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BOOK OF ABSTRACTS

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2D Polymers: Synthesis in single crystals and on water

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Two-dimensional materials (2DM) are sheet-like entities and of great interest for their manifold properties. Famous representatives are graphene, boronitride or molybdenum disulfide. 2DMs are often provided by nature or are obtained under harsh conditions. Such conditions exclude the synthetic arsenal of organic chemistry to be used for rational sheet creation and sheet structure variation on a molecular level.

Recently it was shown that covalent monolayer sheets can be accessed at room temperature by genuine two-dimensional polymerization of organic monomers applying simple protocols.¹ They include spreading of monomers at an air/water interface into long-range ordered reactive monolayer packings or crystallizing them into layered single crystals, followed by light-induced growth reactions. These growth reactions result in macroscopic sheets of considerable mechanical strength, whose structures resemble molecular fishing nets (2D polymers).

The contribution addresses strategic, synthetic and analytical issues and provides a view into the future.

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1D and 2D Nanocarbon Materials for Solar Energy Conversion Schemes

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Carbon is the key to many technological applications that have become indispensable in our daily life. Altering the periodic binding motifs in networks of sp^3 -, sp^2 -, and sp -hybridized C-atoms is the conceptual starting point for a wide palette of carbon allotropes. To this end, the past two decades have served as a test-bed for measuring the physico-chemical properties of low-dimensional carbon with the advent of fullerenes (0D), followed in chronological order by carbon nanotubes (1D), carbon nanohorns, and, most recently, by graphene (2D). These species are now poised for use in catalysis.

Expanding global needs for energy have led to a significant effort to develop alternatives to fossil fuels. While alternative sources for energy are already in use, they comprise a small percentage of the energy demands needed to carry us through the 21st century. No single source will solve the global needs, but the development of photocatalysis has vast potential as a point-of-use power source.

I report on our efforts regarding a unifying strategy to use the unprecedented charge transfer chemistry of 0D fullerenes, the ballistic conductance of 1D carbon nanotubes, and the high mobility of charge carriers in 2D graphene, together in a groundbreaking approach to solving a far-reaching challenge, that is, the efficient use of the abundant light energy around us. For example, hybrid materials based on nanocarbons and metaloxides are the ideal design for realizing breakthroughs in high photon conversion efficiencies suitable for the catalysis of water.

Covalent organic frameworks (COFs): Extending organic chemistry into two and three-dimensions.

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As Nobel laureate Roald Hoffmann pointed out in 1993, the field of synthetic organic chemistry with structures that extended “infinitely” into 2-dimensions and 3-dimensions were non-existing at that time¹. The challenge has been in developing crystallization and linkage chemistry for such synthetic targets. This situation changed in 2005 when our group created the first 2D covalent organic frameworks (COFs)², followed by the synthesis of the first 3D COFs in 2007³, thereby extending the field of organic chemistry beyond discrete molecules (0D) and polymers (1D). Because these materials are entirely constructed from strong covalent bonds (C-C, C-O, C-B, and B-O), they have high thermal stability (400 to 500 °C) and extremely low density (0.17 g/cm³). Within a short period of 5 years after the first report of COFs, our group has established their permanent porosity², their reticular design that pushed them into the mesoporous range⁴, their applications in hydrogen⁵, methane⁶, ammonia⁷, and carbon dioxide⁶ storage. In terms of linkages, in addition to the boroxine and boroeester linkages of the 2D and 3D COFs mentioned above, we also demonstrated within that early period the use of borosilicate linkages⁸, imine linkages⁹, and hydrazine linkages¹⁰. The successful determination of the structure of COF-320 directly from single-crystal samples in 2013 using 3D rotation electron diffraction (RED) is an important advance in the development of COF chemistry¹¹. We also showed how reticulating molecular catalysts into COFs can produce porous structures capable of capturing carbon dioxide and converting it into useful feedstock chemicals¹². This cobalt porphyrin based COF has the best performance of any homogenous or heterogeneous catalyst for conversion of carbon dioxide to carbon monoxide. Recently, we showed how molecular weaving could be accomplished in COFs to make the first truly molecularly woven material in the history of science¹³. This discovery combines the porosity and robustness of frameworks with mechanically deformable materials, thus has the potential of revolutionizing the way we make materials. In this presentation, efforts to make large single crystals for x-ray diffraction and future directions will be discussed.

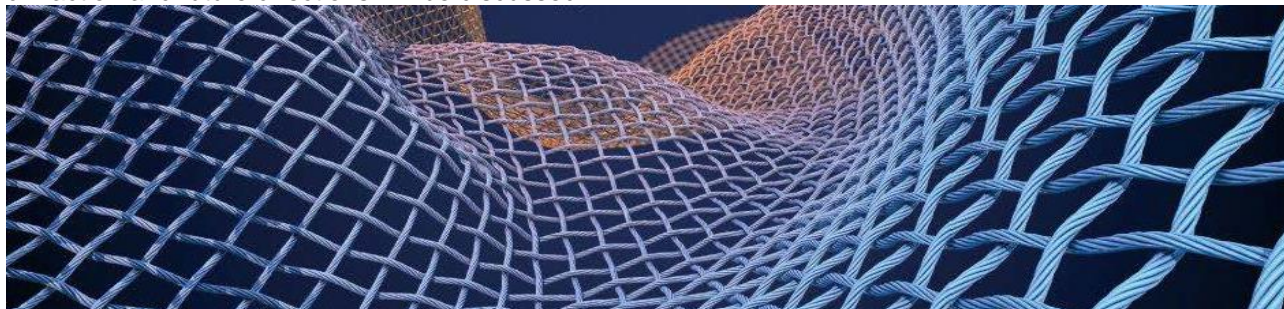


Figure 1. Molecular weaving concept

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Defect-free functionalized magnetic 2D coordination polymers

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Chemical functionalization of two-dimensional materials is an important approach to tune their stability or functionalities.¹ Current post-synthetic methodologies typically result in defective materials with no control of the position of the functional molecules. Two-dimensional hybrid organic-inorganic polymers are an emerging group of materials analogues of graphene², whose molecular composition allows, by chemical design, a surface tunability and the presence of various functionalities.

Here we present a new family of this type of hybrids materials based in magnetic Fe(II) centres, denoted **MUV-1-X** (MUV = Materials of the University of Valencia, X = H, Cl, Br, CH₃, NH₂),³ which can be easily exfoliated mechanically down to the monolayer retaining the magnetic properties. The molecular nature of these crystalline solids based on coordination chemistry allows a pre-synthetic functionalization, yielding an homogeneous functionalized surface, and permits to tailor the physical properties of the layers, exemplified with the tuning of the wettability (Figure 2). Finally, the high robustness and chemical stability of the exfoliated monolayers has enabled us to study the mechanical properties of these molecularly-thin layers.

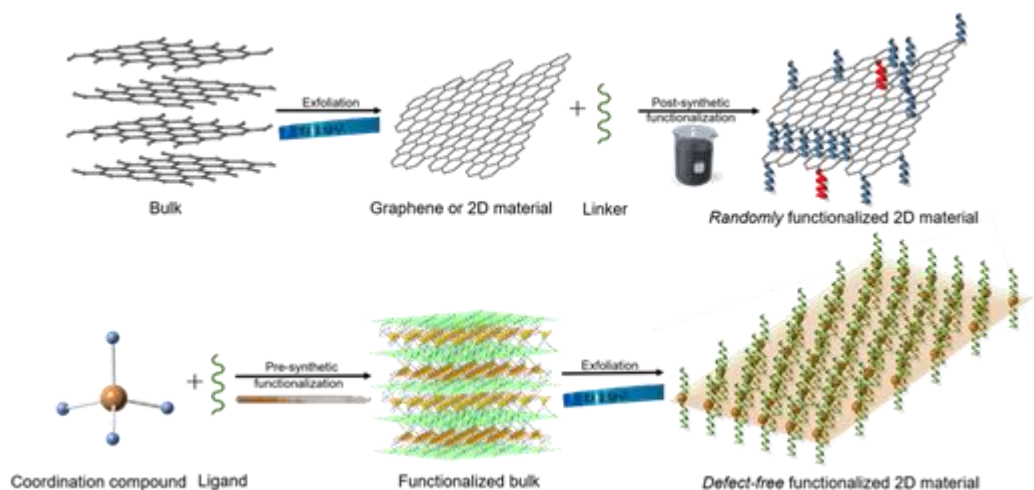


Figure 1. Schematic representation of the covalent functionalization in a post-synthetic manner (top), exemplified with graphene, and the pre-synthetic functionalization used in this study (bottom).

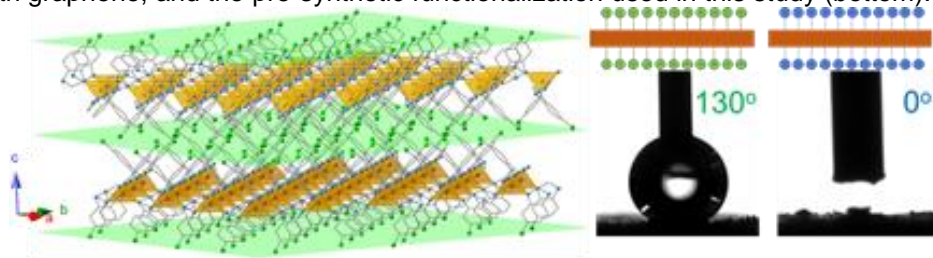


Figure 2. Crystal structure of **MUV-1-X** and the surface functionalization from hydrophobicity (X = Cl) to hydrophilicity (X = NH₂).

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A Wavy and Highly Crystalline 2D Covalent Organic Framework

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Two-dimensional organic frameworks are a class of crystalline porous polymers that enable controlling the pore sizes, surface areas and channel functionalization. In general 2D-COFs are planar, but in recent years the effect of introducing non-planar monomers have received increasing attention.

In this lecture, the synthesis of a new wavy 2D-COF (Marta-2D-COF-1) will be discussed. This wavy structure is the result of the presence of highly complementary twisted polycyclic aromatic hydrocarbons in the framework's nodes.

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Charge transport in Ultrathin Films of Metal-Organic Frameworks

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Metal-Organic Frameworks (MOFs) are porous coordination polymers built from the interlinking of metal clusters and organic linkers. MOFs have already demonstrated great potential in gas storage, separations, sensing and catalysis. Nowadays there is an increasing interest in developing an advanced generation of electronic and optoelectronic devices that make use of electrically active MOFs to exploit combination of electrical conductivity and porosity.^[1] However, this type of applications preferably requires the processing of these bulk materials as high-quality nanometric thin films with exquisite control over several parameters that are important for device performance like morphology, density, crystallinity, roughness and orientation. Research involving electrically conductive MOFs is just starting to blossom,^[2] but investigation of the electrical conductivity of MOF thin films at the nanoscale (<100 nm) is still challenging due to the synthetic difficulties in producing smooth films with homogenous coverage and low roughness with nanometric accuracy. We will comment on the use of bottom-up techniques to produce homogeneous ultrathin films of MOFs with exquisite control over their nanometric thickness. Electrical properties of these ultrathin films can be then analysed in a vertical configuration by using the hanging-drop electrode technique^[3] or by integration into MOF-FET architectures for measuring lateral charge transport^[4] and investigate on the origin of their chemoresistive response.^[5]

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Water-based and Inkjet printable 2D-Inks: From formulation engineering to all-printed heterostructures

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The isolation of various two-dimensional (2D) materials allows to combine them into heterostructures. Such a concept can be used to make functional devices. Solution processing of 2D materials [1] allows simple and low-cost techniques such as inkjet printing [2, 3] to be used for fabrication of heterostructure of arbitrary complexity. However, the success of this technology is determined by the nature and quality of the inks used. Furthermore, these formulations must be suitable for all-inkjet printed heterostructure fabrication - the remixing of different 2D crystal gives rise to uncontrolled interfaces, resulting in poor performance and lack of reproducibility of the devices.

In this work we show a general formulation engineering approach to achieve highly concentrated, and inkjet printable water-based 2D crystal formulations, which also provide optimal film formation for multi-stack fabrication [4]. Examples of all-inkjet printed heterostructures, such as arrays of photosensors [4], logic memory devices [4], strain sensors [5] and capacitors [6] will be discussed. In particular the capacitors are used to demonstrate all-2D fully printed band pass filters and graphene-based field-effect transistors.

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Dynamic Covalent on-surface Chemistry at the solid-liquid interface

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Single-layered covalent organic frameworks (sCOFs) have attracted great attention due to the appealing properties anticipated for graphene-like two-dimensional (2D) polymers.¹ Much effort has been focused on reaching high-quality, large-scale sCOFs; and impressive results have been achieved in the last years. However, controlling the topology, size, shape and dispersity of the material is still difficult. In order to tackle this challenge, a better understanding of the on-surface reaction is needed.

Here, the effect of covalently modified graphitic surfaces on the formation of sCOFs at the solid-liquid interface will be presented, using scanning tunneling microscopy (STM).^{2,3} The impact of variable density of grafted aryl species will be tested on the on-surface synthesis of DCC-based 2D-sCOFs. The grafted aryl species that act as defects provide steric barriers to the progress of the on-surface reactions, and can be locally removed to restart the 2D polymer healing process. This unique strategy provides a general approach to study in situ this dynamic covalent on-surface chemistry (Figure 1).⁴

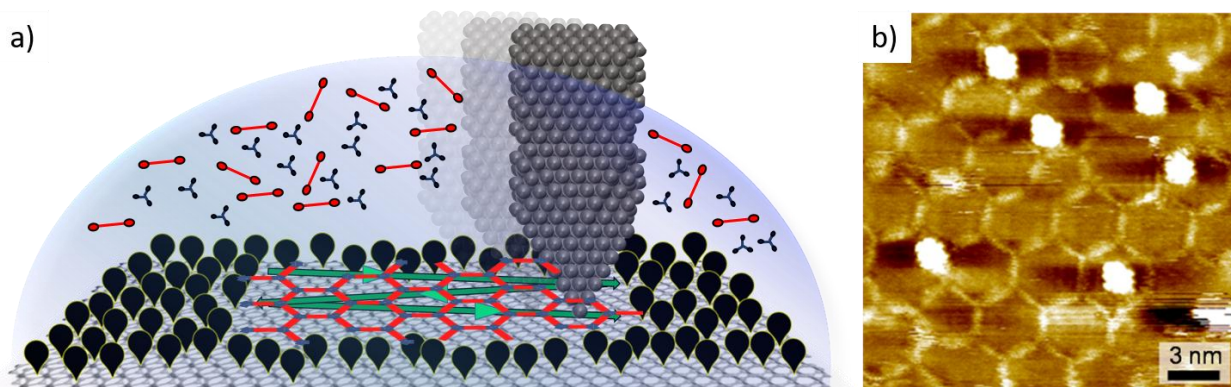


Figure 1. On-surface COF formation on covalently modified substrates. (a) Schematic model of the followed strategy. (b) STM image of a imine-based sCOF on aryl-grafted HOPG.

Acknowledgements

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Engineering of two-dimensional highly crystalline free-standing polymer networks based on calixarenes

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Two-dimensional (2D) organic networks, fabricated with molecular precision via bottom-up methods, receive rapidly increasing attention as tuneable matrices to investigate host-guest interactions in a wide range of applications.¹ Recently, we presented the first crystalline coordination network of propyl and carboxy functionalized calix[4]arene (**1**) as it forms a Cu²⁺ coordinated network at the air-water interface.² In our more recent work, we replaced the carboxy groups with methyl cyano functional groups: *p*-methyl cyano-calix[4]arene (**2**) forms a free-standing and crystalline 2D supramolecular organic network (SON) in absence of any organic/inorganic linkers.³ In our in-depth investigation, we identify this system as the first which is stabilized by only weak dipole-dipole interactions. The presence of the methyl amino functional groups at the upper rim of calix[4]arene leads to the formation of a covalent organic network at the interface. Large mono-crystalline networks have been assembled at the air-water interface and have been transferred onto solid substrates. Analysis has been performed by Brewster angle microscopy, molecular-resolution atomic force microscopy (AFM), surface ellipsometry, contact angle measurements, X-ray photoelectron and near-edge X-ray absorption fine structure spectroscopy and transmission electron microscopy.

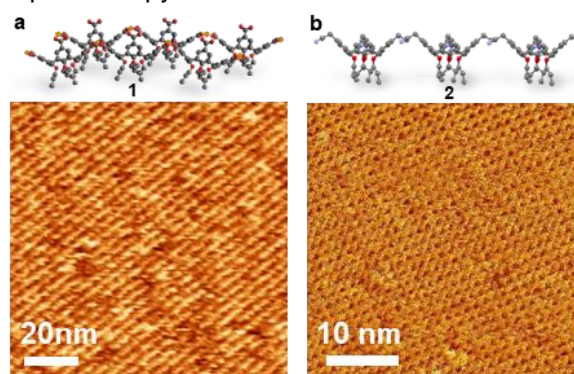


Figure 1. **a**, High-resolution AFM image of the crystalline coordination network of **1** and its corresponding molecular model. **b**, Molecular-resolution AFM image of the SON of **2** and its corresponding molecular model.

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Constructing surface-confined ordered molecular architectures from a hydroxamic acid linker molecule

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Hydroxamic acids are biologically relevant functional groups with high potential in supramolecular chemistry. However, unlike carboxylic acids they are far less investigated in this regard and hitherto unexplored when confined in a two-dimensional environment. Here we show that a simple ditopic linker functionalized with hydroxamic acids self-assembles to different two-dimensional networks at noble metal surfaces. By means of scanning tunneling microscopy, atomic force microscopy and density functional theory calculations, we unveil the molecular configurations underlying the intricate interfacial assemblies. It is concluded that hydroxamic acids are versatile building block units capable of forming nodes encompassing from two to six molecules. On both Au(111) and Ag(111) surfaces regular structures are achieved by densely packed straight nodes between 2 molecules. Additionally, on Ag(111) 4-fold nodes with varying opening angles result in regular porous networks. The latter include an aesthetically appealing network featuring hexagrams and a square-like network with chiral nodes. Thus we conclude that the hydroxamic acid guided supramolecular assembly is offering a rich playground and it is sensitive to the template used, thus providing access to novel intricate surface tessellations.

Bottom-up Approach to Graphene Materials by Combining Organic Synthesis with Surface Science

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The development of atomic force microscopy (AFM) and scanning tunnelling microscopy (STM) with functionalized tips has allowed the visualization of molecules adsorbed on different surfaces with submolecular resolution. This advance, together with the possibility to induce on-surface chemical reactions, opens up exciting applications in chemistry and materials science.

In this talk I will comment on how these breakthroughs in AFM/STM, in combination with organic synthesis, allowed us to obtain and characterize graphene-like nanostructures. In particular, I will include recent examples on the synthesis of graphene molecules (Fig 1A² and 1B³), the on-surface preparation of graphene nanoribbons (GNRs) and the bottom-up construction of nanoporous graphenes (Fig 1C).⁴

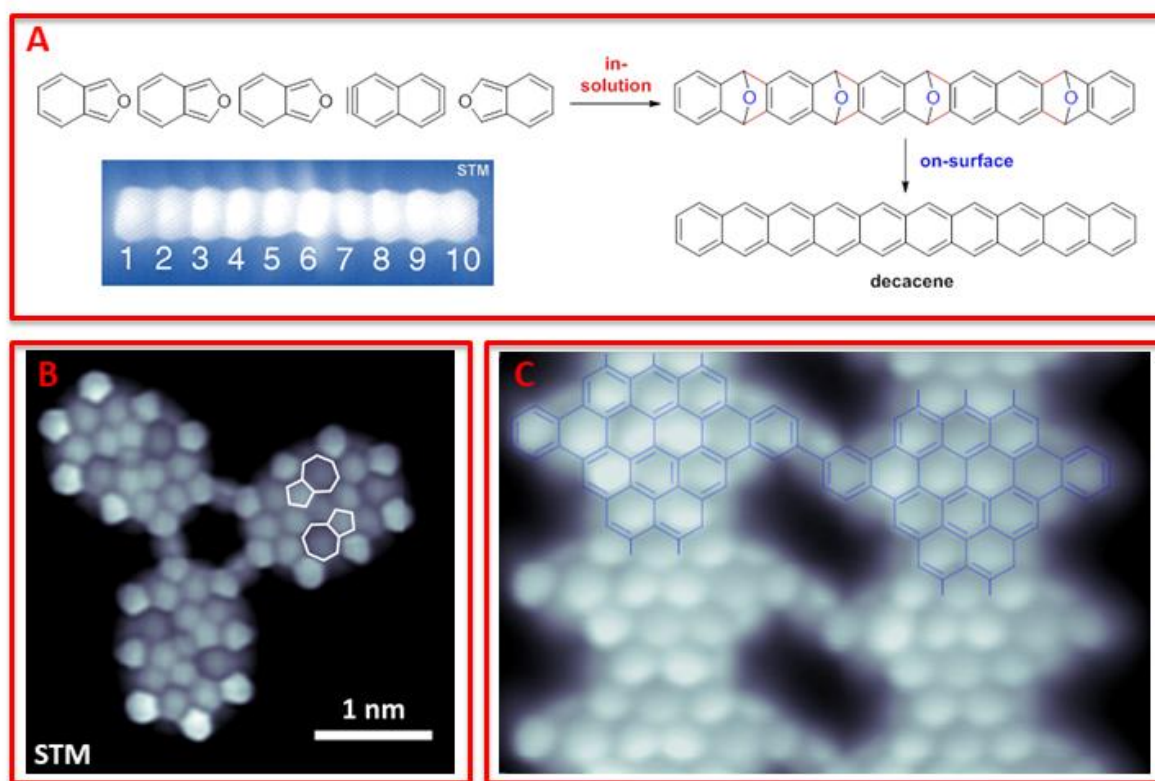


Figure 1. Selected examples of graphene materials obtained by combining in-solution and on-surface chemistry

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π -Electron Conjugation in 2D Polymers

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One-dimensional conjugated organic polymers are important optoelectronic materials with tunable properties and myriads of applications. Two-dimensional (2D) inorganic materials, such as graphene, display a spectrum of unprecedented properties that fundamentally impact the solid state physics. It would thus be intriguing to be able to combine the *tunability* of an organic polymer and 2D electron confinement in a single material – a 2D π -conjugated polymer.^[1] The lecture will discuss how a 2D polymer network can be assembled from π -functional building blocks, and how the structure and connectivity of the latter define the properties of the material. It will present our approaches to growing such materials via surface-templated polymerization^[2] and through dynamic covalent polymerization in solution.^[3] The novel properties resulting from the π -electron delocalization (conjugation) in 2D systems will be also be discussed.

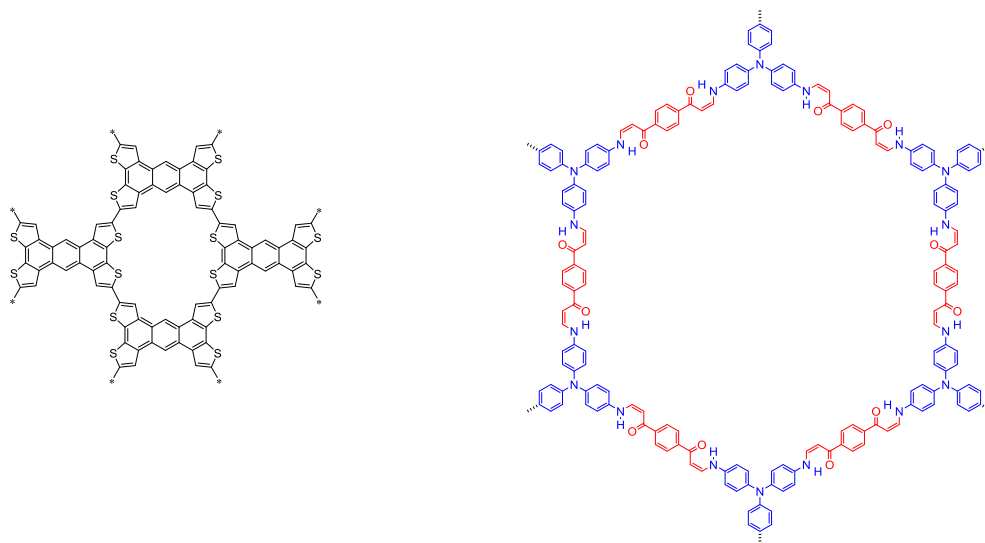


Figure 1. Structure of some of discussed 2D polymers

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Molecular spectroscopy in a solid-state device

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Modern technological devices based on organic semiconductors strongly rely on the energy position of the molecular orbitals as well as in their associated energy gap¹. So far there is not any reliable technique that can determine the transport energy gap in the bulk of an organic semiconductor². This often results in the adoption of inadequate substitutes, such as the fundamental, first-principles, optical or interface gaps². In this work, we demonstrate for the first time a non-destructive in-device approach based on in-device molecular spectroscopy (i-MOS)^{3,4,5} technique that allows both mapping the relative energy of molecular orbitals and extracting the transport energy gap of a molecular semiconductor⁶. Moreover, through the injection of energetic electrons into the organic semiconductor, we can access and manipulate unprecedented electronic transport regimes, such as negative differential resistance (NDR)⁷ arising from a Marcus inversion⁸ phenomenon⁶. Our results demonstrate that i-MOS is an immensely powerful spectroscopic technique for organic electronic community as well as a tool for exploring new charge injection physics in organic semiconductor with novel NDR possibilities for electronic circuiting⁸.

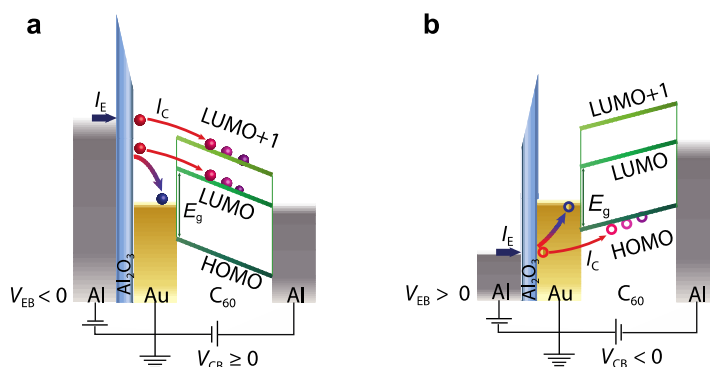


Figure 1. In-device molecular spectroscopy (i-MOS) operation under a negative emitter-base bias, $V_{EB} < 0$ V (a) and $V_{EB} > 0$ V (b).

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Multifunctional hybrid materials based on conjugated porous polymer for solar fuel production

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The growing emission of CO₂ and its contribution to climate change have stimulating research activities towards the utilization of CO₂ as carbon source for the production of fuels and chemicals.¹ The development of artificial photosynthesis procedure for the reduction of CO₂ with H₂O to produce solar fuels as well as the partial reaction to produce hydrogen from water are one of the most promised areas at the same way that suppose a challenge due to the high stability of the CO₂ molecule.² In this sense, a large number of semiconductors have been used as heterogeneous photocatalyst among which TiO₂ is one of the most common.^{3,4}

Herein, we bring forward new organic-inorganic hybrid with the aim of obtain a best performance in artificial photosynthesis process. As organic counterpart we propose the use of conjugated porous polymers (CPPs) which have been used until data as photocatalyst in the hydrogen production from water.⁵ The designed CPPs, are based on dithiophene unit, BOPHY moieties, among others, which provide to the whole polymer with enough conductivity and the adequate redox potentials for both hydrogen production and CO₂ photoreduction. This metal free approach shows up 40-fold increase in the hydrogen production from water/mehtanol mixture and up to 9-fold increase in the photoreduction of CO₂. Besides, a multidisciplinary effort at different timescales has been developed in order to determine the structure- activity. So, the charge transfer pathways (Figure 1) and the chemical mechanism have been established.

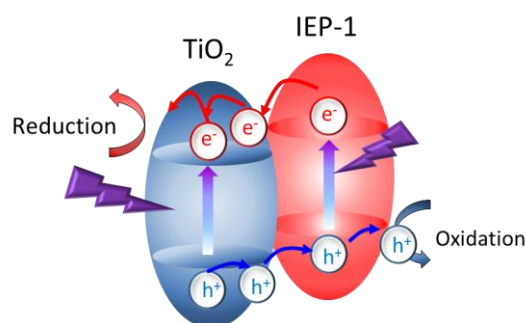


Figure 1. Schematic charge transfer interfaces in an organo-inorganic hybrid heterojunction

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Hierarchical nanostructures in multi-functional electrocatalysts for the artificial leaf

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Nanomaterials are nowadays at the forefront of materials science research. The design and realization of hierarchical nanoarchitectures, in which selected components are arranged to leverage their expected mechanistic functions are obtaining a wide range of applications, from the aerospace industry to bio-medicine, and as benchmarks for many catalytic reactions.

Carbon-based nanomaterials have been the main actors of nanotechnology since their very first discovery, and their unique morphological/electronic properties are particularly suited to be used in electrocatalytic applications. CNTs and graphene are indeed ideal supports in catalysis as they have an optimal electronic conductivity and provide percolation routes for charge transfer reactions to occur. The integration of nanocarbons into hierarchical materials is an effective strategy to further boost the potentiality of nanostructured catalysts. The generation of multiple interfaces in such hierarchical assemblies is responsible for their exceptional activity, whose origin is however only rarely understood.

We will show that, once embedded within nanoarchitectures made of multi-wall carbon nanotubes or graphene and metal oxide shells, the catalytic properties of nanoclusters (1,2,5) and metal nanoparticles (3,4) can be dramatically enhanced according to mechanisms which likely involve the concerted and synergic participation of all component building blocks in the electrocatalytic steps.

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Chemical Functionalization of Synthetic Carbon Allotropes and the Advent of Black Phosphorus

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Chemical functionalization of new C-allotropes is of fundamental interest and opens the door to unprecedented materials applications. In principle, the physical and chemical properties of fullerenes, carbon nanotubes (CNTs) and graphene are related to each other, although their levels of development vary considerably. In order to efficiently explore the reactivity of the less developed CNTs and especially that of graphene it is our goal to provide a unifying approach for the chemistry of all three new carbon allotropes. The fullerenes present the first family of synthetic carbon allotropes. Since their availability in macroscopic quantities numerous investigations with respect to their physical characterization and chemical functionalization have been carried out. CNTs - the second new family of C-allotropes - exhibit at least the same potential for unprecedented applications. Their chemistry, however, is much less developed. Although many protocols for covalent and non-covalent CNT functionalization have been published there are still many fundamental problems to be solved. This includes *inter alia* the highly selective functionalization of metallic- or semiconducting SWNTs, the high throughput isolation of SWNTs with single helicity, the development of general concepts allowing for tunable doping of individualized tubes with single helicity or least defined transport characteristics (metallic – semiconductive). Finally, the youngest representative in the list of new C-allotropes is graphene and the exploration of its chemistry has just begun to start. So far only investigation on the functionalization of defect rich graphene oxide (GO) but not intact graphene itself have been published. Compared to the various flavours of CNTs (broad variation of helicities, single walled, multi walled) graphene is a much more uniform material. This will facilitate the development of its chemistry considerably. We will present a series of new results of covalent and non-covalent functionalizations of fullerenes, carbon nanotubes and graphene. Moreover, we will present first results on the chemical functionalization of other 2D-materials such as black phosphorus (BP) and molybdenum disulphide MoS₂.

Predicting the Properties of Mono- and Bidimensional Covalent Organic Frameworks

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Computer modelling has become a fundamental tool to understand and rationalize new nanomaterials. We will present, with a **special emphasis in experiment and in a fully non-technically manner**, how models can be used to understand and predict quantitatively the electronic properties of 1D and 2D Covalent Organic Frameworks (COFs) based on polyaromatic building blocks¹²⁻². In addition, the advantages, difficulties and shortcomings of computer models and how modelling can help with the characterization of these systems will be highlighted.

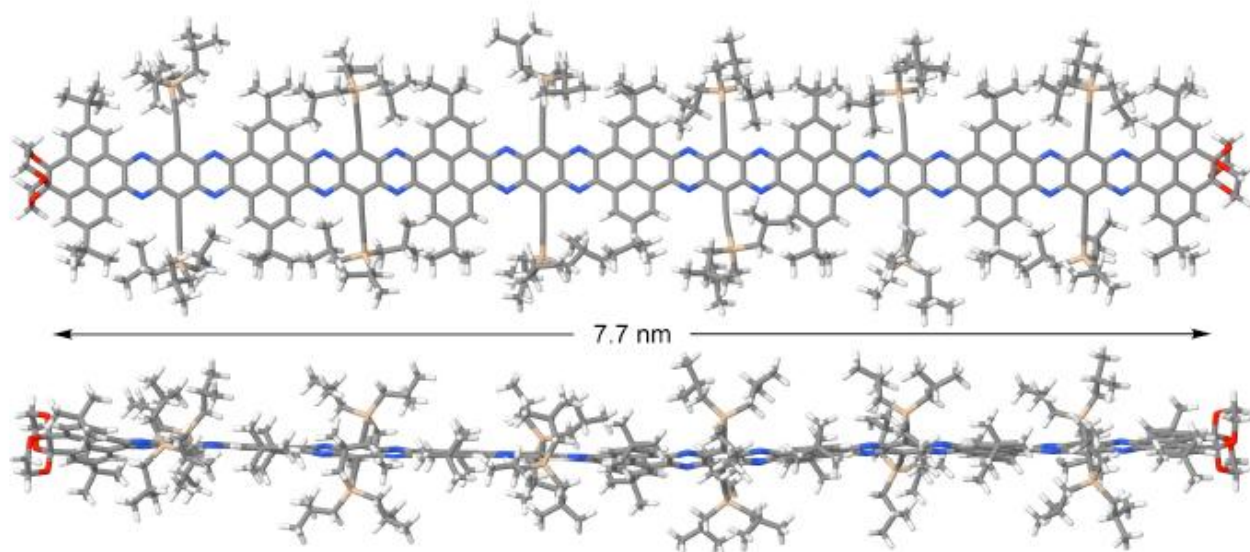


Figure 1. Monodisperse soluble carbon nanoribbon made from iterative synthesis.

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Engineering controlled reaction-diffusion environments for materials synthesis

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Still now, systems present in nature that feature non-equilibrium states continue to inspire researchers in their quest to engineer materials with advanced functionalities. For example, appealing biological systems such as proteins or cells (that undergo sophisticated functions, e.g. molecular recognition or cell division, respectively) are some inspiring examples considered to design new functional artificial systems. However, these biostructures feature non-equilibrium states not only based on their organization at the molecular level; it has been demonstrated that the control diffusion and reaction of chemical species with them is key to assess their extraordinary degree of sophistication. For example, the controlled diffusion of intracellular calcium atoms in confined spaces, and their reaction with proteins and/or cells, has proved to have a regulating effect in vital cellular functions like motility, cell growth, or fertilization. Therefore, we believe that these reaction-diffusion (RD) processes found in nature should be a source of inspiration to gain new insights in both: i) the isolation and study of non-equilibrium states and ii) for the preparation of advanced functional materials.¹

In my talk, I will show how the laminar flow regime present in microfluidic devices enables a fine control over reagents mass transfer in time and space, with mixing only based on reagents diffusion (i.e. controlled RD processes are established), which is in sharp contrast to the situation present in conventional flask synthesis. In common synthetic methods, the diffusion of reagents cannot be easily controlled, and only intense turbulence stirring can ensure a rapid mixing of reagents. This situation clearly positions microfluidic technologies as a unique advanced tool-box technology to rationally design controlled RD environments where materials can be engineered under bio-inspired conditions.

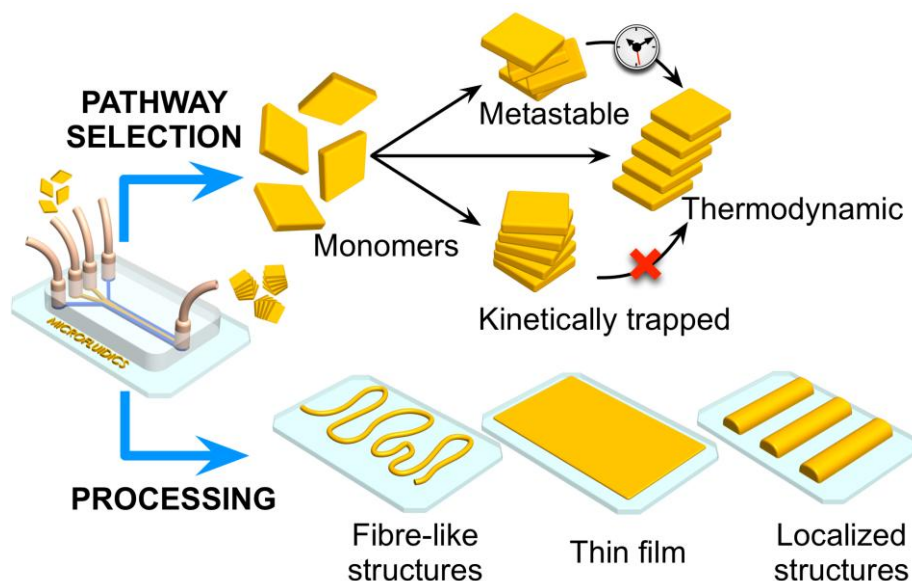


Figure 1. Schematic illustration of the effect of reaction-diffusion processes ongoing in microfluidic environments.

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Simple Clues for Imine-based Organic Frameworks Processability

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Covalent organic-frameworks (COFs) are an emerging class of porous and ordered materials formed by condensation reactions of organic molecules. Recently, the Schiff-base chemistry or dynamic imine-chemistry has been explored for the synthesis of new COFs. The main reason of this tendency is higher chemical stability, porosity and crystallinity that they show in comparison to those previously reported, e.g. boronate ester-based COFs.¹

In this talk I will summarize some interesting aspects concerning the synthesis of imine-based COFs that enable their processability using several techniques such as ink-jet printing,² soft-lithography,² microfluidic,³ spray drying,⁴ 3D-printing, as well as the formation of new large membranes and functional composites.⁵ Perspectives of potential applications of these materials will be presented.⁶

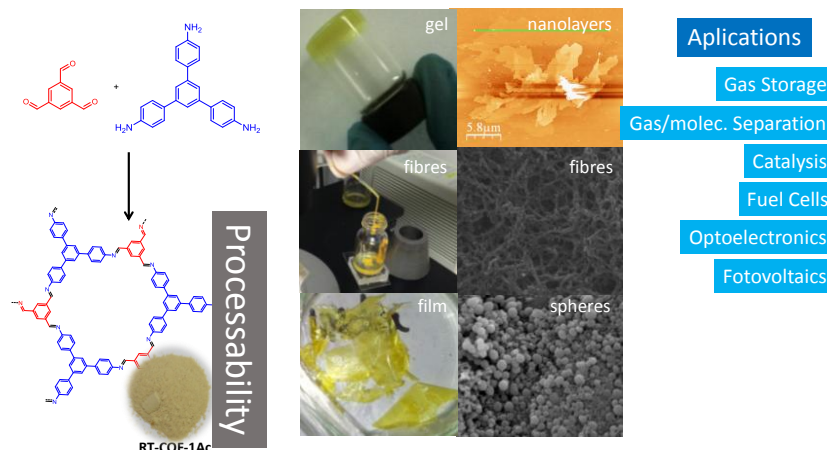


Figure 1. Scheme summarizing the talk

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Covalent Organic Frameworks – A Platform for Controlling Photophysical Processes

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New opportunities emerge by spatially integrating photoactive molecular building blocks into the crystalline lattice of covalent organic frameworks (COFs), thus creating models for organic bulk heterojunctions and porous electrodes for photoelectrochemical systems. In this presentation, we will address means of controlling the morphology and packing order of COFs in thin films (1) and with spatially locked-in building blocks.(2) Regarding the latter, the design of well-defined periodic docking sites enables us to achieve remarkably high crystallinity with several multidentate building blocks and a series of linear bridging units.

We will discuss different strategies aimed at creating electroactive networks capable of light-induced charge transfer. For example, we have developed a COF containing stacked thienothiophene-based building blocks acting as electron donors with a 3 nm open pore system, which showed light-induced charge transfer to an intercalated fullerene acceptor phase.(3) Contrasting this approach, we have designed a COF integrated heterojunction consisting of alternating columns of stacked donor and acceptor molecules, promoting the photo-induced generation of mobile charge carriers inside the COF network.(4) Moreover, additional synthetic efforts have led to several COFs integrating extended chromophores capable of efficient harvesting of visible light, for example (5). Extending newly developed thin film growth methodology to a solvent-stable oriented 2D COF photoabsorber structure, we have recently established the capability of COF films to serve in photoelectrochemical water splitting systems.(6) The great structural diversity and morphological precision that can be achieved with COFs make these materials excellent model systems for organic optoelectronic systems.

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Microscopic analysis of pyrazine-fused conjugated microporous polymers reveal a layered mesoporous structure

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Structural characterisation of low-crystalline materials remains one of the biggest challenges faced by contemporary chemists, but such analysis is vital in order to fully harness the properties of these enigmatic structures. Here we report the use of two alternative but complementary microscopic techniques to innovatively yet comprehensively study complex low-crystalline nanomaterials in direct space and real time, presenting previously unseen features.

High-resolution transmission electron microscopy (HR-TEM) of a pyrazine-fused conjugated microporous polymer (Aza-CMP, figure 1a) synthesised from a solvothermal method shows a highly mesoporous surface,¹ the nature of which is unclear. However, exposing a particle of Aza-CMP to a focussed ion beam (FIB) of Ga⁺ ions leads to the gradual etching of the particle's surface to reveal the internal arrangement and confirms the omnipresence of such pores, consequently revealing intricate channels running deep into the structure. As an alternative to FIB etching, TEM tomography, a process of tilting a CMP particle and acquiring images over an obtuse angular range, has given a three-dimensional analysis of the particle, showing the terrace-like nature of the material in addition to deep channels with diameters of 20-50 nm (figure 1b). The application of a simultaneous iterative reconstruction technique has generated a cross-section and isosurface model (figure 1c) of the particle, demonstrating that the mesopores delve deep into the particle and are not just confined to the surface, hence corroborating the results obtained from FIB etching.

The origin of such channels can be traced back to the synthetic procedure, whereby the polymer nucleates from a solvent particle which disappears leaving a cavity, and thus in addition to microscopic analysis being used to determine the fascinating basis on which such materials form, the results here will also lead the way for a paradigm shift in structural characterisation of CMP and covalent organic framework nanomaterials.

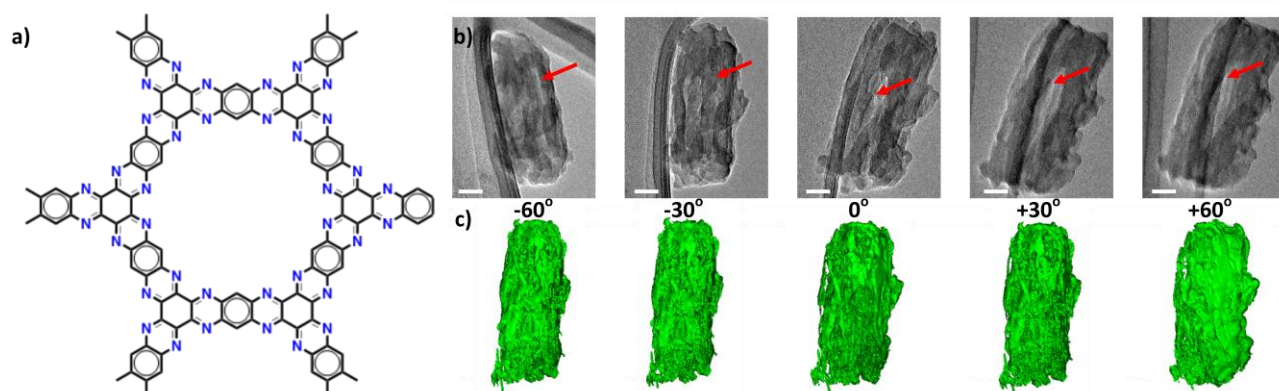


Figure 1. a) The structure of Aza-CMP. A TEM tomographic series (b) shows a CMP particle tilted through various angles; the scale bars are 50 nm, and red arrows point to an example of an internal channel observed within this CMP. A corresponding isosurface model (c) confirms the presence of channels running through the interior of the particle.

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Multi-functional Porous Calix[n]arene Polymers

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Owing to the increasing level of attention focused on the preservation of the environment, there is a growing need for novel multi-functional materials that can meet the increasing demands from society on water resources and pollution remediation. Porous organic polymers (POPs) composed of light elements that possess high specific surface areas, large pore volume, and multiple functionalities are good candidate to fulfil the requirements.¹ In particular, porous covalent organic polymers (COPs) are a promising class because of their ultrahigh hydrothermal stabilities and high yielding synthetic polymer chemistry. Calix[n]arenes (n = 4, 6, 8) have long been recognized as versatile supramolecular scaffolds, however, many previous studies report the syntheses and properties of monomeric calixarenes, fewer describe their incorporation into polymers, and in most of these, the macrocycles serve only as side-chain pendants. Very recently we reported the successful synthesis of a first-in-class calix[4]arene-based porous covalent polymer (**CalP2**) and tested its adsorption ability toward oil, organic solvents, and dyes.² The calix[4]arene-based porous polymer can selectively absorb up to seven times its weight of oil from oil/water mixtures. From aqueous solutions, it can adsorb both anionic and cationic dyes in under 15 minutes. Its uptake capacity is significantly higher than those of the most adsorbent materials reported to date, including commercial activated carbon.

With these positive results and the known advantages of porous organic polymers as adsorbents, we decided to design a series of hyper-cross-linked π -bond-rich porous covalent polycalix[4]arenes (**CalP2-CalP4**), for I₂ adsorption. We enriched the polymers with arenes and alkynes, which are known to endow materials with high surface area and high I₂ affinity. Furthermore, because the phenols of calix[4]arenes are easily lithiated and because alkali metal ions such as Li⁺ are known to enhance adsorption properties of materials by providing sites for charge induced dipolar and quadrupolar electrostatic interactions, we synthesized the corresponding series of lithiated polymers (**CalPn-Li**, n = 2-4) by exposing them to n-butyl lithium at low temperature. We found that both types of polymers (as synthesized and lithiated) performed well as I₂ adsorbents.⁴

For all application, the polymers can be easily regenerated using mild washing procedures and reused several times with no loss of absorption efficiency.



Figure 1. Porous calixarenes polymers for environmental applications

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Unraveling Energy Gaps of 2D Graphene Nanoribbons and 1D Linear Carbon Chains by Resonance Raman Scattering

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Recently we demonstrated synthesis of 2D graphene nanoribbons¹ and 1D linear carbon chains² inside carbon nanotubes. It is very interesting and important to unravel the energy gaps of the new-synthesized 2D and 1D compounds, however, it is impossible if applying the common method like absorption or photoluminescence spectroscopies due to the strong overlapping signals between the studied materials and the carbon nanotubes or screening effect of the nanotubes. In this presentation, I will show our recent results on the synthesis of 2D / 1D compounds and especially on their properties explored by resonance Raman scattering. For example, the obtained energy gaps of two graphene nanoribbons can help to confirm the structures of these nanoribbons. In addition, experimentally determined electronic energy gaps ranging from 2.253 to 1.848 eV follow a linear relation with Raman frequency³ (see Figure1), which can be used for band gap prediction from the Raman spectrum of carbon chains for others in future.

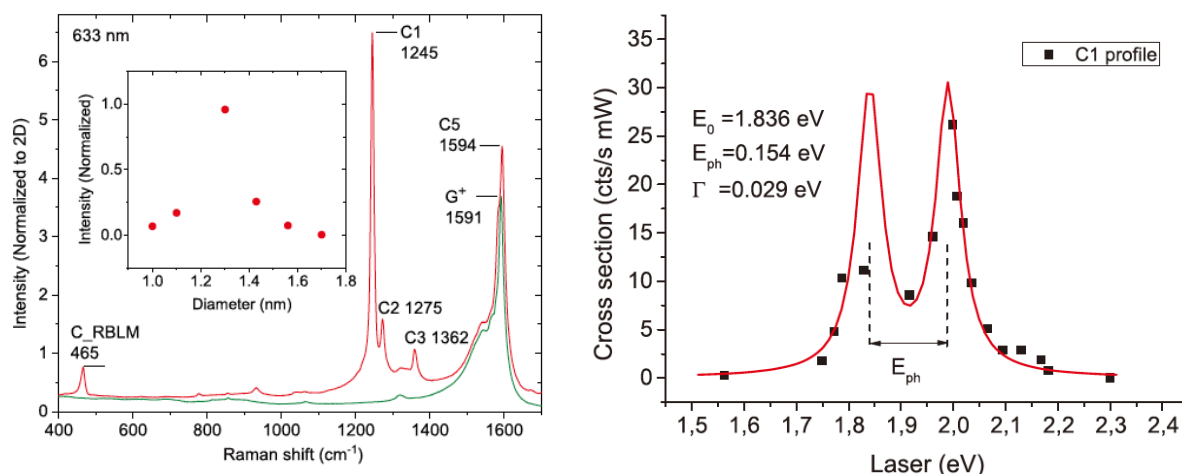


Figure 1. Left: Raman spectra of empty carbon nanotubes (green) and graphene nanoribbon inside carbon nanotubes (red). Right: Excitation cross section for the C1 Raman line of graphene nanoribbon inside nanotubes. The full drawn line is from a fit considering incoming and outgoing resonance.

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Sustainable porous polymers for water treatment, gas capture and catalysis

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Nanopores (< 100 nm) in porous polymers offer confined spaces with vast contact surfaces and tunable functionalities. We have developed a family of nanoporous covalent organic polymers (COPs 1-200) through scalable, catalyst free conditions that feature a wide range of functional groups available for chemical interactions. In water treatment, COPs can selectively capture contaminants such as micropollutants¹. Heavy metals and uranium capture from seawater also benefit from heterogeneous nature of the sorbents with high diffusion rates. In particular, porphyrin containing COPs showed high precious metal uptake capacities. Water capture from air is promoted by quaternary COPs². Carbon capture requires water stable, porous networks and COPs can show remarkable interactions such as N₂-phobic behavior³. By varying chain length of a covalently tethered amine within a nanopore, we optimized CO₂ binding energy, leading to new CO₂ sorbent designs⁴. Nanopores with heterocyclic pore wall chemistries (e.g. benzoxazoles) enable catalytic, oxidative, metal-free coupling of amines⁵. Another, pyridyl salicylimine based system converts epoxides and CO₂ into cyclic carbonates with unprecedented selectivity and conversion at ambient conditions⁶.

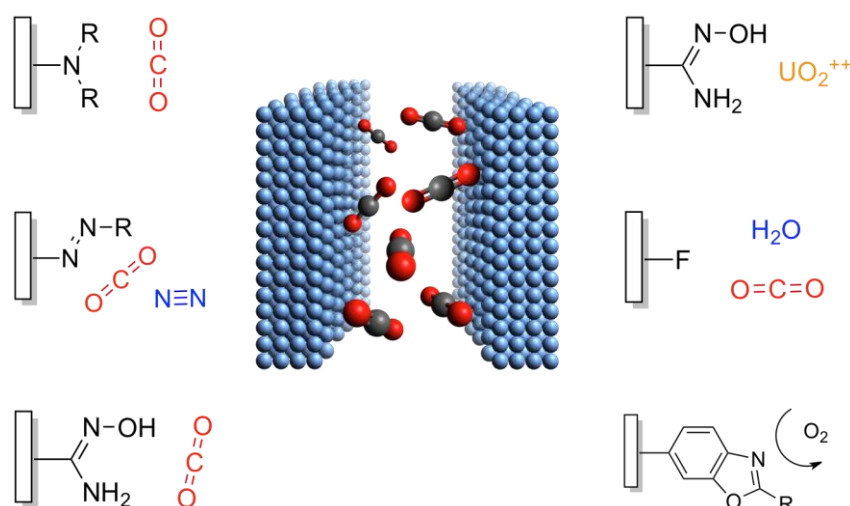


Figure 1. Nanoporous polymers can be tuned to capture and convert CO₂ and clean up water.

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Supramolecular Design Principles for the Synthesis of 2D Covalent Organic Frameworks

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2D Covalent organic frameworks¹ (COFs) are a class of crystalline, porous polymers with 2D layers that are constructed from rigid monomers connected through dynamic covalent bonds. These sheets are stacked in three dimensions through non-covalent interactions. The interplay between these interactions can determine the mechanism of polymerization, or even whether or not the final polymer is crystalline or amorphous. We have recently published² work that aims to explain how the structural features non-planar monomers can affect COF polymerization using molecular dynamics simulations in combination with experiment. We have designed and synthesized several polyphenylene and polycyclic aromatic hydrocarbon COF monomers with variable structural topologies and functionality. These structures were designed to probe the importance of features such as planarity, and aromatic stacking on the outcome of polymerization – whether a 2D layered structure, or an amorphous 3D network, is formed. This talk will encompass our efforts to expand upon our previously published work and explain how the electronic and conformational structure of monomer units can be used to improve crystallinity and long-range order within 2D COFs.

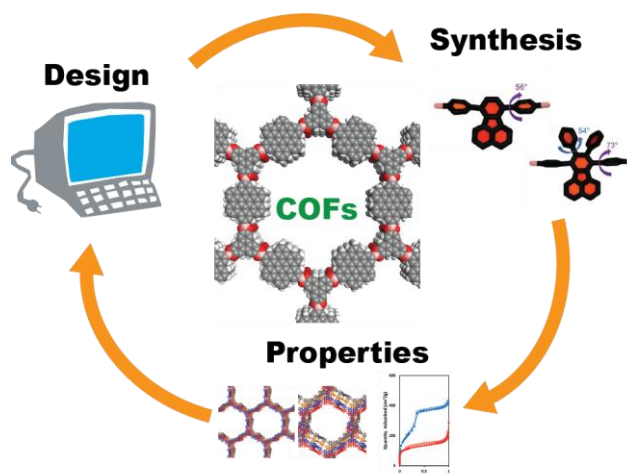


Figure 1. Illustration of the combined synthetic and computational approach to study the formation of crystalline 2D COFs

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Versatile Materials based on Carbon Nanohorns and Graphene Quantum Dots for Wide Applications

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Nowdays a huge number of different carbon nanomaterials are under studies for obtaining better properties, higher solubility, to attach the desirable molecules to them....in summary to tune them for any possible application. Carbon nanohorns¹ (CNHs) are horn-shaped tubular structures (similar in structure to single-walled carbon nanotubes) capped with a conical tip. Individual nanohorns tend to cluster and form a globular structure between 80 and 100 nanometres in diameter with the tips of individual nanohorns projecting outward from the centre in all directions. The high purity and the lack of metal particles of produced CNHs is their major advantage compared to carbon nanotubes. On the other hand, graphene quantum dots² (GQDs) are nanometer-sized carbon nanomaterials which present photoluminescent properties due to the quantum confinement and the edge effects.

This communication focuses on the chemical transformations used for modification of carbon nanohorns and the synthesis of graphene quantum dots. It will be also presented some composite hydrogels/GQDs and the effect of the morphology of these carbon nanomaterials on the new materials and how we can take the advantages of the properties of the carbon NANOMaterials in MACROScale systems.

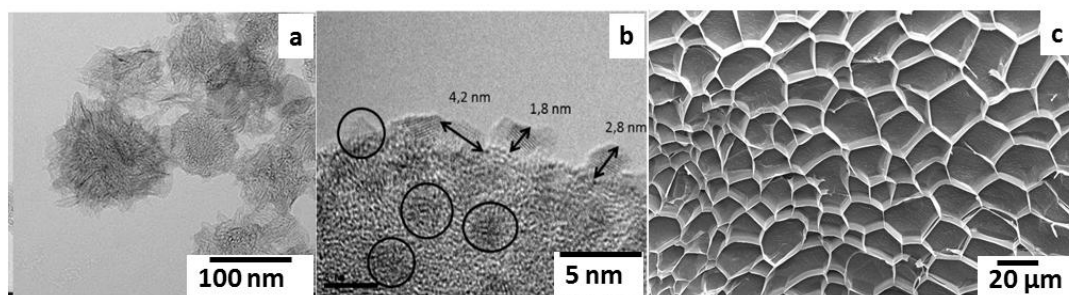


Figure 1. 1a GQDs, 1b CNHs, 1c Composite Hydrogels/GQDs

The different systems could be modulated in the search of a wide range of applications based on an appropriate surface modification. Any applications require a better understanding of the structure-property correlations. For this reason, a whole set of techniques such as AFM, TEM, SEM, TGA and NMR are often used in our group to characterize the structure of these ensembles. Therefore, in this communication we report our latest development on the functionalization and synthesis of the different materials, with overview at the most important applications, such as materials and medicinal science.

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Polymer-covered Graphene Sheets at Biointerfaces

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2D nanomaterials have recently received much attention for their strong biointeractions¹. However, any control over these interactions and practical application of the 2D devices relay on understanding their mode of action. Due to their undefined structures, the mechanisms of interactions between 2D nanomaterials and biosystems is a controversial topic². For a systematic study of these interactions, the structure of these nanomaterials and in particular their exposure should be defined.

Recently, we have developed a method for a controlled functionalization of graphene derivatives with which we have synthesized different graphene-based 2D nanomaterials with well-defined functionalities, polymer coverage, and isoelectric points (pI)³. We found that cellular uptake pathways, pathogen interactions and intracellular localization of these 2D nanomaterials strongly depended on their surface structure and functionality⁴. By manipulating these factors, we were able to tune interactions between the synthesized 2D nanomaterials and biosystems⁵.

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Electrochemically Controlled Drug Delivery by Breaking Imine Bond of Graphene-aniline Platform

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On-demand release of drug molecules is interesting and important in various therapeutic applications to improve the precise and targeted dosing, which can remarkably accelerate efficiency of treatments.¹ Recently, a large variety of delivery systems based on graphene are achieved due to the unique properties of mechanical compatibility, cell adhesion and low toxicity properties.²

Here we describe an electrochemically controlled drug delivery system based on graphene-aniline platform (1) with breaking imine bond between graphene and drug (9-anthracenecarboxaldehyde (A9) and 2,3,4,5,6-Pentafluorobenzaldehyde were used as models, Figure 1a). The results indicated that the drugs can be released under electrochemical oxidation, which were confirmed by increase of fluorescence intensity of the solution after electrolysis of 2-1 (Figure 1b, AE 2-1) compared to before electrolysis (Figure 1b, BE 2-1), and by lower atomic ratio of F/N of graphene-based materials, 1-2' (after electrolysis, 0.8) vs. 2-2 (before electrolysis, 1.5). Moreover, the products of electrolysis of (*E*)-N-(anthracen-9-ylmethylene)-4-methylaniline showed the highly selective imine bond breaking, as characterized by ultra performance liquid chromatography-mass spectrometer (UPLC-MS).

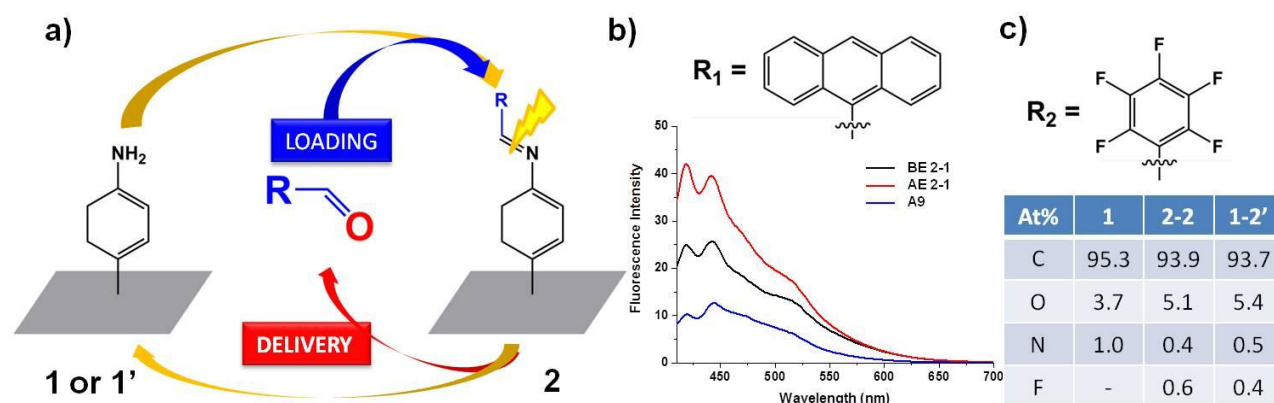


Figure 1. a) scheme of loading and delivery with drug models. b) Fluorescence spectra of before and after electrolysis of 2-1, 9-anthracenecarboxaldehyde (A9). c) Atomic concentration (%) in XPS of 1, 2-2, and 1-2'

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Stimuli responsive polymeric nanoparticles for drug delivery applications

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The development of functional polymeric nanoparticles is essential for breakthroughs in nanomedicine. By tuning the polymer characteristics and subsequently applying optimized formulations for the procedure of nanoparticles, tailored nanoparticles with varying release properties, degradation behavior, targeting groups and size distributions can be developed. For the preparation of polymeric nanoparticles, nanoprecipitation is a good choice since it is a facile, mild, and low energy input process. In combination with high-throughput devices such as microfluidics, pipetting robots, inkjet printers, and automated analytical instrumentation, the abilities of nanoprecipitation can broaden tremendously with significant effects on new applications. Selected examples in the field of gene- and drug delivery vehicles will be presented, e.g. dual pH-value and redox responsive nanoparticles and polymersomes based on a methacrylate copolymer library [1,2,3]. Also natural polymers, in particular dextran, are a great platform for the manufacture of responsive nanoparticles for gene delivery applications.

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Improved Synthesis of Two-Dimensional Covalent Organic Frameworks

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Polymerizing monomers into periodic two-dimensional (2D) networks provides structurally precise, layered macromolecular sheets that exhibit desirable mechanical, optoelectronic, and molecular transport properties. 2D covalent organic frameworks (COFs) offer broad monomer scope but are generally isolated as powders comprised of aggregated nanometer-scale crystallites. Here we control 2D COF formation using a two-step procedure, in which monomers are added slowly to pre-formed nanoparticle seeds. The resulting 2D COFs are isolated as single-crystalline, micron-sized particles. Transient absorption spectroscopy of the dispersed COF nanoparticles provides two to three orders of magnitude improvement in signal quality relative to polycrystalline powder samples and suggests exciton diffusion over longer length scales than those obtained through previous approaches. These findings will enable a broad exploration of synthetic 2D polymer structures and properties.

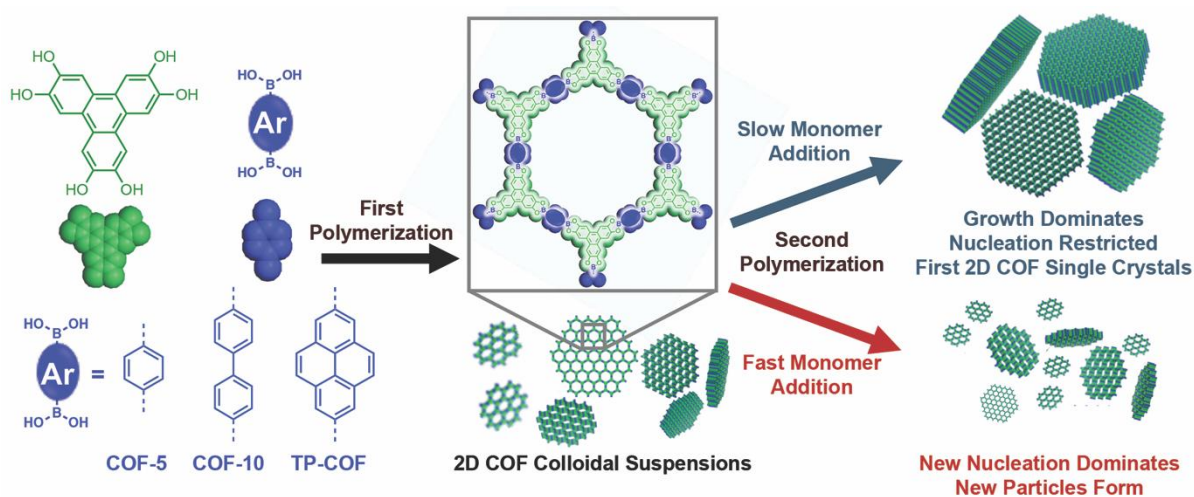


Figure 1. Schematic of controlled 2D polymerization. A two-step seeded growth approach provides 2D COF single crystals. When HHTP and a linear bis(boronic acid) monomer are condensed in a solvent mixture containing CH_3CN , crystalline 2D COF nanoparticles are formed as stable colloidal suspensions. These nanoparticles are enlarged in a second polymerization step in which the monomers are added to the solution slowly.

Spin Crossover in an Exfoliated 2-D Coordination Polymer and its Implementation in Thermochemical Films

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Development of novel 2D materials with singular and thrilling properties has aroused large interest due to the novel unexpected applications that can be derived from there. In this sense, coordination polymers (CPs) have appeared as matching candidates thanks to their rational chemical design and the added-value properties given by the presence of metal ions. This is the case of switchable spin crossover systems that have been proposed as excellent candidates for data storage or sensing, among others. Here we report the delamination of crystals of the 2D spin crossover (SCO) $\{[\text{Fe}(\text{L}_1)_2](\text{ClO}_4)_2\}_\infty$ (**1**) CP by liquid-phase exfoliation (LPE) in water. The application of this top-down technique results in the formation of flakes with controlled thicknesses, down to 1–2 nm thick (mostly mono- and bi-layer) that retain the chemical composition and SCO interconversion of the bulk material. Moreover, these flakes can be handled as stable colloidal dispersions for many days allowing for its transfer in a controlled manner to solid substrates and the formation of thermochemical polymeric films as a proof-of-concept of device. These maiden results will definitely open new venues and opportunities for the investigation and future integration of these original switchable 2D materials in devices..

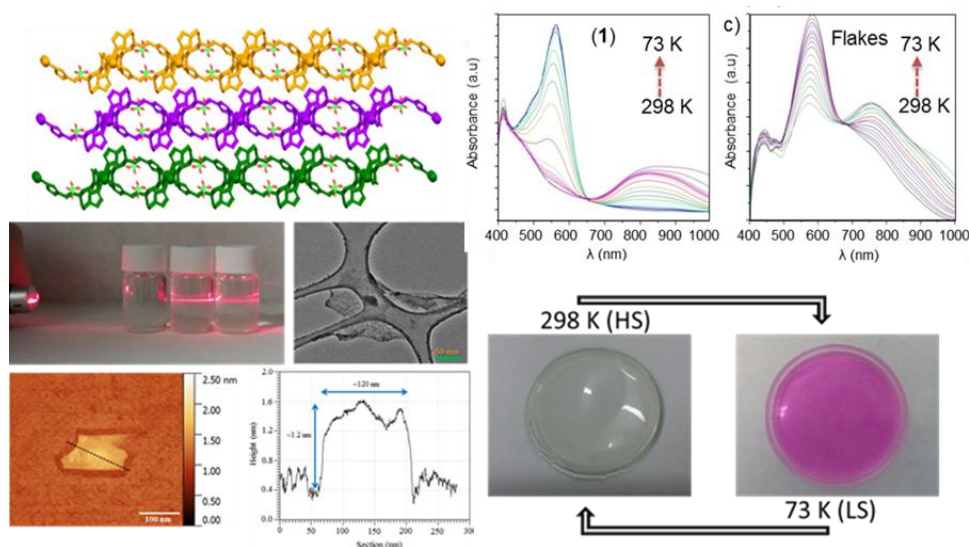


Figure 1. (Left) X-ray structure: packing of 2D-corrugated sheets along b axis (adjacent sheets are shown with orange, purple and green); Tyndall effect of the colloidal suspension in water; TEM image of a single isolated corrugated flake; tapping mode AFM topography of the layers on silicon substrate; height profile corresponding to the dashed lines in panel. (Right) Variable-temperature absorption spectra for the bulk crystals (**1**) and flakes over the 73–298 K temperature range. Films of 2D flakes on a poly(vinyl alcohol) (PVA) at room temperature (HS, left) and 73K (LS, right)

Photocatalytic Hydrogen Evolution from Covalent Organic Frameworks with Molecular Cobaloxime Co-catalysts

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Owing to the easy tunability of electronics and structure, hence crystallinity and porosity, light induced hydrogen evolution with covalent organic frameworks (COFs) has garnered significant recent attention.^{1,2,3,4} However, photocatalytic hydrogen evolution with COFs has only been explored with rare and expensive platinum co-catalyst.^{1,2,3} We present here our results on light induced proton reduction catalysis with COFs using cobaloximes as noble metal free molecular co-catalysts.⁵ Efficient hydrogen evolution ($782 \mu\text{mol g}^{-1} \text{h}^{-1}$ and TON 54.4) is seen with an azine linked N2-COF and a chloro(pyridine)cobaloxime co-catalyst in the presence of triethanolamine as a sacrificial electron donor in water and acetonitrile mixture under AM 1.5 illumination. The methodology can be seen to be extended to other COFs and cobaloxime co-catalysts. The proton reduction mechanism by the cobalt complex in the photocatalytic system will be discussed as well. The results lead way to the development of efficient noble metal free COF-molecular-co-catalyst based photocatalytic systems with a precise control over the nature, density and arrangement of the photocatalytically active sites.

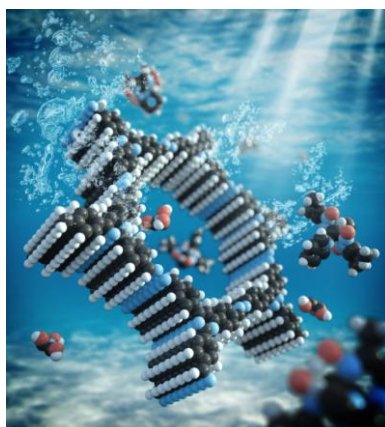


Figure 1. Schematic representation of photocatalytic H_2 evolution with N2-COF and chloro(pyridine)cobaloxime co-catalyst. Image courtesy: Christoph Hohmann, NIM Munich

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Porous Framework Materials: Spheres, Films and Membranes

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Covalent Organic Frameworks (COFs) represent a new class of highly porous, crystalline polymers with uniformly arranged ordered pore channels.¹ Even though COFs have been used for storage of a wide variety of molecular species like gases, nanoparticles, enzymes and drugs; the benefits of their ordered pore channels for molecular separation is hardly extracted. The key issue behind this problem is the difficulty of fabricating COF particles into a self-standing, stable membrane form. Apart from the processability, the other formidable obstacle that prevents utilization of COFs in real life applications are i) chemical stability, ii) difficult synthetic procedures, and iii) scalability. In this context, we have successfully overcome the chemical stability problem of COFs, by synthesizing β -ketoenamine based frameworks. Irreversible enol to keto tautomerism resulted in phenomenal stability within the frameworks.² While processability, synthetic hurdles, and scalability of COFs still remain unexplored. In order to address these key issues, we have developed a very simple, scalable and novel methodology by which COFs can be synthesized by simple mixing and heating of the reactants. Using this method COF can be processed in to self-standing covalent organic framework membranes (COMs).³ The resultant COMs display higher porosity and crystallinity over their reported powder form. These self-standing COMs are flexible, continuous, devoid of any internal defects or cracks, show long-term durability. It retains structural integrity in water, organic solvents and even in mineral acid (3 N HCl). We have utilized these COMs for separation applications such as waste water treatment and recovery of valuable active pharmaceutical ingredients [APIs] from organic solvents.³ Our result highlight, that COMs could satisfactorily address world's most challenging separation problems including waste water treatment, drug recovery from organic solvents in pharma industries.

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Functional Microporous Polymers for Catalysis and Energy Applications

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Microporous Polymer Networks (MPNs) and covalent organic frameworks (COFs) are emerging new classes of functional porous materials, which combine several advantages of polymeric materials with conventional porous matter, like zeolites, activated charcoals or metal organic frameworks.^[1] MPNs and COFs exhibit exceptionally high porosities and surface areas, while their covalent nature ensures sufficient thermal and chemical stability. Furthermore as solely composed of organic compounds an exquisite control over the chemical nature of the large accessible surface areas as well as the physical properties of the resulting networks is possible. All these properties make MPNs and COFs interesting for emerging applications such as energy storage^[2] or organic electronics.^[3] Furthermore, MPNs and COFs open new prospects in the field of catalysis, as various functionalities as active sites can be introduced into the polymer backbones, which can be applied in diverse fields from asymmetric organocatalysis^[4] to photocatalysis^[5]. Novel work has also shown the potential of functional MPNs to immobilize organometallic catalysts (Figure 1). Finally, MPNs and COFs with permanent ionic charges in the organic backbone will be discussed.^[6] Extra-framework cations or anions within the cavities of these charged porous networks can be easily exchanged, which allow to tailor their properties for further advanced applications.

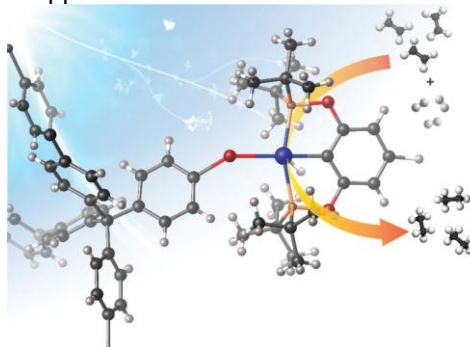


Figure 1. Surface organometallic chemistry using a functional microporous polymer network as support

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Zr(IV)-MOF confined in mesoporous silica for the activation of carbonyls: synthesis of steroid derivatives

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Defective sites in the crystal are considered the active sites in some metal-organic frameworks (MOFs) catalysts.¹ The selective growth of MOF nanocrystals within mesoporous materials (MPMs) via novel '**solid-state**' **crystallization** allows for an outstanding loading of the mesoporous cavities with **very small MOF nanocrystals**.² This approach maximizes the concentration of defective sites at the outer crystal surface, by reducing the MOF crystalline domain down to a few nanometers via **confinement within the mesoporous scaffold** and also confers additional stability to the highly active MOF nanocrystals used as catalysts. In order to demonstrate these advantages, zirconium containing MOF nanocrystals have been confined within mesoporous silica materials.

These composite materials are employed as active, selective and stable heterogeneous catalysts for the conversion of large molecules exhibiting low diffusion coefficients, such as **testosterone** and **epiandrosterone**, which show a high pharmacological interest.³ TEM images show the selective loading of the SBA-15 monodimensional channels with (Zr)UiO-66(NH₂), which is confirmed also by the FTIR spectra and N₂ physisorption. The advantage of using the mesoporous silica component is confirmed by the higher TOF for the **testosterone esterification**, obtained with the hybrid material (0.38 h⁻¹) respect those obtained with the similar MOF sample in the absence of SBA-15 (0.19 h⁻¹). A clear correlation between **catalytic activity** of the dispersed Zr sites present in the confined MOF and the **loading of the mesoporous SiO₂**. We also carried out the **selective reduction of testosterone** by substituting the use of homogeneous catalysts by our heterogeneous hybrid catalysts, employing for the first time Zr as a Lewis acid in catalytic amounts obtaining the desired androst-4-ene-3,17-diol in quantitative yield and excellent **chemoselectivity** after just one hour of reaction at **room temperature**. Finally, we have test the activity of the hybrid MOF/MPM in the synthesis of 16-(E)-benzylidene-androsterone by **aldol condensation** with benzaldehyde, which is an intermediate in the synthesis of anti-cancer steroids.⁴ Using the 6.6 wt.% loaded catalyst, the aldol condensation produces 83% yield of with respect to the 41% obtained in the presence of the bulk MOF after 24 h. The hybrid material also presents a **good reusability**, obtaining 70% yield after five reaction runs. In conclusion, we have demonstrated the superior catalytic performance of the MOF/MPM materials with respect to bulk microporous solids for the **activation and further transformation of carbonyl groups in steroids**, generating pharmaceutically interesting compounds. The use of such novel heterogeneous catalysts containing **catalytically active (Zr) MOF nanocrystals well-dispersed on mesoporous supports**, will encourage the adoption of this approach for other catalytic applications. The increased catalytic activity and **mechanical stability** of this hybrid MOF nanocatalysts confined in the mesoporous scaffolds allows for **multiple reuse** of the catalyst without significant leaching of the active sites in batch and in **continuous mode**, important for its commercial use in industrial processes.

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Practical Synthesis of *N*-Rich Functional Porous Organic Polymers

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Porous Organic Polymers (POPs)^{1,2} have been attracting much attention owing to their potential applications in many areas, including gas adsorption³, separation⁴, heterogeneous catalysis⁵, drug delivery⁶ and water treatment⁷. And the introduction of functional groups to the backbone of POPs can further enhance their performance. In addition, the practical synthesis of POPs is highly demanded by the development of novel materials. In this presentation, the design and facile syntheses of three classes of functionalized POPs with well-defined structure will be discussed (Figure 1). NO₂-PAFs were prepared by robust Cu-mediated Ullmann coupling reaction⁸, Azo-POPs were synthesized by NaBH₄-mediated reductive coupling on nitrated monomers in half hour⁹, and TAAzo-POP-2 was made by azo-coupling between 1,3,5-triaminobenzene and 4,4'-diaminobiphenyl-derived bis(diazonium) salt at room temperature¹⁰. All these functional POPs were carefully characterized by multiple spectral methods, their BET surface area and porosity were well studied, and their adsorption towards gases and organic pollutants in water were investigated. Nitro groups were proved to enhance the CO₂ uptake of NO₂-PAFs⁸, NaBH₄-mediated reductive coupling and azo-coupling on 1,3,5-triaminobenzene were found to be very efficient for the practical synthesis of azo-POPs. These results represent the state-of-art research in the area of porous organic polymers and will attract interests from the society of functional polymer materials.

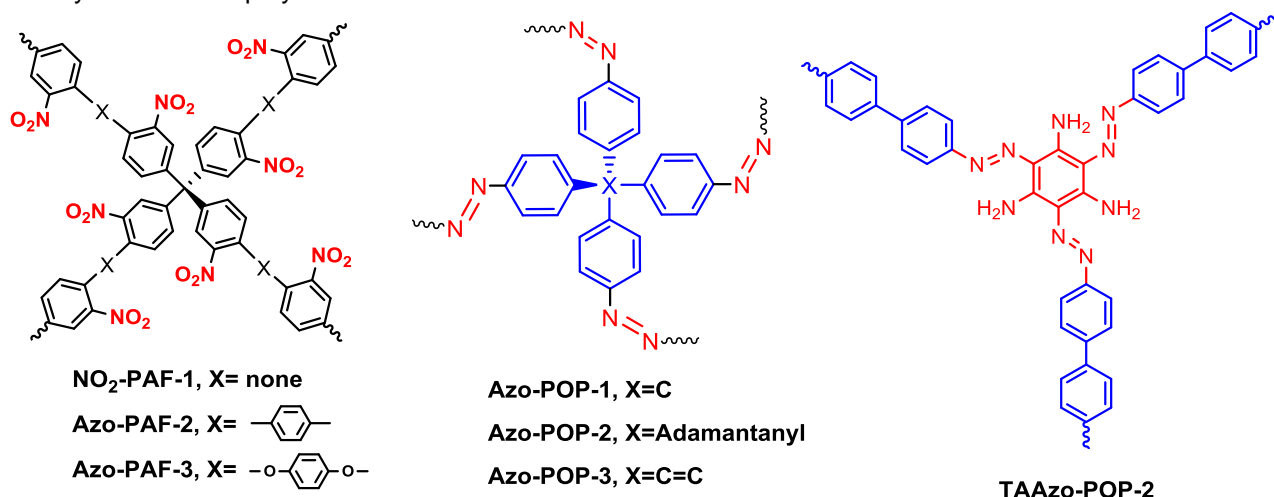


Figure 1. Functional POPs developed by Huang group in the past 3 years

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Recent strategies in the synthesis of 2D polymer and 2D COF

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I will introduce recent work carried out in our laboratory on the synthesis of 2D polymer and 2D covalent organic framework (COF). The synthesis of crystalline two dimensional (2D) polymer linked by C-C bonds can be considered as one of the holy grails of synthetic chemistry. In the first part of my talk, I will introduce a highly scalable, C-C coupling-based 2D conjugated aromatic polymer (2D-CAP) synthesized via thermal debromination of the phenazine ring-fused precursor 2-TBQP in its crystalline state. Isothermal gas-sorption measurements of the bulk material reveal a dominant pore size of ~0.6 nm, which indicates uniform open channels from the eclipsed stacking of the sheets. 2D polymers synthesized by such endogenous polymerization methods show excellent performance when used as supercapacitors and sodium ion batteries. By using interface polymerization, monolayer 2-D polymer can be synthesized. In the second half of the talk, we discuss how we can make a white-light emitting 2-D COF. We utilize the eclipsed stacking structure of 2D COFs to turn on, as well as tune, the solid-state photoluminescence (PL) from non-emissive molecular building blocks. The emissive state is turned on by the restriction of intramolecular bond rotation (RIR) *via* intralayer and interlayer hydrogen bonds among highly organized layers in the eclipse-stacked 2D COFs. The 2D COFs serve as a framework for varying the size of the conjugated linkers and side-chain functionalities, rendering the COFs emission-colour-tuneable from blue to white. Through our structure-property correlation study, this work provides a guide to design new solid-state emitters for potential applications including as photosensitizers and sensors and in lighting and supramolecular encryption.

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Flash/Poster Presentations

Wondrous NanoCarbons

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Carbon, the element 6 has a unique ability to form diverse structures, including the wonder-materials such as fullerenes, graphene, carbon nanofibres and nanotubes. Nanotubes, for example, possess record-breaking strength, conductivity and chemical stability, which are harnessed and developed in nanoscale test tubes and nano-reactors at Nottingham. Chemical reactions of individual molecules entrapped in nanotubes can be triggered, studied and controlled by heat, light or electron beam (e-beam). In the latter case molecular dynamics and mechanisms of reaction can be directly imaged in real time and with atomic resolution. Molecular reactions in nanotubes often deliver products inaccessible by other means, such as nanoribbons of graphene or unusual polymers, or enable improvements of important reactions such as hydrogenation or halogenation. Furthermore, nanotubes loaded with metal nanoparticles exhibit remarkable catalytic properties that can be exploited in many reactions, including electrocatalysis in fuel cells, outperforming traditional catalysts by selectivity and durability.

Transmission electron microscopy (TEM) is one of the most powerful methods to study chemistry of individual molecules in nanotubes, by kinetic energy transfer directly from the e-beam to atoms of the molecule, displacing them from equilibrium positions – an approach we termed *ChemTEM*.¹ Impact of the e-beam triggers bond dissociation and various chemical reactions which can be imaged concurrently with their activation by the e-beam and can be presented as stop-frame movies. Because the e-beam of TEM acts simultaneously as a source of energy for the reaction and as an imaging tool monitoring the same reaction, *ChemTEM* reveals atomic-level chemical information, such as motion of molecules or pathways of their reactions, which can be correlated with properties of the molecules in nanotube measured in macroscopic experiments. Therefore, carbon nanotubes and other low-dimensional materials, such as graphene, provide a physical bridge between the molecules and macroscopic world, and enable us to harness their functional properties for practical applications in catalysis, and energy conversion or storage.

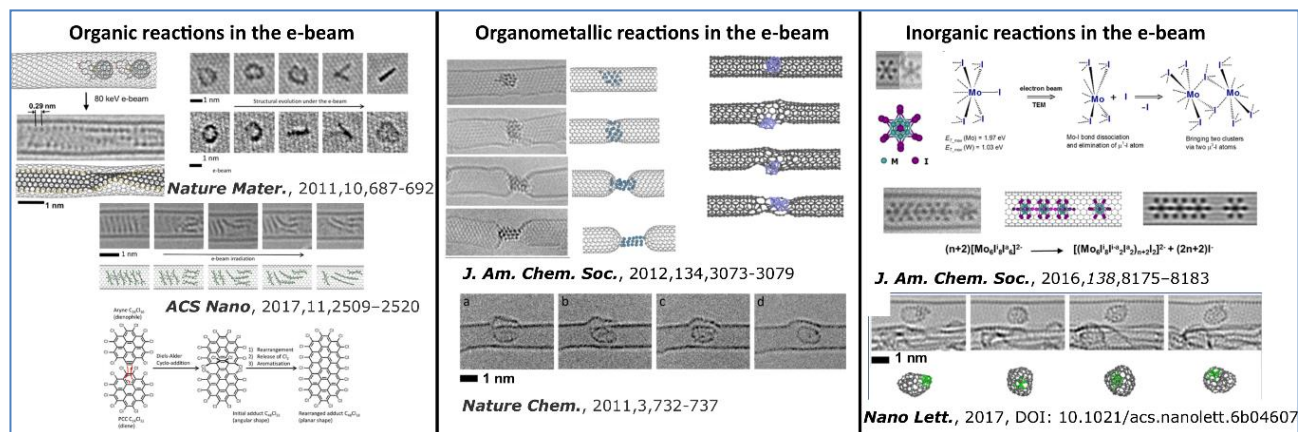


Figure 1. A variety of chemical reactions can be initiated and studied inside carbon nanotubes, many discovered by a new approach in transmission electron microscopy - *ChemTEM*.

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Antimonene: Recent progress.

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Two-dimensional (2D) materials have attracted enormous attention during the last few years because of their outstanding properties and potential applications.¹ Beyond gapless graphene, other elemental 2D materials have been successfully synthesized; being black phosphorus (BP) the only semiconducting material reported so far with a suitable band gap 1.5 eV.² This result together with its excellent charge-carrier mobility and current on/off ratios makes BP a perfect candidate for nanoelectronics and nanophotonics applications. However, its instability represents a major drawback for the development of real applications⁴. Along this front, antimony is a good candidate as it is in the same group in the periodic table as phosphorus and exhibits an allotrope closely related to BP. Indeed, a single layer of antimony, or antimonene, exhibits a band gap of about 1.2–2.4 eV and an outstanding stability under ambient conditions. Antimonene has been recently isolated for the very first time both by mechanical exfoliation⁵ and liquid-phase exfoliation.⁶ A number of theoretical calculations predict extraordinary physical properties like high carrier mobility, thermal conductivity, and strain-induced band transition among others.

In this work, we have studied in detail the liquid-phase exfoliation process of antimony. By adjusting exfoliation conditions we demonstrate control over the surface oxidation of the antimonene flakes. Additionally, we have shown the use of antimonene as a material for energy storage applications,⁶ and its non-covalent functionalization with a tailor-made perylene bisimide through strong van der Waals interaction.⁷

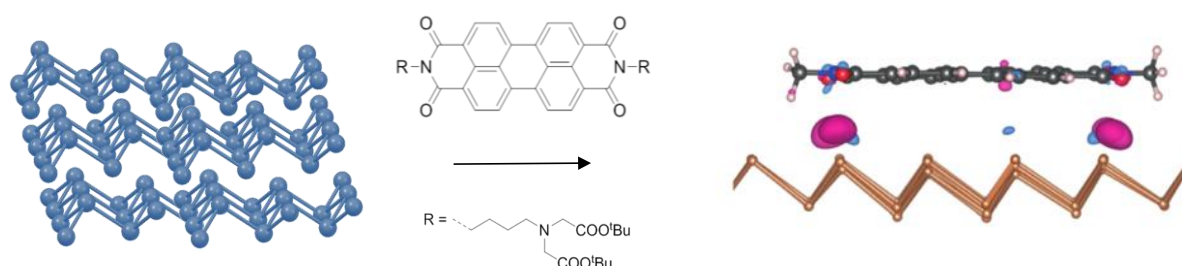


Figure 1. Schematic diagram and side view of the optimized geometries of PDI core on single-layer Sb.

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Flexible C-C bonded network polymers for high-density methane storage

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Natural gas is abundantly found on earth and environmentally cleaner than petroleum. However, low density of natural gas makes it difficult to transport and store, limiting its applications. Adsorbed natural gas (ANG) technology is a safer and cheaper alternative to conventional liquefied or compressed natural gas storage particularly for on-board applications including the shipment of natural gas. Conventional rigid porous materials, such as activated carbons, zeolites, metal organic frameworks, and porous organic polymers demonstrate way lower performance than the target capacity (0.5 g/g, 263 L/L) set for commercial applications. Here, we report flexible dimethylene-linked network polymer, which is easily made from industrially cheap chemicals, and scaled up to kg scale in one batch, to show record high working capacities (5-100bar) of methane 0.625 g/g (294 L/L). The flexible linker groups provide both the rapid desorption and the thermal management, while its hydrophobicity along with the carbon-carbon bonded framework ensures robust use over many cycles and conditions. The method we have developed here is highly scalable, and could be extended to different variabilities depending on the monomer and linker choice. The high methane storage capacity, inexpensive and scalable production of this material makes it a prominent candidate for commercializing ANG technology.

A Supramolecular Strategy to High-Quality Covalent Organic Frameworks and Their Post-Synthetic Modification

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Two-dimensional covalent organic frameworks (2D COFs) are crystalline nanoporous materials formed by the self-assembly of purely organic building blocks into sheets, which undergo aromatic stacking interactions in the third dimension, giving access to an open porous structure.¹ COFs feature high surface area, low density, tunable pore size and shape, as well as high thermal stability and stability in various organic solvents.² All of these properties highlight the potential of COFs to be used in a wide range of applications, such as gas storage, catalysis, adsorption, and optoelectronics. Therefore, the construction of new 2D COF structures with high quality remains a priority.

Aromatic interactions play a central role in the formation, stability, and layer alignment of 2D COFs.³ Despite the importance of these interactions in both formation and properties of 2D COFs, few experimental studies have been dedicated to their optimization. We have employed a supramolecular strategy taking advantage of dipole moments to gain access to COFs with high crystallinity and large surface area.⁴ As a proof-of-principle, we have prepared boronic ester-linked Dione-COF based on pyrene-4,5-dione and hexahydroxytriphenylene. The strong dipole moment of the pyrene dione building block (~ 6.1 – 6.7 D),⁵ is proposed to favor columnar stacking within the pore wall and resulting in high crystallinity and surface area of the obtained material.

Post-synthetic modification (PSM) of COFs is an effective strategy to incorporate functional groups within the pore walls, tailoring their structural and chemical environment. Herein, we present a novel functionalization method for COFs by converting the dione moieties of Dione-COF by PSM, giving access to various functionalized COF materials. Overall, the supramolecular strategy for COF formation combined with post-synthetic modification of the constituting building blocks is a powerful approach to give access to more diverse and versatile COFs.

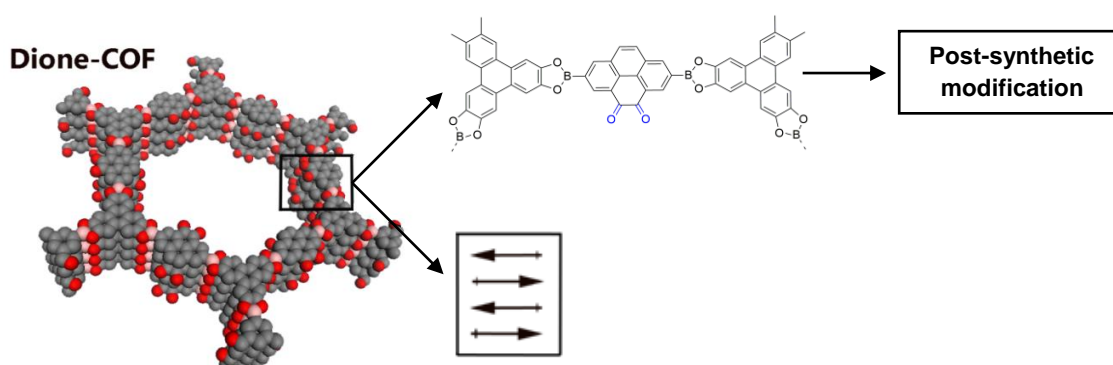


Figure 1. Supramolecular strategy and post-synthetic modification of Dione-COF.

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Layer-Stacking-Driven Fluorescence in a Covalent Organic Framework

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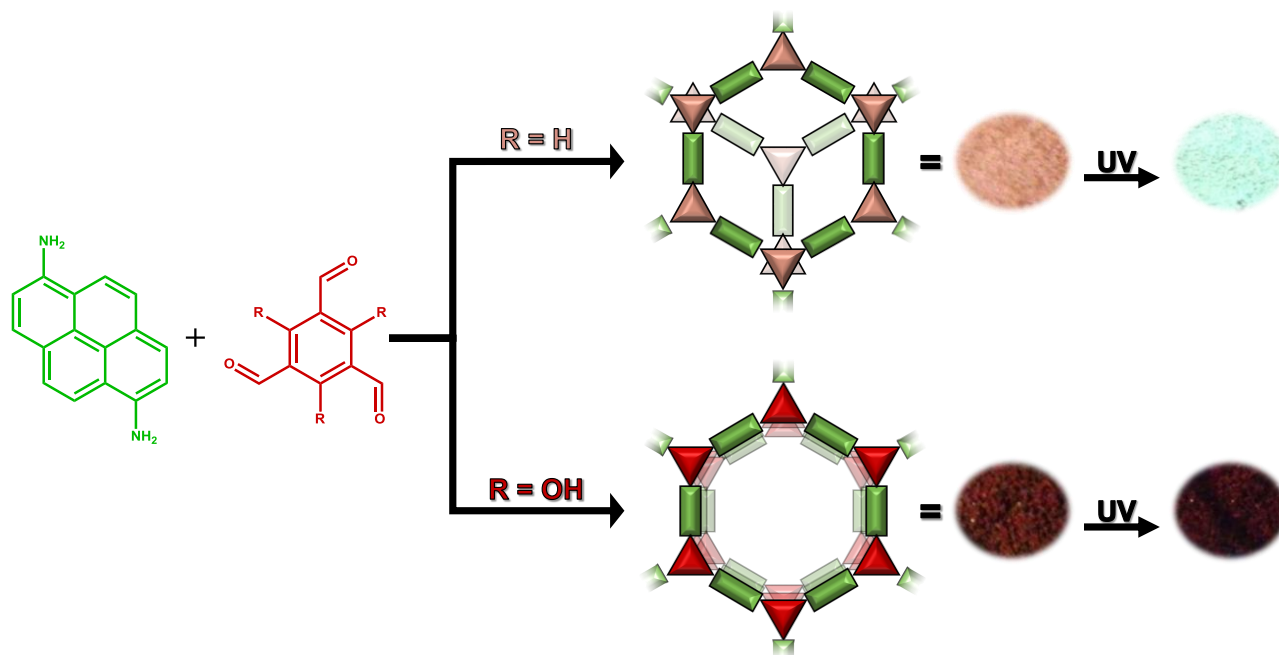
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Two-dimensional covalent-organic frameworks (COFs), being their crystalline architectures exclusively composed of porous organic layers, offer new platforms for sensing and photoelectric applications. Emission properties are often compromised in layered systems due to aggregation-caused quenching driven by π - π interactions. Highly emissive 2D-COF have been reported by incorporation, though synthesis, of certain structural flexibility, resulting in less efficiently packed structures.^{1,2} In this way, it is imperative to harness local modifications within 2D-COFs that can result in improved fluorescence for applications. Herein, we report a new family of imine-linked 2D covalent organic frameworks (COFs) bearing fluorescent pyrene-units, named IMDEA-COF. Notably, this 2D-COF shows dramatic layer-packing-driven fluorescence in solid-state arising from the three-dimensional arrangement of the pyrene units among layers. Stacking of the COF layers within these materials (either AA eclipsed or AB staggered) can be controlled through simple chemical functionalization of the native organic ligands used in the synthesis.



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Modelling the Electronic structure of Two-Dimensional Conjugated Microporous Polymers

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1D and 2D Covalent Organic Frameworks (COFs) that are readily dispersible in solvents were recently synthesized and studied^{1,2}. Computational studies of the full series of crystalline of 2D Covalent Organic Frameworks based on these systems¹ together with several molecular analogues were performed. The objective was to understand how the variation of the pore size alters the electronic properties. Preliminary work indicates that structures with pore sizes > 10 nm are feasible and should be chemically stable³.

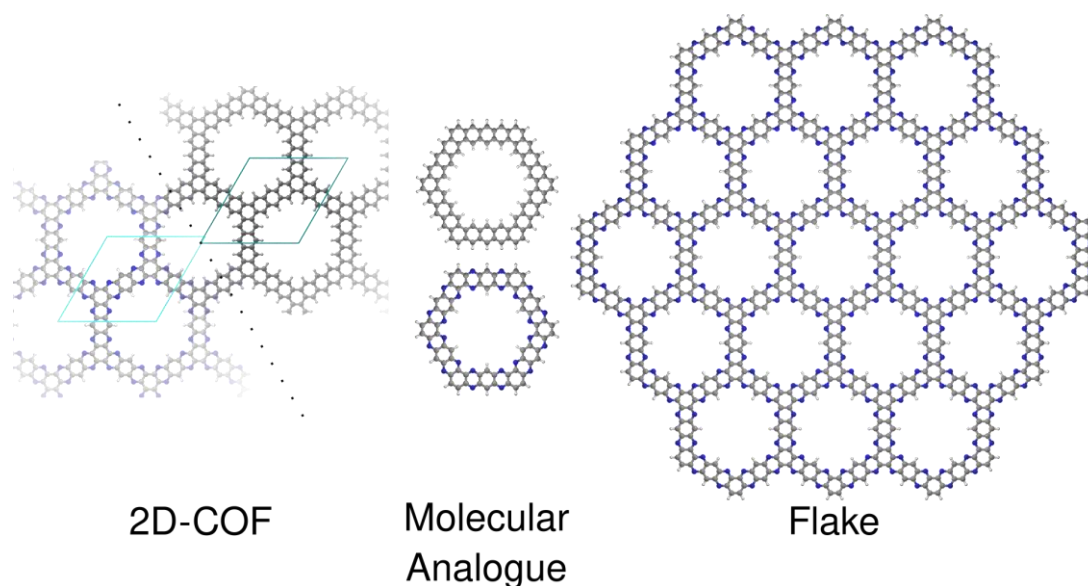


Figure 1. 2D COF (periodic) and two molecular analogues models.

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Improvement the crystallinity of twisted aromatic frameworks with potential energy applications

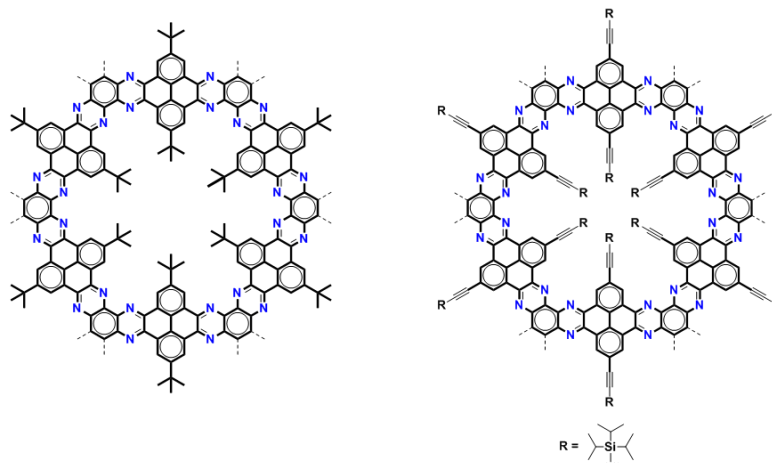
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A new family of twisted aromatic frameworks based on pyrazine moiety has been synthesized. This group of 2D polymers presents high crystallinity comparing with their counterparts. Furthermore, the crystallinity of this COF can be improved once they have been synthesized. Considering the properties of these materials, they are promising candidates for energy application, such as electro-catalysts for the oxygen reduction reaction (ORR) the hydrogen evolution reaction (HER), supercapacitors, and batteries.



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Dynamic study of the 2D-COFs at solid/liquid interface

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Two Dimensional Covalent Organic Frameworks (2D-COFs), which consist of single-layer thick sheets of crystalline polymer networks, have attracted significant research interest due to their promising potential applications in sensing, energy storage, and optoelectronic devices [1]. The condensation of boronic acids to boroxines is one of the most commonly employed reactions to fabricate 2D-COFs on solid surfaces [2,3]. Despite this, very little is known about the dynamics of the boronic acid condensation reaction on solid surfaces. The dynamics of surface reactions is of significant interest to understand the mechanism of 2D-COF formation and potential manipulation strategies.

To this end, self-condensation of pyrene 2,7-diboronic was studied using scanning tunneling microscopy (STM) at the highly oriented pyrolytic graphite (HOPG)/octanoic acid interface at room temperature. Dynamics of unreacted molecules in the vicinity of small domains of already formed 2D-COFs was studied in-situ using high-resolution STM. We report in-depth characterization of the 2D-COF formation process where we identify monomers, oligomers and small flakes of 2D COFs at submolecular resolution and also study their interconversion as a function of time.

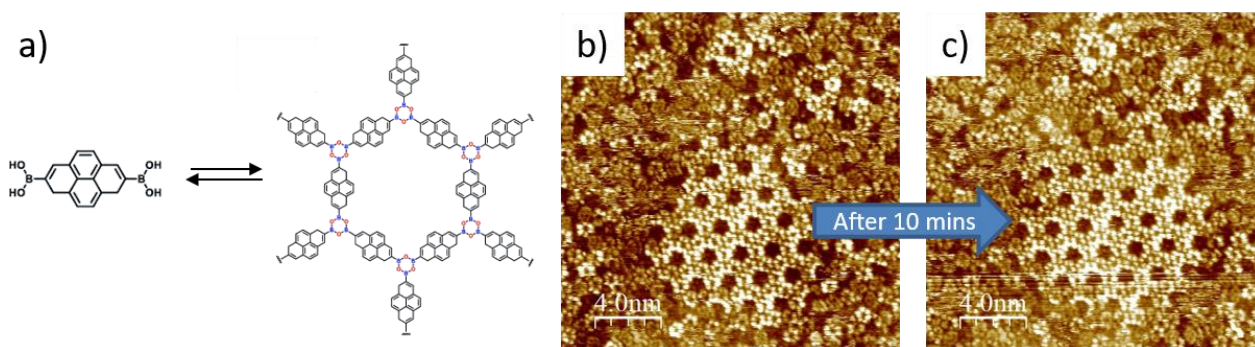


Figure 1. a) Scheme of the condensation reaction; b-c) STM images showing the dynamic change of COF at HOPG-octanoic acid interface. Scanning parameters: $V_s = -0.2$ V, $I_t = 20$ pA

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Antimicrobial Poly(ϵ -caprolactone)/Chloramphenicol Blends for Drug Eluting Medical Devices

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In the last few years, medical devices have evolved from being a mere support to being smart appliances that help with the healing process. Polymeric materials offer a broad range of possibilities and contribute to substantially improving the effectiveness of the drugs, directing them towards the objective, as well as reducing the side effects of an overdose. Furthermore, the low bioavailability of most drugs can be countered with the formation of amorphous solid dispersions (ASDs)¹ by incorporating the drug into a polymeric matrix, due to the establishment of strong specific intermolecular interactions. Miscibility between the two components favors the formation of ASDs, preventing the crystallization of the drug, and as a result, enhancing its solubility. In this work, mixtures of Poly(ϵ -caprolactone) (PCL) with the broad-spectrum antibiotic Chloramphenicol (CAM) were studied². Since it is a drug sparingly water-soluble, it can remain undissolved in the gastrointestinal tract when administered orally, instead of being absorbed. Hence, the combination of this antibiotic with the PCL would allow to keep it in an amorphous form, obtaining a greater solubility and bioavailability. PCL/CAM blend miscibility has been confirmed using the single glass transition temperature (T_g) criterion, intermediate between those corresponding to the two components in the blend. In turn, the analysis of the melting point depressions using the expression of Flory indicates negative interaction parameters for both PCL-rich (χ -1.8) and CAM-rich (χ -0.2) blends. Then, hydrogen bonding specific interactions ($-C=O \cdots H-O-$) between the polymer and the antibiotic were proved using infrared spectroscopy. In addition, the analysis of the spherulitic morphology of the blends by AFM showed that when the amorphous drug enters into the interspherulitic region, it displays a laxer morphology characteristic of miscible blends³ (see Figure 1).

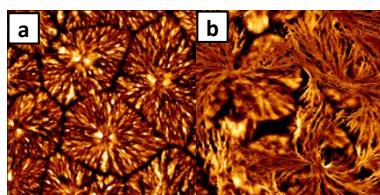


Figure 1. AFM topographic images: a) pure PCL, and b) PCL/CAM 50/50

The study of the release behavior demonstrated that when the entire antibiotic is in an amorphous state, there is an initial burst, followed by a constant release rate. This mechanism responds to an ideal drug delivery from biomedical devices, since the initial burst serves to deal with the risk of infection during implantation and the subsequent constant release at an effective therapeutic concentration, to combat a possible latent infection⁴. Moreover, the antibacterial activity of the polymer-drug system was analyzed by agar diffusion test against *Escherichia Coli* (bacteria frequent in implant-associated infections), and the results confirmed that Chloramphenicol can be released in a controlled way without losing antibacterial activity (see Figure 2).

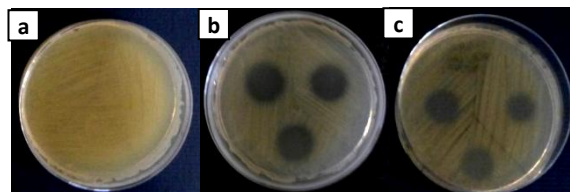


Figure 2. Images of inhibition zones created after pouring on LB agar plates with *E. Coli* 5 μ L of the leachates obtained from a) PCL, b) chloramphenicol solution of 1 mg/mL and c) PCL/CAM 80/20, after 24 h in PBS buffer solution at 37 $^{\circ}$ C.

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Photophysical Characterization of Dibenzozahexacene Monomers and Dimers

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Lately, nitrogenated polycyclic aromatic hydrocarbons (N-PAH) have attracted increasing attention, as they serve as a cornerstone for the design and synthesis of organic semiconductors.¹ With the advent of their acene derivatives the impact of replacing carbon by nitrogen and, in turn, changing the overall nature of these kind of molecules, have been demonstrated.² Pyrene-fused azaacenes, in particular, have proven to be of great interest due to their outstanding length/stability relationship and the implication on the construction of narrow nanoribbon inspired structures.³ In addition, their resemblance to linear acenes, such as pentacene or hexacene, renders them a promising candidate for singlet fission. To this end, we opted for the investigation on a dibenzozahexacene monomer (DAM; Figure 1) and a set of three dibenzozahexacene dimers. The goal was to analyze the differences between the monomer and dimer derivatives, as well as between the different conformations of the dimers by means of steady state spectroscopic and ultrafast transient absorption pump-probe techniques.

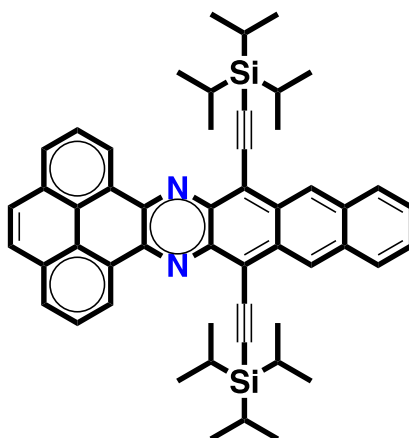


Figure 1. Basic structure of the investigated dibenzozahexacene derivatives.

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Poster Presentations

Ambipolar Vertical Organic Field-Effect Transistors and Inverters.

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Organic devices aim at opening the path towards a forthcoming generation of low cost, flexible¹ and biocompatible² electronic technology. In particular, and having in mind logic operations, an important goal is to perform Boolean functions through logic gates. In this work we present an inverter built upon ambipolar vertical field-effect transistors (VOFETs). The VOFET have been fabricated on standard Si wafers and using CVD graphene and aluminium as source and drain contacts. In this particular case, diketo pyrrolo-pyrrole derivative (DPP-4T)³ is employed as ambipolar semiconductor. In our devices, the graphene weak electric field screening allows the gate voltage to influence both the charge injection into the semiconductor as well as the charge transport in the organic material^{4,5,6}. Adopting an ambipolar material we achieve both n-type and p-type operations without the need of combining different molecular species, and with a simplified device fabrication process.

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Stacking triangular open-shell graphene fragments

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Triangular open-shell graphene fragments are non-Kekulé benzenoid molecules which can be considered as triangular graphene subunits (Figure 1).^{1,2} Coupling several of them, it is possible to design high-spin molecular systems with magnetic and transport properties similar to those of typical inorganic materials. Triangular open-shell graphene fragments take advantage of the possibilities offered by the molecular world: increasing control of molecular magnetism by chemical design; structural and electronic versatility; low density and high flexibility.

This work digs into the possibility of designing molecular ferromagnets by columnar stacking of triangular open-shell graphene fragments.³ Phenalenyl and triangulene dimers are considered as representative examples (Figure 1). We will review the relevance of these two molecules in the design of new materials as well as their structure and bonding.

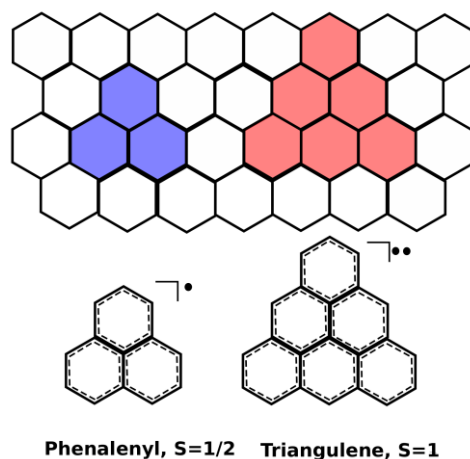


Figure 1. A graphene sheet and triangular open-shell graphene fragments phenalenyl and triangulene. Whereas phenalenyl exhibits a doublet ground state with a total spin (S) $\frac{1}{2}$ and one unpaired electron, triangulene has a triplet ground state ($S=1$) with two unpaired electrons.

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Supramolecular Organic Frameworks via Watson-Crick Pairing

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Supramolecular Organic Frameworks (SOFs) present advantages over other types of materials as COFs or MOF's because of their lower molecular weight and better processability. On the other hand, SOFs present the disadvantage of being more unstable because of the lower energy of the bonds that connect the building blocks. Nevertheless, recent studies have achieved new 2D SOFs that significantly improve previous results, obtaining promising materials that are of great interest in different fields.¹

Our aim is to take advantage of the knowledge acquired in our group regarding the use of ditopic nucleobase monomers to form supramolecular structures² and use them to obtain 2D networks (Figure 1). Previously, we have obtained STM images at the solid-liquid interphase that prove the formation of 2D networks³ of cyclic tetramers formed by cooperative Watson-Crick interactions between complementary bases. The network is stabilized by other interactions between macrocycles, as H-bonding or Van der Waals interactions between peripheral groups.

In this work, we present a couple of molecules in which two of these monomers have been joined using a “fusing-motif”, so that network formation depends essentially on Watson-Crick interactions between G and C nucleobases, as well as the preliminary characterization of the self-assembled systems formed.

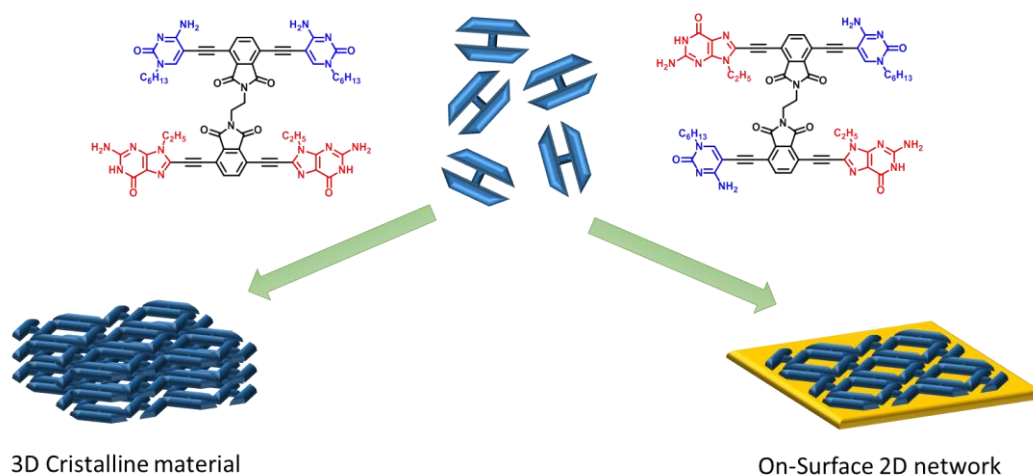


Figure 1. Ways of study of the different Supramolecular Organic Frameworks via Watson-Crick Pairing.

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Porous Carbons Derived From Metal-Organic Frameworks on Functional Polymer Membranes for the Enhanced Extraction of Pollutants

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Keywords: Metal-organic frameworks, porous carbons, membranes, extraction

Metal-organic frameworks (MOFs) have been used recently as precursors to obtain porous carbons with high chemical and thermal stability and high adsorption capacity.^{1,2} Porous carbons were prepared via calcination of MOFs under inert atmosphere. MOFs derived porous carbons have been tested for the extraction of different pollutants from water samples.³ One of the most important problems for the use of this kind of materials as adsorbents is their recovery. To overcome this limitation, different strategies have been designed. Among them, the incorporation of porous carbons in membranes is a desirable approach due to their reusability and excellent flow-through properties enabling high extraction yields, and the straightforward automation of the process, increasing the extraction throughput and reproducibility.⁴

In this communication, we have explored the use of MOF-74 as precursor to obtain porous carbons, and their subsequent processing into mechanically stable filtration membranes by coating of nylon disks with a 0.45 µm pore size with a mixture of the MOF-74 derived carbon with polyvinylidene fluoride. The structure, morphology, and porosity of the materials prepared were studied using X-ray diffraction, electronic microscopy and nitrogen adsorption-desorption isotherms. MOF-74 derived carbon membranes were tested as sorbent materials for the extraction of organic pollutants.

Acknowledgements

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Synthesis and characterization of a novel Green cationic polyfluorene and its potential use as a fluorescent membrane probe

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Most of fluorescent probes currently used in literature are based on small organic dyes, luminescent proteins or even quantum dots. However, these fluorescent materials show important limitations such as photobleaching, self-quenching and chemical decomposition, or potential cytotoxicity risk associated with their heavy metal components which restrict their applications. For that, fluorescent probes based conjugated polymers (CPs) have been introduced, in particular, conjugated polyelectrolytes (CPEs) which have improve solubility in aqueous media. Among CPEs, emit in blue region, but color emission can be shifted to longer wavelengths by copolymerization with other aromatic monomers. In our group, we were synthesized and characterized copolymers (fluorene-based CPs and CPEs) based on this strategy by Suzuki coupling (1). In the present work, we have synthesized by microwave-assisted Suzuki coupling reaction a novel green light-emitting conjugated polyelectrolyte of Copoly-([9,9-bis(6'-N,N,N-trimethylammonium)hexyl]-2,7-(fluorene)-*alt*-4,7-(2-(phenyl)benzo[d][1,2,3]triazole)) bromide (**HTMA-PFBT**, **Figure 1**). HTMA-PFBT exhibited two absorption band around 325 and 425 nm as well as a fluorescence emission band between 470 to 600 nm, depending on the solvent. The behavior of HTMA-PFBT in buffer and in presence of model membranes of different lipid composition was characterized by fluorescence spectroscopy and microscopy in order to explore the potential use of this polyelectrolyte as a green fluorescent membrane probe. High affinity to lipid membranes was confirmed by the increase in the emission spectrum of HTMA-PFBT. The polyelectrolyte rapidly was embedded within the lipid bilayer where it exhibited high fluorescence efficiency and large stability. HTMA-PFBT showed lower affinity to zwitterionic membranes as compared to anionic ones, as well as a more external location, near the membrane-aqueous interface. Fluorescence microscopy studies confirmed the interaction of HTMA-PFBT with the model membranes, labeling the lipid bilayer without perturbing its morphology and showing a clear preference towards anionic systems. In addition, HTMA-PFBT was able to label the cell membrane of bacterial and eukaryotic cells. All these results suggest the potential use of HTMA-PFBT as a green membrane marker for bioimaging purposes.

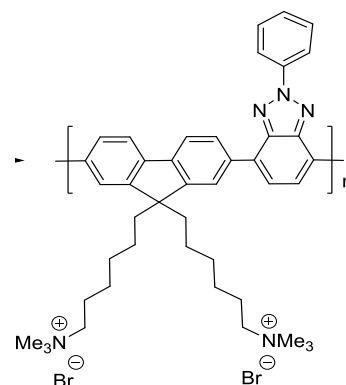


Figure 1. Chemical structure of **HTMA-PFBT**

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3D printed devices with immobilized porous materials for pollutant extraction and degradation

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Nowadays, emerging technologies, such as 3D printing, have a broad scope of application.¹⁻³ However, 3D printed polymers have a rather small surface area, and a limited chemical functionality. In this work, we explore different strategies to immobilize highly porous materials into 3D printed devices fabricated using stereolithography. Two different approaches have been developed to immobilize hypercrosslinked polymer-derived hyperporous carbons,⁴ and metal-organic frameworks.⁵ As proof of concept, cylinders composed by a matrix of small interconnected cubes have been coated with hypercrosslinked pyrrole-derived carbon by a direct photo-immobilization approach. Alternatively, the metal-organic framework ZIF-67 has been coated into a similar device via the preparation of ZIF-67/polymer “inks” and their subsequent immobilization after solvent removal. The developed 3D printed devices have been shaped as magnetic stirrers or pipette tips enabling the fast and efficient extraction or degradation of environmental pollutants.

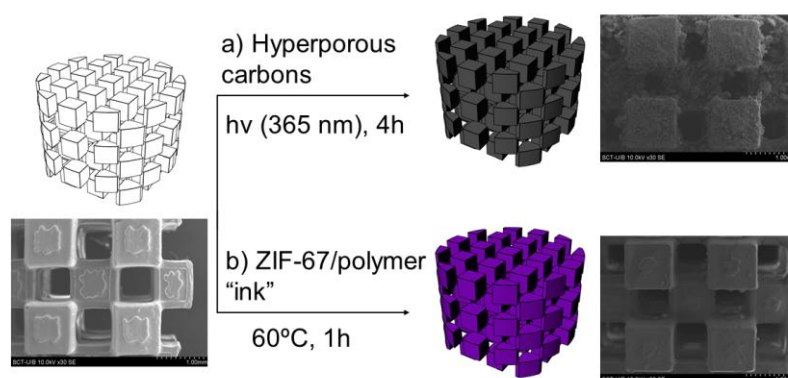


Figure 1. a) Direct photo-immobilization of hypercrosslinked pyrrole-derived hyperporous carbon. b) ZIF-67 immobilization via polymer “inks”.

Acknowledgements

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Chemical Engineering of Photoactivity in Heterometallic Titanium-Organic Frameworks by Metal Doping

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Metal-Organic Frameworks (MOFs) are a relatively new class of crystalline porous materials composed of metal-oxo clusters connected by polytopic organic ligands to assemble porous structures with applications in catalysis, gas separation and storage or sensing to cite a few.¹ These materials have generated a great interest in the community due to the easy tuning of their structure and properties by judicious choice of the metal and/or linkers used in the synthesis. In this regard, Ti^{IV}-based MOFs have attracted a lot of interest due to their high stability and the photocatalytic properties intrinsic to titanium centers.² However, the synthesis of this class of materials remains a synthetic challenge due to the difficulties in avoiding the formation of amorphous titanium oxides in the solvothermal conditions common to MOF synthesis.

Here we present a new family of chemically robust, photoactive heterometallic titanium-organic frameworks coined MUV-10 (*MUV = Materials of Universidad de Valencia*) with [Ti^{IV}₂M^{II}₂(μ₃-O)₂(H₂O)₂(CO₂)₈] units connected by trimesate anions to build a very robust porous architecture with a surface area of 1000 m²·g⁻¹ (Figure 1). Interestingly, despite the presence of divalent metals in the metallic building units, this system shows a high stability in water in a broad range of pH values ranging from 2 to 12, without affecting its crystallinity nor its surface area. Compared to other methodologies based on the post-synthetic modification of MOFs, the heterometallic clusters in the structure of MUV-10 provides a platform to manipulate their electronic structure and photoactivity by metal doping rather than linker functionalization. Our approach is well fitted for controlling the positioning of dopants at an atomic level to gain more precise control over the band gap and electronic properties of the porous solid. Changes in the band gap are rationalized with computational modelling and experimentally confirmed by photocatalytic H₂ production.³

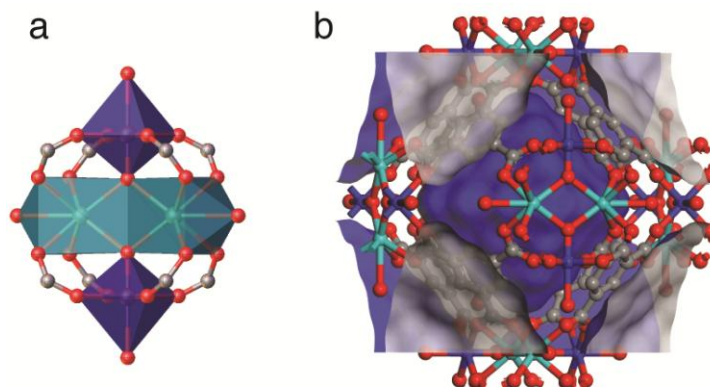


Figure 1. Structure of MUV-10. a) Ti^{IV}₂M^{II}₂(μ₃-O)₂(H₂O)₂(CO₂)₈ tetramers acting as SBUs. b) Internal structure of the sodalite-type octahedral cages.

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Synthesis and Characterization of Novel Hole Conducting Pyrene-based precursors for Perovskite Solar Cells

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Hybrid perovskites solar cells have irrupted with power conversion efficiencies > 20% in the last five years. The development of perovskite solar cells (PSC)¹ requires the design and synthesis of new materials to meet the optimal optoelectronic properties, solubility and processability. Organic synthesis is an useful tool for the generation of less-expensive organic hole transporting materials for PSC. So far, the most promising charge transport material, the so called spiro-OMeTAD (2,2',7,7'-tetrakis[*N,N'*-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene), gave the best results in terms of power conversion efficiency. This molecule presents triphenylamine units, which are known to be conducting hole moieties, and simultaneously present a three dimensional structure due to the central unit spiro-bifluorene. This allows the formation of a globular structure type with hole conducting units at the periphery.

Pyrene-based π -conjugated derivates have shown a lot of potential in semiconducting, such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) and organic photovoltaics (OPVs). We have designed and synthesized a series of pyrene derivates with arylamine side groups containing fragments with high hole conducting ability, while maintaining efficient blocking of the flow of electrons² via Buchwald–Hartwig and Suzuki couplings. Among these, PSC were fabricated with JP-04 as hole transporting material giving a PCE of $\approx 15.28\%$ which is comparable with spiro-OMeTAD as the reference. JP-04 is thus a promising HTM with the potential to replace the expensive spiro-OMeTAD due to its comparable performance and much simpler and less expensive synthesis route.

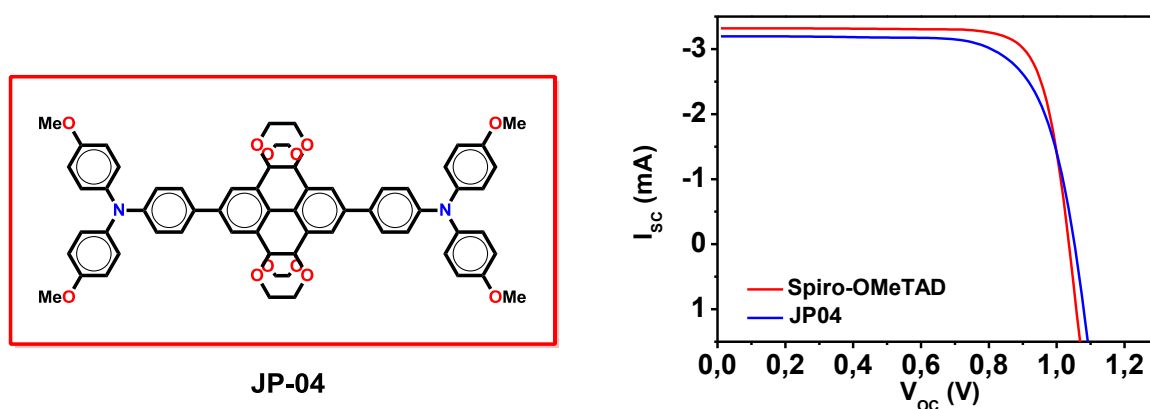


Figure 1. A: Chemical structure of the hole conducting material of Pseudo-pyrene. B: Comparison of the current density vs. voltage of the pseudo-pyrene with spiro-OMeTAD as the reference.

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High-conductance values in π -folded molecular junctions

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Folding processes play a crucial role in the development of function in biomacromolecules. Recreating this feature on synthetic systems would not only allow understanding and reproducing biological functions but also developing new functions that align with our technological needs. This has inspired the development of conformationally-ordered synthetic oligomers known as foldamers, which are able to adopt folded conformations through non-covalent intramolecular interactions encoded in their primary structure. Herein, a new family of foldamers, consisting of an increasing number of anthracene units that adopt a folded sigmoidal conformation by a combination of intramolecular hydrogen bonds and aromatic interactions is reported.¹ Such folding process opens up an efficient through-space charge transport channel across the interacting anthracene moieties. As a matter of fact, single molecule conductance measurements carried out on this series of foldamers, using the scanning tunneling microscopy based break junction technique, reveal exceptionally high conductances in the order of $10^{-1} G_0$ and a low length decay constant of 0.02 \AA^{-1} that exceed the values observed in molecular junctions that make use of through-space charge transport pathways.

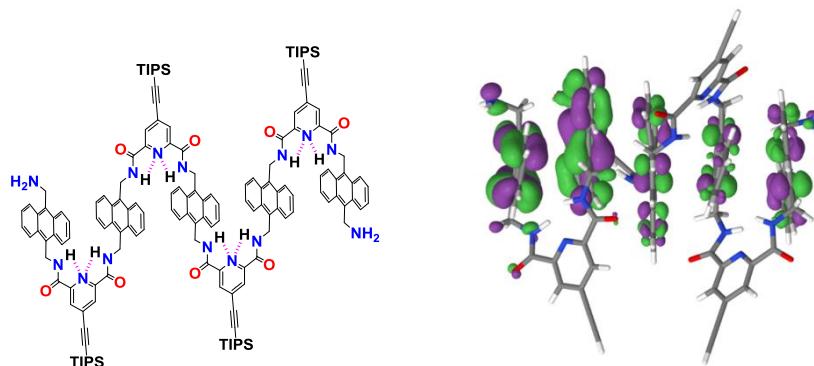


Figure 1. Representative foldamer and its degenerate HOMO orbitals in the folded conformation

Moreover the sigmoidal shape of our foldamers offers some pockets suitable for host-guest interactions, that can be exploited to extend our system to the polymeric level. The introduction of small structural modification allowed us to synthesize a self-recognizing foldamer, able to form a supramolecular polymer thanks to hydrogen bonds and aromatic p-stacking.

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Atomic-Precision: From Small Molecules To The Largest Nanoribbons

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Linear and ribbon-like polycyclic aromatic hydrocarbons such as acenes and graphene nanoribbons have recently attracted large interest from the scientists, as they can be considered as graphene “cut outs” designed *ad libitum*. By careful and wise control of their synthesis, the major drawbacks of the graphene, such as zero band-gap or negligible solubility, can be overcome while retaining the one-atom thickness of graphene with the structure-dependent metallicity of carbon nanotubes.

In general, the nanoribbons can be obtained by following either a top-down or bottom-up approach. Although, the former has been widely used by cutting graphene or unzipping carbon nanotubes to prepare NRs, the NRs do not show atomic precision over any structural variable. Bottom-up can provide atomically-precise control over the edges of the NRs, but do not provide control over the length. Solution polymerisation methods provide control over the edge and width, but no control over the length. The properties of NRs are highly dependent on the width, length and edge structure, and therefore, a precise atomic control over these three structural variables is necessary for establishing their fundamental properties and exploring their potential applications. NRs have unique electronic, optical and mechanical properties and are considered promising candidates to develop new technologies for electronics, photonics, and energy conversion, among others.

Here, we present the largest atomically precise NRs which are based on pyrene-fused pyrazaacenes.^{1,2} Due to the introduction of pyrene units into the backbone, this type of nitrogenated polycyclic aromatic hydrocarbons show very high stability in air. The nanoribbons were easily characterised due to the large solubility in common organic solvents and the photoconductivity measured (**Fig. 1**).

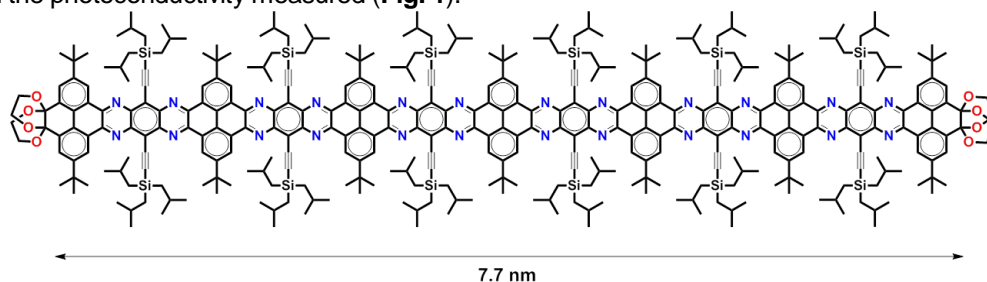


Figure 1.

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Towards Functionality from Trivial Starting Materials: Gaining Processability in 2D Conjugated Microporous Polymers.

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Two-Dimensional Conjugated Microporous Polymers (2D-CMPs) composed of fused aromatic rings combine an extended 2D π system with permanent nanometer-sized pores and appeared as a highly tunable alternative to nanopore-grafted graphene. Furthermore, the synthesis by bottom-up approaches, allows the incorporation of heteroatoms into the framework, providing an additional feature to modulate their electronic structure and properties.^{1,2}

The preparation of stable dispersions of individual layers of 2D-CMPs would provide enormous advantages since it would facilitate the sorting of layers by size, composite preparation by solution mixing, chemical modification, and structural and optoelectronic characterization. In addition, it would enable the formulation of such 2D materials in inks and thus would enable low-cost, large-area liquid-deposition methods, such as spin coating, spray coating, or inkjet printing.³

In this sense, a 2D-CMP was prepared from a building unit leading to the formation of a lattice with two different sized nodes. These nodes are overcrowded with bulky and rigid substituents that enhance the dispersion properties in polar organic solvents by substituent-solvent interactions and by twisting the structure.

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2D materials for efficient CO₂ capture

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Global warming resulting from the emission of greenhouse gases has received widespread attention with international action from governments and industries. Among the greenhouse gases, CO₂ contributes more than 60% to global warming because of its high emission levels from diverse sources. CO₂ capture process represents typically about 70% of the total cost of the CCS (Carbon Capture and Storage) chain, and therefore, novel adsorption technologies that can offer various advantages over conventional adsorption, are gaining support nowadays. One of the most promising technologies for CO₂ capture is based on the adsorption process using solid sorbents. In this context, GRAPHENEA is part of the GRAMOFON project in which the main objectives are:

- 1) to develop and prototype a new energy and cost-competitive dry separation process for post-combustion CO₂ capture based on innovative hybrid porous solids Metal organic frameworks (MOFs) and Graphene Oxide (GO).
- 2) to optimize the CO₂ desorption process by means of Microwave Swing Desorption (MSD) and Joule effect, that will surpass the efficiency of the conventional heating procedures.

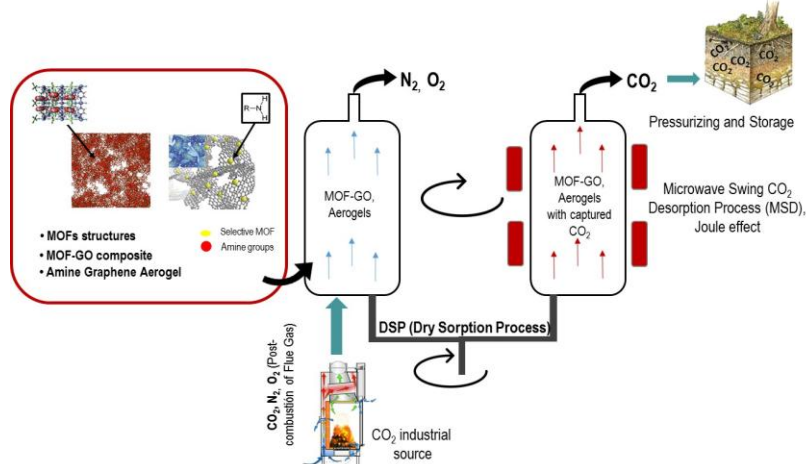


Figure 1: strategy of the global process we aim to design in GRAMOFON.

In the first period of the project graphene oxide aerogels and graphene oxide/MOF composites have been synthesized and characterised obtaining promising results.



The GRAMOFON project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement nO 727619. The sole responsibility for the content of this presentation lies with the GRAMOFON project and in no way reflects the views of the European Union.

Polycyclic Aromatic Hydrocarbons from Asymmetric Pyrene Derivatives

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Pyrene and its derivatives have been intensively explored as organic semiconductors¹. Among these, pyrene-fused acenes are a family of ribbon-like polycyclic aromatic hydrocarbons in which linear annulations are combined with periodic off-linear bisannulations (Figure 1). Such off-linear bisannulations, in the form of fused pyrene residues, increase the number of aromatic sextets in the electronic structures of pyrene-fused acenes, increasing their stability. Although pyrene-fused acenes have been known for several decades, the development of straightforward and solid synthetic routes in recent years has allowed their modification, the introduction of heteroatoms into their aromatic frameworks, and their solubilisation, and therefore, the exploration of their properties^{2,3}.

Our research group has recently described a series of nitrogenated ribbon-like pyrene-fused acenes with planar and twisted structures.^{4,5,6} The synthesis of such derivatives requires desymmetrisation of pyrene with different functional groups with very specific groups that in some cases require harsh or unselective protection and deprotection protocols. Our research endeavors towards the development of a simple method to obtain asymmetric pyrene derivatives through reductive alkylation of ketones that can be unmasked at a later stage through oxidative cleavage of alkyl chains will be described.

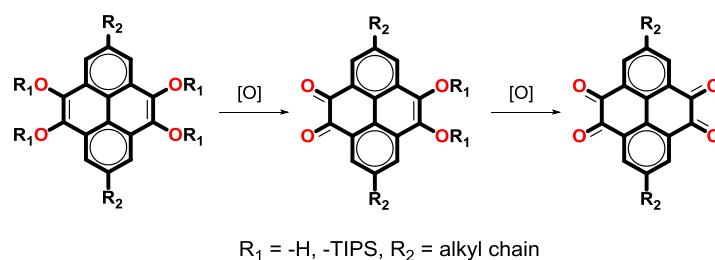


Figure 1. Route of oxidative cleavage of tetraalkylpyrene derivatives.

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Oxidative Fusion Reactions of *ortho*-Phenylene-Bridged Cyclic Oligopyrroles/thiophenes: From Planar [8]Circulene to Helicenes

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[*n*]Circulenes refer to a class of polyaromatic hydrocarbons (PAHs) having a central *n*-membered ring surrounded by benzenoids or other aromatic segments.¹ Although [*n*]circulenes have demonstrated interesting structural and optical properties, the synthesis still remains challenging. Recently, we reported a "fold-in" oxidative fusion reaction of *ortho*-phenylene-bridged cyclic tetrapyrrole (**[4]CPPy**) to afford a tetrabenzotetraaza[8]circulene (Figure 1).² This novel PAH shows a perfect planar structure, well-structured absorption/emission bands, and overall aromatic features.

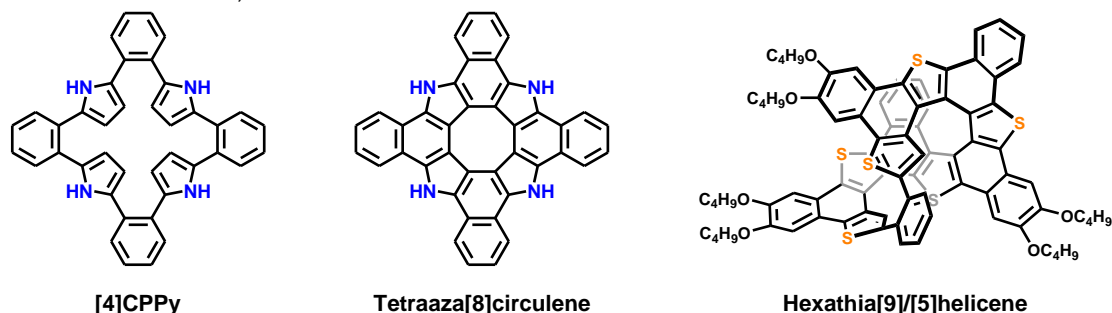


Figure 1 Chemical structures of **[4]CPPy**, **[8]circulene** and **hexathia[9]/[5]helicene**.

When *ortho*-phenylene-bridged cyclic hexapyrrole (**[6]CPPy**) was subjected to the same oxidation reaction conditions, a closed pentaaza[9]helicene was obtained with only four new C-C bonds formed.³ On the other hand, an unexpected double-helical hexathia[9]/[5]helicene was furnished when the *ortho*-phenylene-bridged cyclic hexathiophene (**[6]CPTh**) was oxidized under the same condition. This hexathiahelicene presents an interesting but rare asymmetric double helicene, whose formation was assumed to result from multiple oxidative fusion along with a 1,2-aryl shift. Detailed synthesis, single crystal structures and optical properties of these π -conjugated systems will be discussed.

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Covalent immobilization of biomedical dysprosium-based metal–organic chains on silicon-based polymer brush surfaces

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We report on a process for immobilizing metal–organic chains constructed of dysprosium and sodium ions based on 5-aminopyridine-2-carboxylic acid, onto silicon-based surfaces coated with poly(acrylic acid) (PAA) polymer brushes. Atomic force microscopy (AFM) and fluorescence microscopy were used to study the film morphology before and after the deposition of the 1D metallo-organic polymer. The covalent linkage of the dysprosium complex is also confirmed using X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (SEM-EDS) analysis. Using magnetic force microscopy (MFM) we particularly addressed the magnetic properties of the grafted metal–organic structure.

These results suggest a simple and effective method for incorporation of such molecules onto nanometric surfaces.

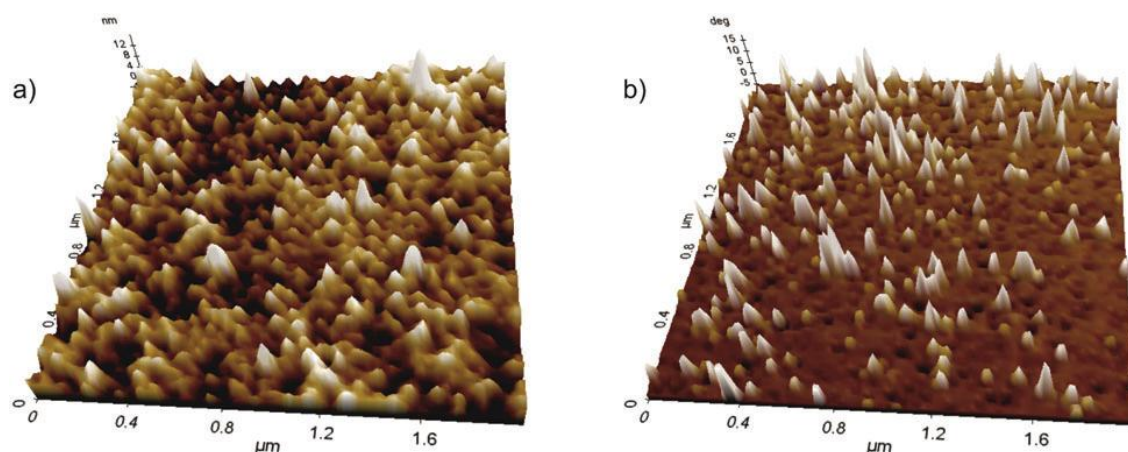


Figure 1. (a) Topographic AFM image of functionalized PGMA surface ; (b) MFM image measured at 30 nm lift height. Both 2.0 _ 2.0 μm of size.

Poly(ethylene glycol)–[60]Fullerene-Based Materials for Perovskite Solar Cells with Improved Moisture Resistance and Reduced Hysteresis

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ChemSusChem 2018, 11, 1032 (Very Important Paper)

A series of [60] fullerenes functionalized with poly-ethylene glycol (PEG) moieties is presented (Figure 1). Fullerenes are known for their nature of electron acceptors and both pristine [60] fullerene and its derivatives have been widely used in perovskite solar cells (PSCs), either as electron transporting layers (ETLs) or in the same perovskite, as additives. On the other hand, PEG was observed to be able to protect perovskite against moisture by attracting and retaining water molecules.

The molecules synthesized for this study are incorporated in $\text{CH}_3\text{NH}_3\text{PbI}_3$, the simplest and most known hybrid perovskite. Increasing the efficiency and the long-term performances of these PSCs is the aim of this study. As a matter of fact, it is known that fullerene molecules inside the perovskite layer have beneficial effects on these cells, for example reducing hysteresis and bettering the performances.

In this case, the cells containing our fullerenes maintained up to the 97% of their original efficiencies after several days exposed to ambient atmosphere.

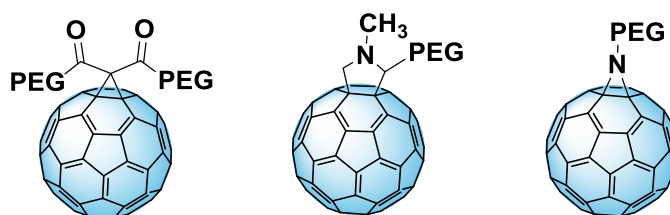


Figure 1. Series of novel PEG-fullerenes synthesized for the purpose

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