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9th International Symposium on Nano & Supramolecular Chemistry

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PLENARY ABSTRACTS

PL1: Perspectives in Chemistry: From Supramolecular Chemistry towards Adaptive Chemistry

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Supramolecular chemistry is intrinsically a dynamic chemistry in view of the lability of the interactions connecting the molecular components of a supramolecular entity and the resulting ability of supramolecular species to exchange their components. Similarly, molecular chemistry becomes a dynamic covalent chemistry (DCC) on introduction into the molecular entity of covalent bonds that may form and break reversibly, so as to allow a continuous change in constitution by reorganization and exchange of building blocks. Taken together, these features define a Constitutional Dynamic Chemistry (CDC) covering both the molecular and supramolecular levels.

CDC introduces a paradigm shift with respect to constitutionally static chemistry. It takes advantage of dynamic diversity to allow variation and selection and operates on dynamic constitutional diversity in response to either internal or external factors to achieve adaptation.

CDC generates networks of dynamically interconverting constituents, constitutional dynamic networks, presenting agonistic and antagonistic relationships between their constituents that may respond to perturbations by physical stimuli or to chemical effectors. It applies in chemistry as well as in materials science.

The implementation of these concepts points to the emergence of adaptive and evolutive chemistry, towards systems of increasing complexity.

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PL2: TiO₂ Photocatalysis and Diamond Electrode

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The tremendous amount of research that has been carried out in the two closely related fields of semiconductor photoelectrochemistry and photocatalysis during the past three decades continues to provide fundamental insights and practical applications. The principles and measurements obtained TiO₂ with photoelectrochemical studies have led to the research activity on heterogeneous photocatalysis, where the strong photooxidative activity of TiO₂ has been applied to environmental cleanup. This resulted in the concept of “light cleaning”, i.e., deodorizing, disinfection, and decontamination of air, water and surface with TiO₂ thin films and light. In 1997, we reported the novel photo-induced superhydrophilicity of TiO₂ and proposed the concept of self-cleaning superhydrophilic properties of TiO₂.

We have the research center in our Noda Campus of Tokyo University of Science, named “Photocatalysis International Research Center”. In this center, we have three research groups, Artificial photosynthesis group (Demonstration experiment using sun light), Self-cleaning group (Performance evaluation using windows and walls), and Environmental cleanup group (Environmental cleanup with composite photocatalyst). Now we have three more research projects of Plant factory PJ, Liquid light-tube PJ and CO₂ reduction using diamond electrode PJ. In this meeting, I will explain and introduce the recent progress and our main targets of this research center.

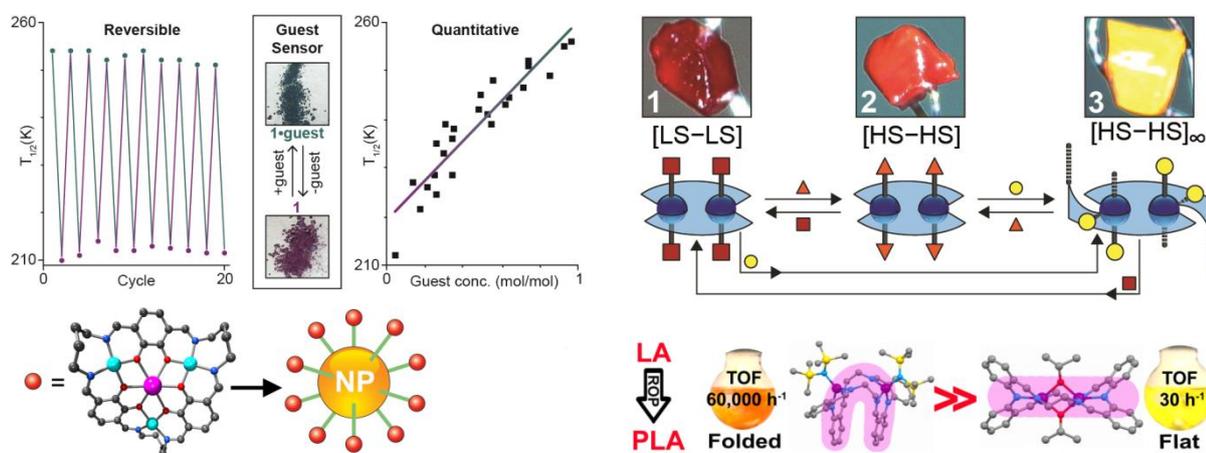
PL3: Guest sensors, switches, and macrocyclic catalysts

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In my research group we focus on the design of polydentate and macrocyclic ligands that provide a lot of control over the bound metal ions, as well as producing stable, robust complexes. Our aims include working towards spin crossover-based guest sensors, immobilizing magnetically interesting complexes on solid supports, and producing stable highly active catalysts [1-11]. Highlights of our recent work will be presented.



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PL4: Emergent Applications in Nano and Supramolecular Chemistry

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The time has come for us to embrace complexity—despite the fact that everyone has their own definition of it—and put much more emphasis into studying mixtures of interacting molecules. An excellent reason for responding positively to the intellectual challenge posed by systems chemistry is that complexity very often gives rise to emergent properties that are not present in the components of a complex mixture but come to light only as a result of interactions between molecules. One example of emergent behavior, which I will highlight, is provided by a class of wholly organic materials based on 1:1 and 2:1 mixtures of neutral aromatic compounds—where donors and acceptors, which also encompass stabilizing hydrogen bonding interactions—form mixed stacks that boast the welcome but elusive property of room temperature ferroelectricity. While the materials' behavior was unexpected, the molecular basis for it is extremely simple and the superstructure leads directly to the complexity that emerges once the act of crystallization is complete. The result is a material with properties not shared by its components. Another example is provided by the self-assembly, in aqueous alcohol, of infinite networks of extended structures, which we call CD-MOFs, wherein γ -cyclodextrin (γ -CD) is linked by coordination to Group IA metal cations to form metal-organic frameworks (MOFs). CD-MOF-1 and CD-MOF-2, which can be prepared on the gram scale from KOH and RbOH, respectively, form body-centered arrangements of (γ -CD)₆ cubes linked by eight-coordinate alkali metal cations. These CD-MOFs exhibit very different properties than γ -CD itself. For a time, I was of the opinion that the nature of the anion accompanying the K⁺ or Rb⁺ cation was unimportant. Not so, because if it is AuBr₄⁻, the situation changes quite dramatically. Yet another example of emergent behavior comes to light in the isolation of gold. We need to come to terms with complex networks that can be periodic, aperiodic or completely random. Complex networks are everywhere to be found: they are all around us. Consider the world-wide web or global stock markets. Reflect on the way birds adopt formations in the sky during migrations or the response of different ecosystems to climate change. In the superorganism formed by certain ant colonies, the ants operate as a unified entity, working together collectively to support the colony. Prediction in the case of complex networks is nigh impossible. Uncertainty rules the roost—and the unexpected is always just lurking round the corner. While research into complex networks is commonplace in mathematics, physics and biology, as well as in computer science, economics and the engineering disciplines, when it comes to creating and understanding complex networks, chemists have been conditioned by their education and training to avoid them. We have an aversion to working with mixtures of molecules, yet complex mixtures no longer constitute an intractable problem with rapidly growing access to modern analytical tools, increasingly enlightened approaches to chemical synthesis—often involving one-step procedures starting from inexpensive and readily available starting materials—and the ability to carry out computations on integrated systems over multiple length scales in time and space.

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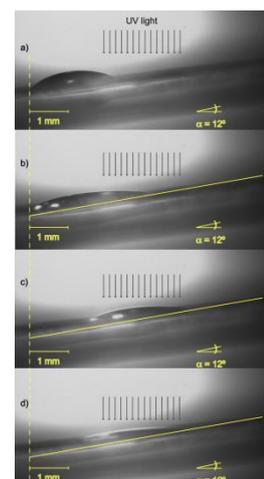
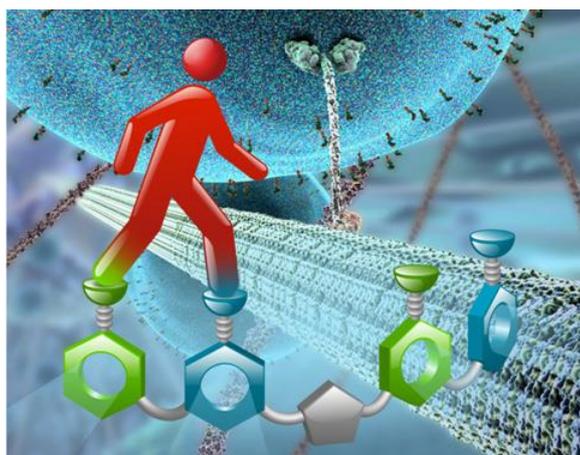
PL5: Making the Tiniest Machines

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Over the past two decades some of the first examples of synthetic molecular level machines and motors—all be they primitive by biological standards—have been developed. Perhaps the best way to appreciate the technological potential of controlled molecular-level motion is to recognise that nanomotors and molecular-level machines lie at the heart of every significant biological process. Over billions of years of evolution Nature has not repeatedly chosen this solution for achieving complex task performance without good reason. In stark contrast to biology, none of mankind's fantastic myriad of present day technologies exploit controlled molecular-level motion in any way at all: every catalyst, every material, every polymer, every pharmaceutical, every chemical reagent, all function exclusively through their static or equilibrium dynamic properties. When we learn how to build artificial structures that can control and exploit molecular level motion, and interface their effects directly with other molecular-level substructures and the outside world, it will potentially impact on every aspect of functional molecule and materials design. An improved understanding of physics and biology will surely follow.



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PL6: Multifunctional Hybrid Carbon Interfaces

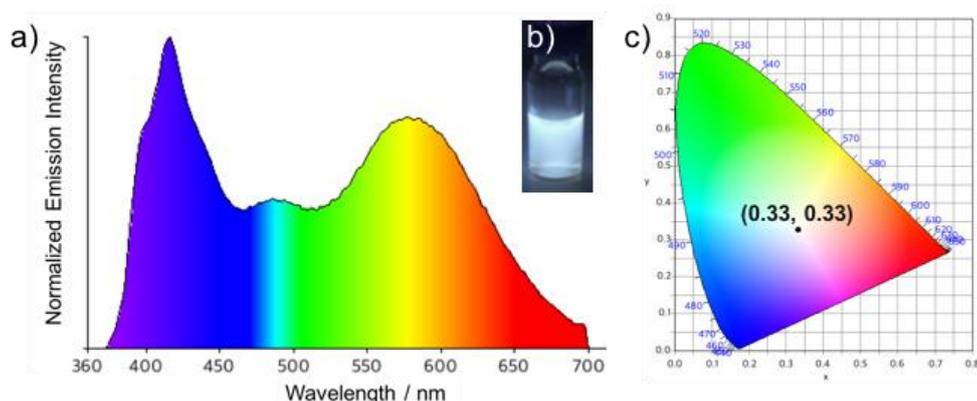
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Carbon nanodots, quasispherical nanoparticles with size below 10 nm, are the next generation nanostructures, possessing even more intriguing properties compared to other carbon nanomaterials: their intriguing photoluminescence properties have led people to label them “carbon nanolights”, making them promising candidates in a wide range of applications, including biosensing and bioimaging, photoacoustic and thermal theranostics, inexpensive and environmentally friendly sensitizers in mesoscopic solar cells.

We have recently described a simple, scalable, reliable and cost-effective synthetic process for producing high-quality nitrogen-doped carbon nanodots (NCNDs), by employing arginine and ethylenediamine as precursors [1]. The new material displays among the smallest size and the highest fluorescence quantum yields reported so far. Moreover, they can be easily post-functionalized, due to the abundant presence of amino groups.

These new NCNDs can act as powerful alternative to the conventional co-reactant species for electrochemiluminescence generation [2]. We have also presented a rational synthetic design for mastering CND properties, showing the importance in the choice of the precursors. By using properly designed functional units, the desired properties can be modulated, from the molecular to the nanoscale level in a controlled fashion. CNDs with customized emission can therefore be approached [3].



In combination with suitable catalysts, other carbon nanoforms (nanotubes and nanohorns) can serve as versatile interfaces for the splitting of water molecules to give oxygen, but, especially, molecular hydrogen, ideal for clean energy generation.

During this talk, we will show the latest and most exciting results obtained in our laboratories in these fast developing fields.

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PL7: Electrocatalysis for Energy Conversion Processes

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Replacement of precious metal catalysts by commercially available alternatives is of great importance among both fundamental and practical catalysis research. Nanostructured graphene-based and transition metal materials have demonstrated promising catalytic properties in a wide range of energy generation/storage applications. Specifically engineering graphene with guest metals/metal-free atoms can improve its catalytic activity for electrochemical oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), thus can be considered as potential substitutes for the expensive Pt/C or IrO₂ catalysts in fuel cells, metal-air batteries and water splitting process. In this presentation, we will talk about the synthesis of nonprecious metal and metal free elements-doped graphene, and their application on electrocatalysis [1-8]. The excellent ORR, OER and HER performance (high catalytic activity and efficiency) and reliable stability (much better than the commercial Pt/C or IrO₂) indicate that new materials are promising highly efficient electrocatalysts for clean energy conversion.

Keywords: Transition metal, metal-free, electrocatalysts, oxygen reduction reaction, oxygen evolution reaction, hydrogen evolution reaction, energy conversion

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PL8: Critical design of heterogeneous catalysts for sustainable production of chemicals and energy: current approach and emerging prospects

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Catalytic technologies play a critical role in the economic development of both the chemicals industry and modern society, underpinning 90 % of chemical manufacturing processes and contributing to over 20% of all industrial products. Concerns over dwindling oil reserves, carbon dioxide emissions from fossil fuel sources and associated climate change is driving the urgent need for clean, renewable energy supplies. Two important sources (i) biomass derived from waste agricultural/forestry materials or non-food crops and (ii) large natural gas resources, offers the most easily implemented and low cost solution to produce transportation fuels, and for biomass the only non-petroleum route to organic molecules for the manufacture of bulk, fine and speciality chemicals necessary to secure the future needs of society.

However, to facilitate such a transition requires innovations in catalyst and process design for the selective conversion of these hydrophilic, bulky feedstocks into fuels or high-value chemicals. This presentation will discuss the challenges faced in these two areas: catalytic biomass processing, as well as in natural gas processing and highlight recent successes in catalyst design which have been facilitated by advances in nanotechnology and careful tuning of catalyst formulation.

The catalytic systems have been categorized into subgroups such as metal oxides and phosphates, supported metals, functionalized porous materials, and carbonaceous materials to discuss their structural features and active sites towards intrinsic reactivity and selectivity in the catalytic transformation via reactions such as: hydrolysis, dehydration, hydrodeoxygenation and oxidation. Specific case studies will explore how the effects of pore architecture and acid/base strength can impact upon process efficiency.

KEY LECTURES ABSTRACTS

KL1A: A light-driven artificial molecular pump

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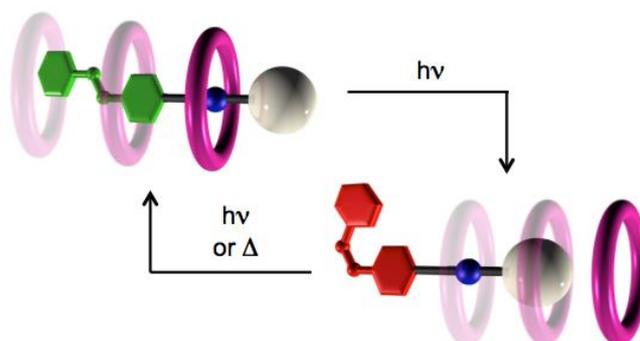
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The development of dynamic chemical systems that exploit dissipative (non-equilibrium) processes is a challenge in supramolecular chemistry and a premise for the realization of artificial nanoscale motors [1]. Here we will describe investigations undertaken in our laboratories aimed at photo-inducing and -controlling large-amplitude molecular motions, both under thermodynamic and kinetic viewpoints, in multicomponent (supramolecular) species that comprise photoreactive units [2]. This work has recently culminated with the design, construction and operation of a system in which light irradiation causes the relative unidirectional transit of a nonsymmetric molecular axle through a macrocycle (see Figure) [3]. The device rectifies Brownian fluctuations by energy and information ratchet mechanisms and can repeat its working cycle under photostationary conditions. The conceptual and practical elements forming the basis of autonomous light-powered directed motion are implemented with a minimalist molecular design. As a matter of fact, this is the first example of a photochemically driven artificial molecular pump [4]. Systems of this kind can not only lead to radically new approaches in catalysis, materials science and medicine, but also disclose unconventional routes for the conversion of light energy into chemical energy.



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KL1B: All-Inorganic Perovskite Quantum Dot Composites for Backlight Display

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All-inorganic CsPbX_3 ($X = \text{I}, \text{Br}, \text{Cl}$) perovskite quantum dots (PQDs) have been extensively investigated because of their unique optical properties, such as tunable wavelength, narrow band, and high quantum efficiency. These fascinating features of inorganic nanocrystals have been utilized in light emitting diode (LED) devices. The common method that uses LED on-chip fabrication is mixed green (520 nm) and red quantum dot (620 nm) with silicon gel. With its strong ion exchange effect, this phenomenon widens the narrow emission spectrum. Quantum dots cannot be mixed because of anion-exchange. This research aims to address this issue by designing a mesoporous PQD nanocomposite that can prevent ion exchange and increase its stability. We mixed green quantum dot-containing mesoporous silica nanocomposite with red PQDs, which can prevent the anion-exchange effect and increase thermal and photo stability. After resolving this problem, we further applied wide color-gamut in PQD-based LEDs for backlight display. We also successfully used PQDs in an on-chip LED device. Our white LED device for backlight display pass through a color filter with an NTSC value of 113% and Rec. 2020 of 85% as shown in Fig. 1 [1-3].

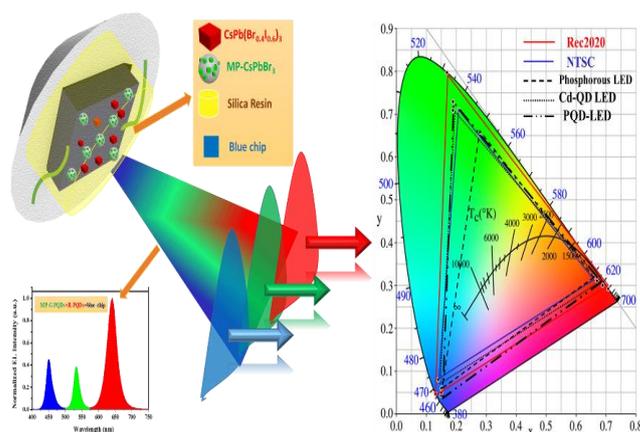


Figure 1. Green CsPbBr_3 PQDs and red $\text{CsPb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ mixed in silicone resin were fabricated and placed on the InGaN blue chip. The green and red QDs were excited by 450 nm blue light and emitted green and red lights. This device was called PQD-white LED. PQD-white LED exhibits a wide color gamut because of its narrow emission wavelength.

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KL2A: Self-organization of supramolecular receptors in the nanoparticle-coating monolayer

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Gold nanoparticles protected by a monolayer of organic molecules offer a straightforward route to the realization of complex chemical systems. Indeed, several groups have already demonstrated that such nanoparticles can be turned by appropriate functionalization into sensors and catalysts. Such an activity intrinsically implies the cooperative (or collective) recognition of substrate by the monolayer molecules. The functional groups implemented the structure of the coating molecules provide the interactions for substrate recognition. Whereas, their radial organization on the particle surface can multiply the number of interactions and provide some degree of preorganization. Spatial proximity of functional groups in the monolayer can be exploited to obtain cooperative functions. Still, the design of receptors with programmed affinity using monolayer protected nanoparticles is a challenging goal. In this lecture, we will discuss our recent results on the exploitation of nanoparticles recognition abilities to enable new detection protocols (“NMR chemosensing”) [1] that conjugate the selectivity of chemosensors with the large structural information provided by NMR. The rationale of our methods rests upon the slow diffusion rate of 2-nm gold core nanoparticles with respect to small analytes, and on the intermolecular dipolar interactions as a pathway to transfer magnetization between two interacting species. Diffusion ordered spectroscopy, NOE or STD experiments allow the extraction of the NMR spectrum of the analyte from the mixture. The main advantage is hence the fact that the signal produced by the sensing system is the full NMR spectrum of the analyte, and not just a variation of one sensor property. This allows not only a detection and quantification of the analyte, but also its unambiguous identification. Application of this protocol include detection of relevant metabolites in biological fluids, analysis of mixtures, quality validation of drug formulations. In additions, our protocols provide tools to identify, rank and investigate the recognition ability of the nanoparticles. Such information, integrated with extensive computational simulations, reveals a protein-like recognition mode for monolayer protected nanoparticles [2].

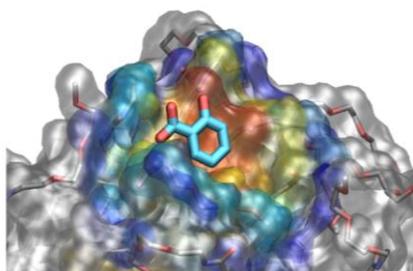


Figure 1. Docking pose of salicylate to a monolayer-protected nanoparticle

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KL2B: Lanthanides-Redox Ligands for Single Molecule Magnets and Luminescence

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Lanthanide-based complexes have greatly contributed to the development of molecular magnetism in the last decade and more particularly in the branch of single molecule magnets (SMMs) [1]. The main reasons are their large magnetic moments associated to their intrinsic large magnetic anisotropy. The splitting of the multiplet ground state of a single-ion in a given environment is responsible of the trapping of the magnetic moment in one direction in SMMs. However, the analyses of the crystal field effects on the magnetic anisotropy are not so common [2]. A better understanding of the magneto-structural correlations in lanthanide-based complexes should provide tools to improve their potentialities.

In this presentation we will focus on the specific magnetic properties of TTF-based lanthanide mononuclear and polynuclear complexes. We will show how optimize the SMM behavior playing on i) the modulation of the supramolecular effects via chemical modifications of the TTF ligand [3], ii) simple molecular engineering modifying the electronic distribution and symmetry of the coordination polyhedron, iii) magnetic dilutions (solution and doping) and iv) isotopic enrichment of the dysprosium [4,5].

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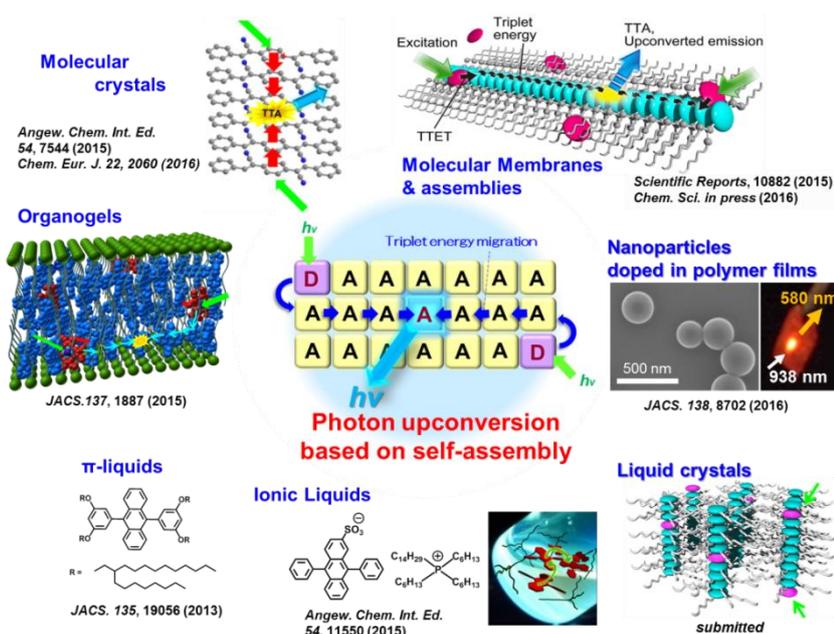
KL3A: Photon Upconversion based on Energy Migration in Molecular Assemblies

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Triplet-triplet annihilation-based photon upconversion (TTA-UC) is a promising methodology which can be applied to many sunlight-based energy conversion systems. To date, efficient TTA-UC has been achieved in solution based on the molecular diffusion of excited triplet molecules. However, the diffusion of chromophores in such low-viscosity solvent is not high enough to maximize the UC quantum yield at low solar irradiance. To solve these problems, we introduced the concepts of energy migration in ordered molecular self-assemblies [1] to achieve efficient TTA-UC in molecular systems [2-10]. Interestingly, some of the molecular self-assemblies dispersed in solution or organogels revealed oxygen barrier properties, which allowed TTA-UC even under aerated conditions [2,3,5,8-10]. In this talk, our recent development on the supramolecular TTA-UC in varied molecular systems will be discussed.



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KL3B: Detection of reactive oxygen species *in vitro* and *in vivo* based on nanomaterials

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Reactive oxygen species (ROS) play important roles in the biological systems. Excessive concentration of ROS will lead to the oxidative damage to biomolecules such as protein, DNA, and lipid layers, resulting in various diseases. Although electron spin resonance (ESR) as a conventional method shows the capability for the detection of overall ROS, the selectivity for the specific ROS and the application on *in vivo* detection is still a great challenge. As a result, it is of significant importance to establish alternative methods to accomplish the detection of ROS rapidly, accurately and selectively. Alternatively, electrochemical sensors exhibit the outstanding performance in the selectivity, which is also promising for the real time detection *in vivo*. In this report, we will give an introduction on the electrochemical sensors based on nanomaterials for ROS detection. An outlook on the future development of ROS electrochemical sensors and the corresponding application on the research and prevention of some diseases will also be presented.

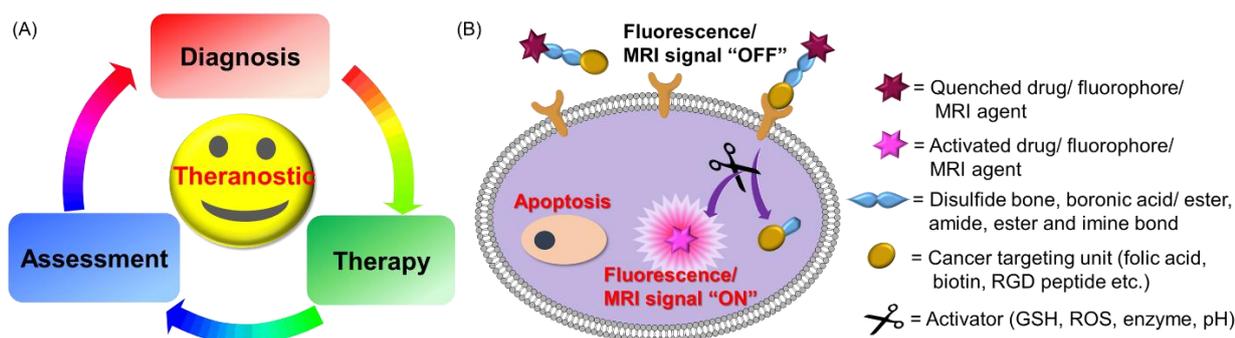
KL4A: Antitumor Theranostics and Its Delivery Sensing

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The advances in genomics, proteomics, and bioinformatics have directed the development of new anticancer agents to reduce drug abuse and increase safe and specific drug treatment. Theranostics, combining therapy and diagnosis, is an appealing approach for chemotherapy in medicine which exhibit improved biodistribution, selective cancer targeting ability, reduced toxicity, masked drug efficacy, and minimum side effects. The role of diagnosis tool in theranostic is to collect the information of diseased state before and after specific treatment. Magnetic particle-, mesoporous silica-, various carbon allotrope-, and polymer nanoparticle-based theranostic systems are well accepted and clinically significant. Currently, small conjugate-based systems have received much attention for cancer treatment and diagnosis. The structural architecture of these systems is relatively simple, compact, biocompatible, and unidirectional. In this talk, the latest developments on small conjugate based theranostic agents for tumor treatment and diagnosis using fluorescence undertaken in my lab will be given.



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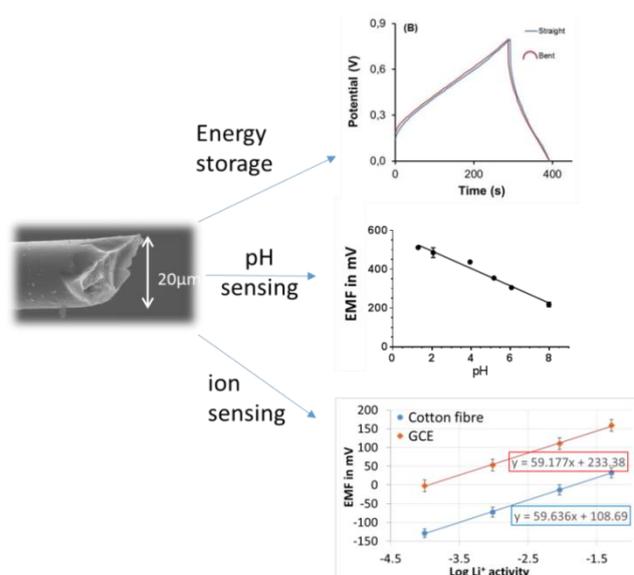
KL4B: Nanocarbon and Conducting Polymer Fibre-Based Electrodes—From Energy Storage to Electrochemical Sensing

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Wearable electronic devices have attracted much attention in recent years because of their widespread applicability from personal electronics, to healthcare applications. Lightweight, flexible energy storage is essential to power such electronics. Fibre-shaped electrodes are emerging as a versatile design for wearable applications since they can be easily incorporated into clothing [1]. In this study we used nanoparticles to produce flexible fibre electrodes and evaluated their properties in terms of energy storage and as sensing electrodes.

We investigated the wet-spinning of fibers containing different nanocarbons (e.g. carbon black, carbon nanotubes (CNTs)), conducting polymers and metal oxide nanoparticles. These fibre electrodes were compared to nanoparticle-coated cotton thread. The electrical and electrochemical properties were evaluated for the different fibers in addition to fiber morphology and mechanical performance. Incorporating redox materials like MnO₂ and further conducting polymer layers, resulted in a large increase in specific capacitance and stability upon repeated cycling. The resulting solid state wire-based devices show promising electrochemical performance with respect to energy storage [2]. The electrochemical performance of these fiber-based electrodes was also evaluated in terms of sensing. Physiologically significant ions, such as the anti-psychotic drug lithium, were detected using these flexible fiber electrodes, in addition to measuring skin pH. An excellent Nernstian response was generated by these wearable sensors. Their performance was compared to glassy carbon electrodes and both electrode types functioned identically.

The combination of both fiber-based sensors and fiber-based energy storage will allow for fully integrated wearable sensing.



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KL5A: Chemical Function based on Redox-active Ligands

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Since the 1970s, many research groups have reported numerous metal complexes with redox-active ligands based on, for example, homo- or heterolytically *ortho*-disubstituted benzenes. Metal complexes with redox active-ligands are able to transfer electrons and protons not only at the metal center but also at their ligands. Furthermore, the intramolecular charge distribution of metal complexes with redox-active ligands can be modulated by external stimuli as reported by Pierpont *et al.* [1]. In the 1990s, the first reports on the catalytic activity of metal complexes with redox-active ligands started to emerge, and since then, the electron-transfer properties of the ligands have been identified as key features for the catalytic activity. These results thus indicate that the research area for metal complexes with redox-active ligands, which has since become a widely studied field.

More recently, we have aimed to develop new chemical function based on these redox-active ligands, spread over bistable molecular system synchronizing with macroscopic bistability [2] to redox-active liquid crystals [3] multi-electron transfer system [4] and light-induced hydrogen evolution materials [5]. In this invited presentation, recent progresses on these research topics will be given.

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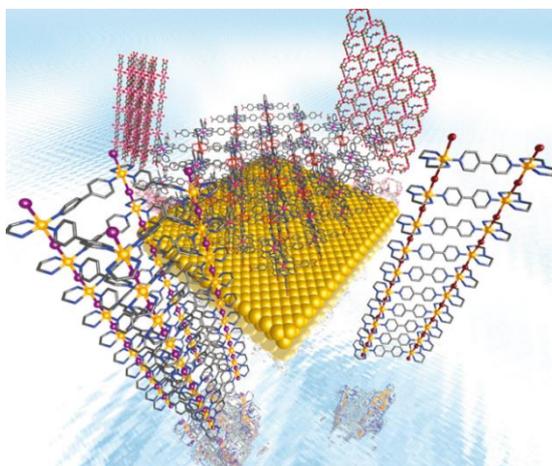
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KL5B: Highly Conductive Coordination Polymers

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Recent studies on metal–organic frameworks (MOFs) have shown that their designable framework architectures and specific pore surfaces are of potential interest to chemists studying various functionalities of solid-state materials, such as selective gas sorption, heterogeneous catalysis, magnetism, and electrical conductivity. Electron or proton conductivity is now regarded as a new functionality of the porous MOFs, and has attracted much interest, not only for scientific studies, such as biological systems, but also for practical investigation. MOFs can provide well-designed pores for electron- or proton-conducting pathways and include various conducting media, such as frameworks and/or water molecules in the pores. To date, we have studied the introduction of acid molecules and water molecules into the pores as proton carriers and conducting media, respectively, and have succeeded in synthesizing highly proton-conductive MOFs. We have also investigated on the MOF electron conductors including conductive tubular and surface MOFs as shown in the figure [1-4]. We demonstrate a bottom-up approach for the fabrication of well-defined dimensional-crossover nano-architectures with high tunability using metal ions and organic molecules as building blocks. We succeeded in rationally constructing an assembly of square prism-shaped metal-organic nanotubes with aside of 2 nm. A uniform 1D channel is fabricated inside the tube, and H₂O and alcohol can be selectively adsorbed. Its optical gap is about 0.76 eV of semiconductive region, and X-ray and theoretical studies revealed its unique electronic structure of CDW quartets. In addition, its electronic states can be successively controlled by exchanges of structural components and guest molecules. The results presented here demonstrate a rational route to the creation of nanotubes with high tunabilities of structures and electronic states, and might also offer valuable insights into nanomaterials.



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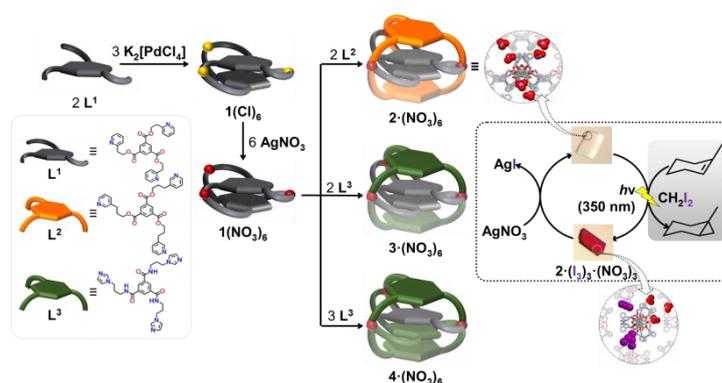
KL6A: A synthetic strategy for multi-layered Pd(II) complexes via transannular $\pi\cdots\pi$ interactions and its application as a scavenger in photoreaction

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The palladium(II)cyclophane systems, constructed by previously reported proof-of-concept self-assembly, represent a crucial landmark in the field of effective and recyclable scavenging triiodide (I_3^-) in photo-cyclopropanation of alkenes with CH_2I_2 . The scavenger's driving force behind photo-cyclopropanation is the efficient *in situ* crystallization of triiodide-exchanged species. The exact quantitative photoreaction yields according to the mole ratios of the cyclophane system are impressive. The recycling behavior can be ascribed to the rigidity and stability of the four-layered tripalladium(II)cyclophane.



Scheme 1 Stepwise synthetic procedure and recyclable photoreaction scavenger for four-layered tripalladium(II)cyclophanes (PdCl₂, yellow; Pd(NO₃)₂, red; L¹, black; L², orange; L³, green)

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KL6B: NANOPOROUS-CRYSTALLINE POLYMERS AND INDUSTRIAL INNOVATIONS

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For two commercial thermoplastic polymers, syndiotactic polystyrene (s-PS) [1-3] and poly(2,6-dimethyl-1,4-phenylene)oxide (PPO) [4,5], crystalline phases including empty cavities of molecular size in their unit cell have been obtained and named *nanoporous-crystalline* phases. These nanoporous-crystalline phases unprecedentedly exhibit density lower than the corresponding amorphous phases and are obtained by guest removal (e.g., by carbon dioxide in supercritical conditions) from co-crystalline host-guest phases, between a polymer host and low-molecular-mass guest.

These nanoporous-crystalline phases are able to absorb guest molecules also from very dilute solutions. Most studies have been devoted to s-PS, which exhibits two different nanoporous-crystalline phases, δ^1 and ϵ ,² whose nanoporosity is organized as isolated cavities and channels, respectively.

Physically crosslinked monolithic aerogels, whose physical knots are crystallites exhibiting a nanoporous crystalline form, will be also discussed [6-8]. These *aerogels* present beside disordered amorphous micropores (typical of all aerogels) also all identical nanopores of the crystalline phases. Their outstanding guest transport properties combined with low material cost, robustness, durability and easy of handling and recycle make these aerogels suitable for applications in chemical separations, purification and molecular storage [6-8].

The final part of the presentation will be devoted to possible industrial innovations of materials based on co-crystalline and nanoporous crystalline s-PS phases. In particular, applications of nanoporous films for active packaging of fruit and vegetable (by removal of ethylene and carbon dioxide) [9] of nanoporous staple for removal of pollutants from water and air [10] and of nanoporous aerogels as support for nanostructured catalysts [11] will be presented.

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INVITED LECTURES ABSTRACTS

IL1A: Multi-component nanomachinery - From rotation to catalysis

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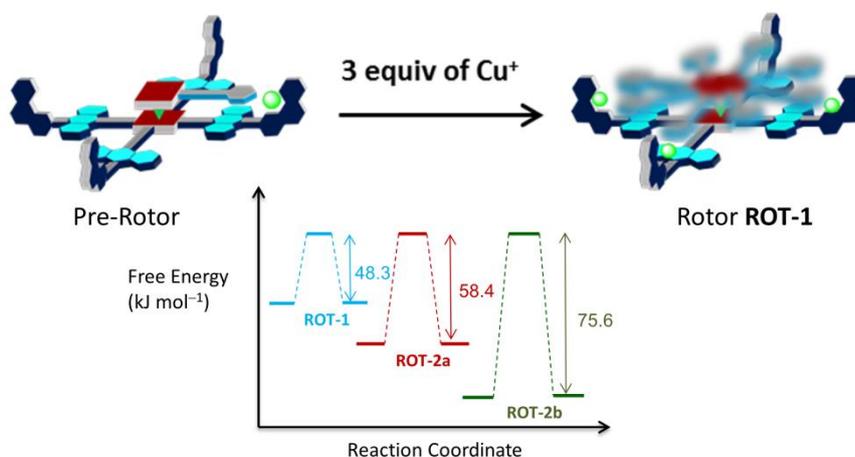
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Biological machines and processes have been serving as insightful masterpieces for chemists working in the field of artificial machines (see Nobel-prize laureates 2016) and systems chemistry. Despite some outstanding progress in more recent years, the benchmark achieved with artificial molecular machinery is still rather modest and far below the level of intricacy reached by biological machines. Organisms, cells, machines and every-day devices are typically made up from more than 10-100 distinct components.

Thus, implementation of emergent machine functions in multicomponent assemblies is at present one of the chief challenges. Our heteroleptic coordination tool kits with their high level of constitutional control in combination with self-sorting offers new chances for the rational design of multicomponent assemblies with tuneable properties [1]. As a result, our research has led to functional nano-assemblies in diverse areas, such as novel nanoswitches [2] and nanorotors [3].

The present talk will address a topical selection of functional multi-component machinery from our recent work, including multi-component rotors (Figure 1), oscillators and sliders, some of which are equipped with catalytic properties. Keeping an eye on the importance of biological motor enzymes, the talk will additionally reveal some interesting results on how the speed of rotary machinery is correlated with the rate of catalytic processes.

Figure 1.
Four-component rotors with different rotators exhibiting distinct barriers for rotation. **ROT-2a** and **ROT-2b** (not shown) have two-arm rotators.



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IL1B: Recent Progress on Fluorescent Probes and Activatable Photosensitizers

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Fluorescence is an important detection method due to its simplicity and high detection limit [1]. In this presentation, we focus our recent contributions to fluorescent chemosensors and imaging probes for ROS and GSH for various biologically important species. For example, HOCl is a biologically important reactive oxygen species (ROS).¹ Previous reports have shown that HOCl is involved in the oxidative burst of phagocytes, a process by which phagocytic cells generate highly reactive HOCl via the myeloperoxidase-H₂O₂-Cl⁻ system to kill pathogens [2]. Recently, we reported **R19S** [3] and **PIS** [4] as new fluorescent probes for HOCl, which have high selectivity, sensitivity and short response time in a broad range of pH. We also developed the ratiometric fluorescent probe, **QG-1**, for quantitatively monitoring cellular GSH. The probe responds specifically and reversibly to GSH with an ideal dissociation constant K_d of 2.59 mM and a fast response time ($t_{1/2} = 5.82$ s) [5]. The development of multifunctional reagents for simultaneous specific near-infrared (NIR) imaging and phototherapy of tumors is of great significance. A synergic methodology of phototherapy, photothermal therapy as well as imaging will be presented [6]. Finally, we reported a *o*-phenylenediamine-pyronin linked dye that is capable of both fluorogenic and colorimetric discrimination between phosgene and the prototypical nerve agent mimic, diethyl chlorophosphate (DCP) in the solution or gas phase [7].

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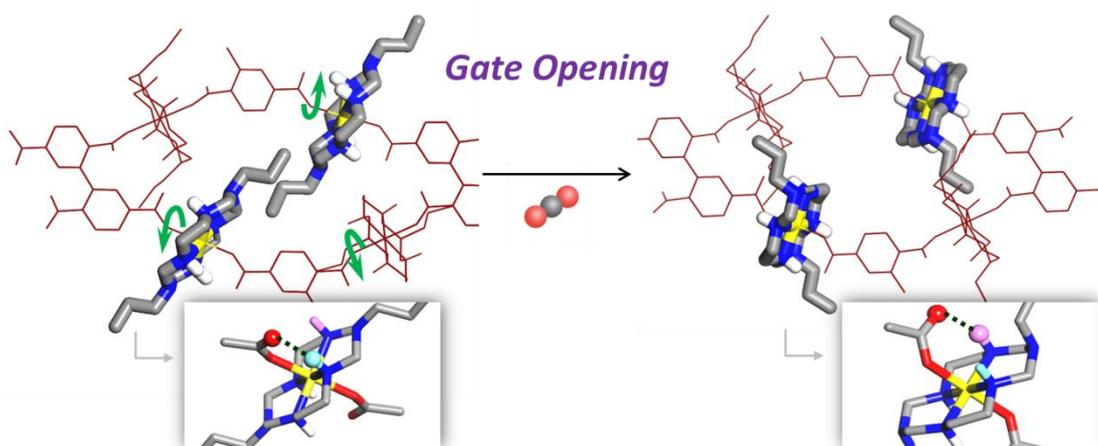
IL2A: Exploration of Gate-Opening and Breathing Phenomena in a Tailored Flexible Ni^{II} Macrocyclic-based MOF

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Flexible metal–organic frameworks (MOFs) show the structural transition phenomena, gate opening and breathing, upon the input of external stimuli. These phenomena have significant implications in their adsorptive applications. In this work, we demonstrate the direct capture of these gate-opening and breathing phenomena, triggered by CO₂ molecules, in a well-designed flexible MOF composed of rotational sites and molecular gates. Combining X-ray single crystallographic data of a flexible MOF during gate opening/closing and breathing with in situ X-ray powder diffraction results uncovered the origin of this flexibility. Furthermore, computational studies revealed the specific sites required to open these gates by interaction with CO₂ molecules.



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IL2B: Electronic-Structure Informatics for Materials Design in Nano and Supramolecular Chemistry

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“Electronic-Structure Informatics (ESI)” is an emerging field in computational chemistry, combining the electronic-structure theory and cheminformatics for design and discovery of functional molecules [1]. In ESI, the key issue is to find correlations between electronic-structure information and knowledge information of chemical materials. It is noted here that the electronic-structure information may be either of experimental, theoretical, or computational data as far as it is concerned with electronic structures of materials. On the other hand, the knowledge information may be described in any ways: it may be either written texts, numerical values, or mathematical formula as far as it provides either predictions of materials, suggestions of material-design principles, or mechanisms/rules/laws in chemical phenomena. Once a good correlation between the two types of information would be found, we would be able to suggest promising materials for a particular purpose. This is expected to be achieved by deploying computational tools for database search, machine learning, and experimental design.

In this lecture, we will discuss about our recent developments in ESI. It includes molecular design of efficient hole transport materials for the perovskite solar cell [2], discovery of skin-whitening compounds included in plants [3], classification of cancer-related compounds [4], and classification of organic molecules and its relation to biological classification of metabolic systems [5]. Based on these applications, we will point out that development of “operations research” for chemistry would be the key in computer-aided (artificial/augmented intelligence-based) functional materials design, in particular, in the field of nano and supramolecular chemistry.

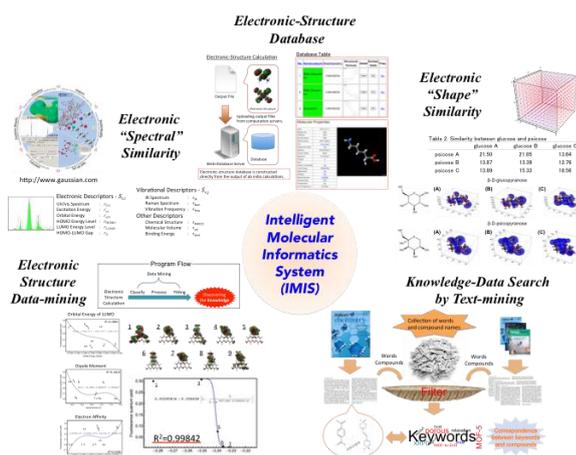


Figure 1. Electronic-structure informatics system developed in Kumamoto University. This system consists of (1) database of calculated electronic structures of molecules, (2) electronic-spectral similarity analysis based on the calculations, (3) electronic-shape similarity analysis based on the calculations, (4) data-mining (machine learning) for the computational results, and (5) text-mining obtaining knowledge data from literatures and internet documents.

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IL3A: Generation Of Functional Nanostructures Via Self-Assembly Process

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Abstract

Supramolecular chemistry investigates chemical systems and large architectures build from simple molecular components connected *via* weak, non-covalent and reversible interactions. The same holds for molecular chemistry when the molecular entity contains covalent bonds that may form and break reversibly, so as to allow a continuous modification in constitution by reorganization and exchange of building blocks. These features define a Dynamic Combinatorial Chemistry (DCC) on both the molecular and supramolecular levels.¹ The field of DCC is currently undergoing a revival, largely on account of our increased understanding of supramolecular phenomena and the subsequent development of self-assembly processes. The results obtained so far show the huge potential of complex and functional chemical systems generated by implementation of supramolecular and DCC approach, however the full understanding of controlled synthesis of multicomponent molecular and supramolecular architectures (2D and 3D), with predicted physicochemical parameters was not yet achieved.

Taking into account the big potential of supramolecular and dynamic covalent chemistries in the creation of functional architectures we decided to investigate the formation of complex chemical systems by means of dynamic/reversible covalent and non-covalent bonds. The purpose of our studies is the development of new complex supramolecular and molecular dynamic systems of different topologies and functions. The influence of the employed dynamic bonds on the structural, physicochemical and functional properties of the synthesized architectures is of our main interest.

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IL3B: Supramolecular-Cation Approach for Constructing Crystalline Molecular Electronic Materials

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Supramolecular cations based on crown ethers are promising building blocks for constructing molecular assemblies expressing a variety of functions. We have already reported electronic functions arising from dynamic motion of supramolecular cations in the solid state. A one-dimensional stack of [15]crown-5 with lithium cation in $(\text{Li}^+)_x([\text{15}]\text{crown-5})[\text{Ni}(\text{dmit})_2]_2$ showed a lithium ion conduction in the crystal, which controlled electronic conduction in the $[\text{Ni}(\text{dmit})_2]$ column [1]. A ferroelectric transition was observed in $(m\text{-fluoroanilinium}^+)(\text{dibenzo}[18]\text{crown-6})[\text{Ni}(\text{dmit})_2]$ due to the flip-flop motion of the aryl group by applying outer electric field [2].

Supramolecular rotator cations were embedded in functional anions to form multifunctional crystals. We chose $[\text{MnCr}(\text{oxalate})_3]^-$ complexes as an anion, which is known to form two-dimensional honeycomb structure exhibiting ferromagnetic transition at around 5 K, aiming at constructing multiferroic crystals. Supramolecular cations were also utilized to regulate the cation-anion assembly-structures in the solid state, which strongly affect the functions of crystals. Figure 1 shows the crystal structure of $(\text{anilinium}^+)(\text{trans-syn-trans-dicyclohexano}[18]\text{crown-6})[\text{Ni}(\text{dmit})_2]$ (**1**). The supramolecular cations formed one-dimensional columnar structure with the disorder of anilinium due to the planar conformation of the crown ether with C_{2h} symmetry [3]. $[\text{Ni}(\text{dmit})_2]$ anions were inserted in the spaces between the crown ethers. In case we used a distorted supramolecular cation, $(3\text{-AP}^{2+})(\text{dibenzo}[30]\text{crown-10})$ (AP = aminopyridine) (Fig. 2), we could induce a chiral space group of the crystal, which can be used to develop chiral magnets [4].

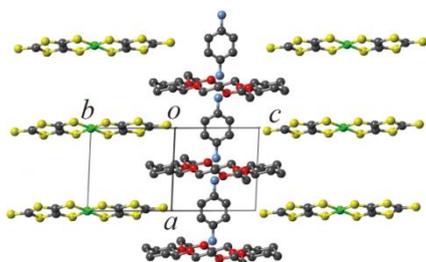


Fig. 1 Crystal structure of **1**.

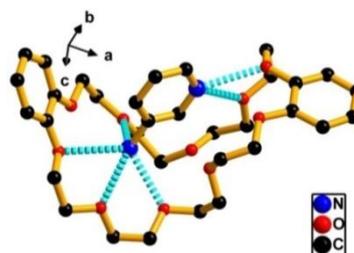


Fig. 2 Supramolecular structure.

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IL4A: Smart recognition by macrocyclic hosts

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Smart properties of solid calixarenes and other hosts were observed boosting their selectivity and clathrate stability. Absolute selectivity of host response to guest inclusion and release was found, which goes far beyond the capability of ordinary key-to-lock mechanism. While current concept of molecular recognition is based on the preferential binding of complementary species, the present work uses specific cooperative properties of host crystals such as their memory of previously bound guest, pseudopolymorphism of host-guest clathrates with more than one step of guest inclusion, favorable hydration effect on binding of hydrophobic guests by hydrophilic hosts, and effect of clathrate preparation history on guest inclusion capacity and clathrate stability. Thus, small guest molecules having no more than one functional group capable of H-bonding or donor-acceptor interactions can be discriminated even from their close homologues.

A true recognition was found in a two-step formation of benzene clathrate with tert-butylthiacalix[4]arene derivative both on vapor sorption isotherm and in kinetic response of mass-sensitive sensor. This experiment is extremely selective being capable to detect benzene qualitatively and quantitatively in mixtures with any other compounds. Inclusion cooperativity of glassy calixarenes makes possible also a visual detection of organic vapors in mixtures giving a response to a very small step in guest concentration [1,2].

An observed ability of several calixarenes to remember evolved guests does not have any precedents by selectivity. This memory can be read in simultaneous TG/DSC experiment as an exothermic effect of host collapse from loose to dense phase without mass change. The memory parameters (enthalpy and temperature of polymorphic transition) strongly depend on the guest structure. This smart property persists also for guest mixtures [2]. In some cases, such memory effect can be found only after a solid-phase guest exchange in calixarene clathrates [3]. When combined, these effects give a controlled polymorphism of calixarenes with long-chain substituents with H-bonding capability [2]. The procedure of clathrate preparation by guest exchange is rather selective itself and gives a surge in guest inclusion capacity and clathrate stability both for calixarenes and beta-cyclodextrin [4]. This may produce clathrates that cannot be formed by host-guest interaction in binary systems. The highest clathrate stability was found for calixarene capable of special anti-sieve effect, so that larger guests can be bound, while smaller ones are excluded [5-6].

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IL4B: Coordination complexes of tetradentate ligands: molecular magnetism and catalysis

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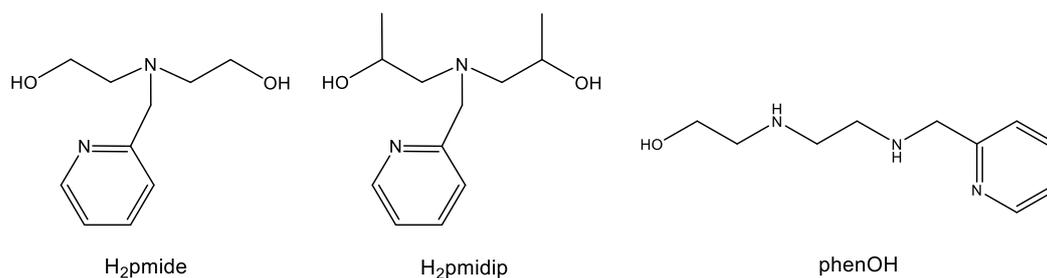
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The design and preparation of di- and trinuclear transition metal complexes has enabled the understanding and development of molecule-based magnetic materials and the structural elucidation of metalloenzymes in biological systems, as well as the development of catalysts for hydrocarbon oxidations. It has been recognized that the metal ions and the binding ligands as capping molecules may play important roles in the formation of desirable compounds, due to the molecular shape, charge, and size.

In order to get the desired transition metal complexes, we have used three tetradentate ligands, i.e., *N*-(2-pyridylmethyl)iminodiethanol (H₂pmide), *N*-(2-pyridylmethyl)iminodiisopropanol (H₂pmidip), and *N*-(2-pyridylmethyl)-*N'*-(2-hydroxyethyl)ethylenediamine (phenOH). We have prepared a series of dimeric and trimeric metal complexes from the reaction of metal (Fe, Co, Ni) ions and H₂pmide/H₂pmidip/phenOH in MeOH: [(Hpmide)Fe(NO₃)₂](NO₃)₂•2CH₃OH (**1**), [(pmide)Fe(N₃)₂]₂ (**2**), [(Hpmide)₂Ni₃(CH₃COO)₄] (**3**), [(Hpmide)₂Co₃(CH₃COO)₄] (**4**), [(pmidip)₂Co₃(CH₃COO)₄] (**5**), [(phenO)Fe(N₃)₂](NO₃)₂ (**6**), and [(phenOH)Ni(N₃)₂]₂ (**7**). These are basically characterized by EA, IR, UV/vis, and X-ray crystallography. Further researches were done through both magnetic and catalytic data. For example, both **1** and **2** showed Fe(III) dinuclear geometries with each octahedral structure as well as efficiently catalyzed the oxidation of a variety of alcohols under mild conditions. **1** showed a strong antiferromagnetic interaction within the Fe(III) dimer, while **2** had a weak antiferromagnetic coupling within the Fe(III) dimer. Likewise, the other complexes (**3-7**) are also displayed interesting structures, magnetochemistry, and catalysis. Thus in this talk we will show the detailed preparation of the transition metal complexes, crystal structures, magnetism, and catalytic properties.



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IL5A: Supramolecular Approaches to Homogeneous Catalysis

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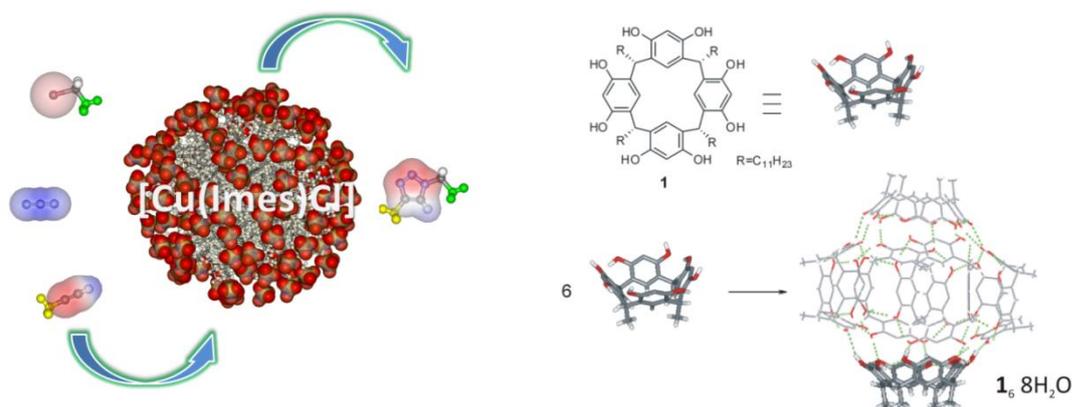
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Enzymes are basically polypeptides that, in some cases in combination with metal centers and other units, operate in solution as homogeneous catalysts accelerating the rate of reactions by up to 15-18 orders of magnitude, thus representing the source of inspiration for all chemists involved in catalysis. Moreover, the outstanding substrate and product selectivity together with the mild experimental conditions and the impressive turn over numbers and frequencies typical of enzymes are all features that homogeneous and heterogeneous catalysis can hardly imitate.

Several lessons can be learnt from enzymatic catalysis. One very simple is that substrates are recognized within a cavity of enzymes before the true catalytic event and this is the base for the substrate selectivity and provide further intermediate stabilization and consequent rate acceleration thus steering product selectivity. Inspired by the efficiency displayed by enzymes, artificial capsular structures as reaction hosts represent an interesting but challenging goal.

In this contribution two possible approaches will be presented for the creation of encapsulated catalysts reminiscent of enzymes. The first one is based on the use of micellar media to dissolve catalysts and substrates in water as a benign solvent in order to exploit the confinement effects imparted by the hydrophobic effect that enhance selectivity and catalytic activity [1]. Examples of traditional metal catalysis as well as catalysis with metal nanoparticles [2] will be provided.

An alternative approach operating in organic media is based on the resorcin[4]arene **1** molecule that in organic solvents leads to a spherical hexameric capsule $1_6 \cdot (H_2O)_8$ held together by 60 hydrogen bonds with a cavity of about 1375 \AA^3 . Results related to the application of this capsule as i) a nano-reactor where reagents as well as catalysts can operate within the cavity of the host observing unique substrate and product selectivities [3] and ii) as a nano-catalyst itself able to accelerate reactions involving cationic intermediates [4] will be presented.



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IL5B: Photoinduced Processes in Macrocyclic isoalloxazine–anthracene systems

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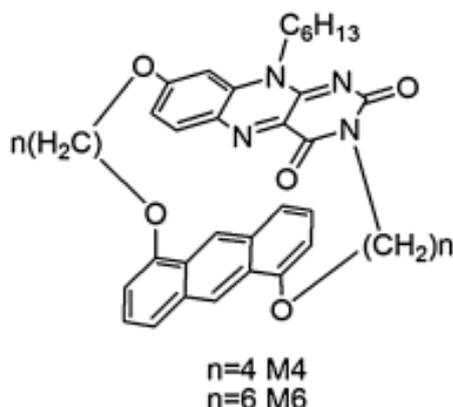
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Two new macrocyclic structures containing 8-hydroxyisoalloxazine and 1,5-dihydroxyanthracene moieties linked by aliphatic chains of different lengths ($n = 4$ and 6) were designed and synthesized in order to study photoinduced electron transfer (PET) processes from the anthracene unit towards the isoalloxazine singlet excited state induced by structural changes due to different intrachromophoric distances and orientations. The compounds have been fully characterized by NMR spectroscopy and the X-ray solid state structures of both macrocycles have been elucidated. Photophysical measurements, including continuous wavelength photoinduced absorption (cw-PIA), at room temperature and 77 K have been carried out in order to investigate the influence of the close contacts between the aromatic groups (π – π stacking) on the photophysical properties of the macrocycles.



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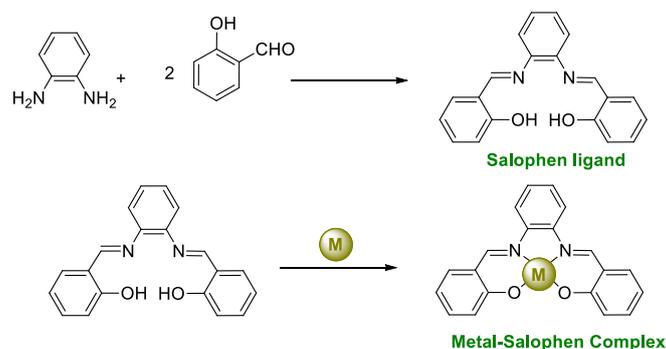
IL6A: Metal-salophen complexes: highly versatile scaffolds for the supramolecular design of host-guest systems

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Salophens are a quite popular class of Schiff base ligands [1]. They are obtained by a modular synthesis involving the condensation of 1,2-phenylenediamine, with two equivalents of salicylaldehyde. The two starting building blocks can be easily functionalized and this gives access to a large variety of ligands with subtle variations in steric and electronic configuration. The resulting coordination site, an N_2O_2 binding pocket, is capable of bonding to metals in a tetradentate fashion, stabilizing them in various oxidation states. The role of the metal center in determining the characteristics of these complexes is fundamental and the majority of such derivatives can be described as immobilized Lewis acids able to coordinate Lewis bases. Remarkably, the introduction on the ligand skeleton of additional, appropriate binding motifs can lead to a well-defined pattern of intermolecular interactions that can enhance the efficiency and selectivity of the recognition processes.



Currently our research focuses on the use of suitably designed metal-salophen complexes as supramolecular receptors for the recognition of anions [2], ion pairs [3] and neutral substrates. The contribution of secondary weak interactions on which the selectivity of the recognition processes relies (i.e. cation- π [4], anion- π [5], hydrogen bonding, van der Waals interactions etc) can be unambiguously identified in our systems.

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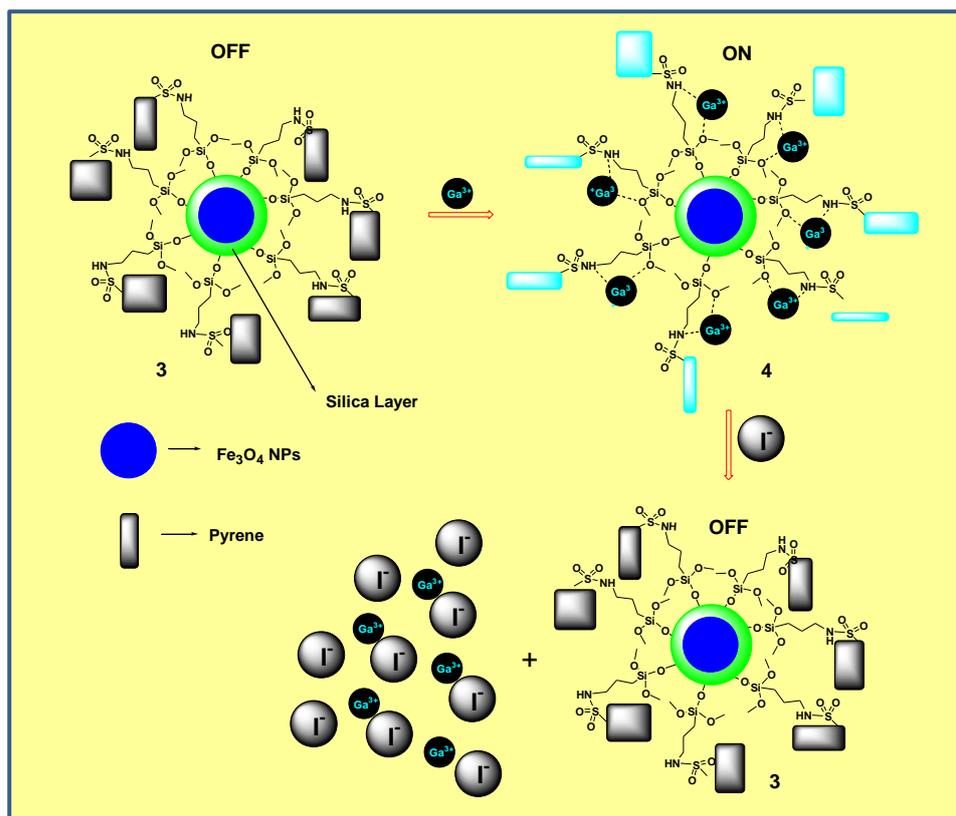
IL6B: Sensitive and selective fluorescence *OFF-ON-OFF* sensor for cascade detection of Ga^{3+} cation and I^- anion based on pyrenesulfonamide-functionalized nanoparticles

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Pyrenesulfonamide derivatives have been known to sense the salicylic acid and 2,4,6-trinitrophenol selectively [1-3]. Pyrenesulfonamide-functionalized inorganic/organic hybrid $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles were prepared and investigated for the selective and sensitive detection of metal ions. The fluorescence monomer emission intensity of pyrene at 380 nm was “switched on” by interaction with Ga^{3+} . The *in-situ* prepared Ga^{3+} -complex with inorganic/organic hybrid $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles led to the selective and sensitive sensing of I^- ions with “switch off” fluorescence emission. Thus, inorganic/organic hybrid $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles act as a switch with “*OFF-ON-OFF*” operation for sequential detection of Ga^{3+} and I^- ions. Characterization and sensing mechanism of the inorganic/organic hybrid $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles using FT-IR, TGA, XRD, and TEM techniques are described [4].



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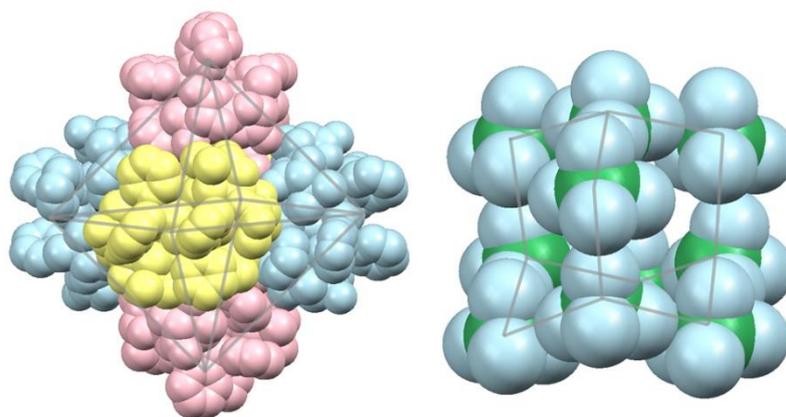
IL7A: Metalloligand Approach That Leads to the Creation of Non-Coulombic Ionic Solids

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In recent years, considerable attention has been directed to the design and creation of polynuclear and supramolecular coordination compounds. To construct highly organized structures for these compounds, metal-mediated self-assembly processes, which spontaneously afford molecular aggregates from relatively complicated organic ligands and metal ions via coordination bonds, are commonly employed. On the other hand, we are interested in metalloligand approaches, in which isolated metal complexes with sulfur-containing ligands are stepwise aggregated by metal ions [1]. Recent our studies showed that the aurate(I) complex with two D-penicillaminates, $[\text{Au}(\text{D-pen})_2]^{3-}$, functions as a chiral multidentate metalloligand that can bind to metal ions through coordinated thiolato and non-coordinated amine and carboxylate groups, producing a variety of chiral polynuclear and supramolecular species. To expand the range of this chemistry, it is worthwhile to introduce a digold(I) unit having bis(diphenylphosphino)alkane as a linker, in place of the Au^{I} atom in $[\text{Au}(\text{D-pen})_2]^{3-}$ [2]. Here we report on the coordination functionality of digold(I) metalloligands of this class, focused on the creation of ionic crystals that show an unusual aggregation of complex cations and inorganic anions.



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IL7B: Calixarene Based Fluorescent Chemosensors

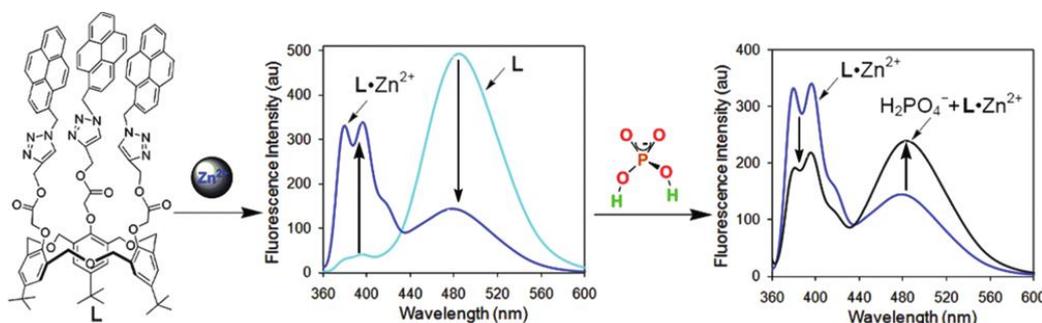
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Hexahomotrioxacalix[3]arene derivatives with C_3 symmetry are useful as a basic skeleton for the design of new ionophores, complexation with metal ions, anions and alkylammonium ions which play important roles in both chemistry and biology. The design and application of new heteroditopic receptor systems capable of simultaneous coordination of both anionic and cationic guest species has recently attracted a great deal of interest, as these systems have the potential to act as salt solubilisation, extraction, and membrane transport agents.

A ratiometric fluorescent receptor with a C_3 symmetric structure based on a pyrene-linked triazole-modified homooxacalix[3]arene (**L**) was synthesized through click chemistry and characterized. This system exhibited an interesting ratiometric detection signal output for targeting cations and anions through switching the excimer emission of pyrene from the “on-off” to the “off-on” type in neutral solution. ^1H NMR titration results suggested that the Zn^{2+} center of receptor $\text{L} \cdot \text{Zn}^{2+}$ provided an excellent pathway of organizing anion binding groups for optimal host guest interactions. It is thus believed that this receptor has potential application in sensing, detection, and recognition of both Zn^{2+} and H_2PO_4^- ions with different optical signals. In addition, the fluorescence emission changes by the inputs of Zn^{2+} and H_2PO_4^- ions can be viewed as a combinational R-S latch logic circuit at the molecular level [1-3].



In this presentation a series of calixarene-based chemosensors incorporating click-derived triazoles for metal cations, anions as well as neutral molecules with pico level detection limits will be also demonstrated [4-7].

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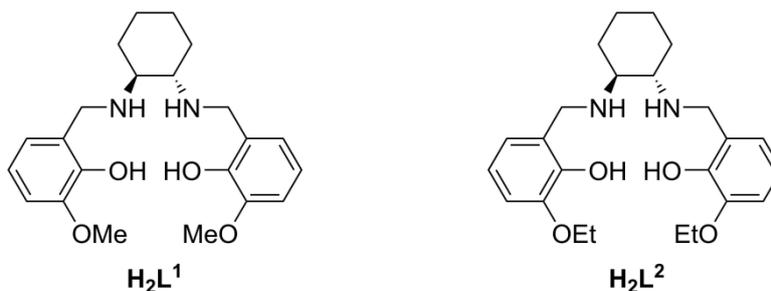
IL8A: New Heterodinuclear Zn(II)/Ln(III) Complexes of *N,N'*-Bis(3-alkoxy-2-hydroxybenzyl)cyclohexane-1,2-diamines

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The coordination chemistry of heteropolynuclear 3d/4f metal complexes with multifunctional N,O-donor ligands has received increasing attention over the last 20 years [1-2]. Whereas the chemistry of heterodinuclear Zn(II)/Ln(III) Schiff base complexes has been described in a number of papers [3,4] related amine derivatives are only scarcely studied [5,6]. Here we report the synthesis and structural characterisation of five isostructural heterodinuclear Zn(II)/Ln(III) complexes (Ln=Gd, Tb, Er, Yb) with the substituted cyclohexane-1,2-diamines **H₂L¹** and **H₂L²** [7]. In the complexes zinc(II) is coordinated by the inner N₂O₂ donor set of the ligand and an oxygen of a bridging acetate anion; the lanthanide(III) ions possess an O₉ coordination environment involving the ligand's outer O₄ donor set, two bidentate nitrate ions and the bridging acetate.



Acknowledgement

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IL8B: Molecular Rotor Dynamics in Nanoporous Architectures

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Molecular rotors, especially when bearing dipoles, are a challenging research field entailing a number of useful phenomena, such as switchable ferroelectricity, and the fabrication of dynamic elements of molecular motors in solids. The combination of remarkable porosity with ultra-fast rotor dynamics was discovered by our group in molecular crystals and covalent frameworks, by ^2H spin-echo NMR spectroscopy and T_1 relaxation times [1-3]. Molecular rotors, as fast as 10^7 Hz at 200 K, are exposed to the crystalline channels, which absorb CO_2 and I_2 vapors even at low pressure. Interestingly, the rotor dynamics could be controlled by I_2 absorption/desorption, showing a remarkable change of material dynamics and suggesting the use of porous crystals in sensing and pollutant management. Novel mesoporous organosiloxane frameworks, obtained by a self-assembly process, allowed to realize periodic architectures of fast molecular rotors containing dynamic C-F dipoles in their structure (Fig. 1a) [4]. The dipolar rotors showed not only the rapid dynamics of the aromatic rings (ca. 5×10^8 Hz at 325 K) (Fig. 1b), but also a dielectric response typical of a fast dipole reorientation under the stimuli of an applied electric field.

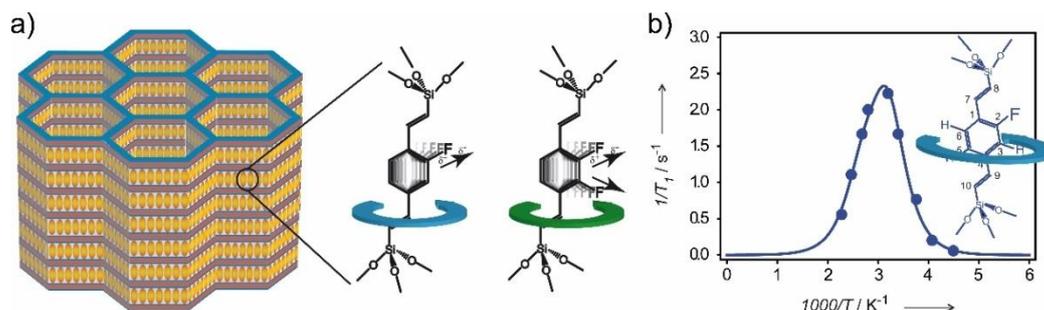


Figure 1. a) Mesoporous organosiloxane frameworks with 2-fluorodiviny- and 2,3-difluoro-divinylbenzenesiloxane moieties. b) ^{13}C relaxation rates for C_3 nucleus of organosilica versus the reciprocal of temperature.

Molecular rotors were mounted on crystal surfaces exploiting the formation of surface inclusion compounds. Guest molecules engineered as three segments comprising a shaft, a stopper, and a rotator can interact with a porous crystal and insert the shaft into the bulk crystal, while the rotator lies on the surface [5]. The host-guest relationships were established by 2D solid state NMR and low rotational barriers were found by dielectric spectroscopy.

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IL9A: Supramolecular bio-sensing with cavitands: challenges in prostate cancer diagnostics and epigenetic histone modifications

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The direct, clean and unbiased transduction of molecular recognition into a readable and reproducible response is the biggest challenge associated to the use of synthetic receptors in sensing. All possible solutions demand the mastering of molecular recognition at the solid-liquid interface as prerequisite [1]. In this contribution the following cases will be discussed, which have in common the use of phosphonate cavitands as specific receptors for *N*-methylated species in water: [2]

1. Detection of sarcosine in urine. Sarcosine is the new marker for the aggressive forms of prostate cancer [3]. Three different detection modes will be presented, all featuring tetraphosphonate cavitands as specific receptors for sarcosine: (i) fluorescent displacement detection using a cavitand-decorated silicon wafer [4]; (ii) conductimetric sensing using cavitand-decorated single-walled carbon nanotubes [5]; (iii) electrochemiluminescence (ECL) sensing with cavitand-decorated magnetic nanoparticles [6].

2. Epigenetic histone modification monitoring. Histone methylation on lysines residues is one of the most intensely studied epigenetic modifications in mammals, due to its relation to cancer development. The covalent addition of a methyl group occurs generally on several lysines of histone H3 tail peptide. Sequencing studies have shown how H3K4, H3K9, H3K20 and H3K27 are often the preferred methylation sites, although species-specific differences do exist [7]. Unfortunately mono-methylation of lysines is a very challenging moiety to identify and measure, due to the lack of significant difference in both molecular weight and charge between the modified and unmodified peptide. A method for sensing mono-methylated peptides will be presented. Recognition results robust and specific regardless the position of the methylated lysine along the amino acid chain and the number of methylated lysines in the chain. The recognition event is transduced into an optical signal thanks to a specifically designed SiO₂-TiO₂ core-shell non-plasmonic resonator [8], which allows to trap the peptide-cavitand binding partners and “gently” enhance their Raman fingerprint.

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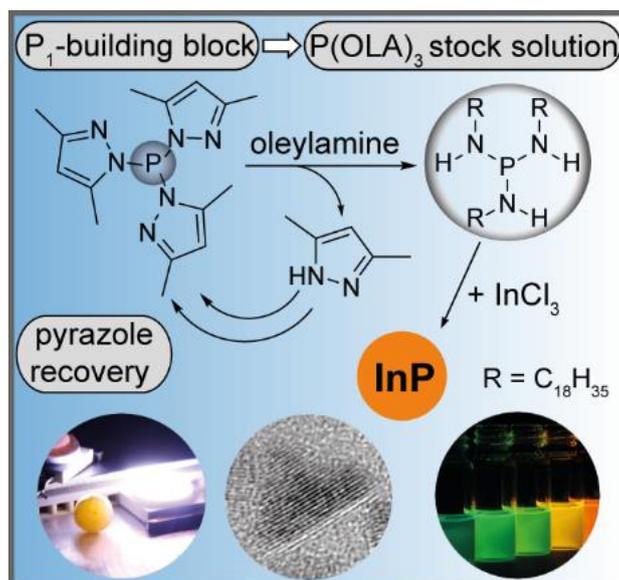
IL9B: Versatile Tri(pyrazoly)phosphanes – Application as phosphorus precursors for the synthesis of highly emitting InP/ZnS quantum dots

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Tri(pyrazoly)phosphanes [1] are utilized as an alternative, cheap and low-toxic phosphorus source [2] for the convenient synthesis of InP/ZnS quantum dots (QDs) [3]. From these precursors, remarkably long-term stable stock solutions (>6 months) of P(OLA)₃ (OLA = oleylamine) are generated from which the respective pyrazoles are conveniently recovered. P(OLA)₃ acts simultaneously as phosphorus source and reducing agent in the synthesis of highly emitting InP/ZnS core/shell QDs. These QDs are characterized by a spectral range between 530–620 nm and photoluminescence quantum yields (PL QYs) between 51–62%. A proof-of-concept white light-emitting diode (LED) applying the InP/ZnS QDs as color conversion layer was built to demonstrate their applicability and processibility.



Acknowledgement

Financial support from the European Research Council (ERC) (*SynPhos*, project number 307616 and AEROCAT, ERC-2013-AdG), M-ERA.NET Network (ICENAP, project number GA 1289/3-1) and the Deutsche Forschungsgemeinschaft through the research training group Nano- and biotechnologies for packaging of electronic systems (project number DFG 1401/2) are acknowledged.

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IL10A: New Gold N-Heterocyclic Carbene Chemistry: Porphyrin-Like Gold(III) Complexes, Dinuclear Gold(II) Complexes, and Gold(I)/Gold(III) Mixed-Valence Complexes.

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This presentation will describe some of our recent work on Au complexes of N-heterocyclic carbene (NHC) ligands derived from bis- and tetrakis(imidazolium) salts.

We have synthesized new Au(III) complexes containing a porphyrin-like Au(NHC)₄ core. Usually, reduction of Au(III) to Au(I) seriously compromises attempts to synthesize Au(III)-NHC complexes directly from Au(III) sources and imidazolium ions in the presence of base [1,2]. We find, however, that when the NHC precursors are bis- and tetrakis(imidazolium) ions, Au(III) compounds of form [Au(NHC)₄X₂]X or [Au(NHC)₄]X₃ can be obtained in high yield. These remarkably robust complexes have been structurally characterised by X-ray diffraction studies, and their solution behaviour has been explored using NMR spectroscopy and conductance measurements. In D₂O solution, ligands in the [Au(NHC)₄]³⁺ cation undergo base-catalyzed H/D exchange reactions without reduction of the Au(III) centre.

We have also explored the oxidation of dinuclear Au(I) complexes of form [Au₂L₂]²⁺ where L is a cyclophane-bis(NHC) ligand derived from an bis(imidazolium) cyclophane [3-5]. The structure of the cyclophane-bis(NHC) ligand determines the separation of the two Au centres in the dinuclear Au-NHC complex, which in turn determines the outcome of the oxidation reaction. Where the cyclophane-bis(NHC) ligand enforced a short Au...Au distance, strongly luminescent Au(II) complexes containing an X–Au–Au–X core were obtained. Where the cyclophane-bis(NHC) ligand enforced a longer Au...Au distance, Au(I)/Au(III) mixed-valence complexes were obtained. For the mixed valence complexes, an exchange process in solution resulted in interconversion of the Au(I) and Au(III) sites.

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IL10B: Rational Design of Highly Active M–N/C Electrocatalysts for Oxygen Reduction Reaction

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The development of highly active, durable, and low-cost oxygen reduction reaction (ORR) catalysts is central to making polymer electrolyte fuel cells commercially viable. During the last decade, tremendous recent efforts have been devoted to replacing expensive, scarce Pt-based electrocatalysts with non-precious metal catalysts (NPMCs) for the ORR. Among various NPMCs, M–N/C (M=Fe or Co) catalysts have emerged as the most promising ORR catalysts due to their high ORR activities. In this direction, we have endeavored toward the rational design of high-performance M–N/C catalysts and the identification of active species in M–N/C catalysts [1-4].

We have prepared a family of transition metal-doped ordered mesoporous porphyrinic carbons (M-OMPCs; M=Fe, Co, Ni, or their combinations) by nanocasting mesoporous silica templates with macrocyclic compounds such as metalloporphyrin and metallophthalocyanines [1-2]. The M-OMPC catalysts have a high density of molecularly dispersed M–N_x sites and have large surface areas and tunable pore structures. Among the M-OMPC catalysts, the FeCo-OMPC catalyst exhibited an excellent ORR activity in an acidic medium, higher than other non-precious metal catalysts.

We have developed a general design strategy based on “silica-protective-layer-assisted” method that can preferentially produce catalytically active Fe–N_x sites towards highly efficient Fe–N/C electrocatalysts [3]. This method is applicable to any type of carbon supports as well as Fe–N precursors. One of resulting catalysts, consisting of CNT wrapped with thin porphyrinic carbon layer (CNT/PC), contained relatively high density of Fe–N_x sites, and showed very high ORR activity and remarkable stability in alkaline media. Importantly, the CNT/PC-based cathode demonstrated excellent performances in both an alkaline anion exchange membrane fuel cell as well as an acidic proton exchange membrane fuel cell.

We have also made efforts toward identifying a new active species in M–N/C catalysts [4]. We constructed archetypical hybrid catalysts by the reaction of an organometallic complex, [CoII(acac)₂] (acac=acetylacetonate), with N-doped graphene-based materials at room temperature. In the hybrid structure, the cobalt-containing species is coordinated to heterocyclic groups in N-doped graphene as well as to its parental acac ligands. The hybrid material shows high electrocatalytic activity for the ORR in alkaline media, and superior durability and methanol tolerance to a Pt/C catalyst. Based on the chemical structures and ORR experiments, we could identify a new active species for the ORR: “Co–O₄–N” structure.

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IL11A: C_{3v} -Symmetric tripodal anion receptors based on trindane molecular skeleton with urea-, diamide-, urethane-, guanidine-, and triazole-recognition motifs

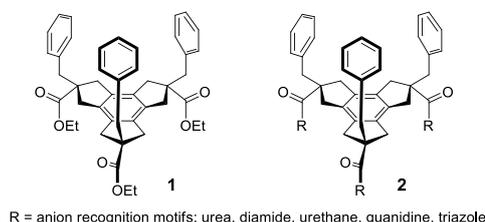
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One of the most useful studies in supramolecular chemistry is on the molecular receptors for various purposes, such as recognition, isolation, extraction, transport, sensing in the biological systems or in the nature. Many cation receptors such as Li^+ , Na^+ , K^+ ionophores are currently well developed and used in selectively sensing ions in medical applications by a ion-selective electrodes. However, the development of anion receptors with high selectivity and stronger anion binding ability are hampered by relatively bigger size with low charge density, complex geometry, highly hydrated water and pH sensitivity. With the concept of preorganization and shape complementarity from supramolecular chemistry anions receptors with high selectivity and stronger anion binding ability can be achieved by designing multi-dimensional receptors with increased number of binding sites and binding dimensions. Most biologically important anions are spherical halide anions, and phosphate ions, sulfate anion, nitrate anions, which all have C_3 symmetric element. The C_3 symmetric tripodal anion receptors with tri-recognition binding motifs are well fit for those requirements for preorganized multiple binding and shape-selective binding dimensions. We have developed a C_{3v} -symmetric trindane molecular skeleton, **1** for selective recognition of C_3 -symmetric anions, which has a nonpolar benzylic moieties on a molecular plane and a polar carboxylic moieties on the other molecular plane for further functionalizing anion recognition motifs conjugated with chromophores and fluorophores. Anion receptors **2** with urea, diamide, urethane, guanidine, and triazole anion recognition motifs were designed, synthesized and studied on anion recognition by NMR titration, UV-Vis spectrometer and fluorescent spectroscopy, and discussed with molecular modeling study. All recognition motifs we studied here show the anion binding ability by H-bonding to relatively selective to F^- anions over others. As an example, receptor with naphthoimidazole groups as guanidine anion binding motif showed 40 nm red-shift in the UV-vis spectral study and a significant fluorescence enhancement at 410 nm in the presence of fluoride. Fluoride induced visually detectable color change allowed to detect F^- ratiometrically with the detection limit down to 208 nm.



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IL11B: Engineered Nano-adjuvants: Bridging Multiscale Molecular/Nano Structures and Immuno-adjuvanticity

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Recent progresses in nanostructured immuno-adjuvants have offered great opportunities in promoting immune responses for prevention or treatment of disease (e.g. cancer). However, challenges exist in developing potent and safe adjuvants for generating robust and long-lasting adaptive immunity, presumably due to the lack of proper fabrication strategy and limited understanding on the roles of nanostructure and composition.

Recently, we have reported the synthesis organic-inorganic hybrid silica materials with multi-shelled dendritic architectures [1]. It is shown that compared to conventional single shelled structure or pure silica composition, double-shell organosilica nanoparticles exhibit significantly improved adjuvant effect for antitumor *in vivo*. Using a micro-emulsion assisted approach, it is also demonstrated that mesoporous silica nanoparticles with a unique asymmetrical head-tail structure can be successfully synthesized [2]. The asymmetrical nanoparticles exhibited a higher level of uptake and maturation of antigen presenting cells compared to conventional symmetrical ones; and delivered an antigen peptide *in vivo* with improved immune response. We have also shown that silica nanoparticles with a rough surface [3] are better delivery vehicles for DNA transfection and potentially DNA vaccination. Our studies have provided new insights in the rational design of effective nano-adjuvants with controllable nano/molecular for vaccine development and immunotherapy.

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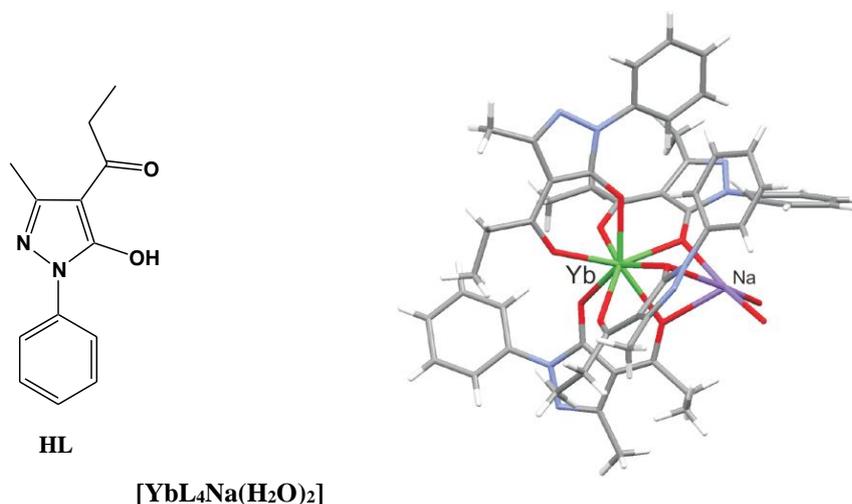
IL12A: New *d*- and *f*-Block Metal Complexes with 4-Acylpyrazolones

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4-Acylpyrazolones have received remarkable attention as versatile chelating agents in material chemistry, medicine, catalysis and solvent extraction [1,2]. Due to their simple synthesis fine-tuning and modification of their physico-chemical properties are straightforward. For a long time we were interested in using acylpyrazolones as extractants [3]. Now we have synthesized a series of *d*- and *f*-block metal complexes (Fe(III), Co(II), Cu(II), Zn(II), Nd(III), Eu(III), Gd(III), Yb(III) and UO₂(VI)) with two 4-acyl-3-methyl-1-phenyl-5-pyrazolone ligands (**HL**). Whereas most of the complexes are characterized by the typical composition [ML_n·(H₂O)_s], we have also isolated two novel heterodinuclear complexes for Nd(III) and Yb(III) with the composition [ML₄Na(H₂O)₂]. The different structures will be compared and discussed in detail.



Acknowledgement

The author thanks the German Federal Ministry of Education and Research (BMBF - project 02NUK014A) for financial support.

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IL12B: Nanomagnetite: from biomedical to environmental and energy applications

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The development of nanoscale technologies has led a revolutionary change in a multitude of fields. Many nanomaterials have proved effective in various applications. As a case study, magnetite, thanks their exceptional properties, were successfully applied in more and more field: biology, biomedicine, energy, catalysis, environmental applications, as electrochemical sensors, and many others. Among the nanoprobe, magnetic core/shell Fe₃O₄/silica nanoparticles (NPs) loaded with dyes molecules and covered by functionalities are very promising. They allow the development of biomedical platforms for simultaneous imaging, diagnosis and therapy. We demonstrated a facile and general strategy for the fabrication of robust fluorescent magnetic nanoprobe with high payloads of dye molecules and their use as multimodal nanoprobe for cell imaging [1,2]. These nanoprobe not only effectively keep photochemical stability of dyes, but also provide a platform for grafting other functional or targeted moieties into silica surface via primary amines. Moreover, the nanoprobe have uniform spherical morphology and can be dispersed well in aqueous solution, which are very desirable for biomedical applications. Another very interesting field regard the energy storage, high surface area monodispersed nanoparticles of Fe₃O₄ with low tendency to aggregate, showed excellent electrochemical behavior as electrode material for supercapacitors [3]. The high surface area Fe₃O₄ NPs exhibited remarkable pseudocapacitive activities, including the highest specific capacitance over reported for Fe₃O₄ (300 F g⁻¹ at 0.5 A g⁻¹). Further electrochemical studies concerned new and cheap catalyst for hydrogen evolution reaction (HER), in particular the focus is on the use of metal oxides, able to favor the increase of the electronic population on the most conductive areas, leading to unexpected high performance and at low cost. We obtained controlled Pt/PtO₂ NPs directly grown on a magnetite surface to exploit the intimate connection of the different components, e.g. junction and interaction with a metal oxide, oxide based improvement of electron population on Pt. MNPs, with an appropriate functionalization, showed excellent behavior as sorbent for Magnetic Solid Phase Extraction (MSPE) of Polycyclic aromatic hydrocarbons (PAHs), combining strong adsorption ability of carbon materials, superparamagnetism of magnetite, and high surface area of nanomaterials. In addition, citric acid functionalized monodispersed Fe₃O₄ nanoparticles (NPs) in presence of a small amount of hydrophobic functionalities was used to bond directly Lipase (E.C.3.1.1.3) from *Thermomyces lanuginosus* (TL), through multiple physical interactions. Immobilized lipase showed a very high activity recovery up to 144% at pH = 7 and 323% at pH = 7.5 (activity of the immobilized enzyme compared to that of its free form). The enzyme, anchored to the Fe₃O₄ NPs, to be easy recovered and reused, resulted more stable than the native counterpart and useful to produce flavors and biodiesel from food industry wastes.

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IL13A: Ag⁺-Triggard *pseudo*-capsule assembly: A Silver Complex System Like the PPAP (Pen-Pineapple-Apple-Pen)

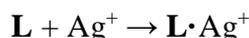
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A Japanese comedian broke through as a worldwide star last year. His name is **Pikotaro**TM. He sings a short song (just 45 seconds!) entitled **PPAP**TM (**Pen-Pineapple-Apple-Pen**TM) while comical dancing. The song was ranked as #1 and #77 in YouTube and Billboard, respectively. His momentum does not stop even now, and there are no days when I do not watch him on TV in Japan. In this talk, I introduce a silver complex system like the **PPAP**TM.

It is known that Ag⁺ ions interact with aromatic rings by the Ag⁺-π interaction between LUMO (5s orbital) of Ag⁺ and HOMOs of aromatic rings.¹ Recently, we have reported² that tetra-armed, triple-armed, and double-armed cyclens with aromatic side-arms behave like an *insectivorous plant* (insect-eating plant, for example, flytrap) when they form complexes with Ag⁺. The aromatic side-arms in the armed-cyclens cover the Ag⁺ incorporated into the cyclen rings by Ag⁺-π interactions and CH-π interactions in an organic solvent and water. We named the armed cyclens "argentivorous (silver-eating) molecules." The "argentivorous" is a coined word that was made by a combination of *argentum* (silver) and *vorous* (eating) in the Latin. It is important to note that the word "argentivorous" is different from "argentophilic." The word "argentophilic" has been used in the sense of Ag⁺-Ag⁺ interactions.³ In the argentivorous molecules previously reported, aromatic side-arms have been connected by methylene (-CH₂-) groups. When the -CH₂- groups are replaced by allyl (-CH₂-CH=CH-) groups, we expected that the -CH=CH- part of the allyl group would interact with the Ag⁺ incorporated into the cyclen ring, and a *pseudo*-cavity constructed by the four aromatic side-arms would bind neutral organic guests with polar functional groups. Therefore we prepared new argentivorous molecule (**L**) which has -CH₂-CH=CH-Ph groups as side-arms. As we expected, an Ag⁺ complex with **L** (**L**·Ag⁺) incorporates an acetonitrile (CH₃C≡N) molecule in the *pseudo*-cavity. In addition, when α,ω-dinitriles (N≡C-(CH₂)_n-C≡N, n=2-6) are employed as a neutral guest molecule, the system forms a *pseudo*-capsule type Ag⁺ complex like the **PPAP**TM.

"I have a ligand (**L**). I have a silver (Ag⁺). Ah! Silver complex (**L**·Ag⁺)!"



"Silver complexes. Neutral guest. Ah! Complex-Neutral Guest-Complex!"



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IL13B: In vitro/in vivo evaluation of nanoparticulate drug carriers

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Our research interests are focused on the development of novel multifunctional nano/micro-particulate drug delivery systems, in vitro and in vivo evaluation of their therapeutic efficacy and biological safety for treatment of various diseases including cancer. Some key research findings and achievements relevant to the nanocarrier & supramolecular chemistry are summarized as follows.

We synthesized and characterized chitosan-grafted-cyclodextrin (CD-g-CS). Ketoprofen was used as a model drug to prepare drug-loaded nanoparticles with controllable size by the ionic crosslinking method. In-vitro drug release profiles were investigated and optimized [1]. We prepared and characterized the FK506/dimethyl- β -cyclodextrin (DM- β -CD) inclusion complex using the ultrasonic method. Prepared and characterized bovine serum albumin nanoparticles incorporating the FK506/DM- β -CD inclusion complex using the desolvation method [2]. We developed other CS/CD-based NDDS: (i) Prepared and characterized DM- β -CD/CS, PEG/DM- β -CD/CS, PEG/CS particles using DM- β -CD, CS and PEG with different MWs. They had the controllable particle size, uniform size dispersion, spherical morphology and good stability. (ii) develop a novel drug delivery system based on carboxymethyl-cyclodextrin-grafted-oligochitosan derivatives (CM- β -CD-g-CSO) and adamantane modified paclitaxel (AD-PTX) via supramolecular micellar assembly [3]. (iii) Developed a microsphere drug delivery system with an excellent sustained-release profile by the one-step or two-step solidification method. The formation mechanism of microspheres was elucidated [4]. We also studied the morphology of mPEG grafted chitosan (mPEG-g-CS) forms self-assembled nanoparticles depending on the ratio of α -CD to mPEG, and a likely mechanism for the morphological transition of the rod-coil graft copolymer (Figure 1) was proposed.

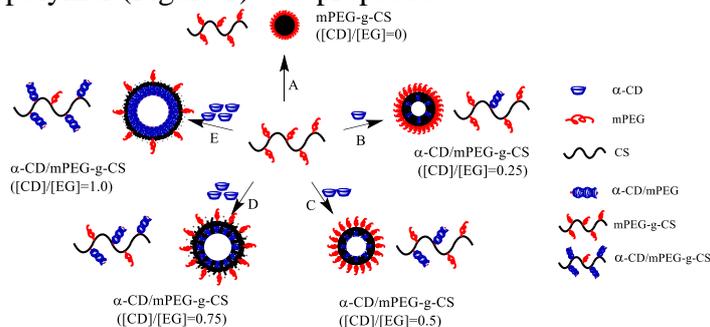


Figure 1. Schematic illustration of the formation of α -CD/mPEG-g-CS nanoparticles.

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IL14A: Targeting DNA G-quadruplex structures in vivo: towards a High Throughput Screening analysis of putative ligands

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Effective ligands able to recognize with high affinity and selectivity DNA G-quadruplex (G4) structures spontaneously self-assembled in telomeres or in oncogenes can be putative drugs in targeted anticancer therapies. For rapid screenings of large libraries of potential G4 binders, fast and reliable methods for the selection of compounds specifically targeting G4 structures are urgently required.

In this frame, we recently developed an innovative affinity chromatography-based assay, named G4-OAS (*G-Quadruplex on Oligo Affinity Support*), first optimized for different known G-quadruplex binders and then applied to a set of novel potential ligands [1]. In this binding assay, the analyzed compounds are flown through a resin functionalized with a G-rich oligonucleotide forming a G4 structure. Upon cation-dependent control of the folding processes of the immobilized G4-forming oligonucleotide, the molecules specifically binding the G4 structure are captured and then released using suitable G4-denaturing solutions.

The screening of focused libraries of small molecules, selected as potential G4 groove binders of the 5'(TTAGGG)₄TT^{3'} telomeric sequence, allowed selecting a small set of putative G4 ligands, studied in solution in their interaction with DNA through several biophysical techniques. Evaluation of their bioactivity showed that 3 ligands of this sub-library induced marked telomere-localized DNA damage response in human tumour cells [2].

The tandem application of virtual and experimental screenings proved to be a successful strategy to identify new bioactive chemotypes able to target the telomeric G4 DNA. Our current efforts are devoted to expanding the potential of the G4-OAS binding assay by extending it to a variety of biologically relevant G4-forming DNA/RNA sequences [3].

Acknowledgement

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IL14B: Tiny Goldworks: Gold Clusters in the Subnanometer Regime

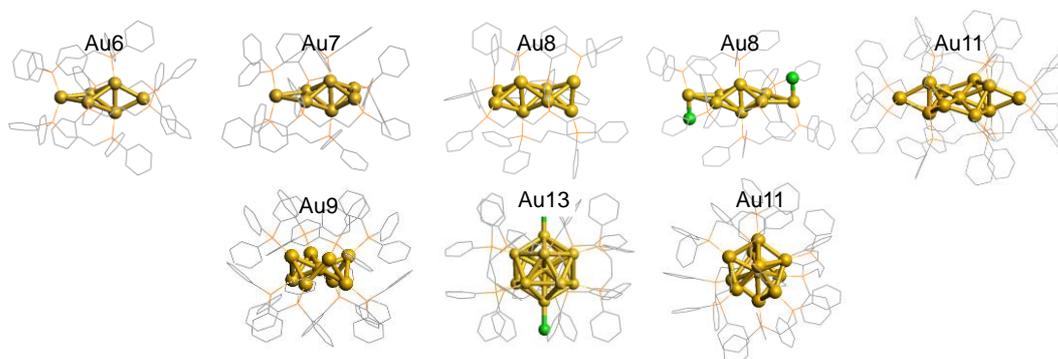
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It is well known that colloidal metal nanoparticles with a diameter of several nanometers are characterized by their prominent size-dependent properties, which have been widely exploited in diverse applications. However, when the object's size approaches 1 nm (metal number ~ 100), colloidal characters disappear and instead molecule-like features associated with discrete electronic structures emerge. In this talk, I shall talk about our recent studies on subnanometer gold clusters with nuclearity (metal number) of ~ 10 , and show that their properties are critically dependent on the inorganic microstructures and surface environments.

Phosphine-ligated gold clusters with defined nuclearity have a long history of studies, offering a library of 'tiny goldworks' with various geometrical and electronic features. During our recent studies on diphosphine-ligated gold clusters, we have found some exceptional Au₆, Au₇, Au₈, Au₁₁ clusters with non-spherical geometries [1,2]. Unlike conventional sphere-like clusters, these non-spherical clusters exhibit isolated absorption bands in the visible region, which are strictly dependent on the geometrical structures rather than the nuclearity. We also show that the exterior organic environments can be used as toolboxes for the modulation of the cluster properties. Among them, electronic coupling of the gold moieties with π -systems is noteworthy, which cause substantial perturbations on their optical absorption and photoluminescence features [3]. These features imply unique potential of subnanometer gold clusters to exhibit stimuli-responsive chromism behaviors. Elaborate ligand choice based on host-guest and supramolecular chemistries would allow the evolution of novel cluster-based materials, which may be applied to chemical sensors and smart luminescent materials.



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IL15A: Post-Synthetic Modification with Triple Events: Anion Exchange Coupled with Reduction and Dimerisation of Cu(II) Complex via SCSC

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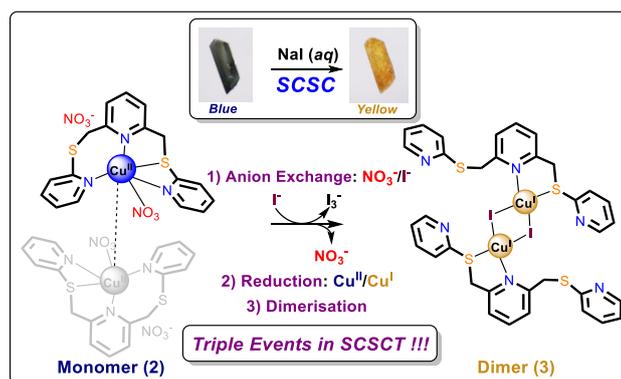
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Post-synthetic modification (PSM) of metallosupramolecules via an SCSC transformation provides a powerful tool, not only for creating of new materials, but also for understanding mechanistic pathways [1,2]. Hence it is a challenge to develop methodologies involving multiple transformations for preparing new materials that cannot be obtained via direct synthesis.

We report an anion exchange process accompanying cation reduction and dimerisation via the SCSC transformation [3]. First, a reaction of the flexible tripyridyl dithioether **L** with CuI afforded a mixture of four bis(ligand) complexes (**1a-1d**). To avoid the formation of undesired mixed products, a copper(II) nitrate complex-mediated approach involving anion exchange and cation reduction was employed to give a monomer complex, [Cu^{II}(**L**)NO₃]₂NO₃·toluene (**2**). When the blue crystals of **2** was immersed in an aqueous NaI solution, the crystals were transformed to a pale yellow dimer-type copper(I) iodide complex, [(μ-Cu^I₂I₂)(**L**)₂] (**3**). The observed anion exchange promotes the reduction of copper(II) to copper(I) at the expense of I⁻/I₃⁻ oxidation as well as dimerisation via the formation of a Cu₂I₂ cluster.

This result corresponds to the synthesis of a compound that otherwise was not able to be prepared via a direct synthetic procedure. As far as we are aware, the present PSM is the first example exhibiting triple events occurring during the SCSC transformation; an anion exchange coupled with the reduction and dimerisation of a metal centre of a complex. It is expected that this approach might provide a promising and efficient post-synthetic strategy.



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IL15B: Anti-adhesives: Future Therapy for Bacterial Infections?

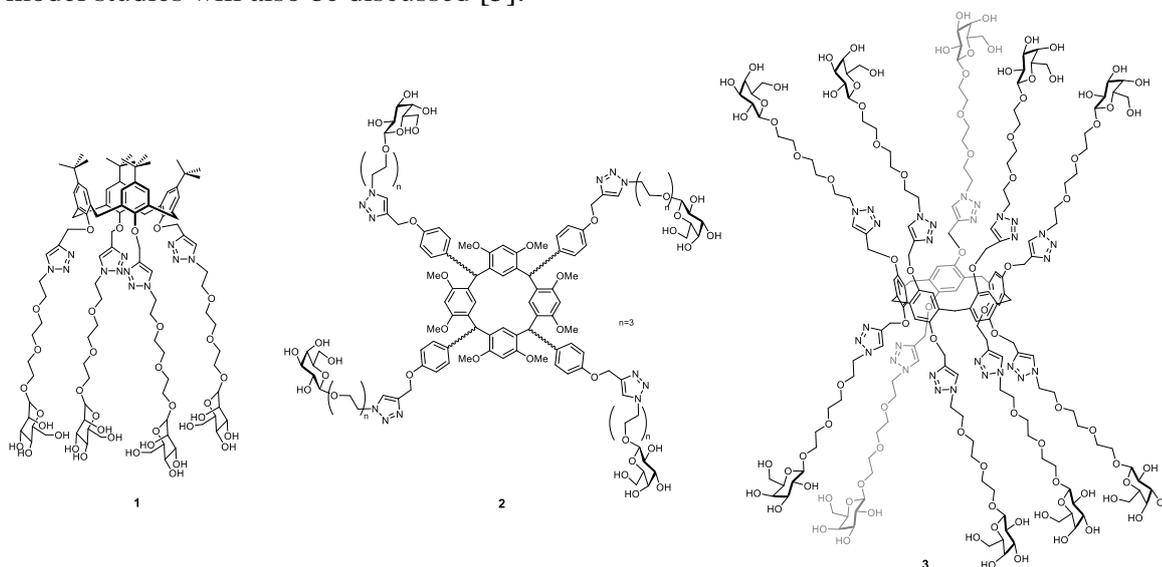
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The challenge of increasing bacterial resistance to classical antibiotics is leading to the development of alternative strategies for treating bacterial infections. Anti-adhesive molecules that inhibit the interaction between bacterial and human cells offer an intriguing possibility for reducing bacterial load without a bactericidal effect.

This talk will focus on the development of anti-adhesives, based on macrocyclic glycoclusters, which inhibit two lectins from *Pseudomonas aeruginosa* (LecA and LecB) that are implicated in adhesion, biofilm formation and infectivity. The importance of ligand topology in achieving high binding strength and selectivity between different lectins will be described through comparison of libraries prepared from calix[4]arenes **1** [1,2], resorcin[4]arenes **3**, **2** and pillar[5]arenes **3** [4]. Additionally, the potential modes of action and evaluation of the most effective inhibitor of LecA to-date in mouse model studies will also be discussed [5].



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IL16A: Size-discriminative allosteric extraction of alkali metals with propyl-acetic acid crossed type calix[4]arene

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Calixarenes are macrocyclic oligomers and their derivatives provide three-dimensionally arranged coordination sites for target metal ion. They also exhibit structural effects such as size-fitting effect, converging effect of functional groups, and complementary effect [1]. The allosteric effect is one of structural effects and is known as an effect caused by a certain effector in an enzyme. Tetraacetic acid type of calix[4]arene exhibited allosteric coextraction of metal ions in the presence of sodium ion [2]. The extraction of the second ion was driven by the first uptake of sodium showing high affinity with calix[4]arene, consequently the second dissociation of acetic acid was facilitated. It was found that sodium ion itself was coextracted with the first sodium-loading calix[4]arene [3].

In the present work, the extraction behavior of alkali metal ions with propyl-acetic acid crossed type *p*-*t*-octylcalix[4]arene was investigated. This calix[4]arene derivative exhibited allosteric coextraction for lithium and sodium ions. The stoichiometries of lithium, sodium and potassium in individual system were 1 : 2, 2 : 3, 1 : 1 (derivative : metal ion), respectively, while that in competitive system was 1 : 1 : 1 (derivative : sodium ion : lithium ion) as shown in Fig. 1. These stoichiometries are well explained by size-discriminating property, that is, the second sodium ion is too large to be extracted with a single molecule of the derivative, and the third sodium was extracted with two first sodium-loading derivatives.

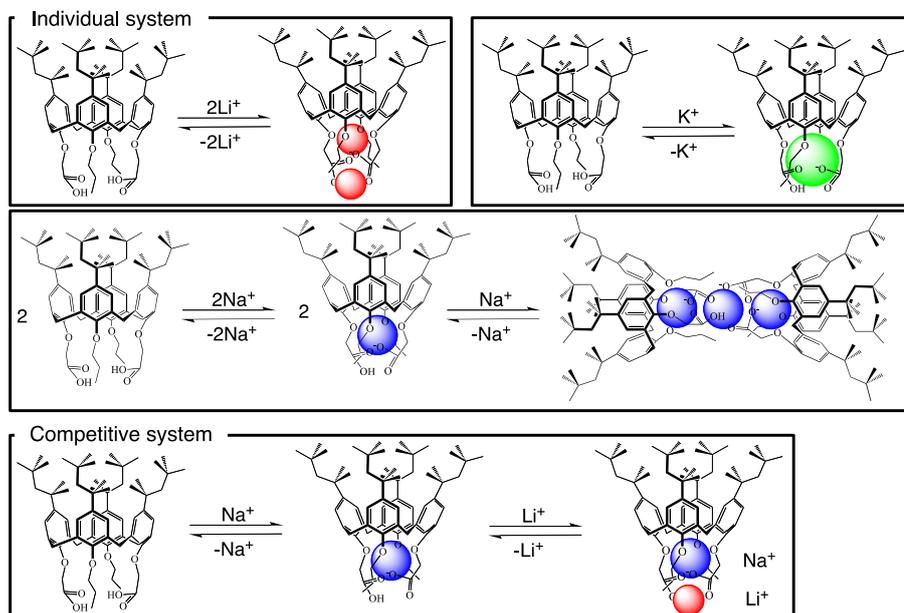


Figure.1 Alkali metal extraction scheme with propyl-acetic acid crossed type *p*-*t*-octylcalix[4]arene.

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IL16B: Ti³⁺ self-doped materials from a hybrid TiO₂-acetylacetonate gel

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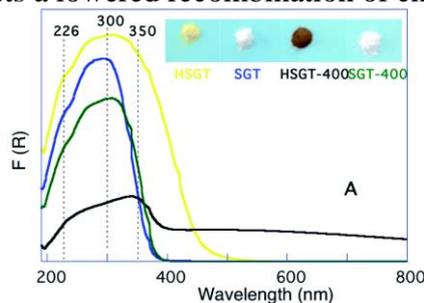
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TiO₂ based semiconductors are considered the most promising photocatalysts for applications as pollutants degradation, water splitting, CO₂ reduction and solar cells. Despite their favorable properties, the limited light absorption and high recombination rate of electron-hole pairs result in low efficiency of solar energy conversion. Recently an alternative to the common strategies employed to overcome these drawbacks modifying the electronic structure of TiO₂ has been proposed: the possibility to obtain partially reduced oxides, containing Ti³⁺ or oxygen vacancies. This kind of materials show a dark color (often black or blue) with visible light absorption owing to electronic states in the band gap. Their preparation usually requires hydrogenation or other harsh reducing conditions [1].

Here we report a simple and economical route, the calcination in air at 400 °C of a hybrid xerogel containing acetylacetonate prepared by sol-gel, to synthesize a visible light responsive TiO₂. After thermal treatment the yellow amorphous xerogel (HSGT), which exhibits interesting catalytic properties itself [2], turns to dark grey anatase TiO₂ (HSGT-400, see figure). It was characterized by complementary spectroscopic techniques to clarify its electronic features [3]. A diffuse absorption in the visible range is observed by UV-DRS (see figure, absorbance reported as Kubelka-Munk). XPS spectra demonstrate a very high content of Ti suboxides in the sample and EPR measurements support the formation of Ti³⁺ self-doping in the bulk of the material, while photoluminescence gives insight in the electronic states and suggests a lowered recombination of charge carriers [3].



HSGT-400 seems to possess high stability in ambient conditions, unlike many other black TiO₂ materials. Preliminary tests of photocatalytic activity show interesting results in the degradation of a dye as a model pollutant under visible light irradiation. The material studied is a promising candidate for the use of TiO₂ in different applications requiring extended photoresponsivity and stability.

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IL17A: Electrochemical anions recognition in water using gold electrodes modified with dipodal or di-peptide anion receptor attached to dipyrromethene- Me(II) complex

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In recent decade, the intermolecular recognition of anions in water has been attracted the attention of numerous scientific groups involved in supramolecular chemistry.^{1, 2} The most of literature reports the recognition of anions in one organic phase. Developing systems for the recognition of anions in water medium is still a challenging task. Here, we proposed the first anion recognition study of dipyrromethene modified dipodal anion receptor or dipeptide attached to electrochemically active dipyrromethene-Cu(II) complex or dipyrromethene-Co(II) complex in highly diluted water medium (in the picomolar range). The developed systems were characterized electrochemically using cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV). Both of them were successfully applied for the electrochemical recognition of anions (Cl⁻, Br⁻, and SO₄²⁻) in highly diluted aqueous medium. The results obtained allowed establishing the mechanism of communication between the redox centre and receptor anion complex as well as analytical signal generation.

IL17B: Heteroelectrode Structure for Solar Water Splitting: Integrated Cobalt Ditelluride across TiO₂-passivated Silicon Microwire Array

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Cobalt ditelluride as a cocatalyst on the surface of silicon microwires array (Si-MWs), as a heterocathode for hydrogen evolution reaction was synthesized via one-step drop-casting method. The improvement in photo-electrocatalytic efficiency, including the 0.9 V anodic shifting in onset potential and -15 mA cm^{-2} photocurrent density, are comparable to that of other cocatalyst systems for water reduction. The photocurrent decay of CoTe_2 @Si-MWs further improved to roughly -10 mA cm^{-2} by depositing 10 nm atomic-layer-deposited TiO₂ on Si-MW photocathode for 67 min. Outcomes of this study may demonstrate the possibility of introducing a new class of $\text{M}_x\text{Co}_{(1-x)}\text{Te}_{(2-x)}$ cocatalysts as an alternative to noble metals in facilitating water splitting reaction.

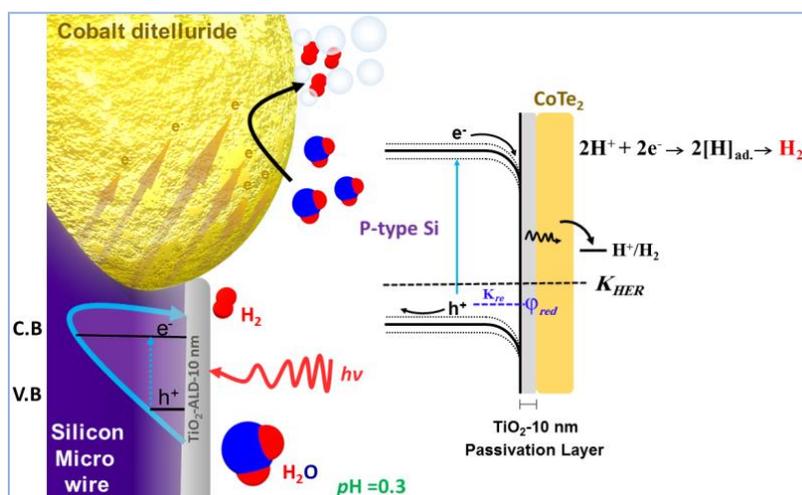


Figure 1 CoTe_2 @TiO₂-Si-MWs provides active sites for proton reduction and combines surface hydrogen atoms into molecular hydrogen. Φ_{red} stands for the corrosion potential of the p-type semiconductor, which is more negative than the KHER.

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IL18A: Anion binding with transition metal helicates and mesocates

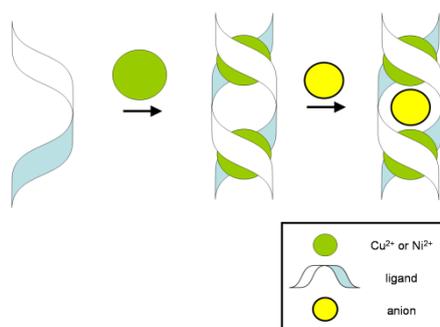
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Supramolecular architectures continue to find utility as hosts for anionic guests. Frequently, these structures self-assemble, trapping or encapsulating the anion within,[1] and, depending on the design of the ligand can form a myriad of supramolecular shapes including helicates [2,3].

By linking salicylaldimine units via a strap containing tertiary amines, we have shown that these ligands adopt helical and box shaped supramolecular cages upon complexation with transition metal cations (figure) [4]. The now protonated amines of the zwitterionic form of the ligand are available for anion binding. The structures and anion binding properties of these complexes will be presented.



Schematic of anion binding with helicates.

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IL18B: Renewable fuels via hydro-pyrolysis of biomass – Performance of cheaper, non-noble metal catalysts

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Aiming the replacement of costly noble metal catalysts in the hydrodeoxygenation of pyrolysis vapors for bio-oil upgrading, this work evaluated the performance of cheaper $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$ catalyst for the hydro-pyrolysis of pinewood biomass and found that it removed all the oxygenated compounds and produced aliphatic and aromatic hydrocarbons, being comparable with $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ catalyst.

Figure 1 shows that thermal pyrolysis leads to the formation of high amounts of oxygenates (9% acids, 38% carbonyls, 12% furans and 28% phenols). When pure $\gamma\text{-Al}_2\text{O}_3$ was used as catalyst, the acids and phenols were reduced completely, 70% of carbonyls were converted and interestingly 77% of hydrocarbons were formed. This might be due to the dehydration of acids and phenols over the acid sites of $\gamma\text{-Al}_2\text{O}_3$ [1]. Over $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ catalyst, all the oxygenates were completely converted into aliphatic (42%) and aromatic (58%) HC. Promisingly, $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$ catalyst only produced aliphatic and aromatic HC (57% and 43%, respectively), as well.

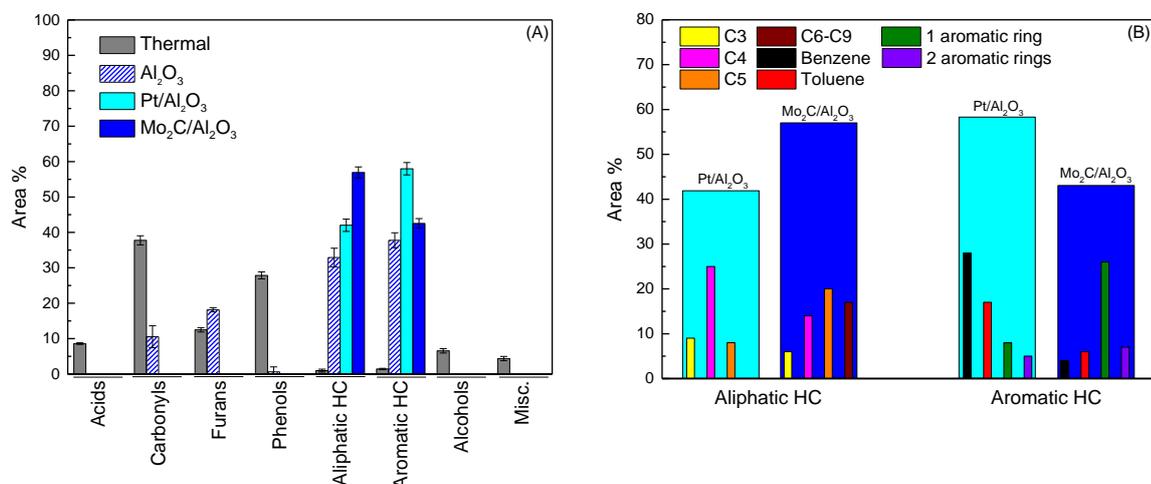


Figure 1. Product distributions of biomass hydro-pyrolysis over different catalysts.

It was demonstrated that $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$ removed oxygenated compounds completely and produced aliphatic and aromatic hydrocarbons, which are the most compatible fuel components. Comparing it with $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ performance, it can be claimed that $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$ catalyst is a promise and cheap alternative to noble metal catalyst for catalytic hydro-pyrolysis of biomass to liquid fuels.

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IL19A: Polyion Complex Vesicles with Surface Phosphorylcholine Groups

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The fabrication of giant vesicles using low-molecular-weight surfactants and polymers has been reported. The present study describes a novel preparation method of G-PICsomes through dialysis of 1.5 M NaCl aqueous solution containing a mixture of oppositely charged diblock copolymers against pure water. A cationic diblock copolymer (P₂₀M₁₉₀, $M_n(\text{NMR}) = 4.95 \times 10^4$, $M_w/M_n = 1.05$) composed of hydrophilic polyphosphobetaine, poly(2-(methacryloyloxy)ethyl phosphorylcholine) (PMPC) blocks and cationic poly((3-(methacrylamido)propyl)trimethylammonium chloride) (PMAPTAC) blocks was prepared via reversible addition-fragmentation transfer (RAFT)-controlled radical polymerization [1]. Anionic diblock copolymer (P₂₀A₁₉₆, $M_n(\text{NMR}) = 4.85 \times 10^4$, $M_w/M_n = 1.07$) composed of PMPC blocks and anionic poly(sodium 2-(acrylamido)-2-methylpropanesulfonate) (PAMPS) blocks also was prepared via RAFT polymerization (P, M, and A indicate PMPC, PMAPTAC, and PAMPS blocks, respectively). Subscript numbers indicate the degree of polymerization (DP) of each block estimated by ¹H NMR.

When P₂₀M₁₉₀ and P₂₀A₁₉₆ were added to 0.1 M NaCl aqueous solutions in proportions that resulted in charge neutralization, PICsomes formed with an R_h of about 80 nm [2]. Adding NaCl to adjust [NaCl] = 1.5 M caused dissociation of the PICsomes to unimers due to disruption of the electrostatic interactions. In contrast, when a mixture of P₂₀M₁₉₀ and P₂₀A₁₉₆ in 1.5 M NaCl was dialyzed against pure water, G-PICsomes with a radius of ca. 1 μm were formed along with coacervates as [NaCl] decreased [3]. The G-PICsomes in pure water were formed by electrostatic interactions of the oppositely charged diblock copolymers, and were covered with PMPC shells. The G-PICsomes were able to encapsulate hydrophilic guest molecules into the interior of the aqueous phase. These G-PICsomes covered with PMPC shells can be used as simple and easily prepared cell models.

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IL19B: Clay Mineral Nanofiber and Nanosheet Catalysts FOR catalytic glycerol OXidehydration to ACROlein and acrylic acid

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In the search for novel solid acid catalysts for the gas-phase catalytic oxidehydration of glycerol to acrylic acid, sepiolite and montmorillonite clay minerals were activated with hydrochloric acid to produce solid acid nanofiber and nanosheet catalysts [1-3]. The effects of the activation process on the texture and acidity of nanofiber and nanosheet, and their roles in gas-phase catalytic oxidehydration of glycerol to acrylic acid were investigated through X-ray diffraction, X-ray fluorescence analysis, scanning electronic microscopy, thermogravimetric analysis, N₂ adsorption-desorption isotherms, NH₃-temperature-programmed desorption, Fourier transform-infrared spectroscopy and pyridine adsorption followed by in situ infrared spectroscopy. Hydrochloric acid-activated clay minerals have proved to be active solid acid catalyst for the gas-phase oxidehydration of glycerol with air to acrolein and acrylic acid. Both the texture and the acidity of clay minerals can be tuned by the acid activation. Such activation had several effects, including part of removal of magnesium and aluminum in the octahedral sheets of clay minerals, and the unbundling of aggregated sepiolite fibers, the delamination of montmorillonite platelets, and even some breakage of the Si-O-Si bonds in the tetrahedral sheets of clay minerals. Those changes depended upon the concentration of hydrochloric acid used for activation. The type, the amount, the strength of the acid sites on the catalysts can also be tuned by acid activation. The medium to strong Brønsted acid sites from Si-O-H⁺ and H⁺ adsorbed on the surface were responsible for yielding acrolein. Loading WO_x and CuO_x onto the nanofiber and nanosheet of clay minerals can enhance the catalytic oxidehydration of glycerol, leading to a higher yield of acrylic acid. (The authors wish to acknowledge the financial support from the National Natural Scientific Foundation of China (21373185;41672033)).

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IL20A: Bio-inspired photocatalytic hybrid materials for sustainable hydrogen production

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Energy is one of the most prominent concerns of the 21st century. The increase on global warming, environmental pollution and exhaustion of fossil fuels owing to the raise of world energy demand, urgently requires the development of technology which can derive energy from renewable resources. In this regard, artificial photosynthesis via solar-driven water splitting [1] is of interest for producing clean fuels such as hydrogen (H₂). Considerable effort has been devoted to the development of stable and visible-light active photocatalyst semiconductors for H₂ evolution based on the principles of natural photosynthesis [1]. In this presentation we report the development of highly stable heterogeneous visible-light-active hybrid catalysts for photocatalytic H₂ production from water, inspired by nature's photosynthesis. We combine the components of the multimeric complex of Photosystem II, such as *free*-base and metallo-porphyrins (*m*-TCPP and Zn-*m*-TCPP), with the semiconductor g-C₃N₄ [2], to extend visible light absorption and enhance the intermolecular donor-acceptor electron transfer process between the porphyrin and the semiconductor, a key parameter to construct efficient electronically coupled nano-hybrids. By tuning the morphology (porous and nanosheet structure) of the semiconductor g-C₃N₄, an improvement of the photocatalytic activity of the hybrid material was observed due to the enhancement of the electronic and optical properties of g-C₃N₄. Our work shows that the sensitization of g-C₃N₄ with porphyrin dyes, and the control of its morphology, can be an effective approach to create stable and efficient materials for photocatalytic applications, such as hydrogen production.

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IL20B: Nanocatalyst of Ni-Al₂O₃-bentonite for hydrocracking of palm oil into biofuel

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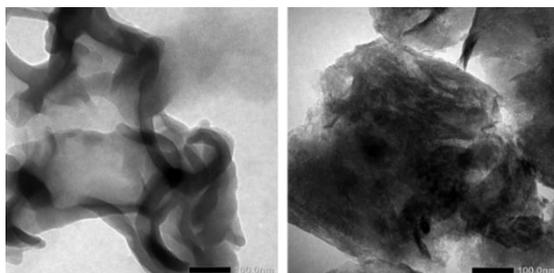
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Preparation of Ni-Al₂O₃-bentonite for hydrocracking process of palm oil into biofuel has been conducted. The purposes of this research were to synthesize Ni-Al₂O₃-bentonite, to study the physicochemical properties of the bentonite, and to test its ability as the hydrocracking catalyst of palm oil. The research began by cleaning up bentonite with distilled water and HF of 1%. Bentonite was then activated with sulphuric acid of 1.2 M and pillarized with pillaring agent [Al₁₃]⁷⁺ polyoxocation and calcined to be Al₂O₃-pillared bentonite. Finally, the pillared bentonite was wet impregnated with NiCl₂·6H₂O and calcined to be Ni-Al₂O₃-pillared bentonite. Modified bentonites were characterized with AAS, XRF, XRD, BET, TEM, FT-IR, and ammonia acidity test. To test the catalytic activities, modified bentonites were used to be the catalysts of hydrocracking reactions of palm oil. the hydrocracking processes were conducted on 500 °C for 1 hours. The products of hydrocracking reactions were characterized with GC-MS. The results showed that modifications of bentonite, which were activated, pillarized, and impregnated with Ni can increase the physicochemical properties of the bentonites, such as the acidity and the basal spacing. Ni-Al₂O₃-bentonite had the highest acidity, was 3.25 mmol/g. Pillarization and impregnation generally lowered the surface area, average pore size and pore volume. The hydrocracking process of palm oil using modified bentonite catalysts resulted in solid, liquid, and gaseous products. The analysis results showed that the liquid products have similar compositions to that of diesel oil and gasoline fraction. Hydrocracking with Ni-Al₂O₃-bentonite resulted the most liquid product, which is 46.32%, and had the highest percentage of diesel oil fraction, which was 61.20%.

Keywords: bentonite, pillarization, impregnation, palm oil, hydrocracking.



Acknowledment.

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IL21A: Effort on the promotion of iron sulfide to an efficient hydrodesulfurization catalyst

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The SO_x released from fossil fuels is one of the main source of air pollution. Extensive efforts have been devoting to develop desulfurization catalysts to effectively remove sulfur from fuel. Active phase metals including cobalt, nickel, molybdenum, and tungsten are extensively used in industry for hydrotreating/hydrodesulfurization catalysts for over 50 years. However, while it is desirable to use inexpensive materials to do the same job, it is a grand challenge. Herein, we report a novel iron-based sulfide catalyst that is tuned by zinc with extremely high activity for hydrodesulfurization, which shows an industrial application potential to replace industrial Mo-based catalysts. With an optimal configuration, the reaction rate constants of the dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) HDS are increased by 9.2 and 17.4 times, respectively, compared with the sum of that on the mono-iron and zinc sulfides. HDS activity for the sterically hindered 4,6-DMDBT on the FeZn sulfide catalyst is even close to that of Co-MoS₂. The experiments indicate that the addition of zinc greatly modifies the electronic properties of iron sulfide by transfer electron from zinc to iron, which tunes the d band center to modulate the adsorption behavior of dibenzothiophene and 4,6-dimethyldibenzothiophene. Combined with theoretical calculations, our experiments show that the addition of zinc dramatically tunes the formation of sulfur vacancies. We propose that the sulfur vacancy formation is the critical factor for designing highly efficient iron-based sulfide catalysts.

IL21B: Tunable Pressure Effects in Graphene Oxide Layers

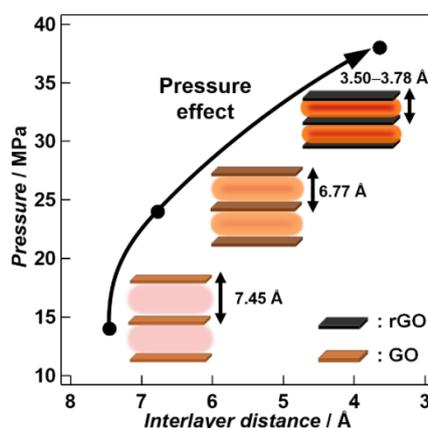
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The van der Waals interactions in pores of micro-porous materials generate a confinement effect for guest species. Confinement effects, in particular pseudo-pressure effects, are of importance to developments of characteristic states and unique phases of materials in pores under mild conditions. Recently, it has been reported that stacking structures of two-dimensional (2D) nano-sheets of graphene also act as a field to produce the confinement effects. Although there are many types of porous materials, tunable confinement effects arising from pore size tuning in one material remain unexplored. In most cases, the different size pores should be prepared one by one to obtain required pseudo-pressure effects. Materials exhibiting tunable confinement effects will produce a useful platform for the precise control of physical properties of nanomaterials confined in the pores. Accordingly, we have focused on the structural transformation from graphene oxide (GO) to reduced graphene oxide (rGO) for the development of tunable confinement effects.

Tunable pressure effects associated with changing interlayer distances in two-dimensional graphene oxide (GO)/reduced GO (rGO) layers are demonstrated through monitoring the changes in the spin-crossover (SCO) temperature ($T_{1/2}$) of $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ nanoparticles (NPs) incorporated in the interlayer spaces of the GO/rGO layers. The interlayer separation along the GO to GO/rGO-NP composites to rGO series decreases smoothly from 9.00 Å (for GO) to 3.50 Å (for rGO) as the temperature employed for the thermal reduction treatments of the GO-NP composites is increased. At the same time, $T_{1/2}$ increases from 351 K to 362 K along the series. This $T_{1/2}$ increment of 11 K corresponds to that observed for pristine $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ NPs under a hydrostatic pressure of 38 MPa. The influence of the stacked layer structures on the pseudo-pressure effects has been further probed by investigating the differences in $T_{1/2}$ for $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ that is present in the composite as larger bulk particles rather than as NPs.



ORAL COMMUNICATIONS ABSTRACTS

O1A: Supramolecular Interactions of Solid Cyclodextrins with Guest Vapors

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Cyclodextrins (CDs) and their clathrates are widely used due to host's encapsulating ability. However, conventional methods of CD clathrates preparation are related to a complicated search of optimal conditions and procedures for every included guest. Intricate problem is an optimization of water contents in CD-guest system. The host hydration can reduce an inclusion threshold for large hydrophobic guests by their activity giving favorable hydration effect for their inclusion [1]. Besides, water competes guests for binding sites in CD at high water activities.

These difficulties can be removed using guest or water exchange in anhydrous solid CD clathrate. This is a new method shown to be a better preparation procedure for clathrates of beta-cyclodextrin (bCD) with guests of moderate hydrophobicity and molecular size, such as 1-propanol, 2-propanol or propionitrile. Clathrates with more than 2 mol of these guests per 1 mol of host were prepared ($S > 2$). Such inclusion capacity is unreachable by other methods. In comparison with other studied "leaving guests", the exchange of benzene allowed preparing bCD clathrates with higher guest contents. An exchange of THF and ethanol for other guests was shown to be more selective and less complete in some cases.

Saturation of intermediate hydrate with controlled water contents in molecular cavity and interstitials can be used for effective preparation clathrates of alpha-cyclodextrin (aCD) with volatile organic compounds. As a result, clathrates with higher guest contents can be prepared than by saturation of dried aCD.

All available thermodynamic models of guest inclusion by CDs deal with data of complexation in solution, while most inclusion compounds of CDs are prepared and used for practical applications as solid clathrates. Present work gives a first determination of formation Gibbs energy of alpha- and beta-cyclodextrin hydrates and clathrates along with a quantitative thermodynamic description of corresponding hydration process as a phase transition. Together with performed determination of formation Gibbs energy for anhydrous inclusion compounds with organic guests, these results show the extent, in which water may be regarded as a unique guest for initially dried cyclodextrins [2]. The observed structure-property relationships help to find the structural requirements for a guest to be included by dried CDs without water. This gives a way for development of new efficient techniques for preparation of CD clathrates with various organic compounds for practical purposes, where some organic component may be used instead of water as the agent activating inclusion of a target compound.

The work was supported by Russian Government Program of Competitive Growth of Kazan Federal University and by RFBR, grant No. 17-03-01311.

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O1B: Solid-state optical and electrical properties of new chiral oligothiophenes: the central role of supramolecular organization

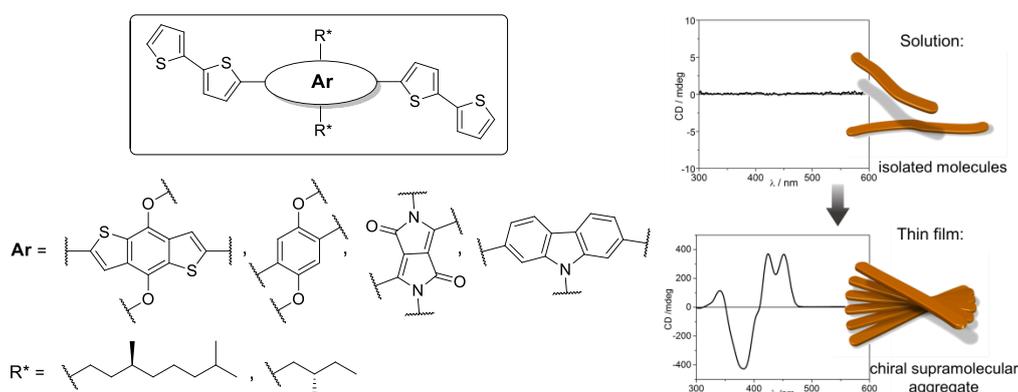
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Thanks to the possibility to modulate electronic and optical properties, organic semiconductors based on π -conjugated polymers and oligomers have opened the way to the development of innovative optoelectronic devices. Their fundamental electro-optical properties (charge and exciton transport, light absorption and emission, response to external stimuli, etc.) depend not only on their chemical structure and the conformation assumed, but also on the supramolecular interactions and the nano/mesoscale organization in the solid-state [1]. Chirality represents one of the most sophisticated expedients to control the supramolecular aggregation of similar systems (in particular their interchain spacing and/or alignment) [2]. As a further bonus, chiral π -conjugated systems may be used as active layers in sensors able to discriminate enantiomers [3] or in circularly polarized (CP) light detectors [4].

We decided to work with new oligothiophenes – which have well known applications in optoelectronics – functionalised with some inexpensive alkyl chiral groups derived from natural sources, seeking self-assembly properties, which would ensure supramolecular chirality and the onset of extraordinary optical and electrical properties.



Herein we describe: *i*) the synthetic route developed for the preparation of these oligomers; *ii*) their spectroscopic characterization (UV-Vis, ECD, fluorescence) to investigate the supramolecular organization in thin films prepared by drop casting or spin coating; *iii*) preliminary studies of CP-light detection in organic field-effect transistors (OFETs) based on the most promising oligothiophenes as semiconducting layers.

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O2A: Identification of specific noncovalent interactions between proteins and nanoparticles based on site-resolved NMR spectroscopy

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The successful application of nanoparticles (NPs) in the biosciences necessitates an in-depth understanding of how they interface with biomolecules [1]. Protein–NP interactions are also of interest for the development of hybrid devices. Thus, methodologies aimed at characterizing biomolecules associating with NPs represent an indispensable tool.

Solution NMR spectroscopy is a mature technique for the investigation of biomolecular structure and intermolecular associations, however its use in protein-NP interaction studies remains highly challenging [2]. We show that noncovalent protein-NP interactions are accessible by NMR, and we describe novel approaches based on site-resolved protein signal perturbations.

To contribute to an understanding of the interactions between fundamental biomacromolecules and NPs, we investigated the adsorption of fullereneol onto ubiquitin (Ub). NMR data were consistent with the reversible formation of soluble aggregates incorporating fullereneol clusters [3]. The specific interaction epitopes were identified, coincident with functional recognition sites in a monomeric and a dimeric Ub.

The incorporation of paramagnetic centers into NPs offers new opportunities to explore bio-nano interfaces with increased sensitivity and in heterogeneous biomolecular mixtures. The adsorption of Ub onto Gd-doped NPs produced residue-specific NMR line-broadening effects mapping to a contiguous area on the surface of the protein. Importantly, an identical paramagnetic fingerprint was observed in the presence of competing protein-protein association equilibria representative of those encountered in biological media [4].

Besides the mapping of binding surfaces, we also successfully applied NMR approaches to describe the dynamics of proteins adsorbed onto NPs [5].

The developed approaches offer new opportunities for an improved characterization of the biomolecular corona of NPs and of designed protein-NP systems.

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O2B: Metal Ions Turn-on Phosphorescence Sensors in Water With Concomitant Self-Assemblies

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Carboxylic acids provide supramolecular assemblies due to directional hydrogen bonds or coordination to metal ions.¹ However, most of them do not combine exalted luminescent properties. Hexakis(phenylthio)benzene derivatives carrying six carboxylic acid groups at their periphery are designed to couple aggregation-induced phosphorescence, water-solubility and metal-binding properties. These asterisks are non-emissive in solution, but phosphorescence is turned-on in the solid state or when rigidity occurs from restricted intramolecular motions.² They are then highly phosphorescent, due to the well-known AIE phenomena.³ Under slightly basic aqueous solutions, carboxylates complex divalent metal ions to create self-assemblies, leading to phosphorescence, by hindering molecular motions. For instance, when an asterisk is titrated with Pb(NO₃)₂, changes in the absorption and phosphorescence spectra are observed with a plateau at ca. 3 equiv. of Pb²⁺ ions per molecule.

Alkali and alkaline earth cations like Li⁺, Na⁺, K⁺, Mg²⁺ and Ca²⁺ do not turn on phosphorescence and do not perturb Pb²⁺ complexation, indicating an excellent selectivity for this metal ion. Also, 3d metal ions like Mn²⁺, Fe²⁺, Co²⁺, Cu²⁺ and Zn²⁺ do not turn on phosphorescence. The self-assemblies can be disassembled with EDTA due to Pb²⁺ scavenging by a strong EDTA-Pb complex. This sensing process is thus reversible by turning ON or OFF phosphorescence by consecutive additions of Pb²⁺ and EDTA⁴.

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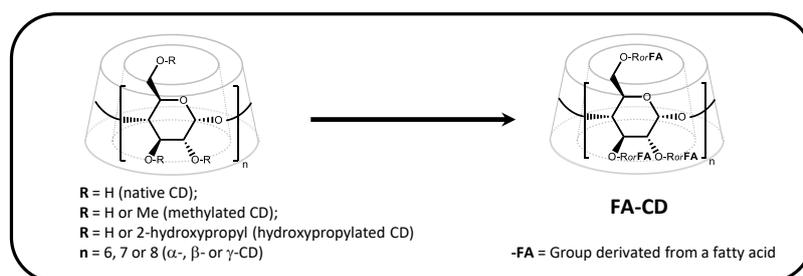
O3A: Biphasic aqueous hydrogenation catalyzed by ruthenium nanoparticles promoted by fatty acid-modified cyclodextrins

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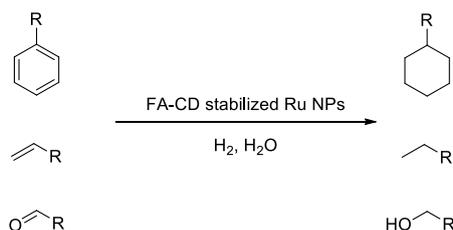
New cyclodextrins, called **FattyAcid-CycloDextrins (FA-CDs)**, have been synthesized in high yields starting from native or modified CDs.



Various **FA-CDs** can be obtained. Indeed, the following characteristics can be easily changed:

- the nature of the CD (native CDs, *i.e.* α -, β - or γ -CD; randomly methylated or 2-hydroxypropylated CDs)
- the type of the fatty acid derivatives
- the substitution degree, *i.e.* the number of **-FA** group grafted per CD.

These modified CDs have shown good solubilities in water and good aggregation properties. Tested as protective agent of ruthenium nanoparticles dispersed in aqueous phase and as mass transfer promoters in unsaturated compounds aqueous biphasic hydrogenation catalyzed by ruthenium nanoparticles, these cyclodextrins led to good stability of colloidal suspension and fast reactions.



These very good catalytic results were attributed to the good stability of the so obtained colloidal suspension and the inclusion properties of these new chemically modified cyclodextrins.

This work was performed in partnership with the SAS PIVERT, within the frame of the French Institute for the Energy Transition (Institut pour la Transition Énergétique (ITE) P.I.V.E.R.T. (www.institut-pivert.com) selected as an Investment for the Future ("Investissements d'Avenir"). This work was supported, as part of the Investments for the Future, by the French Government under the reference ANR-001-01.

O3B: Fluorescently-labeled TBAs conjugated to nanoparticles for capture or activity-control of thrombin

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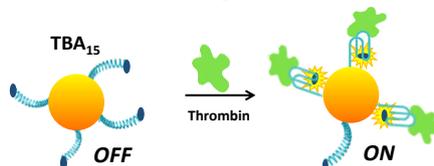
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Nucleic acid aptamers are single-stranded DNA/RNA molecules identified to recognize with high affinity specific targets including proteins, small molecules, ions, whole cells and even entire organisms, such as viruses or bacteria [1]. Interestingly, many of the aptamers selected against biologically relevant protein targets are G-rich sequences that can fold into stable **G-quadruplex** (G4) structures [2]. Despite having an overall similar scaffold, a large variety of different structural arrangements are available for G4s, accounting for their notable diversity in the target recognition events, also ensuring high specificities and binding affinities.



The 15-mer G-rich oligonucleotide known as **thrombin-binding aptamer** (TBA₁₅) is a DNA aptamer targeting with nanomolar affinity thrombin, a serine protease involved in coagulation processes, and able to inhibit the thrombin-catalyzed polymerization of fibrinogen [3]. It folds into an intramolecular G4 consisting of two planes of guanine tetrads. Due to its intrinsic instability in physiological media, several modified TBA analogs have been proposed in the literature, containing backbone/base modifications, or specific conjugations with several entities to improve thermal and enzymatic stability [3]. Recently, with the goal of optimizing *in vivo* stability and activity of unmodified TBA, we prepared and characterized new TBA analogs conjugated to magnetic (dextran-magnetite) [4] or silica (Sicastar®) [5] **nanoparticles** (NPs) carrying structure-sensitive **fluorescent systems**. The selected NPs have been chosen for their low cytotoxicity and high biocompatibility. The use of nanoparticles for the *in vivo* delivery of TBA, expected to allow *per se* an increased nuclease resistance and bioavailability of the oligonucleotide, offers as additional advantage the possibility to exploit **multivalency** effects, due to the presence of multiple copies of TBA on a single scaffold [3].

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O4A: Porphyrin-edged $[M_4L_6]^{8+}$ capsules for cage controlled catalysis

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Confinement of the catalytically active site is the key reason for high activities and selectivities observed in enzymatic transformations. The intrinsic complexity of natural enzymes has urged chemists to study simpler supramolecular cage analogues [1] to ultimately achieve higher activity and selectivity in known catalytic transformations. Selective encapsulation of catalysts in cages, which should remain throughout the catalytic cycle in competition with substrate molecules, is challenging. [2] One strategy involves the use of ligand templates, i.e. building blocks that can coordinate to the active metal center and simultaneously to the building blocks that form the cage. [3] Here we demonstrate two new examples of cage controlled catalysis, namely size-selective hydroformylation of a series of aliphatic and aromatic alkenes [4] and efforts towards light-driven proton reduction. In both cases the encapsulation of the catalytically active complex within the $[M_4L_6]^{8+}$ capsule is coordination-driven, relying on the supramolecular pyridine-zinc porphyrin interaction. The windows in the faces of the tetrahedral cage are limited in size due to the steric bulk imposed by the porphyrin units, occupying the edges of the capsule. In the first example this results in substrate size selective catalysis, as only smaller substrates can access the Rh(I) catalyst in the cage, and these alkenes are converted into the corresponding aldehydes (Figure 1). In our second example, we encapsulate a Fe-Fe hydrogenase mimic inside the cage, also by coordination to the Zn(II) porphyrin edges. The porphyrin-based edges are also used for light induced electron transfer to the catalyst inside the sphere (Figure 2), with the aim to achieve efficient light-driven proton reduction. In both examples the cage acts as a second coordination sphere around the catalytically active site, which bears a strong resemblance to nature where enzymes embed the active site deep inside the hydrophobic pocket of a bulky protein structure. In this talk the latest results of this project will be presented.

Figure 1

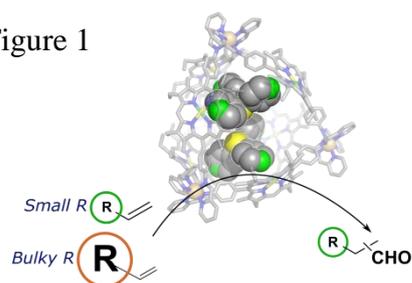
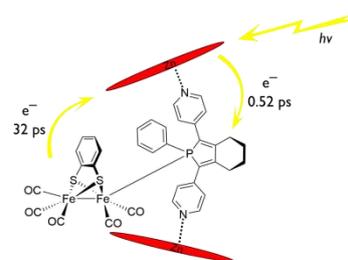


Figure 2



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O4B: Restricted-access supramolecular solvents for biomonitoring of polycyclic aromatic hydrocarbons with mosses

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The European Monitoring and Evaluation Programme (EMEP) monitors 34 sites to evaluate the emission and deposition of persistent organic pollutants (POPs), mainly polycyclic aromatic hydrocarbons (PAHs). This coverage is insufficient to provide sound insights into the spatial and temporal variations of pollution levels within the EMEP region. An easier and cheaper alternative to the conventional precipitation analysis of POP is their biomonitoring using mosses. Regular measurements of PAHs concentrations in mosses can provide much higher sample density and consequently they can greatly improve the quality of official emission data.

Here we report a fast, low-cost and eco-friendly method for quantification of 14 priority PAHs in mosses based on the combination of restricted-access supramolecular solvents (SUPRAS-RAM) and liquid chromatography-fluorescence detection (LC-FLD). The SUPRAS-RAM selected was made up of inverted hexagonal aggregates of decanoic acid, that spontaneously formed in a THF:water solution through self-assembly processes [1]. The nanostructures in the SUPRAS offered an external hydrophobic phase, consisting of hydrocarbon chains extended and surrounded by THF, and internal aqueous cavities, whose size was tailored by controlling the THF:water ratio for amphiphile self-assembly. These nanostructures in the SUPRAS permitted fast and efficient extraction of PAHs while excluded macromolecules by chemical and physical mechanisms. Thus, proteins precipitated by both the decrease of the dielectric constant of solution and the formation of complexes with decanoic acid, while polysaccharides and humic acids did not incorporate to the internal aqueous cavities due to size exclusion. Method detection and quantification limits for PAHs were in the ranges 0.04-0.24 and 0.14-0.80 µg/kg, respectively. The method was applied to the determination of different moss species collected in both polluted and unpolluted sites in the South of Spain. Recoveries were within the range 71-110%. The method fulfilled the criteria of the European Commission Decision 2002/657 and fitted the requirements for biomonitoring of PAHs.

Acknowledgments

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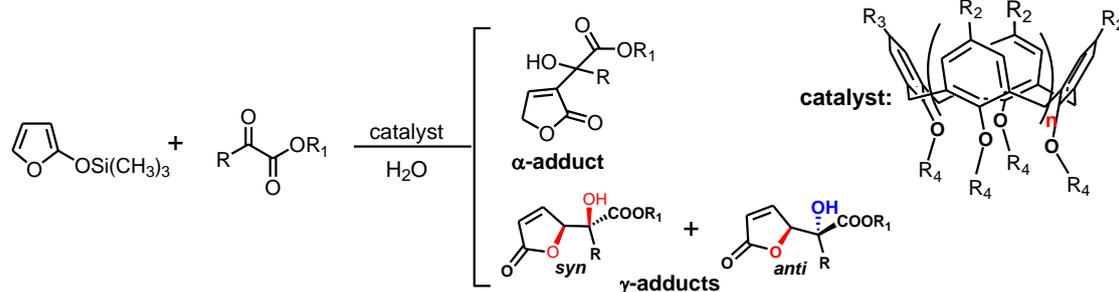
O5A: Supramolecularly organocatalyzed C-C bond formation under "on-water" conditions or inside nanocavities

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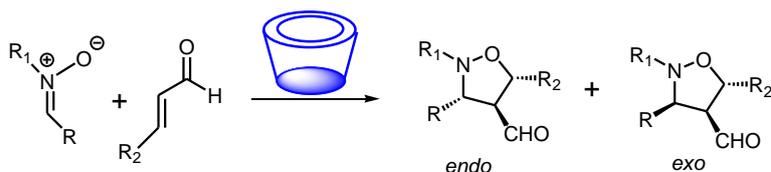
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During the last years and with the advent of green and sustainable chemistry, a particular attention has been paid to the development of new and efficient synthetic strategies able to mimic the attractive levels of performance, selectivity and specificity observed in biological processes [1,2]. In this context, the use of water as a reaction medium and the design of "artificial" enzymes with the attractive features of natural ones but without the drawbacks of their intrinsic vulnerability and poor substrate versatility, represent promising fields [3,4]. We report here our recent studies on these two issues based on the use of calixarene derivatives. In fact, their remarkable hydrophobicity and their recognition abilities make them valid organocatalysts for the vinylogous Mukaiyama aldol reaction under "on-water" conditions [5,6] and provide a nano-environment to efficiently conduct 1,3-dipolar cycloaddition of nitrones to α,β -unsaturated aldehydes [7].

Calixarenes as organocatalysts under "on-water" conditions



Catalysis inside nanocavities



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O5B: Silica-Eumelanin Hybrid Nanoparticles Engineered by Covalent Conjugate Polymerization

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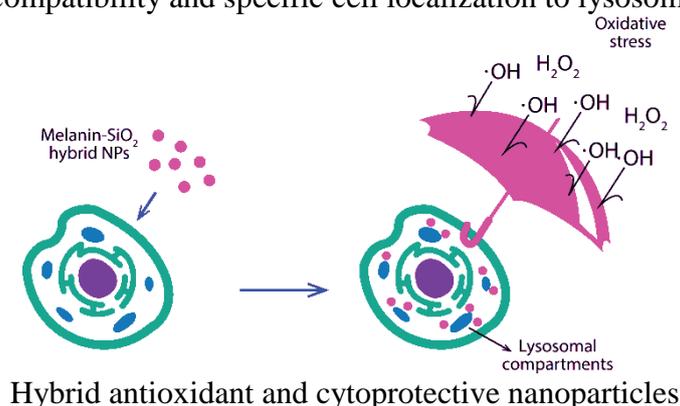
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Organo-inorganic hybrids, made by coupling inorganic nanostructures to organic molecules, provide the opportunity to invent a huge set of new multifunctional materials with a large spectrum of known and as yet unknown properties. Eumelanins, hydrophobic natural pigments, are emerging as a powerful organic component for developing biologically active materials because of their numerous biological functions, such as photo-protection, photosensitization, free radical quenching, metal ion chelation and even intrinsic antimicrobial behavior [1]. Silica is one of the few inorganic material recognized as 'safe' by the US FDA. In addition, the endogenous nature of silica and its functional versatility make it one of the most intensively investigated among inorganic materials in the field of biotechnology, health and medicine both for imaging and delivery. Furthermore, it is biocompatible and easy to functionalize to guarantee active targeting, as well as long circulation times.

Following a bioinspired approach, herein we propose a novel synthesis strategy to the design eumelanin-silica hybrid nanoparticles integrating the potent antioxidant properties of DHICA eumelanin into a stable, bioactive and biocompatible silica matrix. These systems prove that eumelanin's biofunctional and physico-chemical properties can be markedly enhanced, if its formation occurs through templated polymerization in the presence of a ceramic phase [2]. Particularly, this approach presents manifold potentialities that can ultimately lead to cutting-edge functional hybrid materials featuring relevant antioxidant and cytoprotective nanoparticles endowed with high stability, biocompatibility and specific cell localization to lysosomes.



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O6A: Pillararenes: a mechanistic study of a cation templated synthesis and catalytic application in reaction occurring in organic media

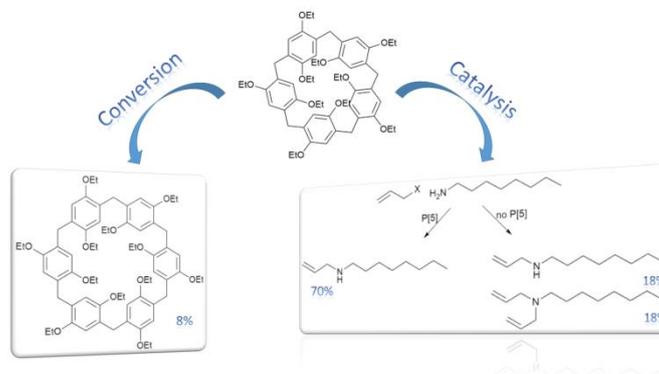
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In 2008 for the first time pillar[n]arenes (P[n]), a new class of macrocyclic aromatic molecules, have been synthesized in the group of Ogoshi [1]. Since then a lot of effort has been put to improve the synthesis to provide a wide range of new host molecules to be employed as supramolecular materials, as nanodevices or for biological applications. Recently we published a paper on some innovative templated syntheses employing small organic and organometallic cations, focused on improving the yield of the P[6] product [2].

So far the mechanism of the cyclo-condensation reaction of pillar[n]arenes has been explained by dynamic covalent bond chemistry [3]. We investigated the phenomenon observing the conversion of P[5] into P[6] at room temperature through MS spectrometry with the aid of an isotopic labelled P[5]. Even though pillar[n]arenes have attracted a lot of interest mainly for their potential applications as supramolecular materials, only few examples of their use as supramolecular catalysts have been reported [4]. Due to the host-guest properties of pillar[n]arenes our group. We disclosed the catalytic effect of P[5] in nucleophilic substitution reactions observing an increase of more than one order of magnitude in rate of the reaction between allyl halides and primary amines. Moreover, P[5] enabled high degrees of product and substrate selectivity, all behaviours that are reminiscent of enzymatic catalysis.



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O6B: A biocompatible chemical process to prepare hyaluronan based material able to self-assemble into stable nano-particles

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New self-assembled nano-particles were developed by chemical conjugation of natural fatty acids to the backbone of hyaluronan (HA).

An environmentally sustainable and energy-efficient synthetic process has been developed, it consists in a microwave-promoted acylation of the hydroxyl function of the polysaccharide with the fatty acids, performed under solvent-free conditions. The efficient interaction of the solid reagents with the MW radiation accounts for the obtained high yielded products. The self-assembly process of the obtained compounds very fast occurred in an aqueous medium under MW-radiation, thus allowing the development of a green protocol for the nano-particles preparation. The chemical structure and the self-association behavior of them were studied by FT-IR, NMR, fluorescence and dynamic light scattering. The HA derivatives form stable spherical shape aggregates, as assessed by transmission electron microscopy.

As subsequent step, the curcumin was loaded in the hydrophobic core of the HA-fatty acid micelles, in order to investigate the delivery and biodistribution of the potential drug delivery systems by monitoring the fluorescence of the loaded probe.

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O7A: Glycan recognition with benzoboroxole-based sensor platforms

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The expression of glycoproteins with structural modifications of the glycan moiety, such as changes in glycosylation and increased branching, is often related to cancer [1]. One of the biggest challenges nowadays is the recognition of such complex structures with high specificity. Benzoboroxoles are synthetic carbohydrate receptors that exhibit binding ability in physiological conditions [2]. In particular, they can bind hexopyranosides, which account for the large majority of biologically relevant carbohydrates, through the formation of cyclic boronate esters with the hydroxyl groups of the sugars. Thus, the integration of benzoboroxoles in sensor platforms has great potential for the detection of cancer-related glycans.

Here, we report a general approach to create a stable complex between a series of selected glycans and the highest possible number of benzoboroxoles. This is an essential and at the same time challenging feature to achieve high specific binding. Each complex is then imprinted on a chemically modified gold surface, creating a pocket that is able to accommodate the targeted glycan only (Figure 1) [3].

The preparation of platforms able to recognize a series of complex carbohydrates (sialylated, fucosylated and multi-antennary) is under investigation. The binding affinity and selectivity of the imprinted surfaces are assessed by Surface Plasmon Resonance analysis. This approach can be extended to any cancer-related glycan and it is expected to provide a powerful diagnostic tool for the detection of glycoproteins, through the development of novel sensor platforms capable of discriminating healthy and cancerous glycoforms.

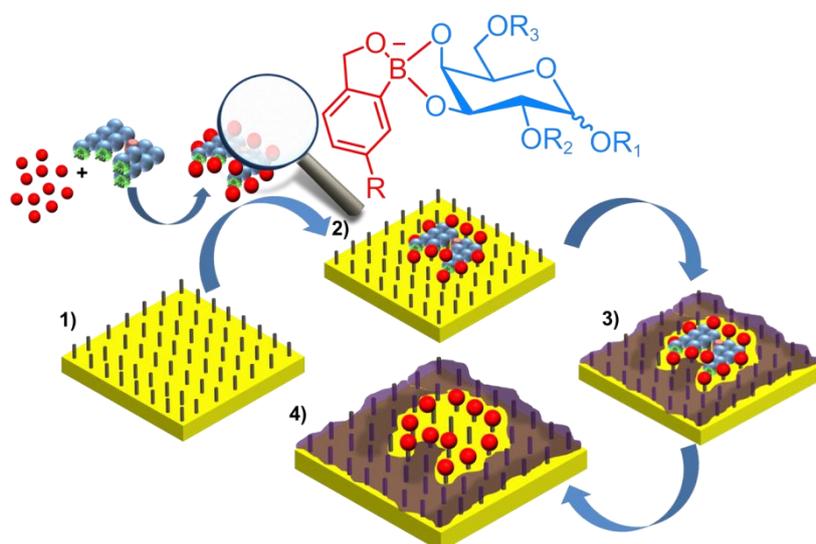


Figure 1. Fabrication of the sensor platform.

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O7B: Chemosensing control of monolayer-protected gold nanoparticles

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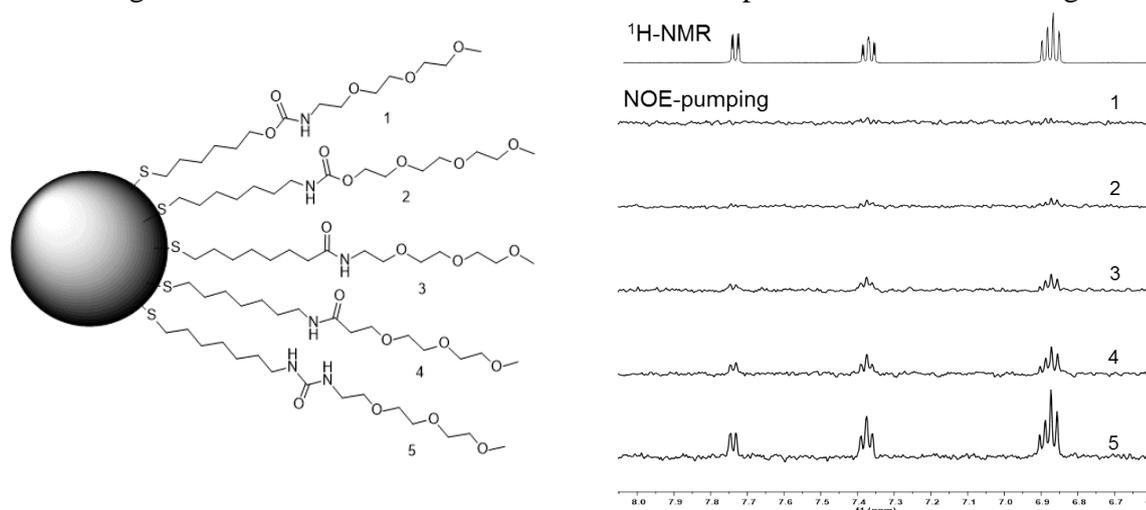
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Our group reported a new chemsensing method recently, which is based on monolayer-protected gold nanoparticles and NMR. The detection experiment we use in this method is called “NOE pumping”² and it consists of two steps: first a diffusion filter is used to cancel the magnetisation of all the molecular species presents in the sample but not of the nanoparticles due to their lower diffusion coefficient. Secondly, the magnetisation is transferred via NOE effect from the nanoparticles, which act as receptors, to the interacting species. Therefore, only signals of the interacting analytes are displayed in the 1D NMR spectrum of the mixture. In this way, detection, identification and quantification of the analyte are possible and also selectivity of the nanoparticles can be simply modified by varying the coating molecules of the nanoparticles.

In our previous study, we found that NP-3 has the ability to detect salicylate in the presence of 3- and 4-hydroxybenzoate and p-toluene-sulfonate, and such selectivity can be essentially ascribed to hydrophobic partition. To further investigate the factors controlling the molecular recognition ability, we prepared a series of nanoparticles coated with thiols having similar structures but featuring an hydrogen bond donating group (NH) at different positions. Based on molecular dynamic simulations, the monolayer of the nanoparticles can self-organise to form transient pockets, which acts like protein binding pockets. The results of the NOE pumping experiments revealed that the different nanoparticles investigate do have different affinity for salicylate even when the NH grouped is located in slightly different positions along the coating molecule chain. This suggests a relevant role of H-bonding in salicylate recognition as well as quite a defined structure of the binding pocket. Further study of the sensing mechanism is still in progress.

ERC-StG grant 259014 MOSAIC and Chinese Scholarship Council are acknowledged.



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O8A: Carboxylic Acids as Chemical Fuels for the Cyclic Operation of a Catenane Based Molecular Switch: Tuning the Motion Rate

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In this work, activated carboxylic acids are presented as new chemical fuels for a catenane based, bistable chemical switch composed of two identical macrocycles incorporating a 1,10-phenanthroline unit. While the transition between two different states of a molecular switch has often been made possible by the sequential addition of a fuel and a proper antifuel [1], here one only chemical species, 2-cyano-2-phenylpropanoic acid **1**, is employed to drive the whole cyclic operation (Figure 1).

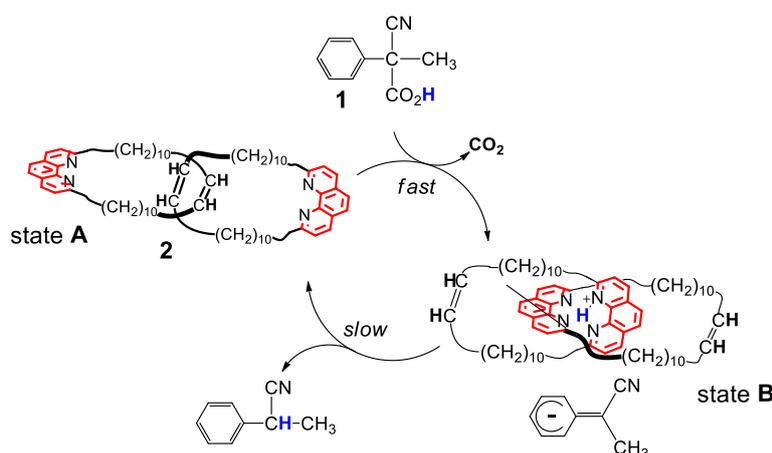


Figure 1. Cyclic operation of the catenane-based switch **2** coupled to decarboxylation of fuel **1**.

Decarboxylation of acid **1** is fast and quantitative when carried out in the presence of 1 molar equivalent of the chemical switch and, when decarboxylation is over, all of the catenane molecules have experienced large-amplitude motions from state **A** (neutral) to state **B** (protonated), then to state **A** again [2].

In this communication, the principle at the basis of the above system will be illustrated. Furthermore, it will be shown that is possible to control the rate of the cyclic motion of the switch (ranging from 100 s to 100 h timescale) by a fine tuning of the fuel chemical structure.

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O8B: Selective nanoparticle-protein interactions. Towards nanoproteomics

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Activity-based protein profiling¹ is one of the most powerful tools for protein quantification. By labelling proteins with an irreversible covalent inhibitor, it reports both protein expression and activity levels. This makes it a very powerful tool for drug discovery and diagnosis. Despite the numerous advantages, experiments are typically too long and expensive instrumentation is required in many cases to make it viable for routine analysis. In our project we use gold nanoparticles as scaffolds to reach the some goal avoiding the aforementioned drawbacks.

We have developed and fully characterized water soluble supramolecular conjugates of gold nanoparticles with a thiol-based mixed-monolayer with the capability to interact via site-specific probes with the protein active site.

Biotinylated nanoparticles were capable to bind avidin displacing weaker ligands from the active sites. The formation and disposition of the protein corona have been quantified at the molecular level and visualized by electron microscopy.

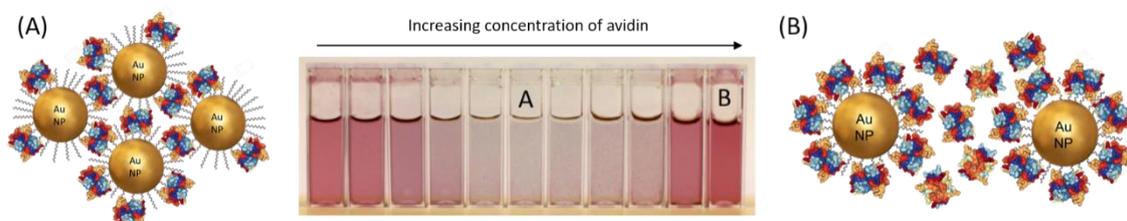


Figure 1. Avidin titration of biotinylated gold nanoparticles with increasing amounts of protein. Crosslinked (A) and dispersed (B) protein-nanoparticle conjugates are illustrated.

The approach has been extended to additional moieties and selective control of the formation of the protein corona has been achieved by exploiting differences in binding strength between the protein and the nanoparticle functional group.

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O9A: Formation of Imidazo[1,5-a]pyridine Derivatives Due to the Action of Fe²⁺ on Dynamic Libraries of Imines

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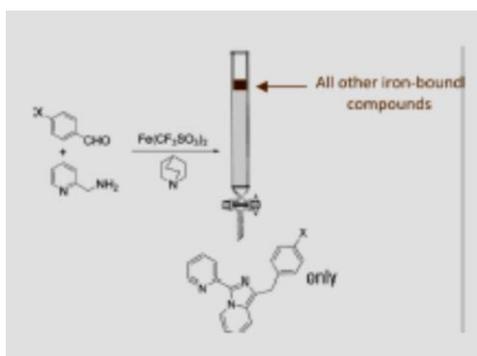
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A renewal of interest in imine chemistry is witnessed by the large number of papers published in recent years. The main reason for this is the reversible character of most of the reactions involving imines, which qualifies them as attractive reagents in the fields of supramolecular and dynamic combinatorial chemistry, organic synthesis and materials science [1].

With the aim of investigating the possibility to exploit simultaneous transamination/transamination (TATI) reactions [2] for synthetic applications, an imidazo[1,5-a]pyridine derivative was unexpectedly obtained through the action of Fe²⁺ on a dynamic library [3] of imines generated in situ via condensation of benzaldehyde and 2-picolylamine under TATI conditions. This reaction product was easily isolated as the only nitrogen-containing product eluted from the chromatographic column. A reaction mechanism has been proposed, in which combined kinetic and thermodynamic effects exerted by Fe²⁺ on the various steps of the complex reaction sequence are discussed. The Fe²⁺ nature of the added metal cation was found to be pivotal for the achievement of the imidazo[1,5-a]pyridine derivative as well as its amount in the reaction mixture. When the electronic effects were evaluated, gratifying yields were obtained only in the presence of moderately electron-releasing or moderately electron-withdrawing groups on the aldehyde reactant.



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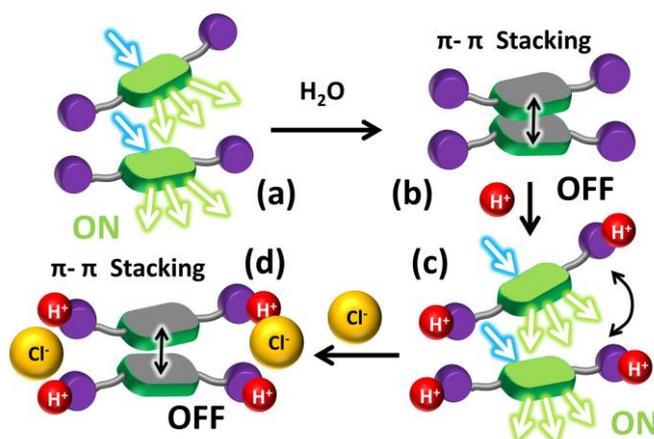
O9B: Self-assembling supramolecular structures as stimuli-responsive systems for sensing pH and anions in water

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Stimuli responsive materials are finding increasing importance in fields of high social and economic impact that include drug delivery, diagnostics, tissue engineering and ‘smart’ optical systems, as well as microelectronics, biosensors, microelectromechanical systems, coatings and textiles [1]. Although different design approaches have been proposed, the **self-assembly** of molecular or nanostructured building blocks is, without any doubt, one of the most versatile, straightforward and powerful strategy to achieve stimuli-responsive materials [2]. The response of these materials, either to environmental or external solicitation, can be, in fact, achieved by exploiting the same inter-components interactions that brings to their assembly.

Here we demonstrate that self-assembly of properly designed perylene bisimide amino derivate can be controlled by pH in water solution [3,4]. As shown in the figure the dye molecules (a) self-assemble in water because of p-p stacking interaction (b), causing fluorescence quenching. The system can be disaggregated and the fluorescence switched on by protonation exploiting the electrostatic repulsion between the positive cations (c).

Even more interestingly we observed that the protonated system can be re-assembled by increasing the concentration of anion that partially shields the positive charge of the ammonium substituents. Finally our molecules show a unique response to protonation and anion concentration in water. These features make them very promising tools for ion sensing in view of biological and environmental applications.



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O10A: An efficient Ru NPs stabilizer with a cyclodextrin based polyammonium polymer for the hydrogenation of unsaturated compounds in aqueous medium

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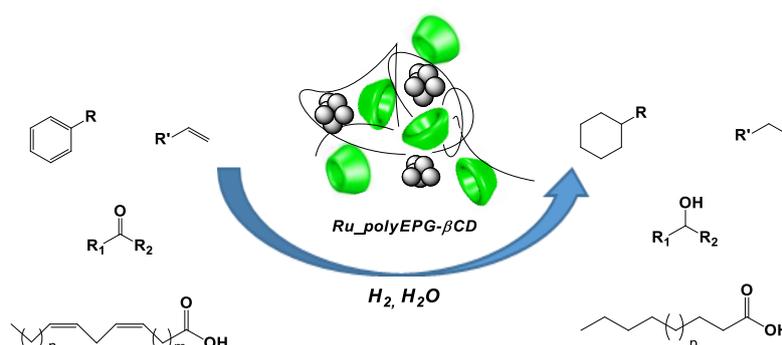
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In order to better respond to environmental standards, the development of metal nanoparticles (NPs) using green approaches has exponentially grown for the last decade [1]. Cyclodextrins (cyclic oligosaccharides that are composed of α -D-glucopyranose units connected by α -(1,4)-linkage) have appeared to be interesting candidates for the synthesis of size-controlled zerovalent NPs active for the hydrogenation of unsaturated substrates carried out in aqueous media [2].

We have recently reported that polyCTR- β -CD (polymer made of β -cyclodextrin crosslinked with citric acid) allows to stabilize water dispersed ruthenium nanoparticles for the hydrogenation of furan derivatives [3]. Nevertheless, it shows a sensitivity towards the acidity through a metal sedimentation for pH values below five.

To overcome this stability issue, we decided to use a β -CD polymer containing ammonium groups, named polyEPG- β -CD, *i.e.* β -CD crosslinked with both epichlorhydrin (EP) and glycidyltrimethyl ammonium chloride (GTMAC). Well dispersed ruthenium NPs with an average size of 3.8 nm have been obtained. Several experiments have highlighted the beneficial effect of the cyclodextrin *via* supramolecular interactions leading to a high robustness and great catalytic activities of the ruthenium NPs allowing their recyclability even after ten catalytic runs. Moreover their stability towards acidity allows to study the hydrogenation of unsaturated carboxylic acids such as fatty acids or aromatic acids.



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O10B: Ratiometric Optical Sensors for the Visible Detection of Cu(II) Ions in an Aqueous/Methanol Mixture

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Chemoreceptors are a flourishing region of supramolecular chemistry that has demonstrated potential as efficient, budget friendly alternatives for the detection of neutral molecules, metals and/or anions in various systems. As a continuation of our studies [1-2], presented in this work are two ratiometric optical sensors utilising the naphthalene and julolidine or salicylaldehyde molecular units. In a neutral buffered water/methanol mixture, these sensors show visible detection for Cu(II) ions by a colourless to yellow change in solution colour (Fig. 1). Ultraviolet – Visible spectrometer (UV-Vis) titration studies have shown that the limit of detection for both ligands with Cu(II) is in the nanomolar region. Significantly lower than the 2 ppm World Health Organization guidelines for safe drinking water. These sensors have potential applications for monitoring Cu(II) ions in environmental systems including waterways and soils. Furthermore, the detection may be measured quantitatively using Beer's law when combined with UV-Vis or fluorescent studies.

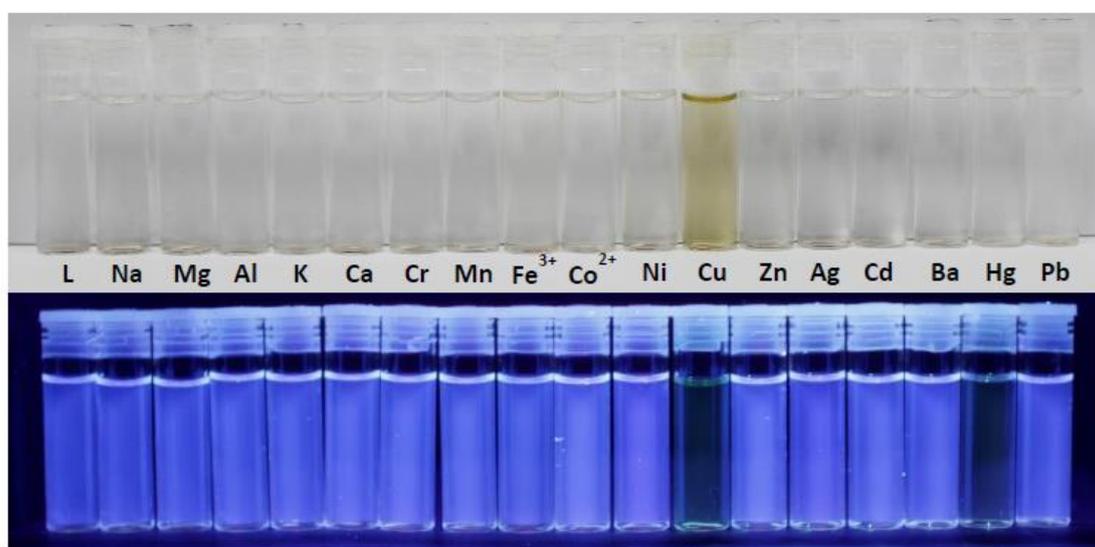


Figure 1. Chemoreceptor solutions in a 1:1 MeOH/water pH 7.2 mixture, with 5 equivalent units of metal salt solutions. Detection for Cu(II) is observed by a solution colour shift from colourless to yellow.

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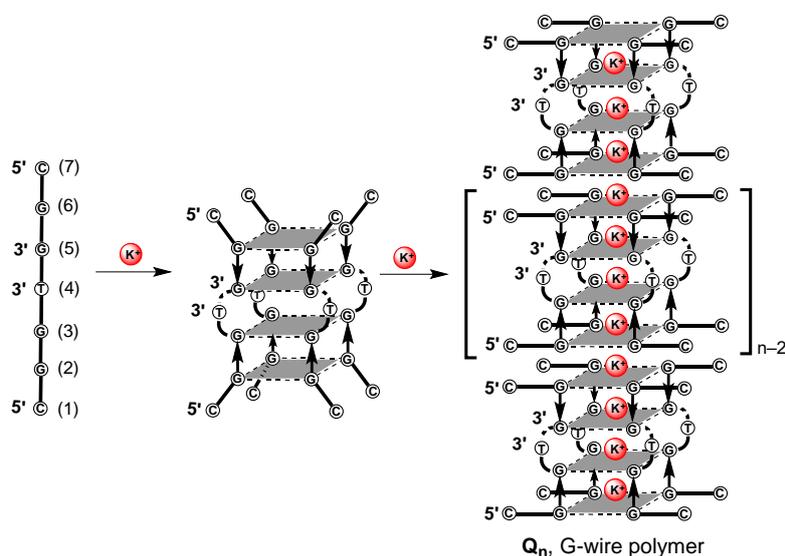
O11A: Design of tailored DNA G-wire nanostructures by self-assembling of short G-rich oligonucleotides incorporating a 3'-3' inversion of polarity site

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The obtainment of tailored DNA nanostructures of known size and composition in simple and affordable ways represents one of the most important avenues in both nanotechnology and medical sciences. In the past years, several DNA strands having suitable sequences proved to be useful building blocks for the obtainment of higher-order supramolecular DNA structures, such as DNA origami and nanotubes, to be used for the construction of DNA-based nanocircuits [1–3]. However, despite favorable theoretical models [4] and some positive preliminary results, it has been established that long strings of duplex DNA adsorbed on solid surfaces show no significant charge transport. Thus, the above-mentioned DNA nanostructures are not suitable for DNA nanocircuitry. Conversely, long-range charge transport properties have been demonstrated for long G-quadruplex DNA assemblies (known as G-wires) [5]. In this communication, I will present a new route towards the construction of short-to-long G-wire segments of known length *via* multimerization of G-quadruplex building blocks [6,7] obtained by short G-rich ODN sequences incorporating a 3'-3' inversion of polarity site [8].



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O11B: Supramolecular solvents based on Hexanol/Tetrahydrofuran for the forensic determination of amphetamine derivatives in a comprehensive pool of biological matrices

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Supramolecular solvents (SUPRASs) are nanostructured liquids originated in a spontaneous process of self-assembly and coacervation from a ternary solution of water, a water-miscible organic solvent and an amphiphile. SUPRASs constituents are coordinated in an ordered system that confers them unique properties, different from those shown by organic solvents and ionic liquids. They are very good extractants for the analysis of complex samples, not only because they offer different interactions in terms of energy and polarity, but also because they can act as volatile restricted-access materials (RAM-VOL-SUPRASs) eliminating, in that way, common interferents such as proteins and/or phospholipids. In the case of the hexanol/THF/water SUPRAS, its nanostructure (Fig 1) is made by inverted hexanol micelles, where the hydroxyl groups arrange around an aqueous cavity while alkyl chains are dissolved in tetrahydrofuran (THF).

Amphetamine and Amphetamine-like drugs such as Ecstasy (MDMA), belong to the big family of synthetic illicit drugs of abuse. Their popularity among consumers is due to their biological effects on SNC that increase energy, endurance and sociability. On the other hand, Amphetamine-like substances decrease the physical and mental capabilities to drive vehicles with predictable endings which has motivated several laws around the world to test and punish drivers under the influence.

In this work, a supramolecular solvent has been used to develop a single and quick method capable of detecting amphetamines and amphetamine-like drugs in oral fluid, urine, serum, sweat, breast milk, hair and nails by HPLC-MS/MS. Limits of detection were in the low ng mL⁻¹ range, well below those proposed by international Governments and Agencies as cut-offs. The method proposed can be used as a confirmatory tool for counter-analysis and allows to easily take advantage of the different detection windows established for each matrix, ranging from hours (e.g. saliva) to months (e.g. nails).

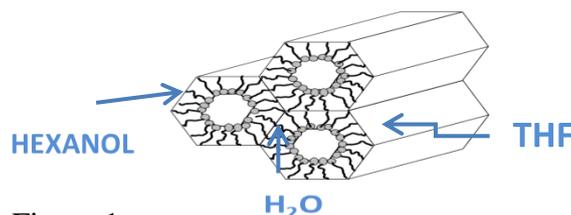


Figure 1

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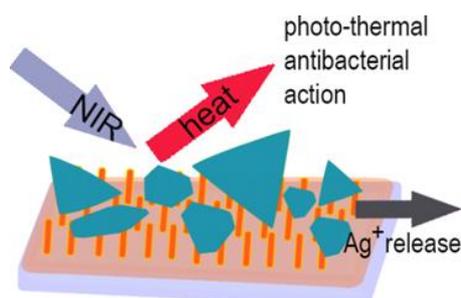
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O12A: Inorganic nanochemistry for antibacterial applications: the heat is on for silver and gold

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Since the ancient times, the charm of Silver and Gold never decreased. In the last two decades, anyway, the rise of nanotechnologies has boosted a new, enormous interest in these shiny elements: Au and Ag nano-objects of different dimensions and shapes are showing to work for a plethora of applications, particularly in the biomedical field. One of most interesting is their antibacterial use, which could respond to the problems coming from pan-drugs-resistant bacteria and from bacterial and biofilm-associated infections involving medical, surgical, and prosthetic surfaces.

Noble metal anisotropic nano-objects can be prepared tuning their size, shape and Localized Surface Plasmon Resonance (LSPR) features, in order to obtain an intense absorption in the Near-Infrared (NIR) region. Subsequently, bulk glass samples can be easily decorated with these nano-objects, yielding model surfaces which are able to exploit two different mechanisms to gain an intense antibacterial activity: (i) the well-known bactericidal action caused by Ag⁺ release from Ag nanoparticles [1,2]; (ii) the hyperthermia caused by photo-thermal effects observed under NIR Laser irradiation of Ag and Au nano-objects[3]. This behaviour allows to imagine promising in vivo applications, if we are able to impart cooperation to the two mechanisms, thus ensuring a long-term antibacterial protection (given by Ag⁺ release) which can be reinforced on need by a fast photo-thermal action, switchable by a Laser treatment [4,5] in the NIR region, the so called “therapeutic window”, in which biological tissues are almost transparent. Starting from our early results on antibacterial action of spherical silver nanoparticles layers grafted on glass, this contribution will show our latest results obtained with systems which exploit anisotropic objects, silver nanoplates and gold nanostars. In this way, one can obtain the functionalization of bulk surfaces with safe and efficient antibacterial layers, a strategy which could be useful for the coating of biomedical devices.



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O12B: Kinetic model heterogeneous reaction self-assembly on nanocomposit sorbent and them peculiarity

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All-round deep physics-chemistry understanding catalytic process and them kinetic conformity with law appear importance problem [1] of catalysis. Catalysis belong to region chemistry kinetic, therefore reliable kinetic model, describe speed reaction on nanocomposite sorbent, necessary for modeling complicated reaction.

Distinctive peculiarity nanocomposite is high sorption activity them surface and chemistry activity, which manifestation in geometry active center and its energy state (electronic factor). Such material provide easy active center for substrat. Catalytic center nanocomposit apper active component catalisator on its surface, also time, dislocation, arise by technology drawing film. Energetic unequal active [2] center on surface further formation less active or notactive complex. This bring to inhibition catalysts.

Therefore new kinetic model, tace into account idea nothomogeneous surface, manycenter adsorption, reconstruction surface by chemisorption, interaction between adsorption particle have topical meaning. Examine model heterogeneous-catalytic reaction and its kinetic equation, comfortable for numerical modeling flow on nothomogeneous surface nanosorbent reaction self-

assembly. By formation molecular complex in micelle use equation: $k_{\text{экснер.}} = \frac{k_e + k_{H^+}}{k_s} = k_{\text{ass.}} \cdot k_{H^+}$ (1).

By formation dimer in process self-assembly by gas solvation: $k_{\text{ass.}} \cdot k_e' = k_{\text{exp.}} = \frac{k_e + k_{H^+}}{k_s}$ (2). k_s -

constant bind final product micelle or solvent accordingly; k_e ; k_{H^+} - constant transfer electron and proton accordingly; k_{ass} - constant association. Experimental establishment, what k_{exp} by gas solvation on order less reaction in micelle. Effect inhibition reach not much meaning k_{ass} in solvent. Probably [3], what solvent electron appear ion clyster slime $X_n^-(\text{organic.molecul})_2$ (n- numbersolvent electron in clyster, X- number molecule solvent in clyster). Reaction analyse equation Brensteda-Poljani. Coefficient α from equation I.N. Brensted $\alpha = \frac{\Delta G}{8G_o^\ddagger}$ (3) is 2,5 ÷ 3,4. Such

anomalies be formed then, when happen important charge in structure solvation sphere.

Constant prohibition electron singlet-triplet conversion for calculation exchange interaction compose $\sim 10^{30} \text{ c}^{-1}$; constant spin-catalyst at barrier reaction $k \sim 10^{15} \div 10^{22} \text{ c}^{-1}$.

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O13A: Supported nanoparticles for catalysis and biomedical applications

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In recent years considerable attention has been drawn to the possibility of deposition of metal nanoparticles onto conducting or not conducting substrates due to its great importance in the fabrication of materials suitable for a wide range of applications. Within this frame, we have prepared a large variety of stable supported metal nanoparticles ($M_{NPs} = Au, Ag, Cu$) by using a great variety of supports such as silica, alumina, titania (hereafter generally termed as Oxides Supports, OS) [1], Indium Tin Oxide (ITO) [2] and hydroxyapatite (HA) [3] to be employed as heterogeneous catalytic systems and biomaterials.

In this contribution we will present an overview of our more recent work with OS and HA supports. With regards to the OS, we started using commercial polyethyleneimine-functionalized silica beads [1a,b,c] and we went on preparing nanoparticles anchored to OS functionalized with alkynyl carbamate moieties [1d,e] that, through its derivatization by radical thiol-yne chemistry, was subsequently used to fabricate a novel amino-sulfide branched support [1f]. In the HA case we have reported an easy, green and low cost method to support Ag_{NPs} onto functionalized HA crystals obtaining a material that combines the absence of cytotoxicity with a significant long-standing antibacterial activity towards both *Staphylococcus aureus* and *Escherichia coli* [3a]. We also functionalized HA with (9*R*)-9-hydroxystearate (HSA) which has been shown to play an important role as natural negative regulator of tumor cell proliferation. The synthesized new materials are able to dramatically affect proliferation, viability, and activity of SaOS2 osteosarcoma cell line. In particular, all of the samples displayed significantly reduced viability with respect to pure HA and a dose dependent effect on cytotoxicity parameters, suggesting that these materials could be usefully applied at specific bone sites for the local treatment of bone metastases [3b].

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O13B: Doped graphene-metal interfaces as ORR and OER electrocatalysts for fuel cells applications

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Hybrid organic-inorganic systems are widely applied in different technological devices thanks to the peculiar combination of molecular functions (*e.g.*, molecular recognition) and solid-state inorganic features (*e.g.*, fast charge and heat transport) [1,2]. For instance, graphene nanostructures (GNS) can be easily combined with inorganic substrates for designing new materials for energy conversion devices [3]. In particular, there is an active research community addressing the optimization of effective and cheap alternatives to traditional expensive platinum-based cathodes for oxygen reduction reaction (ORR) in intermediate temperature fuel cells. Recent experiments support the idea that dopants or interfacing with a metallic support can enhance GNS catalytic activity [4,5].

In this context, we have investigated the energy conversion capabilities of a hybrid material based on GNS and doped-GNS on a metallic substrate with first-principles calculations. Starting from a *in-house* modified DFT-D approach (DFT-DM) [6] for treatment of metal-GNS dispersion forces, we characterized how the structural, electronic and catalytic properties of GNS are tuned by dopants and by direct interaction with a metal surface. In this contribution, we will first discuss minimum-energy geometries, binding energies and electronic structure features of pristine and doped graphene on the hexagonal Ag(111) surface slab. Both p- and n- doping effects have been investigated using boron and nitrogen as dopant atoms, respectively. Then, we address the ORR catalysis at the surface of the hybrid electrode in the framework of the theoretical hydrogen electrode (TSHE) [7]. We focus on the reaction intermediates and the minimum energy pathways for the ORR in order to understand the effects of the metal substrate on the physical and chemical properties of GNS. Our final objective is to design a new and effective GNS-silver hybrid cathode for low temperature fuel cells by identifying the dopants and/or defects that can boost ORR catalysis without weakening the excellent electronic features of graphene.

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O14A: A novel secondary pore-forming agent: The catalytic performance of vanadium in zeolite Y post treatment

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Over the past decades, vanadium and zeolite Y are considered as a pair of irreconcilable contradictions in the oil refinery industry, especially the FCC process [1]. This is because the vanadium could cause the structure collapse of the zeolite Y in the FCC process, which lead to the deactivation of the catalyst. Specifically, a part of vanadium is present in the form of vanadic acid under the hydrothermal conditions, which easily combine with the framework aluminum of zeolite Y to form aluminum vanadate [2]. The aluminum vanadate can be decomposed into vanadium pentoxide and alumina under high temperature. Then, the vanadic acid which is formed by vanadium pentoxide combining with steam continues to attack the framework aluminum of zeolite Y. This cycle will not stop, until all the framework aluminum is removed. We wonder if we can take the advantage of the unique performance of vanadium to induce secondary pore formation on zeolite Y through the control of the experimental conditions.

In this work, the NH_4Y_v was prepared by the incipient wetness impregnation method using ammonium vanadate aqueous solution and NH_4Y which prepared from NaY by ammonium exchanges, followed by subsequent hydrothermal treatment. The proper conditions were studied by changing the ammonium vanadate content in the precursors, the length and the temperature of the hydrothermal conditions. Under proper conditions, the secondary mesopore volume of the treated USY_v zeolite increased by 72% from $0.085 \text{ cm}^3/\text{g}$ to $0.146 \text{ cm}^3/\text{g}$.

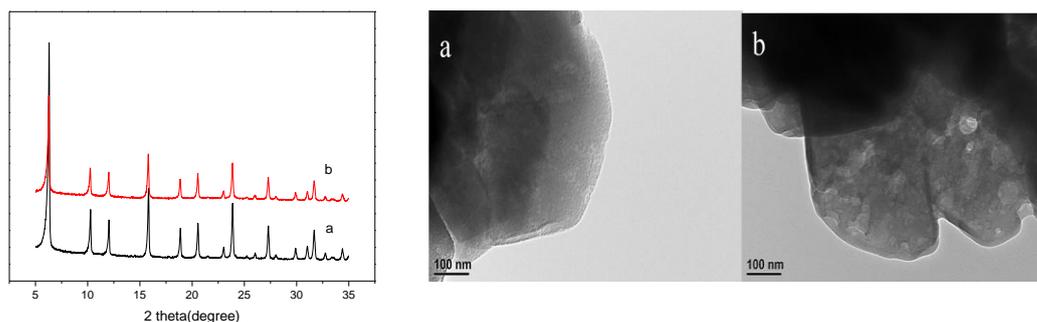


Figure 1. XRD patterns and TEM images of the samples: (a) USY; (b) USY_v

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O14B: Design of coordination framework from O₂N₂-diaza-crown macrocyclic ligand substituted with pyridine side arms

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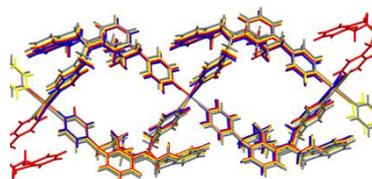
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Azacrown macrocyclic ligands are well-known compounds for their important roles in the coordination chemistry [1]. Meanwhile, incorporating pyridine side arms to the macrocycles has received great attention particularly in the preparation of coordination networks [2]. As a significant network, coordination polymers (CPs) encompass one-, two or three dimensional networks made of metal ions/clusters interlocked by organic linkers. CPs are among the most remarkable crystalline compounds in material science and chemistry for their potential and practical applications in catalysis, magnetism and molecular recognition [3].

Numerous organic linkers have been found applicable in coordination networks but those linkers based on macrocycles such as azacrown ethers, calix[4]-arenes, cucurbit[n]urils, and porphyrins are interesting tectons because of their appropriate donor-atoms preorganization and conformational restrictions [4].

Due to the ability of pyridine arms in coordination of metal ions, they widely used in preparation of CPs [2,4]. In 2005, the first CPs of azacrown ethers with pyridine arms was reported [5] and later their potential capability to adjust their bridging length when integrated into CPs, was studied [6]. Basically, the position of the N donor atom on the pyridine arms (N_{py}) is essential in determining final topology of CPs as well as the formation of CPs versus discrete complex [4]. This fact persuade us to study on the effect of the position of the N atom on the pyridyl moiety of a O₂N₂-diaza-crown macrocyclic ligand reported by Lindoy et al. 1992 [7] in terms of probable formation of CP in the presence of a series of metal ions.



Scheme 1. The isostructural CPs' of **L** with M(II): M=Ni(red), Pb(grey), Mn(yellow), (Cu Blue)

The single crystal study on the ortho substituted N-py side arm of **L** has already indicated on the formation of a discrete complex of the substituted **L** with metal-ion⁸. As in inferred from Scheme 1, employing the para substituted N-py side arms on **L** affords several isostructural CPs **L** even in the presence of different metal ions in DMSO and DMF.

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O15A: Catalytic Hydrogenation of Lignin Model Compounds Using TiN Supported Copper Nanoparticles

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Lignin is the second major constituent of Lignocellulosic biomass which mainly consists of aromatic compounds that are a potential source for production of fine chemicals. Catalytic conversion of lignin is a possible option for lignin valorization into aromatics and fuels. Despite the potential, conversion of lignin to chemicals, specifically to aliphatic and aromatic compounds, has always been a challenging mission due to propensity of macromolecular composition of lignin to make a condensable, intractable solid residue in biorefinery processes. The complex and variable structure of lignin has encouraged utilization of several simpler, low molecular weight lignin model compounds during the depolymerisation reaction of lignin. Utilization of lignin model compounds has several advantages; firstly, their intermolecular linkages resemble those that can be found in native lignin polymers, hence their reaction provides a simple but realistic insight into the depolymerisation of lignin polymers. Secondly, lignin model compounds are similar to different products of the lignin depolymerisation process, hence can be effectively used for the development of a strategy to convert lignin depolymerisation products to high value added chemicals such as, phenols and aromatics. Catalytic valorization of lignin often needs a strong catalyst to resist harsh environment of lignin cleavage process such as, strong resistance in corrosive media of reaction with high temperature and pressure. Utilization of expensive noble metals (e.g. platinum, palladium, ruthenium) proved to be an effective catalyst for lignin cracking, however their high price make them less competitive for this process. Recent studies on hybrids of early transition metals have proven that they can be a potential replacement for noble catalysts; according to low cost, high availability, and high resistance of these compounds. Titanium nitride nanoparticles can act as highly active supported catalyst when they are promoted with active metal such as nickel. In recent studies TiN supported nanoparticles have been used as an active catalyst for hydrogenolysis of lignin model compounds and real lignin samples, which shown high activity and selectivity. In this work the depolymerisation of lignin model compound is investigated using hydrogenation cleavage, which carried out using TiN supported copper catalyst (TiN-Cu) as a new hydrogenation catalyst. This test revealed high activity of TiN nanoparticles loaded with 30 Wt. % copper in hydrogenolysis reaction comparable to industrial noble catalysts. Monitoring the conversion of lignin model compounds revealed that these compounds have high tendency to undergo the cleavage reaction in β -O position (Figure 1).

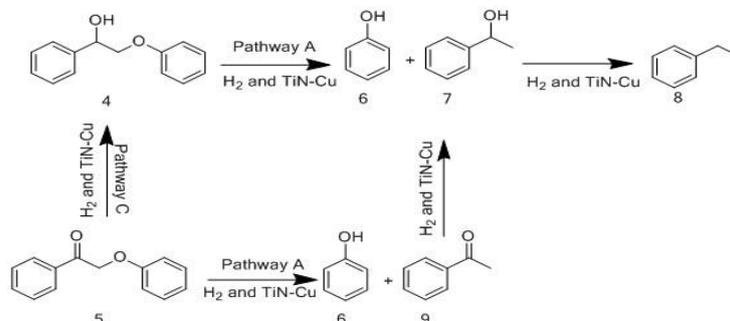


Figure 1: The reaction mechanism for cleavage of 4 and 5 with TiN-Cu Nanoparticles.

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O15B: Acidity tuning by tin isomorphous substitution of aluminium in AlPO₄-5 and its application in the hydrodesulfurization reaction

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MeAlPO₄-5 materials prepared by using metal cations to substitute framework Al³⁺ and P⁵⁺ ions of AlPO₄-5 zeolite have attracted great interest in acid, redox properties, as well as catalytic activity [1,2]. Tin is widely used in many catalytic reactions, its catalytic ability, together with its similarities to Si (both belong to the same group in periodic table), make tin to apply to many reactions. SnAlPO₄-5 molecular sieves have been hydrothermally synthesized using triethylamine as structure directing agent and two hydrated stannous chloride as tin source. The as-synthesized and calcined samples have been investigated with the different characterization techniques. All samples with the similar specific surface area, pore structure and highly ordered hexagonal crystals have AFI topology with a high crystallinity, and no impure crystalline phase is detected. The presence of divalent tin incorporated into the framework of zeolite by isomorphous substitution Al³⁺. According to the NH₃-TPD, FT-IR spectroscopy of pyridine and MAS NMR, the existence of P(3Al, Sn) environments make the materials have stronger acidity (both Bronsted acid and Lewis acid) than pure AlPO₄-5 zeolite. The structural Bronsted acid sites generated by the incorporation of Sn²⁺ for Al³⁺[3]. The desorption pattern of SnAlPO₄-5 samples consists of two distinct peaks concentrated at 160°C and 305°C. In addition to the peak observed for SnAlPO₄-5 samples shows a strong shoulder around 305°C. Al₂O₃ and SnAlPO₄-based NiW catalysts were tested hydrodesulfurization (HDS) of DBT. Supporting the characterization results, the SnAlPO₄-based catalysts have efficient activity in such reactions which require acid centers.

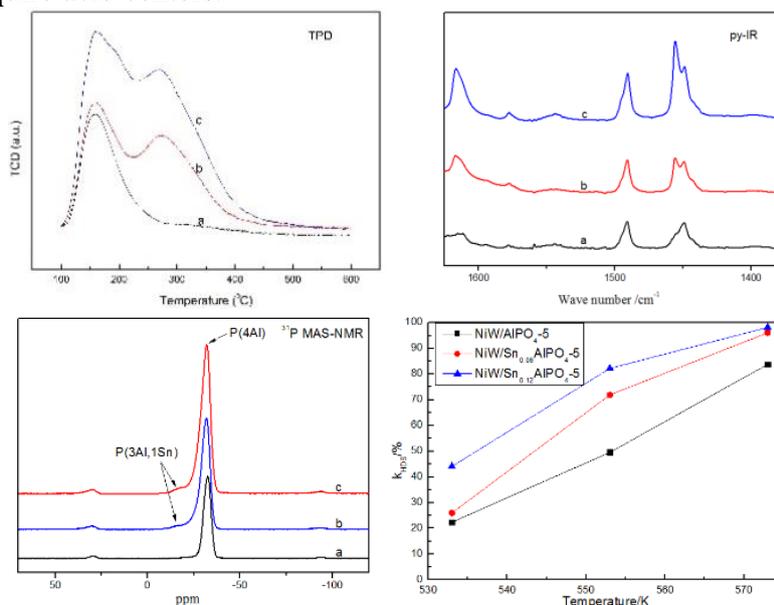


Figure 1. Characterization of the samples: (a) AlPO₄-5, (b) Sn_{0.06}AlPO₄-5 and (c) Sn_{0.12}AlPO₄-5.

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POSTER ABSTRACTS

P1: Single-step supramolecular solvent-based sample treatment for the control of Ochratoxin A in spices subjected to EU regulation

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Spices contaminated by Ochratoxin A (OTA) contribute around 8% to the dietary intake of OTA in European population. Regulatory restrictions (tolerable limits: 15 µg/kg) demand for fast and reliable monitoring of OTA in spices for surveillance purposes [1]. Spices are classified within the group difficult or unique commodities owing to their high content in carotenoids, essential oils and/or dyes, as well as carbohydrates and/or fats, which cause poor recoveries and interferences in OTA determination. Immunoaffinity columns (IACs) have been extensively used for sample cleanup but their high cost, limited storage time, cross-reactivity with Ochratoxin C and the need for filtration of around 100-200 mL of the extracts and evaporation to dryness of the eluates makes the process quite slow and expensive for surveillance programs.

In this paper, a single-step supramolecular solvent (SUPRAS)-based sample treatment has been developed for the efficient isolation of OTA in spices subjected to regulation by the EU (i.e. chilies, chili powder, cayenne, paprika, white and black pepper, nutmeg, ginger and turmeric). Recoveries for OTA (at the µg/kg level), in the presence of high concentrations of carotenoids, essential oils and/or dyes (at the g/kg level), were in the range 87-104% and extracts were directly analyzed by LC-FD. Such high extraction efficiency and selectivity for OTA, independently of the matrix composition, was the result of the mixed-mode mechanism and high number of binding sites offered by the SUPRAS as well as its capability to act as a restricted access solvent based on chemical and physical mechanisms. The method involved the stirring of the sample (0.2 g of spice) with 0.4 mL of SUPRAS for 10 min, subsequent centrifugation and direct analysis of the crude extract by liquid chromatography/fluorescence detection using solvent calibration. From a practical point of view, the most valuable asset of the method here reported is the combination of extraction and sample cleanup in a single step, that permitting reliable quantification of OTA without the need for extensive IAC based cleanup, which results in considerable savings on time and costs. The method meet the requirements to be used in enforcement and surveillance programs related to the monitoring of OTA in spices.

Acknowledgments

Authors gratefully acknowledge financial support from Spanish MINECO (Project CTQ2014-53539-R) and FEDER.

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P2: Supramolecular Tuning of Photochromism in Mechanically Interlocked Molecules

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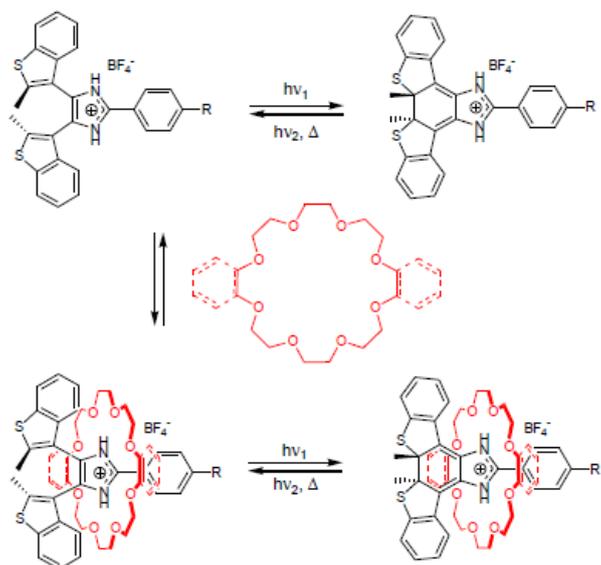
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Pseudorotaxanes have been widely exploited in the field of Mechanically Interlocked Molecules (MIMs) [1], since, with a proper design, they can be applied in both solution and solid materials as molecular switches or machines [2].

Here we report photochromic pseudorotaxanes based on the imidazolium-crown ether recognition pattern [3].

The imidazolium moiety in the axles has been functionalized with two 2-methylbenzothiophene groups, as shown in the figure, and exhibits typical photochromic properties of diarylethenes. [4] In suitable non-protic solvent, the photochromism of these axle can be tuned by means of association with either [24]crown-8 or dibenzo-[24]crown-8. In fact, when the axle is threaded into the macrocycle, the photoinduced cyclization and the thermal cycloreversion reactions are strongly affected, in terms of mechanisms, rates and quantum yields.



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P3: New nanohybrid for dehalogenation and contemporaneous removal of halocarbon from water

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Metal nanoparticles with their small particles size, large specific surface area [1], excellent adsorption and high reduction reactivity [2] are promising materials for remediation of contamination with chlorinated organic pollutants.

In the case of the dechlorination, a reduction reaction takes place, involving the gain of electrons coupled with the oxidation of the nanoparticles. Therefore, metals with a more positive oxidation potential have a higher ability for degrading chlorinated contaminants in water. Among zero valent metals (ZVMs), nickel has a relative greater negative reduction potential. On the other hand, carbon materials are widely used supports for dispersing catalytic metal nanoparticles, due to their high surface area and effective porous structure for transferring reactants and products. Molecular adsorption on graphene/graphene-based composites and their applications in water purification have gained momentum recently. Nanocomposites metal nanoparticles/graphene, in particular nanoparticles supported by graphene, are very effective reducing agent for dehalogenation and can contemporaneously catalytically reduce various halogenated organics into non- or low- toxic compounds [3], followed by subsequent adsorption of the degraded products by the graphene surface. Here we report the chemical reactivity of Ni nanoparticles supported on graphene, prepared in a one-step synthesis, by very promising bottom-up chemical strategy [4,5] in the presence of graphene nanosheets obtained by physical exfoliation of graphite [6], in the degradation of halogenated compounds in water. The sample obtained was characterized by Raman Spectroscopy, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy – Energy dispersive X-ray spectroscopy (TEM-EDS), thermogravimetric analysis coupled with mass spectrometry (TG-DTG-MS), X-ray diffraction (XRD), high performance liquid chromatography (HPLC). This paper demonstrate the dehalogenation of 2,4 chlorophenol, and at pH <8 a two step degradation mechanism of more chlorinated compounds (e.g. Chlordane), by Ni nanoparticles supported on graphene followed by the subsequent adsorption of the degraded products by the graphene surface.

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P4: Immobilization of β -glucosidase onto mesoporous wrinkled silica nanoparticles for cellobiose hydrolysis

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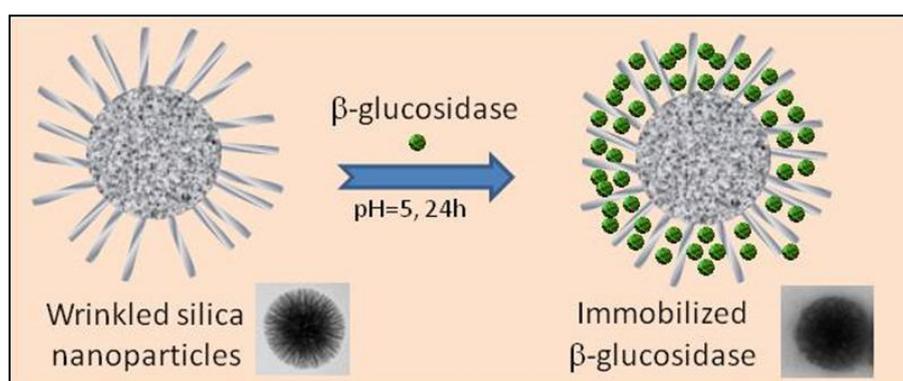
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Wrinkled silica nanoparticles (WSNs) with central-radial pore structure were synthesized using a modified procedure compared to the one in [1] and utilized as insoluble support for the immobilization of the enzyme β -glucosidase (BG) by adsorption. BG is biotechnologically relevant because it is involved in the conversion of lignocellulosic biomass into fermentable sugars [2]. The enzymatic hydrolysis of cellulose involves a set of enzymes, referred to as cellulase, which work sequentially releasing cellobiose. BG acts hydrolyzing cellobiose to glucose.

The WSNs synthesized showed an unprecedented hierarchical trimodal micro/mesoporous pore size distribution. The resulting nanocomposite BG/WSNs contained about 70 mg/g of BG, that was in the interior of the pores. Conformational analysis performed by fitting the amide I band of the FT-IR spectrum pointed out to a preserved enzyme native conformation except for a slight aggregation. The ability of BG in promoting the hydrolysis reaction was assessed by evaluating the conversion yield of cellobiose to glucose, i.e. using its natural substrate for cellulose degradation. The results showed that the immobilized BG promoted the complete hydrolysis of cellobiose to glucose, so as the free enzyme. The biocatalyst was reused for several times, showing total conversion at least for three subsequent reuses.

The results of this study indicate that wrinkled silica nanoparticles are a promising candidate for β -glucosidase immobilization, to supplement enzymatic cocktails used in the degradation of cellulose into fermentable sugars, i.e. for bioethanol production.



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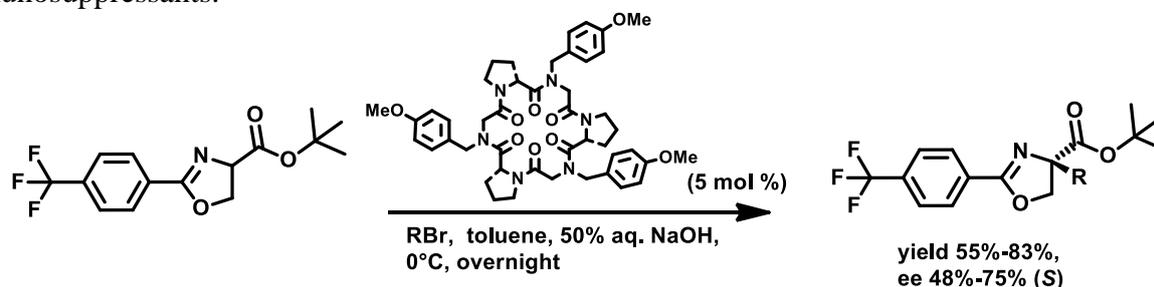
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P5: Enantioselective alkylation of 2-aryl-2-oxazoline-4-carboxylic acid esters catalyzed by cyclopeptoids

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The enantioselective synthesis of α -substituted and α, α -disubstituted amino acids is a process of great interest in organic synthesis, as the products themselves are extremely important for the research and synthesis of biologically active compounds. In the last decades the enantioselective alkylation of protected amino acid substrates by chiral phase-transfer catalysis (PTC) has been greatly investigated. Among the phase-transfer catalysts (PTCs), quaternary ammonium salts, derived from cinchona alkaloids, and binaftyl and biaryl quaternary ammonium salts [1], exhibit good enantiomeric excesses. The difficulties associated with the synthesis of the above-mentioned classical catalysts have led to investigate the development of catalytic systems with comparable performances, but easier to synthesize. The validity of cyclopeptoids, cyclic oligomers of *N*-alkylated glycine, as an alternative to classical PTCs has been widely demonstrated [2], mainly due to their excellent properties as hosts and metal cations carriers [3].

In this poster communication will be described the synthesis and the application of cyclopeptoids containing L-Pro residues and variously substituted benzyl side chains in the enantioselective alkylation of the 2-aryl-2-oxazoline-4-carboxylate esters to obtain α -substituted serine derivatives (scheme 1), which are fundamental for the synthesis of natural products, peptidomimetics and immunosuppressants.



Scheme 1. Enantioselective alkylation of the 2-[4-(Trifluoromethyl)phenyl]-2-oxazoline-4-carboxylic Acid *tert*-Butyl Ester, catalyzed by chiral cyclopeptoids

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P6: Calix[6]arene threading with weakly interacting tertiary ammonium axles: generation of chiral pseudorotaxane architectures

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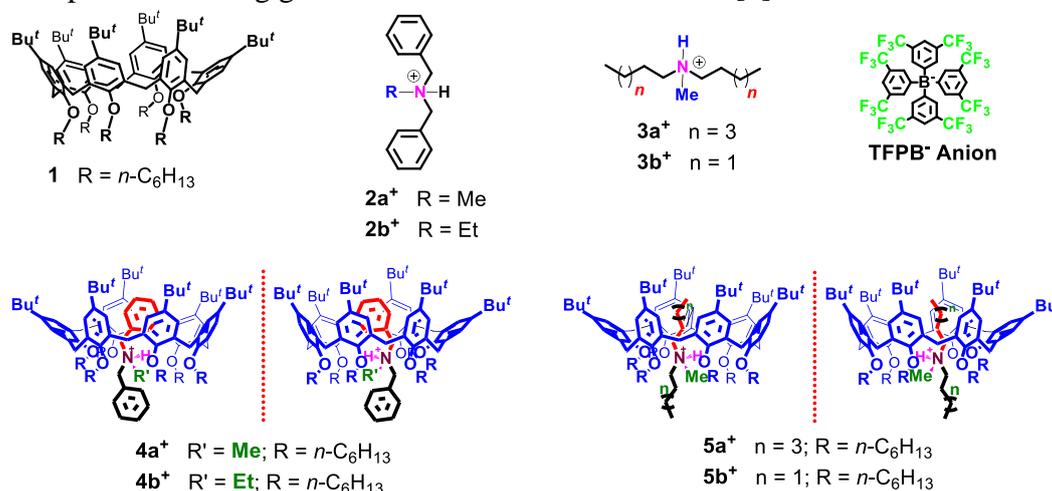
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Supramolecular interlocked architectures such as rotaxanes and catenanes [1] are gaining more and more attention in fields as nanotechnology [2] and molecular machinery [3]. Both catenanes and rotaxanes could derive from a common pseudorotaxane precursor, obtained by threading a linear axle through the cavity of a macrocyclic wheel thanks to non-covalent interactions. The most studied protocol uses threading of secondary ammonium derivatives through the cavity of crown-ether macrocycles, mediated by H-bond and ion-dipole interactions. Importance of ammonium/crown-ether rotaxanes relies in the fact that they act as molecular shuttles by reversibly deprotonating/reprotonating the ammonium site. In order to make the switch clearer and cleaner it's preferable to use weakly interacting tertiary ammonium sites [4], but here a problem arises because tertiary ammonium/crown-ether pseudorotaxanes are extremely labile, so direct threading occurs with low yields [5].

It's known that "super-weak" tetrakis[3,5 bis(trifluoromethyl)phenyl]borate anion (TFPB) allows threading of secondary ammonium axles through the cavity of scarcely preorganized calix[6]arene macrocycles [6]. Inspired by these considerations we decided to investigate the direct threading properties of calix[6]arene macrocycle **1** with tertiary ammonium salts **2TFPB** and **3TFPB**. The study surprisingly pointed out the formation of chiral pseudorotaxanes **4⁺** and **5⁺** as a consequence of the first example of threading generated chiral ammonium center [7].



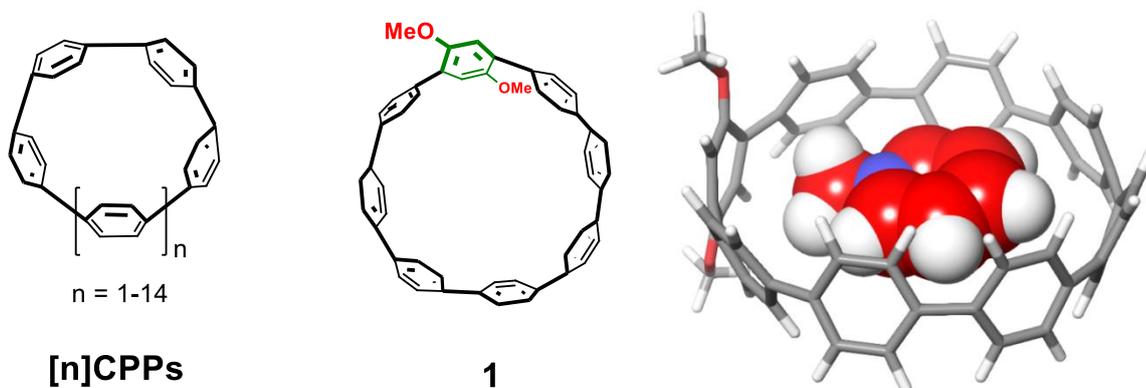
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P7: Recognition of Pyridinium Guests by [8]Cycloparaphenylene Host

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CycloParaPhenylenes ([n]CPPs) are fully conjugated macrocycles constituted by n para-linked benzene units (Figure), which exhibit size-dependent optical and electronic proprieties [1,2]. [n]CPPs exhibit the narrowing of the HOMO-LUMO gap as the number of aromatic units decreases, consequently, the emission spectra of CPP derivatives are blue-shifted and quantum efficiency increases as the macrocycle become larger [2]. This optoelectronic properties make the [n]CPPs excellent candidates for applications in nanoelectronics and photonics. [n]Cycloparaphenylene (carbon nanorings) are considered as potential templates for the bottom-up synthesis of uniform single wall carbon nanotubes [3]. Differently by other macrocycles, such as calixarenes, pillararenes and resorcinarenes, the recognition properties of [n]CPP macrocycles have been scarcely investigated and the few examples in the literature mainly regarded the complexation of fullerenes [4,5]. In the present work, we have designed and synthesized the [8]CPP derivative **1** bearing a 1,4-dimethoxybenzene electron-rich moiety which is considered as useful supramolecular synthon able to interact with cationic electron-poor pyridinium guests. We wish to describe here the synthesis of the 1,4-dimethoxybenzene-incorporating [8]CPP **1** derivative (Figure) the its optical and electronic properties. Finally, for the first time we report here on the molecular recognition abilities of a [8]CPP derivative towards pyridinium guests (Figure) [6].



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P8: Regeneration Performances of a Ceria-Coated Diesel Particulate Filter

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Catalytic regeneration of diesel particulate filters (DPFs) has been proposed as an alternative or complementary approach to bypass or mitigate the drawbacks associated with thermal regeneration. In principle, the catalyst may be used to achieve soot oxidation at lower temperatures (250-550°C) than those required for thermal regeneration (> 600°C), and/or to shorten the regeneration time period, thus allowing for energy saving. However, there is still no general consensus regarding the ability of catalyst-coated DPFs (CDPFs) to oxidize soot at low temperatures and under conditions relevant to practical applications [1]. Indeed, the regeneration performances of a CDPF are strictly dependent on the efficiency of the contact between the soot particles and the active sites of the catalyst particles.

The improvement of the soot/catalyst contact has motivated a number of experimental studies (see, e.g., [2-4]). These works are mainly focused on ceria as the catalyst for soot oxidation owing to its redox properties, oxygen storage capacity, and low cost as compared to noble metals. Novel ceria-based materials (in the form of nano-fibers, nano-cubes, nano-rods, self-assembled stars, etc.) have been proposed with the aim of enhancing the contact between the two solid phases. Such materials have been successfully tested under conditions of soot/catalyst/gas contact that, even in the case of the “loose” contact, which represents the most realistic testing conditions [5], are quite far from those actually established during filter regeneration.

In the present work, the regeneration performances of diesel particulate filters wash-coated with highly dispersed nano-metric ceria particles were assessed. The aim was at gaining insight into how the filter regeneration performances are dependent on the soot/catalyst/gas contact. To this end, the selectivity to CO₂, the onset temperature for catalytic oxidation, and the share of catalytic oxidation (with the respect to the overall amount of combusted soot) were evaluated from the results of regeneration tests carried out on filters having different catalyst/soot ratios. Physico-chemical characterization of the filter samples was also performed.

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P9: Polyfunctional ligands for supramolecular assemblies of Mn(II) catalysts in aqueous systems

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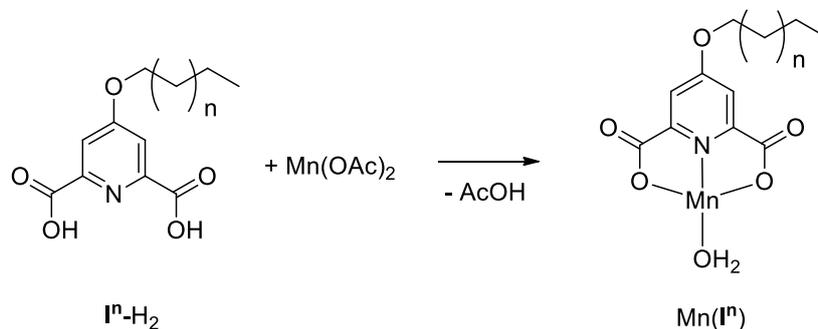
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It is well known the interest of the chemical industry towards oxidation reactions [1]. In this context, complexes of Mn(II) occupy a privileged role, for their well-known ability to activate hydrogen peroxide through group transfer mechanisms [1].

The ideal catalysts meets certain parameters: stability, low environmental impact, efficiency at low temperatures and cost-effectiveness. Furthermore, it should present compatibility with aqueous systems, and also the ability to interface with apolar environments, given the organic nature of typical substrates. With regard to this last consideration, it is well known that the insertion of catalysts in micellar systems has a beneficial effect on their performance [2]. On this basis, and in order to satisfy the just mentioned constraints, we have started a systematic study on the synthesis and characterization of Mn(II) complexes containing ligands derived from chelidamic acid [3] with tailored ponytails (I^n-H_2):



The complexes will differ in the length of the chain present on the pyridine ring, introduced in order to verify its effect on aggregation in aqueous systems and disclose any beneficial result on their ability to activate the hydrogen peroxide.

The poster will present the synthesis of the complexes, and preliminary studies on their chemophysical characterization and reactivity.

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P10: Halloysite nanotubes as innovative carriers for (bio)organic molecules

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The recent growth in nanoscale technology has led to advanced investigations of various types of nanocarriers. Among those, Halloysite nanotubes (HNTs) arrive as the best inorganic material for potential applications in a wide range of areas, including anticancer therapy, sustained delivery for certain agents, as a template or nanoreactor for biocatalyst [1].

HNTs are inexpensive, biocompatible and naturally occurring vehicles that exhibit high specific surface area and large aspect ratio. They are composed of rolled bilayer of aluminol (Al-OH) inner-layer and siloxane (Si-O-Si) outer-layer. The two mentioned layers exhibit different properties including the surface charge and potential reactivity. Specifically, the outer lumen surface is negatively charged while the inner lumen surface is positively charged and on average more reactive. Moreover, there is a significant content of hydroxyl groups present on defects and edges of the HNTs tubes. Taking into account mentioned properties HNTs exhibit prominent potential in various modifications and loading possibilities. The inner-lumen hence promoting the loading of negatively charged molecules while the outer surface opens the possibility for the adsorption of positively charged molecules and its relative functionalization.

In our study we have explored the complete HNTs analysis, including physical characterization, investigation on the HNTs functionalization with several different bi-functional organic molecules and their loading capacities for certain pharmacological agents in the context of bladder cancer treatment.

We characterized HNTs with respect to the length and inner-/outer-lumen diameter size, the specific surface area, the main pore size and its decomposition with respect to the temperature increase. Mainly we focused our attention on HNTs functionalization capacities taking into account the influence of naturally adsorbed water molecules on its outer surface. A series of functionalized HNTs have therefore been obtained and completely characterized by means of FT-IR, zeta potential, BET, TEM. We performed mimics of HNTs inner-/outer-lumen and compared their reactivity. In this communication we will show the results of the study of HNTs loading procedure, loading efficiency and drug release.

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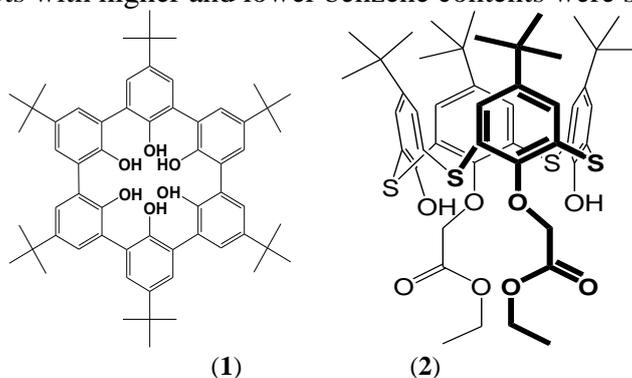
P11: Controlled selectivity of guest inclusion by calixarene derivatives

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Selective memory for volatile organic compounds and controlled selectivity of guest inclusion are smart properties of calixarenes. In the present work, the mutual influence of two guests benzene and tetrachloromethane in their binary mixture on the memory effect for tert-butylcalix[6]arene (**1**) was studied. The first example was found for an ability of these two guests to erase the host memory for each of them when included simultaneously with formation of a ternary clathrate. This clathrate has a much higher thermal stability than corresponding binary clathrates according to the data of simultaneous TG/DSC method combined with mass-spectrometric analysis of the evolved guest vapors. Besides, to characterize ternary clathrate $1 \cdot 0.3C_6H_6 \cdot 0.9CCl_4$ as a new crystalline phase and not a mechanical mixture of binary clathrates formed separately with each guest, these clathrates and four other ternary products with higher and lower benzene contents were studied using XRPD.



Prepared mixed inclusion compounds perform a unique ability for fractional guest release on the separate steps of clathrate decomposition, which may be used for separation of pure volatile compounds from their mixtures.

For calixarene **2**, the possibility to control the direction of solid-phase guest exchange in its clathrate and the inclusion selectivity for the guest mixture components were studied. The effect of a small additive of the non-included fourth component on the calixarene sorption capacity, the selectivity and direction of the guest exchange process in clathrate has been found. Depending on the content of the fourth component, it is possible to obtain ternary and quaternary clathrates of different composition, or transfer the "host" to a state without guest.

Acknowledgment.

The work was supported by RFBR (grant no. 17-03-01311).

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P12: Ferromagnetic Behaviors of Wheel-Type Heterometallic Clusters

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Multinuclear transition metal clusters have attracted tremendous attention in the field of molecular magnetism due to their diverse magnetic properties [1]. Heterometallic clusters are particularly useful for developing the Single-Molecule Magnets (SMM), since the magnetic interactions are controllable by selecting the combination of metal ions and designing the coordination structures. There are problems, however, which are difficult to prepare any desired multinuclear structures [2,3]. We recently prepared ferromagnetic heptanuclear nickel(II) complex $[\text{Ni}_7(\text{HL})_6(\mu_3\text{-OMe})_6]\text{Cl}_2$ (**1**) and heterometallic multinuclear clusters $[\text{Ni}_{7-x}\text{M}_x(\text{HL})_6(\mu_3\text{-OMe})_6]\text{Cl}_2$ ($\text{M} = \text{Mn}, \text{Co}$) based on complex **1**. These heterometallic clusters showed ferromagnetic behaviors in the same way as complex **1**. From these complexes, it is possible to obtain the high anisotropy and the large spin ground state for developing the SMM. We report here their syntheses, structures and metal-dependent magnetic properties. Complex **1** was crystallized in the cubic space group $Pa\bar{3}$. Seven nickel(II) ions were linked by six monoanionic ligands and six methoxy groups, which showed in a wheel-type structure. The $[\text{Ni}_7]$ core of complex **1** was incorporated to a central nickel(II) ion which is surrounded by a $[\text{Ni}_6]$ hexagon. The temperature-dependent magnetic susceptibility of complex **1** gave the following values: $J_1 = 6.87 \text{ cm}^{-1}$, $J_2 = -3.41 \text{ cm}^{-1}$, $g = 2.24$, and $zJ = +0.024 \text{ cm}^{-1}$ with an agreement factor $R = 9.0 \times 10^{-3}$ [R is defined as $R = \sum(\chi_m T_{\text{exp}} - \chi_m T_{\text{calc}})^2 / \sum(\chi_m T_{\text{exp}})^2$]. An unusual spin ground state of $ST = 5$ due to coexisting antiferromagnetic and ferromagnetic couplings between the nickel(II) ions was revealed.

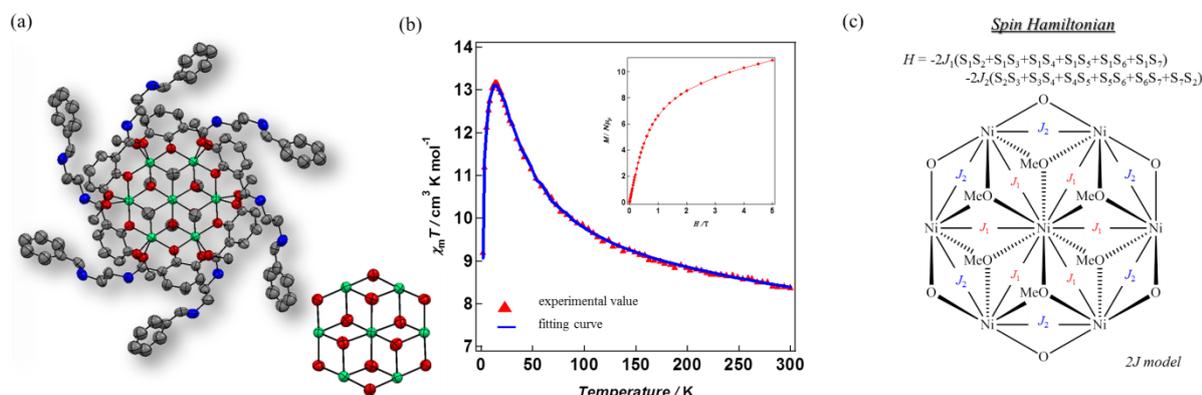


Figure 1. (a) Crystal structure and $[\text{Ni}_7]$ core of complex **1**. (b) Plots of $\chi_m T$ vs. T and fitting curves in a 5000 Oe field (inset; Plots of M vs. H at 2 K) for complex **1**. (c) Spin Hamiltonian and spin topology for complex **1** ($2J$ model).

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P13: Synthesis and characterisation of dimeric cubane Ni(II) capsules

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In recent years, molecular capsules are being garnered considerable interest as vehicles capable of selective molecular recognition or catalyst [1-3]. We have recently prepared dimeric cubane Ni(II) capsules by introducing two kinds of alkylamines, propanediamine and pentamethylenediamine, to each salicylic acid derivatives. Herein is the characterisation of dimeric cubane Ni(II) capsules, $[\text{Ni}_8(\text{HL}^{c=3})_6(\text{CH}_3\text{O})_6(\text{CH}_3\text{OH})_6\text{Cl}_2]\text{Cl}_2$ (**1**) and $[\text{Ni}_8(\text{HL}^{c=5})_6(\text{CH}_3\text{O})_6(\text{CH}_3\text{OH})_6(\text{OH})_2](\text{BF}_4)_2$ (**2**) by X-ray crystallography, elemental analysis and FT-IR. Counter anions, Cl^- , in the complex **1** having shorter alkyl chain (*n*-propyl) exist outside capsules but those, BF_4^- , in **2** having longer alkyl chain (*n*-pentyl) are included within the cavity. The space-filling model shows that complex has no enough space to accommodate the counter ion (Figure 1).

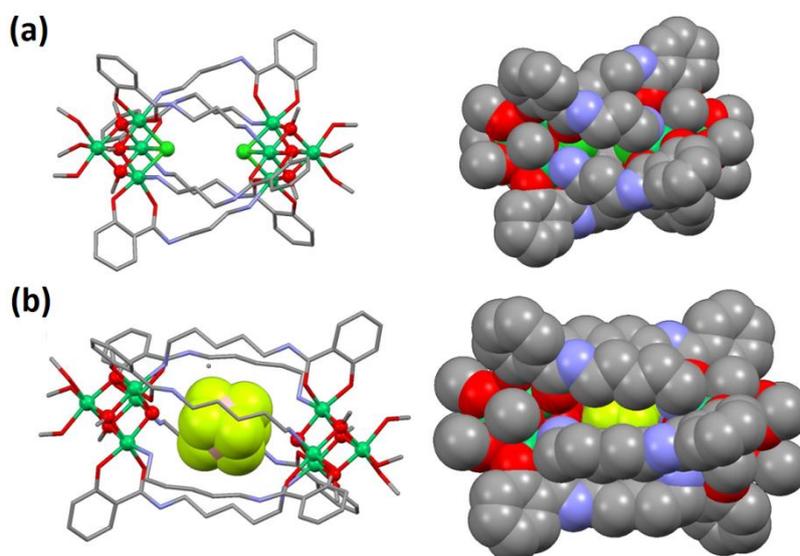


Figure 1. The crystal structures and space-filling models of complex **1** and **2**.

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P14: Resorcin[4]arene-Based Hexameric Capsule as Nanoreactor for 1,3-Dipolar Cycloadditions

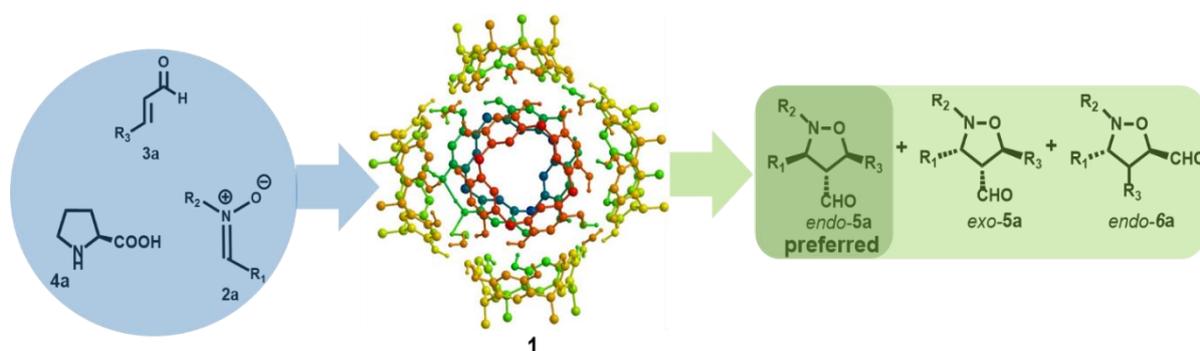
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In the last decade, many efforts have been devoted to the study of self-assembled supramolecular architectures as nanoreactors for organic reactions [1]. The self-assembled nanoreactors show selective encapsulation of substrates [2], reaction rate acceleration and the stabilization of reactive species. In addition, many reports show that in the presence of nanoreactors, well known organic reactions proceed with an unconventional regio- and stereochemistry [3]. Self-assembled resorcin[4]arene-based hexameric capsule **1** [4] has been largely exploited as nanoreactor, thanks to its capacity to host selectively the substrates and to its [5] ability to stabilize cationic reactive intermediates [6]. These capsules have been used as nanoreactors for the hydration of aromatic alkynes [7] and terpene cyclization [8]. In this communication, we will show that hexameric resorcinarene capsule is a highly efficient nanoreactor for the proline-catalyzed 1,3-dipolar cycloaddition between nitrones and unsaturated aldehydes (see Figure) with unexpected control on the regio- and stereochemistry of the reaction. The stereochemical outcome of the reaction was also investigated and rationalized by *in silico* computational studies.



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P15: Halides binding with uranyl-salophen receptors: unambiguous evidence of anion- π interactions in solution and in the solid state.

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Uranyl-salophen compounds are efficient receptors for anions and suitable supramolecular systems to be studied both in solution and in the solid state for many supramolecular applications spreading from recognition to catalysis [1].

In such systems, the driving force for anion complexation is provided by the interaction with the hard Lewis acidic uranyl center. The presence of electron-deficient aromatic pendants on the main skeleton, beside the metal center, increases the selectivity of the recognition of anions through an additional supramolecular interaction, i.e., anion- π interaction [2].

To elucidate the contribution of this quite elusive interaction, a series of uranyl-salophen complexes with one or two properly substituted aromatic pendant arms, Fig 1, have been synthesized.

Investigation has been undertaken in solution and in the solid state using a series of tetralkylammonium halide salts. The data here reported represent the first example of the occurrence of anion- π interactions in systems in which the main driving force for recognition is controlled by Lewis acid-base interactions.

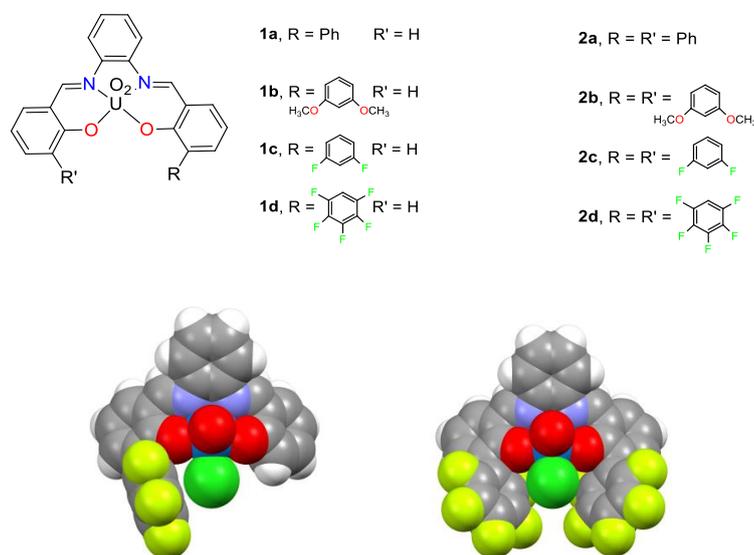


Figure 1. Above: Uranyl-salophen receptors used in this study; below: X-Ray crystal structures of **1d**@Cl⁻ and **2d**@Cl⁻ complexes respectively.

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P16: Superparamagnetic iron oxide nanoparticles functionalized by peptide nucleic acids

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The dysregulation of microRNAs (miRNAs) has been implicated in a variety of pathologies, such as inflammatory and autoimmune diseases, neurological disorders, as well as several types of cancer. Anti-miRNA platforms highly effective in in-vitro cell assays have been reported, but translation to the clinic is hampered by poor in-vivo stability of nucleic acids and ineffective uptake of nucleic acids by target cells. This study aims to overcome these obstacles by designing, producing and testing new miRNA targeting materials constituted by Peptide Nucleic Acids (PNAs, synthetic mimics of natural DNA and RNA) [1]. Indeed, PNAs conjugate the effectiveness of the natural nucleic acids targeting with chemical/thermal stability and resistance to enzymatic biodegradation.

A novel efficient method has been developed for covalently linking Peptide Nucleic Acid (PNA) oligomers and superparamagnetic iron oxide nanoparticles (SPION), to produce water soluble hybrid nanomaterials that can act as MRI contrast agents, as hyperthermia promoters and as PNA carriers. The multistep procedure involved: (i) preparation of oleate-stabilized SPION by using the thermal decomposition method, to control the size of the magnetic core; (ii) exchange of the oleate layer by dimercaptosuccinic acid (DMSA), to impart water solubility and to provide functional groups for PNA grafting; (iii) functionalization of a PNA oligomer with a terminal maleimide moiety, to allow SPION–PNA conjugation by thiol-maleimide Michael addition reaction, exploiting the SH groups of DMSA on the SPION surface. The method was tested using a model PNA decamer containing all four nucleobases (–CTAGATCACT–). SPION–PNA conjugation by SH addition was found more efficient than conjugation through amide bond between the COOH groups of DMSA and the terminal NH₂ groups of PNA. Elemental analysis, UV-Vis and IR spectra, ζ-potential, TEM, AFM, relaxivity and magnetic measurements of the SPION used for PNA binding is reported, and compared to the one relative to the SPION–PNA conjugate.

Reference

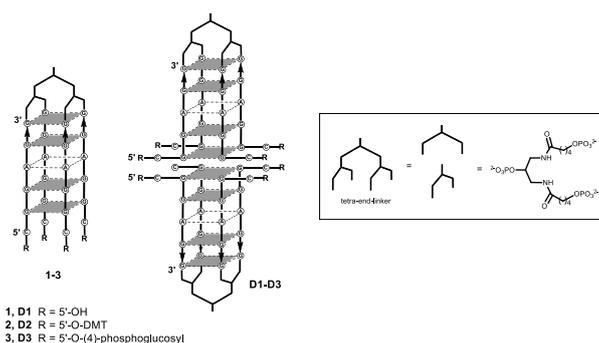
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P17: Studies on G-rich Tetra-End-Linked Oligonucleotides Forming Dimeric G-Quadruplex Structures with *in Vitro* anti-HIV Activity

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In the last decades, many RNA and DNA aptamers targeting HIV proteins have been reported. Among these, several G-quadruplex (G4)-forming ODN aptamers have shown the ability of protecting human cell cultures from HIV infection because of their binding to the V3 loop of the glycoprotein 120 exposed on the surface of HIV spikes. To improve the kinetics of G4 formation and considering that all the gp120-binding aptamers present in the literature needed chemical modifications to increase their resistance against nucleases, in recent years we synthesized a series of new monomolecular anti-HIV aptamers [1,2] by exploiting the Tetra-End-Linker (TEL) strategy proposed by us in 2004 [3]. By exploring different TEL lengths and orientations and different ODN sequences, we produced a small library of TEL-aptamers capable of protecting human CD4⁺ CEM cell cultures from HIV infection at submicromolar concentrations. In this poster communication we present our latest results on the synthesis and structural characterization of three new dimeric TEL-G4-forming aptamers based on the ODN sequence 5'CGGAGG3' (**1-3**, Figure). In **1-3** each arm of the TEL moiety is linked to the 3'-ending guanosine of one ODN strand, whereas the 5' hydroxyl groups of cytosines are left unprotected (**1**) or capped with either the dimethoxytrityl (DMT) group (**2**) or with glucose (Glu) (**3**). The *in vitro* anti HIV activity of G-Quadruplexes **1-3** is also reported.



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P18: Supported gold nanoparticles catalysts for alkynes hydroamination

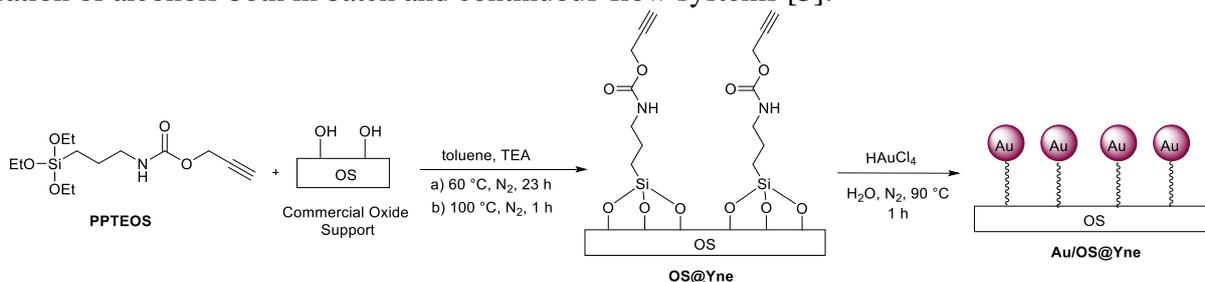
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Our research group has recently reported the preparation of gold nanoparticles (Au_{NPs}) supported on different functionalized silica supports. We started using commercial polyethyleneimine-functionalized silica bead [1] and we continued preparing silica nanoparticles functionalized with alkynyl carbamate moieties [2].

Furthermore, we have focused on the straightforward synthesis of Au_{NPs} anchored on commercial, micrometric oxide supports (i.e. SiO_2 , Al_2O_3 , TiO_2) previously modified with the di-functional organosilane [3-(2-propynylcarbamate)propyl]triethoxysilane (PPTEOS) by a grafting procedure (Scheme 1). After being thoroughly characterized by several complementary techniques (XPS, TEM, SSNMR, AAS etc.), the catalytic activity of these systems ($\text{Au}/\text{OS}@Yne$) has been evaluated in the oxidation of alcohols both in batch and continuous-flow systems [3].



Scheme 1. Preparation of $\text{Au}/\text{OS}@Yne$.

We now present the latest results obtained in the study of the catalytic application of $\text{Au}/\text{OS}@Yne$ in the alkynes hydroamination reaction, which is considered the most atom efficient process for the formation of a series of nitrogen-containing compounds.

Indeed, this transformation takes place without the formation of any side product and leads to the production of enamine, imine or substituted amines, which have a significant importance as bulk and fine chemicals or building blocks in organic synthesis.

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P19: Poly(ethylene-co-vinyl alcohol)-based microgels prepared through salting-out: phase behavior and structural properties

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Poly(ethylene-co-vinyl alcohol) (EVOH) is a biocompatible water-soluble polymer of great interest thanks to its large-scale applications as a material for drug-delivery, pollutant removal or for building sensors and membranes which prevent the diffusion of O₂. Above the different techniques used for the preparation of vinyl alcohol-based physical hydrogels, the cryogenic route is one of the most studied and widely employed [1], even though other protocols can be followed. The advantages of such gels is the absence of toxic chemicals for their preparation and the consequent possibility to obtain a completely eco-friendly product [2]. In this work we propose a new route for the preparation of EVOH-based microgels through the salting-out effect. Firstly, a previous screening of different salts belonging to the Hofmeister series was performed: sodium chloride represented the best kosmotropic species to use in order to favour the polymer aggregation over a reasonable time-scale. Secondly, the thermodynamic properties and the kinetics of the aggregation process were deeply studied through Static Light Scattering (SLS) and Dynamic Light Scattering (DLS), which allowed rationalising how such process is influenced by different parameters like salt molality, polymer concentration and time from the preparation (fig. 1). Finally, a combined Small Angle Neutron Scattering (SANS) Cryogenic Transmission Electron Microscopy (CryoTEM) and SLS study threw light on the structural and morphological properties of such microgels, showing the role of the salt in the aggregation process and its effect on the supramolecular organization (fig. 2 and fig. 3). In particular, we determined the molar weight and the radius of gyration of the aggregates and we estimated the packing degree of polymer chains within the aggregates, strongly influenced by the presence of sodium chloride, whose concentration could represent a crucial parameter affecting the internal chain dynamics.

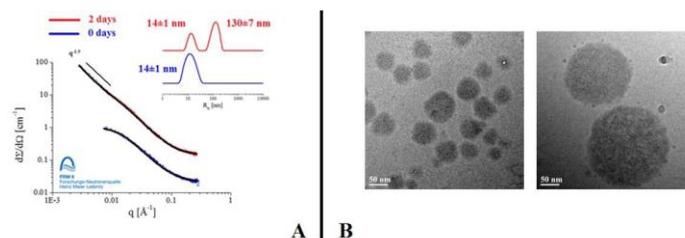


Fig. 2 - Panel A: SANS profiles and DLS measurements for EVOH microgels at time 0 (blue line) and after 2 days from the preparation (red line); Panel B: Cryo-TEM measurements of EVOH microgels after 2 days from the preparation

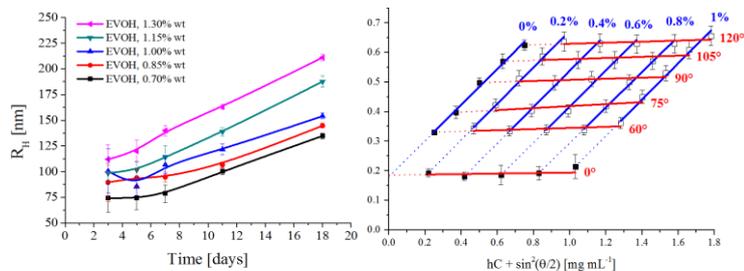


Fig. 3 - Evolution of hydrodynamic radii over time at different copolymer concentrations and constant NaCl molality (0.65 mol/kg)

Fig. 3 - Zimm plot for EVOH aggregates obtained after 7 days from the preparation

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P20: Conformation-sensitive detection of secondary structure-forming oligonucleotides on nanoporous glass beads

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Guanine-rich oligonucleotide sequences can fold into supramolecular structures called G-quadruplexes (G4s). The core G4 unit is the G-tetrad, a cyclic planar arrangement of four guanines linked through Hoogsteen-type hydrogen bonds. Stacking of two or more G-tetrads generates a G4 motif, which is further stabilized by cations hosted in the central cavity of the G4. G4s exhibit a marked structural polymorphism, which depends on strands stoichiometry and orientation, types of linking loops and guanine residues conformation. In particular, G4s can be arranged in different topologies, defined as parallel, antiparallel or hybrid-type, depending on the relative orientation of the G4-forming strands [1].

G4s have been recognized to play crucial roles in human telomeres or in genome regions associated with human or viral gene regulation, thus resulting into novel, effective targets for potential anticancer or antiviral therapies. Thus, for the development of effective and minimally toxic anticancer and/or antiviral drugs, a major challenge is the identification of conformation-selective G4-targeting ligands. With the aim of obtaining supports for affinity chromatography-based High Throughput Screening of putative conformation-selective G4-ligands [2-3], we have recently functionalized nanoporous glass beads with oligonucleotide sequences able to fold, in proper conditions, into different unimolecular G4 structures. To gain a deeper insight into the conformation adopted by the G4s on the glass beads, we have exploited a fluorescent and water-soluble core extended naphthalene diimide, designed to give different fluorescence responses in the presence of different secondary structure-forming oligonucleotides [4]. Preliminary on-resin experiments by confocal microscopy will be here presented.

In principle, our in vitro approach can be extended to in cellulo selective visualization of conformationally different G4 structures in human and viral genomes, thus overcoming the poor conformation-specificity of previously used antibodies [5].

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P21: Core-Shell Mo₂C/MoO₃ Nanowires for HER

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Hydrogen is being vigorously pursued as an ideal energy carrier and its production by water splitting is attracting growing attention. The electrolysis efficiency is enhanced when Pt is used as the catalyst in acidic media. In particular, the main effective catalyst are Pt group metals but it remains challenging to look for alternative catalyst that are more abundant and at lower cost. Group VI transition metal carbides exhibit catalytic properties analogous to platinum group metals because of their unique d-band electronic structures. Tungsten carbide has been explored for the hydrogen evolution reaction (HER) finding interesting results, but an high overpotential if compared with Pt-group metals [1,2]. On the other hand, molybdenum carbide was been demonstrated able to reduce the overpotential.

Many approaches including chemical vapor deposition (CVD) and pyrolysis of metal complexes have been developed for the preparation of metal carbides [3,4]. Among them the more explored is CVD using hydrocarbons or carbonaceous gases (e.g. CO...) and Mo gaseous precursors (MoF₆, Mo(CO)₆, MoCl₅...). On the other hand, the gas-phase syntheses required in general elaborate equipment, and involve the use of costly and toxic reagents, and the product is usually contaminated by chars from the pyrolysis of carbonaceous gases.

Here we report the preparation of core-shell Mo₂C/MoO₃ nanowires by a solid precursor (ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O)) thermolysis, that permits to simplify the precursors inlet to the reactor, which was fed by nitrogen (200 cm³ (STP)/min) from room temperature to 800°C, followed by a controlled CVD of CH₄ 10 vol.% in nitrogen for 10 minutes monitored on-line by ABB analyzers.

The characterization was obtained by the combined use of different techniques: Raman Spectroscopy, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy – Energy dispersive X-ray spectroscopy (TEM-EDS), thermogravimetric analysis coupled with mass spectrometry (TG-DTG-MS) and X-ray diffraction (XRD) analysis. The nanohybrid is able to efficiently drive the HER. MoO₃ serves as a highly nanostructured, conductive core, while the thin Mo₂C coating serves as both a HER catalyst and a protective layer.

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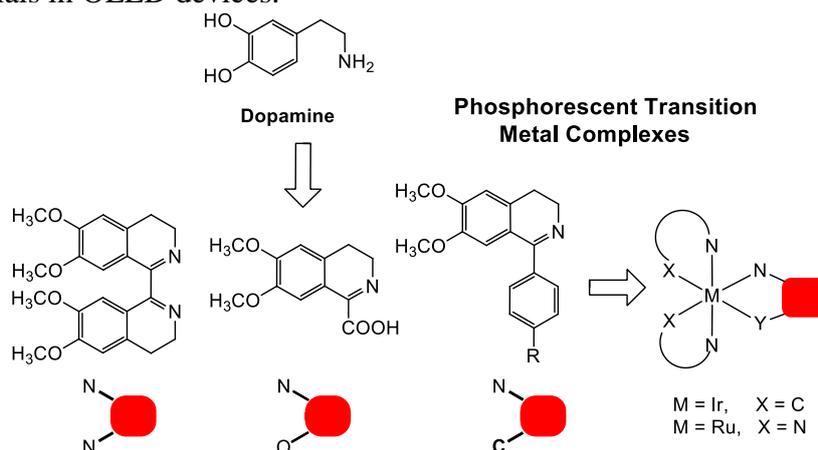
P22: Designing dopamine-based electroluminescent complexes for innovative melanin-inspired OLED devices

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The growing expansion and impact of OLED devices in our everyday life have stimulated the synthesis of a variety of electroluminescent materials with the aim of improving the efficiency and the life-time of the device as well as of selectively tuning the wavelength of the emitting light. In the frame of our research activity aimed at exploring the role of melanins, the dark pigments found in mammalian skin, hair and eyes, as soft organic semiconductors in bio-electronic devices [1,2], we have undertaken a new challenge to obtain innovative electroluminescent bio-inspired materials. Herein we report on the use of dopamine, the catecholic neurotransmitter and monomer precursor of polydopamine, as starting compound for the synthesis of phosphorescent metal complexes to be used as emitting materials in OLED devices.



The synthesis of a set of dopamine-inspired electroluminescent compounds and the relative photo-physical and electrical properties will be reported; the fabrication and characterization of the corresponding OLED devices will also be presented.

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P23: Conformational behaviour and molecularity studies of natural and modified AS1411 aptamers

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AS1411 is a 26-mer G-rich DNA oligonucleotide, currently in Phase II clinical trials, targeting nucleolin, a multifunctional protein involved in cell survival, growth and proliferation, overexpressed on the outer membrane of cancer cells [1].

In the last decade, the interest in using AS1411 as a ligand for the tumor-selective delivery of therapeutic or imaging agents has tremendously increased, especially in view of its potential applications in anticancer strategies.

In order to exploit AS1411 as an active targeting agent for multifunctional, theranostic nanoplateforms, we have selected a set of AS1411 derivatives (*i.e.*: 5'-stearyl-AS1411, 5'-cholesteryl-C6-AS1411 and 5'-cholesteryl-TEG-AS1411) decorated with lipophilic tails at their 5'-end so to allow their subsequent insertion into liposomes or lipid coated-NPs.

The solution behavior of the AS1411 derivatives has been investigated using different techniques, in comparison with the unmodified aptamer. In particular, CD, CD-melting, UV-melting, gel electrophoresis, size exclusion chromatography and DLS analysis have been carried out to get information on their secondary structure and thermal stability of their preferred conformations. This study has been performed in two different pseudo-physiological buffer solutions, mimicking the extracellular and intracellular media, and at different concentrations; special attention has been devoted to the investigation of the effects of the lipophilic tail and of the linker on the overall structure and conformation of the aptamers.

AS1411: 5'-GGT GGT GGT GGT TGT GGT GGT GGT GG-3'

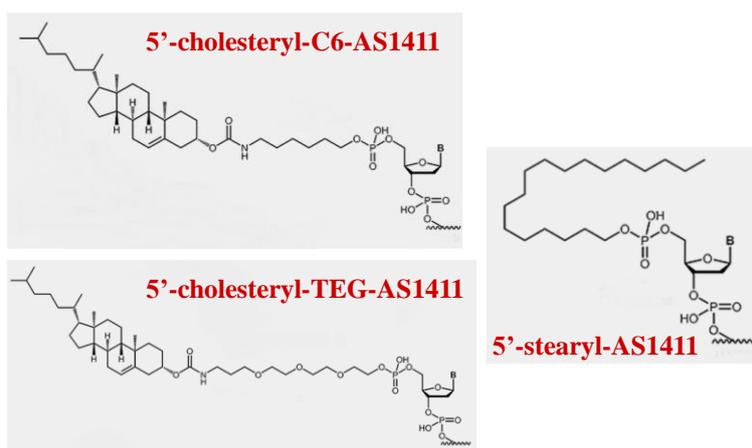


Figure. AS1411 derivatives selected as potential active targeting ligands in the construction of liposome or NP-based anticancer multifunctional systems.

Reference

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P24: New calixarenes act as cation recognizer in asymmetric phase-transfer catalysis

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The growing demand for enantiomerically enriched compounds by industry enforces research towards the development of new synthetic asymmetric methodologies. For this purpose, the asymmetric phase-transfer catalysis has been recognized as a good methodology in organic synthesis, that can be applied both in industry and academia research [1]. Chiral ammonium or phosphonium salts have been largely and efficiently applied in asymmetric phase-transfer catalysis. An interesting alternative to chiral quaternary onium salts are nonionic metal complexing macrocycles. More recently, we reported the ability of cyclopeptoids to act as good phase-transfer catalysts [2].

Calix[*n*]arenes are a leading class of macrocyclic systems efficiently able to complex metal ions. In particular, calix[4]arene-amides showed high affinity for alkali metal cations [3].

Surprisingly, applications of calixarenes as catalysts for asymmetric phase-transfer processes remain scarce. Although examples of chiral ammonium catalysts anchored on a calixarene scaffold have been described, the cation-recognition ability of the macrocyclic structure itself has never been exploited in asymmetric phase-transfer catalysis [4-5]. In this communication is reported the synthesis of new chiral calix[4]arene-amides (e.g. **1-7**, figure 1), the first enantioselective alkylation of *N*-(diphenylmethylene)glycine esters using calixarenes (scheme 1) and their binding affinity toward Na⁺ cation.

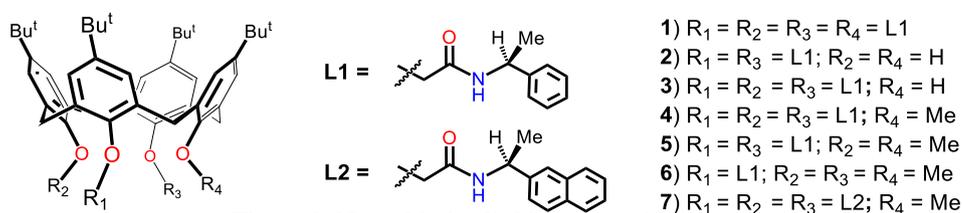
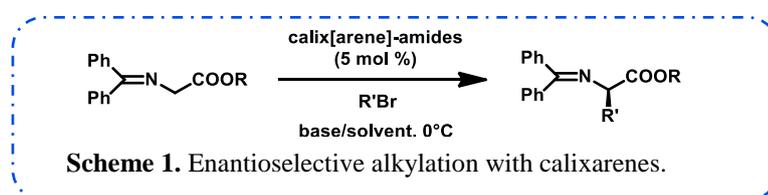


Figure 1. New chiral calix[4]arene-amides.



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P25: Highly sensitive electrochemical detection of Arsenic (III): Fe₃O₄ nanoparticles covered graphene oxide

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Arsenic compounds are known for their ecotoxicological consequences, geochemistry and their effects on human health and environmental. In natural waters arsenic (As) is mostly found as inorganic oxyanions such as trivalent arsenite (As(III)) or pentavalent arsenate (As(V)). There are several techniques for detection of arsenic compounds. Among them, voltammetric methods are preferred to analytical ones because the first present relatively lower cost, lower power consumption and higher sensitivity in the analysis of As amount. Noble metal nanoparticles (Au, Ag, Pt) electrodes have been studied as electrochemical sensor for detection of As in aqueous solution [1]. These electrodes need to work in strongly acidic media and their production is expensive. On the contrary, non-precious metals, such as iron oxide-based materials, are cheaper and environmentally friendly [2]. In particular, magnetite (Fe₃O₄), founded very effective in the removal of heavy metals [3] and used in combination with nanocarbons to improve stability and ability to work in continuous flow systems, have never been studied for detection porpoise. GO is considered an excellent nanoplatform to develop electrochemical sensors, due to the nature of the atoms on its surface, and its controllable defects density that modulates the sensor sensitivity. Moreover, it has been proved that ultra-thin GO nanosheet is high sensitive and selective to arsenic by using an electrode based on GO coupled with leucine molecules [4].

In this work, we present a novel and stable electrochemical sensor made of Fe₃O₄/GO deposited on a glassy carbon (GC) electrode for electroanalytical detection of As, via cyclic voltammetry in aqueous and phosphate buffer solutions. The electrode shows a very good relation between current response and amount of arsenic in a concentration of pollutants ranging from micromolar to nanomolar. Our sensor is easy to use, inexpensive and has allowed fast, sensitive and selective detection of As in non-acid media (pH7), showing excellent reproducibility and stability response.

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P26: Synthetic Complexes of new Quino[7,8-h]quinoline Derivatives

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The properties and applications of coordination cages and complexes are dependent on the synthons they are built from. The proton sponge quino[7,8-h]quinoline is an attractive target as a functionalisable base structure for new synthons. With a destabilizing lone electron overlap between the central nitrogen atoms and a helical torsional twist that can be relieved by monoprotection or complexation, these compounds are both extremely basic and excellent chelators that can accommodate ions of vastly different sizes.

The recent breakthrough in the synthesis of the quino[7,8-h]quinoline core¹ has opened this family of compounds for further exploration, allowing multiple derivatives and complexes to be formed. One of these, 4,9-dipyridylquino[7,8-h]quinoline (fig 1.) is shown below.²



Figure 1: Crystal structure of 4,9-di(4-pyridyl)quino[7,8-h]quinoline

This compound has the potential to form larger coordination structures instead of being limited to mononuclear discrete complexes, opening up a host of exciting possibilities.

This presentation will explore the metallo-organic complexes and structures formed with some of these derivatives, and their potential for supramolecular cage formation.

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P27: Synthesis and application of polymeric zinc organic framework derived zinc oxide composite with conducting polymer

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The presentation will cover the synthesis of zinc organic framework, the preparation of polymeric zinc organic framework-derived zinc oxide composite with conducting polymer, and its application to sensitive and selective detection of nitric oxide (NO) in biological systems. We prepared a new type of electrochemical NO biosensor based on zinc- dithiooxamide (ZnDTO) framework derived porous ZnO nanoparticles (ZnO NPs) and polyterthiophen-rGO composite. By taking advantage of the synergetic effect between ZnO and poly(TTBA-rGO) (TTBA = 3'-(*p*-benzoic acid)-2,2':5',2''-terthiophene, rGO = reduced graphene oxide) nanocomposite layer, the poly(TTBA-rGO)/ZnO sensor probe displayed excellent electrocatalytic activity and explored to detect NO released from normal and cancer cell lines. The ZnO was immobilized on a composite layer of poly(TTBA-rGO). The highly porous ZnO offers a high electrolyte accessible surface area and high ion-/electron transport rates that efficiently catalyze the NO reduction reaction. Amperometry with the modified electrode displayed highly sensitive response and wide dynamic range of 19 nM to 76 μM with the detection limit of 11.2±2 nM. The sensor probe was demonstrated to detect the NO released from living cells by drug stimulation. The proposed sensor provided a powerful platform for the low detection limit that is feasible for real time analysis of NO in a biological system.

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P28: Switchable diastereoselective Michael addition catalyzed by crown ethers

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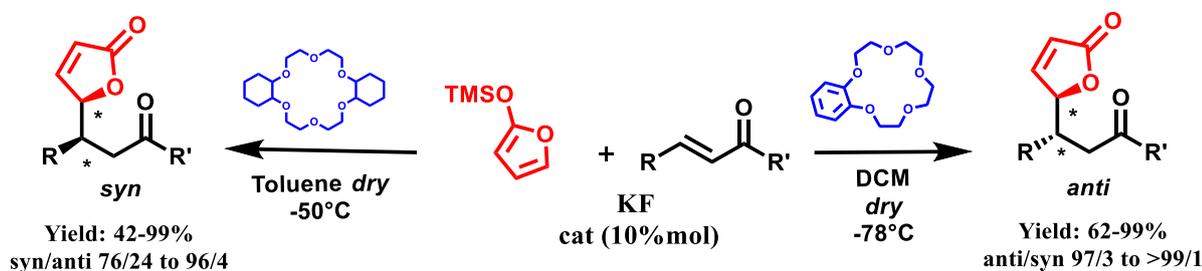
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The great interest towards the stereoselective construction of γ -butenolides arises from their wide distribution in a large number of natural products and from their versatility in the synthesis of drug and biologically active compounds [1]. During the last decade, the vinylogous Michael reaction of 2(5*H*)-furanones or 2-silyloxyfurans has emerged as a highly efficient stereoselective method to afford chiral γ -butenolides. However, most of the known synthetic methods provides *syn* or *anti* Michael adducts employing chiral organocatalysts or ligands, which are often expensive or not commercially available [2-3]. In addition, *syn* adducts has been obtained only by reaction with chalcones.

In this communication, we report an unprecedented switchable diastereoselective fluoride promoted vinylogous Mukaiyama-Michael reaction (VMMR) with diverse α,β -unsaturated ketones, catalyzed by simple achiral crown ethers. *Anti*-adducts were obtained with excellent diastereoselectivities when benzo-15-crown-5 in CH₂Cl₂ was employed, while high *syn*-diastereoselectivities were achieved by employing dicyclohexane-18-crown-6 in toluene (Scheme 1).



As demonstrated by DFT calculations, the diastereoselectivity inversion is attributable to the involvement of loose or tight cation-dienolate ion pairs, depending on catalyst and solvent used. Furthermore, we applied this methodology to vinylogous Michael reaction of 5-phenylfuran-2(3*H*)-one with chiral substrates. The appropriate selection of the chiral auxiliary, the crown ether's cavity size and the solvent has enabled, after removal of the chiral auxiliary, the stereoselective synthesis of all the possible stereoisomers.

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P29: Semiconducting Property of Reduced Graphene Oxide by Using Various Reduction

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Graphene is 2D nanosheet consisted on carbon and attractive material with various property which are unique thermal and electrical conductivity, charge carrier mobility and mechanical property [1]. Graphene is applied to transparent electrode, sensor and catalyst widely. In generally, pristine graphene fabricated by the method such as chemical vapor deposition (CVD) is known that band gap is zero. It is important to investigate synthesis of graphene with unipolar (p- or n-type) semiconductor property because of semiconductor property of graphene is ambipolar. However, semiconducting property of graphene is generally p-type in the atmosphere due to the presence of moisture and oxygen. Synthesis of n-type graphene is especially studied in this field. Synthesis of n-type graphene by doping method with heteroatom is generally used and However, synthesis of non-doped graphene with n-type semiconductor property is hardly reported. In addition, it is difficult to synthesize graphene with ambipolar or unipolar semiconductor property by CVD method because of severe condition.

In this work, we reported non-doped graphene with n-type semiconductor property by using photo-reduced graphene oxide (PRGO). Graphene oxide (GO) have many oxygen functional group on graphene sheet and is synthesized by hummers' method. The ratio of oxygen functional group of GO was decreased by photo irradiation and PRGO was generated. In XPS measurement, PRGO has many C-H bond and the ratio of C=C bond was decreased.

In Kelvin probe force microscopy (KFM), PRGO was show n-type semiconductor property. In FET measurement, PRGO was also indicated n-type semiconductor property, but will be discussed in further details.

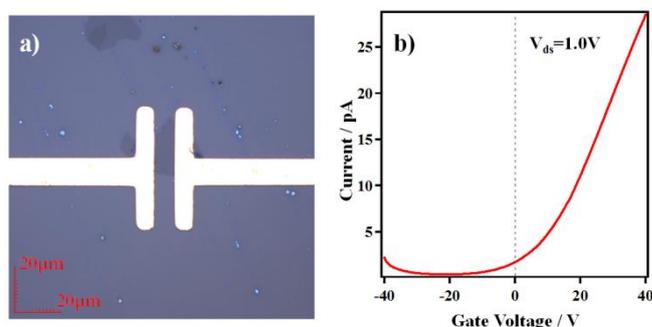


Fig.1 (a) Optical image of PRGO FET device. (b) I-V curve of PRGO.

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P30: ZnO nanoparticles coupled with up-conversion phosphors for the removal of methylene blue under visible light irradiation

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Every day a large amount of products is released by chemical and pharmaceutical industries threatening the environment and human health. Moreover, their removal using conventional oxidation methods is difficult, because a lot of pollutants are biorecalcitrant. Photocatalysis, an advanced oxidation technology, appears one of the most viable solutions, due to its ability to oxidize a wide range of toxic organic compounds into harmless compounds such as CO₂ and H₂O by irradiation with UV light.

Organic pollutants can be removed from water by a UV driven photocatalytic process involving ZnO, as photocatalyst. However, ZnO has a very low efficiency when used in a photocatalytic process using the emission spectrum of solar light and its use in a photoreaction system suffers from the disadvantage due to the non uniform photon distribution inside the reactor core.

With this respect, we propose the use of ZnO coupled with up-conversion phosphors, able to convert visible light into UV light. Therefore, this photocatalytic system was studied for the removal of methylene blue in the presence of visible light irradiation.

The prepared up-conversion phosphors nanoparticles emit UV light (with main emission at 365 nm), when excited with visible light.

The photoreactivity was measured in a pyrex photoreactor irradiated with four visible lamps (nominal total power: 32W). Experimental investigations were performed on physical mixtures of up-conversion phosphors and commercial ZnO nanoparticles, evaluating the decolorization of the target dye. The experimental results showed that the photocatalytic performances obtained using ZnO coupled with phosphors nanoparticles are strongly increased compared to the results achieved in the presence of only ZnO. In particular, the complete dye degradation has been reached in approximately 120 minutes of irradiation, confirming the enhancement of photocatalytic performances induced by UV photons emitted by up-conversion phosphors. These preliminary results show that the use of up-conversion phosphors nanoparticles in photocatalytic systems can be an alternative to the traditional UV lamps, thus preserving human health, environmental and, at the same time, allows to save the energy in process management.

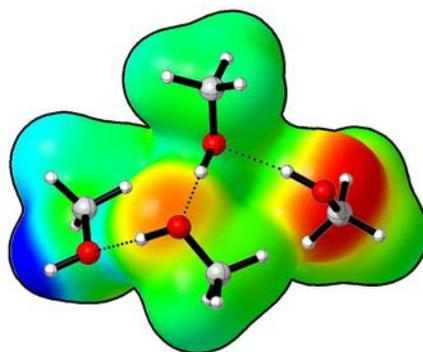
P31: Polarisation of H-bonds on solvation equilibria in alcohols

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The association constants for complex formation of H-bond donor and acceptor pairs have been measured in mixtures of *n*-octane and several aliphatic alcohols. Alcohol solvents are known to undergo self-association leading to linear and cyclic aggregates, which have been modeled in order to access the concentrations and H-bond properties of the different alcohol entities present in the mixtures [1]. Formation of a H-bond between two alcohol molecules leads to polarization of the OH groups, resulting in an increase in binding affinity of the unbound donor and acceptor sites. OH acceptor sites involved in a H-bond remain available, but the donor site becomes unavailable towards further interactions upon binding, so that the overall solvation property of the alcohol depends on the concentration of bound and unbound OH groups in the alcohol aggregates. At low alcohol concentrations, solutes are solvated by alcohol monomers, while with increasing concentrations the solutes will bind mainly to chain ends and not to internal alcohols. These findings are also reproduced by quantum chemical calculations of the electrostatic potential of the alcohols aggregates [2].



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P32: Novel production of core-shell N-doped magnetic nanoparticles of Titania (FM/N-TiO₂) by means of a spinning disk reactor

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Nanotechnology is an emerging field that covers a wide range of technologies which are presently under development. It plays a significant role in the development of innovative methods to produce new products, to substitute existing production equipment and to reformulate new materials and chemicals with improved performance resulting in less consumption of energy and materials and reduced harm to the environment as well as environmental remediation. Because of its chemical and physical properties, TiO₂ has not only emerged as one of the most fascinating materials for environmental applications, but has also succeeded in engaging the attention of chemists, physicists, material scientists and engineers in exploring distinctive semiconducting and catalytic properties.

A novel approach to produce nitrogen doped magnetic core TiO₂ nanoparticles (FM/N-TiO₂) is here investigated. The treatment of wastewater streams by photocatalysis appears a feasible pretreatment for many subsequent purification steps, such as membranes. In order to keep high efficiencies in dealing with the turbid wastewater streams, the photocatalyst requires to be suspended in order to reach the water surface for proper irradiation and operation. A main drawback is the recovery of the suspended photocatalyst, that may be accomplished by magnetic filters (up to 99.9%) as soon as the titania nanoparticles are attached to magnetic nanocores. Moreover, the photocatalyst should react to visible light and not only to UV (as pure titania), to operate with a high energy efficient process that may use LED lamps instead of UV lamps. This property can be acquired through nitrogen doping.

Therefore, the production of FM/N-TiO₂ may represent a general solution to all these problems. The FM/N-TiO₂ were synthesised starting with the production of magnetic nanocores by SDR and their coating of silica by using the Stroeber method. Finally, N-doped titania is produced by means of two different procedures, based on the use of titanium tetraisopropoxide (TTIP) in ethanol as a precursor: by using a 97% N-ethylmethylaniline or a urea solution, respectively. In the final stage of production, the N-doped titania solution is put in contact to the silica coated nanocores, washed and calcinated at higher temperatures. At the end, a core-shell-shell nanoparticle is obtained.

Dependant of the used procedure, different nitrogen loss may occur during the elevated temperature calcination process. The experimental runs performed in an air lift reactor for phenol degradation shows that generally the produced FM/N-TiO₂ are efficient for purification purposes and can be recovered back by magnets with ease; moreover, the particles doped by urea sensibly improved the phenol degradation kinetics at same operating conditions, thus nitrogen loss during their production processes was less.

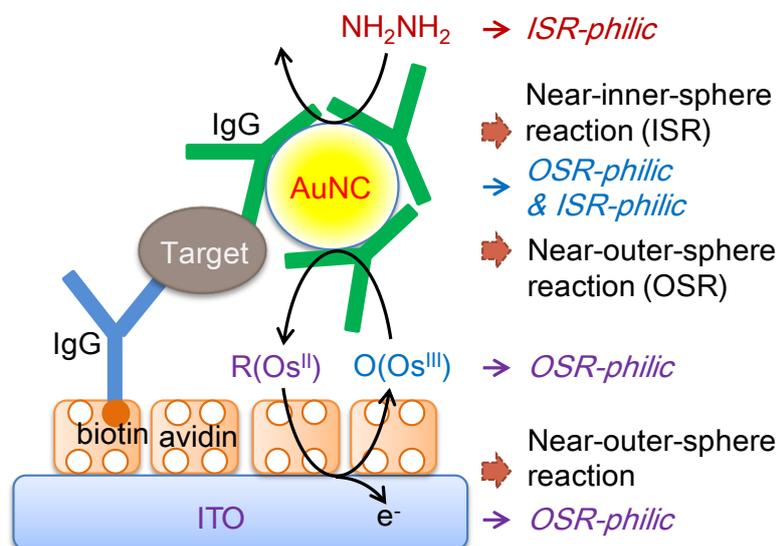
P33: Ultrasensitive Electrochemical Immunosensor Using a Gold-Nanocatalyst Label Mediating Outer-Sphere-Reaction-Philic and Inner-Sphere-Reaction-Philic Species

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We report a new nanocatalytic scheme based on the facts that the redox reaction between a highly outer-sphere-reaction-philic (OSR-philic) species and a highly inner-sphere-reaction-philic (ISR-philic) species is slow that an OSR- and ISR-philic Au-nanocatalyst label can mediate the two different types of redox species. This scheme allows highly sensitive and incubation free detection of creatine kinase-MB (CK-MB). Outer-sphere to inner-sphere redox cycling occurs in the sequence of a highly OSR-philic ITO electrode, highly OSR-philic $\text{Os}(\text{bpy})_2\text{Cl}_2^+/\text{Os}(\text{bpy})_2\text{Cl}_2$, OSR- and ISR-philic AuNC, and highly ISR-philic hydrazine. Ultimately, using outer-sphere to inner-sphere electrochemical-nanocatalytic (EN_c) redox cycling that allows high signal amplification. When the EN_c redox cycling was applied to a sandwich-type immunosensor for the detection of CK-MB, the calculated detection limit was approximately 20 fg mL^{-1} for mouse IgG, reconfirming that the EN_c redox cycling allowed ultrasensitive detection. In the case of another cardiac target (myoglobin), the chronocoulometric signal was similar to that of zero CK-MB, indicating that the immunosensor is selective. The results for clinical serum samples showed that the charge increased with increasing concentration of CK-MB with good reproducibility, indicating that the immunosensor is practically appealing.



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P34: The Binding Interaction of Imazapyr with Cucurbit[n]uril (n=6-8): Combined Experimental and Molecular Modeling study

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The inclusion complexes of imazapyr (IMA) with cucurbit[n]uril, CB[n] (n=6-8), have been investigated. Fluorescence spectroscopy, MALDI-TOF, and ¹HNMR were used to investigate and characterize the inclusion complexation of IMA and CB[n] in solutions. Whereas the solid state complexes have been characterized by Fourier transform infrared spectroscopy (FTIR), and powder X-ray diffraction (PXRD). IMA was found to form 1:1 complexes with CB[n] with association constants ranging from 5.80×10^2 – 2.65×10^3 . The guest molecule IMA was found to encapsulate into the larger cavities of CB[7] and CB[8], whereas with CB[6] the molecule remains outside the cavity. Molecular dynamic (MD) simulations were used to follow the inclusion process at an atomistic level to study the mechanism and stability of inclusion. The results obtained showed that inclusion complexes of IMA with both CB[7] and CB[8] are highly stable in aqueous media, but the smaller cavity size of CB[6] prohibited the formation of complex with the guest. The results clearly show that in addition to hydrophobic interactions the presence of hydrogen bonding has added greatly to the stability of the complexes

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P35: Synthesis and Property of Nickel Dithiolene Complex with Herringbone Structure Based on Lone Pair- π Interactions

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Abstract

Lone pair- π (lp- π) interaction has gained much interest because of its potential to play an important role in the supramolecular system as seen in not only biological activity [1, 2] but also crystal engineering [3]. In molecular solids, lp- π interaction as well as π - π interaction is expected to make a contribution to their electronic structures based on orbital overlapping. However, there are few studies to investigate the role of lp- π interaction in physical properties of molecular solids.

In this study, we attempt to demonstrate that not only intermolecular π - π but also lp- π interactions cause sufficient orbital overlapping in a molecular solid and contribute to its transport property. In order to achieve this aim, we focused on a cyano-substituent metal dithiolene complex as a component of molecular solid. Metal dithiolene complexes are known to show rich physical properties such as electrical, magnetic, or optical properties due to their planar structures and delocalized molecular orbitals by using d- and π -orbitals. To this end, we synthesized Ni(Hdcdmp)₂ (H₂dcdmp = 2,3-dicyano-5,6-dimercaptopyrazine; complex **1**) having four cyano groups. Slow diffusion of diethylether into the solution of **1** affords single crystals of **1**. **Figure 1** shows the crystal structure of **1** obtained from the result of single crystal X-ray diffraction measurement. In this crystal, **1** assembles in the form of herringbone through a - b plane where one-dimensional π -stack columns are connected with each other by lp- π interaction between lone pair of nitrogen atoms in cyano group and π -electron in pyrazine moiety. In addition, hydrogen bond interaction between **1** and diethylether molecules along c axis stabilizes this crystal structure. Because of the herringbone structure, **1** is a promising candidate for molecular solids with 2D transport property based on closed shell system. In this presentation, we discuss the physical properties and the band structure of **1**.

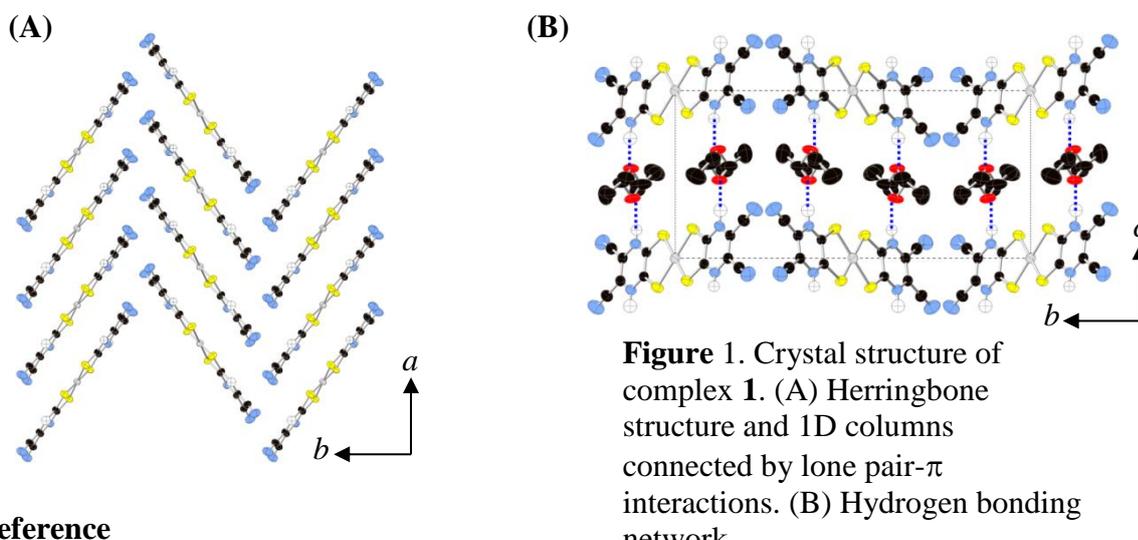


Figure 1. Crystal structure of complex **1**. (A) Herringbone structure and 1D columns connected by lone pair- π interactions. (B) Hydrogen bonding network

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**P36: Phase transition behavior of a [2-pyrrolidone]-[chloranilic acid]
molecular complex with hydrogen-bonded straps**

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Abstract

In molecular crystals, structural phase transition has been widely investigated because of its potential to cause drastic change in physical properties attributed to reformation of intermolecular interaction^[1]. We have focused on a molecular complex composed of two 2-pyrrolidone (Py) and one chloranilic acid (CA) molecules named as PyCA and investigated its structural phase transitions. Py and CA are worked as proton acceptor (A) and donor (D), so that the crystal structure of PyCA consists of hydrogen-bonded straps with an alternating A-A-D component stabilized by interstrap π - π overlap (**Fig.1**). At room temperature, PyCA has two polymorphs, metastable Phase HT_a and stable Phase HT_b. Up to now, it is revealed that the transition from Phase HT_a to Phase HT_b by using temperature cooling and heating processes is a successive phase transition via intermediate phases at low temperature (**Fig.2**). However, crystal structures of these intermediate phases at low temperature are still not clarified. In this study, we carried out the variable temperature measurements of ³⁵Cl NQR and X-ray diffraction (XRD) and DFT calculation, to find out the low temperature structures of PyCA and discuss its transition behavior.

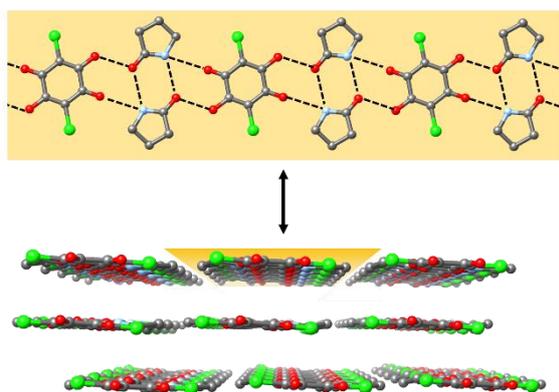


Fig.1 1D hydrogen-bonded strap (upper) and crystal structure (down) of PyCA

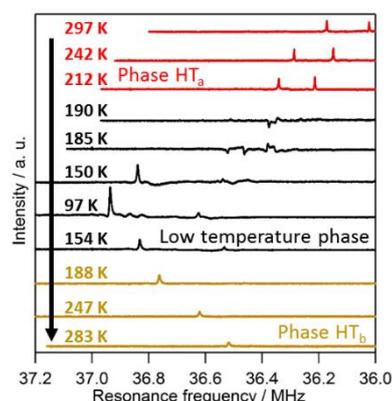


Fig.2 Temperature dependence of ³⁵Cl NQR freq. of PyCA

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P37: Niobia based catalysts for oxidation reaction

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Epoxidized soybean oil and epoxidized methylesters derived by oils play an important role as building blocks for the preparation of a wide variety of consumer products, such as plasticizers and stabilizers for PVC, and components of lubricants. On the industrial scale, the epoxidation reaction is currently carried out with peroxocarboxylic acids, obtained in situ by using mineral acids as catalysts according with the Prileshajew method. However, several drawbacks of this method have been recognized over the years, such as the occurring of side reactions (ring opening and polymerization) caused by the presence of homogeneous acids in the reaction system, and the environmental pollution of the waste acids [1]. New efficient and environmentally friendly systems, such as the use of alternative oxidants and heterogeneous catalysts, may overcome these limitations. In particular, the use of hydrogen peroxide as oxidant is very attractive because the only one by-product of the reaction is water.

Recently, many niobium oxide (niobia) based materials ($\text{Nb}_2\text{O}_5/\text{SiO}_2$) were proposed for the epoxidation reaction with hydrogen peroxide, due to the high leaching stability and good water tolerance. In particular, it was demonstrated that the niobia-silica based materials, containing the same amount of Nb_2O_5 and prepared by different synthesis methods, have different catalytic activity in methyloleate epoxidation with H_2O_2 [2,3]. This singular behavior was ascribed to the presence of different species of niobium (isolated or bulk) depending on the nature of the niobium precursor and the synthesis method. Different methods of synthesis lead to the presence of different structures and surface distribution of active sites (Brønsted and Lewis sites), influencing in this way the activity and selectivity in the epoxidation reaction. Commercial alumina was reported as an efficient catalyst for the epoxidation of methyloleate with hydrogen peroxide, also in the presence of a large substrate like soybean oil [4] moreover it has recently been demonstrated that catalysts obtained supporting Nb_2O_5 on alumina are very good catalyst with high activity and selectivity [5].

The aim of this work is to study deeper the catalytic system ($\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$). In particular, the influence of the preparation conditions on catalyst structure and on catalytic performance will be examined.

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PLENARIES

PL1: Jean-Marie Lehn (University of Strasbourg, Germany)

Perspectives in Chemistry: From Supramolecular Chemistry towards Adaptive Chemistry

PL2: Akira Fujishima (Tokyo University, Japan)

TiO₂ Photocatalysis and Diamond Electrode

PL3: Sally Brooker (University of Otago, New Zealand)

Guest sensors, switches, and macrocyclic catalysts

PL4: Fraser Stoddart (Northwestern University, U.S.A.)

Emergent Applications in Nano and Supramolecular Chemistry

PL5: David A. Leigh FRS (University of Manchester, UK)

Making the Tiniest Machines

PL6: Maurizio Prato (UniTs, Italy)

Multifunctional Hybrid Carbon Interfaces

PL7: Shizhang Qiao (University of Adelaide, Australia)

Electrocatalysis for Energy Conversion Processes

PL8: Jorge Norberto Beltramini (University of Queensland, Australia)

Critical design of heterogeneous catalysts for sustainable production of chemicals and energy: current approach and emerging prospects

KEY LECTURERS

KL1A: Serena Silvi (UniBo, Italy)

A light-driven artificial molecular pump

KL1B: Ru-Shi Liu (National Taiwan University, Taiwan)

All-Inorganic Perovskite Quantum Dot Composites for Backlight Display

KL2A: Fabrizio Mancin (UniPd, Italy)

Self-organization of supramolecular receptors in the nanoparticle-coating monolayer

KL2B: Lahcène Ouahab (Université de Rennes, France)

Lanthanides-Redox Ligands for Single Molecule Magnets and Luminescence

KL3A: Nobuo Kimizuka (Kyushu University, Japan)

Photon Upconversion based on Energy Migration in Molecular Assemblies

KL3B: Minbo Lan (East China University, Japan)

Detection of reactive oxygen species in vitro and in vivo based on nanomaterials

KL4A: Jong Seung Kim (Korea University, Korea)

Antitumor Theranostics and Its Delivery Sensing

KL4B: Carol Crean (University of Surrey, Guildford, UK)

Nanocarbon and Conducting Polymer Fibre-Based Electrodes—From Energy Storage to Electrochemical Sensing

KL5A: Ho-Chol Chang (Chuo University, Tokyo)

Chemical Function based on Redox-active Ligands

KL5B: Hiroshi Kitagawa (Kyoto University, Japan)

Highly Conductive Coordination Polymers

KL6A: Ok-Sang Jung (Pusan National University, Japan)

A synthetic strategy for multi-layered Pd(II) complexes via transannular $\pi \cdots \pi$ interactions and its application as a scavenger in photoreaction

KL6B: Gaetano Guerra (UniSa, Italy)

Nanoporous-crystalline polymers and industrial innovations

INVITED LECTURES

- IL1A:** Michael Schmittel (Universität Siegen, Germany)
Multi-component nanomachinery - From rotation to catalysis
- IL1B:** Juyoung Yoon (University of Seoul, Korea)
Recent Progress on Fluorescent Probes and Activatable Photosensitizers
- IL2A:** Hoi Ri Moon (UniST, Italy)
Exploration of Gate-Opening and Breathing Phenomena in a Tailored Flexible NiII Macrocycle-based MOF
- IL2B:** Manabu Sugimoto (University of Tokyo, Japan)
Electronic-Structure Informatics for Materials Design in Nano and Supramolecular Chemistry
- IL3A:** Artur R. Stefankiewicz (Adam Mickiewicz University, Poland)
Generation Of Functional Nanostructures Via Self-Assembly Process
- IL3B:** Takayoshi Nakamura (Hokkaido University, Japan)
Supramolecular-Cation Approach for Constructing Crystalline Molecular Electronic Materials
- IL4A:** Valery V. Gorbachuk (University Kazan, Russia)
Smart recognition by macrocyclic hosts
- IL4B:** Kil Sik Min (Kyungpook National University, Korea)
Coordination complexes of tetradentate ligands: molecular magnetism and catalysis
- IL5A:** Alessandro Scarso (UniVe, Italy)
Supramolecular Approaches to Homogeneous Catalysis
- IL5B:** Ángeles Farrán (UNED, Spain)
Photoinduced Processes in Macrocyclic isoalloxazine–anthracene systems
- IL6A:** Antonella Dalla Cort (Uniroma, Italy)
Metal-salophen complexes: highly versatile scaffolds for the supramolecular design of host-guest systems
- IL6B:** Hong-Seok Kim (Kyungpook National University, S. Korea)
Sensitive and selective fluorescence OFF-ON-OFF sensor for cascade detection of Ga³⁺ cation and I⁻ anion based on pyrenesulfonamide-functionalized nanoparticles
- IL7A:** Takumi Konno (Osaka University, Japan)
Metalloligand Approach That Leads to the Creation of Non-Coulombic Ionic Solids
- IL7B:** Takehiko Yamato (Saga University)
Calixarene Based Fluorescent Chemosensors
- IL8A:** Karsten Gloe (TU Dresden, Germany)
New Heterodinuclear Zn(II)/Ln(III) Complexes of N,N'-Bis(3-alkoxy-2-hydroxybenzyl)cyclohexane-1,2-diamines
- IL8B:** Silvia Bracco (UniMib, Italy)
Molecular Rotor Dynamics in Nanoporous Architectures
- IL9A:** Enrico DalCanale (UniPr, Italy)
Supramolecular bio-sensing with cavitands: challenges in prostate cancer diagnostics and epigenetic histone modifications
- IL9B:** Jan J. Weigand (TU Dresden, Germany)
Versatile Tri(pyrazolyl)phosphanes – Application as phosphorus precursors for the synthesis of highly emitting InP/ZnS quantum dots
- IL10A:** Murray V Baker (University of Western Australia, Perth, Australia)
New Gold N-Heterocyclic Carbene Chemistry: Porphyrin-Like Gold(III) Complexes, Dinuclear Gold(II) Complexes, and Gold(I)/Gold(III) Mixed-Valence Complexes
- IL10B:** Sang Hoon Joo (UniSt, Republic of Korea)
Rational Design of Highly Active M–N/C Electrocatalysts for Oxygen Reduction Reaction
- IL11A:** Heung-Jin Choi (Kyungpook National University, Korea)
C_{3v}-Symmetric tripodal anion receptors based on trindane molecular skeleton with urea-, diamide-, urethane-, guanidine-, and triazole-recognition motifs
- IL11B:** Chengzhong Yu (University of Queensland, Australia)
Engineered Nano-adjuvants: Bridging Multiscale Molecular/Nano Structures and Immuno-adjuvanticity
- IL12A:** Kerstin Gloe (TU Dresden, Germany)
New d- and f-Block Metal Complexes with 4-Acylpyrazolones

IL12B: Maria Sarno (UniSa, Italy)

Nanomagnetite: from biomedical to environmental and energy applications

IL13A: Yoichi Habata (Toho University, Japan)

Ag⁺-Triggard pseudo-capsule assembly: A Silver Complex System Like the PPAP (Pen-Pineapple-Apple-Pen)

IL13B: Gao Feng (East China University, China)

In vitro/in vivo evaluation of nanoparticulate drug carriers

IL14A: Daniela Montesarchio (UniNa, Italy)

Targeting DNA G-quadruplex structures in vivo: towards a High Throughput Screening analysis of putative ligands

IL14B: Katsuaki Konishi (Hokkaido University, Japan)

Tiny Goldworks: Gold Clusters in the Subnanometer Regime

IL15A: Shim Sung Lee (Gyeongsang National University, South Korea)

Post-Synthetic Modification with Triple Events: Anion Exchange Coupled with Reduction and Dimerisation of Cu(II) Complex via SCSCT

IL15B: Susan E Matthews (University of East Anglia, UK)

Anti-adhesives: Future Therapy for Bacterial Infections?

IL16A: Keisuke Ohto (Saga University, Japan)

Size-discriminative allosteric extraction of alkali metals with propyl-acetic acid crossed type calix[4]arene

IL16B: Antonio Aronne (UniNa, Italy)

Ti³⁺ self-doped materials from a hybrid TiO₂-acetylacetonate gel

IL17A: Jerzy Radecki (Polish Academy of Sciences, Poland)

Electrochemical anions recognition in water using gold electrodes modified with dipodal or di-peptide anion receptor attached to dipyrromethene- Me(II) complex

IL17B: Shu-Fen Hu (National Taiwan Normal University, Taiwan)

Heteroelectrode Structure for Solar Water Splitting: Integrated Cobalt Ditetelluride across TiO₂-passivated Silicon Microwire Array

IL18A: Paul G. Plieger (Massey University, New Zealand)

Anion binding with transition metal helicates and mesocates

IL18B: Victor Teixeira da Silva (NUCAT, Rio de Janeiro, Brazil)

Renewable fuels via hydro-pyrolysis of biomass – Performance of cheaper, non-noble metal catalysts

IL19A: Shin-ichi Yusa (University of Hyogo, Japan)

Polyion Complex Vesicles with Surface Phosphorylcholine Groups

IL19B: Chun Hui Zhou (AMSC of Zhejiang University of Technology, China)

Clay Mineral Nanofiber and Nanosheet Catalysts For catalytic glycerol Oxidehydration to ACROlein and acrylic acid

IL20A: Eliana S. Da Silva (LSRE-LCM, Universidade do Porto, Portugal)

Bio-inspired photocatalytic hybrid materials for sustainable hydrogen production

IL20B: Karna Wijaya (Gadjah Mada University, Indonesia)

Nanocatalyst of ni-al₂o₃-bentonite for hydrocracking of palm oil into biofuel

IL21A: Baojian Shen (CNPC, China University of Petroleum, China)

Effort on the promotion of iron sulfide to an efficient hydrodesulfurization catalyst

IL21B: Shinya Hayami (Kumamoto University, Japan)

Tunable Pressure Effects in Graphene Oxide Layers

ORAL COMMUNICATIONS

O1A: Gatiatulín Askar (Kazan Federal University, Russia)

Supramolecular Interactions of Solid Cyclodextrins with Guest Vapors

O1B: Gianluigi Albano (UniPi, Italy)

Solid-state optical and electrical properties of new chiral oligothiophenes: the central role of supramolecular organization

O2A: Michele Assfalg (UniVr, Italy)

Identification of specific noncovalent interactions between proteins and nanoparticles based on site-resolved NMR spectroscopy

O2B: Marco Villa e Paola Ceroni (UniBo, Italy)

Metal Ions Turn-on Phosphorescence Sensors in Water With Concomitant Self-Assemblies

O3A: Sébastien Tilloy (University of Artois, France)

Biphasic aqueous hydrogenation catalyzed by ruthenium nanoparticles promoted by fatty acid-modified cyclodextrin

O3B: Domenica Musumeci (UniNa, Italy)

Fluorescently-labeled TBAs conjugated to nanoparticles for capture or activity-control of thrombin

O4A: Sandra S. Nurtila (University of Amsterdam, Holland)

Porphyrin-edged [M4L6]8+ capsules for cage controlled catalysis

O4B: Noelia Caballero-Casero (University of Córdoba, Spain)

Restricted-access supramolecular solvents for biomonitoring of polycyclic aromatic hydrocarbons with mosses

O5A: Margherita De Rosa (UniSa, Italy)

Supramolecularly organocatalyzed C-C bond formation under "on-water" conditions or inside nanocavities

O5B: Brigida Silvestri (UniNa, Italy)

Silica-Eumelanin Hybrid Nanoparticles Engineered by Covalent Conjugate Polymerization

O6A: Marta Da Pian (UniVe, Italy)

Pillararenes: a mechanistic study of a cation templated synthesis and catalytic application in reaction occurring in organic media

O6B: Stefania De Luca (CNR, Italy)

A biocompatible chemical process to prepare hyaluronan based material able to self-assemble into stable nano-particles

O7A: Stefano Tommasone (University of Birmingham, UK)

Glycan recognition with benzoboroxole-based sensor platforms

O7B: Sun Xiaohuan (UniPd, Italy)

Chemosensing control of monolayer-protected gold nanoparticles

O8A: Chiara Biagini (Uniroma1, Italy)

Carboxylic Acids as Chemical Fuels for the Cyclic Operation of a Catenane Based Molecular Switch: Tuning the Motion Rate

O8B: Alvaro Martínez (UniPd, Italy)

Selective nanoparticle-protein interactions. Towards nanoproteomics

O9A: Simone Albano (CNR, Italy)

Formation of Imidazo[1,5-a]pyridine Derivatives Due to the Action of Fe²⁺ on Dynamic Libraries of Imines

O9B: Valeria Caponetti (UniBo, Italy)

Self-assembling supramolecular structures as stimuli-responsive systems for sensing pH and anions in water

O10A: Sébastien Noël (Université Lille Nord de France, France)

An efficient Ru NPs stabilizer with a cyclodextrin based polyammonium polymer for the hydrogenation of unsaturated compounds in aqueous medium

O10B: Daniel J. Fanna (Western Sydney University, Australia)

Ratiometric Optical Sensors for the Visible Detection of Cu(II) Ions in an Aqueous/Methanol Mixture

O11A: Nicola Borbone (UniNa, Italy)

Design of tailored DNA G-wire nanostructures by self-assembling of short G-rich oligonucleotide incorporating a 3'-3' inversion of polarity site

O11B: Francesca Accioni (University of Córdoba, Spain)

Supramolecular solvents based on Hexanol/Tetrahydrofuran for the forensic determination of amphetamine derivatives in a comprehensive pool of biological matrices

O12A: Angelo Taglietti (UniPv, Italy)

Inorganic nanochemistry for antibacterial applications: the heat is on for silver and gold

O12B: Kibalnikova O.V. (Saratov State University, Russia)

Kinetic model heterogeneous reaction self-assembly on nanocomposit sorbent and them peculiarity

O13A: Maria Cristina Cassani (UniBo, Italy)

Supported nanoparticles for catalysis and biomedical applications

O13B: Eduardo Schiavo (UniNa, Italy)

Doped graphene-metal interfaces as ORR and OER electrocatalysts for fuel cells applications

O14A: Lei Li (University of Petroleum, China)

A novel secondary pore-forming agent: The catalytic performance of vanadium in zeolite Y post treatment

O14B: Bahram Ghanbari (University of Technology, Iran)

Design of coordination framework from O2N2-diaza-crown macrocyclic ligand substituted with pyridine side arms

O15A: Masih Rashidi (University of Queensland, Australia)

Catalytic Hydrogenation of Lignin Model Compounds Using TiN Supported Copper Nanoparticles

O15B: Houxiang Sun (University of Petroleum, China)

Acidity tuning by tin isomorphous substitution of aluminium in AlPO4-5 and its application in the hydrodesulfurization reaction

POSTERS

P1: Noelia Caballero-Casero (University of Córdoba, Spain)

Single-step supramolecular solvent-based sample treatment for the control of Ochratoxin A in spices subjected to EU regulation

P2: Lorenzo Casimiro (UniBo, Italy)

Supramolecular Tuning of Photochromism in Mechanically Interlocked Molecules

P3: Claudia Cirillo (UniSa, Italy)

New nanohybrid for dehalogenation and contemporaneous removal of halocarbon from water

P4: Aniello Costantini (UniNa, Italy)

Immobilization of β -glucosidase onto mesoporous wrinkled silica nanoparticles for cellobiose hydrolysis

P5: Assunta D'Amato (UniSa, Italy)

Enantioselective alkylation of 2-aryl-2-oxazoline-4-carboxylic acid esters catalyzed by cyclopeptoids

P6: Nicola Alessandro De Simone (UniSa, Italy)

Calix[6]arene threading with weakly interacting tertiary ammonium axes: generation of chiral pseudorotaxane architectures

P7: Paolo Della Sala (UniSa, Italy)

Recognition of Pyridinium Guests by [8]Cycloparaphenylene Host

P8: Valeria Di Sarli (CNR, Italy)

Regeneration Performances of a Ceria-Coated Diesel Particulate Filter

P9: Antonio Fabozzi (UniNa, Italy)

Polyfunctional ligands for supramolecular assemblies of Mn(II) catalysts in aqueous systems

P10: Katarzyna Fidecka (UniMi, Italy)

Halloysite nanotubes as innovative carriers for (bio)organic molecules

P11: Muhammet Gabdul Khaev (Kazan Federal University, Russia)

Controlled selectivity of guest inclusion by calixarene derivatives

P12: Fumiya Kobayashi (Kumamoto University, Japan)

Ferromagnetic Behaviors of Wheel-Type Heterometallic Clusters

P13: Sotaro Kusumoto (Kumamoto University, Japan)

Synthesis and characterisation of dimeric cubane Ni(II) capsules

P14: Pellegrino La Manna (UniSa, Italy)

Resorcin[4]arene-Based Hexameric Capsule as Nanoreactor for 1,3-Dipolar Cycloadditions

P15: Luca Leoni (UniRoma1, Italy)

Halides binding with uranyl-salophen receptors: unambiguous evidence of anion- π interactions in solution and in the solid state

P16: Daniela Maggioni (UniMi, Italy)

Superparamagnetic iron oxide nanoparticles functionalized by peptide nucleic acids

P17: Maria Marzano (UniNa, Italy)

Studies on G-rich Tetra-End-Linked Oligonucleotides Forming Dimeric G-Quadruplex Structures with in Vitro anti-HIV Activity

P18: Chiara Parise (UniBo, Italy)

Supported gold nanoparticles catalysts for alkynes hydroamination

P19: Marco Perfetti (UniNa, Italy)

Poly(ethylene-co-vinyl alcohol)-based microgels prepared through salting-out: phase behavior and structural properties

P20: Chiara Platella (UniNa, Italy)

Conformation-sensitive detection of secondary structure-forming oligonucleotides on nanoporous glass beads

P21: Eleonora Ponticorvo (UniSa, Italy)

Core-Shell Mo₂C/MoO₃ Nanowires for HER

P22: Carmela Tania Prontera (UniNa, Italy)

Designing dopamine-based electroluminescent complexes for innovative melanin-inspired OLED devices

P23: Claudia Riccardi (UniNa, Italy)

Conformational behaviour and molecularity studies of natural and modified AS1411 aptamers

P24: Rosaria Schettini (UniSa, Italy)

New calixarenes act as cation recognizer in asymmetric phase-transfer catalysis

P25: Carmela Scudieri (UniSa, Italy)

Highly sensitive electrochemical detection of Arsenic (III): Fe₃O₄ nanoparticles covered graphene oxide

P26: Rebecca Severinsen (Massey University, New Zealand)

Synthetic Complexes of new Quino[7,8-h]quinoline Derivatives

P27: Yoon-Bo Shim (Pusan National University, Republic of Korea)

Synthesis and application of polymeric zinc organic framework derived zinc oxide composite with conducting polymer

P28: Marina Sicignano (UniSa, Italy)

Switchable diastereoselective Michael addition catalyzed by crown ethers

P29: Hiroshi Takehira (Kumamoto University, Japan)

Semiconducting Property of Reduced Graphene Oxide by Using Various Reduction

P30: Vincenzo Vaiano (UniSa, Italy)

ZnO nanoparticles coupled with up-conversion phosphors for the removal of methylene blue under visible light irradiation

P31: Hunter (University of Cambridge, UK)

Polarisation of H-bonds on solvation equilibria in alcohols

P32: Marco Stoller (Uniroma1, Italy)

Novel production of core-shell N-doped magnetic nanoparticles of Titania (FM/N-TiO₂) by means of a spinning disk reactor

P33: Haesik Yang (Pusan National University, Korea)

Ultrasensitive Electrochemical Immunosensor Using a Gold-Nanocatalyst Label Mediating Outer Sphere-Reaction-Philic and Inner-Sphere-Reaction-Philic Species

P34: Maali Saad Mokhtar (Sultan Qaboos University, Sudan)

The Binding Interaction of Imazapyr with Cucurbit[n]uril (n=6-8): Combined Experimental and Molecular Modeling study

P35: Yojiro Kimura (Kyoto University, Japan)

Synthesis and Property of Nickel Dithiolene Complex with Herringbone Structure Based on Lone Pair- π Interactions

P36: Masaki Donoshita (Kyoto University, Japan)

Phase transition behavior of a [2-pyrrolidone]-[chloranilic acid] molecular complex with hydrogen-bonded straps

P37: Martino Di Serio (UniNa, Italy)

Niobia based catalysts for oxidation reaction