Suzuki cross-coupling reactions in the construction of C-C bond with a focus to improve protocol for economical and environmentally friendly reactions. The reactions are catalyzed using Pd(PPh$_3$)$_2$Cl$_2$, a commonly used palladium catalyst and aqueous Poly-ethylene Glycol 400 (PEG 400) as solvent. We have synthesized a number of biaryls starting from a range of aryl halides. Results of these experiments will be presented.

**ABCChem 12**

Aerosol-based synthesis of nanosized and nanostructured materials as versatile and sustainable synthetic methodologies

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The global need of improved efficiency of energy conversion devices such as photovoltaic and fuel cells pushes the materials science community to explore the existing plethora of synthesis, shaping and processing methods. Among them, the spray generation synthetic methods have solved many of the challenges associated to photovoltaic cell assembly and light emitting diode (LED) production. Additionally, such continuous synthetic process, allows large scale production, solvent recovery and environmentally-friendly chemistry, leading to a more sustainable process. This work will show some of the examples in which such synthetic procedure can be considered as a versatile strategy to produce nanostructured materials, and nanoscale-based devices.

**ABCChem 13**

Catalytic conversion of ethanol to butadiene: Detailed DFT investigation of the complex reaction mechanism

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Butadiene is one of the most important bulk chemicals produced in the petrochemical industry. At present, butadiene is mainly obtained from petrochemical sources, but the development of a cheap and sustainable process for its production from biomass-based resources would result in a reduced reliance on oil resources. In this context, great interest has been addressed on the possible conversion of ethanol to butadiene. Several mechanisms have been proposed in the last years. One of those was suggested by Toussaint and co-workers on the basis of which two acetaldehyde molecules are first formed by dehydrogenation of ethanol. In a second step, an aldol condensation reaction occurs leading to the formation of 3-hydroxybutanal. Dehydration of 3-hydroxybutanal produces crotonaldehyde, which is further hydrogenated and dehydrated to form the final product butadiene. On the basis of these findings, we performed a DFT investigation of the reaction mechanism. The ethanol to butadiene conversion reaction was studied using two different oxides, ZnO and MgO. The choice of these catalysts relays on their observed activity for both dehydration and dehydrogenation thanks to the presence on their surface of both electron-donating oxygen ions and partially electron-accepting Mg/Zn cations. Our investigation has shown that ZnO performs better than MgO leading to lower energy barriers. The reaction mechanisms involving the two catalysts are very similar and for both of the two oxides the rate determining step corresponds to the H transfer of an H from a methyl group of the crotyl alcohol to one of the O of the surface. However, the energy barrier is higher when MgO is used. Computed atomic charge evaluated using NBO scheme have shown a higher positive and negative charges on H and O ions, respectively, in Zn-based cluster models in comparison with MgO clusters, suggesting that the hydrogen atom can be transferred in an easier way on the more negative O ions of the ZnO cluster than MgO.

ABCChem 14

Optical confinement to induce forbidden phosphorescence in BAlq

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Bis(2-methyl-8-quinolinato)-4-phenylphenolate aluminum (BAlq) is a fluorescent organometallic molecule used in organic electronics. It is fluorescent but it does not show phosphorescence. The existence of a triplet energy level was predicted theoretically and physically revealed with the help of an emitting sensitizer, a molecule that transfers the energy from the excited singlet to the forbidden Triplet energy level, and at a very low temperature. In the present study, we report phosphorescent emission from BAlq at room temperature and in the absence of a sensitizer. The emission from the Triplet state was achieved thanks to the optical confinement provided by a colloidal photonic crystal. The photonic crystal was engineered to suppress the fluorescence emission of the molecule which enhances the probability of phosphorescent radiation. The wavelength of the new peak observed agreed with theoretical calculations and with the previous observations using a sensitizer. The optical confinement suppresses the available energy modes for fluorescence and favors the unusual intersystem crossing, giving rise to phosphorescent-triplet emission from BAlq. The molecules were included in an inner layer of a colloidal photonic crystal to ensure a more effective optical confinement and subsequently inserted within two colloidal photonic crystal forming a sandwich like structure. Emission was recorded at different temperatures, from 80 K up to room temperature, in order to study the temperature dependence of the phosphorescent emission peak.

ABCChem 15

Toward a thermodynamic profile for Cadmium-based quantum dot surface chemistry using isothermal titration calorimetry

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For a number of decades, the study and development of colloidal semiconductor quantum dot (QD) chemistry has proven to be a rich field with application goals ranging from photovoltaics and photocatalysis to bio-imaging and drug delivery. Cadmium-based colloidal QDs are some of the most studied nanomaterials and represent a model system for much needed surface chemistry investigations in the field. Essentially, the challenges in providing a full thermodynamic profile for QD surface chemistry must be overcome if QD-based technologies are to ever reach their full potential. This work highlights how even
in such a well-studied nanocrystal system, there are several caveats for appropriately compiling a thermodynamic profile for the dynamic nature of QD surfaces. It is imperative to consider the impact on the QD surface in the various surrounding media from the purification stage and on through surface modification reactions. Our lab has focused on further developing metrics for investigating colloidal QD surfaces while perturbing the QD environment as little as possible. We have established a highly effective and novel gel permeation chromatography approach to QD purification, which is ideal for investigating QD surface interactions with common spectroscopic tools as well as investigating QD–ligand thermodynamics with isothermal titration calorimetry (ITC). In fact, where spectroscopic techniques have been limited in providing a full description of QD-ligand interactions, we have demonstrated the capacity of ITC to elucidate binding phenomena responsible for the most drastic effects on QD photo-physical properties.

ABCChem 16

Bis and tris-chelate pyridylimidazolyl-2-chalcogenone M²⁺ (M = Fe, Co, Ni and Zn) complexes: Structural and magnetic properties

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Spin crossover (SCO) materials can reversible switch between the high and low spin states by means of an external stimulus such as temperature, light, applied magnetic field or pressure. This type of promising bistable complexes may find application as memory devices, molecular switches, MRI contrast agents, nanosensors, etc. This phenomenon has been observed in octahedral first-row transition metal complexes with d⁴-d⁷ electronic configurations, being iron(II) complexes the most widely studied systems, particularly in Fe⁷(N₆) coordination spheres. Recently, Fe⁷(N₄S₂) SCO complexes have been obtained containing exclusively thioether based ligands. Thus, we have centred our attention to imidazolyl-2-chalcogenones, in which the chalcogen atom, E = S or Se, is immersed in a C=E group. Interestingly, there are no examples in the literature of tris or bis-chelate complexes of potentially bidentate imidazolyl-2-chalcogenones, comprising a pyridine or pyrimidine pendant-arm.
In this work, we present the synthesis and characterisation of two bidentate imidazolyl-2-chalcogenones ligands possessing a pyridine pendant arm, namely 1-pyridyl-3-methylimidazolyl-2-chalcogenone, thione and selone, L$_5$ and L$_{Se}$ respectively. In order to evaluate the effect of the C=E group in the magnetic properties of the metal complexes, and specially the possible SCO properties for Fe$^{II}$, we have synthesised, to the best of our knowledge, the first tris- and bis-chelate metal complexes containing imidazolyl-2-chalcogenone, in (N$_4$E$_2$) and (N$_3$E$_3$) coordination spheres: [M$^{II}$($L$E)$_2$(X)$_2$] and [M$^{II}$($L$E)$_3$](BF$_4$)$_2$, E = S, Se; M = Fe, Co, Ni, Zn; X = NO$_3^-$, NCS$^-$. Fig. 1. The complexes have been characterised by standard spectroscopic techniques and by single crystal X-ray crystallography. The latter technique, allowed us to perform a structural analysis to determine the spin state for the Fe and Co complexes. Moreover, it was possible to study remarkable almost face-to-face π-π inter- and intra-molecular interactions among other classical and non-classical contacts.

**ABCChem 17**

**Unraveling the mystique of mixed halide lead halide perovskites**
Metal halide perovskites have drawn significant attention because of its ability to deliver high efficiency solar cells. Mixed halide lead perovskites offer a useful strategy for continuous tuning of the semiconductor bandgap. For example, by varying the halide ion composition of methylammonium lead iodide/bromide it is possible to tune the bandgap between 1.55 eV and 2.43 eV. In addition to photovoltaic applications these mixed halide perovskites offer rich photophysical properties with applications in lasing and optoelectronic devices. An intriguing property of mixed halide lead perovskites (e.g., CH$_3$NH$_3$PbI$_{3-x}$Br$_x$) is phase segregation to create iodide-rich and bromide-rich regions under visible irradiation. The halide ion movement in mixed halide films can be tracked from the changes in the photoluminescence and absorption spectra. Photoinduced segregation in mixed halide perovskite has a direct influence on decreasing the solar cell efficiency as segregated I-rich domains serve as charge recombination centers. The recovery of loss in the external quantum efficiency mirrors the dark recovery of the absorption showing the reversibility of the photoinduced halide segregation. Implication of such halide ion migration in mixed halide perovskite solar cell will be discussed.
heterocyclic carbene complexes (M-NHC). The materials were fully characterized using several techniques and particularly by advanced solid state NMR using Dynamic Nuclear Polarization which allowed us to have a molecular description of surface Metallo-NHC sites. Different M-NHC (M = Ru, Ir, Pd...) based catalysts were prepared and tested several reactions of which selective hydrogenation (Ir) and olefin metathesis (Ru). Their performances were compared to those of homogeneous homologues in solution. In the worst cases, the materials were found as active as homogeneous counterparts. In the best cases, the developed systems were more than 50 times more active (in term of rate and TON). These remarkable performances were attributed to surface site isolation which suppresses bimolecular deactivation processes and to beneficial interactions between the silica surface and the M-NHC.

Figure 1. Schematic drawing of the surface sites of an Ir-NHC based material

ABCChem 19

Synthesis of NHC-stabilized metal nanoparticles and their catalytic application in the selective hydrogenation of alkynes

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Metal nanoparticles (NPs) display physical and chemical properties which confers them high potential for application in diverse areas such as catalysis. In this area metal NPs combine advantages of both homogeneous and heterogeneous catalysis, namely high activity /selectivity and recovery and reuse. To enhance their catalytic performance, it is necessary to selectively
produce small and well-defined nano-objects stabilized by species that will restrict the approach of the substrate and as such, induce selectivity. It is well known that strongly coordinating ligands can stabilize and limit the growth of the particles. A new procedure to synthesize NHC-stabilized metal NPs based on the in situ generation of free carbenes will be presented in this communication. Using this new approach the basic pretreatment of an imidazolium salt and the subsequent filtration is unnecessary. This methodology is based on the in situ formation of free carbenes taking advantage of the decarboxylation of 1,2-dimethylimidazolium-2-carboxylate (Me$_2$Im-CO$_2$) to the 1,2-dimethylimidazol-2-ylidene (Me$_2$Im). Small spherical colloidal NiNPs with size range between 2 and 4 nm and narrow size distribution (~20%) have been obtained through the reduction of (Ni(COD)$_2$) precursor in the presence of the NHC-transfer agent (Me$_2$Im-CO$_2$). This new methodology was successfully applied in the immobilization of nickel nanoparticles onto multiwall carbon nanotubes (MWCNTs) by a “one-pot” procedure and can be extended to other metals as Pd and Cu. The new supported nickel nanocatalyst behaves as an efficient heterogeneous catalyst in the partial selective hydrogenation of terminal alkynes to afford the corresponding (Z)-alkenes under very mild reaction conditions (50°C and 5 bar H$_2$ pressure). Those products were produced in excellent yields at low nickel loading (3 mol%) and the heterogeneous catalyst can be readily recovered by simple filtration and reused four times without a noticeable loss in its catalytic activity.

Figure 1. Immobilized NHC-stabilized Ni NPs as catalyst in alkyne hydrogenation

ABCChem 20
Electrocatalytic behaviour of cobalt phthalocyanines in the presence of graphene quantum dots

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Graphene quantum dots (GQDs) are carbon-based nanomaterials characterized by good electron donating abilities, robust chemical inertness, excellent photostability, high biocompatibility, low toxicity, and high solubility in aqueous and non-aqueous solvents [1,2]. GQDs have been used to modify electrode surfaces for electrochemical sensing [3]. On the other hand, metallophthalocyanines (MPcs) are well known as electrocatalysts [4]. In this work we combine the two electrocatalysts: MPcs and GQDs for enhanced electrocatalysis by synergistic effect. We report on the electrochemical behaviour of reduced graphene quantum dots (rGQDs) compared to amino functionalized graphene quantum dots (NH$_2$GQDs). Reduction of the GQDs entails the elimination of the excessive carboxyl and hydrogen groups on the GQDs surface, thereby reducing the energy band gap. The two GQD types were conjugated to a novel cobalt phthalocyanine (CoPc) derivative (Fig. 1) via covalent interactions. The resulting conjugates were adsorbed onto a glassy carbon electrode (GCE), using the drop and dry method and used for the detection of hydrazine.
Selective electrochemical reduction of CO$_2$ into energy-dense organic compounds is a promising strategy for using CO$_2$ as a carbon source. However, efficient and selective earth abundant metal catalysts for the two reactions typically required for efficient CO$_2$ electrolysis, namely the oxygen evolution reaction (OER) and CO$_2$ reduction, are still scarce. We will present here the synthesis and electrochemical properties of a rationally designed nanostructured copper/copper oxide electrocatalyst for OER$^1$, and of a series of iron-based catalysts synthesized by pyrolysis of Fe-, N-, and C-containing precursors for the electroreduction of CO$_2$ to CO under aqueous conditions$^2$ (Figure 1). We will show that their selectivity for CO$_2$ reduction can be easily modulated with the amount of iron present during the synthesis of the materials, and will report their structure-activity relationship.
Analytical aspects of biosensors based on enzyme inhibition

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Biosensors based on enzyme inhibition represent a cost-effective device for fast screening of inhibitors. They could be used as a complementary approaches to traditional methods. A biosensor is an analytical tool, which combines a bioreceptor with a physical transducer to detect specific components of a sample.

In the present conference, we would like to underpin the recent advances in biosensors based on enzyme inhibition field, focusing on:

- the investigation of a new theoretical approach in order to easily understand the type of inhibition and calculate the kinetic parameters;
- the evaluation of the performances of the biosensor in the case of reversible and irreversible inhibition, in terms of time of analysis, detection limit, matrix effect;
- the use of nanomaterials;
- the development of biosensors based on enzyme inhibition embedded in labs on a chip;
- The applications of biosensors based on enzyme inhibition in real samples.
In this lecture, the experimental results obtained with biosensors developed in our laboratory for the detection of pesticides aflatoxins, cyanide, sulfide, methylmercury, nerve agents, antibiotics, and various other drugs and toxins will be presented. These inhibitors were usually detected at levels of ppb. Given the low concentrations found of these contaminants in water samples, the Solid Phase Extraction is required prior to analysis and was commonly used in combination of biosensors for a wide range of compounds. The diagnosis of type of inhibition greatly improves sensitivity by a judicious choice of the enzyme concentration, substrate concentration and incubation time.

The effect of the use of the nanomaterial on the analytical performances of the biosensor such as sensitivity, detection limit and linearity will be highlighted.

ABCChem 23

Integrative metabolomics analysis of the Brazilian Biodiversity

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Plants and other living organisms have long been used as source for different useful human products. Traditional medicines have always been a source for the cure of many diseases since antiquity. However, their rational use was possible only after the understanding of how the compounds present in plants had their activities proved. Then the search for new bioactive compounds had a huge development and as consequence, a number of new molecules with different spectra of activities were found. Numerous examples of bioactive natural products are known, however their discoveries have always been associated with the development of new analytical techniques. Recently metabolomics strategies based on mass spectrometry improved dereplication process and also open new perspectives for chemical biology investigations. Even though the search for new drugs from plants and other organisms is still exciting and attractive, chemistry has played a key role in the explanation of biological and biochemical observations, opening a number of opportunities in the area. Each single organism (plant, marine or terrestrial animals, microorganism, algae, among others) interacts with ecosystem by different strategies including chemical signals and/or chemical defenses. Compounds involved in this process are usually secondary metabolites, than we can accept the concept that organism actions are governed by the flux of energy and
information through an enormous number of molecules. Also, the natural products can have unknown physiological functions that must be deeply understood in the future. In this talk we provide an integrative overview of mass spectrometry strategies helping integrative metabolomics analysis for the Brazilian Biodiversity.

**ABCChem 24**

**Synthesis of halogenated furanones with bactericidal activity against drug-resistant strains of Pseudomonas aeruginosa**

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Antimicrobial resistance (AMR) happens when microorganisms (such as bacteria, fungi, viruses, and parasites) change when they are exposed to antimicrobial drugs (such as antibiotics, antifungals, antivirals, antimalarials, and anthelmintics). Patients with infections caused by drug-resistant bacteria are at increased risk of worse clinical outcomes and death and consume more health-care resources than patients infected with non-resistant strains of the same bacteria.

Considering the above, we decided to synthesize the 8 furanones shown in Table 1 and to evaluate them against 4 drug-resistant strains of Psuedomonas aeruginosa (RME 101, RME 118, RME 124, RME 125). Our results showed that only F1, F2, and F5 were active against the four drug-resistant strains of P. aeruginosa tested. Our findings indicate that structurally simpler furanones are more active than those with aromatic substituents, regardless of the presence of halogens in their structures.
Vinylaziridines useful intermediates for synthesising sphingosines

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Sphingolipids, essential components of cell membranes, have emerged as key signaling molecules involved in the regulation of many physiological and pathophysiological functions. Thus, they play an important role in the regulation of cell proliferation, differentiation, survival, trafficking and cell death. They are interconvertible by different metabolic enzymes in a complex lipid signaling system. Modulation of this sphingolipid metabolism is a promising strategy for cancer, and many connections between cancer therapies and sphingolipid metabolism having been implemented.

In this communication we present our recent results in the synthesis of sphingosine analogues using vinyl- and alkynyl aziridines as intermediates. Procedures for synthesising these intermediates based on metal- and organo-catalyzed oxyamination reactions will be presented.
Synthesis of solvatochromic probes to label the mycobacterial cell wall and their use in studies of the effect of host microenvironment on anti-tuberculosis drug efficacy in vivo

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Tuberculosis (TB), an infectious disease caused by the bacterial pathogen Mycobacterium tuberculosis (Mtb), is one of the top ten causes of death worldwide and the leading cause of death by a single infectious agent according to the World Health Organization (WHO). Rapid diagnosis, treatment, evaluation of treatment efficacy, and development of new antibiotics against drug resistant TB are ongoing challenges. Moreover, until recently, a dearth of appropriate chemical probes for noninvasive monitoring of infection in a living model organism has impeded investigation of the effect of the host microenvironment on the epigenetic and metabolic state of the bacterium. In the past few years, the Bertozzi Group has developed a mycobacteria-selective turn-on probe consisting of trehalose, a sugar that is incorporated into an extremely hydrophobic layer of the mycobacterial cell wall called the mycomembrane, attached to a solvatochromic fluorophore, a dye that only fluoresces strongly in hydrophobic environments. The probe’s negligible fluorescence in less hydrophobic surroundings produces good signal over background even without washing away excess unincorporated probe, a requirement for in vivo applications. However, though the original probe is a promising new labeling reagent, its relatively low fluorescence intensity combined with its particular excitation and emission wavelengths make background autofluorescence a problem, especially for in vivo applications. Early experiments with alternate solvatochromic dyes have been encouraging, resulting in brighter, red-shifted mycobacteria-selective probes. Here we describe the synthesis and characterization of a range of solvatochrome-trehalose probes as well as their use in studies of anti-tuberculosis drug efficacy in zebrafish, a model organism for Mtb infection.
A simplified view of mycobacterial trehalose analog uptake. The solvatochromic trehalose probe only becomes fluorescent after lipidation by Ag85 followed by incorporation into the hydrophobic mycomembrane. The probes’ color gradient encompasses the range of fluorescence emission wavelengths for the synthesized dyes.

ABCChem 27

Supramolecular approaches to control selectivity in transition metal catalysis via the second coordination sphere

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The interface between supramolecular chemistry and transition metal catalysis has received surprisingly little attention in contrast to the individual disciplines. It provides, however, novel and elegant strategies that lead to new tools for the search of effective catalysts, and as such this has been an important research theme in our laboratories. In this presentation I will focus on supramolecular strategies to control activity and selectivity in transition metal catalysis, which is especially important for reactions that are impossible to control using traditional catalyst development. For substrates with functional groups we use substrate orientation effects to control selectivity, whereas for non-functionalized substrates we create cages around the active transition metal. What these strategies have in common is the contribution of the second coordination
sphere to the catalytic properties, which is quite different from the traditional ligand effects. More recently, we also explored the use of large nanospheres that allows to perform catalysis at high local concentrations, leading to rate acceleration for several different reactions. These nanospheres can also be used for electrochemical events and as such for proton reduction catalysis. The lecture will focus on our most recent results.

Figure An example of substrate pre-organization at the metal complex for selective hydroformylation and a nano-cage for catalyst/substrate pre-organization

ABCChem 28
**Full property recovery after multiple recycling steps of melt-reprocessed polymer networks and cross-linked polymer composites: Novel one-step synthetic approaches for models of fully recyclable, reprocessable rubber tires and non-isocyanate-based polyurethanes**

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Conventional polymer networks cannot be reprocessed in the melt state and recycled into high-value products because of permanent covalent crosslinks. Reprocessable networks, or covalent adaptable networks, are cross-linked polymers that contain sufficient reversible covalent bonds for network reconfiguration under proper conditions. Such networks contain dynamic linkages that can dissociate or exchange with others at the reprocessing condition. We focus on two reprocessable networks that do not require pre- or post-polymerization functionalization but instead involve simple one-step chemistry with reaction of monomer and/or polymer. In one case, we show how novel use of nitroxide-mediated polymerization (NMP) involving reactions of a multifunctional radical initiator and a polymerizable monomer incorporating a stable nitroxide radical with polybutadiene or natural rubber and styrene lead to models for crosslinked tire rubber. This novel approach for improving sustainability also works in the presence of large levels of carbon black, a filler commonly used in commercial tires, making the approach equally applicable to polymer networks and polymer network composites. The strongly temperature-dependent reversible capping/uncapping step in NMP provides crosslink reversibility. Based on the rubbery plateau modulus from DMA and tensile properties, these networks can be reprocessed multiple times in the melt state with the product exhibiting full recovery of properties related to crosslink density. Robust recovery is also observed in polymer composite networks made by NMP with filler such as carbon black. This one-step NMP method also yields polymer network structures that are possible with only a limited few other reaction methods or have yet to be obtained by any other method. In the second case, a step-growth polymer network based on polyhydroxyurethane has been synthesized and also exhibits full property retention after multiple reprocessing steps. We show that both reversible and exchange reactions are present for this particular polymer at reprocessing conditions. It is important to
appreciate that reversible reactions may accompany exchange reactions in some vitrimers, because the extent of reversible reactions will alter the required reprocessing time. Also, if reversible reaction products are volatile and lost during reprocessing, it will be impossible for the reprocessed material to achieve full property recovery.

**ABCChem 29**

Withdrawn

**ABCChem 30**

**Ethical and societal implications of nanotechnology: Practical information for nanoscientists**

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Nanotechnology is being heralded as a driver of the next technological and economic wave and business enterprise development in this globally emerging field holds much promise. Applications utilizing nanomaterials are increasingly prevalent in many commercial arenas including manufacturing and consumer products.

An understanding of the major issues involved with the application of nanomaterials and nanotechnology is important to gain an appreciation of the safety and health, ethical and societal implications for nanoscientists. The unique properties of nanoparticles that yield many of the far-reaching societal benefits may also pose possible risks. The challenge is to determine whether the nature of engineered nanostructure materials and devices may also present new and unique safety and health risks, within the research laboratory as well as with downstream applications. At the same time, there is a need to address how the benefits of nanotechnology can be realized while proactively minimizing the risk. Growing concern over the potential and perceived risks of nanomaterials may also lead to regulatory action that will impact organizations conducting research or developing new applications in the nanomaterials area.

This presentation will provide an overview of the safety, health, ethical and societal implications associated with emerging technologies, using
nanotechnology as a case study. Better understanding of these related elements will help the nanoscientist researcher be better prepared in the application of their work in nanotechnology development.

**ABCChem 31**

**Polymers to patterns: Using self-assembly to produce complex nanopatterns on semiconductors and flexible substrates**

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Nanopatterned surfaces are of central importance for a variety of areas and applications, such as computer chip architectures, tissue interfacing, biosensors, light management and plasmonics, among many others. Typically, the various approaches to nanopatterning of surfaces are broken into two major classes: top-down methods such as photolithography, e-beam lithography, and scanning force microscopy variants, and bottom-up synthetic techniques, including self-assembly. Since lithography is the single most expensive step in computer chip manufacturing, the use of self-assembled block copolymers (BCPs) templates on surfaces is being seriously considered by the semiconductor industry to pattern sub-20 nm features on semiconductor surfaces; the Industry Technology Roadmap for Semiconductors (ITRS) terms this approach ‘directed self-assembly’, or DSA. Here we will describe how self-assembly of BCPs can be used to produce useful nanopatterns on technologically relevant surfaces, and in some cases, bypassing native equilibrium structures to form higher density patterns, and forms of higher complexity.
Self-assembly of block copolymers on silicon surfaces. Linear polymer nanopattern converted to platinum (left), and dot nanopattern converted to silica (right).

**ABCChem 32**

**Anchored metal polymers derived from metal complexes of the Group 11 with unsaturated N-heterocyclic carbene ligands**

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Transmetalation reactions of complexes with 2-imidazolylidene ligands have been used as a powerful tool to achieve the synthesis of new coinage metal-N-Heterocyclic carbene complexes. Although several systematic studies of NHC containing alkyl or aryl N-substituents have been carried out, only a few examples of compounds with unsaturated groups have been reported; therefore, it is important to establish synthetic, spectroscopic and structural behavior of copper, silver and gold NHC complexes with allylic or vinylic N,N-substituents. Furthermore, metal unsaturated moieties have been used as a
synthetic tool to prepare anchored metal polymers. In this work, we present the reactivity of asymmetric-alkene functionalized imidazolium salts with Ag₂O to obtain N-heterocyclic dimer silver carbenes, and their behavior as transmetalation agents onto [Au(SMe₂)Cl] and Cul to produce mixed silver-gold and silver-copper biscarbene complexes respectively, Fig. 1. In addition, polymerization reactions were carried out using the imidazolium salt 1-methyl-3-(4-vinylbenzyl)-1H-imidazol-3-ium chloride and its silver and gold complexes as monomers, through a free-radical polymerization (FRP) using a MW reactor and AIBN as initiator. They produced three amorphous macromolecular compounds Poly-L4, Poly-1d and Poly-2d, the last two bearing different NHC-metallic repeating units accordingly to its IR, NMR, DSC, TGA, XRD and SEM-EDX spectroscopic characterization.

Fig. 1. Molecular structure of mixed silver-gold compound bis[[1-(4-vinylbenzyl)-3-methylimidazol-2-ylidene]₂Au]{AgCl₂}

ABCChem 33

Withdrawn

ABCChem 34

Effect of temperature in the isomerization of 1-butene using supported Al₂Br₆ catalysts

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Al₂Br₆ is a strong Lewis acid that finds applications in Friedel Crafts alkylation and acylations. It can be supported on solid inorganic supports like SiO₂, Al₂O₃ or even zeolites to overcome the inherent waste problem associated with pure aluminum bromide. In the current study, anchoring aluminum bromide was achieved using vapor phase grafting, in which a surface reaction between aluminum bromide and the hydroxyl groups of the support takes place. As expected, the acidity of the silica gel (SiO₂) was enhanced by supporting aluminum bromide, confirmed by NH₃-TPD and FTIR with pyridine as a probe molecule. Acid sites were observed to be stable even at temperatures of 400 °C. The work here has shown that grafting Al₂Br₆ produces a solid acid that is active for 1-butene isomerization. We are aware of no reports of Al₂Br₆ supported on an inorganic support to create a solid acid catalyst.

Primary products observed in this reaction were trans- and cis-2-butenes although, small amounts of C₃, isobutene as well as C₅-C₇ also were observed. Even at room temperature 1-butene isomerizes into 2-butenes. The conversion of 1-butene increases with temperature and product distribution changes. At 200 °C, cracking produces some C₃ products that are not formed at lower temperatures. At these lower temperatures, negligible levels of <C₄ hydrocarbons are observed. In terms of the ratio of cis/trans, higher temperatures favored the trans- isomer and lower temperatures favored the cis-isomer.
Effect of temperature on 1-butene isomerization

ABCChem 35

Increasing metabolite coverage and data quality in untargeted LC-MS metabolomics

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The main objective of untargeted metabolomics is the measurement of as many small molecular weight metabolites as possible using single or multiple analytical methods. However, these current gold standard protocols are biased towards the detection of medium to high abundance metabolites, whereas many biologically significant metabolites are present at very low concentrations. To address this major challenge in the field of metabolomics, separation science can play a critical role. In this talk, I will summarize several different strategies to improve the detection of low abundance and unstable metabolomes, respectively. First, the role of sequential extraction in global metabolomics will be explored. The proposed method combines sequentially MTBE removal of lipids, methanol deproteinization and mixed-mode SPE to yield four fractions enriched in neutral, anionic, cationic and zwitterionic compounds. Method repeatability, recovery, fraction splitting and matrix effects were evaluated in
detail to show the performance of the method for human plasma. The results show that sequential extraction can significantly improve metabolite coverage without increasing MS analysis time, and achieve gains comparable to the metabolite coverage obtained using seven different extraction methods in parallel. Additional strategies for further improvement of metabolite coverage, such as use of new extraction materials including ionic liquids and nanomaterials will also be briefly discussed. Secondly, the influence of mobile phase additives on metabolite coverage will be illustrated, with the focus on improving metabolite detection using negative electrospray ionization. The clear advantages of using acetic acid as mobile phase modifier for mid-polar metabolites and lipids will be presented. Finally, in vivo solid-phase microextraction, and its capability to preserve unstable metabolome and lipidome will be briefly discussed.

ABCChem 36

Development of monolithic capillary columns and µ-chip for separation of intact proteins for nanoscale liquid chromatography

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One of the key challenges for top-down proteomics (analysis of intact proteins) is the lack of a high-efficiency and high-resolution intact protein separation technique. With this in mind, we are developing new strategies for separation of intact proteins via top-down proteomics mass spectrometry based on hybrid monolith material. For that, we have synthesized in situ in nano-column and multidimensional µ-chip platforms. We obtained advances in the preparation of monolithic nano-columns, regarding: i) understanding the photopolymerization reaction in-situ in the silica capillary ii) the homogeneity of polymer along all nano-column; iii) the development of instrumentation for analysis on nano-LC with UV-Vis capillary detector, and iv) intact protein separations. For the multidimensional liquid chromatography µ-chip, we advanced regarding: i) microfabrication (limit of pressure, sealing glass-glass chip, and canal characterization), and ii) understanding of photopolymerization reaction along the channel of glass platform. We are optimizing the polymer monoliths in both microfluidics channels by Design of Experiments (DoE). This way, we expect to
improve the porosity of the material by adjusting the percentage of the porogen solvent and the crosslinking monomer in the polymerization mixture. Here, we present the first results in separation of intact proteins for nano-columns. Figure 1 shows the chromatogram for bovine serum albumin and myoglobin indicating good run-to-run repeatability. Moreover, we obtained a plate height \( (H) \) of 98.21µm and column efficiency \( (N) \) of 2,197.16 plates/m for myoglobin protein. To our best knowledge, previous studies have investigated column efficiency only to small molecules as alkylbenzenes, with typical plate height of 9.0 µm and efficiency values of 111,000 plates/m. We expect that our studies on optimization of monolithic material can create a reproducible synthesis, to reach better column efficiency and separation of complex mixtures of proteins.

![Chromatogram](image)

**Figure 1.** Separation of a mixture of albumin serum bovine and myoglobin on the nano liquid chromatography with UV-Vis capillary detector.

**ABCChem 37**

Withdawn

**ABCChem 38**

Fighting low quality pharmaceuticals through the development and optimization of an affordable paper-medium antibiotic assay
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Low quality and falsified pharmaceuticals are an unfortunate reality many live with around the world, especially in Low and Middle Income Countries (LMICs). The need for comprehensive analysis in limited resource settings has turned researchers to develop inexpensive tools such as paper-based analytical devices (PADs). The antibiotic PAD (aPAD) utilizes a standard titration assay for beta-lactam antibiotics that has been downscaled to function on paper. The current aPAD methodology uses a glassware addition of sodium hydroxide, carefully prepared triiodide and hydrochloric acid followed by a reaction on the paper test card consisting of a reduction with thiosulfate and a color producing complexation with starch. Through this scheme, the aPAD has the capability to semi-quantify the quality of beta-lactam antibiotics. These drugs, such as amoxicillin and ampicillin, are crucial and widespread in any healthcare system. I performed a field reproducibility test of the aPAD in Eldoret, Kenya. This test, while successful, revealed a need to optimize the process for the end user—pharmacists in LMICs that lack capacity for postmarket surveillance. I created a shortened scheme that requires the placement of triiodide in quantitative amounts onto the aPAD, which will make the final reduction step using thiosulfate redundant. This will simplify both the creation and use of the aPAD and lower cost. Testing was performed to simulate this simplified reaction scheme which gave results similar to the current readout of the aPAD and initial degradation tests show promising results of the “shelf life” of dried triiodide, the crucial new addition to the aPAD.

ABCChem 39

Withdrawn

ABCChem 40

Direct C(sp²)–H trifluoromethylation of enamides using Ruppert-Prakash reagent

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Extensive attention has been devoted towards the development of efficient and versatile methods for introducing the –CF₃ group into diverse organic molecules, as it imparts favorable physicochemical properties. C(sp²)–H bond functionalization is an area of increasing interest, and the corresponding trifluoromethylation still poses a synthetic challenge. Recently, different approaches have been described in which pre-formed electrophilic CF₃ reagents afford the C(sp²)–CF₃ bond formation from the C(sp²)–H, however, given the expensive and/or hazardous nature of these reagents, more efficient, cost-effective and sustainable methods are still ardently needed.

In addition, enamides are important synthetic intermediates and are often found in compounds of pharmacological and agrochemical interest, as well as naturally-occurring products, thus, their direct trifluoromethylation is of significant interest. In this work, we present our results on the C(sp²)–H trifluoromethylation of enamides under oxidative conditions, using Ruppert-Prakash reagent, TMSCF₃ as a sustainable, inexpensive and readily available –CF₃ source. A late-stage trifluoromethylation of complex pharmaceutical compounds is thus established, which has allowed us to prepare CF₃-analogues of various FDA-approved pharmaceuticals.

**Direct C(sp²)-H trifluoromethylation**

Direct C(sp²)-H trifluoromethylation of enamides

**ABCChem 41**

Withdrawn
ABCChem 42

Sustainable approaches to iron-catalyzed cross-coupling of aryl chlorides and tosylates

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Development of new strategies encompassing cross-coupling of unreactive bonds has revolutionized organic synthesis. In this context, iron-catalyzed coupling of halides and C–O electrophiles holds a significant potential for widespread green applications due to low price, abundance and virtually lack of toxicity of iron catalysts. Herein, our recent studies on sustainable approaches to cross-coupling of aryl chlorides and tosylates with high selectivity will be presented. These environmentally benign methods accomplish traditionally challenging C(sp²)–C(sp³) cross-coupling with organometallics possessing β-hydrogens with efficiency matching or superseding current state-of-the-art. The reactions are compatible with a variety of electrophilic functional handles. Applications to double and site-specific alkylations will be described. Representative examples to be presented include reaction optimization, scope studies and investigation of the mechanism.

ABCChem 43

Withdrawn

ABCChem 44

Maximizing catalysis of nanoparticles via their monolayer assembly on nitrogen-doped graphene

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We report a facile interface assembly method to assemble a monolayer array of nitrogen-doped graphene (NG) and nanoparticles (NPs) and then to transfer the dual monolayers onto a solid substrate. Using 3 nm NiPd NPs as an example, we demonstrate that NiPd-NG-Si can function as a catalyst probe and show maximum NiPd catalysis for the hydrolysis of ammonia borane (H₃NBH₃, AB) with
its TOF = 4896.8 h\(^{-1}\) and \(E_a = 18.8\) kJ/mol. The NiPd-NG-Si is equally active for catalyzing one-pot reactions among AB, 2-nitroacetophenone and aldehydes, leading to the high-yield syntheses of quinazolines in water. Our assembly method can be extended to other graphene and NP catalyst materials, providing a new 2D NP catalyst platform for catalyzing reactions in one-pot with maximum efficiency.

**ABCChem 45**

Withdrawn

**ABCChem 46**

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**ABCChem 47**

**Cellulose-based nanostructured composites and devices: The case of graphite and metal oxide films**

*Bruno C. Batista, bruno.batista@iqm.unicamp.br, Pompeu Abreu Filho, Jeferson Santos, Ramon dos Santos, Fernando Galembeck, University of Campinas, Campinas, Brazil*

There are many interesting challenges and opportunities in designing the sensors and actuators of the future. It is important that they are made of inexpensive, robust materials that can be easily discarded after use, and some will have to fulfill foldability and wearability requirements. Paper-based materials offer one interesting solution to these challenges and their usefulness has been demonstrated in recent studies and new emerging devices [1]. They benefit from cellulose unique properties, its renewability and wide availability [2]. Our group has been exploring the use of microcrystalline cellulose [3] and cellulose derivatives to prepare stable dispersions containing nanographite, metal oxides and other particles [4]. Casting these dispersions on top of paper and other lignocellulosic substrates results in functional composite films [4]. While the substrate contributes with mechanical properties, inorganic additives impart desirable conductive and sensing characteristics. The resulting films display an intricate layered microstructure (a) and possess tunable sheet resistance values that can be as low as 0.2 \(\Omega\) sq\(^{-1}\). They are incorporated into a series of paper-
based devices (b) that include geometrically defined conductive tracks and heaters, sensors for water, ethanol and many liquids, pressure sensitive conductors, among others. In this contribution we describe some of the relevant film properties and examples of applications.

(a) Microstructure of cellulose/graphite nanocomposites containing inorganic additives. (b) Example of a paper-based device used for localized heating.

ABCChem 48

Self-cleaning membrane to control fouling by suspended particles

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Membrane filtration is finding more and more applications in modern pharmaceutical, chemical engineering, and advanced water and wastewater treatment. Nevertheless, membrane fouling still remains as one of the biggest problems/hurdles of membrane filtration technology. Conventional methods for membrane fouling control such as chemical cleaning have to generate and handle hazardous waste chemicals. Consequently, with the advancement of polymer science, an innovative approach of green chemistry is to utilize a
piezoelectric polymeric membrane for self-cleaning via controlled vibrations. The filtration tests were conducted with feeding of 0.5 g/L kaolin suspension to the system. The results showed the vibration magnitude of the membrane was still weak (about 40 pico-meter at 5.4 V driving power). However, when the piezoelectric membrane vibrated at its resonant frequency during the pause of filtration process (i.e. pressure was nulled), membrane fouling was significantly reduced compared to the control tests. The advantages of the new membrane system include chemical free and automatic cleaning.

ABCChem 49

Poly(acrylic acid) grafted ceramic microfiltration membrane to mitigate fouling of natural organic matter

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Membrane surface modification is an effective method to mitigate fouling and extend membrane life. This study investigated using poly(acrylic acid) (PAA) grafting g-Al2O3 ceramic membrane to make the membrane more negatively charged in neutral pH range, in order to mitigate fouling caused by natural organic matter (NOM). The isoelectric point dropped from pH 7.8±0.3 of unmodified membrane to pH 5.5±0.4 of the grafted membrane with the degree of grafting (DG) of 67.49 mg cm-2. At the same time, the hydrophilicity of the membrane remained high with the contact angle less than 30°. The filtration tests indicated that PAA-grafted membrane had a greater permeate flux and less fouling by Aldrich humic acid (HA) than unmodified g-Al2O3 membrane. Consistently, FT-IR analysis showed stronger absorbance of the functional groups of HA occurred on the unmodified membrane than the PAA-grafted. In addition, the unmodified membrane had slightly higher rejection of HA determined by UV254, UV280 and Color400, likely due to adsorption of HA from the permeate by the unmodified membrane and the foulant serving as a secondary membrane.

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Poly and pseudomorphism of a crystalline carbazole-xylene-carbazole rotor and their characteristic intramolecular dynamics

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The study and control of the intramolecular motion in crystalline solids has been the main goal in the field of molecular rotors and motors. Recently, we and others had reported that not only changes in the temperature, but also the diffusion of vapor guests could modify the dynamics of rotors in the solid state. In line with the previous findings, in this poster presentation we will discuss in detail the dynamic and polymorphic behavior of a biscardazole-p-[diethynyl-xylene] rotor, where, in addition to the changes in temperature, the inclusion of appropriate substituents in the rotary component offered the opportunity to modulate the internal rotary motion by means of steric interactions.

ABCChem 53

Synthesis, characterization and photophysics properties of carbazole-acceptor-carbazole molecular compasses

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In recent years, the synthesis of organic molecules featuring strong internal dipoles have received tremendous attention, due in part to the possible applications that result from the control of the reorienting dipoles under external electric fields. In addition, if these crystalline organic compounds are highly conjugated, they may show solid state luminescence, enabling several applications in technological devices. Thus, the present poster presentation will discuss in detail the design and synthesis of organic solids with alternating Donor-
Acceptor-Donor moieties, which impart unique emissive properties that combined with the intramolecular rotation, might enable fascinating properties.

**ABCChem 54**

**Amphidynamic behavior in crystalline rotors with bromo-carbazole stators**

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Crystalline molecular rotors are tailored materials inspired in the wheel-axle design, that consist in the appropriate combination of a stator (bulky group) and a rotator (mobile moiety). New molecular devices featuring halogen bonds have been recently reported, with these directional interactions favoring certain crystalline packing of the rotors under study. In this field, our research group has also reported molecular rotors with halogen bonds, emphasizing its role in the isotropic solid-state dynamics.

In this work, we will present the synthesis and solid-state characterization of a new series of molecular rotors assembled through covalent or supramolecular bonds, featuring bromide atoms in the periphery of the carbazole stator. The crystalline structure of these compounds will be discussed to highlight how the intermolecular interactions affect their rotational dynamics, as detailed by solid state NMR.
Unexpected reactivity of phosphorene in dry DMSO

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The search for new highly functionalised materials based on the new 2D material so-called Phosphorene, formed only by P atoms is very promising due to its fascinating electrical and optical properties. In this regard, the understanding of its chemical reactivity with different organic, inorganic and organometallic compounds is mandatory for the rational use of such innovative material in different devices. In a previous study we have shown that the quality of exfoliated black phosphorus (BP) in DMSO is strongly dependent from the water content. Thus, when the exfoliation is carried out in DMSO with a molar ratio P/H₂O ≥ 15, reaction with DMSO occurs and trimetaphosphate is quantitatively formed. This new and unexpected finding led us to study in detail the behaviour of the other phosphorus allotropes under the same reaction conditions. Surprisingly, while red-P shows the same reactivity of BP, the more reactive white allotrope does not react at all. This finding is apparently counterintuitive proving for the first time that both black-P and red-P may show, in a specific reaction, a higher reactivity than white-P. Preliminary results of a theoretical study well support this unexpected reactivity of elemental-P and help to rationalize the elementary steps bringing about the BP hydrolytic degradation and the non innocent role of DMSO in the process.
Magnetic coordination polymers built from oxamate and oxamidate ligands

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The first preparation of heterobimetallic Mn^IICu^II magnetic chains containing oxamato as a ligand were carried out by O. Kahn and co-workers having in mind the rational preparation of molecule-based magnets (MBMs). Kahn’s approach consisted of using organic ligand that can act as a molecular bridge connecting paramagnetic metal ions of different spin states. This will outcome in a system with a net spin resulting from the non-compensation of the antiferromagnetically interacting local spins being at the base of the obtention of heterobimetallic ferrimagnetic systems. Since then, many other magnetic coordination polymers (MCPs) containing functionalized oxamate/oxamidate bridging ligands have been described paying special attention to their multifunctional character. The synthesis of MCPs is still a challenge because of the difficulties in organizing ions in one- (1D), two- (2D) or three-dimensional (3D) networks. This is still a hot subject as confirmed by the impressive number of articles devoted to molecular-programmed self-assembly, crystal engineering and metal-organic frameworks (MOFs). Some illustrative results are the achievement of magnetic sponges, multielectron transfer systems, molecular switches for reversible biphasic processes, Single-Ion Magnets (SIMs), Chiral Single-Chain Magnets (CSCMs), chiral homo- and heterobimetallic wheels, dynamic, chiral and luminescent porous 3D magnets, three-dimensional (3D) proton conducting chiral biological metal-organic frameworks (bioMOFs), SIM hosting into magnetic MOFs and palladium(II) compounds exhibiting catalytic activity. These compounds were synthesized by means of the “complex as ligand” strategy, a preparative route which requires the use of notions of metallosupramolecular chemistry and some tools of crystal engineering. It allows the rational design of chemical objects of different dimensionality nD (n = 0-3). They display several molecular architectures such as metal grids, ladders, racks, polyhedral metal cages, metallodendrimers, interlocked networks, corrugated planes, etc. In this work, we will describe the synthesis, crystal structure and magnetic characterization of supramolecular magnetic coordination polymers with the opba ligand [H₄opba stands for N,N’-1,2-phenylenebis(oxamic acid)]
and their derivatives, among them the flexible edpba \([H_4 edpba= N,N'-\text{ethylenediphenylenebis(oxamic acid)}]\).

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In vitro evaluation of a coordination compound copper (II) mixed chelates (Casiopeina® III-ia) loaded in a niosomal system

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Casiopeinas® are a new generation of antitumor agents which are coordination complexes with copper, they show cytostatic, cytotoxic and antineoplastic activity on in vitro and in vivo studies; between this compound group, the Casiopeina III-ia \([\text{Cu}(4,4\text{-dimethyl 2,2-bipyridine})(\text{acetylacetonate})]\NO_3\) is one of the most studied and actually, this casiopeina stays in the clinical phase I in Mexico. On other hands, it is well known that the chemotherapeutics, due to its cytotoxicity, they can cause various adverse effects; is for this, that the nanocarriers have emerged as an alternative to administration of these drugs. In this work, non-ionic surfactant based vesicles (niosomes) were used for the nanoencapsulation of casiopeina III-ia. The niosomes loaded were prepared by method of ether injection with Span60 and cholesterol in molar ratio 1:1, with increasing total Span60/Cholesterol (S/C) concentration with goal to measure the encapsulation efficiency of drug. The best concentration was 400 \(\mu\text{M}\) and 90 \(\mu\text{M}\) for S/C and casiopeina III-ia, respectively; in this concentration the encapsulation efficiency was 75 \% and the particle size was around 60 nm. The morphology was evaluated by TEM where was observed spherical systems. The kinetic of release was first order and the release was 65 \% inside 69 hours. The release profile was biphasic that was produced by weak interaction between casiopeina and niosomes studied by spectrophotometric UV-visible and FTIR. The essays of cellular viability say that
the niosomes don’t have activity, the casiopeina in noisome showed activity,
but it was less than casiopeina free.

ABCChem 62

Synthesis and reactivity of transition metal clusters containing functionalized
alkynes as ligands

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One important aspect that promoted the study of organometallic compounds is
the greater reactivity of some ligands when that are coordinated to a metal
atom or ion. The case of transition metal clusters is particularly interesting since
the ligand is often coordinated to several metal atoms, affecting the electronic
distribution in the complex.
In this work, we will present reactivity studies of the compounds [(m-
H)Ru₃(CO)₉(CC(CR)) (R=SiMe₃, SiPh₃) with phosphines, amines and sulfur ligands as well as the reactions of [Ru₃(CO)₁₂] with tin containing alkynes.

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Learning about molar ratio curves: The case of several non-quantitative formation reactions

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In the last quarter of 20th Century molar ratio experiments were used to teach a method to determine stoichiometry and equilibrium constants. The three hypothesis of the mathematic model used were:

* There is only one complex formation reaction in the system to produce MaLb
* This reaction is quantitative
* The linear response only depends of the product MaLb concentration

In this work we present a mathematical model, with analytic solution, to predict and interpret, molar ratio curves in systems with the formation of several complexes with reactions partially quantitative. In the figure some figures are shown considering the curves calculated for two successive reactions with different quantitativities.
Frustrated Lewis pair chemistry: An avenue to metal-free synthesis and catalysis

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Main group Lewis acids and bases are used in combination to activate hydrogen in frustrated Lewis pairs (FLPs). This has allowed the development of metal-free reductions of C=N bonds, anilines, N-heterocycles, olefins, polyaromatic hydrocarbons and ketones. This strategy has also led to the synthesis of new boron-based radicals. The design of the applications of new FLPs in the reactions of unreactive substrates is also discussed. Novel approaches to N2 activation is considered while, phosphonium cationic Lewis acids are shown to be effective for C-F bond hydrodefluorination catalysis, hydrosilylations, hydrogenations and C-F bond activations and functionalization. The implications of these findings for applications of main group species in catalysis is considered in this lecture.

Green chemistry with heterogeneous catalysis
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The improvement of chemical process from an environmental point of view can be achieved by designing more integrated process that avoid separation and purification steps. This is useful not only because saves energy and can reduce resids, but also reduces the CAPEX cost. We will show that it is possible to improve process integration by designing bi and trifunctional solid catalysts able to carry out multi step process within a selected reaction window. The different catalytic functions coupled in a single solid catalysts can involve acid and basic sites, metal and acid, metal and basic, and metal plus enzims. Those different situations will be illustrated with reactions that show the important environmental benefit achieved with the multifunctional solid catalyst.

By combining fundamental knowledge on the reaction mechanism with capabilities on material science (synthesis of materials and characterization) it is possible to carry out a given reaction through a different reaction pathway that generates less subproducts or uses a less dangerous reactant or catalyst. We will show that this is the case for carbamoilation, oxidation and coupling reactions. Well defined solid catalysts allow to avoid the use of harmful reactants still with good activities and selectivities.

Finally, we will present the possibility to generate molecules with interesting properties for polymers, surfactants, lubricants and fragrances starting from biomass derived products.

ABCChem 67

Metal-induced aggregation of human lens crystallins: Uncovering the bioinorganic facet of cataracts disease

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Cataracts are the leading cause of blindness in the world, and are formed upon aggregation of lens proteins into high molecular weight complexes, causing light scattering and lens opacity. Several studies implicate metals as a potential etiological agent for cataract, while copper and zinc concentrations in the cataractous lenses are increased significantly, as compared to normal lenses. The monomeric all b-sheet human g-crystallins are among the most abundant
crystallins in the lens and one of the most stable proteins in the human body, but its non-amyloid aggregation is associated with cataracts. In this presentation, the effect of metal ions in the aggregation of these proteins will be discussed. Specifically, Cu(II) and Zn(II) ions induce this aggregation, suggesting site-specific interactions with the g-crystallins. The mechanism for metal-induced aggregation likely involves interaction of the metal ions with the protein, leading to partial unfolding and formation of high molecular weight light scattering aggregates. In this presentation, recent advances in understanding the nature of the metal-protein interactions associated to Cu- and Zn-induced aggregation of the g-crystallins will be discussed. Also, the effect of heavy metal ions on the aggregation of the g-crystallins will be presented. Metal-induced aggregation could be a physiologically relevant phenomenon; thus, understanding its mechanisms will help elucidate the role of metal ions in the aggregation of human crystallins and their potential involvement in the development of cataracts, providing important insights into the unexplored bioinorganic facet of this disease.

ABCChem 68

Bioorthogonal organometallic chemistry: Overview, applications and state-of-the-art

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The goal of performing bio-independent syntheses in complex biological environments, so-called bioorthogonal chemistry, has inspired the search for novel biocompatible transformations for more than a decade and found a niche of application as labelling techniques to study biomolecules in their native state (1). Along with catalyst-free ligations, significant advances have been made in recent years on the development of cell-tolerated bioorthogonal organometallic (BOOM) reactions (2,3), opening up new avenues for the exploitation of the bioorthogonal paradigm in chemical biology and biomedicine. Based on the biocompatibility of some transition metal catalysts (e.g. Pd or Au) and their remarkable catalytic properties, our lab has pioneered the use of heterogeneous catalysis to enable the site-specific activation of chemotherapeutic precursors in specific anatomical locations (e.g. inside tumours). As opposed to biolabile prodrugs, whose activation process relies on metabolic pathways, an efficient BOOM-activated prodrug therapy would be
entirely dependent on the distinct catalytic properties of the metal and therefore the prodrug would remain intact in the absence of the metal source. Palladium (4-7) and, more recently, gold (8) are the transition metals used as catalysts in this unique strategy. In this talk I will present the discovery of N and O-depropargylation reactions that take place under biocompatible conditions and their application as masking methods to eliminate the fluorescence and bioactivity of dyes and clinically-used drugs, respectively, while enabling the bioorthogonal rescue of the compounds’ properties by Pd or Au-functionalized devices in cancer cell culture, living organisms and tumours.

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Exploring the properties of the oxo-centered triruthenium: From fundamental aspects to potential biological applications

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Oxo-centered triruthenium acetate clusters ([Ru3O(CH3COO)6(L)3]n+, L = axial ligands) present important properties owing to their intriguing mixed-valence chemistry and reversible multi-step redox behavior. They are regarded as excellent precursors for the design of molecular assemblies, nanomaterials and more recently studies have demonstrated that clusters present important biological properties. This work is focused on the synthesis, characterization and biological studies of new clusters bearing DPPZ derivatives. The general formula of the new clusters are: (1) [Ru3O(OAc)5(py)2(dppz-Cl)][PF6], (2) [Ru3O(OAc)5(py)2(dppz-CH3)][PF6], (3) [Ru3O(OAc)5(py)2(dppz)][PF6] and (4) [Ru3O(OAc)5(py)2(phen)][PF6]. The absorption spectral of the clusters shows bands around 690 nm, which are characteristic of the intraluster charge transfer transition (IC) and cluster-to-ligand charge transfer transitions (CLCT) in the region between 340-380 nm. The strong and sharp absorption bands at high energy (λ < 350 nm) are assigned to the intraligand (π/π*) transition of the aromatic rings localized on the ligands. The infrared spectra shows asymmetric and symmetric stretching mode ([νas(OCO) and νs(OCO)]) due the presence of
the acetate bridges. For the new clusters, three one-electron oxidation waves were observed in the potential region -1.50 to 0.80 V (vs Ag/Ag⁺) attributed to the processes $E_{1/2}^{1/2} (V) [Ru_3O]^{-1/0}$, $E_{2/2}^{2/2} (V) [Ru_3O]^{0/+1}$, $E_{3/2}^{3/2} (V) [Ru_3O]^{+1/+2}$ respectively. The mass spectra (ES-MS) show the molecular ion peak at $m/z = 1088.9 ([1 - PF_6]^+)$, $m/z = 1068.9 ([2 - PF_6]^+)$, $m/z = 1054.9 ([3 - PF_6]^+)$ and at $m/z = 952.9 ([4 - PF_6]^+)$. Cytotoxicity results (2 to 50 mM, MTT assay) showed the clusters with dppz ligands were more cytotoxic in melanoma murine (B16F10) than the human cancer cell modes (A549). All compounds were not cytotoxic in L929 cells and the clusters were more cytotoxic than the free ligands in all concentrations. These results confirm the relevance of the coordination process and indicate the potential of these clusters as chemotherapeutic agents. Thus, additional studies with target biomolecules (DNA and HSA) will be performed to determine the relationship between structure and biological effect, as well as assays of cellular uptake, internalization, subcellular localization and death mechanisms.

ABCChem 71

Development of drug-eluting transplants

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The clinical success of organ and tissue transplantation is adversely impacted by various trauma including immediate challenges such as ischemia/reperfusion injury (IRI) and the activation of the innate immune system. Fortunately, the process of transplantation provides an exciting opportunity for the ex vivo chemical modification of resected live tissue prior to implantation. Our lab is focused on developing chemical strategies for protecting transplanted tissue, including the generation of covalently modified ‘drug-eluting islets’ reported here.

Controlled release approaches to drug delivery have the potential to provide enhanced efficacy by affording sustained local drug concentrations while avoiding complications such as off-site toxicity. We have been exploring biocompatible methods for the covalent modification of living tissue, including the surface functionalization of pancreatic islets prior to transplantation. These
studies have led us to develop ‘drug-eluting transplants’ – pancreatic islets that release covalently linked small-molecule drugs from their surface in a sustained and controlled fashion. *In vitro* studies of islets modified with a TLR4 antagonist have revealed a significant attenuation of the inflammatory responses that often destroy transplanted islets in the first 24-48 hours after transplantation. Transplantation studies have demonstrated that this protection is maintained *in vivo*, substantially improving the survival of ‘self-protecting’ drug-eluting islets.

We are presently working of further exploring this concept in the context of islet transplantation in addition to extending this work to the transplantation of solid organs. This presentation will describe the organic synthesis, bioconjugation, analytical chemistry, and biological studies involved in this challenging project. The development of drug-eluting tissue functionalized to deliver sustained and localized delivery of a small-molecule therapeutics provides a novel pathway to enhancing success in transplantation.
Global warming is today one of the main concerns of the society. Since the beginning of the industrial revolution, the concentration of CO$_2$ into the atmosphere has increased by more than 40%, due to the burning of fossil fuels. Carbon dioxide is a greenhouse gas and contributes to the increase of the temperature of the planet.

The concept of CO$_2$ utilization is increasing in importance, because it may add value to the production chain. Hydrogenation of CO$_2$ to methanol, dimethyl ether (DME) and hydrocarbons, as well as the production of organic carbonates appears as promising routes to convert CO$_2$ into more valuable products.

Hydrogenation of CO$_2$ to hydrocarbons can be accomplished with the use of Fe and Cr catalysts supported on Nb$_2$O$_5$. Two consecutive reactions take place: reverse water gas shift (RWGS) to produce CO and Fischer-Tropsch synthesis to transform the CO into hydrocarbons. The results indicated that the use of K or Cs as promotors increases the selectivity to hydrocarbons, especially light olefins, of great interest to the chemical industry.

Hydrogenation of CO$_2$ to methanol can be carried out over Cu.ZnO catalysts. The use of metal promotors has a strong effect on the yield of methanol. The results were interpreted in terms of the characterization of the catalysts. The best promotors decrease the reduction temperature and increase the surface area, leading to a more active catalyst. DME can be also produced if the metal catalysts were impregnated over an acidic support, capable of dehydrating the formed methanol.

Finally, we have used zeolites impregnated with metal halides as heterogeneous catalytic systems for the synthesis of cyclic organic carbonates. Styrene oxide reacts with CO$_2$ in the presence of potassium-exchanged zeolite Y impregnated with KI. The reaction occurs inside the zeolite cavity yielding 100% of styrene carbonate at proper reaction conditions. The use of zeolite allows the reutilization of the catalysts, although leaching of K was still observed, leading to a gradual decrease in activity.

**ABCChem 73**

**Catalytic production of chemicals from waste bio-oils**
As oil runs out and becomes more expensive, we shall need alternative resources for chemical manufacture. Bio-derived feedstocks are attractive, but they must not compete for land with food. In this presentation we shall describe the use of Tall Oil, a waste (2 M tonnes per year) from paper manufacture, for the production of alpha, omega diesters as well as the conversion of these diesters into diols and diamines for the production of biodegradable analogues of polyethylene and polyamides. We shall also describe the production of a variety of commodity chemicals from cardanol, a waste from cashew nut processing available at 300,000 tonnes per year. Products will include plasticisers, detergent precursors, tsetse fly attractants and large ring macrocycles.

Homogeneous catalysts are used to promote such reactions as isomerising methoxycarbonylation, hydrogenation of acids, esters and amides, hydrogative amination, heterocycle formation, alkene metathesis and lactonisation.
**Direct arylation as a greener synthetic tool for the preparation of organic materials**

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As an alternative to traditional inorganic materials, conjugated organic materials have received much attention since they combine features of traditional semiconductors with those of synthetic small molecules and polymers. Attractive qualities of organic electronic materials include low density, solution processability, flexibility, and structures that possess tunable properties. In order to fully commercialize these materials, efficient and environmentally friendly methods are needed for their syntheses. This presentation will describe synthetic approaches based on direct arylation reactions that allow the formation of carbon–carbon bonds for both small molecules and polymers. These methods are alternatives to traditional coupling methods (e.g., Suzuki, Stille) and are attractive as they circumvent the need for organometallic intermediates and thus reduce synthetic steps, byproducts, and cost.

**ABCChem 75**

**Novel biofuel synthesis from furfuryl alcohol and butanol over heteropoly acid catalysts**

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Furfuryl alcohol, is readily synthesized from biomass sources that do not compete with ethanol production. Therefore, the development of furfuryl alcohol based fuels may have important ramifications for the biofuel industry. A promising fuel to this end is butyl levulinate. The purpose of the research was to optimize production of butyl levulinate, from furfuryl alcohol and butanol, using salts of phosphotungstic acid as catalysts. These included cesium, copper and silver phosphotungstesates, with varying ratios of cationic substitution. Products detected were butyl levulinate, furfuryl butanoate, dibutyl ether, 1,1-dibutoxy ether, and a claisen condensation product. The catalyst most active towards the target molecule, butyl levulinate, was CsH_2[PW_{12}O_{40}], with a yield of 91% using this catalyst. This work demonstrates that butyl levulinate, a promising
biofuel, can be effectively synthesized via heteropoly acid catalysts and a simple one-pot synthetic route.

**ABCChem 76**

**Greening the organic chemistry laboratory: Comparison of microwave-assisted and classical nucleophilic aromatic substitution reactions**

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An experiment is described for the undergraduate organic chemistry lab which compares microwave-induced organic reaction enhancement (MORE) to that of more traditional synthetic procedures. MORE and traditional reflux procedures for substituting thiocyanate, ethylamine and diethylamine nucleophiles for bromide in nucleophilic aromatic substitution reactions on 1-bromo-2,4-dinitrobenzene are given. Recrystallization affords products of sufficient purity for characterization by C-13 NMR, mass spectrometry and melting point. As students compare the two synthetic methods, MORE procedures are consistently observed to be quicker, easier, greener and result in higher yields. Student instructions, instructor notes and example NMR and mass spectra obtained by students are provided.

**ABCChem 77**

**Carbon nanostructures-based multifunctional nanocomposites obtained as thin films at liquid/liquid interfaces: from preparation to applications**
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We are demonstrating that liquid/liquid (L/L) interfaces are suitable environment to stabilize solid materials as thin films, which can be easily transferred to ordinary substrates (plastics included) aiming different applications. The different approaches to the in situ preparation of carbon nanotubes- or graphene-based nanocomposites with polymers, metal nanoparticles and inorganic materials, directly obtained as thin films at L/L interfaces, will be highlighted in this presentation. The electronic, optical, magnetic and electrochemical properties of these films will be demonstrated, together with several examples of application as transparent electrodes, batteries, supercapacitors, sensors and electrochromic devices.

ABCChem 78

Synthesis and characterization of carbon nanofibers/ Zinc oxide/poly (para-phenylenediamine) ternary nanocomposites

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Nowadays, the nanocomposites have attracted increased attention because their synergistic effect in electrical, optical, catalytic properties [1], and some excellent ternary nanocomposites begin to emerge, such as graphene/CoFe₂O₄/polyaniline [2], reduced-graphene oxide/zinc oxide/poly(p-phenylenediamine) [3] and poly(p-phenylenediamine)/graphene oxide/Au [1]. In this work, a new ternary carbon nanofibers/Zinc oxide/poly(p-phenylenediamine) nanocomposites have been synthesized using one-pot method. The CNFs were mixed with zinc acetate in N,N-Dimethylformamide medium, then the mixture was dried in oil bath, which generates binary CNFs/ZnO composite, finally, the PpPD was incorporate into binary CNFs/ZnO composite via in situ polymerization. The nanocomposite was characterized by Transmission electron microscopy (TEM), Scanning Electron Microscopy (SEM), X-ray photoelectron spectrometry (XPS), and Fourier Transform InfraRed
spectroscopy (FT-IR), the results indicate that the three phases of CNFs, PpPD and ZnO nanoparticles were formed in the system, with a particles size about 30 nm and a very thin layer of the polymer film was deposited on the carbon nanofibers surface. Therefore, the carbon nanofibers/Zinc oxide/poly(para-phenylenediamine) ternary nanocomposite could be used as an electrode material for supercapacitors and other energy storage devices.

ABCChem 79

Carbon nanoreactors: making use of their unique shape

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Hollow carbon spheres (HCSs) have a unique structure in which the sphere and the wall diameter can be changed by synthesis strategies. This can allow for the properties of the carbon layer to be varied. In particular both the transfer of electrons through the layer as well as the transfer of atoms/groups across the layer can be explored by modifying the properties of the carbon layer. Hydrogen spillover is one of the mechanisms by which a noble metal promoter can enhance the reducibility of a metal oxide. In particular a noble metal that can dissociate H₂ molecules at low temperatures to hydrogen atoms can be used to transfer the H atoms to a nearby metal oxide nanoparticle via a spillover mechanism.

In this study Co and Ru nanoparticles were separated by the carbon layer of a HCS by, for example, encapsulating Co nanoparticles inside a mesoporous hollow carbon sphere support (MHCS) while the Ru was exclusively loaded on the outer surface (i.e., Co@MHCS@Ru). Other catalysts, Co/MHCS, and Co@MHCS and promoted CoRu/MHCS and CoRu@MHCS were also prepared. Primary hydrogen spillover was invoked to explain the high Co dispersion of CoRu@MHCS in relation to the Co@MHCS@Ru and Co@MHCS dispersion (pulse chemisorption; reduction at 350. In contrast, a secondary hydrogen spillover process was used to explain the complete reduction of the Co₃O₄ on Co@MHCS@Ru when compared to unpromoted Co@MHCS (in situ PXRD studies). Fischer-Tropsch testing of the catalysts showed that the Fischer-Tropsch activity was proportional to the degree of reduction that increased with the Co-Ru intimate contact. The Ru promoter also enhanced the production of
paraffinic products and methane. The study indicates that the use of hollow carbon spheres are suited to the investigation of reactions in which metals can be separated by a carbon layer of varying thickness and with varying functional groups.

ABCChem 80

Graphene oxide hybrids and composites: applications in energy devices and structural components

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GO and GO-based hybrids or composites have shown great potentials in the applications in the energy and structural engineering sector. GO is a monolayer or a few-layer nanomaterial, which can be obtained by exfoliating graphite oxide through sonicating or mechanical stirring. The functional groups on GO surface (mainly epoxy and hydroxyl groups) act as effective anchoring sites to polymeric chains or ionic liquids. GO is insulating due to the large portion of sp3 hybridized carbon atoms bonded with the oxygen containing groups. However, after reduction, the sheet resistance of reduced GO (namely rGO) can decrease several orders of magnitude, transforming the material into a semiconductor or even into a graphene-like semimetal. The drawbacks of GO for practical applications are due to the combination of structural defects and restacking on multilayer thickness.

We have been applied a fast and reproducible process to prepare GO from graphite using sonication under acidic conditions. The GO and rGO were characterized by transmission electron microscopy, atomic force microscopy, thermogravimetric analysis, X-ray diffraction, Fourier-transform infrared spectroscopy, scanning electron microscopy, X-ray photoelectron spectroscopy, and electrical measurements. Through a three-roll mill, these nanofillers were mixed into resin, obtaining homogeneous dispersion. The influence of GO and GO modified with amminated functions on the enhancements of thermal and mechanical properties of epoxy and polyurethane based composites was studied by our group. Furthermore, composites based on GO and rGO mixed with carbon nanotubes, conjugated polymers and ionic liquids were used in our research to improve electrochemical properties of supercapacitors. The devices based on these
nanomaterials exhibited greater electrochemical performance, such as high specific capacitance, better cycling stability, power, and energy densities.

**ABCChem 81**

**Capping sulfides from mercaptobenzene and mercaptopyridine carbonyl diphosphine ruthenium clusters with potential application as catalytic materials**

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The chemistry of metal carbonyl clusters of group 8 containing sulfur has kept the interest of scientists through the years. Their synthesis, characterization and the understanding of their properties, might lead to potential application of this type of compounds for example, in the hydrodesulfurization process of dibenzothiophene used as model to test complexes catalytic properties. In these work we describe the reactivity studies of [Ru₃(CO)₁₀(diphosphine)]; diphosphine = dppee (1), dppm (2), dppe (3), and dfppe (4) with 6-methyl-2-mercaptopyrindine (L₁), 2-Mercapto-5-(trifluoromethyl)pyridine (L₂) and 3,5-bis(trifluoromethyl)mercaptobenzene (L₃). The reactions of each ligand with every cluster under mild conditions result in the oxidative addition of the thiol moiety giving clusters of general formula [Ru₃(µ-H)(µ-SR)(diphosphine)(CO)₈]. The reaction of L₁ and L₂ with 1 under stronger conditions produced the scission of S-C of the pyridine ring, giving an orthometallated pyridine ring and a sulfide group, and the rupture of one P-C bond gave a phosphide group. In addition, the hydrogenation of the double bond of the dppee diphosphine took place, and the rupture of two Ru-Ru bonds were observed. Fig. 1a. In addition, the thermal hydrogenation reaction of clusters [Ru₃(µ-H)(µ-SR)(diphosphine)(CO)₈] gave the scission of S-C and C-P bonds to obtain sulfide groups coordinated to three metallic centers by the oxidative addition of molecular hydrogen. The presence of fluorinated substituents on the dfppe diphosphine facilitate the rupture of the P-C(aryl) bond to give a compound with a phosphide group, Fig 1b.
Molecular photodissociation and photoinduced ring opening in the gas and solution phase

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Azoles and phenols are common chromophores in the nucleobases and the aromatic amino-acids that dominate the near UV absorption spectra of many biological molecules. π*←π excitations are responsible for the strong UV absorptions, but such molecules also possess excited states formed from σ*←π electron promotions. The πσ* states generally have much smaller absorption cross-sections, but can have profound photophysical importance. We have used photofragment translational spectroscopy (PTS) methods and complementary ab initio calculations to explore πσ*-state mediated bond fission processes following UV excitation of many heteroaromatic molecules in the gas phase, and ultrafast pump-probe studies to explore analogous processes in a range of solvents. This presentation will: (i) summarize photophysical insights gained from PTS studies of pyrroles, phenols and thiophenols in the gas phase, (ii) illustrate the extent to which such knowledge can guide our interpretation of ultrafast pump-probe transient absorption studies.
of the UV photofragmentation of similar molecules in solution, (iii) show how such solution phase studies offer a means of exploring \( \pi \sigma^* \)-state mediated ring-opening of heterocycles like thiophenes and pyrones and (iv) describe recent attempts to study the dynamics of such photoinduced ring-opening processes in the gas phase.

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Accurate models for phosphorus organocatalytic design

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Since the last decade scientists have contemplated the possibility of using theoretical assets to predict the outcome of chemical reactions. Therefore, crafting theoretical models capable of reproducing experimental findings with a high degree of confidence has tremendous impact in the future of guided synthesis. This paper presents to the audience state-of-the-art approaches in modern computation aiming to shed light on the reactivity of phosphines, phosphoranes and phosphine oxides in catalytic Wittig reaction, Appel reaction and Staudinger/Aza-Wittig reaction (figure below). Catalytic Wittig reaction is the simplest and cheapest way to achieve versatile olefinic blocks. CW protocols have been proposed and optimized for different ylides, but synthesis alone has not been able to overcome challenges in stereoselection during the last 60 years. An apt example is represented by the inertia of stabilized ylides in delivering Z-diastereopure olefins. Though catalytic Appel reaction is an easy way to generate alkyl halides from alcohols or to resolve racemic mixtures of phosphine oxides, a full computational investigation is still lacking nowadays. The reactivity of ubiquitous intermediates like phosphoranes has been compared for ylides and nitrogen-based phosphoranes. We hereby propose a
theoretical approach aimed to deepen the understanding of phosphorus reactivity:

**Kinetic Models:** thermodynamic data, extrapolated from electronic structures (M06-2X-D3/def2-TZVP/SMD) and integrated deterministically via simple kinetic laws, mimic the complex network of equilibria underlying the reactions. The rate determining step(s), the importance of fast reduction cycles and, when applicable, the diastereoselection principles are discussed.

**Statistical analysis (for Wittig):** principal component analysis, applied to a statistical sample of catalytic analogs to 3-methyl-1-phenyl-phospholane 1-oxide with diverse electronic/steric profiles, aims to uncover the catalytic motifs behind E/Z-diastereoselective experimental footprints.

Schematic representation of studied reactions

**ABCChem 86**

**Catalysts to the rescue for destroying and monitoring pesticides: from waste to nanomaterials**

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Chemical security has been a global concern because of the imminent risks involved. The abusive and indiscriminate use of pesticides and in the addition the stockpiles of prohibited substances (including chemical warfare) requires effective methodologies to destroy these stocks efficiently. The monitoring of these toxic agents is also of interest. Specifically, organophosphate is a class of pesticides with high toxicity and known stability. Our group has been engaged in developing novel catalysts targeted for degrading organophosphates, hence detoxifying it. The focus is to promote fast and highly efficient catalytic processes. We use different scaffolds from nanomaterials to waste, by chemically modifying with reactive functional groups: imidazole, thiol and hydroxamate. Chemical functionalization is a promising tool for modulating properties and broadening applications of different materials. By the nanomaterial perspective, the feasibility in obtaining the material as thin film or with magnetic property guarantees easy recovery and reuse. In addition, nanomaterials are multifunctional enabling promising applications for sensors. Moreover, waste has been used to anchor groups and have shown prominent activity towards toxic pesticides. We emphasize the reuse of rice husk, one of the greatest agricultural waste and also arabic gum, a tannin industrial waste. This is environmentally friendly since we reuse waste for solving a severe problem involved with chemical security. In addition, we report the development of sensors for monitoring organophosphates. For example, a cheap and homemade colorimeter have been developed and used to analyze the presence of pesticides in only 5 min, that could be promising for field analysis. In summary, we present various catalysts that are able to degrade pesticides, with rate enhancements of up to $10^7$-fold and that were recycled with 3 cycles without significantly losing activity. A thorough mechanistic study is also conducted to confirm the preferable reactions pathways. Further, thin films of the nanocatalysts were applied as surface-enhanced Raman spectroscopy substrate sensor, thus present multiple functionalities: degrades and monitors.
Electrostatics is often described as a mature scientific area but the literature shows many poorly-understood electrostatic phenomena in important systems, from the atmosphere to chemical reactors and living organisms. This is further evidenced in several experiments and effects that have been qualitatively known for a long time but do not have reasonable explanations within the current models and theories for the structure of matter. This situation has been changing substantially since the late 1990s when new experimental methods yielded information on different systems. Efforts to interpret recent data are converging towards wholly new views on charge partition and the formation of domains with charge excess in nearly every material system in our environment. A decisive factor in this situation is the recognition of the importance of chemical reactions in charge build-up and dissipation in any system, including metal and semiconductor solids supported on insulators. This presentation reviews experimental findings and the working hypotheses based on chemical events that are explaining many hitherto challenging electrostatic phenomena. A very recent finding is the conversion of mechanical energy to electricity, by periodically stretching rubber materials. For instance, silicone rubber tubing shows periodic and reversible electrostatic potential variations between ca. -3 kV and 0 V, in phase with the tubing length. Potential change depends on the elastomer used: the stretched natural rubber is positive and becomes negative when relaxed, different from silicone. Every other elastomeric material that was tested also showed periodic potential but following different patterns. The potential oscillation amplitude decreases when the relative humidity lowers from 65 to 25%, as in hygroelectricity. These results are discussed considering piezo-, flexo- or triboelectricity but they are consistent with a mechanism based on the chemical and morphology changes in rubber surface, followed by a change in the surface concentration of H⁺ and OH⁻ ions adsorbed with atmospheric water. Similar variations may occur in other systems (both inert and biological).
Concluding, the recognition and exploration of chemical events in electrostatic phenomena offer many leads to scientific discovery and to new technologies, relevant to the energy, safety, health and environmental engineering areas.

ABCChem 88

Topical drug delivery into skin probed by label-free spectromicroscopy

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Topical drug delivery into skin probed by label-free spectromicroscopy is reported. The role of drug formulations and polymeric nanocarriers is evaluated regarding their penetration into deeper skin layers. Selective and high resolution detection (spatial resolution: <100 nm) of drugs and drug nanocarriers is accomplished by X-ray microscopy. We report on recent results on the penetration of the anti-inflammatory drugs dexamethasone and tacrolimus that are topically applied to human and murine skin samples ex vivo. Drug solutions, formulations, as well as drug-containing nanocarriers (core-multishell nanocarriers and pNIPAM-nanogels) have been investigated regarding their skin penetration, reflecting temporal and local changes in drug distributions as a function of depth. Nanocarriers can only penetrate the stratum corneum, but not into the viable epidermis. High spatial resolution studies allow us to determine the role of nanocarriers altering the drug penetration properties. In the case of nanogels they also facilitate drug penetration into corneocytes. In addition, the influence on drug penetration of damaged skin barriers is
investigated, which is either induced by mechanical impact (tape-stripping) or by inflammatory skin diseases (imiquimod-induced psoriasis in murine skin). The experimental results are modeled by the diffusion of drugs using Fokker-Planck equation. This provides evidence for a diffusion and free energy barrier that controls the drug transport via the stratum corneum into the viable epidermis. Complimentary results from stimulated Raman microscopy are briefly reported allowing us to derive 3-dimensional maps of the compounds under study. Focus of these studies is put on the distribution of lipids and proteins, which are affected by drug delivery processes depending on the drug formulation penetrating the skin samples. Finally, recent results from optical near-field microscopy are reported, which yield after resonant excitation in the infrared regime high spatial resolution of <10 nm, so that details of the penetration of drugs in the stratum corneum are visualized. These results can be correlated with high resolution electron micrographs, which allows us to reach a molecular understanding of drug penetration from label-free spectromicroscopy.

ABCChem 89

Investigation of calix[n]arene as drug carriers for tyrosine kinases inhibitors by theoretical methods

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Tyrosine Kinase Inhibitors (TKI’s) have proven to be effective for the treatment of lung cancer, chronic myeloid leukemia and gastrointestinal tumors. These inhibitors are basically actuate by impeding phosphorylation and breaks the communication signals within the cell to deregulate the cellular activity. Therapeutic use of first generation TKI’s i.e., Imatinib (Gleevac™) is continuously increasing which led to the development of drug resistance. This adverse scenario prompted the investigators to think for other alternatives that can provide improved ailment against the tyrosine kinases. Analysis performed on possible second generation TKI’s alternatives (Gefitinib, Regorafenib, Iapotinib, dasatinib and Sunitinib) show bioavailability and other pharmacokinetics discrepancies in early clinical testings. Therefore, aiming to improve the bioavailability profile of Tyrosine kinase inhibitors (TKI’s), we have proposed the drug carrier based on calix[n]arene macrocycles.
A total of 72 inclusion complexes with the upper rim functionalized calix[n]arene (n=4,5,6,8) via appended groups SO$_3$H, tert-Butyl ($t$-Bu), iso-Propyl ($i$-Pr), COOH, C$_2$H$_4$OH, and C$_2$H$_4$NH$_2$ were theoretically studied for the most probable inclusion complex. The predominantly involved selective interactions were explored by Density functional theory, complementary-shape docking based method, Molecular Mechanics-Generalised Born Molecular Volume (MM-GBMA) and Molecular Dynamics calculations. Through this work, we will reveal the important functionalities that are essential for the designing of respective drug carrier for TKI’s.

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**Synthesis and characterization of biogenic selenium nanoparticles with antimicrobial properties made by Staphylococcus aureus, methicillin-resistant Staphylococcus aureus (MRSA), Escherichia coli and Pseudomonas aeruginosa**

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Antimicrobial resistance is a global concern that affects to more than 2 million of people each year all around the world. Thus, new methodologies for the treatment of bacterial infections are needed. One of the most promising approaches might come from metallic nanoparticles since bacteria cannot develop resistance to these nanostructures. For years, metallic nanoparticle synthesis processes are well studied. However, they are often accompanied by significant drawbacks such as cost, extreme processing conditions, requirements of special characterization techniques, and toxic waste production. In this work, we explored the environmentally safe synthesis selenium nanoparticles, which have shown promise in killing bacteria. Using Escherichia coli, Pseudomonas aeruginosa, Methicillin-resistance Staphylococcus aureus and Staphylococcus aureus, selenium nanoparticles with sizes rounded 90-150 nm were synthesized under standard conditions using an environmentally-safe approach. Nanoparticles were characterized using Transmission Electron Microscopy (TEM), Energy Dispersive X-Ray (EDX) to determine the chemical compositions and ICP-
MS to validate the chemistry within the samples. Selenium nanoparticles were also characterized and tested for their ability to inhibit the bacterial growth in different degrees. A decay in the bacterial growth was achieved against both Staphylococcus aureus and Escherichia coli in a range of nanoparticle concentration from 25 to 250 µg/mL, showing no significant cytotoxicity effect when they were cultured with human dermal fibroblasts (HDF) cells for 24 hours. Therefore, biogenic selenium nanoparticles made by bacteria were showing as synthesis approach which overcomes the drawbacks and limitation of synthetic methods.

ABCChem 92

CO2-Switchable materials and surfaces

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Industrial inefficiencies, causing wastage of energy and materials, are often the result of failures to resolve time-separated conflicting requirements. For example, a drying agent needs to strongly absorb water during use, but during regeneration it needs to easily release the water. Stimuli-responsive materials can solve such conflicting requirements, such as a drying agent that switches from a hygroscopic form to a water-repelling form. Of all of the stimuli that can be used to trigger changes in stimuli-responsive materials, CO2 is particularly benign, easy to remove, and does not require the material to be conductive or transparent. This presentation will describe how CO2-switchable materials can solve a variety of environmental problems such as:

- The performance of oil-based paints is far superior to that of water-based paints but the environmental impact of organic vapour emissions is problematic. How can we get the performance without the environmental impact?
- Liquid chromatography uses solvent gradients or solvent mixtures to control retention times and improve separations. How can we obtain such control using only water with no organic solvents or salts added?
- One third of the world’s natural rubber crop is thrown away because it coagulates before it can be processed. How can the coagulated rubber be converted back into latex form without using volatile organic solvents?
Rapid removal and recovery of phosphorus from water using a nanoiron sponge

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Excess nutrients (phosphorus, nitrogen) in water leads to algal bloom, one of the most severe problems associated with surface water. Phosphorus is the limiting nutrient to control algal growth; therefore, removing phosphorus from surface water is a major strategy to prevent algal bloom in lakes and other water bodies. In this study, we present the development and evaluation of a NanoIron sponge as a phosphorus sorbent. Iron nanoparticles are grown directly on a polyurethane sponge using a proprietary technology involving thermal reduction. The results demonstrate that the NanoIron sponge can remove over 99% of phosphorus from water within 5 min. After passing the solution containing 10 mg L\(^{-1}\) phosphorus through the NanoIron sponge, phosphorus concentration dropped to the undetectable level (<2 µg L\(^{-1}\)), below the US-Environmental Protection Agency (US-EPA) limit. The NanoIron sponge has an uptake capacity of over 116 mg g\(^{-1}\), up to 4 times the capacity of commercially available phosphorus sorbents. The used sponge can be regenerated and 100% of phosphorus recovered by simple immersion in the regeneration solution. Furthermore, the sponge exhibits antibacterial properties against cyanobacteria, which prevents biofouling and thus allows a long-term use of the sponge in real-world conditions.

Mixed oxides as novel recyclable catalysts for water treatment by advanced oxidation processes
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Loading of nanomaterials of metal oxides and mixed metal oxides on silica, alumina and various novel supports has received significant attention in the recent years, as such materials, can demonstrate impressive catalytic activity in organic synthesis and other green reaction protocols. Heterogeneous catalysts offer wide range of benefits including, easy recovery for reuse, thermal stability, shape selectivity, with scope to modify their structure and acidic/basic properties. Due to their advantages, heterogeneous catalysts are preferred choices for value added conversions and one-pot synthesis comprising multicomponent reactions. The protocols based on metal oxides as catalysts are eco-friendly with atom efficiency and enhanced selectivity towards targeted products giving excellent yields many toxic chemicals used for varied purposes, in the chemical, agro and pharmaceutical industries are non-biodegradable, due to their nature and characteristics and persist in aquatic systems for prolonged periods, propelling wider health and hygiene challenges. Based on our experiences and successes, the details of various advanced oxidation processes (AOPs) for degradation of non-biodegradable and refractory chemicals and polychlorinated organics, by employing using recyclable mixed oxides and nanomaterials as heterogeneous catalysts and photo catalysts will be described, with focus on the water remediation from toxic pollutants.
In recent years, nanotechnology has shown continuous growth and a considerable increase in applications and potential benefits. It has been demonstrated that the inclusion of nanomaterials improve the efficiency of thermal enhanced oil recovery (EOR) processes through the upgrading of the physicochemical properties of the oil. Accordingly, the aim of this work is to synthesize, characterize and evaluate supported tungsten and nickel oxide nanoparticles for adsorption and catalytic performance on air/steam gasification of Colombian asphaltenes. Silica nanoparticles of 12.5 nm in size were synthesized using the sol-gel method and were characterized by size,
surface area, FTIR, point of zero charge, and thermogravimetric analysis (TGA). Tungsten and/or nickel oxide nanoparticles were synthesized over the silica nanoparticles surface following the incipient wetness technique, using three different solution concentrations and calcination temperatures: 1, 3, 5% wt and 350, 450, 650°C, respectively. X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and N2 physisorption at 77 K were used to characterize the crystal size and surface area of NiO and/or WO$_3$-supported-on-SiO$_2$ nanoparticles. Results demonstrated the enhancing of asphaltenes decomposition by the action of the nanoparticles due to the reduction in the decomposition temperature of the asphaltenes up to 200°C in comparison with the system in the absence of nanoparticles, and that the synthesis temperature plays an important role in the adsorptive and catalytic activity of the materials, possibly due to geometric and electronic effects on the surface and different metal-support interactions. The effective activation energies were estimated with the iso-conversational OFW method, this energy was found to be related to adsorption affinity and interactions of asphaltenes over the nanoparticles surface. Finally, with the results observed in this study, the efficiency of thermal EOR methods will be increased leading to the obtained of oils with higher quality.

**ABCChem 98**

**Phthalocyanine-cobalt ferrite based nanocomposites as bifunctional photocatalysts in water purification**

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The photocatalytic oxidation of pollutants through advanced oxidation process (AOP) using molecular oxygen and a photosensitiser is an important strategy for pollution control, since it does not liberate any additional pollutants. The application of AOP is considered as one of the emerging green technologies for water treatment, due to the possibility of using two natural resources: dissolved oxygen and solar energy. The AOP method is based on the use of reactive oxygen species (ROS) in oxidizing pollutants in water. In this work, nanocomposites based on two photocatalysts; a zinc phthalocyanine (Pc) and glutathione capped cobalt ferrite magnetic nanoparticles (GSH-CoFe$_2$O$_4$ MNPs) (Fig. 1) are used as bifunctional photocatalysts for photodecomposition of methyl orange and photoreduction of Cr(VI), common water pollutants. Due
to the presence of the magnetic nanoparticles, the photocatalysts in the work also offer an added advantage of magnetic regeneration of the photocatalysts and hence reusability.

![Diagram of conjugation between a Phthalocyanine (Pc) and magnetic nanoparticles (MNP)](image)

Fig. 1 – Representation of the conjugation between a Phthalocyanine (Pc) and magnetic nanoparticles (MNP)

**ABCChem 99**

Amine-functionalized magnetite nanoparticles as a reusable nano-adsorbent for the removal of heavy metal ions

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The impacts of heavy metal pollution are severely harmful due it being incapable of biodegradation and are thus persistent in the environment. Many methods have been used in this regard, including chemical precipitation, ion exchange, membrane technologies, coagulation, reduction, biosorption, filtration, adsorption, reverse osmosis, granular ferric hydroxide, electrolysis, and surface adsorption. Most of these methods have economic and technical disadvantages to achieve the discharge standards.

In this work, we aim to take a further step in the application of magnetic nanoparticles on a solid support as highly efficient, recoverable, stable, and cost-effective catalyst which prepared by an environmentally friendly procedure. We synthesize organo-functionalised magnetic nanoparticles on solid supports for the removal of heavy metal cations in wastewater. A core-shell magnetic nanostructure was prepared by performing hydrolysis in alkaline solutions using tetraethylorthosilicate (TEOS) and functionalising the silica coating with a terminal linker which was further modified with organic molecules such as salicylaldehyde for further increase in the adsorption capacity towards metal cations.

The characteristics of these functionalised nanoparticles were assessed at various stages during the production process using (FTIR), (HR-SEM), (HR-TEM) and (XRD). These materials applied as efficient and economical adsorbents for green removal of lead (II) ions from water. Magnetic nanoparticles were strongly influenced by an external magnetic field and resulted in the separation from the aqueous media within one minute. To its adsorption capabilities, the effect of dosage of adsorbent, contact time, initial pH and initial concentration of lead ion are scrutinized. Owing to high adsorption capacity of these catalysts, the lead ion can be removed considerably, up to 80 %, and the adsorption reaches equilibrium within 10 minutes under optimized conditions. Regeneration and reusability of these adsorbents were studied and able to regenerate without significant adsorption capacity loss.

ABCChem 100

Chemical potential and chemical hardness in charge transfer processes
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The chemical potential (\( \mu \)) and the chemical hardness (\( \eta \)) are very important response functions that allow one to describe in a simple, but conceptually meaningful, manner charge transfer processes for a wide variety of chemical interactions. In density functional theory of chemical reactivity these two quantities are identified with the first (\( \mu \)) and the second (\( \eta \)) derivatives of the energy with respect to the total number of electrons at constant external potential (usually the potential generated by the nuclei). Thus, through the use of a smooth quadratic interpolation between the \( N_0 - 1 \), \( N_0 \) and \( N_0 + 1 \) electron systems (\( N_0 \) is an integer), one finds that \( \mu = -(I+ A)/2 \) and \( \eta = I- A \), where \( I \) and \( A \) are the vertical first ionization potential and electron affinity, respectively. It may be seen that (\( \mu \)) and (\( \eta \)) are global quantities that characterize the molecule as a whole, and therefore, from the values corresponding to each of the interacting species when they are isolated, one can analyze the global charge transfer between them, when they are placed together. Additionally, through the use of the chain rule for functional derivatives one can derive the local reactivity indicators that provide information at the local level of the charge transfer processes. In this presentation we will analyze the global and the local situations and will show through several examples the usefulness of the present approach to characterize charge transfer processes between chemical species.

ABCChem 101

Simultaneously determination of traces Cd\(^{2+}\) and Pb\(^{2+}\) using a new hybrid nanocomposite of bismuth nanoparticles-carbon nanofibers/ionic liquid

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During the last decade, nanocomposites formed by combining different materials such as carbon nanomaterials (CNMs), metals nanoparticles (MNPs), and ionic liquids (ILs) have attracted considerable attention in the development of a new electrochemical sensors with a high-performance. Monitoring and
control of environmental pollution are the fields that these nanocomposites have been widely used as sensors to analyze a variety of pollutants including heavy metals ions. Cadmium (Cd\(^{2+}\)) and lead (Pb\(^{2+}\)) ions are the most toxic environmental pollutants even at a very low concentration exposition. Due to their high toxicity, a considerable effort have been made to develop a simple, a highly sensitive and selective analytical methods for the analysis of traces Cd\(^{2+}\) and Pb\(^{2+}\) [1-2].

In the present work a new nanocomposite electrode has been fabricated by combining the unique properties of bismuth nanoparticles (BiNPs), CNFs and the ionic liquid 1-ethyl-3-methylimidazolium bis(tri-fluoro-methyl-sulfonyl)imide, [EMIM][NTf\(_2\)]. The obtained modified electrode have shown very attractive electrochemical performances compared to conventional electrodes using graphite and mineral oil, notably improved the electrical conductivity and the stability. The interface properties of the fabricated electrode were characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and the morphology was examined by scanning electron microscopy (SEM-FEG). This new nanocomposite has demonstrated interesting electrochemical performances for the determination of traces Cd\(^{2+}\) and Pb\(^{2+}\), in addition a better sensitivity and selectivity.

ABCChem 102

Nano biosensors for dengue virus detection

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Dengue virus (DENV) is an arthropod-borne virus transmitted primarily by Aedes mosquitoes and is major cause of disease in tropical and subtropical regions. Since the 1970s, it has spread to urban and semi-urban areas in over 100 countries and the incidence of dengue infections throughout the world has increased 30-fold. More than 3.6 billion people are at risk and an estimated 390 million infections occur annually. With no vaccine or specific treatment, early detection plays a significant role in decreasing fatality rates. Dengue infection has no pathognomonic clinical features, thus diagnostic tools are essential for diagnosis.

We report two nanobiosensors based on semiconducting single-walled carbon nanotubes (sSWNTs) chemiresistor functionalized with bioreceptors for the rapid,
facile, low cost, point-of-care/use detection of DENV. The first biosensor detects whole DENV using Heparin, an analog of the heparan sulfate proteoglycans that are receptors for DENV, as a bioreceptor for detection of whole DENV virions. This permits detection of DENV virions from a variety of viral culture-compatible samples; such as fluid or tissue samples from monkeys, vector mosquitoes, and humans. In the second biosensor anti-dengue non-structural protein (NS1) monoclonal antibodies were used to detect DENV NS1, a clinically accepted biomarker for DENV infection, for early detection and diagnosis of the disease in Aedes mosquitoes and human saliva. The biosensors were selective and sensitive for their target analyte over the clinically relevant concentration range with detection occurring in only 10-20 min.

**ABCChem 103**

**New paper/polymer hybrid microfluidic microplate for rapid quantitative detection of multiple disease biomarkers**

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Enzyme linked immunosorbent assay (ELISA), is one of the most widely used laboratory disease diagnosis methods. However, performing ELISA in low-resource settings is limited by long incubation time, large volumes of precious reagents, and well-equipped laboratories. Herein, we developed a simple, miniaturized paper/PMMA (poly(methyl methacrylate)) hybrid microfluidic microplate for low-cost, high throughput, and point-of-care (POC) infectious disease diagnosis. The novel use of porous paper in flow-through microwells facilitates rapid antibody/antigen immobilization and efficient washing, avoiding complicated surface modifications. The innovative funnel-shaped microwells allows simple transfer reagents to multiple microwells thus avoiding repeated manual pipetting and costly robots. Results of colorimetric ELISA can be observed within an hour by the naked eye. Quantitative analysis was achieved by calculating the brightness of images scanned by an office scanner. Immunoglobulin G (IgG) and Hepatitis B surface Antigen (HBsAg) were quantitatively analyzed with good reliability in human serum samples. Without using any specialized equipment, the limits of detection of 1.6 ng/mL for IgG and 1.3 ng/mL for HBsAg were achieved, which were comparable to commercial ELISA kits using specialized equipment. We envisage that this simple
POC hybrid microplate can have broad applications in various bioassays, especially in resource-limited settings.

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Study of the substituent variation and hydrogenation of 5-X-H$_2$salbu ligand in Cu(II) coordination compounds and their effect on biological activity

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The salen type compounds have been studied due to their generated interest in chemistry and biology. A main characteristic of these ligands is their versatility because steric and electronic properties can be modulated using different amine and carbonile precursor.

In the present work, compounds with Cu(II) and H$_2$salbu ligands were synthetized, this ligands are derivate of H$_2$salen, the differences between them are the four methylene bridge groups in the diimine group. The ligand increases the flexibility and the copper will present a distortion on its geometry. The ligand’s hydrogenation in H$_2$salbu will confer a major flexibility; this change will generate a modification in copper environment.

Ten new copper(II) compounds with 5-X-H$_2$salbu and 5-X-H$_4$salbu ligands were synthesized modifying the substituent R in 5 posicion where R is MeO, Me, H, Cl and NO$_2$. In the same way, a reduction of the imine group was carried out for the other 5 compounds.

It was found that the geometry of compounds with H$_2$salbu ligands is square planar distorted towards tetrahedral due to the impediment of four-carbon chain linking the nitrogen atoms presence. For the compounds with hydrogenated binders present a higher distortion in their geometry. This can be observed in the results of EPR and X-ray crystallography. Likewise, some compounds were found to form dimers in which the ligand chain opens and coordinates to two copper atoms in a µ bridge like.

The modification of the copper reduction potential was studied by cyclic voltammetry, it was found that the compounds with electro-atractor substituents favor copper reduction while the electro-donors do not favor it. For the Cu(5-X-H$_4$salbu) compounds, the reduction process is more favored than in Cu(5-X-H$_2$salbu), because the hydrogenation of the binder generates a higher flexibility generating a major distortion to the tetrahedron, stabilizing the Cu(I) species.

The biological activity of the coordination compounds was tested in different tumor lines, in HeLa, A549, LS180 and ARPE-19. The compounds in generally are more active in HeLa and the hydrogenated compounds are the most active. Recently, these compounds have been tested in Leishmanial, finding that the new ligand and the coordination copper compounds show an important activity against these parasites obtaining IC$_{50} < 0.5$ μM.
Structure-based design and SAR studies of ATP citrate lyase inhibitors as anticancer agents

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ATP citrate lyase (ACL) plays a critical role in generating cytosolic acetyl CoA, a key building block for de novo fatty acid and cholesterol biosynthesis. ACL is overexpressed in numerous cancer cells and considered as an attractive target for developing anticancer drugs. Structural analyses and MD simulation of the cocrystal structure of citrate-ACL led to our identification of an allosteric hydrophobic cleft adjacent to the charged citrate-binding domain of ACL. We implemented a structure-based approach to identify and optimize novel furan and emodin types ACL inhibitors that target specifically this previously unrecognized allosteric binding site. In the emodin series, we synthesized halogenated derivatives, aryl and amine derivatives for structure-activity relationship (SAR) studies. Among them, compound 1e (1,3,8-trihydroxy-2,4-dibromo-6-methyl-anthraquinone) showed IC₅₀ of 2.9 µM in the ACL enzymatic activity assay and Kd of 0.65 µM in the ACL binding assay. Further, 1e dose-dependently inhibited the proliferation of A549 lung cancer cells and significantly reduced the stemness of cancer cells as measured by 3D tumorsphere and FACS analyses. In the furan series, substituted 2-furoic acids and 3-benzofuroic acids were identified as ACL inhibitors via a virtual high-throughput screening (vHTS) of a focused library of 2,000 compounds. Remarkably, the hit rates of the vHTS protocol are 45% - 11 out of the 24 compounds selected from the vHTS potently inhibited ACL enzymatic activity. The IC₅₀ of the most potent furan derivatives ranged from 2 to 10 µM. We will discuss in details the SAR results, in silico protocols, biophysical characterizations, and DMPK analyses of the lead compounds. In addition, we will also provide an update on our on-going efforts in broad cancer cell lines.

Synthesis and characterization of mixed copper (II) compounds with N₂O tridentate Schiff base ligands with possible biological activity
In this paper, we synthesize a series of mixed copper (II) compounds using as main ligand a tridentate asymmetric Schiff base, with donor atoms type N₂O, derived from monocondensation of N-methyl ethylendiamine/propylenediamine with R-substituted salicylaldehydes (HL₁), where R = H, MeO, N₂O. Cationic complexes with formula Cu(L₁)NO₃ were prepared by refluxing Cu(NO₃)₂·2.5H₂O and HL₁, in a 1:1 ratio, in methanol for 1 h. The molar conductance data reveals that these compounds are electrolytes in methanol solution. Single-crystal X-ray determinations show a distorted octahedral geometry with the Cu atom at the center of the complex, three of the equatorial positions occupied by two donor sites of N-azomethine, N-amine and one O atom of deprotonated phenol from ligand HL₁, and the remaining positions occupied by O atoms from the nitrate ions. The reaction between these compounds, Cu(L₁)NO₃, and neutral secondary ligand 1,10-phenanthroline or 4,4'-dimethyl-2,2-bipyridine (L₂), resulted in mixed copper (II) compounds with general formula [CuL₁(L₂)]NO₃, characterized by elemental analysis, infrared spectroscopy, UV-vis spectroscopy, cyclic voltammetry, conductivity, magnetic susceptibility, and single-crystal X-ray determinations. Biological tests are in process.
Synthesis of quinazoline-2,4,6-triamine derivatives and evaluation of their antiproliferative activity on cancer cell lines

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A series of quinazoline-2,4,6-triamine derivatives were synthesized and evaluated for their in vitro antiproliferative activity. The synthesis of target compounds (1–5) began with the cyclocondensation of 5-nitroanthranilonitrile with guanidine hydrochloride led to 6-nitroquinazoline-2,4-diamine; which was treated with acetic anhydride followed by hydrogenation to furnish N,N'-(6-nitroquinazoline-2,4-diyl)diacetamide. Condensation of diacetamide with substituted benzaldehydes gave the corresponding imines. The imine group was reduced to yield the intermediate secondary amine. The condensation procedure was then repeated with a second aldehyde for the formation of the corresponding tertiary amine. Finally, the diacetamides were hydrolyzed to yield 1–5. The results of in vitro biological activity demonstrated that N¹-(4-methoxyphenyl)methyl]-N¹-{4-(trifluoromethoxy)phenyl}methyl]benzene-1,4-diamine (4) and N⁶,N⁶-bis[(4-(trifluoromethoxy)phenyl]methyl]quinazoline-2,4,6-triamine (5) showed broad spectrum antiproliferative activity with mean GI₅₀ of 73, 18, 34 mM on HCT15, HeLa, MCF7, respectively. Additionally, studies of application of compound 5 with acetylcysteine were carried out in order to explore the possible cytoprotective role of this amino acid to the cytotoxic action of 5.

Study of mixed chelate coordination compounds (Casiopeínas®) with DNA one of several targets of these type of compounds

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In the last decades, the search of new compounds as antineoplasticos agents based on essential transition metals, has called the attention of investigators for the design, synthesis and the evaluation of new drugs that have a smaller toxicity but greater biological activity with respect to antitumor like well-known platinum compounds. Antitumoral Casiopeinas® are some of the earlier representative coordination compounds of copper (II) with good potential, since they have shown biological activity on a great amount of tumors as much in vitro, as well as has shown to have activity in vivo. With a general formula \([\text{Cu}(\text{N-N})(\text{N-O})]\) \(\text{NO}_3\) or \([\text{Cu}(\text{N-N})(\text{O-O})]\) \(\text{NO}_3\), where \((\text{N-N})\) corresponds to substituted bipyridines or phenanthrolines; \(\text{(N-O)}\) does correspond to α-aminoacidade or peptides, whereas \((\text{O-O})\) corresponds to acetilacetonate or salicylaldehidate. Several hypotheses on the action mechanism have been developed, and these include the generation of reactive species of oxygen (ROS), mitochondrial toxicity by the Fenton reaction that commonly are associated with copper(II) and his complexes, taking to a cellular death by apoptosis. Experimental data suggests these compounds interact directly with the DNA, nevertheless, the interactions and the specific molecular ways of binding clearly are not been established. In this work, the objective is evaluate the molecular attachment modes of 21 casiopeins with different substituents and different ligands with the plasmid DNA PBR322 of E. Coli RRI; persecuted is to find a tendency with respect to the ways of union of 21 Casiopeinas® by different techniques to determine if these are intercalated or have interaction in the grooves of the DNA helix. Additionally it was observed if it exists some correlation between the obtained results and the results of a previous theoretical study of molecular dynamics with of these same compounds with a fraction of dodecamero DNA, where they propose several types of interaction. It was proposed that these types of compounds can interact in 3 ways with the DNA base pairs. Several techniques were used and results are presented.
Tracking heme loading of a protein in live cells by Fluorescence-Lifetime Imaging Microscopy (FLIM)

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Heme biosynthesis is well characterized. The final steps occur in mitochondria but how heme is transferred to heme-dependent proteins is not known, in part due to current technical limitations in monitoring the heme loading of specific proteins in cells. Cytochrome c peroxidase (Ccp1) is a heme-based mitochondrial H$_2$O$_2$ sensor. Labilization of its heme occurs when H$_2$O$_2$ levels spike in respiring yeast. This leads to the activation of catalase A (Cta1), which directly or indirectly receives Ccp1’s heme. To fully understand this unprecedented H$_2$O$_2$-triggered heme mobilization, we selected Ccp1 fused to green fluorescent protein (Ccp1-GFP) as a probe of Ccp1 heme loading in live cells. Heme efficiently quenches GFP fluorescence. In vitro, we find that heme-free recombinant apoCcp1-GFP exhibits a lifetime of 2.86 ns whereas heme-loaded holoCcp1-GFP displays long (2.45 ns) and short (0.96 ns) lifetimes. The fractional amplitude of the short lifetime increases linearly at the expense of the long-lifetime amplitude as apoCcp1-GFP binds heme. Notably, fluorescence lifetimes
are Ccp1-GFP concentration independent unlike fluorescence intensities. Combined our results allow us to estimate by FLIM the heme status of Ccp1-GFP in 2- and 7-day live yeast cells. Our study not only sheds light on the heme status of Ccp1 \textit{in vivo} but also suggests a novel tool for unraveling intracellular heme trafficking.

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\textbf{ABCChem 117}
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\textbf{ABCChem 119}
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\textbf{ABCChem 120}
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\textbf{ABCChem 121}

\textbf{Self-organization phenomena in surface chemistry and precipitation reactions}
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Self-organization is a ubiquitous phenomenon found in natural and anthropic environments. It allows ordered behavior to be created in systems containing many participants, without the need for a specific directive to each one of the elements involved. The global interactions are mediated via self-enhancing (autocatalytic) and inhibitory processes that can give rise to feedback loops. These mechanisms abound in chemical and physical systems originating exquisite patterns and motifs in time and space, as in the case of the acclaimed Belousov–Zhabotinsky reaction. In biology, they are thought to be responsible for complex behavior, such as homeostasis. Overall the understanding and control over self-organized processes is leading to a welcomed expansion in the ways one can synthesize complex materials or run complex reactions. The present contribution describes the emergence of complex behavior in a few selected physical-chemical examples. In acidic solutions, a platinum surface covered with oxides react with small organic molecules producing CO$_2$ and other intermediaries. The pace of reaction is found to be self-accelerating and a mechanism based on the autocatalytic production of platinum free sites is proposed. On another front, interaction between aqueous metal solutions and hydroxides (or sulfides) produce precipitate structures in the form of plumes or tubes. An experimental model system is proposed and studied, to understand the basic phenomena behind self-organized precipitate formation. The two, dissimilar reactions are found to be connected by similar mechanisms which will be discussed in the meeting.

ABCChem 122

Analysis of the adsorption isotherm in optical sensing of ammonia in polyaniline

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A thin film of polyaniline chemically deposited on a basis of transparent glass changes trasmitancia/absorbancia when being exposed to gas ammonia. If we place to the film among a light source, as a light emitting diode (LED), of well-known wavelength, and of a phototransistor coupled optically, this trasmitancia/absorbancia change generates a voltage to the exit of the
phototransistor that can be used like an indirect measure of the concentration of the gas, the temporary behavior of this electric answer has the same functional form of the function that describes the isotherm of Langmuir. Using the method of least squares a function is fitted to the experimental data of voltage and the parameters of this function are determined, it is compared with the theoretical function of the isotherm and it is possible to determine the time in which the rates of adsorption and desorption are balanced, these speeds are also determined. In addition to an analysis of the parameters of the adjusted functions, the adsorption and desorption energies are determined.

ABCChem 123

Determination of pKa value and study of the decomposition of O-ethyldithiocarbonate

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O-ethyldithiocarbonate is a substance that can be used to functionalize polymers and confer it different properties. The pKa value in aqueous solution of its conjugated acid was determined by UV spectrophotometry and it was attempted to corroborate it by potentiometry. The pKa value obtained by UV spectrophotometry was 2.79, using the computational program SQUAD to fit the UV absorption spectra set. By potentiometry a similar pKa value could fit the titration pH/V curve; nevertheless it seems that a decomposition in the pH medium takes place, as it has been reported in the chemical literature.
Potassium O-ethyldithiocarbonate K-EDTC.

Figure. UV Absorption spectra set for EDTC 5 10^{-5} M at several pH values (left) and pH-metric titration curve for EDTC 0.1M (right).

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Electrochemical sensor based on modified carbon paste electrode for carbaryl determination

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Carbaryl (1-naphthyl-1-methylcarbamate) is one of the major active ingredients of many commercial formulations of carbamate pesticides. Due to the toxicity of this compound for the human being and the environment, considerable attention has been focused on the development of novel nonenzymatic electrodes for carbaryl detection.

The modification of the electrode surface can enhance the properties of electrochemical sensor and biosensor by increasing the surface area, improving the selectivity and promoting the electrocatalytic effects. Several materials were exploited in the electroanalytical determination of carbaryl. Nevertheless, some sensors such as zeolite or aromatic diamines polymer-ionic liquid modified carbon paste electrodes have never been used to carbaryl detection. The present work aims to use modified carbon paste electrode for the determination of carbaryl. The development of such sensor has been investigated by voltammetric and electrochemical impedance measurements. The morphological characterization has been done by scanning electronic microscope.

The influence of incorporating zeolite in the sensor platform will be shown. The zeolite enables the selectivity and the electrocatalytic activity of electrochemical sensor by the size selectivity property and the framework structure of zeolite. The response given by carbon paste electrode with and without zeolite has been compared and the influence of the incorporation on surface structure and morphology and on the sensing behavior has been evaluated. This new material presents a good sensitivity and selectivity. Different parameters affecting the determination of carbaryl were studied; such as, zeolite proportion, preconcentration time and pH, DPV parameters. Applications will be illustrated by the sensing of key analyte in tomato samples.

ABCChem 128

Withdrawn
Exploration of the haem detoxification pathway in the malaria parasite \textit{Plasmodium falciparum} in the search for new antimalarials

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During the blood stage of the malaria parasite lifecycle, during which symptoms of the disease are manifested, the organism lives within the host red blood cell and digests most of its haemoglobin, releasing vast quantities of toxic free haem which it needs to dispose of. It does this by converting it to a crystalline form known as malaria pigment or haemozoin. We have shown that at least 90\% of the haem in the most pathogenic of the malaria species, \textit{Plasmodium falciparum}, is incorporated into haemozoin. A number of important past and present clinical antimalarials, including chloroquine are able to inhibit the formation of the synthetic counterpart of haemozoin, \(\beta\)-haematin. More recently, it has been possible to demonstrate that these antimalarials inhibit haemozoin formation and cause a buildup of free haem within the parasite cell itself. The mechanism of haemozoin formation remains uncertain, but studies using neutral lipids have shown that these very efficiently mediate \(\beta\)-haematin formation and inspired the use of neutral detergents as mediators. These advances have prompted a number of efforts to discover new antimalarial scaffolds using high throughput screening and this has not only permitted a break out from the well established quinoline haemozoin inhibiting antimalarials, but has also opened the way to molecular docking techniques that may allow virtual screening for new antimalarials in this class.
A benzimidazole docking into corrugations on the fastest growing face of a β-haematin crystal

**ABCChem 132**

**Nanosystems built through self-assembled nanobuilding blocks: Towards responsive and programmable materials**

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In the last decade, a significant advance took place in materials chemistry. Two key factors of this progress are the development of reproducible nanomaterials synthesis, and the control of self-assembly processes. The combination of these powerful concepts leads to produce multiscale materials with hierarchical architectures, which mimick the complexity of those found in Nature.

Mesoporous materials (MM) with high surface area and controlled mesopore diameter are an example of these complex materials. The combination of sol-gel synthesis and supramolecular templating leads to highly controlled pore
systems that can be “decorated” with organic, biological or nanoscale functions. In the last decade, this field evolved from the mere production of high surface area matrices, to programmable nanosystems, in which confinement effects, responsivity, or collaborative functionality can be imparted into the structure through the control of positional chemistry of different chemical building blocks.

In this presentation, we will illustrate the richness of this emergent field by analyzing the designed synthesis of mesoporous materials made up of Self-Assembled Nanobuilding Blocks, which present finely tuned pore size, connectivity or wall nature. Mesopores can be then modified by small molecular species, biomolecules or polymers, leading to hybrid MTF with an amazing variety of chemical behaviors, from tunable catalysis to light guiding or responsiveness. In addition to synthetic and characterization tools, theoretical models and simulations are essential to understand the complexity of the synthesis paths and the final properties. This in-depth knowledge is key to evolve from materials synthesis to ultimate nanosystems design.

The combination and feedback of synthesis, characterization and modeling leads to pre-designed nanosystems. Plus, each highly controlled mesoporous system is in itself a building block for more complex structures. Confinement, interactions and localized reactivity can be used as topological tools for building nanosystems able to host different chemical or biochemical groups with well-defined positioning. These concepts permit to build tunable catalysts, enzyme cascade hosts, intelligent bioscaffolds, remotely activated nanoparticles, chemical-to-optical transducers or perm-selective membranes. A potentially infinite variety of nanosystems with externally controllable behavior is at our disposal, opening the path to design intelligent matter

ABCChem 133

ACS safety initiatives: Impact on the global chemistry enterprise

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Catalyzed by tragic events at UCLA, Texas Tech University, and Yale, the American Chemical Society has moved forward with initiatives aimed at recognizing the importance of chemical safety to the chemistry enterprise. The
two most significant - adoption of "Safety" as a Core Value of the Society and a mandatory requirement for including safety information in manuscripts (as appropriate) will have major impact on the global chemistry community. This presentation will examine all of the initiatives and discuss their impact on other chemistry societies and how those organizations, and their members, might react.

ABCChem 134

Risk perception in academic laboratories

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In this study, we examined researchers’ risk perception. Due to potential liability and negative impact on an institution’s reputation, details about injury numbers and types are most often not released by universities and colleges. In research laboratories this can result in a false sense of security. The study is based on the analysis of a safety climate survey that was distributed nation-wide in 2012. Our study demonstrates that researchers in academia underestimate their risk when working in a laboratory. Hard and soft facts influencing risk perception as they pertain to the research environment will be discussed. Safety behavior was found to be strongly correlated with how researchers view their risk when working in their laboratories. Principal Investigators and laboratory supervisors did not affect researchers’ risk perception but positively influenced safety behavior alluding to the complexity of the relationship between risk perception and safety behavior. An example from a recent accident investigation will be used to illustrate how a researcher’s risk perception changed when confronted with a different culture of a safety. The impact of safety culture on how researchers view their risk and safety will be discussed.

ABCChem 135

US safety initiatives as influences on global laboratory safety

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US environmental, health & safety regulations have guided lab safety procedures in the US for several decades. This paper will explore how those regulations and numerous non-government initiatives have helped to improve lab safety procedures on a global scale. The American Chemical Society and other scientific organizations in the US have stressed the importance of reducing chemical research risks in academia and industry on a global scale, and numerous resources have been developed to help improve safety information and procedures in other countries.

**ABCChem 136**

**Analyzing academic laboratory accidents to prevent accidents**

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Safety training often relies on a mixture of generalized and research-specific training topics. But can safety training instead be focused on areas of greatest need? The UC Center for Laboratory Safety conducted research on laboratory accidents at UCLA and the ten campuses of the University of California system in order to gain insight on the types of accidents and their rates of occurrence. The objective is to set accidents in academic research laboratories in perspective and guide recommendations for accident prevention. The results highlight deficiencies and successes that can direct improved researcher safety training and an overall improvement in laboratory safety culture.

**ABCChem 137**

**Approaching research and scale-up safety through process-oriented solutions**

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Research safety is often hampered by a mindset that does not think through process conditions which can substantially contribute to an unacceptable risk profile for the experiment or scale-up. We will analyze research incidents where the neglect of process conditions led to unacceptable consequences and introduce a better way of doing research safely.
The role of nanostructured materials in enhancing the photophysical behaviour of phthalocyanines

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Nanomaterials have attracted a great deal of interest since they display properties that are not present in the macroscopic materials. The surface of NPs may be modified with different functional groups for different applications. The combination of phthalocyanines with nanomaterials such as carbon nanotubes, quantum dots, fullerenes, upconversion and metal nanoparticles has been shown to improve their photosensitizing behavior. Phthalocyanines (Pcs) are now well known as photosensitizers for photodynamic therapy (PDT) and photodynamic antimicrobial chemotherapy (PACT). Photophysical properties of interest for Pcs in the presence of nanomaterials include triplet state yields and lifetimes, singlet oxygen quantum yields and nonlinear optical behavior. The various methods for the conjugation of nanomaterials with MPCs, Fig. 1, such as adsorption, covalent bonding by click chemistry or amide bond formation, will be discussed.

The conjugates formed are characterized by several methods including laser flash photolysis, time correlated single photon counting, steady state fluorescence, Raman, X-ray diffraction (XRD), X-ray phoroelectron and UV/Vis spectroscopies. Microscopy techniques such as atomic force microscopy and scanning electron microscopy are also used in characterizing the conjugates.

Fig. 1. Attachment of phthalocyanines to gold nanoparticle (AuNP)
Thorium has been attracted a lot of attentions because of the possibility of its usage as a nuclear fuel instead of Uranium. Thorium is more abundant and generates more power for the same amount of fuel as Uranium. The energy cost from Thorium is even cheaper than coal with less environmental issues than Uranium. Mining and processing of monazite are a source of Thorium, which involves the separation of Thorium from rare earth elements. Industry uses liquid-liquid extraction with tributylphosphate as the chelating ligands. Solid state absorbents, especially mesoporous carbons, are of great interest for metal ion separation since they can be reused with less waste and harmful chemicals. In this study, Wrinkled Mesoporous Carbon (WMC) with surface modification has been prepared and tested as an absorbent for selective recovery of Thorium from rare earth elements. The surface oxidized WMC is highly selective for Thorium absorption. The performance of the WMC is orders of magnitude larger than that of activated carbon, which might due to the high surface area and pore structure as well as the abundance of oxygen functional groups on the
WMC. The WMC also shows excellent absorption capacity for rare earth elements.

**ABCChem 140**

**Holmium based metal-organic frameworks for gas separations and cancer therapy**

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Metal-organic frameworks (MOFs) are highly ordered hybrid organic-inorganic materials with properties such as defined crystallinity, permanent porosity and high surface area. By carefully selecting the building blocks in a MOF, i.e. the metal cluster and the organic linker, it is possible to tailor the specific properties of these materials.

Lanthanide based MOFs have interesting properties due to the nature of the metal node. Lanthanide ions have high coordination numbers and diverse coordination geometries, making it difficult to prepare porous materials. By binding solvent molecules to these ions, along with the organic linker, nonporous extended 3D structures are formed. The removal of the solvent molecules can lead to the formation of microporous framework materials with accessible free metal sites. The presence of accessible coordinatively unsaturated lanthanides in the framework which can act as Lewis acid sites, imparts the MOFs with properties suitable for diverse applications such as drug delivery, photoluminescence, chemical sensing, heterogeneous catalysis and gas adsorption.

The research to be presented focuses on the synthesis and characterization of Holmium based MOFs (Ho-MOFs) and their applications. The crystal structures of three novel Ho-MOFs based on rigid linkers will be described (see images). Since free sites can selectively bind specific gases, membranes with enhanced gas separation properties can be developed. Recent results for gas separations and cancer treatments will be discussed.
Facile fabrication of crack-free large-area 2D and 3D inverse opal films of transition metal oxides

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One of the remarkable properties of monodisperse spherical colloidal particles (PS spheres for instance) is their ability to auto-assemble in periodic structures called colloidal crystals (CC). When the interstitial space between the CC PS spheres is filled with a transition metal oxide (TMO), an opal composite is obtained. Upon elimination of the CC skeleton, a periodic macroporous structure, inverse opal (IO), is obtained. We developed a new, very fast, successful and efficient route for low temperature synthesis of large area crack free 2D IO of TMOs (TiO$_2$, WO$_3$, V$_2$O$_5$, etc.) with a high periodicity macroporous structure. We called this route « dynamic-hard-template infiltration strategy ». It is built upon the formation of 2D assemblies of PS opal structures by the floatation method, followed by the infiltration of TMO guest material in the floating self-assembled 2D PS spheres, thus retaining the opal structure. This is achieved by exploiting the capillary action of the TMO sol which was prepared by careful consideration of colloidal stability. After a PS/TMO opal composite monolayer structure floating over water has been formed, a substrate (rigid or flexible) is introduced under the opal composite monolayer and the solution is sucked out in order to deposit the composite opal monolayer onto the substrate. After drying, a PS/WO$_3$ composite opal monolayer is obtained. To obtain a 2D TMO IO film, the PS spheres template was removed by applying a room temperature solvent treatment. Furthermore, the PS/TMO opal composite monolayers were used as building blocks for the synthesis of 3D TMO IO films in a bottom-up approach. To achieve this, a PS/TMO opal composite monolayer serves as support upon which another PS/TMO opal composite monolayer is added, and so on, one over the other, rendering possible, after removal of the PS spheres template, the fabrication of large area 3D TMO IO films. Similarly, bilayer, and trilayer TMO IOs with large area, having the same pore sizes from layer to layer, can be obtained by repeatedly applying this strategy. This approach also allows control over hierarchical porosity and film thickness by simply changing the diameter size of the sacrificial colloidal template and/or the inorganic precursor used in each layer. The 2D and 3D TMO IO films fabricated with this technique exhibit good electrochemical reversibility, cycling stability, and increased coloration efficiency (CE).

ABCChem 142

Physicochemical properties of metallophthalocyanines when conjugated to magnetic nanoparticles
Metalphthalocyanines (MPcs) are versatile macrocycles that have attracted attention for various applications including as photosensitizers in photodynamic therapy (PDT) of cancer, photodegradation of pollutants, and photodynamic antimicrobial chemotherapy (PACT). For these applications, efficiency at generating singlet oxygen from the excited triplet states of the MPC is essential. MPcs may be linked to magnetic nanoparticles for ease of separation (in PACT and photocatalysis) and for improved triplet state parameters. The work reports on the successful synthesis and chemical linking of carboxylic acid functionalized asymmetric zinc phthalocyanine (ZnPc) complexes to amino functionalized magnetic nanoparticles (AMNPs), Scheme 1. The photophysical and photochemical parameters of linked complexes and the ZnPc complexes alone were then compared in relation to the structural differences of the Pc complexes. High triplet quantum yields ranging from 0.62 to 0.87 when phthalocyanines were alone or linked to AMNPs were obtained.
Nanoparticles, porous materials and capsules are interesting nano/micro system able to entrap desired molecules and act as delivery or imaging species. They can be created using soft species such as gels or polymers or inorganic precursor. In this talk I will focus on silica-based materials able to be destroyed on demand. Indeed the issues related to the use of materials for therapy in living
organism, are their accumulation in vital organs and their slow elimination that often prevent their use in clinical applications. Recently, a new generation of breakable hybrid nanoparticles, able to respond and degrade upon external stimuli (e.g. enzymatic, redox, pH, etc.), have been developed in our group\textsuperscript{1,2}. The insertion of responsive linkers in the framework of these particles, results not only in the destruction and safe excretion of the nanoparticles from the cells, but also in a faster and better delivery of the payloads. Moreover, to expand the breakability properties of this material for other purpose, the possibility to entrap proteins into a breakable silica shell has also been realized in our laboratory\textsuperscript{3}. After careful analysis of the kinetics of release of small molecules, their cytotoxicity and the influence that shape and size can have \textit{in vitro} and \textit{in vivo}, we are currently investigating their use for siRNA release, in devastating diseases such as hepatocellular carcinoma. Some data will be presented to show the potential of the systems.

The implementation of these nanoparticles as active component in hydrogels confers functionalities and elasticity properties to the system. We have shown that the hybrid hydrogels allow the growth and proliferation of mesenchymal stem cells (MSC) that infiltrating into the implant and have effects on the scaffold integration by improving the healing process\textsuperscript{4}. The hydrogels that contain such containers are perfectly biocompatible and can be made fully degradable. Interestingly they can be injected as liquid and are able to solidify in less than 2 seconds in different tissues and organs. Some examples of their use \textit{in vivo} in large animals will be presented.

**ABCChem 144**

**Advancing functional materials for biomedical applications using laser metal deposition**

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Implementing molybdenum into the currently used Ti6Al4V alloy can have a major effect on the biomedical industry. The use of laser metal deposition as an additive manufacturing method used to make hip or other implants could be a way to customize the medical industry for each patient receiving treatment, which would help with their comfort and everyday life. One way of doing this is
by using functionally graded material, where different properties could be obtained in different areas of an implant. Through the surface modification process known as Laser Metal Deposition, Ti6Al4V and Mo can be combined together in powdered form and parts can be made quickly and effectively. Several functionally graded samples were produced, in which there are alternating layers of deposition of Ti6Al4V, 5% Mo, 10% Mo and 15%Mo at a few different laser powers. Scanning electron microscopy and Vickers hardness instrument were used to characterize these alloys and determine properties such as microstructure, grain size and hardness. This research showed that functionally graded materials have superior properties for a variety of different applications, specifically within the biomedical industry. Results will also include some challenges encountered related to etching such functionally graded samples. This work involved US undergraduate students conducting research at South Africa’s centers of excellence.

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**Crystalline carbazole-based rotors as promising organic materials**

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In recent years, the synthesis of molecules that emulate the form and function of macroscopic machines have been the focus of many research groups around the world. Current reports have shown that the motion in some molecular machines, namely rotaxanes, rotors and motors, can be controlled to perform very interesting functions in the condensed phase. Given the interest in this field, this presentation will be centered in our recent progress in the design, synthesis and characterization of molecular rotors that contain peripheral carbazole, an emissive compound commonly found in organic electronics. Due to our design, the synthesized compounds not only show rotary motion within their crystals, but also display interesting sorption and solid-state emission properties. The implications of combining such rapid dynamics and sorption or solid-state fluorescence, might enable potential technological applications, which will also be discussed.
Intramolecular motion in carbazole-based rotors with sorption properties

ABCChem 147

Towards heterobimetallic supported catalysts through a surface organometallic chemistry approach

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Catalysis is widely accepted as an essential tool of sustainable development, improving chemical industry’s competitiveness, while minimizing its environmental impact. The direct activation of strong bonds by organometallic catalysts could substantially impact the feedstock pool for tomorrow’s industry, allowing for the catalytic conversion of abundant raw materials into valuable organic compounds or the direct functionalization of organic products in an atom-efficient fashion.

A current frontier area in organometallic catalysis is cooperative activity between two distinct metal centers in order to foster new transformations not possible with monometallic species. Catalyst stability and robustness is a key feature for success in multimetallic systems, in particular for tandem catalysis where one major issue is catalysts incompatibility - i.e. inhibition of one metal center by the second one - which can be circumvented upon immobilization of the metallic active sites on a solid support. The Surface OrganoMetallic
Chemistry (SOMC) approach has shown to be particularly efficient to afford low-coordinate metal species not achievable in solution, having a well-defined and uniform structure to facilitate establishing reliable structure-activity relationships and featuring unique reactivity. Yet so far heterobimetallic edifices supported at the surface of a material are exceedingly rare and there is no straightforward methodology to isolate such species. This presentation will present our latest research efforts aiming at developing innovative synthetic methodologies based on SOMC to enable the preparation of original heterobimetallic active sites at the surface of oxide materials.

**ABCChem 148**

**Imaging mycobacteria**

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Mycobacteria and related pathogens can cause devastating human diseases, including diphtheria (_Corynebacterium diphtherie_) and tuberculosis (_Mycobacterium tuberculosis_). The increased dissemination of infectious diseases and the rise of the antibiotic resistance are spurring efforts to understand how these species build and maintain their protective cell envelope. The mycobacterial cell envelope is constructed from saccharide and lipid building blocks not found in human hosts. It is radically different than that of even other Gram-positive bacteria. Mycobacteria use unique building blocks combine to assemble a barrier that is durable, largely impermeable, and dynamic. These attributes facilitate their survival. We are exploring key enzymes involved in mycobacterial cell envelope construction to facilitate the generation of new diagnostics and anti-infective agents. To this end, we have used chemical synthesis to assemble NMR and fluorogenic probes that co-opt the biosynthetic machinery and can be used to detect mycobacteria and image mycobacterial cell division in real time.

**ABCChem 149**

**Green Chemistry: A tool to sustainable development in Africa**

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With the increasing human population, industrialization, environmental concerns and depletion in supply of nonrenewable resources, Africa needs to develop new process routes, synthetic methods, analytical tools and policies that are more affordable, reliable and safer. Green chemistry can play a pivotal role in making this a reality with sustainable path that meets current scientific and technological development without compromising the progress and success of future generation. The fundamentally attractive concept of green chemistry is solvent free reactions. These are interesting alternative approach, mainly when this condition eliminates the use of a solid support or solvent from reaction. When less waste is generated, environmental compliance casts go down while treatment and disposal become unnecessary.

In our studies, we have developed a route for solvent free hydroxylation of the methyl esters from underutilized seed oil in the presence of cetyltrimethylammonium permanganate which also covers the synthesis of alkanolamide. The process was monitored with FTIR and NMR. Further evaluations with biomass in environmental studies were characterized using X-Ray diffractometer, TG, SEM, Particle size analyzer, CHN and BET. This has shown interesting results in waste water treatment and corrosion control as the processes are green, cheap and sustainable. Our finding has revealed that green chemistry is the key to a less polluted and safer environment in Africa.

ABCChem 150

25 years of green chemistry and policy

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Green chemistry was born out of the Pollution Prevention Act of 1990 and, although the 12 Principles of Green Chemistry were not published until 1998, I think it’s fair to say that green chemistry is at roughly the quarter century mark, and this is an appropriate time to step back and look at where we stand.

Practitioners throughout the chemical enterprise are looking to make their
current processes greener. In industry, this is often associated with cost-cutting and efficiency efforts, which brings us to a simple reality: cost-benefit analysis is a key driver in the greening of any given process. Green chemistry doesn’t automatically win. It has to make economic sense. The vast majority of all organic chemicals in commerce are still derived from petroleum, which presents a whole other host of challenges - challenges which can be solved through the practice of green chemistry throughout the chemical enterprise.

This presentation will look at the evolution of policy drivers for green chemistry, including government policy, retail policy, sector supply chain initiatives, and NGO movements that promote the development and adoption of green chemistry and engineering. Government policy is intended to set the framework for the management and use of chemicals in commerce. While the implementation of US federal reform remains unresolved, the trend in Europe, Asia, and individual US states is toward greater disclosure of chemical identities, assessment of hazard, and restrictions on the use of high hazard chemicals, with some explicit encouragement for the adoption of safer chemicals.

Beyond government policy, consumers are increasingly creating demand for products that are perceived to be safer. In recent years, various NGOs have also brought considerable pressure on retailers, manufacturers, and brands, publicly drawing attention to high hazard chemicals in products and demanding alternatives that are designed to be less hazardous.

The brief history of green chemistry is marked with extraordinary creativity and accomplishments in meeting the “triple bottom line” of sustainability in economic, social, and environmental performance. This has generally been accomplished by improving a single crucial element or characteristic such as toxicity, persistence, or energy consumption. Green chemists and engineers are working to get their research and innovations into everyday products and processes, redesigning the basic building blocks of our economy in sustainable ways.

**ABCChem 151**

**Green chemistry through external partnership**
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Over the past 10 years, MSD Process R&D has established an effective model for contract research and manufacturing. With MSD scientists working shoulder-to-shoulder with our external partners, the model allows us to tackle highly challenging projects without first having to address the problems internally. Under this model, we have been able to make our chemistry greener for our outsourced projects by emphasizing innovation. So far, more than 800 projects have been successfully completed with the delivery of >20 metric tons of advanced intermediates/active pharmaceutical ingredients (APIs). The annual average process mass intensity (PMI) for these projects has been reduced by more than 50% throughout the years from 2011 to 2016. The presentation will focus on process-development case studies on the synthesis of advanced intermediates/APIs. Details will be discussed on chemistry innovation and PMI reduction.

ABCChem 152

Life Cycle Inventory (LCI) as an excellent tool for teaching fundamentals of sustainability to chemistry and chemical engineering students

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Life cycle assessment (LCA) has become the method of choice for assessing the environmental impacts of chemical products and manufacturing processes in academia and industry. Life Cycle Inventory (LCI) is the foundation of LCA. For a viable LCI assessment, access to real manufacturing data is critical. However, proprietary and confidential manufacturing data is not publicly available. Patent literature and specially process patents offer the best alternative. LCI assessment of commercial products was the core element of a sustainability course that we designed for advanced undergraduate and graduate students in the Schools of Chemistry & Biochemistry and Chemical and Biomolecular Engineering at the Georgia Institute of Technology. Student teams completed the LCI studies of three different manufacturing routes to vanillin and production of polyethylene terephthalate (PET), PlantBottle, and polyethylene furanoate (PEF). In this presentation, we will first discuss the LCI methodology, intellectual
property landscape, patent selection, and mass data collection from patent literature. Then, we will share the results of the LCI studies and the benefits and challenges of this approach for teaching fundamentals of sustainability.

ABCChem 153

Super-structured nanomaterials

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Metamaterials are artificially structured materials whose properties derive from structure instead of function of their constituent units. As a result, they exhibit properties not usually observed in nature, such as negative refraction and electromagnetic cloaking for optical metamaterials and negative Poisson’s ratios for mechanical metamaterials. However, conventional metamaterials are limited when derived from building units having a single characteristic length scale. This talk will discuss two broad classes of super-structured nanomaterials whose properties can be exquisitely tuned by the interplay of short-range and long-range interactions. We will describe massively parallel, unconventional nanofabrication tools that can realize these superstructures in both hard and soft materials. We will highlight the exceptional optical properties from multiscale metal (plasmonic) materials as well the unique mechanical and dynamic wetting properties of hierarchical polymeric structures. Other applications that can result from super-structured nanomaterials will also be discussed.

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Relocation of a small molecule in a biocompatible supramolecular gel

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Sodium deoxycholate (NaDC) forms thixotropic supramolecular gels, which can bind hydrophobic guest molecules. In solution, NaDC forms aggregates that
also provide binding sites for hydrophobic guests. Our objective was to characterize the mobility of the NaDC gel components at different temperatures. The gel network is formed from NaDC aggregates, but some of these aggregates remain soluble in the trapped aqueous phase of the gel. Pyrene was used as a fluorescent probe molecule, which is hydrophobic and is solubilized within the gel. Cucurbit[6]uril (CB[6]), a macrocyclic host, was added to mechanically strengthen the gel and also served as a host for the weak binding of pyrene. At low temperatures pyrene was located in the aqueous phase of the gel and bound to CB[6], whereas pyrene relocated into the network of the gel as the temperature was raised. Hysteresis was observed during cooling which led to the release of pyrene at low temperatures. The release temperature for pyrene was dependent on the concentration ratio between NaDC and CB[6]. These results show that the relocation of a small hydrophobic guest, akin to a drug, can be induced by the addition of additives and changes in temperature.

**ABCChem 156**

**Phosphorene as a hosting platform for metal nanoparticles**

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Recently it was discovered that black phosphorus (BP) can be exfoliated down to the monolayer, named phosphorene, either by Scotch tape method or by ultrasound activation. Exfoliated BP represents a highly promising 2D material due to its peculiar physico-chemical properties and the first applications in the field of storage and conversion of energy have been already achieved. Our contribution addresses the chemical functionalization of 2D BP by decorating its surface with transition metal nanoparticles. It was studied in depth the nanohybrid constituted by nickel nanoparticles immobilized on exfoliated BP which revealed an increased stability in ambient conditions in comparison to pristine phosphorene. Additionally, it was successfully applied in the catalytic semihydrogenation of phenylacetylene, affording high selectivity and efficiency that were unchanged after recycling tests.
Green sample preparation methods for challenging matrices and trace element determination

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Nowadays, with a few exceptions most of equipment used in atomic spectrometry require a previous step for sample preparation, generally a digestion step, that is generally necessary for a suitable analysis. However, conventional methods for sample digestion and further elements determination by atomic spectrometry involve the use of a relatively high volume of concentrated reagents (inorganic acids in case of further metals determination) and a relatively long time for digestion. The use of concentrated reagents generally requires a dilution step before analytes determination that could negatively affect the limits of detection. Moreover, the digestion efficiency of some systems presents some limitations for many matrices. In this sense, even using methods based on microwave-assisted closed vessels some drawbacks
can occur and incompleteness of digestion is frequently reported. Nowadays, there is a trend for the development of methods requiring lower reagent consumption, less analytical steps and lower waste generation combined with high efficiency of digestion. In addition, it is important obtaining digests that are suitable for determination techniques avoiding excessive dilution or higher blank levels. On this aspect, the main trends for sample preparation for a variety of matrices will be presented in this lecture for further metals and also non-metals determination by atomic spectrometry. The use of diluted solutions using oxygen pressurized systems with or without UV radiation, use of combustion systems, etc, will be covered and the main aspects of sample preparation for the determination of metals and halogens will be discussed. Recent applications will be presented showing the advantages of methods using diluted reagents (microwave-induced combustion, UV digestion, etc) for metals and non-metals determination using a variety of techniques as ion chromatography, ICP-MS and ICP-OES.

ABCChem 158

Hadamard-transform fluorescence EEM spectroscopy

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We present a fluorescence excitation emission spectrometer with superior data acquisition rates over previous instruments. White light from a white light emitting diode (LED) source is dispersed onto a digital micromirror array (DMA) and encoded using binary $n$-size Walsh functions (“barcodes”). The encoded excitation light is used to irradiate the liquid sample and its fluorescence is dispersed and detected using a conventional array spectrometer. After exposure to excitation light encoded in $n$ different ways, the 2-dimensional EEM spectrum is obtained by inverse Hadamard transformation. Using this technique we examined the kinetics the acid-driven demetallation of chlorophyll-a into pheophytin-a. For these experiments EEM spectra with 31 excitation channels and 2048 emission channels were recorded every 15 seconds. In total, data from over 3000 EEM spectra were included in this report. It is shown that the increase in data acquisition rate can be as high as 500-fold over conventional EEM spectrometers and spectral acquisition rates of more than two spectra per second were demonstrated.
Spirocyclohexadienones as an unusual scaffold for acetylcholinesterase inhibition

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The potential of inhibition of a set of spirocyclohexadienones, readily synthesized in 2 steps and good overall yield from Morita-Baylis-Hillman adducts, was evaluated in vitro against acetylcholinesterase. We found that some of them are able to inhibit the acetylcholinesterase activity, with IC₅₀ values ranging from 0.12 to 12.67 μM. Molecular docking study indicated that the spirocyclohexadienone, 9e (IC₅₀ = 0.12 μM), an uncompetitive AChE inhibitor, showed a good interaction at active site of the enzyme. Thus, we have identified a hit for further studies aimed at the discovery of more potent acetylcholinesterase inhibitors. As far as we know, this is the first report describing the anti-cholinesterase effect of this class of compounds.
Search of secondary metabolites with potential biological activity by screening of plants using $^1$H-NMR spectroscopy

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The study of biologically active secondary plant metabolites requires prior knowledge and understanding of structure-activity relationships. This is necessary because the infrastructure needed to measure biological activity in oncology, bacteriology, immunology, and virology—to cite some examples—may be expensive and difficult to access in many laboratories, so this methodological approach allows accelerating the identification of candidates to study. In our laboratory we start this activity with secondary plant metabolites by running $^1$H-NMR spectra for each plant extract. These spectra indicate the type of compounds the plant might have, and whether its study might be useful according to the specific aims. Once a plant with compounds of interest is identified, we proceed to their separation and identification with chromatographic and spectroscopic techniques. Collaborations with external institutions allow the study of their biological activity.
Figure 1. $^1$H-NMR spectrum of Rutaceae Zanthoxylum monophyllum extract.
Several inactive protein precursors are converted to biologically active proteins by self-cleaving under a controlled chemical reaction, all of them initiated by a N-O or N-S acyl shift. Some examples of self-catalyzed protein rearrangements have been widely studied (e.g. hedgehog proteins, N-terminal nucleophile hydrolases and pyruvoylenzymes). Others, like alpha-amylases, are still under scrutiny regarding their rearrangement mechanisms. Some authors propose that amylases isoforms may be the result of post-translational modification events or an expression of multigene families, but others suggest autoproteolytic events.

In *Lactobacillus amylovorus*, the alpha-amylase coded by the amyA gene is translated as a multidomain protein with an amino-terminal catalytic domain (CD) and a carboxy-terminal starch binding domain (SBD) arranged in five identical carbohydrate binding modules (CBM) in tandem. An self-cleavage process has been observed in this amylase, where hydrolysis seems to occur at the SBD both in presence or absence of the CD and regardless of the genetic background in which the enzyme is expressed, native or heterologous environment.

Purified SBD undergo proteolysis when incubated at pH above 7 and this process seems to accelerate when divalent ions such as MgCl$_2$ are included in the incubation buffer. PMSF and pepstatine had no inhibition effect on proteolysis. On the other hand, stability increases in presence of EDTA and at pH close to 5, in correlation with the pH of amylase maximal activity. Importantly, we observed that proteolysis fragments are always the same and retain the ability to bind to insoluble starch. The *L. amylovorus* a-amylase autoproteolytic mechanism is currently under characterization.
Chemical labeling of silica (SiO$_2$) and magnetite (Fe$_3$O$_4$) nanoparticles with fluorescein for biomedical applications

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Nanoparticles of magnetite, Fe$_3$O$_4$, and carboxylated silica, SiO$_2$-COOH, were synthetized following standard procedures and then their surfaces modified to attach a fluorescent label in order to explore their use as drug delivery systems and/or imaging agent. Citrate stabilized magnetite nanoparticles were chemically modified by coating their surfaces with a biocompatible polysaccharide (carboxymethylcellulose) labeled with fluorescein (Fluo-CMC), while silica nanoparticles were modified by directly attaching fluorescein on its surface using DCC coupling. These nano-platforms were characterized using FTIR, fluorescent spectroscopy, dynamic light scattering (DLS), scanning electron microscopy (SEM) and fluorescent microscopy. The biocompatible nanoparticles were intranasally administered to a set of male Wistar rats to evaluate its biological response and biodistribution in the brain. To verify if these nanoparticles were located at different regions of the brain, a histopathological analysis was performed, using fluorescent microscopy and hematoxylin – eosin as a contrast staining. Preliminary results indicate that these systems are potentially useful biocompatible platforms for the design of theranostic imaging agents and drug delivery nanocarriers.

Synthesis of all stereoisomers of pallantione, the male-produced sex pheromone of Pallantia macunaima (Heteroptera: Pentatomidae)

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Semiochemicals are chemical cues used by organisms for inter or intraspecific communication. Pheromones are the most studied class of semiochemicals and
are substances that are released to trigger a response in individuals of the same specie. The most abundant indentifieds are the sex and aggregation pheromone. The study of this compounds are useful for applying in integrated pest managements programs that aim to lower the use of pesticides by using the pheromones to attract the pest in to the trap.

*Pallantia macunaima* (Heteroptera, Pentatomidae) is an important heteropteran pest that occurs in grain plantations in Southern Brazil. In a previous study it was reported the identification and determination of the absolute configuration of the sex pheromone of this stink bug. It was the first ketone found in the Pentatomidae family, the isomer of the sex attractant pheromone released by males is (6R,10S)-6,10,13-trimethyltetradecan-2-one, termed pallantione. In this work we report a new enantioselective synthesis of the four possible stereoisomers of this compound. The synthesis was conceived as the connection of two chiral building blocks, employing (R)- or (S)-citronellol and methyl (S)-3-hydroxy-2-methylpropionate as the source of chirality, which are commercially available in high enantiomeric purity. The synthetic route included as key steps Grignard reactions and lithium anion of the sulfones, for connection of the chiral building blocks.

With the work developed it was possible to obtain all four stereoisomers with good global yields; comparison with data from the literature it was possible to observe that racemization did not occur in any steps of the synthesis.
Biocompatible magnetic nanoparticles as intranasal drug delivery carriers for the brain

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Magnetic nanoparticles, in particular magnetite (Fe₃O₄), have been explored for their potential use as drug delivery systems and agents for magnetic medical imaging (MRI) and hyperthermal therapy [1, 2]. We have evaluated the use of nearly monodispersed, water soluble and stable Fe₃O₄ nanoparticles (~30 nm) modified with a biocompatible polysaccharide coating as novel drug delivery carriers to the brain. The nano-platform used was characterized using FTIR and Raman spectroscopy, SEM and TEM electron microscopies; drug loading and release of dopamine in different mediums was followed in a closed vessel until a
pseudo-equilibrium was reached during periods up to 48 hours using a UV-Visible spectrophotometer. The biocompatible magnetic nanoparticles were administered via intranasal to a set of male Wistar rats and the biological response at different concentrations as well as its biodistribution in the brain was evaluated as a preliminary test. The presence of nanoparticles distributed in different regions of the rat’s brains was confirmed by histopathological analysis, using Perls’ Prussian blue staining to detect exogenous Fe(III) and verified by magnetic resonance imaging (MRI) tracking [3]. A HPLC analysis was made to quantify the dopamine released by the nanoparticles in an animal model of Parkinson’s disease. Our results suggest that this biocompatible, nanostructured system may become an interesting, non-invasive method to introduce therapeutics into the brain for the potential treatment of several neurodegenerative disorders.

ABCChem 167

Derivatization and evaluation of Ersindole: A rapid inducer of endoplasmic reticulum stress and immunogenic cell death

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Cytotoxic compounds that can trigger a concatenate anticancer immune response are of great interest to the scientific community. Previously, we identified novel anti-cancer tetracyclic indole compounds that were generated by diverting synthetic intermediates from the total synthesis of (±)-actinophyllic acid. Utilizing a Lewis acid mediated cascade reaction between stabilized carbocations and a π-nucleophile, a library of structurally diverse tetracyclic indole derivatives were synthesized and anticancer properties evaluated against the human lymphoma cell line U937 and human triple-negative breast cancer cell lines Hs578t. Mode-of-action studies determined that the compounds elicited immunogenic cell death via rapid induction of endoplasmic reticulum (ER) stress. A well tolerated derivative was evaluated in a syngeneic mouse model for metastatic breast cancer and demonstrated a significant reduction in mouse tumor burden.
Highly diastereoselective aminocatalytic protocol for the synthesis of spiroisoxazol-5-ones

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A number of spiro-isoxazol-5-ones have been identified with antibacterial, antitubercular and cytotoxic properties, which make these molecules valuable synthetic targets. However, just a limited number of strategies to access such structures have been developed until today.

In this context, we developed an aminocatalytic protocol employing α,β-unsaturated methyl ketones and alkylidene isoxazol-5-ones, in order to produce spiro-isoxazol-5-ones. The reaction proceeds via a double Michael addition mechanism and affords the thermodynamically more stable product, which contains three contiguous stereocenters. This transformation displays high efficiency (yields up to 96%) and a remarkable control of the relative stereochemistry (dr > 20:1).

Synthesis and evaluation of N-phenylquinazolin-4-amine derivatives as cytotoxic agents in cancer cell lines

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Cancer is a condition that is characterized by the uncontrolled growth and spread of the cells, and that at a certain moment can invade surrounding tissue and affect any part of the body in a process called metastasis. Epidemiological data report that the majority of cancers cause high mortality rates worldwide, and the main cancers with the highest mortality rate include lung, breast, colon, and prostate cancer. However, the treatments that exist today are very aggressive and have no effect on patients in advanced or terminal stages, arising the need to look for new options for the treatment of this pathology. One of the strategies in the drugs design is the use of privileged structures, as is the case of the quinazolines. In that context, in the present project 8 (eight) N-phenylquinazolin-4-amine derivatives were synthesized, characterized by $^1$H NMR and $^{13}$C NMR, and evaluated in five tumor cell lines (PC-3, HCT-15, MCF-7, MDA-MB-231 and SKALU, prostate cancer, colon, positive estrogen breast, triple negative breast, and lung, respectively). The results of the chemical part showed the successful obtaining of the compounds when they were characterized spectroscopically and obtained with excellent yields (85-95%). On the other hand, in the biological evaluation it was observed that the presence of the nitro group and the trifluoromethyl group in the structure 6-nitro-N-(4-(trifluoromethyl)phenyl)quinazolin-4-amine (2c) was essential to achieve a cytotoxic activity in the five tumor cell lines. A similar behavior although with less cytotoxic activity was observed in the structure N4-(4-(trifluoromethyl)phenyl)quinazoline-4,6-diamine (3c) where the nitro group was changed to the amino group, in this case the preliminary results suggest that the nitro group is indispensable for cytotoxicity. We can conclude that the synthesized compounds presented cytotoxic activity in the five cell lines and are possible drug candidates.
Syntesis, characterization and biological evaluation of heterocyclic chalcones' analogs as anticancer agents in breast cancer cell line MDA-MB-231

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Chalcones consist of two phenyl rings joined by a, β-unsaturated carbonyl system (enone), possesses a wide variety of biological properties. They have been structural modifications object. These variations have led to the discovery of compounds with specific pharmacological activity, for example, they have been reported chalone with activity anticancer, antibacterial, antifungal, among others. In this research, four compounds chalone type (C1-C4) were synthesized using the well-known Claisen-Schmidt condensation, a simple and low cost method that is amenable to the practice of green chemistry according to the semi-quantitative analysis of the Ecoscale. The cytotoxic properties of these compounds were evaluated using the MTT method in vitro assay against the breast cancer cell line MDA-MB-231. Were obtained yields that oscillated
between 65 and 85%, observing for each compound a characteristic color. The methodologies used resulted acceptable based on the semi-quantitative analysis proposed by Van Akan, et al., (2006) and Clavo, et al., (2009), being favored by the use of a solvent harmless to the environment as well as the obtained yield. The chemical shifts and coupling constants of the protons of the α,β-unsaturated systems determined the trans geometry (notation E, J = 15.6-16 Hz) of the double bond. Hydrogens and carbons of the synthesized compounds possess chemical shifts and coupling constant own according to the chemical structure. The anti-proliferative effect of the compounds C1-C4 indicates cytotoxic effects in the breast cancer cell line MDA MB-231. Effectivity of C1-C4 can be associated to the structural composition, since the A-ring is replaced by a heterocyclic and hydrogen is replaced by fluor atom in the B-ring. The changed of hydrogen by a fluor atom enhance the cytotoxicity. The replacement of a proton with a fluor atom is a strategy used in the development of drugs to alter biological function. The remarkable biological potential of these chalcones is due to their possible interactions with various proteins related to cell apoptosis and proliferation. It great interests to investigate the effects of compounds C1-C4 on some of the proteins that regulate the cell cycle progression.

ABCChem 171

Withdrawn

ABCChem 172

Mass spectrometry imaging by LA-ICP and DESI of liver cancer

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Mass spectrometry imaging (MSI) emerged in the last decades as an option in the prospection of the new biomarkers, and has open many doors for clinical
analysis, especially in the oncological area. These MSI show the spatial distribution of molecular or atomic composition, evidencing different regions as carcinogenic or healthy tissue, necrotic area, and others. The main techniques of ionization used for MSI analysis can be divided into two types: molecular and atomic analysis.

DESI is an ambient ionization technique and MSI, is possible to be performed under atmospheric pressure and without or minimal sample preparation. LA-ICP-MS has been developed as a powerful and sensitive micro-analytical methodology enabling multi-elemental analysis and isotope ratio measurements at the trace and ultratrace level. Figure 1 displays the workflow for liver tissue analysis. Firstly, the tissue is sectioned into thin slices and the glass slides for MSI analysis are mounted. The same glass slide used for DESI imaging was subsequently analyzed by H&E.

Preliminary results show the difference between healthy and cancer tissue by lipidomic and atomic profile. The concentration and distribution of the metals Ca, P and Mn are very similar of the arachidonic acid (ion m/z = 303), PS (ion m/z = 792) and PI (ion m/z = 885), respectively (Figure 2). Others ions too present differences between healthy and cancer tissues.
**Figure 1:** Analytical workflow for glass slides preparation, tissue chemical analysis by LA-ICP-MSI and DESI-MSI, and morphological analysis by H&E.

![Image of analytical workflow](image)

**Figure 2:** Molecular analysis by DESI-MSI of Arachidonic acid, Phosphatidylserine (PS) and Phosphatidylinositol (PI) \((m/z = 303, 792\) and 885, respectively) and atomic analysis by LA-ICP-MSI of metals \(^{42}\text{Ca}, ^{31}\text{P}\) and \(^{55}\text{Mn}\).

ABCChem 173

**Annopurpuricin A: New acetogenin from the roots of Annona purpurea; structural characterization and anticancer activity**

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*Annona purpurea* is a tree native to America. Its fruit known as “cabeza de negro” is edible and several parts of the tree are used in traditional medicine. In previous chemical studies, alkaloids and acetogenins were isolated from bark, leaves and seeds. The roots are employed against kidney diseases and a hydroalcoholic extract of the seeds and leaves have been used as insecticide to *Aedes aegypti*. Taking into account the long worldwide ethnomedical history,
it was proposed, the chemical study of the root, with the aim of carrying out the isolation and structural elucidation of secondary metabolites of *A. purpurea*. From 2.3 kg of roots several ascending polarity extracts (hexane, dichloromethane and methanol) were prepared. After, each extract was chromatographed by further Si gel column and reversed-phase HPLC. The results show that the dichloromethane extract was rich in acetogenins. The chromatographic purification allowed to obtain the principal compound (annopurpuricin A) 0.018% (500 mg). The complete structure analysis was made by spectroscopic techniques and chemical methods (silylated derivatives and Mosher esters). In vitro analysis performed against three cell lines (MSTO-211H, HeLa and HepG2), demonstrated that, in HeLa cell line, annopurpuricin A is the most potent acetogenin isolated from nature (IC$_{50}$ = 0.063 nM) and it is 119 times more potent than bullatacin. The mechanism of action involves a death by a dual apoptosis/necrosis with a collapse in the mitochondrial membrane potential, without the induction of volume increase swelling.

**ABCChem 174**

Validation of 3M™ MLSII (microbial luminescence system) method vs. traditional method, for microbial evaluation of UHT pasteurized beverages

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Food industry requires microbiological testing of products before releasing them for distribution and market. There has been an intense development of methods to shorten time-to-results, especially for microbial tests. 3M™ Microbial Luminescence System MLSII is an emerging fast methodology to test UHT pasteurized milk, based on the biochemical reaction of ATP, present in all living beings, with the enzyme luciferase; the test gives results in few minutes after product incubation. The aim of this research has been the validation of the methodology for mexican non-milk beverages, processed by UHT, as a microbiological monitoring alternative for quick and dependable results. Validation was carried out vs. traditional plate streaking method to determine presence or absence of microbial growth.

Procedure included inoculation of standardized cultures of 4 reference
microbial strains that have developed in UHT beverages. Inoculated beverages acquired in retail stores were incubated for 48 h. Parallel samples were taken for both methodologies, under controlled conditions. Results were statistically processed to establish acceptance threshold, detection limit and specificity of the 3M MLSII. Conclusions indicate that MLSII is acceptable and adequate for S. cerevisiae detection in the three studied beverages, detection limit being 10 UFC. It is, however not adequate to detect populations < 10 UFC of P. aeruginosa, A. niger nor G. stearothermophilus in any of tested beverages. Threshold acceptances were established for the three products tested. Specificity, regarded as the fraction from total negatives correctly identified as such by the tested method, is acceptable for the tested microorganisms, except for S. cerevisiae.

**ABCChem 175**

**Hydrolysis and biotransformation of citrus flavonoids by Penicillium digitatum, P. italicum and P. expansum**

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Green and blue molds, caused by Penicillium digitatum and P. italicum respectively, are the main diseases that affect citrus fruits in the worldwide postharvest, resulting in great economic loss. Brazil is the world's largest orange producer, responsible for 61% of all the orange juice consumed on the planet. Thus, due to the great economic impact that these fungi cause to Brazilian industry and to the greater control of food quality, we are looking for methods to control citrus infection. The mechanism of pathogen-host interaction has already been determined in several biological systems, but they have not yet been fully clarified for P. digitatum and P. italicum. LC/MS analyzes of extracts from in vivo assays to obtain the metabolic profile of the fungus during the infection process showed that P. digitatum acts on the citrus flavonoids, naringin and hesperidin, hydrolyzing the two sugar units linked to the polyphenols. The ions [M+H]+ m/z 303 and 273 for the aglycone part for hesperidin and naringin respectively were found in three retention times on the chromatograms of the assays (complete polyphenol, no rhamnose, no rhamnose and no glucose). The ions [M+H]+ m/z 319 and 333 were also found in the extracts and have the same fragmentation characteristic of the aglycones, indicating that they are possibly biotransformation products. In vitro biocatalysis
assays using the citrus flavonoids as substrate were performed and confirmed the results obtained in vivo: P. digitatum and P. italicum hosts specific for citrus fruits demonstrated the ability to hydrolyze the sugar units of flavonoids at a rate much higher than P. expansum that is able to infect other types of fruit. These results show that the ability to hydrolyze and modify citrus flavonoids through rhamnosidases and other enzymes may be one of the factors responsible for pathogenicity in citrus, since flavonoids are fruit defense compounds and have inhibitory activity against fungi of the genus Penicillium.

**ABCChem 176**

**Microbiological control service for Food Tech Lab: Relevance of microbiological analysis for food products, made by students of Food Microbiology Lab**

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Food Technology Lab (LABTEC) for undergraduate students is an experimental course of 20 credits, taken in the 8th (or 9th) semester. Its course manual indicates the physicochemical tests that students must perform in the products that they process thru the modules of the course: Cereals, Dairy, Meat products and Vegetables. Results are analyzed to establish if specifications from related standards are met; if they aren’t, then adequate corrective actions must be undertaken.

Microbiological testing is also part of national and international regulatory standards; however, complexity in cost and logistics required to perform such testing in LABTEC drew us to develop a joint program with groups of 6th semester, taking Food Microbiology Lab. Through the program, 216 food units were collected and tested with 232 analyses to determine Salmonella spp, *Staphylococcus aureus*, coliforms, aerobic count as well as yeast and mold. Live and inert surfaces related to food process were also analyzed.

Final results indicated that LABTEC started with 9% of processed food samples meeting all physicochemical and microbiological specifications; at the end of the project, 92% of samples met all quality and safety specifications. Corrective actions were established in every module, every time non-compliance samples
appeared. This were undertaken by LABTEC students as soon as Food Microbiology Lab results were known. Students of this latest course benefited from the experience of making the microbiological analysis as if it was a professional service and became conscious of good execution importance in order to obtain dependable, useful results.

ABCChem 177

Sensitization of students at food processing: Importance of Food quality in food technology laboratory

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Food Safety is the result of direct and non-direct actions amongst which ingredients handling and environmental monitoring stand out. The most frequent sources of contamination are handlers and food contact surfaces (cutting boards, utensils and equipment for food processing), raw materials and vectors like dust and insects. Live and inert surfaces are some of the most common sources of cross contamination of food, both at home and in food industry.
Food tech lab for undergraduate students is an experimental course of 20 credits, which aims to integrate all the learning background from the curriculum. Therefore, it has been considered a most important matter to sensitize students towards hygienic practices before they start to process food. Through the exercise designed we plan to assure adequate processing of foods and controls to accomplish acceptable hygienic quality and to comply sanitary specifications in related official standards (NOM), as well as to evaluate such compliance through efficient control methodologies.

ABCChem 178

Dairies safety and quality: Filth test in fresh cheese produced by Mexican SME (PyME)

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Mexico has an important gastronomic tradition in dairies, especially artisan cheese. There is large consumer demand for fresh cheese, although it is less stable than processed varieties and, because of its physicochemical attributes, it is associated with larger microbial risk. Therefore, through its process, hygienic practices must be warranted and the end product must comply with specifications stablished in official standards (NOM).

In Mexico “materia extraña” refers to both filth and objectionable matter such as metals or stones. Filth found in food (insects, its fragments or eggs, hairs, rodent feces, fibers, plant residues or splinters) implicates potential risk for consumer health. This research included microbiological analysis for indicators and pathogens, heavy metals and filth test in 12 fresh cheese brands, produced by Mexican SME. Results indicate the need to standardize procedures and reduce the risk related to filth presence. Microbial analysis results are consistent with types of filth found in samples. The protocol for filth test for cheese was developed as well as a visual guide made from optical microscope images, to help students identify the filth found in food, powdered dry milk and other dairies.

ABCChem 179
In order to reduce the pollution by residues of organic solvents, it is necessary to search for non-contaminant solvents in the synthesis of nanostructured materials. Carbon dioxide (CO$_2$), despite being a greenhouse contaminant gas, in its supercritical state can be used as a solvent in the synthesis of nanostructured magnesium carbonate (MgCO$_3$), as an alternative to the use of methanol (used as a co-solvent in this synthesis). In this work, two green synthesis routes of MgCO$_3$ are compared: sequestration of CO$_2$ in aqueous solutions and synthesis with supercritical CO$_2$. 36 experiments were carried out in aqueous synthesis and 3 experiments in supercritical synthesis, obtaining carbonates with different morphologies, including both high density (low porosity) and low density (high porosity) products. Two nanostructured materials were characterized by BET analysis with pore diameters lower than 6 nm. SEM images showed morphologies of micro needles for the supercritical synthesis product and a bundle of rods morphology (BRM), for the product synthetized by the aqueous route; this morphology has not been reported previously. XRD and Raman spectroscopy showed that a mixture of structures was obtained for the nanostructured material BRM, and for the product obtained by the supercritical synthesis there was a correlation of crystalline nesquehonite. Finally, dye and microfluidic adsorption tests were carried out, obtaining that these materials have the potential to be used as adsorbent materials.
Novel Mn-porphyrin catalyst used in cyclohexane oxidation by PhIO under a green chemistry approach

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Porphyrids are a group of organic molecules capable to chelate metal ions. Manganese porphyrins (MnP) have been intensively studied for their properties as catalysts in oxidation reactions of numerous organic substrates, in which they mimic cytochromes P450. Porphyrins' catalytic activity can be improved by adding substituents in its meso-aryl groups. This work presents the study of a novel metalloporphyrin, chlorido-5,10,15,20-tetrakis-(2',3',4'-trimethoxyphenyl)-porphyrinatomanganese(III) ([MnIII\text{T}(2,3,4)MPPCl], Cat. 2), including its obtainment, characterization, and catalytic properties in cyclohexane oxidation by iodosobenzene (PhIO). Two Green Chemistry strategies were adopted: reactions were conducted in 1) dimethyl carbonate, a green solvent, and 2) absence of solvent. [MnIII\text{TPPCl}] (chlorido-5,10,15,20-tetraphenylporphyrinatomanganese(III), Cat. 1), the classic catalyst, was also employed in some systems for comparison purposes. The reactions were realized...
in microscale, under 25 °C and magnetic stirring, for 90 minutes. The only observed products were cyclohexanol (cy-ol) and cyclohexanone (cy-one).

The new catalyst was synthesized following the method of Gonsalves et al. Characterization via UV-vis and infrared spectroscopy, elemental analysis and mass spectrometry indicated the formation of \([\text{Mn}^{III}T(2,3,4)\text{MPPCl}]. \) Cat. 2 had shown higher yields for oxigenated products than Cat. 1 in all three systems (Table 1), and the improvement was even higher in the green systems (especially in absence of solvent, where the cy-ol yield was highest). Cat. 2 had also shown less bleaching percentages than Cat. 1 in all the systems, what can be explained by the stereo impediment created by the methoxy groups, which hamper the auto-oxidation processes — therefore favoring the higher product yields obtained with Cat. 2. Selectivity towards cy-ol was higher when Cat. 2 was employed in absence of solvent, because the greater amount of substrate favors cyclohexane oxidation rather than cy-ol oxidation to cy-one. The green strategies adopted in this work are desirable in order to generate less environmental issues, while increasing reaction efficiency. Thus, we show that poorly reactive substrates such as cyclohexane can be satisfactorily oxidized while adopting principles of Green Chemistry.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Dimethyl carbonate</th>
<th>Dichloromethane</th>
<th>No solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Yield (%)</td>
<td>Yield (%)</td>
<td>Yield (%)</td>
</tr>
<tr>
<td>Cat. 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cy-ol</td>
<td>12</td>
<td>18</td>
<td>15</td>
</tr>
<tr>
<td>Cy-one</td>
<td>7</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>Cat. 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cy-ol</td>
<td>17</td>
<td>18</td>
<td>15</td>
</tr>
<tr>
<td>Cy-one</td>
<td>13</td>
<td>16</td>
<td>15</td>
</tr>
</tbody>
</table>

1 Yield based on PhIO. 2 Sel = product selectivity calculated as (%Cy-ol) × 100/(%Cy-ol + %Cy-one). 3 Ble = The degree of catalyst destruction was calculated from the UV-Vis absorption spectra recorded at the end of the reaction. Mn(II)/PhIO/cyclohexane molar ratio = 1:10:4650 (reactions with solvents) and 1:10:13950 (reactions without solvent).

ABCChem 182

Green chemistry ACS Student Chapter at the Federal University of Rio de Janeiro, Brazil: Prospects and outreach activities

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The first ACS Student Chapter dedicated to Green Chemistry was founded at UFRJ to direct support from the Society to outreach activities in the education of chemistry teachers. Even before the Chapter was officially recognized, professors and students had been developing projects in academic and industrial fields to promote environmental conservation of processes at the molecular level. Some examples are: the National Science and Technology Week (experiments that attract high school students’ attention), courses at academic events such as the national Chemistry Congress and Symposium on education, the Brazilian Green Chemistry School Meetings, Green Chemistry workshops for high school teachers, the Green Chemistry Notebook (news related to research and innovation) and international workshops. The 2016 ACS Global Innovation Imperative (Gii) was awarded to the Green Chemistry School and resulted in a workshop in November (Belém, Brazil), to develop “Green chemistry Experiments for Remote Locations”. It brought together local chemistry professors (from riverside and indigenous communities), municipal and state level officials, high-school teachers, green chemistry lecturers and specialists from the UK, USA and Brazil. It was followed by a meeting for high school teachers offered in May 2017 to discuss the insertion of green chemistry into the curriculum through simple experiments with available materials (Fig. 1). A member of the Chapter received the “Professor Arikerne Sucupira” Award for the best communication at the VII Meeting of the Brazilian Green Chemistry School (a patent on green corrosion inhibitors has just been deposited). The Chapter works in different fields of green chemistry that can be attested by recent communications on CO₂ recovery, natural polymers, sustainable energy and green corrosion inhibitors. The next step is to develop social media networks for outreach activities and evaluate the proposals from the 2016 Gii (Education for Sustainable Development) at an international workshop (August 2018, Rio de Janeiro).
Molecular dynamics: An approach for the understanding of drug delivering systems

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The current demand to discover new drug release systems has lead to the use of novel polymers, with physical and chemical properties. These properties allow them to have a great potential in pharmaceutical formulation for various
functions, such as material packaging and fabrication of drug delivery devices. In spite of this, the polymers themselves are rarely studied: experimentally or computationally. Sodium salt of poly(maleic acid-alt-octadecene), known as PAM-18Na, is an amphiphilic copolymer derived from maleic anhydride that has been studied as a possible form of protection, vehiculation and delivery of drugs. Nevertheless, the molecular structure that this polymer adopts in an aqueous environment is unknown, which limits the advance in this field. Due to this, it is useful to know and predict the conformation of PAM-18Na in aqueous solution using molecular dynamics as a tool. This project studied PAM-18Na at two ionized states: 100% and 0%, and with two lengths of alkyl chain: 16 and 1. This was done in order to visualize the effects that Coulomb interactions and Lennard-Jones interactions have on the conformation of the molecule, evaluated measuring the radius of gyration.

In this project, the molecular dynamics of PAM-18Na is simulated in aqueous environment, for a given ionization state. In order to do this, the program Gaussview was implemented to draw the molecule (20 monomers) that was then classically optimized using Gaussian09. The output file (.opt) is then used in Gabedit to generate a .pdb file for the molecule. This .pdb file was then used to generate the topology (.top) file and the Gromacs file (.gro) using MKTOP and Gromacs, respectively. The latter was again employed to generate the simulation using OPLS-AA force field. Finally, the simulation was visualized using VMD, where the most repeated conformation was chosen. This conformation would give an idea as how this copolymer may interact with an active ingredient or other excipient in a given formulation.

**ABCChem 185**

**Synthesis, characterization and biological evaluation of homo- and heterofunctionalized polyamide dendrimers for application in inflammatory diseases**

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Inflammation is a general pathomechanism associated with numerous diseases of great global impact as many cancers, metabolic disorders and infectious, neurodegenerative and autoimmune diseases. That is why the development of drugs that are able to treat chronic inflammation, in an effective way and are
well tolerated by the patients, becomes an interesting field of research in the search for the treatment and cure of hundreds of diseases.

Dendrimers appear as a convenient starting point for the design of these drugs. These nano-sized and well-defined branched macromolecules have interesting chemical properties and a wide variety of biological applications. Dendrimers’ multivalency has enabled their increasing importance in nanomedicine due to their intrinsic properties in biological activities and for being versatile drug delivery carriers.

In our project, we are synthesizing G3 polyamide dendrimers with potential application in the treatment of diseases that are caused by inflammatory processes. These dendrimers will be homofunctionalized bearing NO-releaser, triethylphosphonium groups and bile acids; and heterofunctionalized, bearing two moieties from combinations between these compounds with recognized biocompatibility and anti-inflammatory properties (Figure 1).

To evaluate the biological potential of the proposed dendrimers, we will study their cytotoxicity and their anti-inflammatory properties in assays as inhibition of NF-κB activation, suppression of pro-inflammatory repertoires such as TNF-α and IL-1β and p53 expression. We expect that this project will result in new knowledge in the area of dendrimer chemistry and inflammatory processes, and possibly allows the development of new multi-target drugs with application in diseases as cancer and Alzheimer’s.
Synthesis of colloidal silver nanoparticle clusters and their application in ascorbic acid detection by SERS

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Ascorbic acid (vitamin C) has an essential role in the human body mainly due to its antioxidant function. In this work, metallic silver nanoparticle (AgNP) colloids were used in SERS experiments to detect ascorbic acid in aqueous solution. The AgNPs were synthesized by a green method using potato starch as reducing and stabilizing agent, and water as the solvent. The optical properties of the
yellowish as-synthesized silver colloids were characterized by UV-visible spectroscopy, in which besides a typical band at 410 nm related to the localized surface plasmon resonance of the silver nanoparticles, a shoulder band around 500 nm, due to silver nanoparticle cluster formation, is presented when relatively higher concentrations of starch are used in the synthesis. These starch-capped silver nanoparticles show an intrinsic Raman peak at 1386 cm\(^{-1}\) assigned to deformation modes of the starch structure. The increase of the intensity of the SERS peak at 1386 cm\(^{-1}\) with an increase in the concentration of the ascorbic acid is related to a decrease of the gap between dimers and trimers of the silver nanoparticle clusters produced by the presence of ascorbic acid in the colloid. The limit of detection of this technique for ascorbic acid is 0.02 mM with a measurement concentration range of 0.02–10 mM, which is relevant for the application of this method for detecting ascorbic acid in biological specimen.

**ABCChem 187**

**Preparation and characterization of nanoparticles of (-)-epicatechin loaded chitosan for studies in breast cancer**

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Breast cancer, the most frequently occurring cancer in women from Mexico and the world, is a major public health problem. The search of new therapeutic strategies against this cancer has focused on natural products, such as polyphenols, specifically flavonoids. In this context, our group has shown that (-)-epicatechin (a flavonoid) has an antiproliferative effect on cell lines of breast cancer. However, flavonoids are molecules typically prone to degrade when exposed to physical, chemical and biological factors, which limits its activity in vivo. Aim: Therefore, we focus on developing and characterization (-)-epicatechin loaded chitosan nanoparticles for to evaluate their anticancer activity in breast cancer models (in vitro and in vivo). Methods: the chitosan nanoparticles and nanoparticles loaded with drug were obtained by supramolecular self-organizing and both its diameter as its polydispersity index (PI) were determined by light scattering dynamic, the superficial charge of nanoparticles was measured by particle electrophoresis, then the nanoparticles were characterized by differential scanning calorimetry, Fourier transform infrared spectroscopy, transmission electron microscopy, atomic force microscopy and confocal microscopy. The entrapment efficiency and drug – loading of (-)-epicatechin in the nanoparticles were determined too. The antitumoral activity in vitro was evaluated in breast cancer cell by MTT assays and the antitumoral activity in vivo was observed in syngeneic transplant model cancer in BALB/c mice. Results: We obtained nanoparticles with size of 200 nm, zeta potential negative, IP smaller than 0.2 and morphology was spherical shape. We observed a major antitumoral effect in vitro and in vivo of nanoparticles with (-)-epicatechin compared with the flavonoid in its free form. Conclusion: The data obtained in this work, suggesting that the (-)-epicatechin loaded chitosan nanoparticles have potential therapeutic values in the treatment of breast cancer.

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The main objective of this study was to analyze the use of solid lipid nanoparticles (SLN) loaded with phenytoin (PHT) as drug carriers to the brain. The SLN were prepared by the high shear homogenization method. The
anticonvulsant and anxiolytic effect of SLN, PHT and SLN-PHT after oral and intraperitoneal administration was evaluated in vivo. The anticonvulsant effect was evaluated using the Pentylenetetrazol (PTZ) model and the anxiolytic effect was evaluated with the elevated plus maze model, open field exploration test and hole-board test.

**ABCChem 189**

**Morphological, thermal and mechanical properties of alginate-oxidized nanocellulose gels for biomedical applications**

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Cellulose nanocrystals (CNC) and cellulose nanofibers (CNF) have attracted great interests of scientific community mainly due to their renewability, biodegradability and ecological properties. In this work we have used eucalyptus as nanocellulose (CNC or CNF) source and TEMPO oxidation reaction to introduce carboxylate groups in their surfaces. The alginate-based gels were prepared from mixing stock solutions of alginate (2% w/v) and nanocellulose suspensions (1% w/v). After mixture, the system was freeze-dried for 48h. This material was added into a calcium chloride solution (2% w/v) for 24h. The impacts of the calcium induced crosslinking were studied by swelling ratio, FTIR, SEM, TGA and DMTA. The swelling ratio tests showed that the alginate-CNF materials presented the highest swelling (20 w/w) in phosphate buffer at 37°C due to 3D-network crosslinked gel. FTIR spectra for both alginate-nanocelluloses showed an increase of absorption bands attributed to carboxylate groups after TEMPO oxidation reaction. When calcium chloride was added in these mixtures a displacement of the bands towards lowest wavenumber was observed due to the formation of calcium bridges between CNC or CNF and alginate. SEM showed that alginate-nanocellulose systems have considerably porosity which is an important parameter to induce cell growth. Glass transition temperature (Tg) values observed in DMTA analyses showed that the addition of nanocellulose did not change the Tg. CNF-alginate material showed a lower storage modulus when compared to the CNC-alginated system due to higher porosity of the nanocomposite prepared with
The results described here are promising and open the possibility to apply these materials in biomedical applications.

**ABCChem 190**

**Simple method for obtention of carbon nanoribbons from multiwalled carbon nanotubes (MWCNTs)**

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Carbon nanoribbons can be produced by exfoliation or unzipping of multiwalled carbon nanotubes using strong oxidants and acids or via metal intercalation-exfoliation in liquid ammonia followed by acid and thermal exfoliation. These unzipping methods tend to produce ribbons of several layers, and it may be difficult to separate individual, monolayer graphene nanoribbons. This work presents the production of single-layer carbon nanoribbons from multiwalled carbon nanotubes by a combination of treatments with acids and hydrogen peroxide. Characterization by scanning electron microscopy (SEM), Raman spectroscopy and atomic force microscopy (AFM) shows that this method can produce long, single-layer, carbon nanoribbons without the use of harsher oxidants such as permanganates or toxic solvents such as liquid ammonia.

**ABCChem 191**

**Polyester-toner microchips for biomolecule analysis**

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The miniaturization of analytical systems is a growing and relevant area in the scientific environment. The development and improvement of micro devices allowed the increase of the efficiency of many analyzes due to the optimization of their processes, which includes a lower volume of reagents and samples.
required, portability facilitated, reduction of the time spent, low cost manufacturing, integration of many steps into a single substrate, besides the microchip’s applications in equipment of gas chromatography (GC), liquid chromatography (LC), and capillary electrophoresis (CE). However, the design and material of the prototype directly influence the analysis’ performance, since the interaction of the internal walls with the analytes or dimensional parameters can cause the loss of reproducibility of the process, for example, the occurrence of the Joule Effect during the measures. Thus, we propose in this microfabrication alternatives an improvement of the analytical performance through different techniques of polyester-toner production, such as laser ablation or manual cutting, using a simple layout composed only of one channel and reservoirs for sample injection and potential application, and conducting tests of the electrosmotic flow by means of capacitively coupled contactless conductivity detection (C^4D). The dynamic coating of the microchips has also been shown to be an innovative and practical strategy for minimizing the undesirable effects of channel’s interaction with the analytes, since it can be done in house and allows versatility in the choice of reagents, once ionic polymers can be employed such as hexadimethrine bromide (polybrene). We obtained the elimination of direct interferences in the channels working with 100 to 180 µm in thickness, as well as a stabilization in migration time after coating in different pHs, aiming at a better analytical reproducibility for future analysis of biomolecules as amino acids, proteins, peptides and biopharmaceuticals.

Polyester-toner microchip with laser ablation: First layer of polyester material with reservoirs, second layer with toner deposited twice on both sides, third layer composed solely of polyester transparency

ABCChem 192
Purification and characterization of hypoglycin A & hypoglycin B

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Blighia sapida, commonly referred to as the ackee, belongs to the Sapindaceae family. Two toxins, namely hypoglycin A (L-α-amino-β-methylene cyclopropane propionic acid) and hypoglycin B (γ -L-glutamyl-a-amino-β-methylene cyclopropyl propionic acid) are associated with the fruit. This study was undertaken to identify a facile method of isolating and purifying both toxins. Hypoglycin A and B were purified from Blighia sapida ethanolic seed extracts using anion exchange chromatography, and were characterized by nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FTIR). A band at 3090 cm$^{-1}$ previously assigned as an amino acid (NH$_3^+$) is believed to be attributed to the CH stretching vibration of methylene cyclopropane, specifically the methylenic stretch in hypoglycin. Hypoglycin A and B co-eluted in a yield of 0.4 % yield.

ABCChem 193

Determination of acidity level in simulated seawater by spectrophotometry

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Visible spectrophotometry is a method currently used to determine pH. It is based on the use of colorimetric indicators that in aqueous solution behave like Brönsted acids and bases. The equation to determine the total hydrogen ion concentration depends on the cologarithm of the dissociation constant (p$K_a$) and the molar absorptivity coefficients ($\varepsilon_i$) of each of the indicator chemical species (HIn and In). The interest in quantifying the pH accurately lies in using spectrophotometry to generate series of temporary pH data in seawater of the coastal zone. The creation of a data base is useful in the coastal observatories of global change in Mexico because it allows to estimate the effect of marine acidification on ecosystems, especially for the coastal ecosystems of Mexico. We present the pH calculations performed by spectrophotometry for simulated
seawater solutions and also the estimation of the uncertainty associated with the determination.

**ABCChem 194**

**Theoretical study of the synthesis and structure of polycyclic saturated "cages"**

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Saturated polycyclic “cages”, commonly referred to as homocubanes, are derivatives of cubane in which one or more of the edges has been replaced by methylene bridges. Most saturated cages molecules contain considerable strain energies which frequently causes unusual patterns of chemical reactivity. However, they present high kinetic stability which makes them ideal systems to controlled energy storage. In this study, we performed computational calculation using PM3, ZINDO/S semi-empirical methods and RHF/3-21g to investigate the thermodynamics of the synthesis of the cubane molecules and the effects of the bridge position on the bond-energies within the molecules. Our results confirm the kinetic stability of the intermediates of the cubane synthesis. In addition, we found that the presence of methylene bridges decreases the strain energy of the molecules, which could help to control and tune the energetics of different systems for their applications in energy storage and other devices that may require high reactivity.
Analyzed homocubanes (HC) structures.

**ABCChem 195**

**Intermolecular hydrogen bonding during proton coupled electron transfer in α-hydroxyquinones**

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Reduction processes of α-hydroxyquinones represent a typical self-protonation case of study, wherein the electrogenerated anion radicals undergo fast and irreversible proton transfer, leading to the formation of the corresponding hydroquinones. Unfortunately, the faradaic efficiency of the process leads to only one third of the starting material being reduced. To improve this efficiency, an external proton source (salicylic acid, pKa (in DMSO) = 6.7) can be added to the medium (Figure 1A), and the corresponding voltammetric signal increases its relative current. Nevertheless, in some compounds (diterpene abietane α-hydroxiquinones Horminone, Taxodione y 7α-O-methyl-conacytone, Figure 1B), the behavior leads to the evolution of a peak prior to the one associated with the selfprotonation step, which increases its current in a similar fashion as with increases of proton donor. This behavior suggests that the latter compounds undergo a prior chemical reaction, probably related to the formation of an hydrogen bonding complex with the original quinone. In this work, experimental details evidencing such process along with theoretical analysis of the possible structure of such adducts will be presented.
Exploring the use of isomerism in heteroleptic complexes for rational design

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Effective proton reduction catalysts are critical for the eventual use of water splitting in energy storage. Rational design through ab initio and density functional computations offers a cost effective and time efficient method for catalyst improvement. Catalysts developed by heteroleptic modifications of the pyridinethiolate moieties of the nickel pyridinethiolate (Ni-pyt) proton reduction catalyst have been explored computationally. The most notable finding is the high variability of the Ni inner coordination sphere and basicity between isomers of heteroleptic compounds. Careful exploration of the Ni-pyt system and simpler model systems provides insight into the mechanism of this variability. The tools of conceptual DFT, namely local softness and the Fukui function, are deployed for discussion of the changes in the coordination sphere. A discussion of intra- and inter ligand electronic structure and nonbonding interactions yields a working model of this effect. Finally, a method for utilizing this effect for more effective optimization of molecular properties is proposed, with particular attention paid to the area of proton reduction. Computations were performed with NWChem.
6.6 for geometry optimization, normal modes, and condensed Fukui functions, and Psi4 1.1 for coupled cluster calculations on isolated ligands.

**ABCChem 197**

**Construction and characterization of solid-state sensors based on tungsten oxides used for the determination of acidity in dairy samples**

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Nowadays, the use of glass electrodes in food industry is the standard for pH and acidity levels determination in direct samples, being the dairy industry one of the most important sectors in which this kind of procedures take part. It has been reported that glass electrodes becoming fouled due to protein and lipid adsorption on the electrode surface and their brittle nature; so, it has made necessary to look for other kind of ion selective electrode in order to determine the concentration of the hydrogen ion in aqueous solution. For this work, solid-state sensors based on tungsten oxides were built and characterized. Such oxides were electrogenerate with an optimized methodology and each kind of electrodes was coated with Nafion (R) with the purpose of protecting the pH sensible film. The performance of this electrodes were evaluated, and the response of the electrode in presence of potassium ion as interference ion was determined.

The procedures used to determine the acidity in milk were based on the Mexican standards NOM-155-SCFI-2003 and NOM-155-SCFI-2012, which differs each other from the addition of water in the samples. To get the equivalence point during the acid-base titration, diverse methodologies were used, and those different values of acidity obtained are attributable to the fouling of glass electrodes in the characteristic of the same sample. Typical acid-base titration shown several problems, as difficulty to see the change of color in the pH indicator. The application of Gunnar Gran functions (using the data obtained from tungsten sensors) gave the most repeatable and trustworthy results. Additionally, a similar parameter to an acid dissociation constant for the caseins in milk was obtained from the G. Gran functions. Such fact was later confirmed with the ones obtained from the titration of pure casein. Finally, in the titration of yogurt was found that, by the association of G. Gran functions, the contribution
of acidity given by the caseins and the one given by the lactic acid, formed in the fermentation process of yogurt, can be differentiated.

ABCChem 198

Tyrosinase biosensor in screen printed carbon modified electrodes with gold-nanoparticles for polyphenols determination in fresh fruits extracts

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There were developed a tyrosinase enzyme biosensors to quantify polyphenols in natural fruit extracts by electrochemical methods using screen printed carbon modified electrodes. For the sensor the experimental and electrochemical techniques parameters were optimized: pH, enzyme immobilization conditions, enzyme and substrate concentrations. Voltammetric techniques such as cyclic and square wave voltammetry as well as amperometry were used with standard addition calibration curves. The biosensor was prepared over screen printed carbon electrodes with gold nanoparticles deposition and immobilized tyrosinase with bovine serum albumin and glutaraldehyde. The substrates used were caffeic acid and gallic acid. The support electrolyte was a phosphate buffer at pH 8.0 for both compounds. Amperometry applied at 0.25 V presented a linear range from 0.3 μM mM to 600 μM, repeatability 1.7 % and reproducibility 1.9 % as RSD. The limit of detection was 0.25 μM and limit of quantification was 0.7 μM for the quantification of caffeic acid and for the gallic acid the limit of detection obtained was 0.27 μM and the limit of quantification 0.9 μM. The biosensor was used to determine polyphenols in fresh ethanolic blackberry and soursop extracts. The biosensor presents acceptable performance and can be used to determine polyphenols in different fruit matrixes and concentrations.
Charge transfer mechanisms determined by chemical reactivity theory within DFT

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In this work we apply the 2-parabolas model that satisfies the discontinuity condition dictated by the ensemble theorem, and that assumes the existence of the second derivative, the hardness, with respect to the number of electrons.
This model leads to the definition of the electrodonating and electroaccepting powers, chemical reactivity descriptors that have been used in the recent literature. Inspired by these ideas, we present a global and local partitioning of the charge transferred predicted by the PP model that allow us to determine which direction of electron transfer, electrophilic or nucleophilic, prevails in a given reaction. Several applications to well known reactions like complexation, hydration of aldehydes and ketones, addition of Br2 to alkenes and Diels-Alder cycloadditions will be presented. The model also serves to explain and quantify back-donation as it is illustrated in its application to the reaction between phosphines and a transition metal atoms. To show the potentiality of this approach, the partitioning of the amount of electrons transferred is applied to the interaction of the iron-sulfur ferredoxin and a set of imidazopyridines, aiding to determine the action mechanism of these compounds. The potential application of the local analysis to propose starting geometries for transition state searches is also discussed.

**ABCChem 201**

**Low-cost minimal instrumentation without salt bridge for microphoto-coulometric detection of SO2**

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A low-cost instrumentation electrolytic cell was obtained to demonstrate a linear quantitative relation between the electrolysis time (equivalency time) and a constant current pulse in redox titrations with electrogenerated iodine without salt bridge; by means of damping, acidity levels had been reached in situ. Both end points of coulometric titration obtained with visual indicator (starch as indicator) and coupled microphotodetection are linear proportional to SO2 levels in standard solution and samples. Typical calibration plots are obtained: 18.2628 s mmol⁻¹ (nHSO₃⁻ [mmol]) + 0.5607 s for visual detection and 11.8404 s mmol⁻¹ (nHSO₃⁻ [mmol]) + 0.7000 s for end point photodetection. Detection of free SO2 levels in red wine samples are shown as an application of the microelectrochemical methodology proposed.
Sequence of coupled chemical and electrochemical reactions, ErCrCr, in coulometric microtitrations of bisulphite with minimal instrumentation with no salt bridge.

Typical calibration plots $A = f(t_{\text{electrolysis}})$: Aliquots of metabisulphite 0.005 N: a) 20 mL, b) 100 mL, c) 180 mL.

ABCChem 202

Evaluation of national refining system’s naphtha reformer units: Internship report
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**Introduction**
The catalytic naphtha reforming is a chemical process to increase the octane of the mixture components to make gasolines. Desulfurized naphtha constitutes the feed of reforming unit. The main products are hydrogen, light hydrocarbons and the reformate. To ensure the continuity of the processes and the proper operation of their equipment, the daily monitoring of the operation is carried out through a Distributed Control System.

**Objectives**
To obtain the trends between reformed octane number and naphtha reforming plants' operating variables.
To determine the causes of the low octane number in National Refining System's catalytic reforming units.

**Methods**
Four catalytic reforming units located in two refineries of the company were selected as follow:
- U-500-1 and U-500-2 from TU
- U-500-1 and U-500-2 from SC

A period of eight months (from January to August 2017) was defined for the monitoring of the reforming units.

Operating conditions of units, feed and reformate specifications were obtained from PI System.
From reformer's operating temperatures, reaction sections' characteristic temperatures for each unit were determined (WAIT, WABT).
Finally, four graphs of WAIT, WABT and RON (Research Octane Number) were constructed along the time the reformers were monitored.

**Data Analysis**
U-500-1 TU and U-500-1 SC are Continuous Catalytic Reformer (CCR) plants, whereas U-500-2 TU and U-500-2 SC are Semi-Regenerative Reformer (SRR) plants.

**Conclusions**
The low octane number on reformate is due to catalyst depletion.
In general, there is a progressive increase in both WAIT and WABT, as well as decrease in the RON over time.
The Conformity Assessment determines the degree of compliance and compliance of Mexican official standards, international standards or other specifications, prescriptions or characteristics for a product, method, process or service. The laboratory of the Metrology Unit seeks to develop methods to demonstrate
the aptitude, traceability and estimation of uncertainty in different measurement methods, both chemical (gravimetry, volumetry, base acid titers) and physicochemical (spectrophotometry, viscosimetry), and the development of methodologies for the metrological confirmation of instruments and equipment. Following the guidelines for the conformity assessment that involves the NMX 9001-2008 and NMX-EC-17025-IMNC-2006 standards, it seeks to detect errors of the proposed methods, correct them, prevent future errors, generate experience and document it. With the information obtained, will serve to achieve the corresponding accreditation for each of the methods before the Mexican Accreditation Entity (EMA, for its acronym in Spanish).

**ABCChem 204**

*Development and validation of an HPLC-MS/MS method for the identification and quantitation of 3,3’-diindolylmethane in newborn-rat plasma*

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In the presented work a method was developed and validated to measure 3,3’-diindolylmethane in plasma through high performance liquid chromatography coupled with a triple quadrupole mass spectrometer. The conditions of the MS spectrometer were tuned to obtain the best possible signal of the analyte. The analyte was determined in human plasma determining an accuracy of 95.7% and factor such as limit of detection (30ng/mL) and limit of quantification (100ng/mL) were determined alongside linearity. No carry over was detected in the method. The flow rate, retention time and run time were overall improved for the application in an investigation regarding the molecule as a candidate for a commercial pharmaceutical.

**ABCChem 205**

*Validated method to determine neurotransmitter in human plasma by HPLC-MS/MS with specific application to suicide cases*

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An HPLC-MS/MS method was developed for the determination of dopamine (DA), serotonin (5-HT), epinephrine (E) and norepinephrine (NE) in human plasma. The analytes were separate in a reverse phase column using a mixture of water, methanol and formic acid. The instrument was operated under the multiple reaction monitoring (MRM) mode using electrospray ionization (ESI) in the positive mode. A good linear relationship with coefficients under > 0.99 was achieved over the concentration ranges of 5-1000 ng mL⁻¹. The detection limit for DA, 5-HT, E and NE were 1, 0.1, 0.5 and 1 ng mL⁻¹ respectively and 5 ng mL⁻¹ of quantification limit for the neurotransmitters analyzed. The method was used to analyze and quantify DA, 5-HT, E and NE in 10 human plasma samples, were 3 who committed suicide and 7 who died from other causes. A low concentration of NT was obtained for the ones who committed suicide, this information is useful to make a relationship with suicide, depression and low concentrations of neurotransmitters.