



Book of abstracts

22 - 27 May 2022

^W
2d_m Workshop on
2D Materials

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May
2022



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Workshop on
2D Materials

	Sunday 22 nd	Monday 23 rd	Tuesday 24 th	Wednesday 25 th	Thursday 26 th	Friday 27 th
09:00-09:30	R. Sessoli (González-Ciamician RSEQ Award)	H. Van der Zant	R. Berndt	F. Guinea		09:00-09:30
09:30-10:00		M. J. López	F. Rivadulla	S. Mañas		09:30-10:00
10:00-10:30		P. Marín	N. Guihery	J. J. Baldoví		10:00-10:30
10:30-11:00	Coffee break	J. Puigmarí	Coffee break	Coffee break	Coffee break	10:30-11:00
11:00-11:30		M. A. Rodríguez	G. Aromí	G. Abellán		11:00-11:30
11:30-12:00	M. Echavarren	E. Vázquez	A. Forment	H. Suderow		11:30-12:00
12:00-12:30	J. Crassous		J. Soriano	S. Pané		12:00-12:30
12:30-13:00	N. Martín	R. Oda				12:30-13:00
13:00-13:30						13:00-13:30
13:30-14:00						13:30-14:00
14:00-14:30	LUNCH	LUNCH	LUNCH	LUNCH	LUNCH	14:00-14:30
14:30-15:00						14:30-15:00
15:00-15:30						15:00-15:30
15:30-16:00						15:30-16:00
16:00-16:30	Registration	D. Peña	L. Bogani	N. Agraït	M. M. Ugeda	16:00-16:30
16:30-17:00						16:30-17:00
17:00-17:30	Welcome	N. Ortiz	M. Souto	Flash presentations and	Flash presentations and	17:00-17:30
17:30-18:00		Flash presentations and				17:30-18:00
18:00-18:30	E. Ruiz	Coffee break	Coffee break	Coffee break	Coffee break	18:00-18:30
18:30-19:00						18:30-19:00
19:00-19:30	E. Ortí	oral communications	and oral communications	oral communications		19:00-19:30
19:30-20:00	Reception cocktail					19:30-20:00
20:00-20:30						20:00-20:30
20:30-21:00						20:30-21:00
21:00	DINNER	DINNER	DINNER	DINNER	BANQUET	21:00

08h00	SUNDAY 22 nd	ESMolNa2022
14h00	Lunch	
16h00	Registration	
17h00	Welcome	M. Ángel Oliveira (Mayor of Tordesillas); M ^a Luz Rodríguez (U Valladolid); Eugenio Coronado (U Valencia) M. Ángel Zamala (CTR1 Director)
17h30	Eugenio Coronado- ICMol- Univ. of Valencia (ES)	Welcome: Introduction to Molecular Nanoscience
18h00	Eliseo Ruiz- Univ. of Barcelona (ES)	Magnetism and Electron Transport at Single-Molecule Level
19h00	Enrique Ortí- ICMol- Univ. of Valencia (ES)	Electroluminescent Materials Based on Ionic Transition-Metal Complexes: A Theoretical Insight
19h30	Reception cocktail	
21h00	Dinner	

08h00	MONDAY 23 rd	ESMolNa2022
09h00	Roberta Sessoli- Univ. of Florence (IT)	Magnetic molecules in quantum nanoscience (González-Ciamician RSEQ Award)
10h30	Coffee break	
11h00	Josep Puigmartí- Univ. of Barcelona (ES)	What can microfluidic technologies offer?
11h30	Antonio M. Echavarren- ICIQ- RSEQ (ES)	Mastering Gold Catalysis for the Synthesis of Complex Molecules
12h00	Jeanne Crassous- Univ. of Rennes- CNRS (FR)	Helicenes : multifunctional chiral platforms
12h30	Nazario Martín- Complutense Univ. of Madrid (ES)	Unveiling the Properties of Chiral Synthetic Nanographenes
14h00	Lunch	
16h30	Diego Peña- CiQUS- Univ. of Santiago de Compostela (ES)	Combining Organic Synthesis with Surface Science: from Nanographenes to Single-Molecule Reactions
17h30	Alba Pejenaute- Univ. Autónoma de Madrid (ES)	Cas9 mutagenesis, expression, purification, and activity for an improved interaction with bovine serum albumin nanoparticles (BNPs)
	Mireia Ruiz Gasent- ICMol- Uv de València (ES)	Coordination and removal of heavy metal ions by boehmite macrocyclic polyamines
Flash Pres 4'+1'	Julia Requena- ICMol- Uv de València (ES)	Cytotoxicity assesment of pristine and oxidized carbon nano-onions
	Andrea Lázaro Gómez- ICMol- Uv de València (ES)	Design, synthesis and evaluation of novel extended triphenylamine derivatives for G-quadruplex detection and visualization in cells
	Tensae Eskinder Bekele- Univ. Autonoma de Madrid (ES)	growth of metallic nanoparticles into flexible substrate for the development of plasmonic effect
	Cristina Fernández Sánchez- Univ. de Valladolid (ES)	Langmuir-Blodgett thin films containing bis-phthalocyanines and galactose oxidase as electrochemical sensors
	Alia Alwedyan- Univ. Autónoma de Madrid (ES)	Metallophthalocyanine-based nanoparticles for photodynamic therapy (PDT)
	Álvaro Gómez Tola- Univ. de Valladolid (ES)	Modification of the molecular diffusion of hydrocarbons through polyolefins
	Norberto Medina Rodríguez- Univ. de La Laguna (ES)	Multivariate MOFs for analytical applications
18h30	Coffee break	
19h00	Gema Pérez de Bustos Canario- Univ. Autonoma de Madrid (ES)	Non-fullerene acceptors based on Subphthalocyanine-perylenediimide systems
	Lydia Ferrer- Univ. Miguel Hernández Elche (ES)	Phthalocyanine Dimers linked with Spirofluorene and Phenothiazine bridges as Hole Transported Materials in Perovskite Solar Cells
	Francisco Sánchez Martínez- Univ. de Castilla-La Mancha (ES)	Steady-state properties of 8-Hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS) in different media
	Laura Mateo Miñarro- Univ. of Alicante (ES)	Study of the dynamic behavior and stability of polyarginine/sodium dodecyl sulfate (PLA/SDS) films spread at the air/water interface
	Diego Aranda Camuñas- Univ. Autónoma (ES)	Synthesis of gold nanoclusters fixed on mesoporous materials and the study of its catalytic activity in oxidation reaction

Oral Comm 8'+2'	Mónica Gutierrez-Salazar- ICMol- Uv de València (ES)	<i>A photoswitchable helical peptide with light-controllable interface/transmembrane topology in lipidic membranes</i>
	Bas Huisman- ICMol- Uv de València (ES)	<i>Understanding the 3D- to 0D-phase transformation mechanism of hybrid organic-inorganic lead halides perovskites</i>
	Masooma Ibrahim- Karlsruhe Inst. of Technology (DE)	<i>Growth of a Poyoxometalate-Capped Giant Iron-Based Molecular Mineral Structure from Water</i>

21h00 *Dinner*

08h00 TUESDAY 24 th ESMolNa2022		
09h00	Herre Van der Zant- TU Delft (NL)	<i>Spin signals in single-molecule junctions</i>
10h00	Maria José López Santodomingo- Univ. of Valladolid (ES)	<i>Nanoporous and layered carbon materials doped with metal nanoparticles for hydrogen energy applications</i>
10h30	Pilar Marín Palacios- IMA- Complutense Univ. of Madrid (ES)	<i>Ball milled graphene for Gigahertz applications</i>
11h00	<i>Coffee break</i>	
11h30	Ester Vázquez Fernández-Pacheco- Univ. of Castilla-la Mancha (ES)	<i>Graphene in water: preparation, detection and applications</i>
12h00	Miguel Ángel Rodríguez Pérez- Univ. of Valladolid (ES)	<i>From the microscale to the nanoscale in cellular materials</i>
12h30	Reiko Oda- IECB- Univ. of Bordeaux (FR)	<i>Helical inorganic nano-platform for chiral Induction, reaction and recognition</i>
14h00	<i>Lunch</i>	
16h30	Lapo Bogani- Univ. of Oxford (UK)	<i>Molecular electronics: how to make and investigate devices</i>
17h30	Nagore Ortiz Vitoriano- CIC EnergíGUNE (ES)	<i>Electrochemical energy storage: from materials to device applications</i>
18h00	Rana Alawar- Univ. Autónoma de Madrid (ES)	<i>Exosomes as natural Nanoparticles encapsulatrd with curcumin for treatment and diagnosis .</i>
	Miriam Mínguez Avellán- Univ. de Valencia (ES)	<i>Facile route for the formation of lead halide nanoparticles in functional thin-film</i>
Flash Pres 4'+1'	Alberto Galindo Caballero- Univ. Autónoma de Madrid (ES)	<i>Physicochemical characterisations of HCIV-1 virus in extreme saline conditions</i>
	Mónica Peláez Lozano- Univ. de Valladolid (ES)	<i>Solubility and diffusivity of hydrofluorolefins in polyurethane foams</i>
	Amalia Coro González- Univ. Autónoma de Madrid (ES)	<i>Synthesis and characterization of semiconductor nanoparticles as luminescence nanothermometers</i>
18h30	<i>Coffee break</i>	
19h00	Hanane El Mansour El Jastimi- Univ. Autónoma de Madrid (ES)	<i>Synthesis of Aza-BODIPY photosensitizers and their application in-vitro for photodynamic therapy</i>
	Laura Mulet Rivero- ICMol- Uv de València (ES)	<i>Synthesis, characterization and application of new silver DNA nanoclusters in the inactivation of microorganisms.</i>
	Hewen Chen -Univer of Oxford (UK)	<i>Memristive Behaviour in Nitronyl Nitroxide Organic Radical Crossbar Array</i>
	Chris Dreessen- ICMol- Uv de València (ES)	<i>High Voc's in spite of High Bulk Recombination in Small-Grain Vacuum-Processed Perovskite Solar Cells</i>
	Giuliana Beretta- Politecnico di Torino (IT)	<i>Modeling and analysis of molecular technologies for the implementation of Field-Coupled Nanocomputing</i>
Oral Comm 8'+2'	Nathan Rodkey- ICMol- Uv de València (ES)	<i>Pulsed Laser Deposition of Cs₂AgBiBr₆: from mechanochemically synthesized powders to dry, single-step deposition</i>
	Lorenzo Pietro Mardegan- ICMol- Uv de València (ES)	<i>Semitransparent Light-Emitting Electrochemical Cells Using Transparent Conductive Oxides as Top Electrode</i>
	Paz Sebastia Luna- ICMol- Uv de València (ES)	<i>Tunable Optical Absorption of Sn-, Ge-, and Zn-Substituted Cs₂AgBiBr₆ Double Perovskites</i>
	Isidora Susic- ICMol- Uv de València (ES)	<i>Wide Bandgap Perovskite Solar Cells with Enhanced Thermal Stability</i>
	Álvaro Peña- Inst. de Magnetismo Aplicado (ES)	<i>UV-assisted graphene-based chemoresistive gas sensors for sub-ppm detection</i>
21h00	<i>Dinner</i>	

08h00	WEDNESDAY 25 th	ESMolNa2022
09h00	Richard Berndt- Kiel Univ. (DE)	<i>STM of functional molecules</i>
10h00	Francisco Rivadulla- CiQUS- Univ. of Santiago de Compostela (ES)	<i>Functional materials for active control of thermal conductivity</i>
10h30	Natalie Guihéry- Univ. Paul Sabatier (FR)	<i>Origin of the Dzyaloshinskii-Moriya vector and interaction with the electric field</i>
11h00	Coffee break	
11h30	Guillem Aromí- Univ. de Barcelona (ES)	<i>Quantum Computing with Heterometallic Lanthanide Coordination Complexes?</i>
12h00	Alicia Forment- ICMol- Univ. of Valencia (ES)	<i>Spin Crossover Systems to tune 2D materials properties</i>
12h30	Joaquín Soriano López- ICMol- Univ. of Valencia (ES)	<i>Water as Energy Vector. Water Oxidation Catalysis Promoted by Polyoxometalates</i>
14h00	Lunch	
16h30	Nicolás Agrait- U Autónoma de Madrid/IMDEA Nanociencia (ES)	<i>Electrical and Thermal Transport in Molecular Junctions</i>
17h30	Manuel Souto- CICECO-Univ. of Aveiro (PT)	<i>Organic electrodes based on redox-active Covalent Organic Frameworks</i>
18h00	Zaida Curbelo Cano- Univ. Autónoma de Madrid (ES)	<i>Developing MnAlC / hydrogel composites for fabricating alternative permanent magnets by bonding and additive manufacturing</i>
Flash Pres 4'+1'	Lydia Abellán Vicente- IMDEA Nanociencia (ES)	<i>Electrical Conductivity Of Single Molecules</i>
	José Troya Martínez- ICMol- Uv de València (ES)	<i>Insertion of Bis(pentamethylcyclopentadienyl)iron(III) cations into new anilate-based networks to obtain isolated single molecule magnets.</i>
	Gonzalo Rivero Carracedo- ICMol- Uv de València (ES)	<i>Chemical tuning of the properties of 2D magnetic materials</i>
18h30	Coffee break	
19h00	Tomasz Charytanowicz- Jagiellonian Univ. (PL)	<i>Opto-electro-magnetic bistability in polar spin-crossover chain material</i>
	Gonçalo Valente- CICECO-Univ. of Aveiro (PT)	<i>Perylene-based Metal-Organic Frameworks: Tuneable Electrical and Optical Properties</i>
	Carlos Sabater- Univ. of Alicante (ES)	<i>Quantum Transport of Single-Molecule Junctions when Theory and Experiment Meet</i>
Oral Comm 8'+2'	Sahar Mahnaee- Univ. de Valladolid (ES)	<i>Computer simulations of the separation of gas mixtures through novel nanoporous boron graphdiyne membranes.</i>
	Saúl Sánchez González- Univ. de Oviedo (ES)	<i>Relevance of Shockley states on the electrical and thermoelectric response of gold-based single-molecule junctions</i>
	Rebecca Rodrigues de Miranda- ICMCB (FR)	<i>Functionalised spin crossover complexes for thin-film based electronic and spintronic devices</i>
	Robert Jankowski- Jagiellonian Univ. (PL)	<i>SHG-active NIR-emissive neodymium(III)-octacyanidometallate(IV) molecular nanomagnets</i>
	Manuel Imperato- Univ. of Modena &Reggio Emilia (IT)	<i>Metal-organic paramagnets as molecular qubits: design and properties</i>
	Safaa Elidrissi Moubtassim - ICMol- Uv de València (ES)	<i>Stacking-enhanced photoluminescence in subphthalocyanine thin films</i>
	Tamara de Ara García- Univ. of Alicante (ES)	<i>STM Study of Dithia[7]helicenes and the Role of an Organic Solvent at Ambient Conditions</i>
21h00	Dinner	

08h00	THURSDAY 26 th	ESMolNa2022 & W2DM
09h30	Francisco Guinea- IMDEA Nanociencia (ES)	<i>Novel phases in twisted bilayer graphene and related materials</i>
10h00	Samuel Mañas- ICMol- Univ. of Valencia (ES)	<i>Magnetic van der Waals heterostructures</i>
10h30	José Jaime Baldoví- ICMol- Univ. of Valencia (ES)	<i>Magnetism in 2D materials: modelling, prospects and opportunities</i>
11h00	Coffee break	

11h30	Gonzalo Abellán- ICMol- Univ. of Valencia (ES)	<i>Hexagonal hybrid bismuthene by molecular interface engineering</i>
12h00	Hermann Suderow- IFIMAC-UAM (ES)	<i>Superconductivity using STM</i>
12h30	Salvador Pané- ETH Zurich (CH)	<i>Materials for Small-Scale Robotics</i>
14h00 <i>Lunch</i>		
16h30	Miguel Moreno Ugeda- Donostia International Physics Center (ES)	<i>Microscopic insights of collective phenomena in two-dimensional materials</i>
17h30	Vanessa Deniz Santana- ICMol- Uv de València (ES)	<i>Electrochemistry as exfoliation tool</i>
Flash Pres 4'+1'	José Ramón Pérez Martínez- ICMol- Uv de València (ES)	<i>Graphene-MoS₂ covalently crosslinked heterostructures for electrochemical applications</i>
	Borja Luis Sánchez Redondo- Univ. Autónoma de Madrid (ES)	<i>Liquid phase exfoliation of Imine-Covalent Organic Frameworks (COF) enhanced by electrostatic repulsion.</i>
	Sergio Ferrer Nicomedes- ICMol- Uv de València (ES)	<i>Optical characterisation of CrSBr metamagnet: From bulk to the monolayer</i>
	Lidia Medinilla Marin- CIC energiGUNE (ES)	<i>The role of perfluorinated binders in graphene-based Na-O₂ battery cathodes: controlling the triple phase boundary</i>
Oral Comm 8'+2'	Marco Marino- Univ. of Milan (IT)	<i>Ab initio calculations of organic molecules (OM) adsorbed on antiferromagnetic materials (AM)</i>
	Arantzazu Letona Elizburu- CIC energiGUNE (ES)	<i>Boosting the performance of graphene cathodes in Na-O₂ batteries by exploiting the multifunctional character of small biomolecules</i>
18h30	<i>Coffee break</i>	
19h00	Miguel Gavara- Edo- ICMol - Univ. de València (ES)	<i>Contactless electrical detection of the thermal and light induced spin transition in hybrid spincrossover/graphene devices</i>
	Alex Gee- Oxford Univ. (UK)	<i>Electron transport in solution processable graphene nanoribbons</i>
	Natalya Vassilyeva- ICMol- Uv de València (ES)	<i>Liquid-phase asymmetrically functionalised 2D layers for design of heterostructures</i>
21h00	<i>Banquet</i>	
	<i>Venue: Parador de Tordesillas</i>	
08h00 FRIDAY 27 th		
	W2DM	
09h30	Brainstorming	<i>Trends and perspectives in 2D materials</i>
11h00	<i>Coffee break</i>	
11h30	Brainstorming	<i>Trends and perspectives in 2D materials</i>
14h00	<i>Lunch</i>	



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Cas9 mutagenesis, expression, purification, and activity for an improved interaction with bovine serum albumin nanoparticles (BNPs)

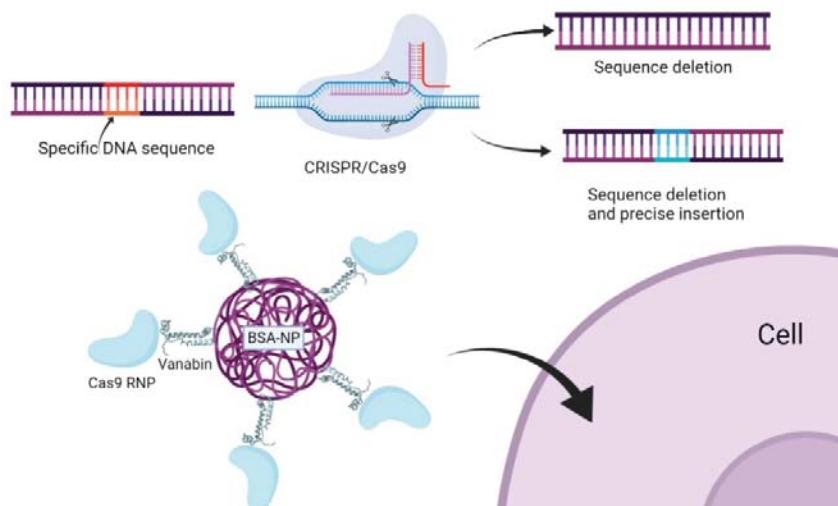
Alba Pejenaute,¹ Catarina Coutinho,¹ Carmen Escalona,¹ María López,¹ Begoña Sot^{1,2}

1- Fundación IMDEA Nanociencia, Madrid, Spain.

2- Unidad de Innovación Biomédica, Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), Madrid, Spain.

CRISPR (Clustered Regularly Interspaced Short Palindromic Repeats) gene editing system is a gene editing tool which allows precise gene editing *in vivo* [1]. It consists of a ribonucleoprotein, meaning an endonuclease protein-RNA complex which acts as a molecular scissor. There are several proteins which belong to the CRISPR system: Cas9, Cpf1, and Cas13 among many others. The SgRNA determines which region of the genome the nuclease will target and cut [2]. Then DNA can be repaired by: i) NHEJ (non-homologous end joining): where random bases are introduced or deleted. ii) HDR (homologous directed repair): where a template substitutes the deleted sequence.

This genetic editing tool has aroused great enthusiasm as it can be used to target and treat genetic diseases *in vivo*. However, its delivery has proven to be a limitation. Nanoparticles have demonstrated to be a vehicle capable of transporting proteins and other molecules into cells. Among them bovine serum albumin nanoparticles have been widely used with biomedical purposes [3]. Here we present a new method to attach Cas9 ribonucleoproteins to albumin nanoparticles. It is based on the addition of a peptide to Cas9, for specific interaction of nanoparticles through disulphide bonds. Cas9 was successfully modified and purified. The modified protein conserves its activity.



[1] Christopher A. Lino, Jason C. Harper, James P. Carney & Jerilyn A. Timlin (2018) Delivering CRISPR: a review of the challenges and approaches, *Drug Delivery*, 25:1, 1234-1257, DOI: 10.1080/10717544.2018.1474964

[2] Mout R, Ray M, Yesilbag Tonga G, et al. (2017). Direct cytosolic delivery of CRISPR/Cas9-ribonucleoprotein for efficient gene editing. *ACS Nano* 11:2452–8.

[3] Lamichhane, S., Lee, S. Albumin nanoscience: homing nanotechnology enabling targeted drug delivery and therapy. *Arch. Pharm. Res.* 43, 118–133 (2020). <https://doi.org/10.1007/s12272-020-01204-7>

Coordination and removal of heavy metal ions by boehmite macrocyclic polyamines.

Mireia RUIZ-GASENT, Álvaro MARTINEZ-CAMARENA, Begoña VERDEJO, Enrique GARCIA-ESPAÑA

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The synthesis, acid–base behaviour and heavy metal (Hg(II), Cd(II), Pb(II)) coordination chemistry of the hexaaazacyclophane ligand (14-hydroxy-3,7,11,14,18,22-hexaaza-1(2,6)-pyridinacyclotricosaphane, **L1**) have been studied by potentiometric, NMR and UV-Vis techniques. Protonation studies reveal that deprotonation of the pyridinol moiety gives rise to a keto-enolic equilibrium, which justifies the higher protonation constant values compared with those analogous pyridine receptors. Coordination chemistry studies reveal the formation of mono and binuclear species above pH 5, highlighting the formation of mostly mononuclear species in the case of Cd(II). The macrocycle has been supported in boehmite nanoparticles for facilitating the metal ion excavenging.

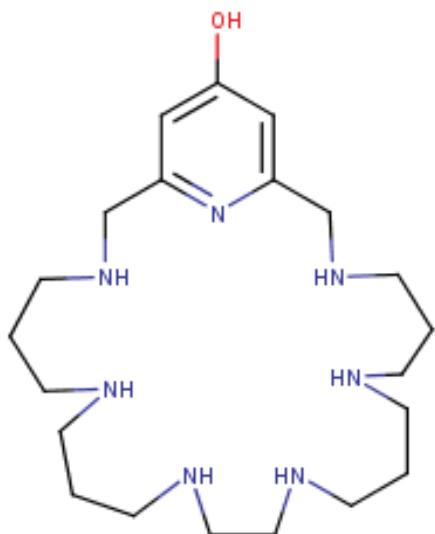


Figure 1: Structure of ligand **L1**

- [1] A. Martínez-Camarena., J. M. Llinares, A. Domenech-Carbó, J. Alarcón, & E. García-España. A step forward in the development of superoxide dismutase mimetic nanozymes: The effect of the charge of the surface on antioxidant activity. *RSC Adv.*, **2019**, 9, 41549–41560.
- [2] A. Martínez-Camarena, E. Delgado-Pinar, C. Soriano, J. Alarcón, J.M. Llinares, R. Tejero, & E. García-España. Enhancement of SOD activity in boehmite supported nanoreceptors. *Chem. Commun.*, **2018**, 54, 3871-3874.
- [3] J. E. Richman and T. J. Atkins, *J. Am. Chem. Soc.*, **1974**, 96, 2268.

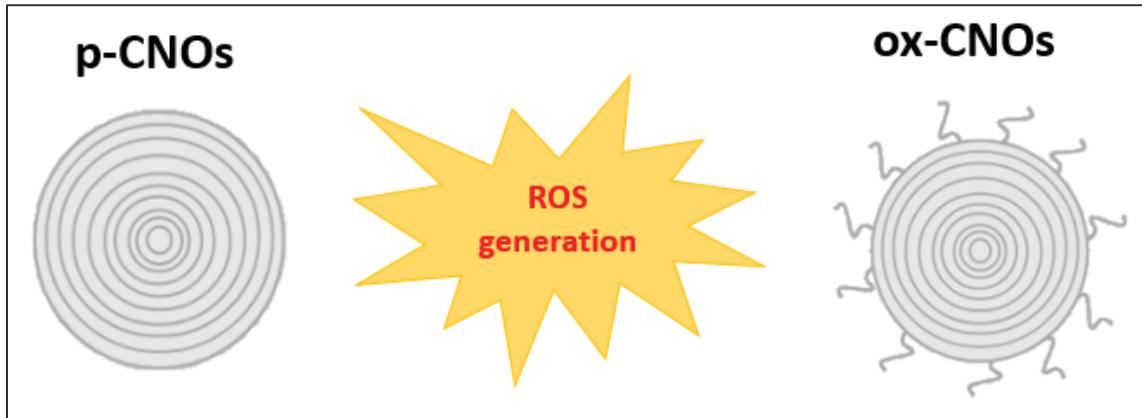
Reactive oxygen species characterization of pristine and oxidized carbon nano-onions

Julia M. Requena-Ramírez, Matteo A. Lucherelli, Jorge González, Gonzalo Abellán

Instituto de Ciencia Molecular (ICMol) - Universitat de València | E-mail: jurera@alumni.uv.es

Carbon nano-onions (CNOs) are nanomaterials with a multi-layered fullerenes-like structure, first reported by Iijima in 1980.^[1] Since their discovery, this carbon allotrope has been researched in a wide range of fields due to its outstanding physicochemical properties, such as graphitic core-shell morphology, large surface area to volume ratio, and biocompatibility, among others. These properties make CNOs excellent candidates in high-ending technological applications, such as energy conversion and storage, catalysis, and nanomedicine.^{[1][2]} In 2005, Ding *et al.* demonstrated the biocompatibility of this nanomaterial, which was even greater than other carbon-based nanomaterials, for example, carbon nanotubes (CNTs).^[2] For this reason, in recent years, studies have investigated their potential in biomedical applications, where they stand out as effective drug delivery systems, bioimaging, sensing and theranostics agents.^[3] In this regard, a very important aspect to consider is the reactive oxygen species (ROS) generation. In most nanomaterials, the main form of cytotoxicity is ROS generation^[2], which lead to oxidative stress causing cell death. In this context, ROS generation can be exploited in some biomedical approaches like photodynamic therapy (PDT), which selectively causes local cell-death through the photo-oxidation of nanomaterials.^[4] For their biological employ, CNOs are commonly submitted to surface modifications aimed to improve water solubility and chemical properties. Commonly, a first oxidative treatment is applied to CNOs (ox-CNOs) to introduce functional groups for further functionalization. Moreover, due to their poor water dispersibility, most of the reported studies focus on the cytotoxicity of functionalized materials, leaving a lack of knowledge about pristine material (p-CNOs). Herein, we investigate and compare the cytotoxicity and ROS generation of p-CNOs and ox-CNOs. ROS generation is studied upon photoinduction and in common biological conditions, to well understand the effect of CNOs in cellular and acellular environments. Finally, with this work we would like to extend the knowledge on CNOs, broadening the horizons of the applicability of this promising carbon nanomaterial in PDT.

ROS generation of pristine and oxidized carbon nano-onions



References:

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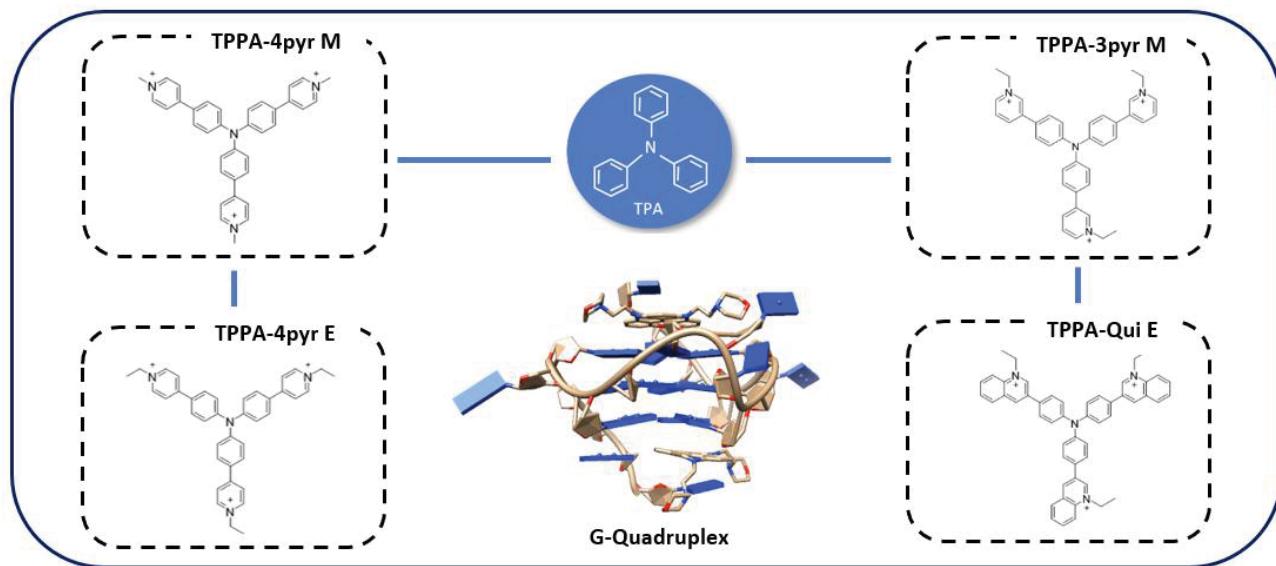
Design, synthesis and evaluation of novel extended triphenylamine derivatives for G-quadruplex detection and visualization in cells

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In the last decade, non-canonical nucleic acid structures have attracted considerable attention of researchers from many science fields, including chemistry, biology, physics, materials and nanotechnology. Non-canonical nucleic acid structures include triplexes, *i*-motifs, three/four-way junctions or G-quadruplexes (G4). The later one is a supramolecular assembly of two or more tetrads, which arise from the hydrogen bonding network of four coplanar guanines. The stability and topology of G4 structures are mainly controlled by the alkali metal cation employed and the nature of the nucleic acid (DNA or RNA). Strikingly, a large number of putative G-quadruplex forming sequences have been identified in the genomes of human and viruses, and evidences suggest their pivotal role in key biological processes such as ageing and cancer.[1] Therefore, these G4 structures have been proposed as potential targets by small molecules for therapeutic intervention.[2-3] In order to unravel the biological processes in which G4s are involved, several strategies have emerged such as antibodies and small molecules. Currently, there is only an antibody for G4 recognition but the limitations of this technology have arisen some concerning in the field. Such limitations emerged from the high affinity of the antibodies for G4s and the application of a fixation agent which can fold these structures in cells and mask the G4s landscape of any biological process. An alternative strategy to detect and visualise G4s is the use of small probe molecules.

In this line, our team has launched a project of G4 probes based on the triphenylamine scaffold and found two ligands with strong interaction and selectivity for G4 structures.[4-5] This project aims to prepare the second generation of triphenylamine-based molecules with extended aromatic core in order to enhance the photophysical features for bioimaging while maintaining the excellent binding abilities for G4s. Herein, we present our synthetic efforts to develop new organic molecules able to interact with G-quadruplex structures. A range of biophysical assays (FRET melting, fluorescence spectroscopy and molecular modelling) has been used to characterise the binding and mode of action. Our results point out the importance of the organic core, the extended aromatic scaffold and the aliphatic conjugation to obtain strong G4 binders and exhibit high fluorescence quantum yields to be applied as bioimaging G4 probes.



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Growth of metallic nanoparticles into flexible substrates for the development of plasmonic devices

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Composites of nanoparticles internalized in polymers have many applications in the field of photonics. Moreover, if the polymer is flexible it brings additional properties like modification of near field coupling. By putting nanoparticles close together, we can localize their electric fields. This is useful for single molecular detection, design of metamaterials, in spectroscopic techniques, among other applications [1].

The aim of this research is to develop composites of flexible conductive polymers and metallic nanoparticles and studying their plasmonic properties. For this, we prepared a material consisting a film of Polyvinyl alcohol (PVA), a layer of a mixture of poly(3,4-ethylenedioxothiophene) and Poly (styrenesulfonate) (PEDOT:PSS) coated with gold nanoparticles (Au-NP).

An aqueous solution of PVA is turned into a flexible thin film. Using a spin coating system a layer of PEDOT:PSS dissolved in DMSO is deposited on the PVA and let it dry. After, using spreading method, 3 layers of gold nanoparticles are applied on top of the PEDOT:PSS layer. The optical properties of the composite are measured using reflection and absorption UV-Vis spectroscopy.

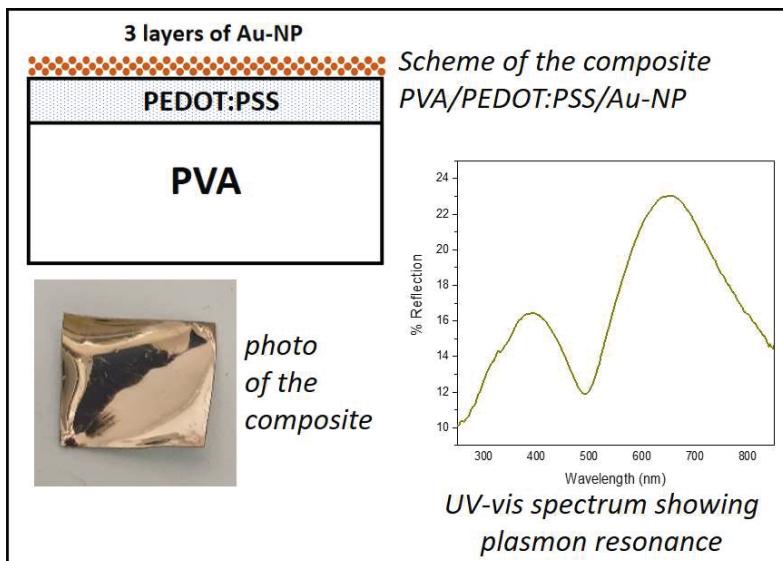


Figure above shows the reflection spectra of the sample prepared. There is a clear dip around 500nm which suggests a manifestation of Au plasmonic effect. Gold nanoparticles typically show plasmonic effects between 500 and 600nm, depending on the size and on the chemical environment.

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Langmuir-Blodgett thin films containing bis-phthalocyanines and galactose oxidase as electrochemical sensors

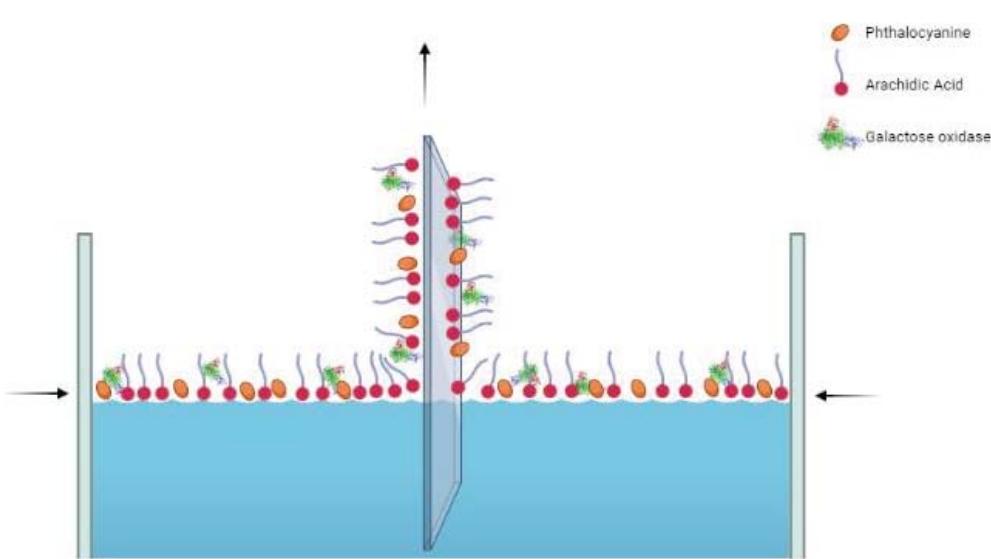
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The need to reduce the physical dimensions and improve the chemical specificity of the devices used in molecular electronics has led to the generation of electrochemical sensing devices based on nanostructured thin films. The Langmuir-Blodgett (LB) technique allows generating nanostructured layers that facilitate electronic transfer, giving rise to an increase in the intensity of electrochemical signals. It has been demonstrated that the modification of electrochemical sensors surfaces with electrocatalytic and/or conductive elements such as nanomaterials or phthalocyanines can improve the sensitivity of the sensor towards certain compounds [1-4]. For this reason, the design of hybrid systems combining different materials has become an interesting tool for the development of new and more efficient electrochemical sensors. Phthalocyanines show the ability to act as electronic mediators in voltammetric sensors by improving the electronic transfer between the analyte and the sensor surface. On the other hand, the use of enzymes stands out for being applied in the generation of biosensors in order to add selectivity and specificity towards specific compounds. In this work, the generation of LB monolayers composed of galactose oxidase (GaOx), gadolinium bis-phthalocyanines (GdPc₂) and arachidic acid (AA) is carried out. The nanostructured films were subsequently deposited on indium tin oxide (ITO) substrates to assess the electrochemical behaviour of the LB layer by voltammetry. The characterization of the LB layers was carried out through the analysis of the π-A isotherms, atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR) and UV-Vis spectroscopy. The deposited LB films were used as voltammetric sensors to test their electrochemical response towards galactose. The intensity enhancement on the voltammograms' peaks allowed to calculate the limit of detection (LOD) and to observe the benefits of the Langmuir-Blodgett method to create ordered nanostructured thin films.



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Metallophthalocyanine-based nanoparticles for photodynamic therapy (PDT)

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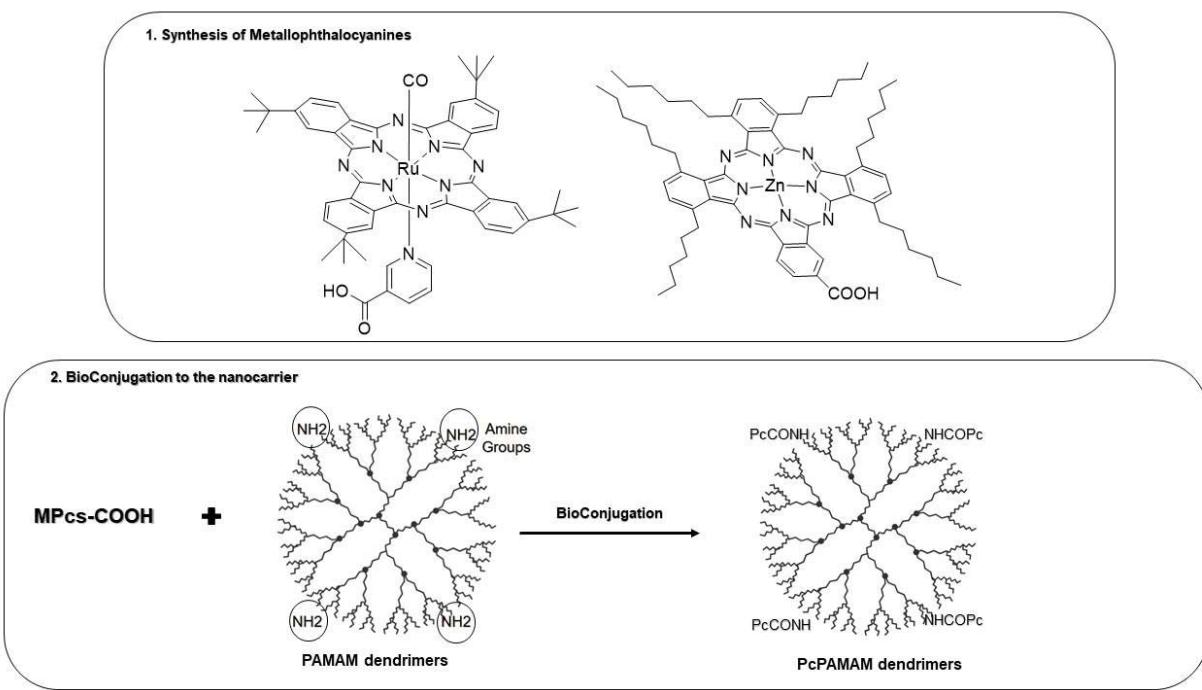
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Photodynamic therapy (PDT) is a non-invasive, clinically approved therapeutic procedure, that has been used to treat malignancies of different types and regions, as well as non-oncological diseases [1]. Phthalocyanines (Pcs) are optimal organic photosensitizing chromophores to be used as active components in singlet oxygen production. They have been widely used as Photosensitizers (Pcs) for PDT owing to their ability to produce singlet oxygen, their non-toxicity and their strong absorption in the phototherapeutic window [2]. The unique cross-like tetrapyrrolic macrocycles is due to an inner porphyrine ring that joins four isoindole subunits, were largely inspired by nature [3], [4].

This work describes the synthesis of Metallophthalocyanine based photosensitizers (MPcs), bearing Zinc(II) and Ruthenium(II) ions within their central cavity. The chromophores have been functionalized at their peripheral or axial positions with a carboxylic acid group for their covalent linkage to a hyperbranched PAMAM dendrimer nanocarrier.



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Modification of the molecular diffusion of hydrocarbons through polyolefins

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Polymer foams are cellular materials mainly composed by two phase materials in which a gas is dispersed in a macromolecular polymer phase by an expansion process. Nowadays polymer foams have a wide range of applications due to their good thermal and mechanical properties. Furthermore, cellular materials allow saving raw materials, contributing to the carbon footprint reduction.

Polyolefins are thermoplastic polymers obtained from oil refining. Polyolefins are semicrystalline, that is, the polymer matrix is composed by two different regions, the crystalline and the amorphous. Many foams found in the industry are prepared using polyolefins due to their versatile properties. Foaming processes include the addition of a blowing agent to generate the expansion. For polyolefins, hydrocarbons are one of the most interesting blowing agents. To achieve a deep understanding of the foaming process and the stability of the foam, it is key to understand the diffusion of the blowing agent in the polymer matrix.

This work is devoted to the measurement of solubility and diffusivity of hydrocarbons in polyolefins with the goal of understanding the mechanics of diffusion of the large molecular weight blowing agents in comparison with air. These properties are of paramount importance for the foaming process and the dimensional stability of the foam. The experiments conducted so far were carried out with different semicrystalline matrixes like LDPE (low density polyethylene), EVA (ethylene octane copolymer) and EBA (ethylene butyl acrylate) using isobutane and air. Different sorption times and sorption pressures were investigated. The preliminary results support the relevance of the processing parameters, the gas nature, and the polymer in the diffusion process.

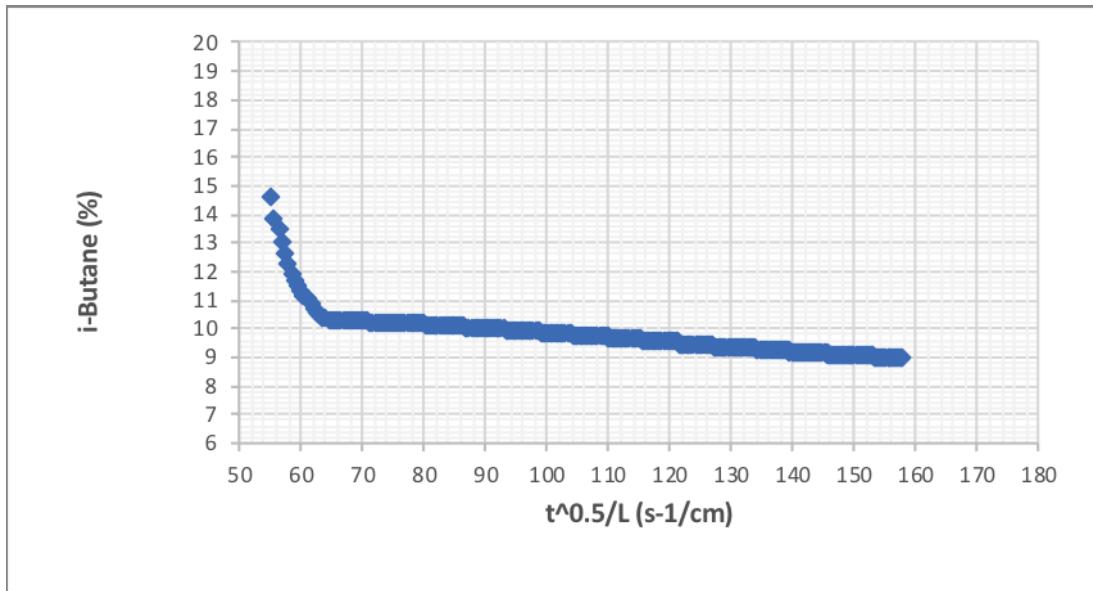


Figure 1. Diffusion curve of isobutane in LDPE matrix

Multivariate MOFs for analytical applications

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Metal-Organic Frameworks (MOFs) are porous crystalline materials formed by the combination of organic linkers with metal cations or metal clusters, also called Secondary Building Units (SBUs). A large number of different MOFs have been reported, showing a wide structural and functional variety. This makes them suitable for different applications, such as gas storage and separation, catalysis, chemical sensing, light-harvesting/solar-energy conversion, drug delivery, and environmental remediation or water harvesting[1].

Most of these reported structures are limited to just one type of organic linker and SBU. In this context, different alternatives for obtaining mixed-component MOFs have been proposed. Among them, multivariate MOFs (MTV-MOFs) include MOFs built of different linkers that share a common backbone but different functional groups. This increases the complexity of the structures, and can provide new sorption capacities[2].

In this work, we are studying multivariations of the already reported[3] DUT-52 MOF with different linkers in order to analyse changes in the adsorption behaviour of emerging contaminants of concern (ECCs) in water. Their synthesis is performed by mixing different proportions of the linkers in a one-pot reaction. Sample characterization is carried out with powder x-ray diffraction (PXRD) and nuclear magnetic resonance (NMR) while adsorption behaviour is studied by a dispersive micro-solid-phase extraction (μ -dSPE) procedure.

Funding for this work has been obtained from the Ministerio de Ciencia e Innovación through the project PID2020-115004RB-I00.

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Non-fullerene acceptors based on Subphthalocyanine-perylenediimide systems.

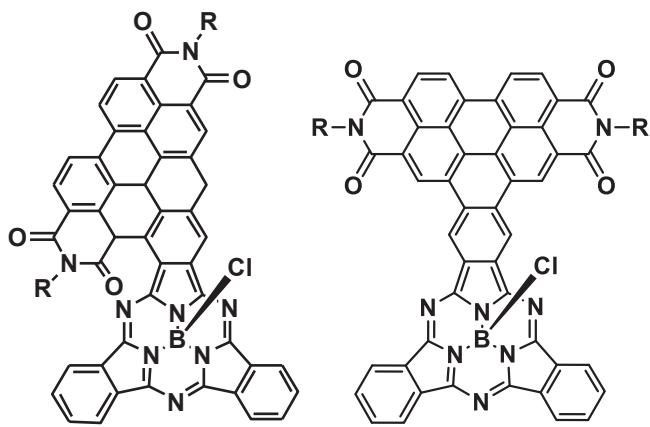
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Subphthalocyanines (SubPc) are an important class of C₃-symmetric organic semiconductors consisting of three diiminoisoindole units assembled around a central boron atom. [1] This particular structure results in a 14 π-electron cone-shaped aromatic skeleton which endow the molecule with intriguing optoelectronic properties, such as strong absorption in the visible range or columnar organization. Importantly, the HOMO-LUMO levels of SubPcs can be easily modulated by peripheral functionalization. Thus, SubPc can be electron donors or acceptors depending on the groups introduced in the peripheral positions. Herein we introduce Perylenediimides (PDI), which are well-known electron-withdrawing units, to the peripheral position of SubPcs with the aim of improving their n-type charge transport properties. Moreover, we will analyse how the structure and symmetry of the PDI-phthalonitriles employed to prepare the SubPc core affects other properties, such as the optoelectronics features, structure, and supramolecular organization.



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Chemical Reviews Subphthalocyanines, Subporphyrazines, and Subporphyrins: Singular Nonplanar Aromatic Systems
2014 **114** (4), 2192-2277

Phthalocyanine Dimers linked with Spirofluorene and Phenothiazine bridges as Hole Transported Materials in Perovskite Solar Cells

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Solar energy is emerging as a strong candidate to replace the fossil fuels that dominate today's energy market^[1]. Perovskite solar cells (PSCs) are a type of photovoltaic device under study that stands out for its extraordinary efficiencies and low cost, however, it has yet to overcome some drawbacks, such as its low long-term stability^[2]. It has been observed that the hole transporting layer (HTL) is closely related to both the stability of perovskite and the conversion efficiencies obtained. The hole transporting material (HTM) insulates the perovskite from damaging environmental conditions, prevents the passage of electrons and transports the holes that allow the potential difference to be generated^[3]. In recent years, phthalocyanines (Pcs) have been widely studied for this purpose,^[4,5,6] due to their high efficiency and low cost. Recently, we have demonstrated how the use of dimer Pcs increase the stability of the PSCs with high efficiencies [7,8]. In this communication, the synthesis of new ZnPc dimers linked with spirofluorene and phenothiazine bridges, with and without the presence of ethynyl spacers, has been carried out (**Figure 1**). The objective is to study the effect exerted by the triple bonds in the Pc structure on their ability to transfer holes in PSC and their implication in the final photovoltaic performance.

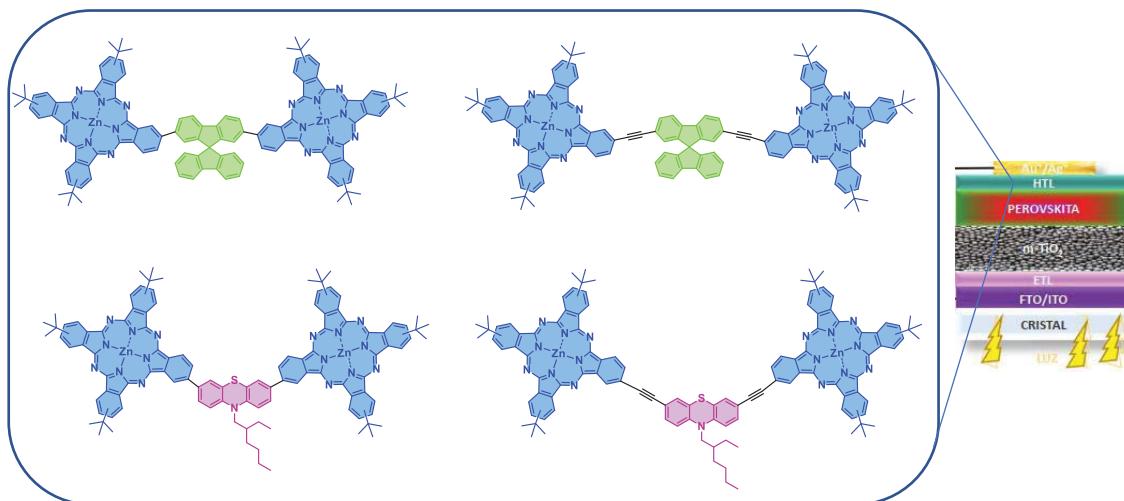


Figure 1. ZnPc dimers used as HTMs in PSCs.

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Steady-state properties of 8-Hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS) in different media

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Organic fluorophores that can undergo a proton transfer (PT) reaction, known as proton transfer dyes (PT-dyes), are one of the most explored dyes owing to their outstanding properties.^{[1], [2], [3]} The PT reaction may occur in their ground or excited state, and may happen within the same molecules frame (excited-state intramolecular proton transfer, ESIPT) or between two different molecular structures (excited-state intermolecular proton transfer, ESPT). PT-dyes present many advantages over other organic fluorophores, as the transfer of their proton to an acceptor moiety, allow a numerous possible chemical structures (enol, keto, anions, cations, zwitterions) with unique optical (absorption and emission) properties. In fact, ESPT dyes have been deployed in a wide number of applications such as optical sensing and detection.^[4]

Herein, we present the steady state characterization of an ESPT dye, 8-Hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS), in different media (basic, neutral and acid) to understand the spectroscopic (absorption and emission) properties of the possible chemical species of the PT-dye. The emission of HPTS in a basic medium is green in color, characteristic of the emission of the anion specie. However, the emission of the HPTS in an acid environment is blue in color, characteristic of the emission of the enol tautomer. On the other hand, in a neutral medium we can observe the presence of both structures (anion and enol) and the transformation of the enol to the anion one after its photoexcitation as a consequence of an ESPT reaction. These studies are the beginning of the future experiments, in which this type of molecules can be encapsulated within different materials to be implemented as active layers of sensors of acids and bases.

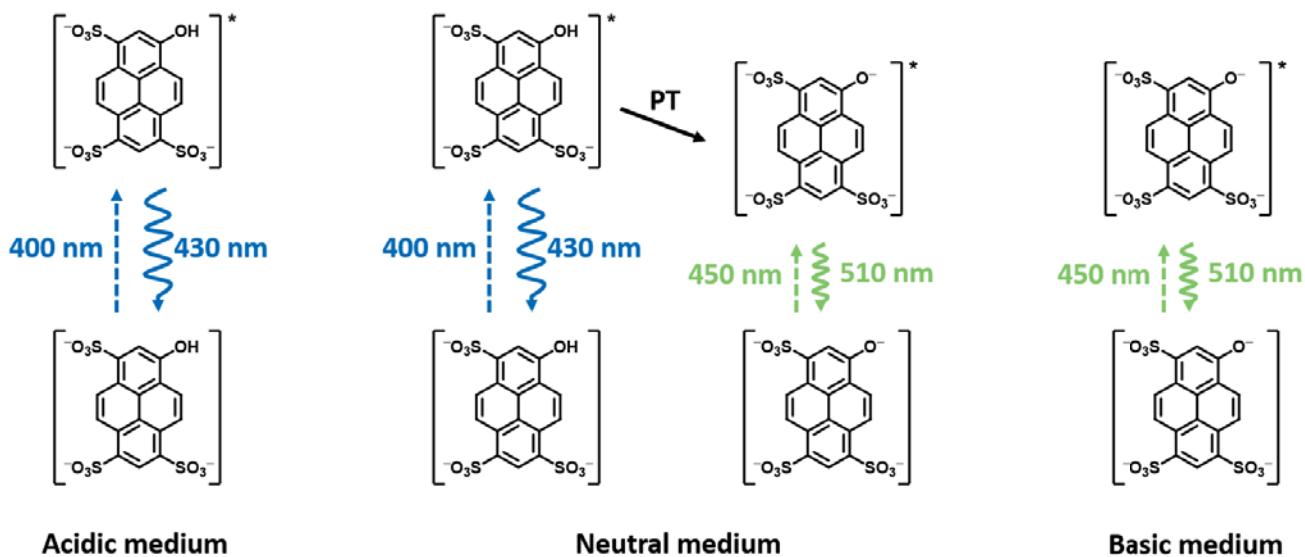


Figure 1. Schematic of the possible structures of HPTS in different media together with their characteristic absorption and emission intensity maxima wavelengths. Moreover, in neutral media we can observe the transformation of the enol to the anion structure through an ESPT reaction.

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Study of the dynamic behavior and stability of polyarginine/sodium dodecyl sulfate (PLA/SDS) films spread at the air/water interface

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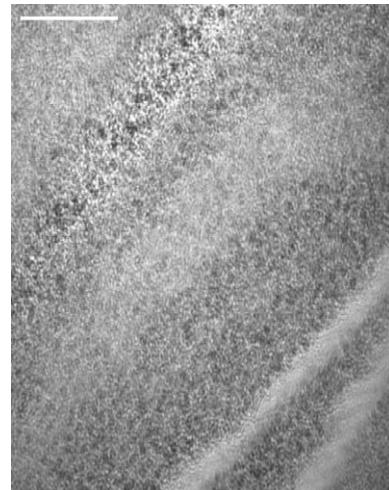
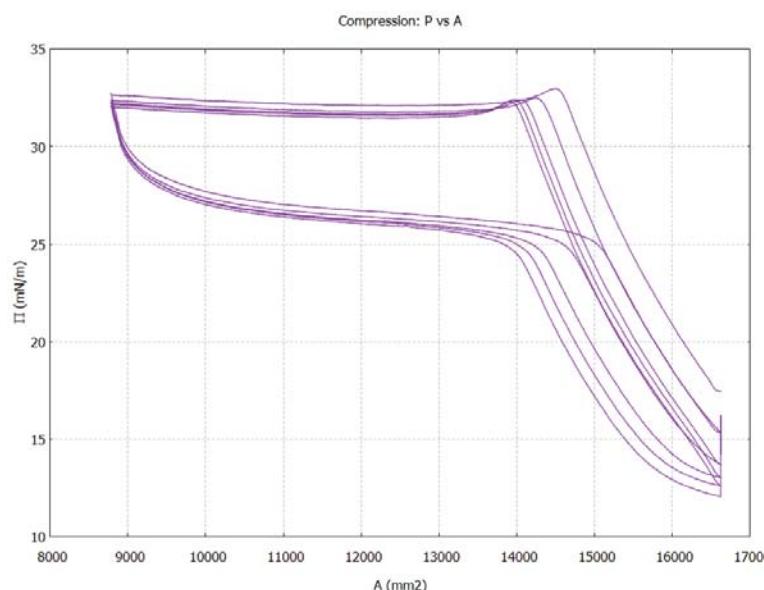
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The properties of oppositely charged polyelectrolyte/surfactant (P/S) mixtures both in bulk and on the surface have increased their interest in colloidal science. The main interested motivation of this type of system is to understand the structure and the formation mechanism of mixed layers at fluid interfaces to find different applications in biocompatible materials, water treatment and everyday life products.

Recent studies have demonstrated the ability to generate extended structures in P/S mixture films at the air/water interface depending on the charge/structure of the aggregates [1]. In addition, studies have also been carried out on different systems to characterize the triggers of the formation of these structures under certain conditions and the shape and behavior of the structures depending on the type of system.

As a possible continuation of these works, this study is focused on the characterization of a new system, using polyarginine as a polyelectrolyte and sodium dodecyl sulfate as a surfactant in the P/S mixture. To accomplish this, we have used a Langmuir trough that allows us to perform surface pressure isotherms in order to study the dynamic response of films to changes in the surface area. We have accompanied this technique with reflectometry techniques such as Brewster Angle Microscopy (BAM) to represent the lateral inhomogeneity on the micrometer scale of the film.

We have carried out the experiments for three different charges of the aggregates (overcharged, undercharged and neutral) to verify if this has a real effect on the formation of the extended structures, obtaining very similar results in the three cases. We have also been able to verify that the behavior of the monolayer in this system is slightly different from those studied previously, comparing the isotherms of the different systems and the BAM images, we can conclude the type of structure formed and its stability is different depending on the type of aggregates.



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Synthesis of gold nanoclusters fixed on mesoporous materials and the study of its catalytic activity in oxidation reaction

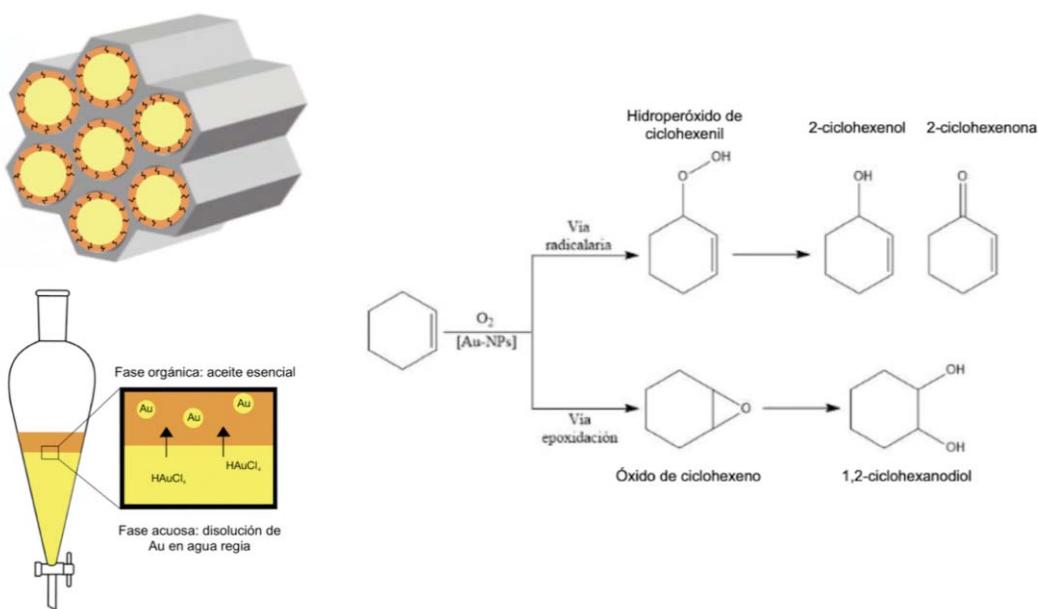
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The present project is focused on the synthesis of gold nanoclusters, supported on mesoporous silica SBA-15 functionalized with thiol groups and amine groups, and the study of its catalytic activity on the oxidation of organic compounds with molecular oxygen. The preparation of gold nanoclusters goes through a process edited by Nicolas Lemery in the eighteen century. This process describes the reduction of a gold solution in *aqua regia* with rosemary oil. The reaction takes place in a two-phase system, where gold is transferred from the aqueous solution to the organic phase. The mesoporous material has been synthesized by the sol-gel method.

Both synthesized materials – silica SBA-15 and the gold catalyst supported on the mesoporous material – are characterized by X-Ray diffraction, N₂ adsorption-desorption isotherms, thermogravimetry and elemental analysis of C, H, N and S. The gold catalyst is also characterized by UV-Vis spectroscopy and inductively coupled plasma atomic emission.

Once the catalyst is synthesized, the effect of light on the photocatalytic selective oxidation of cyclohexene is studied. The reaction is carried out under different light conditions: ambient light, darkness, and under different wavelengths of electromagnetic radiation in the visible region. In order to study the reaction rate, it is followed with gas chromatography analysis.



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A photoswitchable helical peptide with light-controllable interface/transmembrane topology in lipidic membranes

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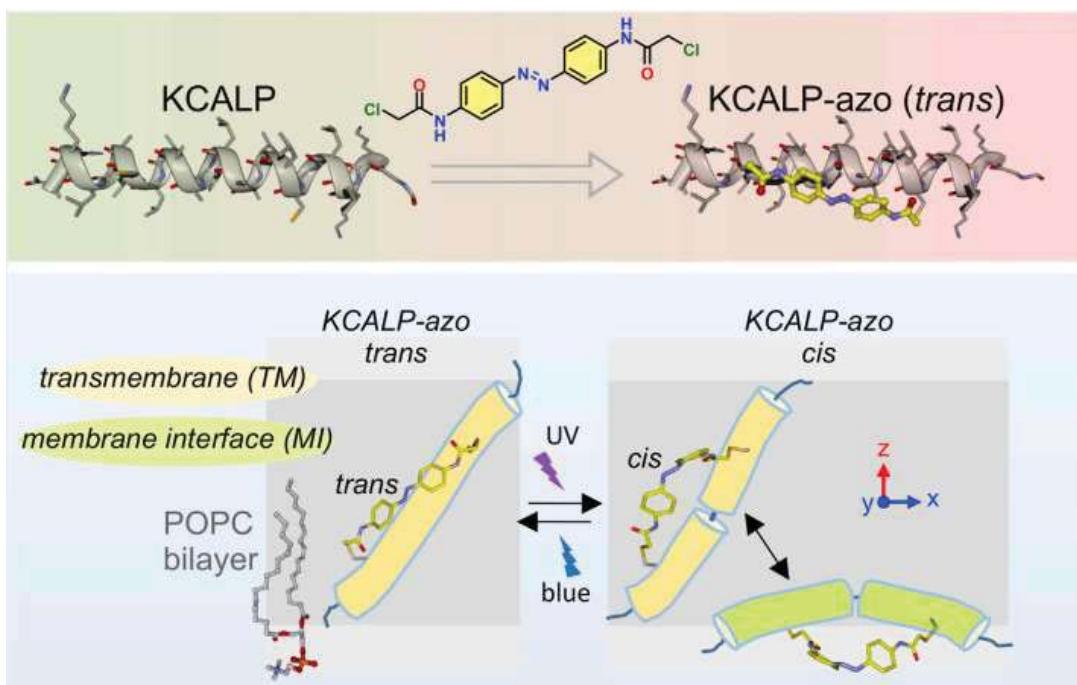
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The spontaneous insertion of hydrophobic helical peptides into lipid bilayers is a process not fully understood [1,2]. This is due to the lack of sensitive experimental procedures allowing to perturb transmembrane peptides (TM) out of equilibrium reversibly and in a small-time frame, being able to measure with sufficient resolution the changes in topology and structure. A practical approach to achieve this sensitivity is photocontrol of peptide folding, using a molecular photoswitch covalently coupled to the peptide. The fast and reversible isomerization of the photoswitch with specific wavelengths can induce changes in the structure -folding/unfolding- of the peptide [3,4] and hence could promote a transmembrane to interphase (TM-to-MI) transition. To measure with time and spatial resolution we used FTIR spectroscopy with modified setups to include a polarizer and LEDs to irradiate the sample, achieving effectively photoisomerization.

In this work [5], we use a 24-residues-long hydrophobic helical peptide, covalently coupled to an azobenzene photoswitch (KCALP-azo), which shows a light controllable TM/MI equilibrium in hydrated lipid bilayer POPC films measured in FTIR spectroscopy, both in ATR and transmission. The results reveal that *trans* KCALP-azo is a transmembrane *a*-helix and after trans-to-cis photoisomerization of the azobenzene with UV light, the helical structure of KCALP-azo is maintained with small changes in its structure, although its helix tilt increased from $32 \pm 5^\circ$ to $79 \pm 8^\circ$, indicating a TM-to-MI transition. After photoisomerization to cis with blue light, we observe a reversible but incomplete MI-to-TM transition, with cis KCALP-azo in a mixture of 90% TM and 10% MI [5].



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Understanding the 3D- to 0D-phase transformation mechanism of hybrid organic–inorganic lead halides perovskites

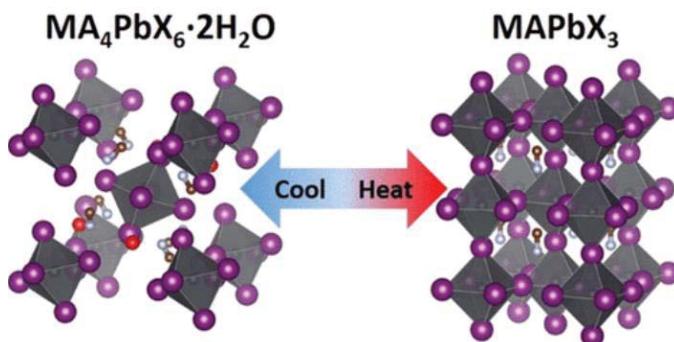
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Halide perovskite materials are the last couple of years very well-studied due to their exceptional properties like, good optoelectronic properties, chemical tenability, relatively high carrier mobility, diffusion length, and radiative lifetime. Not to mention the low cost of material and ease of synthesis of these perovskites, making them an interesting candidate for multiple applications. Therefore, over time hybrid perovskites are integrated in many different types of devices like, Solar cells, LEDs, photoconductors, lasers etc., resulting in some very high efficient devices. While good performing devices are produced, the stability of these hybrid perovskite materials is still poor. To tackle this problem a better understanding of the perovskite behaviour under different environmental conditions is needed. Recent articles have noted a dihydrate organic–inorganic perovskite phase ($\text{A}_4\text{PbX}_6 \cdot 2\text{H}_2\text{O}$) as a degradation or side product of a three dimensional (3D) perovskite. In this talk, the study of this phase is discussed in detail for the $\text{MA}_4\text{PbX}_6 \cdot 2\text{H}_2\text{O}$ perovskite. Having a look into the small organic cation is particularly important as the majority of lead halide perovskites used in optoelectronics is based on such organic cations. It is important to highlight that the reported hybrid organic–inorganic zero-dimensional phase is in fact a hydrated structure: $\text{MA}_4\text{PbX}_6 \cdot 2\text{H}_2\text{O}$. We will show the first solvent-free mechanochemical synthesis of $\text{MA}_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$ and demonstrate its reversible transformation into and from the 3D perovskite analog (MAPbI_3) by controlled (de)hydration under thermal annealing and simple cooling down in moist air. Finally, we will demonstrate the synthesis of mixed $\text{MA}_4\text{Pb}(\text{Br}_1 - \text{xI}_x)_6 \cdot 2\text{H}_2\text{O}$ with $0 < x < 1$, thus expanding the possibilities of these overlooked hybrid organic–inorganic ternary metal halides, which could be implemented for instance in tunable narrow- band near-UV photodetectors.



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Growth of a Poyoxometalate-Capped Giant Iron-Based Molecular Mineral Structure from Water

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Recently, the discovery of naturally occurring polyoxometalates (POMs) in mineral structures demonstrate their importance in geochemical systems.¹ Understanding and identifying of the hydrolysis products of iron in aqueous system is crucial for understanding the formation of iron minerals. Through a “bottom-up” approach, a giant iron-based molecular mineral $\{\text{Fe}_{32}\text{O}_{45}\text{Na}_6(\text{OH}_2)_{18}\}^{12+}$ ($1.7\text{ nm} \times 1.0\text{ nm}$) has been captured from water in the presence of a suitable inorganic ligand via controlled hydrolysis of iron salts. The oxidatively robust POM ligand $[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$ not only stabilizes and crystallizes the iron-oxo cluster but also bestow its intrinsic properties such as solubility, stability and electron trapping capability to the isolated product $[\text{Fe}_{32}\text{O}_{45}\text{Na}_6(\text{OH}_2)_{18}(\text{P}_2\text{W}_{15}\text{O}_{56})_6]^{60-}$ (**Fe**₃₂). The reduction of 32 Fe³⁺ centers to Fe²⁺ while retaining its structural integrity, making it a promising system for electrocatalytic reduction processes. Our synthetic approach provide a molecular pathway for geochemical reactions in the course of mineralization process.

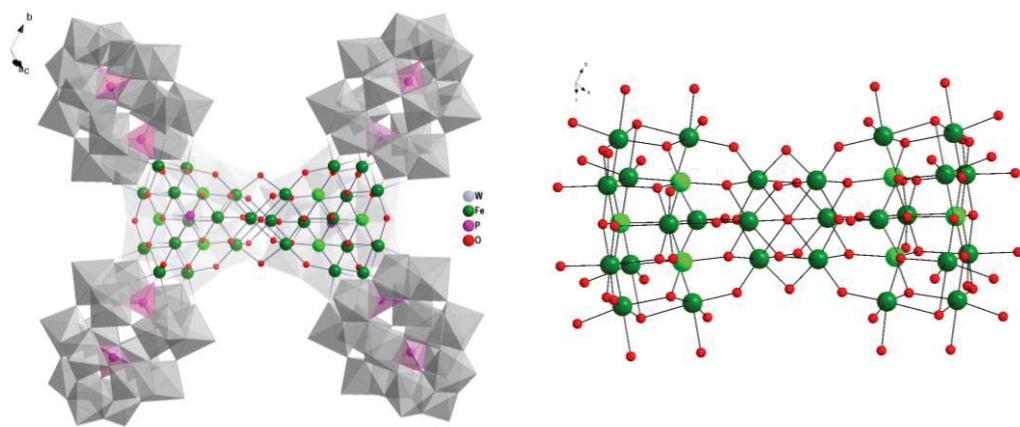


Figure 1. Combined polyhedral/ball-and-stick representation of **Fe**₃₂ POM and **Fe**₃₂ core.

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Exosomes encapsulated with Curcumin, as Natural Nanoparticles for Drug Delivery System

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Exosomes are extracellular vesicles with size (30-150nm), they play an important role in extracellular communication and immune response. Their natural origin, nanometric size and liposome structure allows them to deliver anti-inflammatory agent like curcumin to target cells. Curcumin has addressed good pharmacokinetics properties, stability and safety in human body. However, it has low water solubility and high interaction with lipid membrane, lead it a barrier in its biodistribution and efficacy. Therefore encapsulating curcumin with exosomes will lead to an increased solubility, bioavailability and direct specificity into inflammatory cells. Hepatocellular carcinoma is a primary malignancy of the liver. The diagnosis of HCC remains with low specificity and sensitivity .Here we report the Development of new targeting agent of Exosomal curcumin for therapeutic and diagnosis of HCC.

Exosomes were derived from semi skimmed goat milk then purified and isolated using ultracentrifugation techniques, then protein content for unlabeled exosomes was quantified by Bradford coomasie assay. Later exosomes were characterized by Nanoparticle Tracking Analysis (NTA) and Dynamic Light Scattering (DLS). Following encapsulation of exosomal curcumin probe was done by active encapsulation employing saponin. For this purpose, 200 µg of exosomes were added to 13.5 µl of curcumin (74 mg/ml) and 200 µl of saponin, in 1X phosphate buffer saline, to reach a final reaction volume of 1 ml. Then, the reaction sample was mixed and incubated at 37°C, 300 rpm in darkness for 20 min using a Thermomixer. Lastly, curcumin-encapsulated exosomes were purified by PD10 desalting column, recovering a final fraction of 1.5 ml.

The new ExoCurcumin nanocomplex were fully characterized by NTA, and Nanophotometry. Isolated exosomes showed (135 nm) size by DLS and modal size (120 nm) by NTA. After encapsulation with curcumin the size was (121.8 nm) with NTA, therefore the size of nanoparticle didn't change after encapsulation. Nanophotometry revealed high concentration of curcumin encapsulated inside the exosomes. Finally, in order to evaluate the kinetics of the curcumin released from the nanocomplex, in vitro assays at different time intervals were performed by nanophotometry, which revealed a release of similar values after five and seven days.

In this work we have synthetized the nanocomplex ExomalCurcumin based on the encapsulation of curcumin into milk exosomes. Future studies will evaluate the theragnostic capacity of our agent in optical imaging for treatment of hepatocellular carcinoma.

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Facile route for the formation of lead halide nanoparticles in functional thin-film

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Lead-halide perovskite nanoparticles are a very promising family of materials due to their optoelectronic properties and chemical versatility [1]. By changing the chemical composition, different bandgap energies can be achieved and hence, different absorption and emission spectra, which can be further tailored when the quantum confinement regime is achieved. Additional advantages of perovskite nanoparticles functional thin films include low-cost deposition techniques and less material consumption [2]. However, conventional methods to fabricate perovskite nanoparticles in suspension, such as hot injection, make it challenging to develop functional thin films based on these materials.

The method proposed here uses a metal-organic host matrix based on a sol-gel approach that allows us to obtain perovskite nanoparticles by exposing the films at high humidity atmospheres (70% - 100% RH) after deposition by spin coating. Conductive thin-films with excellent optoelectrical properties can be readily obtained, even without annealing, by this simple mechanism. We will discuss the crystallisation mechanisms and the factors that control the main properties of the nanoparticles.

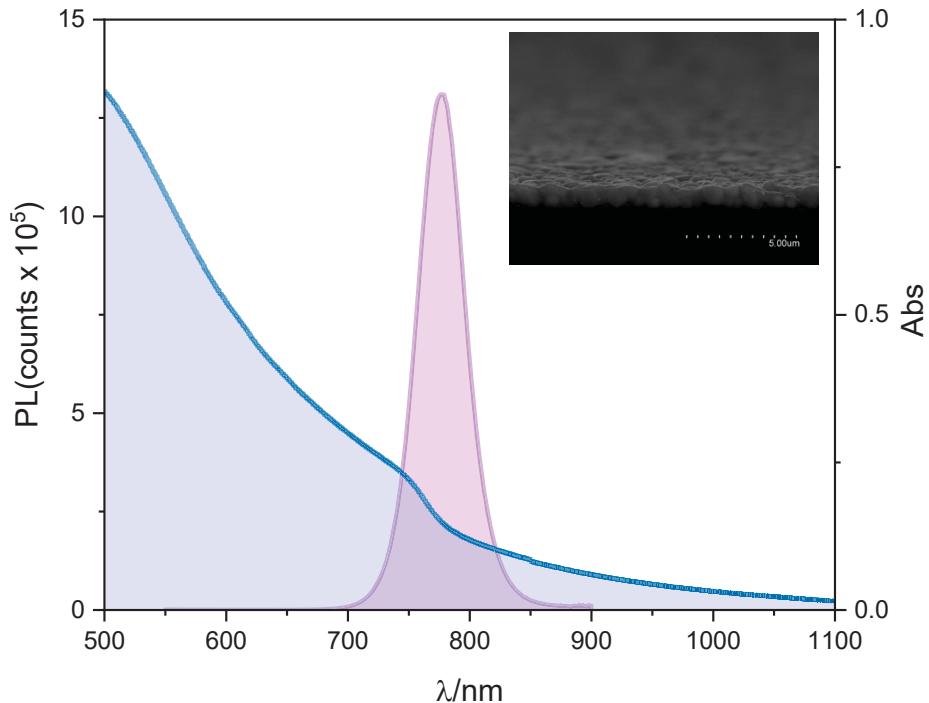


Figure 1. PL and absorbance spectra of a $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film embedded in the organic matrix and crystallized under a 70% of relative humidity atmosphere. Inset : cross-sectional SEM image of the same film.

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Physicochemical characterisations of HCIV-1 virus in extreme saline conditions

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Haloarcula californiae icosahedral virus 1 (HCIV-1) is a halophilic euryarchaeal virus living in salt crystals. It is a tailless icosahedron ~70 nm in diameter, with a lipid vesicle inside protein capsid. Main components are proteins, lipids selectively acquired from the host, and a 31 Kbp linear double helix (ds) DNA molecule. HCIV-1 was isolated from *Haloarcula californiae*, but it can also infect three other strains of Haloarchaea.[1]

Atomic force microscopy (AFM) is a power tool using in nanoscience. AFM in liquid media has been successfully used not only for the topographical characterisation of biological entities such as viruses, but also for single particle characterization, allowing to characterize different physical-chemical properties.[2].

The aim of the current study is to investigate how HCIV-1 adapts to different salinity conditions. For that propose we have performed nanoindentation assays by AFM operating in Jumping Mode + [3], to characterize mechanical and physical changes in virus capsid such us yield force, elasticity, deformation, and height. To explore the adaptation of the viral capsid to the media HCIV-1 capsid has been characterized in two different extreme buffer conditions (1 M NaCl, and 2 mM NaCl) and removing drastically and progressively the salt concentration of the virus environment. In addition, we have studied how the internal lipid vesicle has influenced in the mechanical behaviour of the HCIV-1 virus.

We have observed that a drastic change of the buffer of salt concentration affects increasing in stiffness and yield force of the virus capsid. In contrast, a progressive change in salt concentration do not affect the mechanics of the particle. So far vesicles don't show any relevant difference.

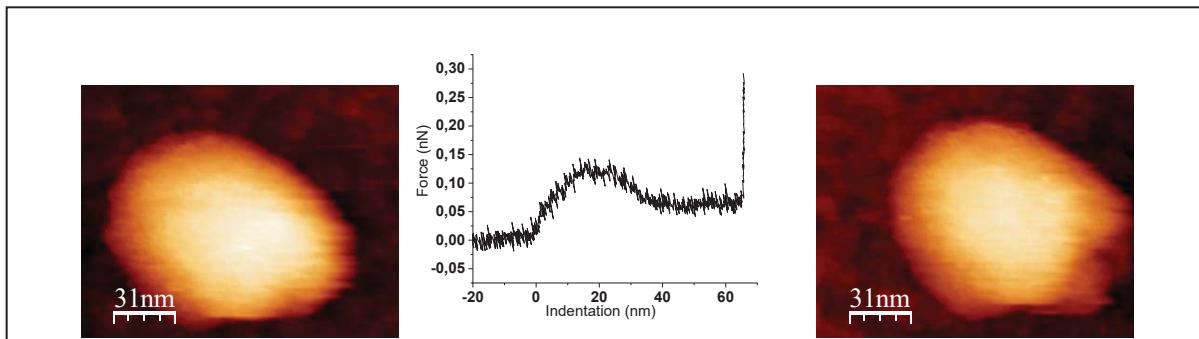


Figura 1. HCIV-1 Left to right, topography of HCIV-1 before the indentation ; Force-Indentation curve example; right image shows the topography of the HCIV-1 after the indentation

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Solubility and diffusivity of hydrofluorolefins in polyurethane foams

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Nowadays, polyurethane foams are mainly used as thermal insulation materials and therefore, knowing the evolution of thermal conductivity over time, i.e., with ageing, is a very relevant factor.

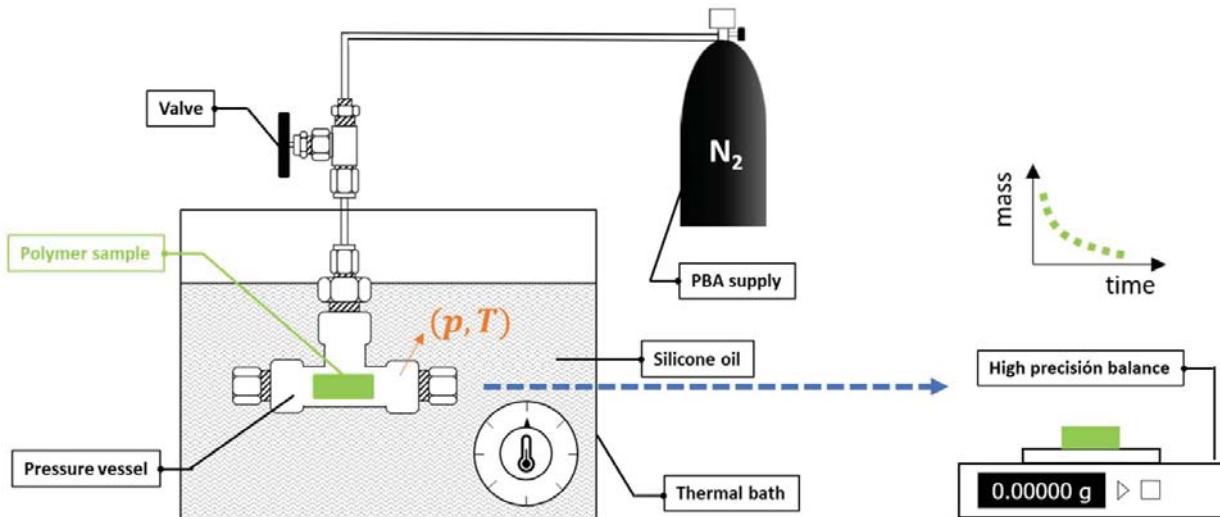
Thermal conductivity grows with time. However, depending on the type of foaming agent used in the formation of the foam, the process of increasing of thermal conductivity can be slowed down to some extent. The foaming agent provides the insulating properties to the foam, and its solubility and diffusivity in the polyurethane matrix directly influences the greater or lesser rise in thermal conductivity over time. Therefore, knowing the solubility and diffusivity of blowing agents in different polyurethane foams is the main objective of this work

Hydrofluorolefins (HFOs) are the blowing agents used in this study. They are olefins, and represent a new group of blowing agents, with a zero Ozone Depletion Potential (ODP), low Global Warming Potential (GWP) and low flammability. They offer an alternative to the preceding generations blowing agents, such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) [1].

The method used to take solubility and diffusivity measurements consists of introducing the polymer sample with blowing agent under controlled pressure and temperature conditions. These terms have been determined by studying the polyurethane foaming conditions.

Solubility and diffusivity are calculated from the mass loss curve of the polymer injected with the blowing agent under pressure [2]. By studying the desorption process, the solubility and diffusivity data in the polyurethane matrix are obtained.

In addition, tests have been carried out to characterise the polyurethane sample at a chemical level. Among the tests that have been carried out are infrared spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).



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Synthesis and characterization of semiconductor nanoparticles as luminescence naothermometers.

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Temperature has a significant role in most of the relevant biochemical processes in living organisms. One of the first signs of many diseases and health dysfunctions is the appearance of local temperature variations.^[1] Consequently, the measurement of temperature and application of heat in biological media has become an essential element in the development of the latest generation of diagnostic.^[2]

The current technology does not comply with the increasing demand for non-contact temperature measurements in deep and localized regions. In order to overcome these difficulties, some of the latest techniques in research rely on nanometric systems that are capable of functioning as remote thermometric or nanothermometer probes. Among the novel methodologies in the measurement of temperature, the exploitation of the thermal dependence of the optical luminescence properties of nanoparticles (NPs) stands out as one of the most promising.^[3] This technique, commonly referred as **luminescence nanothermometry (LNT)**, consists in using NPs deposited on the targeted area to obtain, without contact, a remote temperature reading through the change in its luminescence emission (Figure 1).

In this research, we study the use of silver sulphide (Ag_2S) NPs as luminescent nanothermometers in biological tissue. These NPs (with sizes below 10 nm)^[4] are biocompatible and their photoluminescence, (PL), is centered on 1250 nm (Figure 1a), within the second biological window where light absorption by tissues is minimized. The main objective of this study is to synthesize and characterize the NPs, then to propose a procedure by which information on temperature changes in a biological medium can be obtained using luminescence nanothermometry

This technology could be used for early detection of diseases (e.g., a stroke) and inflammatory processes, which course with the appearance of incipient localized temperature singularities.

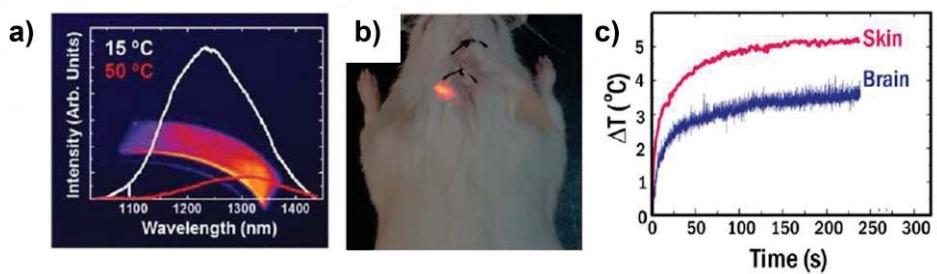


Figure 1. a) luminescence spectra with different intensities and wavelengths as a function of temperature are obtained. b) Merged image of infrared fluorescence *in vivo* and an optical image of a mouse, revealing the presence of Ag_2S NPs injected intracerebrally. c) Comparison of the temperature change obtained on the surface of the skin of the mouse shown in b), measured by infrared thermography and that obtained with Ag_2S NPs by LNT.

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Synthesis of Aza-BODIPY photosensitizers and their application in-vitro for photodynamic therapy

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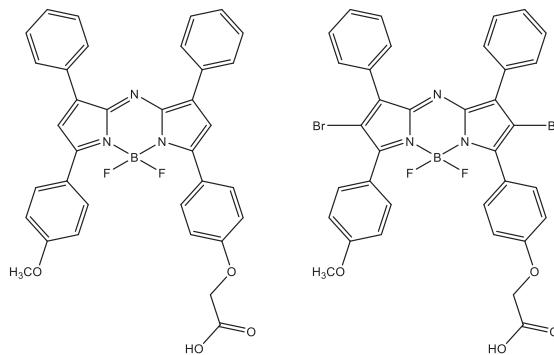
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Photodynamic therapy (PDT) is a two-stage treatment that was discovered more than 100 years ago. This type of therapy depends on three important elements: oxygen, light energy, and a drug called photosensitizer with the goal of destroying cancerous and precancerous cells.^[1] The photosensitizer gets either conjugated to an antibody, peptide, protein, ligand with specific receptors, or linked to a nano-carrier to first target the cancerous cell. Once it gets inside the targeted cell, the photosensitizer absorbs the received light with the suitable wavelength for it to get activated, which results in reactive oxygen species (including singlet oxygen). There are photosensitizers of different classes and Aza-BODIPY (Aza-boron-dipyrromethene) based photosensitizer is the one used in this project. It is known by its high molar extinction coefficients and a broad absorption band spanning from 600 nm to 700 nm. Different techniques were used to get two of these compounds and study their optical properties: chemical organic synthesis, extraction to selectively remove components in the mixture and isolate the compound, thin-layer chromatography (TLC) to analyze the compound mixture knowing the nature of components in it, column chromatography to get the compound purified, pH measurement to neutralize the compound, proton nuclear magnetic resonance spectroscopy (H-NMR) to determine the molecular structure of the compound, and ultraviolet-visible spectrophotometry to study the properties of the photosensitizer and to determine the suitable wavelengths for its light absorption and emission. As results, the two compounds were successfully identified by H-NMR: the first one is with the bromine, and the second one is without. The spectra of UV-Vis spectrophotometry showed the absorption and the emission of 685 nm and 715 nm respectively for the second compound, along with the absorption and the emission of 677 nm and 712 nm respectively for the first compound. Both are successfully ready for bio-applications such as photodynamic therapy and cell imaging.



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Synthesis, characterization and application of new silver DNA nanoclusters in the inactivation of microorganisms.

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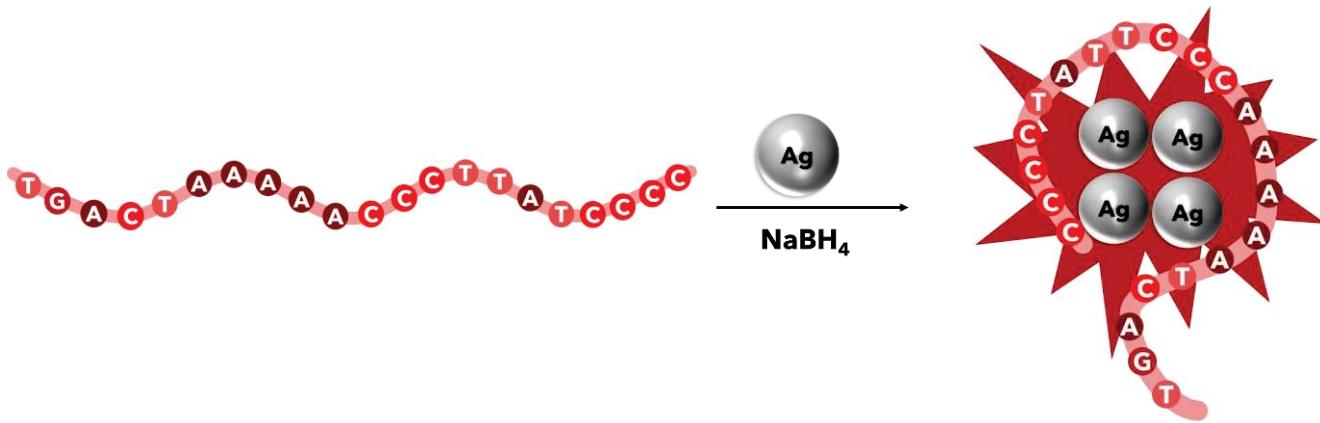
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The spread of resistant bacterial strains is one of the main threats to humanity as recognised by the World Health Organization in its report in 2014 and in its priority list of pathogens published in 2017.[1] The widespread use of antibiotics during the last 30 years resulted in less effective or even, ineffective clinical treatments. Nowadays, antimicrobial infections are treated with drugs developed in the 80s and thus, the pipeline of new drugs has diminished in the last years. Microbial infections have arisen in the last years and are estimated to cause an annual death toll of 10 million worldwide by 2060, which will make many of the medical advances of the 20th century obsolete.

Silver is a non-essential element known for its antibacterial effect used by different civilisations since ancient times. However, the application of silver and silver-based materials is scarce because of the widely use of antibiotics. Nevertheless, the lack of new antibiotics to treat resistant strains has arisen the interest to develop new drugs, targets and therapies of pharmaceutical industry and non-profit organisations. Among silver-based materials, silver nanoclusters have attracted much interest in the last years due to their molecule-like optical properties, in particular, their strong fluorescence. These optical properties of the silver nanoclusters are finely tuned by the capping agents, which are usually chitosan, PEG, PVP or BSA. Recently, DNA has emerged as a new capping agent that can confer additional properties to the material depending on the oligonucleotide sequence used for the material synthesis. [2-3]

In this work, we have developed novel silver DNA nanoclusters showing tunable fluorescence emission depending on the oligonucleotide sequence and characterised them by UV-Vis and fluorescence spectroscopies, DLS and TEM. Taking into account their photophysical properties, photoactivation of the materials have been used to kill bacteria (*S. Aureus* and *E. Coli*) and the mechanisms of action are currently investigated.

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Memristive Behaviour in Nitronyl Nitroxide Organic Radical Crossbar Array

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Memristors are considered as one of the most promising candidates for achieving neuromorphic computing applications. Their abilities to store information as different resistance states and erase and write through various means (e.g. voltage, current, light), allows the integration of processing and information storage [1], which is very similar to how human brain functions. Compared with metal oxides and phase change materials based memristors, molecular memristors surpass them in terms of fabrication difficulty, flexibility, and space for tailoring the properties. Thus, making them competitive candidates for building memristor devices.

Here, I would like to report the distinct memristive behaviour of the nitronyl nitroxide organic radical crossbar array. NIT-PhOPh radical was selected for the creation of crossbar array and unusual memristive behaviours were observed:

- The switching events are stable and have no apparent dependency on the temperature. This implies that the switching mechanisms are likely determined by processes that are not temperature dependent.
- In the 'ON' state (low resistance state), the resistance value is not consistent, and had large variation and even some anomalous points that are far away from the average value. The anomaly likely indicates the existence of an intermediate resistance state.
- With increasing film thickness, switching happens with distinctively higher resistances without any change in the switching voltage, and the switching event starts to become random.

These observations provide interesting perspective on the memristive behaviours of NIT radicals, which is worthy further investigation.

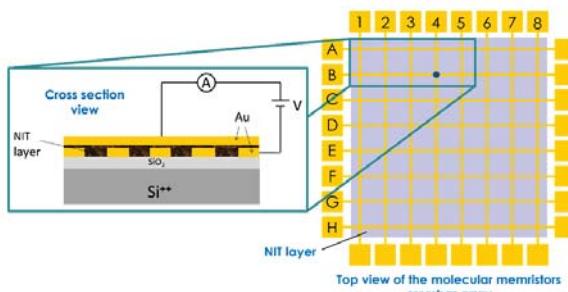


Figure 1 – Cross section and top view of the crossbar molecular memristor device, highlighted dot is cell B4

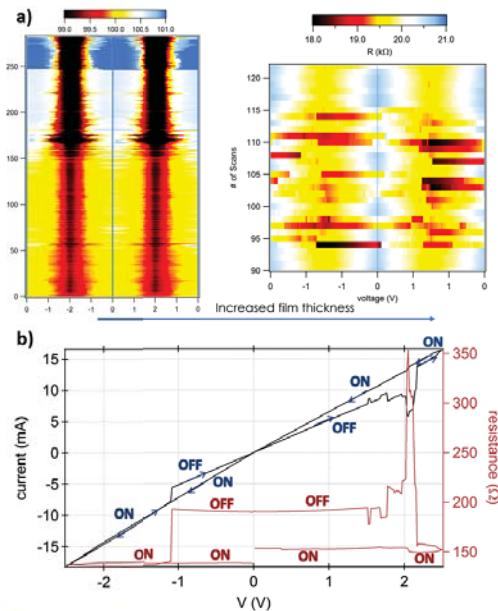


Figure 2 – Preliminary data of a memristive device. a) Switching variability study with increased film thickness. Switching becomes more random with increasing film thickness. b) One complete switching cycle of a NIT organic radical film. All data were obtained by Nicola Dotti.

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High Voc's in spite of High Bulk Recombination in Small-Grain Vacuum-Processed Perovskite Solar Cells

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In a short timescale, perovskite solar cells have reached power conversion efficiencies comparable or higher than established technologies such as Si, GaAs or CIGS based solar cells, still with room for improvement. One important parameter is the open-circuit voltage (Voc) which is mainly influenced by electronic traps in the perovskite bulk or at the interfaces with the charge transport layers (CTLs). Perovskite solar cells are predominantly fabricated via solution-processing methods due to their low cost and good accessibility. These devices are therefore well investigated and set the records for efficiencies and Voc's. It was found that the solution-processed perovskite bulk exhibits big grains, long carrier lifetimes and a high photoluminescence quantum yield (PLQY) when passivated which finally led to the conclusion that the interfaces to the CTLs are limiting the Voc's.[1] Co-evaporation of perovskites offers answers to problems like up-scaling and stackability. However, these films show often different characteristics and are less studied than their solution-based counterpart. Despite their small grains and short photoluminescence lifetimes co-evaporated perovskite solar cells show competitive Voc's.[2] This opens the question about the role of interfacial/bulk recombination connected to this fabrication method. Here, we investigate the apparent contradiction with PL, TRPL and drift-diffusion simulations and show that bulk and interfaces are similarly limiting. We suggest improving the bulk first, as it directly affects the interfaces as well.

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Modeling and analysis of molecular technologies for the implementation of Field-Coupled Nanocomputing

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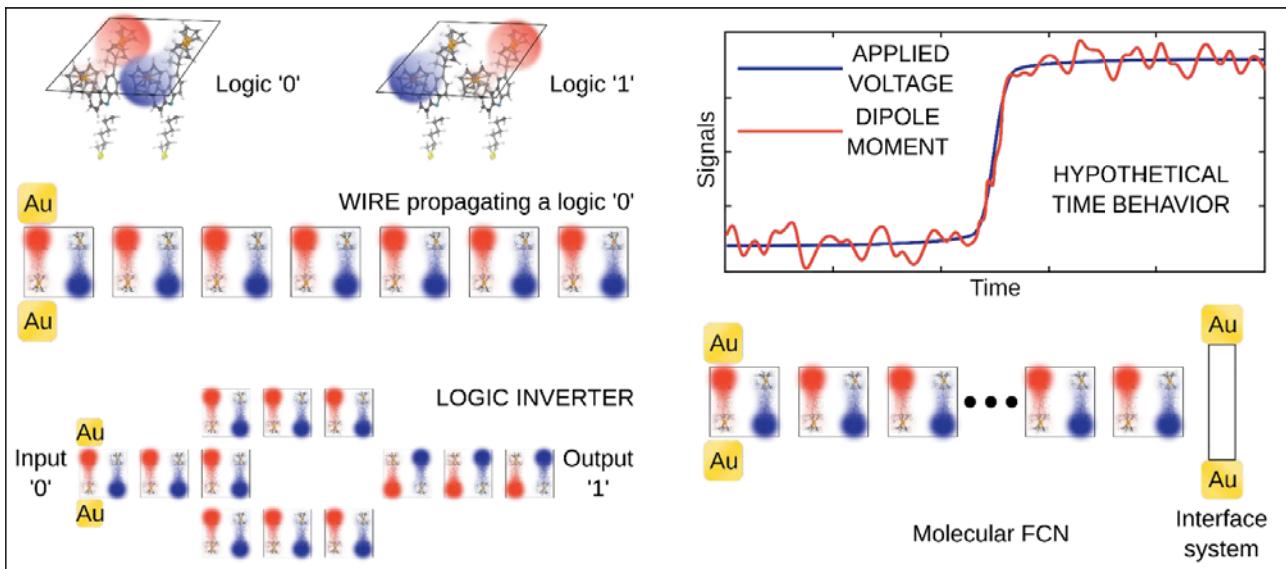
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In recent years, researchers proposed different technologies to face the current demand for ultra-scaled electronic devices. Molecular Field-Coupled Nanocomputing (FCN) is a beyond-CMOS technology that encodes the logic information in the aggregated charge of redox centers of ad-hoc synthesized molecules [1]. Neighboring aligned molecules interact differently depending on their particular electrostatics [2]. Moreover, thanks to Coulomb's repulsion force, it is possible to propagate information or design logic gates. The main advantages of this technology are the high device density per unit area and the ultra-low power consumption since no currents are involved. Moreover, the Coulomb's interaction between neighboring molecules is strong enough for molecular FCN to operate at room temperature [3]. The molecular FCN implementation also offers the possibility to exploit self-assembly techniques. Nevertheless, the need for precise nanopatterned structures slows down the possibility of obtaining a working prototype. A recent result demonstrated the possibility of performing molecular FCN computation on a uniform self-assembled monolayer, though some challenges still must be addressed [4]. Another crucial aspect to consider is the need to measure the charge on a molecule to transduce it into an electrical quantity and enable the interface with conductive electronics.

More specifically, we concentrate on the computational assessment of the molecular FCN to extract useful indications before realizing a working prototype. In our group, we concentrate on mainly two aspects. On one side, we are developing a framework to perform architectural-level simulations of devices implemented in molecular FCN. On the other side, we perform *ab initio* simulations to improve the model description of a single molecule. Indeed, in molecular technologies, it is fundamental to define simple behavioral models that allow the simulations of complex circuits. It is also essential to include all the physical characteristics in the model to obtain precise predictions. One fundamental aspect on which we are currently working regards the dynamic molecule behavior, so we are simulating molecules in the time domain to precisely describe how molecules react to applied electric fields. Indeed, the molecules dynamics characterization will give us essential parameters for electronic devices. Still related to molecular modeling, we are also investigating the possibility of reading the charge distribution on these molecules by interfacing them with conductive systems. We are also currently working to adapt the paradigm to simplify the realization of a prototype and the output measurement, both at the circuit level and the prototypal level with charge measurements, eventually exploiting scanning probe microscopy techniques.



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Pulsed Laser Deposition of $\text{Cs}_2\text{AgBiBr}_6$: from mechanochemically synthesized powders to dry, single-step deposition

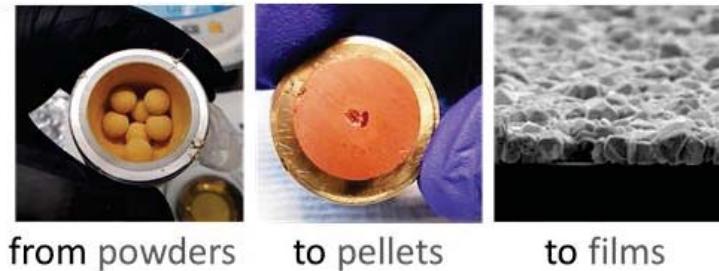
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$\text{Cs}_2\text{AgBiBr}_6$ has been proposed as a promising lead-free and stable double perovskite alternative to hybrid and lead-based perovskites. However, the low solubility of the precursors during wet synthesis, or the distinct volatility of the components during evaporation, results in complex multi-step synthesis approaches, hampering the wide spread employment of $\text{Cs}_2\text{AgBiBr}_6$ films. Here we present pulsed laser deposition of $\text{Cs}_2\text{AgBiBr}_6$ films as a dry, single-step and single-source deposition approach for high-quality film formation. $\text{Cs}_2\text{AgBiBr}_6$ powders were prepared by mechanochemical synthesis and pressed into a solid target maintaining phase-purity. Controlled laser-ablation of the double perovskite target in vacuum and a substrate temperature of 200 °C results in the formation of highly crystalline $\text{Cs}_2\text{AgBiBr}_6$ films. We discuss the importance of deposition pressure to achieve stoichiometric transfer and of substrate temperature during PLD growth to obtain high quality $\text{Cs}_2\text{AgBiBr}_6$ films with grain sizes > 200 nm. This work demonstrates the potential of PLD, an established technique in the semiconductor industry, to deposit complex halide perovskite materials while being compatible with optoelectronic devices fabrication, such as UV and X-ray detectors.



[1] Pulsed Laser Deposition of $\text{Cs}_2\text{AgBiBr}_6$: from Mechanochemically Synthesized Powders to Dry, Single-Step Deposition

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Chemistry of Materials 2021 33 (18), 7417-7422

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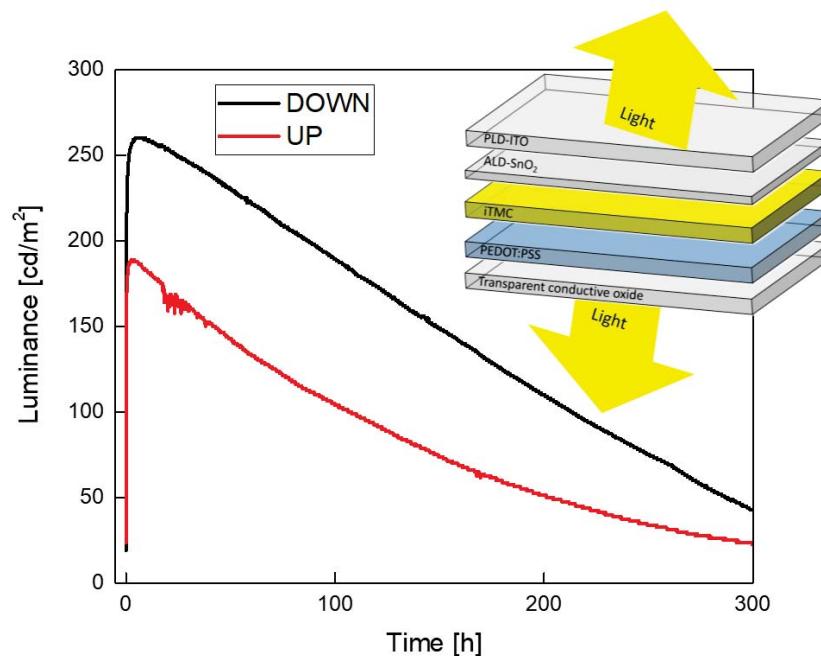
Semitransparent Light-Emitting Electrochemical Cells Using Transparent Conductive Oxides as Top Electrode

Lorenzo Mardegan, Abhyuday Paliwal, Kassio P.S. Zanoni, Daniel Tordera and Henk J. Bolink*

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In recent years, new display technologies have emerged, and with them, the need for development of properties such as large area, stretchability or semitransparency in organic light-emitting devices (OLEDs). In particular, for semitransparent OLEDs, the requirements for the cathode are high light transmittance (over 80%) and low sheet resistance (R_s). Semitransparent light-emitting devices are of great interest as they can enable new applications in consumer electronics. While semitransparent organic light-emitting diodes (OLEDs) have been largely studied, their demonstration in light-emitting electrochemical cells (LECs) remains scarce. Light-emitting electrochemical cells (LECs) currently represent a promising alternative to LED and OLED technologies that in its simplest form consist of a light-emitting active layer, which is composed of a blend of an electroluminescent semiconductor, a salt and an electrolyte, sandwiched between two electrodes. In this work we fabricate a semitransparent ionic transition metal complex based LEC (iTMC-LEC) by developing a transparent top contact based on tin (IV) oxide (SnO_2) and indium-tin oxide (ITO), processed by low-temperature atomic layer deposition (ALD) and pulsed laser deposition (PLD), respectively. ALD and PLD offer the advantages of adjusting the deposition conditions, such as pressure and temperature, to provide a high-quality film, with precise control over thickness and composition moreover the possible harsh effects of the ALD and PLD during processing on the organic underlayers were examined. The resulting devices present a transparency of 75% in the full visible spectrum (380 to 750 nm), with an 82% transmission at the emission peak (563 nm). The devices were characterized from both sides showing high luminance (260 cd m^{-2}) and long lifetime (176 h), with efficiencies reaching 5.2 cd A^{-1} and 3.2 lm W^{-1} , placing them amongst the highest performing semitransparent LECs. These results show the feasibility of using ALD/PLD as top contact for the fabrication of semitransparent LEC devices.

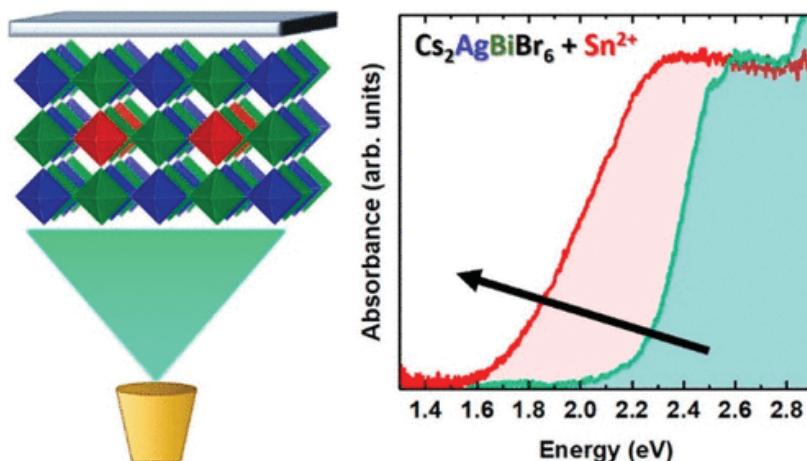


Tunable Optical Absorption of Sn-, Ge-, and Zn-Substituted $\text{Cs}_2\text{AgBiBr}_6$ Double Perovskites

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Lead halide perovskites (LHPs) have emerged as promising materials for future photovoltaics (PV) and other optoelectronic applications. However, their instability against heat and humidity and high toxicity represents a major bottleneck in their commercialization. Herein, we focus our attention on the search for alternative non-toxic materials with similar properties for PV. In particular, the lead-free halide double perovskite (DP) $\text{Cs}_2\text{AgBiBr}_6$ is envisaged as a promising candidate because of its high tunability in terms of chemical composition and optical properties. However, $\text{Cs}_2\text{AgBiBr}_6$ films have been reported to have a relatively wide bandgap of 1.95 eV and a limited charge diffusion length, which limits their performance as photovoltaic absorbers. Herein, we report the dry mechanochemical synthesis of Sn-, Ge-, and Zn-substituted $\text{Cs}_2\text{AgBiBr}_6$ in powder form, whose bandgaps range from 1.55 eV to 2.02 eV. The effect of the different additives inside the DP structure is rationalized through density functional theory (DFT) calculations and linked to lattice disorder, which leads to different optical properties. Finally, the first Sn-doped DP thin films deposited by single-source vacuum deposition techniques are presented, paving the way toward its implementation in photovoltaic solar cells.



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Wide Bandgap Perovskite Solar Cells with Enhanced Thermal Stability

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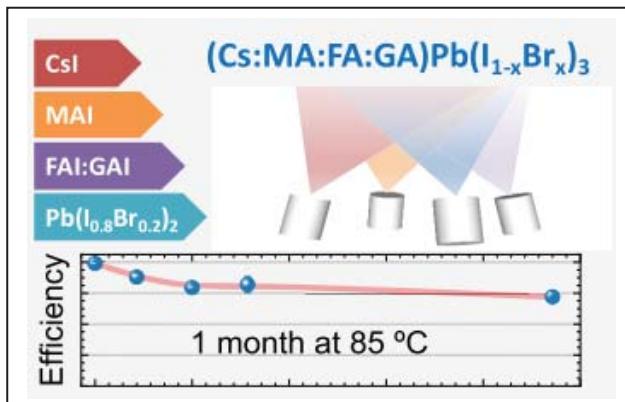
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Metal halide perovskites have proven to be excellent semiconductors, with tuneable band gap, high absorption coefficients and large charge diffusion length. Multi-component lead halide perovskite compositions are widely studied in order to stabilize the perovskite phase, in particular for wide bandgap formulations. The vacuum-deposition of multi-component perovskites is not straightforward, as the number of precursors is in principle limited by the number of thermal sources available in the vacuum chamber. Here we present a process which allows to increase the complexity of the formulation of vacuum-deposited lead halide perovskites films by multi-source deposition and pre-mixing both inorganic and organic components. We apply it to the preparation of wide bandgap CsMAFA triple-cation perovskite solar cells, which are found to be efficient but not thermally stable. With the aim of stabilizing the perovskite phase, we add guanidinium (GA^+) to the material formulation, and obtained CsMAFAGA quadruple-cation perovskite films with improved thermal stability, as observed by X-ray diffraction and rationalized by microstructural analysis. The corresponding solar cells showed similar performance with a remarkable thermal stability, when compared to the triple-cation perovskite devices. This work paves the way towards the vacuum-processing of complex perovskite formulations, with important implications not only for photovoltaics but also for other fields of application.¹



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UV-Assisted Graphene-Based Chemoresistive Gas Sensors for Sub-ppm Detection.

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Chemiresistive gas sensors are electronic devices that can detect a myriad of different molecular species in gaseous environments. As for their working principle, when analytes are adsorbed on the material's surface, changes in its electrical properties, i.e., conductance or resistance, are induced. Such changes are easily monitored with common electronics. Meanwhile, graphene, and its derivatives, are bidimensional materials built from an atom-thick layer of carbon in a honeycomb structure. Thanks to its enormous specific surface ($2630\text{ m}^2/\text{g}$) and low noise-to-signal ratio, it has generated great interest for sensing applications ¹.

In this work, a graphene-based material was synthesized by a novel ball-milling method that meets large-scale production requirements. The product of this synthesis was classified as mesoporous few-layered graphene (MFLG) according to its structural characterization ². MFLG was later deposited onto interdigitated electrodes to create the sensor device ³. The second type of graphene, multilayer graphene (MLG) was synthesized by chemical vapor deposition (CVD) and transferred onto a similar setup thanks to international collaborators ⁴. Both devices demonstrated excellent performance for NO₂ detection.

Under UV irradiation, both graphene-based devices suffered an increase in their sensing performance. Irradiation during the exposure and purge phases of the sensor's operation appears to promote adsorption and desorption respectively (Fig. 1). The mechanisms underlying this increase are yet to be understood and discussion during the event will be welcomed.

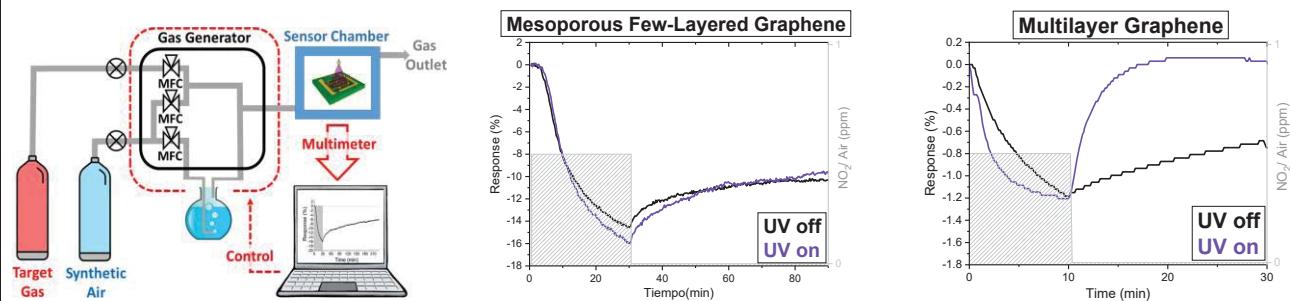


Figure 1 Schematics for the experimental setup (left). NO₂ MFLG sensor (center) and MLG sensor (right) under UV irradiation and dark conditions.

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Developing MnAlC / hydrogel composites for fabricating alternative permanent magnets by bonding and additive manufacturing

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Additive manufacturing (AM) technologies are attracting much interest in high-tech sectors due to the possibility of fabricating complex and high-performance objects with tailored properties and a minimal waste generation [1]. In the permanent magnets (PMs) sector, the manufacturing of magnets by AM requires a high filling factor and no deterioration of the magnetic properties (challenging due to processing temperature issues). Many works on AM of PMs focus on NdFeB, however the present challenge is finding alternative rare earth-free PMs to address the criticality of rare-earths. MnAl-based alloys are promising candidates to partially plug the gap between ferrites and NdFeB magnets, in addition to its high availability and diminished environmental impact [2]. Recently, it has been proven the potential that MnAlC alloy shows to be used for the development of alternative PMs by the AM technology known as Fused Filament Fabrication (FFF) [3].

In this work gas-atomized MnAlC particles consisting of τ -phase (only ferromagnetic phase in Mn-Al) were used as filler for preparing magnetic composites using a hydrogel as matrix material. MnAlC particles showed a quasi-spherical shape with a mean particle size of 50 μm . Firstly, hydrogels were synthesized by chemical route using alginate (ALG) as precursor material, and methylcellulose (MC) that was incorporated as additive for thickening the resulting mixture [4]. Afterwards, the MnAlC particles were added and stirred for obtaining homogeneous composites. Different amounts of MnAlC particles were considered to end with composites with several filler loading. The viscosity of the composites was tuned to make them suitable for additive manufacturing by modifying the proportion between ALG and MC in the composite. Different ALG:MC ratios were analysed (2.5:1 and 1:1), and it was found that a suitable proportion is 2.5:1 as it allows an adequate viscosity of the resulting composite to be loaded in syringes (Fig. 1a) and used in the direct ink writing (DIW) 3D-printing technology. The scalable synthesis process has allowed to load syringes with a volume in a range from 1 up to 8 mL.

According to the Scanning Electron Microscopy (SEM) images, the resulting cured composites (PM particles / hydrogel) show a smooth surface with the MnAlC particles well dispersed along the hydrogel matrix (Fig. 1b). Vibrating Sample Magnetometry (VSM) was used to measure the hysteresis loops of the cured composites with different MnAlC load. Figure 1c shows that the magnetization scales with the MnAlC content in the composite, while the coercive field remains constant showing that the magnetic properties of the MnAlC particles are not deteriorated along the composite synthesis process. The synthesized composites based on MnAlC particles and hydrogel shows suitable and promising properties for their use in the development of a new generation of alternative PMs by bonding and additive manufacturing technologies.

Authors acknowledge Höganäs AB (Sweden) for providing the gas-atomized MnAlC particles through an industrial IMDEA-Höganäs collaboration and the financial support from MICINN by NEXUS (PID2020-115215RB-C21). E.M.P. acknowledges support from AEI through the Juan de la Cierva – Incorporación program (IJC2020-043011-I/MCIN/AEI/10.13039/501100011033) and EU by NextGenerationEU/PRTR.

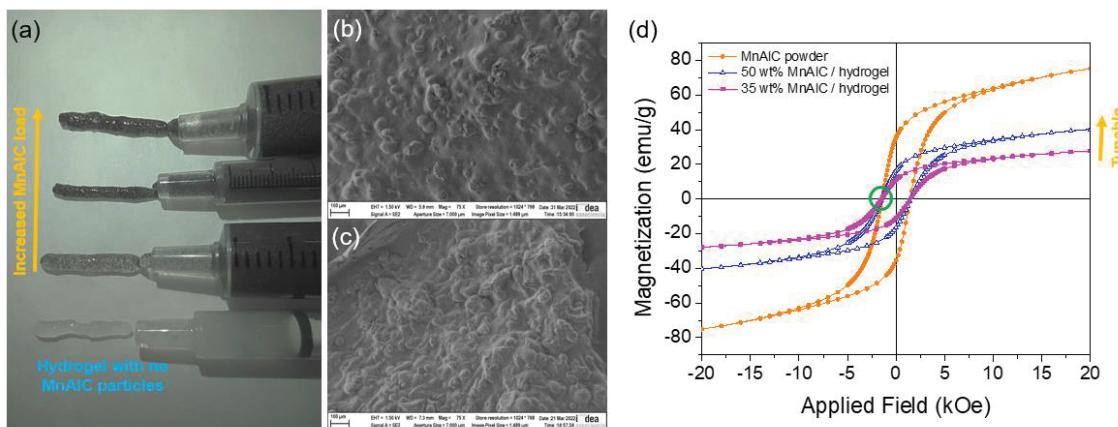


Figure 1: (a) Syringes loaded solely with hydrogel and with composites made of hydrogel and different MnAlC particles load; SEM images of the composites with (b) 35 wt% and (c) 50 wt% content of MnAlC particles [scale bar: 100 μm]; (d) room temperature hysteresis loops measured for the composites with 35 wt% and 50 wt% MnAlC content.

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Electrical Conductivity Of Single Molecules

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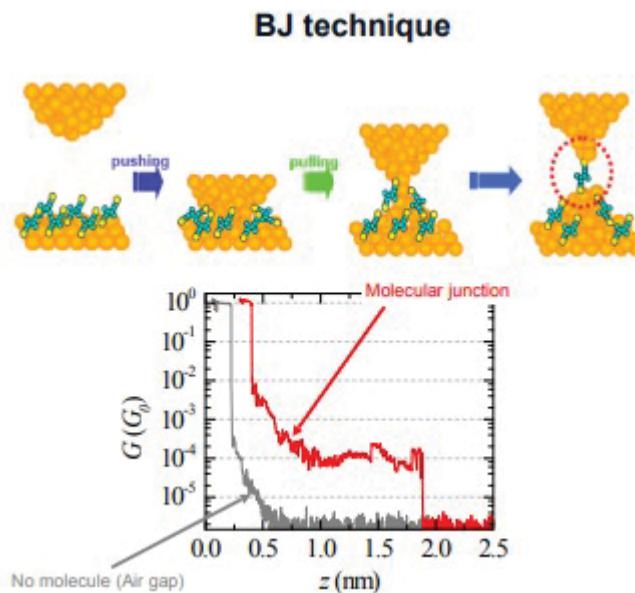
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Abstract:

We will present a room temperature STM break junction study of the single molecule conductance of several novel antiaromatic compounds containing a dibenzopentalene (DBP) unit.¹ The aim of the study is to determine the effect upon the electrical conductance of replacing an aromatic group for a comparable antiaromatic unit. The compounds are based on the well-studied oligo(phenylene ethynylene) backbone with PhSMe anchor groups and we have investigated three different central units: phenyl, anthracene (both aromatic) and DBP (antiaromatic). Our results show that while the molecules with anthracene and DBP are more conductive compared to the phenyl analogue, there is little detectable difference between the former two, which is despite the DBP having the smallest HOMO-LUMO gap thanks to partial antiaromatic character. Theoretical calculations reveal that the reason for this is that the Fermi level lies close to the centre of the HOMO-LUMO in both cases where the difference in transmission curves is small. As the LUMO of the DBP compound is, however, lower than the other two compounds, we hypothesise that tuning the Fermi level alignment with appropriate anchor groups could maximise the difference.



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Insertion of Bis(pentamethylcyclopentadienyl)iron(III) cations into new anilate-based networks to obtain isolated single molecule magnets.

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The chemical synthesis of single-molecule magnets (SMMs) are increasingly being studied in nanoscience, due to the use of these molecules in quantum technology[1]. Recently, a series of ferrocenium complexes has been reported like SMMs in presence of an applied dc field. To reduce the possible effects of dipolar magnetic interactions on the magnetization dynamics, ferrocenium complexes having bulky cyclopentadienyl ring substituents and/or large counterions were prepared[2].

Nevertheless, this is not the unique form to isolate magnetically the Fe(III) ions. In this work we have explored the insertion of decamethylferrocenium cations as counterions of extended anionic networks to separate these magnetic centers in the solid state. We have used anilate-based networks already as they afford numerous examples of anionic extended lattices that can host a great variety of cations[3-5]. A new series of anilate-based network compounds with the formula $[Z^{II}Cp_2^*][M^{II}_2(An)_3]$ (Z^{II} =Fe; M^{II} =Mn, Zn; An= haloanilate; Cp^* = pentamethylcyclopentadienyl) has been prepared. Their structures consist of an anionic-based honeycomb network formed by M^{II} linked through haloanilate group ligands. The bis(pentamethylcyclopentadienyl)iron(III) cations can occupy the hexagon holes of the network or being disposed between layers. Regarding the magnetic behavior, we expect that the networks composed by paramagnetic metals behave as ferrimagnet/antiferromagnet layers together with the intrinsic magnetic behavior of Fe(III) ion. Furthermore, the diamagnetic metals used to make diamagnetic anilate-based networks could magnetically isolate the Fe(III) ions, giving rise to single molecule magnets. Thanks to the protection of the bimetallic network, these single-molecule magnets could increase the magnetic relaxation and spin coherence times. In addition to this, the synthetic method used to make the diamagnetic anilate-based network has resulted in the preparation of a salt of an anionic diamagnetic trimer and decamethylferrocenium counteranions that could be an alternative to isolate magnetically the Fe(III) ions.

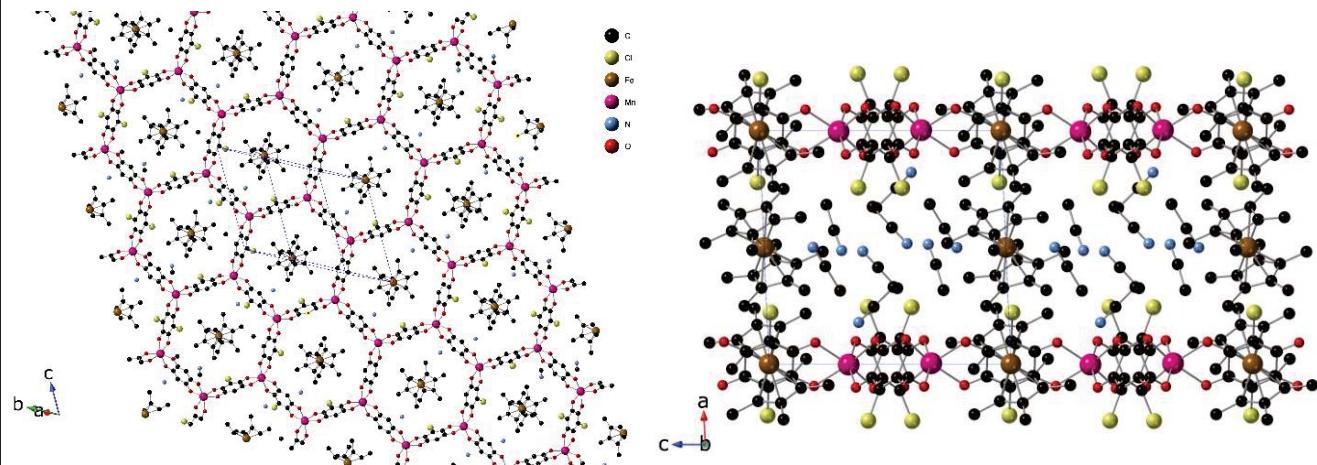


Figure 1 | Structure of $[FeCp_2^*]2[Mn^{II}_2(An)_3]$ (1). Projection of 1 in the space. Fe (brown), Mn (pink), Cl (green), O (red), N (blue) and C (black). Hydrogen atoms have been removed to have a better view of the structure.

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Chemical tuning of the properties of 2D magnetic materials

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Over the last years, two-dimensional (2D) materials have been a great focus of interest due to their outstanding properties and their potential applications in many fields such as electronics, spintronics or magnonics, among others. Recently, the discovery of magnetism down to the monolayer limit in 2D materials [1] has promoted even more insight on them by the scientific community.

In this work, a computational study is presented consisting of the DFT + U calculation of hybrid molecular/2D heterostructures by using Quantum Espresso [2]. In particular, the magnetic materials studied are CrI₃ and CrSBr, which are layered materials whose monolayers are ferromagnetically ordered and antiferromagnetically coupled between them [3]. Here, the heterostructures are formed by placing some organic molecules such as perylene, coronene, TTF and TCNQ above these materials and performing a geometry optimization in order to obtain the ground state of the system. These hybrid interfaces are likely to be formed as it is confirmed by adsorption energy calculations, showing a more stable structure. This approach paves the way for the chemical tuning of the electronic properties of bidimensional materials by molecular adsorption, adding some highly localized electronic states. In addition, these new structures display spin polarization, which allows the creation and propagation of spin waves with promising interest in magnonics for quantum computing or information storage.

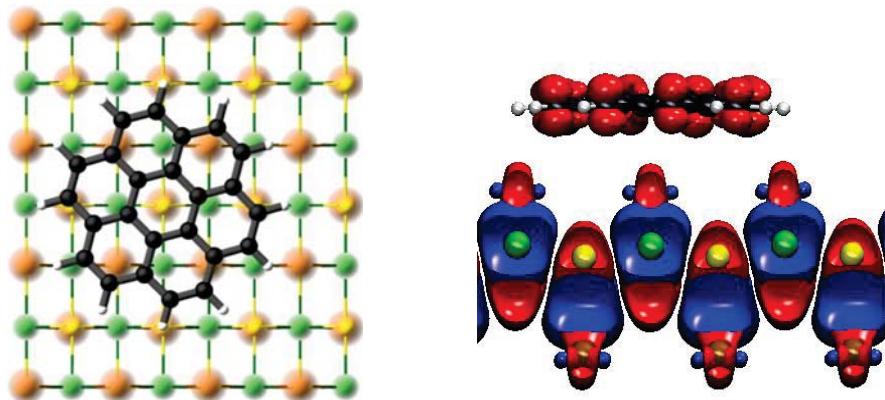


Figure 1. Top view of the hybrid coronene/CrSBr heterostructure (left) and side view of its spin density (right)

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Opto-electro-magnetic bistability in polar spin-crossover chain material

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In the current need for new materials for the construction of chemical sensors, information storage devices or energy conversion systems, the significant scientific attention is devoted to dynamic molecular frameworks which physical properties (magnetic, dielectric, optical) can be switched by external stimuli, such as temperature, light irradiation, or chemical impulse.¹⁻³ One of the most interesting groups of such multifunctional molecular materials are coordination polymers based on octacyanidometallates, as they have already been proven to be a source of diverse functionalities (e.g. SCO effect, slow magnetic relaxation, photoluminescence, chirality, porosity).⁴ Our goal was to obtain a new SCO material that could fit into the current scientific trend of rich multifunctionality. To achieve this goal, we decided to use Fe(II) complexes together with octacyanidorhenate(V) ion ($[\text{Re}(\text{CN})_8]^{3-}$), as the combination of these two building blocks were found to be a fruitful source of SCO-active multifunctional molecular materials.⁵⁻⁶

As the result, we present a novel (TBA) $\{[\text{Fe}^{\text{II}}(\text{phIN})_4][\text{Re}^{\text{V}}(\text{CN})_8]\}$ (phIN) (TBA = tetrabutylammonium cation, phIN = phenyl isonicotinate) coordination polymer. The material consists of nearly straight, anionic, cyano-bridged coordination chains, together with counterions of TBA^+ and a non-coordinated phIN molecules. This material exhibits sharp complete SCO transition around 202 K with a hysteresis loop of 6 K width. The material crystallizes in non-centrosymmetric polar space group Cc, which leads to the significant non-linear optical effect. The second harmonic generation (SHG) signal was observed for both high spin (HS) and low spin (LS) phases, but the SHG signal is remarkably stronger for the LS phase. In addition, the temperature-dependent SHG measurements reveal the hysteretic behaviour of a SHG signal upon cooling and heating cycles. In addition, the spin transition was traced with the UV-vis absorption spectroscopy. The temperature-dependent optical measurements revealed the appearance of new absorption bands as the temperature enters the range of the spin transition. These absorption bands were ascribed to characteristic electronic transitions of LS Fe(II) complexes. Moreover, it was possible to observe the thermal hysteresis loop of the intensity of these absorption bands. Finally, we conducted temperature-dependent conductivity (σ') measurements. We observed hysteretic curves of conductivity temperature dependence of our material. So, herein we report a novel molecular material revealing multifunctional optical, electronic, and magnetic bistability.

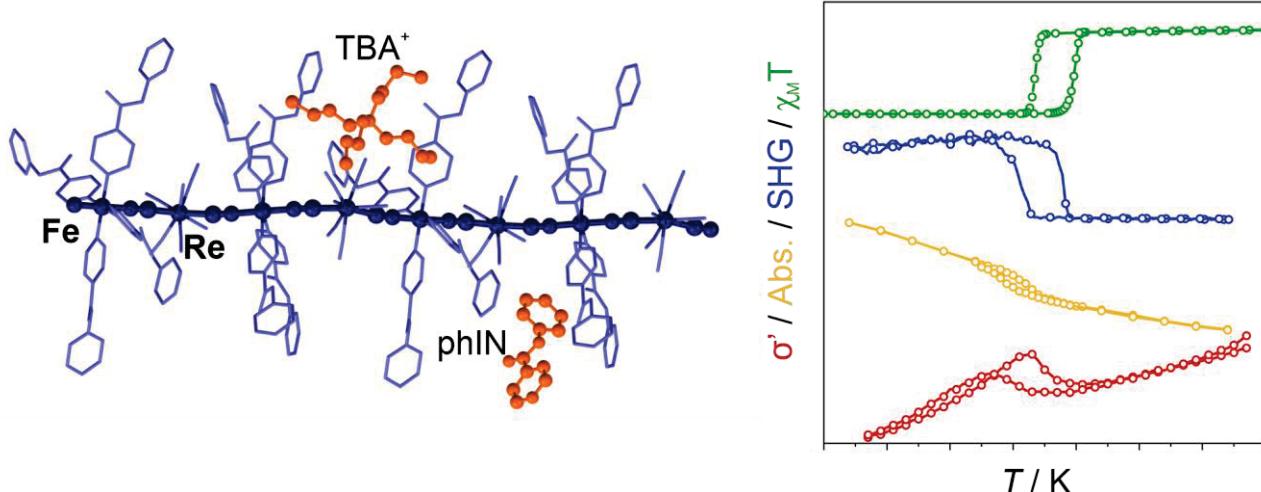


Figure 1. The representative fragment of $\{[\text{Fe}^{\text{II}}(\text{phIN})_4][\text{Re}^{\text{V}}(\text{CN})_8]\}$ coordination chain together with accompanying TBA^+ cations and phIN molecules (left) and the temperature-dependent curves of $\chi_M T$ product (green), SHG signal (blue), absorbance at 550 nm (yellow), and the real part of conductivity (red) (right)

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Perylene-based Metal-Organic Frameworks: Tuneable Electrical and Optical Properties

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Besides their inherent porosity, Metal-Organic Frameworks (MOFs) may also incorporate tuneable electrical and optical properties which strongly depend on the selected building blocks, becoming very attractive for their implementation as integral components in electronic devices.^[1] In recent years, electroactive organic molecules have emerged as promising building blocks for the design and construction of crystalline porous frameworks such as MOFs for different applications in electronics.^[2] In this direction, the construction of new perylene-based MOFs is encouraged due to their remarkable luminescence and promising electrical properties.

Herein we report the electrical conductivity enhancement of an iodine-doped perylene-based MOF by using two-probe single-crystal devices (Figure 1). This conductivity enhancement is ascribed to the partial oxidation of the perylene ligands, as witnessed by spectroscopic studies and supported by theoretical calculations. The charge transport is described by means of a through-space hopping mechanism along the herringbone perylene packing, with highest conductivities of the order of 10^{-5} S·cm⁻¹ measured in two-contact single-crystal devices.^[3]

In addition, we present a new synthetic route to prepare a new family of isostructural perylene-based MOFs with different transition metals (TM = Co, Ni, Zn) exhibiting tuneable optical properties depending on the nature of the metal. We demonstrate the possibility to tune the optical properties by switching the TM while the electrochemical properties of perylene are preserved, as demonstrated by solid-state cyclic voltammetry of PTC-TM.^[4] These studies highlight the great versatility of perlenes as building blocks for the construction of electroactive MOFs.

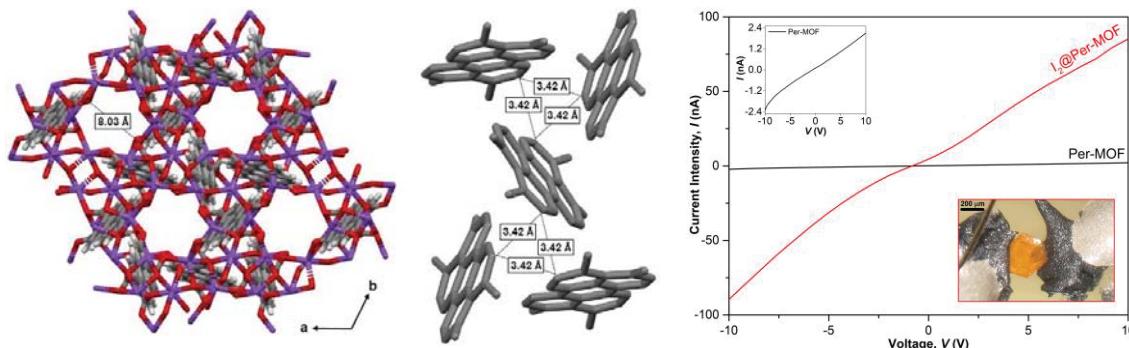


Figure 1. a) Partial views of the crystal structure of Per-MOF on the *abc* plane. b) Representative Current (I)–Voltage (V) plot for crystal devices of Per-MOF (black) and I_2 @Per-MOF (red) at 300 K.

Acknowledgements:

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Quantum Transport of Single-Molecule Junctions when Theory and Experiment Meet

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Molecular electronic transport experiments performed via Mechanically Controllable Break Junctions (MCBJ) or Scanning Tunnelling Microscope on the BJ approach (STM-BJ) don't provide direct information about the bonding of the molecule at the electrodes [1]. However, to unmask the geometrical configuration acquired by the molecules between the electrodes, a combination of atomistic simulations, ab initio calculations, and electronic transport experiments is required.

We modelled the quantum transport of benzene, toluene, cyclohexane, and helicenes molecules over gold electrodes via Molecular Dynamics (figure1) and DFT. We compared them with our experimental results, showing that this model has a high agreement. Our model offers plausible scenarios of the experiment. In summary, this triple comparative clearly reveals the relation between their characteristic electronic transport and the dynamic bonding of the molecule single between the electrodes. Additionally, we shed light on the nature of electrodes and their geometries.

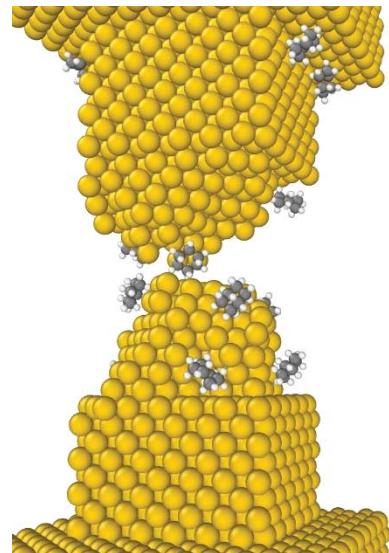


Figure 1. Snapshot of Molecular Dynamic Simulation

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Computer simulations of the separation of gas mixtures through novel nanoporous boron-graphdiyne membranes

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In this study, we use Density Functional Theory [1] and perform calculations with the Quantum Espresso code [2] to investigate if novel nanoporous carbon-based polymers can form suitable membranes for the separation of CH₄/CO₂ gas mixtures with high permeability and selectivity [3]. With this motivation, we examine the utility of boron graphdiyne porous layers as a membrane. Boron graphdiyne is a two-dimensional honeycomb structure with boron atoms at the vertices of the hexagons, linked by carbon butadiyne chains. The structure has large hexagonal holes. Based on the different molecular sizes and different molecule-membrane interaction, we expect that an array of these porous nanostructures can potentially help in the separation of gas mixtures, and in achieving a high rate of gas throughput. We aim to propose a novel membrane design based on two-stage porous graphdiyne bilayers or multilayers. This design might not only improve gas permeation efficiency but also improve selective separation performance.

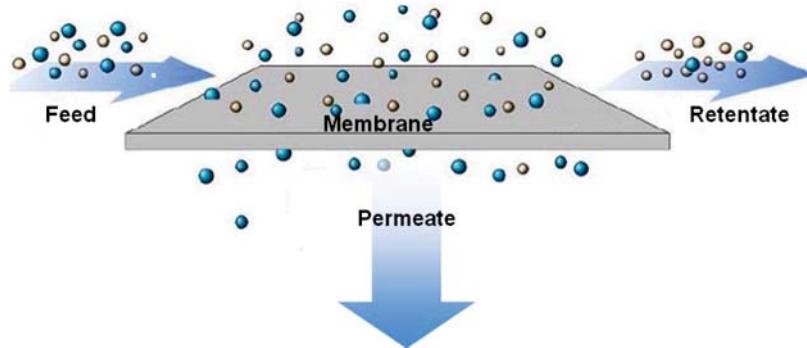


Figure 1. Schematic process of the separation of gas mixtures through membranes

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Relevance of Shockley states on the electrical and thermoelectric response of gold-based single-molecule junctions

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Noble metals break preferably exposing (111)-oriented surfaces, that host Shockley type surface states (Sss) [1]. Nevertheless, the relevance of Sss on the electrical properties of gold-based molecular junctions has not been explored in detail. Here, we present ab-initio simulations that show how the gold (111) SS, that lies approximately 0.5 eV below the Fermi energy, is key to determining correctly the electrical and thermoelectric response of the above junctions. We also show that gold's SS appears in our simulations only if d-orbitals are included explicitly in the valence shell. We discuss in detail Benzenediamine (BDA) and Benzenedicarbonitrile (BDCN) gold (111) junctions, where we also include the DFT+ Σ correction scheme [2].

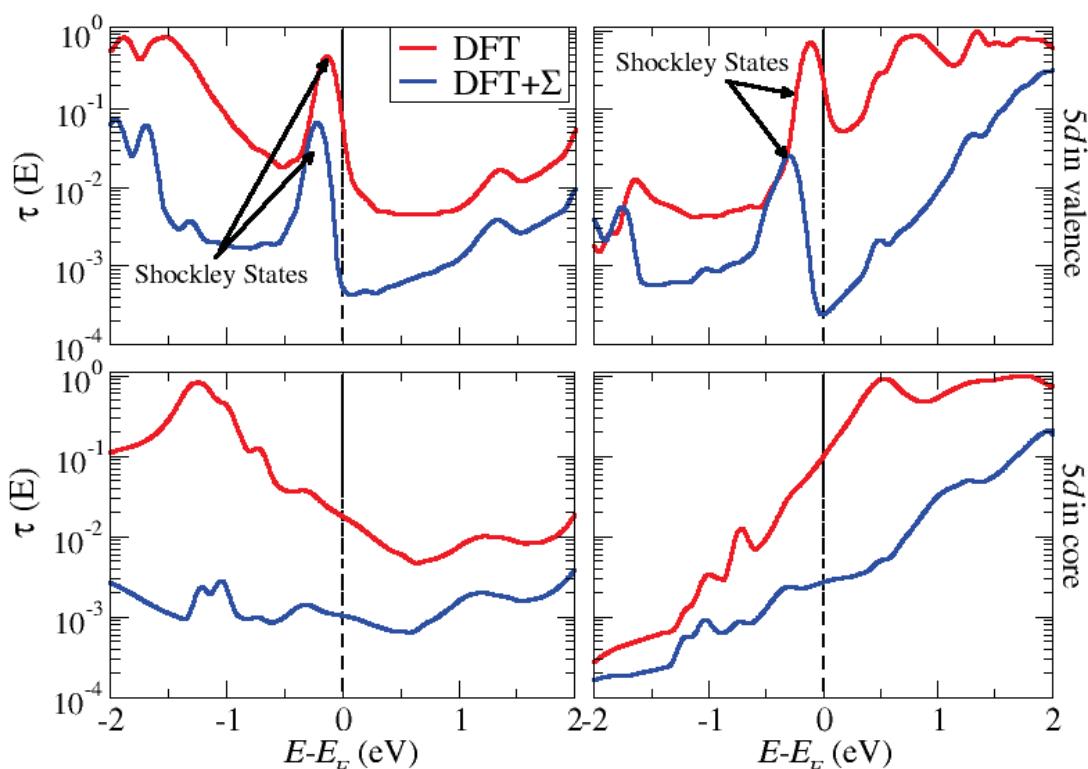


Figure 1: Transmission function of BDA (left panels) and BDCN (right panels). Top (bottom) row corresponds to the junctions where gold's 5d orbitals are explicitly included in the valence (core) shell. The intersection between the graphs and the vertical line gives the low-voltage conductance. The slope of the transmission function at the Fermi energy is proportional to the thermopower.

Take away messages:

- (1) Huge experimental variability is the Achilles heel of molecular electronics, Shockley states are in part responsible for that.
- (2) Having a theoretical model that includes them accurately will help us tune the thermoelectric properties of a given junction, turning the problem of variability into a window of opportunity.

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Functionalised spin crossover complexes for thin-film based electronic and spintronic devices

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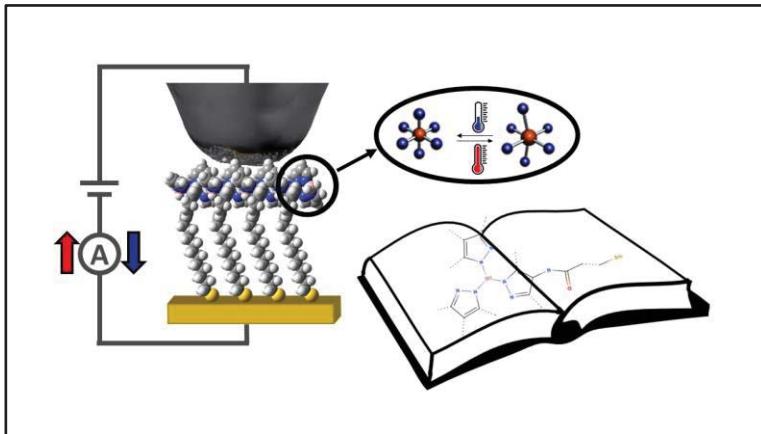
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Spin crossover complexes (SCCs) are transition metal complexes that exhibit reversible state switching at ambient conditions, making them promising candidates for molecular electronics and spintronics, for example in memory devices [1]. In iron (II) complexes, switching occurs between a diamagnetic low spin state ($S=0$) and a paramagnetic high spin state ($S=2$), and is photo- or thermally-induced. The switching is accompanied by a change in the electronic and magnetic properties, such that molecular junctions of these SCCs exhibit a change in conductance depending on the spin state. Resistance switching ratios as high as 400 have been reported for junctions of iron (II) SCCs [2].

A major advantage of SCC thin-film devices over conventional 2D materials is that the organic ligands can be tailored to add any number of desired properties, such as photoactivity [3] or the ability to self-assemble on a surface [4]. However, the structural and electronic complexity of these molecules mean it can be hard to predict the exact conditions where switching will occur. The goal of my thesis is to control the spin state switching of iron (II) SCCs on surfaces. We aim to perform this tuning in two ways: by functionalising the organic ligands [5], or by changing the ‘spinterface’ between the molecules and substrate. The latter is done for example by varying the substrate material, for instance by using a ferroelectric substrate that can be electrically polarised [6].

First, a library of functionalised iron (II) SCCs is being synthesised and characterised: structurally, electrically and magnetically, both in bulk and as (sub)monolayer films. The effect of the substrate on the spin state switching will be investigated, in particular by using polarisable ferroelectric polymer substrates. As a final step, electronic and potentially spintronic devices will be fabricated from thin films of SCCs.

This research aims to increase our understanding of the spin crossover (SCO) phenomenon at the nanoscale and the subtleties of the spinterface, using a variety of substrates controlled by nanostructuration, with the end goal of bringing SCCs closer to technological applications in molecule-based electronics and spintronics.



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SHG-active NIR-emissive neodymium(III)-octacyanidometallate(IV) molecular nanomagnets

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The application of intrinsically emissive lanthanide(III) metal centres in the development of novel molecular nanomagnets led to the emergence of luminescent single-molecule magnets (SMMs).¹ Emissive Ln-based SMMs have aroused notable interest in particular due to the magneto-optical correlations enabling the implementation of emission spectra in the analysis of lanthanide(III) electronic structure.² Moreover, emissive SMMs constitute potential candidates for materials in which emission can be modified by a magnetic field.^{3,4} Utilization of lanthanides in the construction of new molecular systems can be considered a straightforward way to observe both noticeable magnetic anisotropy as well as photoluminescent properties owing to f-f electronic transitions. Another possible way to functionalization of Ln-based emissive SMMs is related to the incorporation of chirality. Molecular systems described by chiral or at least non-centrosymmetric groups are potentially able to exhibit a broad range of fascinating physical functionalities,⁵ such as non-linear optical effects i.a. second harmonic generation (SHG) or magnetization-induced second harmonic generation (MSHG).⁶

Taking the above into consideration, we have focused on generating chirality in bifunctional magneto-luminescent systems. As a part of undertaken studies, we have designed, synthesized and characterized two novel 2-D Nd^{III}-based coordination polymers, described as $\{[\text{Nd}^{\text{III}}_4(\text{H}_2\text{O})_{17}(\text{pzdo})_5][\text{M}^{\text{IV}}(\text{CN})_8]_3\}\cdot 9\text{H}_2\text{O}$ ($\text{M} = \text{Mo}$ (**1**), W (**2**); pzdo = pyrazine N,N'-dioxide).⁷ The abovementioned materials are based on cyanido and pzdo molecular bridges. As the result of the spontaneous resolution process, presumably correlated with the unusual 3:4 ($\text{M}^{\text{IV}}:\text{Nd}^{\text{III}}$) metal ratio as well as supramolecular interactions involving cyanido complexes and pzdo ligands, these compounds crystallize in the non-centrosymmetric C_2 space group. Obtained systems constitute unique examples of multifunctional molecule-based materials combining three various functionalities: (i) second-harmonic generation (SHG) activity (arising from the lack of an inversion centre), (ii) UV-to-vis-light-induced near-infrared (NIR) photoluminescence (originating from the presence of emissive Nd³⁺ ions) and (iii) the effect of slow relaxation of magnetization (related to the single-ion anisotropy of incorporated Nd^{III} complexes).

As in the previous investigated $\text{Ln}^{\text{III}}-\text{[M}^{\text{IV}}(\text{CN})_8]^4-$ systems,⁸ the observed magnetic and optical properties are sensitive to the nature of the incorporated d-transition metal centre. Most of their properties are enhanced upon the substitution of Mo^{IV} centres with W^{IV} ones. In conclusion, the exchange of Mo^{IV} with W^{IV} metal centres in described systems enhances the SH intensity, increases the sensitization efficiency, and slowdowns magnetic relaxation, indicating the modulating role of selected Mo^{IV} and W^{IV} cyanido complexes.

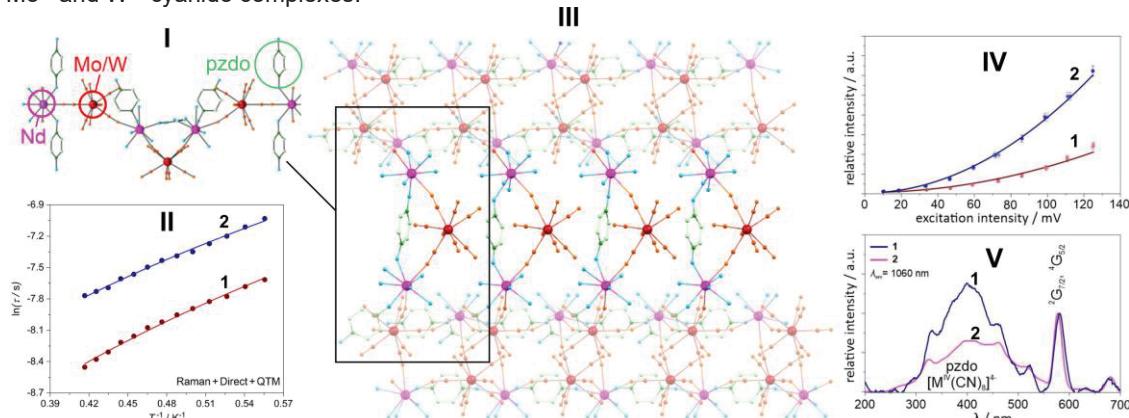


Figure 1. Representative characteristics of **1** and **2**: **I** – molecular building unit; **II** - temperature-dependence of magnetic relaxation times; **III** – fragment of crystal packing along c crystallographic axis; **IV** – power dependence of SHG effect, detected at room temperature; **V** – excitation spectra for the monitored emission at 1060 nm.

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Metal-organic paramagnets as molecular qubits: design and properties

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Exploiting the quantum properties of matter to develop new functional tools and devices is an emerging trend in science and technology. The core of this approach is the quantum bit (qubit), the quantum version of the classic binary bit. Classical bits exist in one of two states, 0 or 1, whereas qubits can be placed into a quantum superposition of their two constituent states, thus simultaneously accessing multiple states [1]. The coherence time is the most important property of a qubit and describes the lifetime of the superposition state before it collapses into one of its constituent classical states.

Among the different physical realizations of qubits, magnetic molecules are a promising option. Simple metal-organic paramagnets with a single unpaired electron ($S = \frac{1}{2}$), like vanadium(IV) complexes, can exhibit sufficiently long coherence times to behave as qubits relevant for quantum computation. To perform as a molecular qubit, these metal-organic complexes need to possess well-established characteristics like chemical and thermal stability, good processability, a functionalizable structure, and of course, a long coherence time. Decoherence is mainly induced by electron-electron and electron-nuclear spin-spin interactions, which can be reduced by chemical design [2].

For all these reasons, our current goal is to design new molecular qubits based on robust, neutral macrocyclic complexes of transition metals, whose O donors contain no nuclear spins. We recently optimized the synthesis and the purification of H₂L (Fig. 1, center), a pre-organized tetradentate proligand containing two fused β -diketones [3]. It should be noted that the metal-binding species (L²⁻) is a binegative ligand and can afford neutral complexes with oxovanadium(IV) ions, thus avoiding the presence of counter-ions. H₂L was characterized by 1D and 2D ¹H-NMR spectroscopy, but the interpretation of the spectra was complicated by the occurrence of keto-enol tautomerism. To obtain unambiguous structural data and to perform also a preliminary study of the chelating ability of our ligand toward a paramagnetic metal, we prepared the cobalt(II) complex of L²⁻. Crystals suitable for X-ray diffraction were obtained from THF/n-hexane solution by adding an excess of pyridine (py) to complete the octahedral coordination geometry of the metal. Surprisingly, the product has a dinuclear structure and its molecular formula is [Co₂L₂py₄] (Fig. 1, left). This new compound was characterized by EA, UV-Vis-NIR, FT-IR/ATR, and ¹H-NMR spectroscopies. We also performed DC and AC magnetic characterization which demonstrated that [Co₂L₂py₄] is a Single-Molecule Magnet in applied static field.

We recently also explored the synthesis [4] of the oxovanadium(IV) complex of L²⁻, which is expected to act as a qubit. Crystals suitable for X-ray diffraction were obtained by vapour diffusion of Et₂O in a DCM solution. Also this product exhibits a dinuclear structure and its molecular formula is *trans*-[(VO)₂L₂] (Fig. 1, right). Significantly, the crystal packing affords a porous, honeycomb-like structure that was never observed before for this type of systems. The structure contains parallel channels ~2 nm in size and ~50% of solvent-accessible voids. This new compound was characterized by EA, UV-Vis-NIR, FT-IR/ATR, and ¹H-NMR spectroscopies.

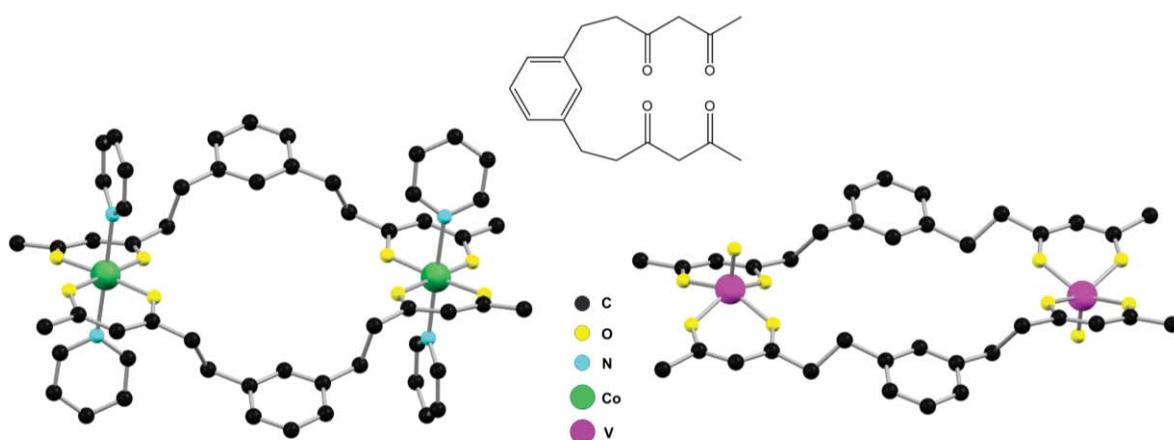


Figure 1. Structures of [Co₂L₂py₄] (left), H₂L (center), and *trans*-[(VO)₂L₂] (right). Hydrogen atoms are omitted for clarity.

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Stacking-enhanced photoluminescence in subphthalocyanine thin films

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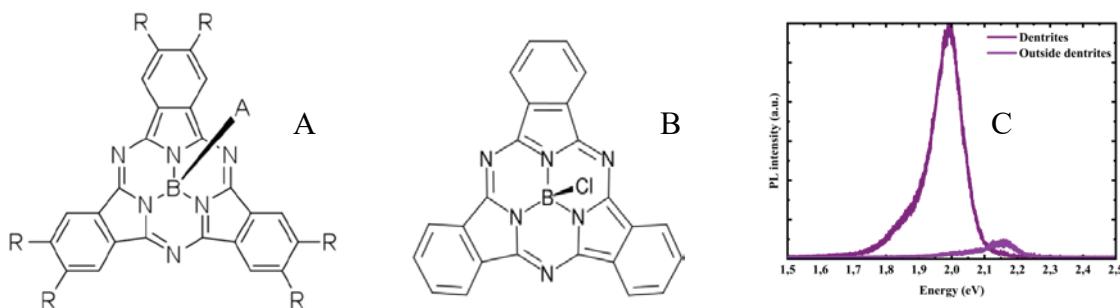
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Subphthalocyanines (subPcs) are contracted homologues of the Phthalocyanines, one of the most investigated porphyrin. They are only known as boron derivatives and are formed with three isoindole subunits. This unique configuration gives rise to a nonplanar bowl-shaped structure contrasting with the planar aromaticity of the above-mentioned phthalocyanines. They are considered to be interesting because their optoelectronic features can be tuned by changing their axial ligand (B-A) and by functionalizing the peripheral positions (R) (figure 1A).

Literature is filled with studies that explore the use of subPcs as organic active layer for optoelectronic devices. It is rare to find a research work that mentions other approaches even though the combination of non-planar aromaticity, permanent electric dipole and photoluminescence can be appealing for a wide range of applications.

The commercially available Boron subphthalocyanine (figure 1B) is the most commonly investigated. Easily sublimed, we started our investigation by preparing thin films with different thicknesses that were deposited on chemically and ultrasonically cleaned substrates by a thermal sublimation technique under a residual air pressure less than 10^{-7} mbar at low rates (0.1 - 0.15 Å). We confirmed the deposition of the molecule by Raman and IR spectroscopies, to investigate as a second step, the surface morphology of the thin films by AFM and optical microscopy. We observed the formation of long dentrite-like organizations parallel to the substrate, where long stem-like assemblies are formed along with smaller leaf-like structures growing outward from these stems. This indicates that the Sub-Pc molecules are stacking along one dimensional direction, with the formation of outward-directed short leafy structures originating from some miss-oriented molecules inside the stem. This is more obvious for thicker films where these structures reach hundreds micrometers length. More interestingly, the optical properties of both areas (amorphous and dentrite-like) are drastically different. In fact, the PL spectrum is narrower and higher in the case of the dentrite-like structures (Figure 1C) and shifted toward lower energies.



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STM Study of Dithia[7]Helicenes and the Role of an Organic Solvent at Ambient Conditions

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Using a Scanning Tunneling Microscope (STM), we study a solution of the chiral molecule dithia[7]helicene ([7]DTH) in benzene [1]. Two different [7]DTH were synthesized with sulfur atoms integrated in different locations displaying two different topologies. After the deposition and evaporation on Au(111), we studied the molecular arrangement over the surface, showing differences due to the interaction of the sulfur atom as a link group with the gold atoms. In our study we could image the different binding configurations of the molecules and characterize their main characteristics including their chirality.

When working with diluted solutions, it was possible to distinguish the solvents from the target molecules [2]. Thus, in the course of the study of the helicenes, we studied three common organic solvents: benzene, cyclohexane and toluene. Our results show thin adsorbed molecular layers of the solvents after evaporation in gold surface. STM images resolve solvent single molecules over the adsorbed film, meaning a good adhesion of the solvent molecules, allowing us to measure the molecular diameter at room conditions.

Finally, we performed electronic transport measurements on solvents by STM-BJ which show the most probable conductance values due to the formation of different molecular bridges. Therefore, helping us to understand the role of physisorbed molecules of solvents in molecular transport experiments at ambient conditions.

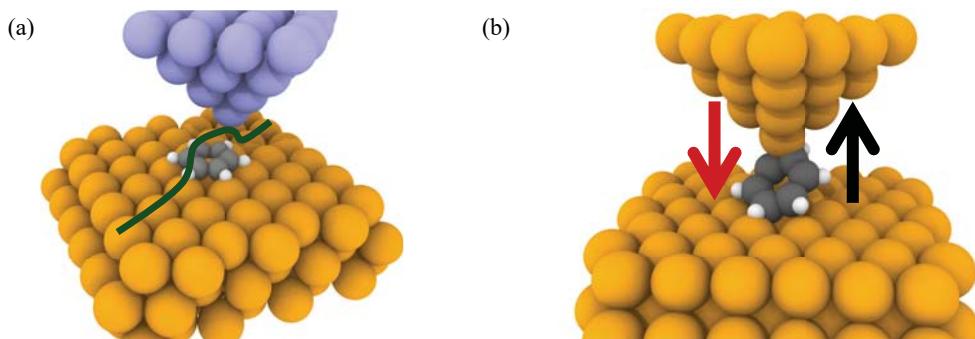


Figure 1. Diagram of a (a) STM performing a scanning along the surface and (b) STM-based break junction (STM-based BJ) performing cycles of pull-push where the conductance values are recorded as a function of the quantum of conductance G_0 .

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Electrochemistry as exfoliation tool

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Since isolation of graphene in 2004, 2D materials have attracted great attention due to the emergent properties arising from the confinement of electrons in two dimensions and to their high surface-area-to volume ratios giving rise to promising new physical/chemical properties. Among these materials, the family of transition metal phosphorus trichalcogenides (TMDCs) of general formula MPX_3 (where M is a transition metal and X is S or Se) has been focus of attention due to their cooperative magnetic properties and a wide range of bandgaps, which envision their potential use in a wide range of applications such as spintronics, electrocatalysis and optoelectronics [1,2]. Within MPX_3 members, $NiPS_3$ has a high interest due to its small bandgap energy (~ 1.6 eV), magnetic properties, and electrochemical activity. [3]

Different approaches have been followed to isolate ultrathin layers from their layered bulk counterparts. [4] Among them, the electrochemical exfoliation method provides several advantages with respect to other strategies such as large production, structural integrity, low cost, and reduced time. Recently, it has been proved that ultrathin $NiPS_3$ flakes can be obtained by this strategy [3]. In this presentation, we will discuss about the electrochemical exfoliation conditions to achieve the best quality flakes and the highest yield, and we will compare with other exfoliation methods. Therefore, we will present a morphological study of the obtained $NiPS_3$ layers by means of atomic force and transmission electron microscopies and we will evaluate the magnetic behavior of the resulting material.

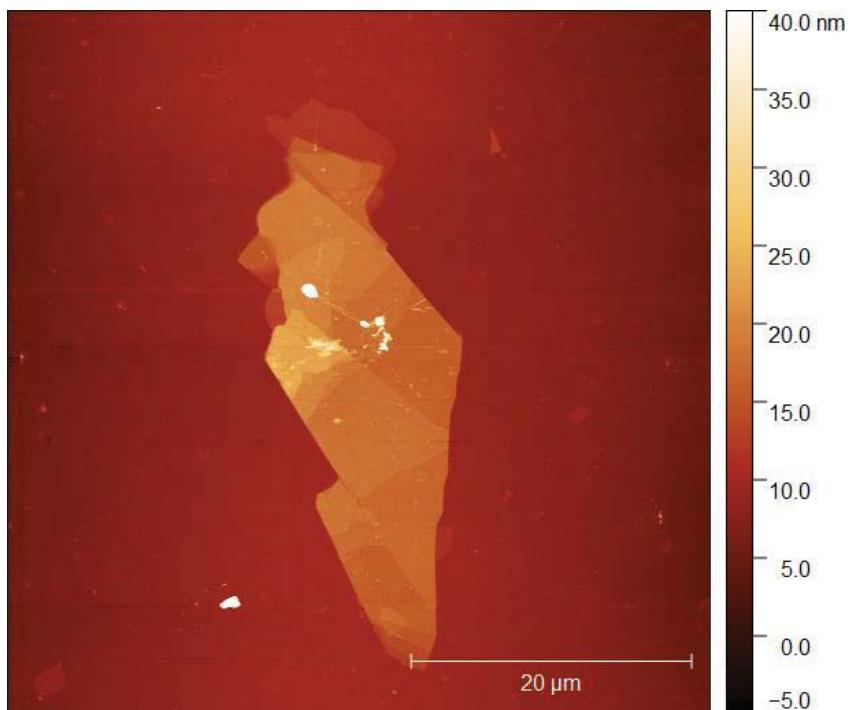


Figura 1. AFM topography image of $NiPS_3$ spin-coated on Si/SiO₂ substrates after exfoliated electrochemically.

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Graphene-MoS₂ covalently crosslinked heterostructures for electrochemical applications

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Graphene was first isolated in 2004, becoming the thinnest material in the world thanks to its mono-atomic flat structure. It is characterized by high transparency, elevated electrical conductivity, and strong Young's modulus [1]. These properties make graphene a promising material for various applications like electronics, spintronics, catalysis and biotechnology to mention a few. Its discovery stimulated the interest of the scientific community and was followed by the isolation of a wide number of other two-dimensional (2D) materials. Among these, molybdenum disulfide (MoS₂), a transition metal dichalcogenide, has raised the attention of researchers because of its tuneable properties. MoS₂ can be found in different polytypes, being 2H-MoS₂ and 1T-MoS₂ the most important ones. 2H-MoS₂ is a diamagnetic semiconductor with poor catalytic efficiency meanwhile metallic 1T-MoS₂ demonstrates higher catalytic efficiency and 10⁷ times higher electronic conductivity [2].

Therefore, a heterostructure formed by the combination of these materials is of great interest for optoelectronic and catalytic applications. Moreover, graphene-MoS₂ hybrids are known for good performance for lithium batteries and aerogels [3]. First results on graphene-MoS₂ devices showed high photonic and electronic performance, combined with improved mechanical properties of the materials. For example, Yu *et al.* fabricated high-performance nanodevices based on Graphene-MoS₂ heterojunctions, paving the way for flexible and transparent electronics [4].

Besides Graphene-MoS₂ heterojunctions in direct contact between the 2D layers, covalently cross-linked 2D materials open the possibility of higher accessibility to the layers and to additional electronic modulations through their covalent functionalization [5]. However, so far, graphene introduced in this heterostructures has been mainly reduced graphene oxide whose properties considerably differ from those found in graphene. In this research, we present our strategy to prepare cross-linked Graphene-MoS₂ heterostructures based on high quality graphene and MoS₂ obtained by chemical exfoliation. After diazonium salts functionalization, a hybrid laminar heterostructure was synthesized via amide bond formation between the 2D layers (Figure 1). Several techniques such as high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy, Infrared spectroscopy (IR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and thermogravimetry (TG) analyses were employed to confirm the formation of the covalently bonded heterostructure.

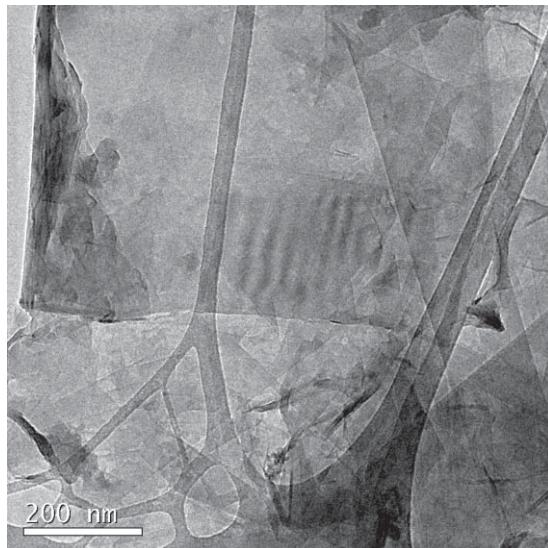


Figure 1 : HR-TEM image of Graphene-MoS₂ crosslinked heterostructure

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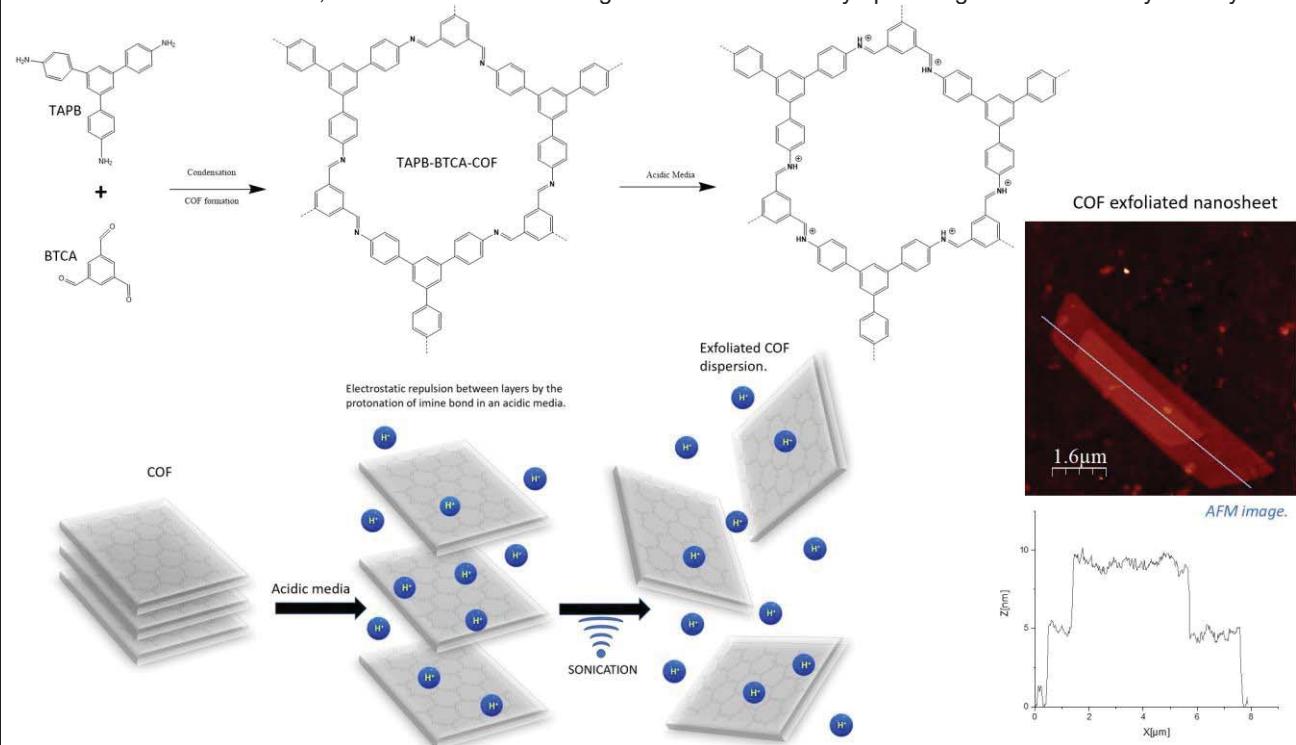
Liquid phase exfoliation of imine-Covalent Organic Framework (COF) enhanced by electrostatic repulsion

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In the last years, research in Covalent Organic Frameworks (COFs) has been growing due to their high porosity, tunable functionality, high stability, and crystallinity.¹ These properties of COFs lead them to an increasing interest for application in energy storage devices, filtration membranes, sensors or catalysis. Nowadays, the majority of COF applications are based on the microcrystalline powder of the bulk COF. However, in many of them, the use of exfoliated COF nanolayers is expected to improve performance, such as it has been shown for Li-ion batteries, for which a side-by-side study of the bulk and exfoliated COF as a cathode material^{2,3} showed the improvement in mass transport, efficiency of redox sites and faster kinetics for Li⁺ storage with COF nanolayers. Thus, COF dimensionality and morphology (2D sheets, nanoparticles, micrometric aggregates) are critical factors to consider and optimize for the final target application. The protocols for COF exfoliation are still specific for each COF, and there is a lack of general guidelines on how to face the challenge of exfoliating new COFs.

Therefore, this work focuses on the development of a robust and universal methodology for the liquid phase exfoliation of imine COFs. We have exploited the pH-dependant, electrostatic repulsion between layers, due to the protonation of the N atom of the imine bonds⁵, and we have also tested different starting bulk materials for the exfoliation experiments, such as gels and aerogels, which are expected to be easier to exfoliate than conventional powders. In addition, the effect of annealing the bulk material was studied, as it enables to obtain larger COF nanosheets by optimizing the bulk COF crystallinity.



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Optical contrast characterisation of CrSBr metamagnet: From bulk to the monolayer

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Optical contrast is a widely used technique in the field of two-dimensional (2D) materials that allows the fast identification of flakes with different thicknesses [1][2], being of great importance for air unstable materials, such as 1T-TaS₂, CrI₃[3] or the CrSBr. As it has been reported for graphene,[4] metal halides [1][3] and other transition metal dichalcogenides [1][5][6] -but not for CrSBr yet-, optical contrast can be done quantitatively in order to identify the thickness of a flake. In this work thin-layers of CrSBr on top of SiO₂/Si substrates are considered.

Due to its highly anisotropic structure, two main axes are easily distinguished. This fact is supported by the different contrast values obtained when the light is polarised parallel to one axis or the other. However, further spectroscopic analysis is carried out to ensure this.

Thanks to this characterisation, van der Waals heterostructures are possible to be built, and transport measurements can be done to determine the behaviour of this metamagnet [7].

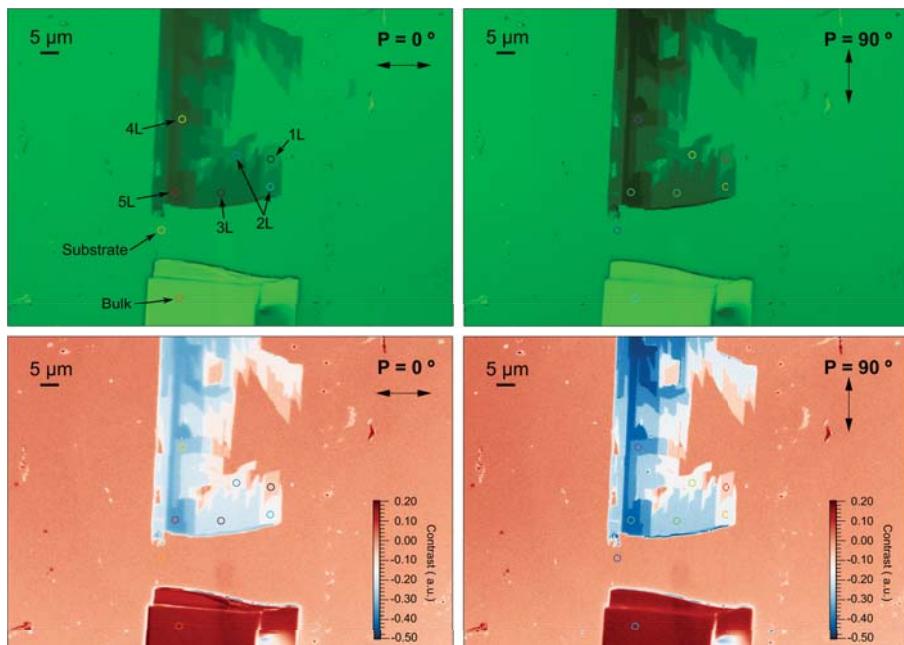


Figure 1. Optical microscopy images of a multilayered CrSBr crystal for the determination of the contrast of each flake. Upper panels are the original microscopy image, while the bottom ones are the contrast analysis. Polarized incident light (at 0° and 90°) shows the high anisotropy of the material.

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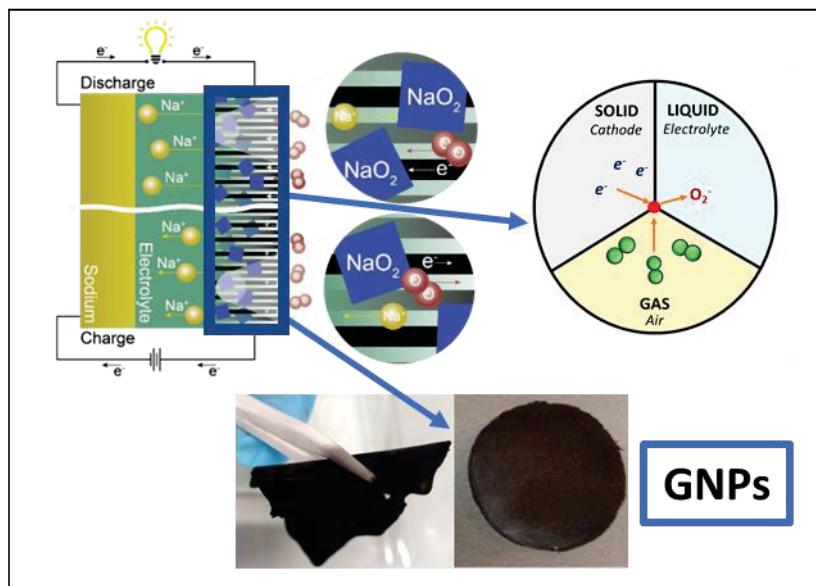
The role of perfluorinated binders in graphene-based Na-O₂ battery cathodes: controlling the triple phase boundary

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Sodium-oxygen batteries (Na-O₂) hold great promise for the transition to a non-fossil fuel economy due to their high theoretical energy density. One of the most important components of these devices is the air-cathode, where a triphasic reaction between the Na⁺ ions present in the liquid electrolyte, the electrons available at the solid cathode and oxygen gas occurs to form solid discharge products. Conventional carbon materials (such as gas carbon fibres, carbon black, carbon nanotubes, activated carbon or graphite) has been largely used as cathodes in Na-O₂ batteries due to their low cost, high surface area, chemical stability, conductivity, and intrinsic catalytic activity toward the ORR/OER.[1]. However, their limited performance at high operating current densities boosted the search for novel air-cathode materials. Graphene has proven to be a promising material due to its outstanding electrical conductivity and open structure, enhancing the O₂ diffusion and facilitating electrolyte impregnation as well as offering many active sites for the formation and decomposition of the discharge products.[2]. The main challenge when using graphene materials, compared with conventional carbons, is a suitable cathode processing due to their low-density. Nevertheless, high density graphene forms such as graphene nanosheets or nanoplatelets (GNPs) presented either good cathode performance while providing much better processability, which is crucial for an industrial applicability in the future.[3]. In order to process graphene, perfluorinated polymers present great advantages; not only as binders but also to favour the diffusion of gaseous components in detriment to liquid electrolytes as well as to alter the electronic conductivity and electrolyte wettability of solid cathodes. Hence, the boundary between the three reaction phases existing in Na-O₂ batteries can be tuned to maximize their efficiency by adding perfluorinated polymers to the cathode formulation. This work examines the influence of polytetrafluoroethylene (PTFE) polymer and its weight ratio on the electrochemical performance of GNP cathodes. The cathodes containing a 10% PTFE yield showed a high full discharge capacity of 4.51 mAh cm⁻² and the largest cycle life among the studied PTFE quantities, delivering 121 cycles with an efficiency of 97%, low overpotential at a high current density (0.2 mA cm⁻²). Finally, the decrease of the electrode wettability by the addition of PTFE polymer was also proven which favours the diffusion of oxygen into the cathode structure.



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Ab initio calculations of organic molecules adsorbed on antiferromagnetic materials

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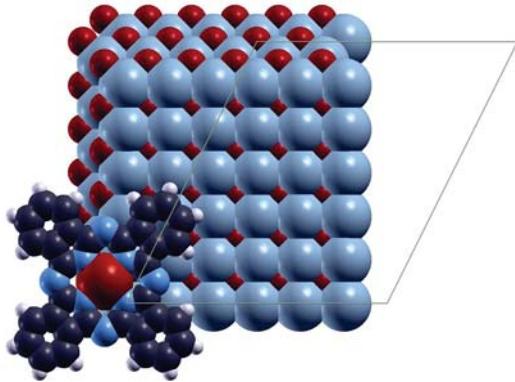
My research is mainly on organic molecules (OM) adsorbed on antiferromagnetic materials (AM). The mutual influence of the magnetic properties at the interface, so called spinterface, will be beneficial from the engineering point of view, to determine spin-polarization of the electronic structure and allow for spin-selected electronic and transport properties. Thus, these complex systems requires a significant understanding of surface physics and of spin dynamics of antiferromagnetic materials.

The first considered system are molecules of FePc adsorbed on a NiO surface. Before looking at the complete system (FePc+NiO), I have studied individually the two subsystems. Transition metal oxides experimentally show an antiferromagnetic behaviour, and in order to reproduce experimental PDOS I have considered U corrections in my DFT simulations (with the Quantum Espresso software). In particular, my main interest has been in NiO AFII, i.e. AF along [111]. As pseudopotentials, I have considered GBRV pseudopotentials, due to their transferability and low convergence threshold (including semicore corrections). At this point in order to deposit my organic molecule, I have considered a NiO[001]-45°(6x3) supercell of 3 layers (surface properties are properly taken into account). I have chosen as organic molecule, a metal phthalocyanine (FePc), because of its relevant electronic properties (acceptor-donor-acceptor molecule). The coupling between the surface and the molecule is described through van-der-Waals corrected xc-potentials.

The results from these preliminary ground state calculations are a local magnetic coupling between the OM and the AM substrate and particular configurations with lower adsorbing energies than others.

The second considered system are molecules of FePc adsorbed on a Cr₃O₂ surface. I am working on the studies of the substrate, before considering the OM's relaxation.

I am not only interested in the ground state properties (DFT - Quantum Espresso), but also in the excited state properties (TDDFT and MBPT - Yambo), on whom I am working, too (excitons and magnons).



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BOOSTING THE PERFORMANCE OF GRAPHENE CATHODES IN Na-O₂ BATTERIES BY EXPLOITING THE MULTIFUNCTIONAL CHARACTER OF SMALL BIOMOLECULES

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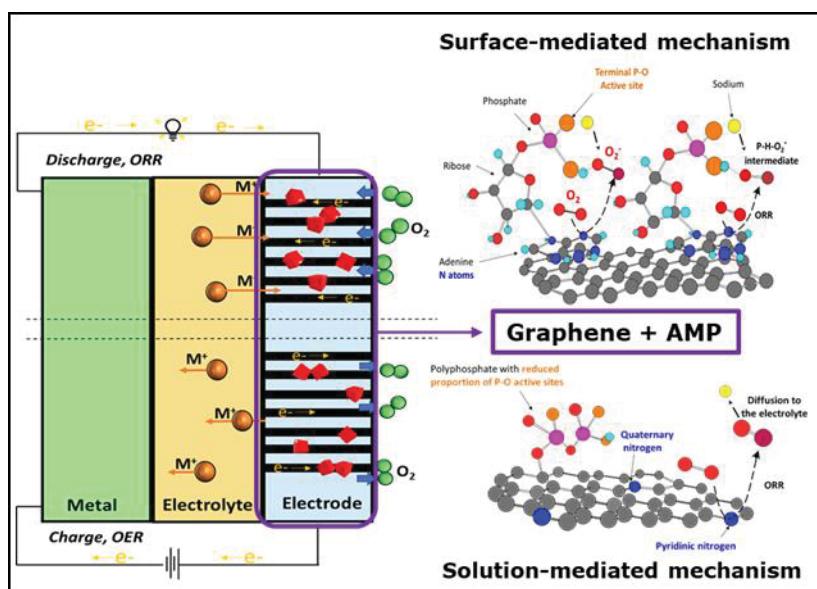
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Rechargeable batteries constitute the nexus between renewable energy sources and stationary and mobile applications. Besides the fact that lithium-ion batteries (LiBs), which currently dominate the battery market, suffer from low energy density, they have nearly reached their limits in terms of theoretical energy density, cycle life, and charge/discharge rate.^[1] For these reasons, “beyond lithium-ion” energy storage systems are urgently needed, such as sodium–oxygen (Na–O₂) batteries, which present high theoretical energy density (\approx 5–10 times higher than that of LiBs, 100–265 vs 1108 Wh kg⁻¹).^[2] Unlike conventional metal-ion batteries, solid discharge products are generated during the cycling of Na–O₂ batteries, with sodium superoxide (NaO₂) being the most interesting product owing to its reversible formation. The use of suitable cathode materials is a point of major concern as they are responsible for achieving efficient deposition/redissolution of the solid discharge products formed during battery operation. Graphene has gained attention as a cathode material due to its superior electrical conductivity and highly accessible 2D area.

In this work, high-quality graphene aerogels via electrochemical exfoliation were prepared using an innocuous biomolecule, the adenosine monophosphate nucleotide (AMP), and tested as Na–O₂ battery cathode using a glyme-based electrolyte. The assembled batteries delivered a discharge capacity as high as 9.64 mAh cm⁻² and endured 95 cycles at a discharge depth of 0.5 mAh cm⁻² with a high current density (0.2 mA cm⁻²). Such a good performance was attributed to the phosphate groups present in the nucleotide, which is adsorbed on the surface of the graphene sheets comprising the porous aerogel cathode. Therefore, the phosphate groups modify the nucleation mechanism of the discharge products by i) enhancing the interaction of the cathode with oxygen reactive species and ii) catalysing the ORR/OER reactions during discharge/charge.



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Contactless electrical detection of the thermal and light induced spin transition in hybrid spin-crossover/graphene devices

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Electronic devices based on hybrid spin-crossover (SCO)/2D heterostructures grant a highly sensitive platform to detect the spin transition of the molecular compound and tune the properties of the 2D material.[1-4] Generally, only the thermal SCO transition has been exploited in these devices and furthermore, the methodologies used for their processing along their fragility upon thermal treatment have limited their applicability. Here, we report an easily processable SCO/2D hybrid device preparation based on thin films of a sublimable SCO compound ($[Fe(Pyrz)]_2$),[5,6]) and CVD-graphene, fully compatible with electronics industry protocols, which integrates a PMMA polymeric interlayer between the two active components in a contactless configuration. This method has allowed to profit the newly discovered properties of a metastable polymorph of this SCO material exhibiting outstandingly fast and effective light-induced spin transition enhanced by the flexible interlayer (100 % yield in few minutes) (Figure).[7,8]

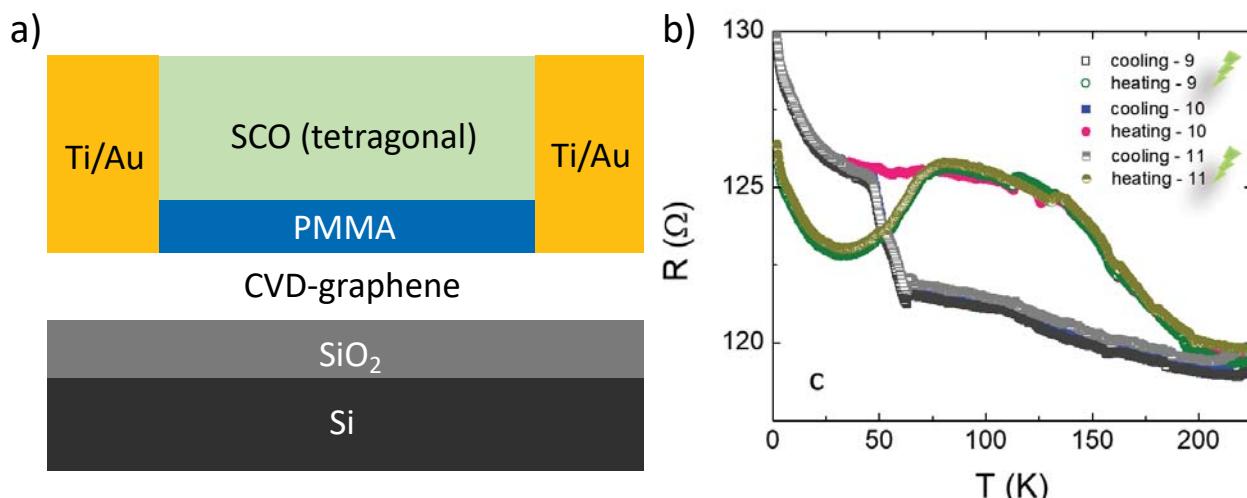


Figure. a) Scheme of the vertical profile of the contactless hybrid SCO/2D device. b) Thermal dependance of the electrical resistance measured in the contactless device for three consecutive thermal cycles, two of them light irradiating the device at 2 K for 5 min (9 and 11) to electrically sense the LIESST effect response of the integrated SCO molecular layer.

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Electron transport in solution processable graphene nanoribbons

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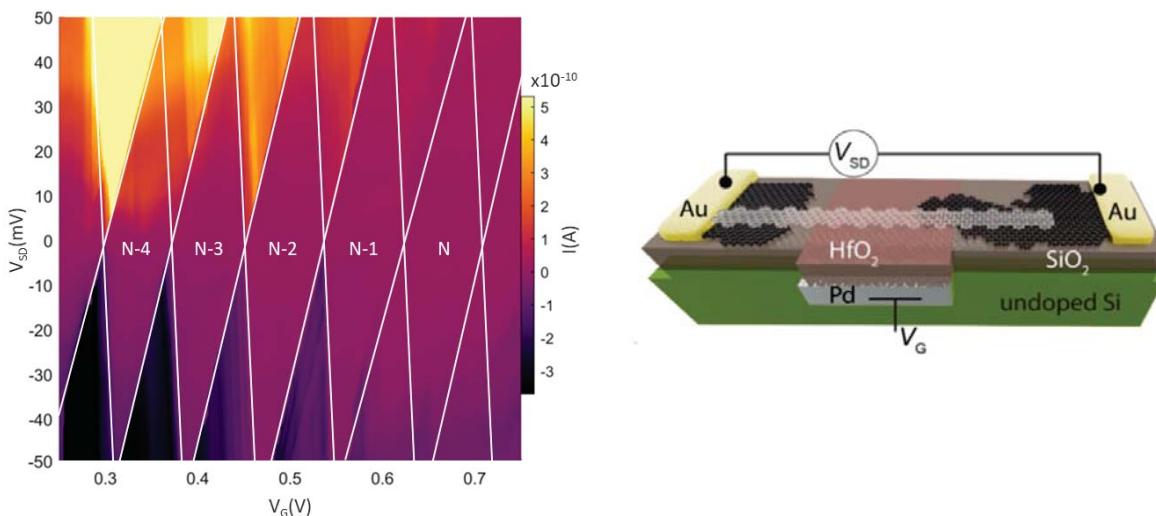
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Quantum transport experiments require ultra clean devices, necessitating dramatic advancements in materials growth processes, new types of chemical synthesis, or unconventional device fabrication techniques. Chemically synthesised molecular graphene nanoribbons (MGNR) now provide carbon nanostructures with single-atom precision but suffer from poor solubility. Here we demonstrate a dramatic enhancement in the solubility of MGNRs via edge functionalization that enables the possibility of achieving exceptionally clean nanodevices directly from solution.

We demonstrate the suitability of these new highly soluble MGNRs by performing low temperature transport measurement using electroburnt graphene nanogap to contact individual MGNRs. The effect of the de-bundling is apparent by the high quality of the transport data which shows well-defined Coulomb diamonds and excited states of varying origin as well as signatures of strong electron-vibron coupling which gives rise to Frank-Condon blockade. Substrate decoupling is shown to be inherent to these types of MGNRs as it seems to be provided by the bulky side groups that suppresses the π -stacking between MGNRs and increase the solubility.



Liquid-phase asymmetrically functionalised 2D layers for design of heterostructures

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Asymmetrically decorated nanoparticles (NPs), also known as Janus NPs, possess two or more differently functionalised surfaces giving rise to a complex combination of properties within one particle. Due to their biphasic morphology Janus NPs exhibit curious coexistence of amphiphilic and anisotropic features expanding boundaries in potential applications [1].

Although the most common Janus NPs are spherical, general synthetic approaches could also be extended towards two-dimensional (2D) monolayers. The conventional synthetic route involves masking of one side of the flake with an inert template, allowing interaction only to flow on the exposed side. Thus, for example, H. Wu et al. achieved fabrication of Janus graphene oxide employing wax-in-water Pickering emulsion [2]. However, Janus 2D materials are not limited to asymmetric graphene and graphene derivatives. During past few years, considerable attention has been drawn towards asymmetric decoration of molybdenum disulfide (MoS_2) known for its appealing properties widely employed in optoelectronics, gas sensing, hydrogen evolution reactions, fabrication of solar cells or lithium-ion batteries [3]. Contrariwise, so far, solution approach for the synthesis of Janus- MoS_2 layers remains almost unexplored.

Here we present a new strategy for asymmetric functionalization of MoS_2 in solution. First of all, flakes of chemically exfoliated MoS_2 are electrostatically displaced onto silica beads template, resulting only one side being exposed to upcoming chemical grafting (Figure 1). Once functionalised, Janus flakes can be recovered by chemical etching of SiO_2 .

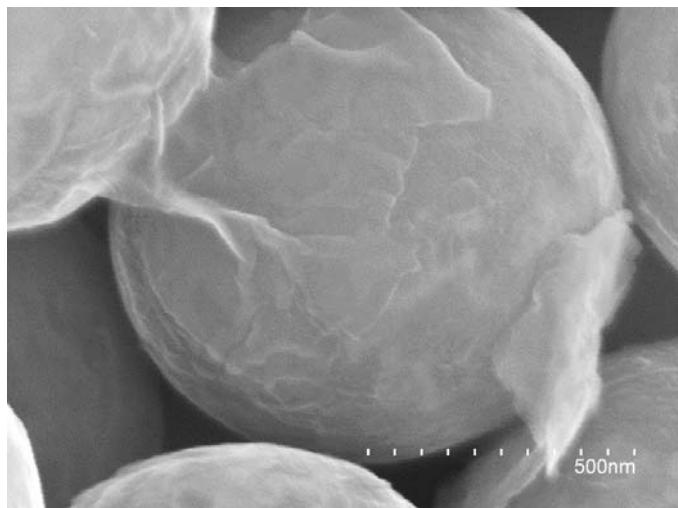


Figure 1. SEM image of MoS_2 flakes on the surface of SiO_2 beads

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