

#ESAM2023

The 1st European School on
Advanced Materials (ESAM2023)

www.icmol.es/esam2023/

#ESAM2023
Gandia (Valencia)
October 15th to 18th
2023



ESAM

*1st European School on
Advanced Materials*

	Sunday 15 th #ICMOLTalks	Monday 16 th ESAM	Tuesday 17 th ESAM	Wednesday 18 th ESAM	
9:00-9:30		Opening	P. Rudolf	K. Pedersen	9:00-9:30
9:30-10:00		L. Bogani			M. Giménez-López
10:00-10:30			M. C. Ruiz Delgado	C. Gómez	10:00-10:30
10:30-11:00		J. Ferrer		J. Rodríguez Navarro	10:30-11:00
11:00-11:30		Coffee break	Coffee break	Coffee break	11:00-11:30
11:30-12:00		M.J. Martínez Pérez	N. Ortiz Vitoriano	R. Martínez Máñez	11:30-12:00
12:00-12:30		D. Peña	L. Aballe	S. Wuttke	12:00-12:30
12:30-13:00		R. Murray	C. Calzado	S. Conesa Boj	12:30-13:00
13:00-15:30	LUNCH	LUNCH	LUNCH	LUNCH	13:00-15:30
15:30-16:00					15:30-16:00
16:00-16:30	Registration				16:00-16:30
16:30-17:00		F. Zamora	J. R. Galán Mascarós	M. Martín González	16:30-17:00
17:00-17:30	Welcome				17:00-17:30
17:30-18:15	N. Martin	Oral communications	Oral communications	Oral communications	17:30-18:00
		Coffee break	Coffee break	Coffee break	18:00-18:30
18:15-19:00	T. Mallah				18:30-19:00
19:00-20:00	Reception cocktail	Oral communications	Oral communications	Oral communications	19:00-19:30
					19:30-20:00
20:00-20:30				Closing	20:00-20:30
20:30-22:30	DINNER	DINNER	DINNER	DINNER	20:30-22:30

All the talks will be in the room MONDUBER I. Hotel RH Bayren & SPA

'Mare Nostrum' Restaurant opening times. Breakfast from 7:30 to 10:30 (8:30 to 11:00 on weekends). Lunch from 13:00 to 15:30. Dinner from 20:00 to 22:30

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AM@ESP
Advanced materials in Spain



The school is part of the integration and collaboration actions of the Advanced Materials Programme of the Complementary R&D&I Plan.
www.materialesavanzados.es

Organizing committee

ESAM2023

Organizers

The school is organized by the Instituto de Ciencia Molecular (ICMol) of the Universitat de València.

Committee



Eugenio CORONADO

Instituto de Ciencia Molecular (ICMol) of the Universitat de València



Enrique ORTÍ

Instituto de Ciencia Molecular (ICMol) of the Universitat de València



Alicia FORMENT

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Venue: Hotel RH Bayren & Spa / Paseo de Neptuno, nº 62 / 46730 Playa de Gandia, Valencia

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Invited Lectures

#ESAM2023



Lapo BOGANI
University of Oxford (UK)



José Ramón GALÁN-MASCARÓS
Inst. of Chemical Research of Catalonia (ICIQ) (ES)



Marisol MARTÍN-GONZÁLEZ
Institute of Micro and Nanotechnology CSIC (ES)



Nazario MARTÍN
Complutense University of Madrid (ES)

Invited Lectures



Kasper PEDERSEN

Technical University of Denmark (DK)



Petra RUDOLF

University of Groningen (NL)



Talal MALLAH

University Paris - Saclay (FR)



Félix ZAMORA

Autonomous University of Madrid (ES)

#ESAM2023

SUNDAY 15th		#ICMol Talks: Molecular Nanoscience
13h-15h30	<i>Lunch</i>	
16h00	<i>Registration</i>	
17h00	Eugenio CORONADO- ICMol- Univ. Valencia (ES)	<i>Advanced Molecular Materials in Spain</i>
17h30	Nazario MARTÍN- U. Complutense Madrid (ES)	Molecular Nanographenes
18h15	Talal MALLAH- U. Paris-Saclay (FR)	Molecular functional materials at the nanoscale
19h00	<i>Reception cocktail</i>	
20h30	<i>Dinner</i>	
MONDAY 16th		ESAM: Graphene and other 2D Materials
09h00	Opening	
09h30	Lapo BOGANI- U. Oxford (UK)	Quantum carbon devices
10h30	Jaime FERRER- U. Oviedo (ES)	<i>Fractionalisation in spin-1 triangulene chains</i>
11h00	<i>Coffee break</i>	
11h30	María José MARTÍNEZ-PÉREZ- INMA- U. Zaragoza (ES)	<i>Magnetic materials: a platform for quantum technologies</i>
12h00	Diego PEÑA- CIQUS- U. Santiago Compostela (ES)	<i>Bottom-up approach to nanographenes by merging organic chemistry and on-surface synthesis</i>
12h30	Richard MURRAY- Wiley-VCH (ES)	<i>Publishing in Wiley's Materials Science and Physics Journals</i>
13h00	<i>Lunch</i>	
16h30	Félix ZAMORA- Autonomous U. Madrid (ES)	Design and Processability of Imine-based Covalent Organic Frameworks
17h30	Henry Andres CORTES PAEZ- BCAM (ES)	<i>Mathematically advanced atomistic modelling of diffusion processes</i>
	Carla BOIX CONSTANT- ICMol- U. València (ES)	<i>Multistep magnetization switching in orthogonally-twisted ferromagnetic monolayers.</i>
	Miguel GAVARA EDO- ICMol- U. València (ES)	<i>Single-step Chemical Vapour Deposition synthesis of MUV-1-Cl magnetic 2D coordination polymer</i>
	Alejandro ORELLANA SILLA- ICMol- U. València (ES)	<i>Symmetry breaking and cooperative spin crossover in a Hofmann type coordination polymer based on negatively charged $\{FeII(\mu-[MII(CN)4])_2\}_n$ layers (MII = Pd, Pt)</i>
18h00	<i>Coffee break</i>	
18h30	José TROYA MARTÍNEZ- ICMol- U. València (ES)	<i>Insertion of SMM in 2D bimetallic anilate/oxalate-based networks</i>
	Juan Carlos ROLDAO- ICMol- U. València (ES)	<i>Ground and Excited State Aromaticity as a Strategy to Design Singlet Fission Chromophores: The Case of Heptalene</i>
	Beatriz SILVA GASPAS- ITQ (UPV-CSIC) (ES)	<i>New lamellar sulfur based materials (ITQ-75) with promising photocatalytic performances</i>
	Juan Pablo CUENCA VARGAS- U. Alicante (ES)	<i>Improvements in Mechanically Controllable Break Junctions Experimental Setup for atomic, molecular and two-dimensional conductors</i>
	F. Enrique GUZMÁN - U. Alicante (ES)	<i>Exploring Electronic Transport in Atomic-Sized Contacts of Sn: Unveiling a Possible Scenario of Topological Insulator</i>
	Andrés MARTÍNEZ GARCÍA- U. Alicante (ES)	<i>Electronic and spin transport of helicenes through ab initio calculations</i>
	Jessica Alejandra CHAPARRO GARNICA - U. Alicante (ES)	<i>Sustainable processes to prepare N-doped activated carbons with high stability</i>
	Vittoria URSO- U. Modena e Reggio Emilia (IT)	<i>Functionalization of 2D materials by intercalation.</i>
	Inés DURÁN RUPÉREZ- U. Politécnica Madrid (ES)	<i>2D Materials for the Implementation of Hot-Carrier Solar Cells</i>
	Jorge RODRÍGUEZ- U. Politécnica Madrid (ES)	<i>Enhancing the absorption of two-dimensional material solar cells</i>
	Jaime LLEDÓ MARTÍN- U. Valladolid (ES)	<i>Influence of the addition of different graphene nanoplatelets in polyurethane aerogels: Study of thermal insulation and mechanical properties</i>
José María BONASTRE ÁLVAREZ- U. Zaragoza (ES)	<i>Sheathed Molecular Junctions for Unambiguous Determination of Charge-Transport Properties</i>	
20h30	<i>Dinner</i>	

TUESDAY 17th		ESAM: Materials for Energy
09h00	Petra RUDOLF- U. Groningen (NL)	Characterization of Advanced Energy Materials by X-ray Photoelectron Spectroscopy
10h00	María del Carmen GIMÉNEZ-LÓPEZ- CIQUS- U. Santiago Compostela (ES)	Advanced Materials for Energy Conversion and Storage
10h30	M. Carmen RUIZ DELGADO- U. Málaga (ES)	<i>Evaluating the structural and electronic properties of stimuli-responsive materials</i>
11h00	<i>Coffee break</i>	
11h30	Nagore ORTIZ VITORIANO- CIC energiGUNE (ES)	<i>Unlocking the potential of metal air batteries through materials development</i>
12h00	Lucía ABALLE- ALBA Synchrotron Light Facility (ES)	<i>The In Situ Correlative Facility for Advanced Energy Materials</i>
12h30	Carmen J. CALZADO- U. Sevilla (ES)	<i>Modelling of spin-crossover molecules interacting with substrates</i>
14h00	<i>Lunch</i>	
16h30	José Ramón GALÁN-MASCARÓS- Inst. Chemical Research Catalonia (ICIQ) (ES)	Advanced materials for the energy transition: renewable fuels and chemicals
17h30	Ilaria LUCENTINI- ALBA Synchrotron (ES)	<i>NiRu supported on CeO₂ obtained by mechanochemical milling as catalyst for hydrogen production from ammonia</i>
	Manuel PÉREZ ESCRIBANO- ICMol- U. València (ES)	<i>Computational insights into the formation of tin halide perovskite nanostructures</i>
	Nicolás Manuel MENÉNDEZ STABILE- ICMUV (ES)	<i>Study of the thermoelectric effect in hydrogels synthesized from lignocellulosic biomass residue.</i>
	Carmen MEJUTO NIEBLAS-INAM-UJI (ES)	<i>Room temperature hydrogen production via electro-dehydrogenation of amines into nitriles: Increasing the efficiency of Liquid Organic Hydrogen Carriers</i>
18h00	<i>Coffee break</i>	
18h30	Emerson VEGA RAMÍREZ- U. ALICANTE (ES)	<i>Development Of Activated Carbons Derived From Chitosan For their Application As Electrodes In High-Durability Supercapacitors</i>
	Francisco FERNÁNDEZ CAÑIZARES- U. Complutense Madrid (ES)	<i>Oxygen vacancies in freestanding complex oxides by advanced electron microscopy</i>
	Andrés MORMENEO-SEGARRA- U. Jaume I (ES)	<i>In operando Characterization of the Ionic Conductivity Dependence on Liquid Transient Phase and Microstructure of Cold-Sintered Bi₂O₃-doped LATP Solid-State Electrolyte</i>
	Sergio FERRER- NICOMEDES- U. Jaume I (ES)	<i>Introducing an ionic conductive matrix to the cold-sintered LATP-based Composite Solid Electrolyte to enhance the electrical properties</i>
	Christian HERNÁNDEZ-ÁLVAREZ- U. La Laguna (ES)	<i>Application of a Remote Sensing Platform using Luminescent Materials</i>
	Sidra IBADAT- U. Milan (IT)	<i>Synthesis and Characterization of Colossal Dielectric Constant Materials for Energy Storage Devices</i>
	Mark WOLF- U. Politècnica València (ES)	<i>Study of the Sulfonation of Chitosan-based Composite Membranes containing fractionated Kraft and Organosolv Lignin for Fuel Cell Applications</i>
	Cristina PINTADO ZALDO- U. València (ES)	<i>Single Ion Magnets based on anilato and ethylene glycol</i>
	Sofía Hidelgar CASAL GARCIA- U. València (ES)	<i>A New Two-Dimensional MOF with field induced Single Ion Magnet behaviour</i>
	Miriam MÍNGUEZ AVELLÁN- U. València (ES)	<i>Moisture-induced formation of perovskite nanocomposite for heterogeneous photocatalysis</i>
	Ismael FERNÁNDEZ GUILLÉN- U. Valencia (ICMUV) (ES)	<i>Perovskite Thin-Film Single Crystal for a High Performance and Long Endurance Memristor</i>
	Alejandro GÓMEZ GONZÁLEZ- U. Zaragoza (ES)	<i>Assembly and characterization of nanostructures for molecular electronics</i>
20h30	<i>Dinner</i>	

WEDNESDAY 18th		ESAM: Smart Materials with advanced functionalities
09h00	Kasper PEDERSEN- Tech. U. Denmark (DK)	Metal-Organic Frameworks Losing Their Innocence
10h00	Carlos J. GÓMEZ GARCÍA- U. València (ES)	Conducting 2D and 3D MOFs. Measurements, mechanisms and types
10h30	Jorge RODRÍGUEZ NAVARRO- U. Granada (ES)	Engineering metal-organic assemblies for the detoxification of harmful compounds
11h00	<i>Coffee break</i>	
11h30	Ramón MARTÍNEZ MÁÑEZ- IDM- U. Politécnica València (ES)	Chemical Communication Principles and Applications
12h00	Stefan WUTTKE- BC Materials (ES)	MOF applications: What is the problem?
12h30	Sonia CONESA BOJ- Delft U. of Technology (NL)	2D Materials at the atomic scale: visualization and design
14h00	<i>Lunch</i>	
16h30	Marisol MARTÍN-GONZÁLEZ- Inst. Micro and Nanotechnology -CSIC (ES)	Nanowire Networks in Optics, Magnetism, and Energy Harvesting
17h30	Joseline IRIBARRA ARAYA- ICMAB-CSIC (ES)	Organic polymers based on curcuminoids linkers
	Anargyros DROLAPAS- ICMol- U. València (ES)	Metal-organic Frameworks in Nanomedicine: DNA Grafting as a Methodology for Building Colloidal & Structural Stability in Biorelevant Media
	Cristina ESTEBAN BARRERA- ITQ (ES)	Multi-component materials based on MWW-type zeolites layers and MgAlCe hydrotalcites
	Isabel TORREJÓN GUERRERO- U. Castilla - La Mancha (ES)	Study of the use of hydrogels as separators in microbial fuel cells
18h00	<i>Coffee break</i>	
18h30	María Victoria AXELRAD TINOCO- U. Castilla La-Mancha (ES)	Additive manufacturing of YSZ scaffolds for bone tissue engineering by Fused Filament Fabrication (FFF)
	Jesús DE LA MORENA DUQUE- U. Castilla-La Mancha (ES)	Real-time control of a hydrogel-based soft actuator with proprioception and self-healing capabilities
	Alicia MORCILLO MORA- U. Castilla-La Mancha (ES)	Self-healing hydrogels for soft robotics
	Irene SÁNCHEZ SÁNCHEZ-AJOFRÍN- U. Castilla-La Mancha (ES)	A Novel and Bioinspired Bilayer Hydrogel System for Engineering Assisted Reproductive Technologies
	Nadia GARCÍA PARRA- U. Politécnica València (ES)	Electroactive membranes for the stimulation of mesenchymal stem cells in vitro
	Alejandro GIL APARICIO- U. Valencia (ES)	Sustainable 3D-printed supports modified with metal-organic frameworks for remediation of organic pollutants. A preliminary study
	Félix LIZALDE ARROYO- U. Valladolid (ES)	Transparent nanocellular high-performance polymers: production, structure and properties.
	Marcos MERILLAS- U. Valladolid (ES)	Nanoporous polymers based on nanostructured polystyrene blends: Fabrication and application to vacuum insulation panels
	Clara AMEZÚA- U. Valladolid (ES)	Development and characterization of new biofoams using microwave radiation
	Mario FERNÁNDEZ DE LA FUENTE- U. Valladolid (ES)	PMMA/acetone gels for the production of completely interconnected PMMA thick membranes: The role of different polymerization methods in structure control
Silvia DEL MORAL PEÑAS- U. Zaragoza (ES)	Enantioselective separation through chiral nanoporous polymers	
Carlota AURÍA- U. Zaragoza-INMA (ES)	Di-block "bent-core" amphiphiles: an approach to functional supramolecular materials	
20h15	Closing and award	
20h30	<i>Dinner</i>	

Book of Abstracts



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Oral communications abstracts

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WEDNESDAY 18th

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Mathematically advanced atomistic modelling of diffusion processesHenry A. CORTES¹, Mauricio R. BONILLA¹ and Elena AKHMATSKAYA^{1,2}¹BCAM Basque Center for Applied Mathematics, Alameda de Mazarredo 14, E-48009 Bilbao, Spain²IKERBASQUE, Basque Foundation for Science, Euskadi Plaza 5, 48009, E-48013 Bilbao, Spain

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Diffusion processes are fundamental in numerous scientific and technological applications, from material science to biological systems. To attain a more profound comprehension of these processes at the atomistic level, advanced computational techniques are imperative. Our group has been contributing to the topic extensively, using as well-established tools such as Density Functional Theory (DFT) and molecular dynamics (MD) as in-house simulation and post-processing methodologies based on hybrid Monte Carlo (HMC) adaptive multistage numerical integration and machine learning. Our research is focused predominantly on the characterization and optimization of advanced battery materials, encompassing diverse aspects that include among others (i) Na⁺ transport in a promising olivine NaFePO₄ cathode material [1]; (ii) The impact of Ga³⁺ and Al³⁺ dopants on the ionic conductivity of solid-state electrolyte (SE) LLZO [2]; (iii) Ionic resistance at polymer/LLZO interfaces in composite SEs [3-5]; (iv) The role of the garnet Li molar content in the conductivity enhancement in the composite SEs [5]. This work describes the methodologies we developed to approach these problems, highlighting our findings on ionic diffusivity and conductivity in stand-alone and composite SEs. It also presents our recently novel technique for post-processing MD trajectories to analyze the spatial distribution of mobile ions around their equilibrium lattice sites in crystalline SEs.

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Multistep magnetization switching in orthogonally-twisted ferromagnetic monolayers.

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The advent of twisting-engineering in two-dimensional (2D) crystals enables the design of van der Waals (vdW) heterostructures exhibiting emergent properties [1]. In the case of magnets, this approach can afford artificial magnets with tailored spin arrangements that do not exist in nature. Here, we fabricate an artificial magnet by twisting 90 degrees two CrSBr ferromagnetic monolayers with an easy-axis in-plane anisotropy, thus forming an orthogonally-twisted bilayer. The magneto-transport properties reveal multistep magnetization switching with a magnetic hysteresis opening, absent in the pristine case. By tuning the magnetic field, we modulate the remanent state and coercivity and select between hysteretic and non-hysteretic magneto-resistance scenarios. This complexity pinpoints spin anisotropy as a key aspect in twisted magnetic superlattices. Our results highlight the control over the magnetic properties in vdW heterostructures, leading to a variety of field-induced phenomena and opening a fruitful playground for creating artificial magnetic symmetries and manipulating non-collinear magnetic configurations [2].

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Single-step Chemical Vapour Deposition synthesis of MUV-1-Cl magnetic 2D coordination polymer

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Since the first isolation of monolayer graphene almost 20 years ago, the research on 2D materials has exponentially grown [1]. However, the typically used mechanical exfoliation technique affords high-quality but small single layer crystals of these materials and is very time consuming with extremely poor yields. Alternatively, the bottom-up Chemical Vapour Deposition (CVD) technique has been deeply studied along the last decade to achieve the production of such materials at large scale and already deposited onto substrates [2]. Still, most efforts have been dedicated to inorganic compounds and, indeed, no results have been achieved for 2D molecular magnets, such as layered coordination polymers, despite the high interest in the chemical and application versatility they present [3]. Here I will show the development of the first CVD synthesis protocol for the synthesis of large ultrathin crystals of one of these materials, the MUV-1-Cl iron (II) layered coordination polymer [4], a spin canted antiferromagnet, that in bulk is synthesized through a solvent free reaction. The adapted CVD protocol yields distributions of rectangular-shaped MUV-1-Cl single crystals as thin as 4 nm (3 molecular layers) with outstanding lateral sizes of over 100 μm (**Figure 1**) that can be grown on different surfaces thanks to the reaction mechanism.

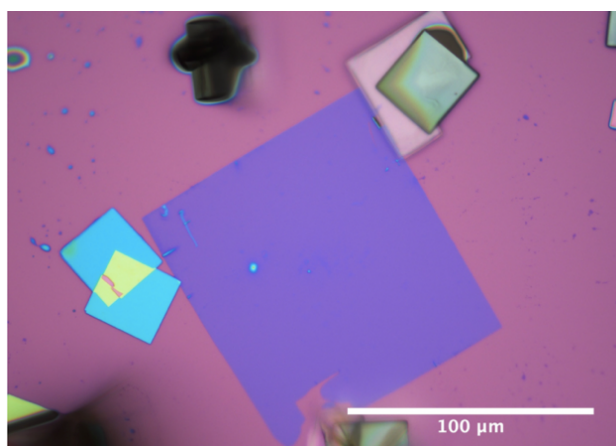


Figure 1: Optical microscope image of a MUV-1-Cl 2D crystal synthesized by CVD.

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Symmetry breaking and cooperative spin crossover in a Hofmann type coordination polymer based on negatively charged $\{\text{Fe}^{\text{II}}(\mu\text{-}[\text{M}^{\text{II}}(\text{CN})_4])_2\}_n^{2n-}$ layers ($\text{M}^{\text{II}} = \text{Pd}, \text{Pt}$)

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Here we describe the synthesis and characterization of two unprecedented isomorphous spin-crossover two-dimensional coordination polymers of the Hofmann-type formulated $\{\text{Fe}^{\text{II}}(\text{Hdpyan})_2(\mu\text{-}[\text{M}^{\text{II}}(\text{CN})_4])_2\}_n$, with $\text{M}^{\text{II}} = \text{Pd}, \text{Pt}$ and Hdpyan is the in-situ partially protonated form of 2,5-(dipyridine-4-yl)aniline (dpyan)^[1]. The Fe^{II} is axially coordinated by the pyridine ring attached to the 2-position of the aniline ring while it is equatorially surrounded by four $[\text{M}^{\text{II}}(\text{CN})_4]^{2-}$ planar groups acting as *trans* μ_2 -bidentate ligands defining layers, which stack parallel to each other. The other pyridine group of Hdpyan, being protonated, remains peripheral but involved in a strong $[\text{M}^{\text{II}}\text{-C}\equiv\text{N}\cdots\text{Hpy}^+]$ hydrogen bond between alternate layers. This provokes a nearly 90° rotation of the plane defined by the $[\text{M}^{\text{II}}(\text{CN})_4]^{2-}$ groups, with respect to the average plane defined by the layers, forcing the observed uncommon bridging mode and the accumulation of negative charge around each Fe^{II} , which is compensated by the axial $[\text{Hdpyan}]^+$ ligands. According to the magnetic and calorimetric data, both compounds undergo a strong cooperative spin transition featuring a 10-12 K wide hysteresis loop centered at 220 (Pt) and 211 K (Pd) accompanied by large entropy variations, 97.36 (Pt) and 102.92 J/K mol (Pd). The breaking symmetry involving almost 90° rotation of one of the two coordinated pyridines together with the large unit-cell volume change per Fe^{II} (ca. 50 \AA^3), and subsequent release of significant short interlayer contacts upon the low-spin \rightarrow high-spin event, accounts for the strong cooperativity.

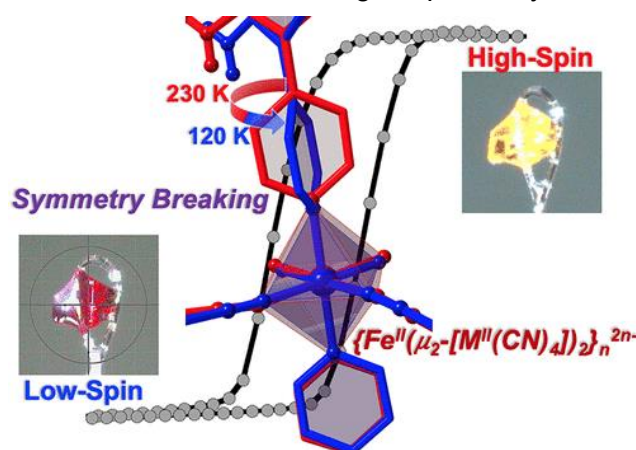


Figure 1. Spin transition of the compounds and its effects.

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Insertion of SMM in 2D bimetallic anilate/oxalate-based networks

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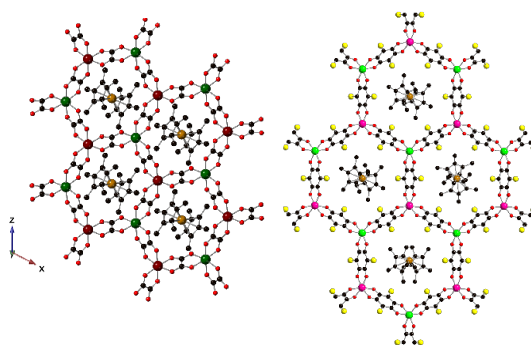
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The oxalate- and anilate-based networks can couple magnetically neighboring magnetic ions. Due to this, they have been studied as molecular-based magnets.[1] The chemical versatility of these compounds can afford new magnetic materials with interesting possibilities as the isolation of Single-Molecule Magnets (SMM).

In this work, we have explored the insertion of decamethylferrocenium cations, which display an SMM behavior,[2] as counteranions of extended anionic networks with the formula $[Z^{III}Cp_2^+][M^{II}M^{III}(X)_3]$ ($Z^{III} = Fe, Co$; $M^{II} = Mn, Zn$ $M^{III} = Cr, Rh$ and Ga ; $X =$ oxalate or haloanilate; $Cp^* =$ pentamethylcyclopentadienyl). In the case of diamagnetic networks, ZnRh or ZnGa, have been used to isolate the inserted decamethylferrocenium cations magnetically. In the anilate-based compounds, the use of a ferrimagnetic MnCr network enabled the study of the magnetic interactions between the extended network and the paramagnetic counteranion. Their structures consist of an anionic-based honeycomb network formed by M^{II}/M^{III} linked through the bis(bidentate) ligands and $[Z^{III}Cp_2^+]^+$ cations between the layers or occupying the hexagonal holes of the network.

Magnetic properties show the magnetic isolation of the decamethylferrocenium cation by the diamagnetic oxalate network results in a field-induced slow relaxation of magnetization and long spin coherence times tested by pulsed EPR. On the other hand, in the anilate-based compounds magnetic data suggest a coexistence of long-range magnetic order, characteristic of the anilate network, and a slow magnetic relaxation of the inserted cation in the compounds formed by the paramagnetic Mn^{II} and Cr^{III} ions in the anilate network and $[Fe^{III}Cp_2^+]^+$. However, the interaction between these two constituents drastically modifies their respective magnetic properties with respect to those of the reference compounds, which present the separate properties of the SMMs (diamagnetic Zn^{II} and Ga^{III} ions in the anilate network and $[Fe^{III}Cp_2^+]^+$) and of the ferrimagnetic network (paramagnetic Mn^{II} and Cr^{III} ions in the anilate network and $[Co^{III}Cp_2^+]^+$).



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Ground and Excited State Aromaticity as a Strategy to Design Singlet Fission Chromophores: The Case of Heptalene

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In recent years, the singlet fission (SF) phenomena appeared as an alternative to reduce thermal losses and increase the efficiency of optoelectronics devices.[1] SF photovoltaic technology requires chromophores with their lowest excited states arranged so that $2E(T_1)$. The success of pentalene derivatives for singlet fission,[3] been a bicyclic 8π -electrons antiaromatic system, gives rise to the question if similar systems, such as the bicyclic 8π -electrons heptalene compound could potentially be explored to produce SF chromophores. In fact, heptalene present some advantages when compared to pentalene, such as, higher stability and synthesis at room temperature.[4] However, the heptalene parent do not fulfill the electronic requirements for SF. In this work, aromatic and electronic features are tuned to design a series of promising compounds for application as SF chromophores.

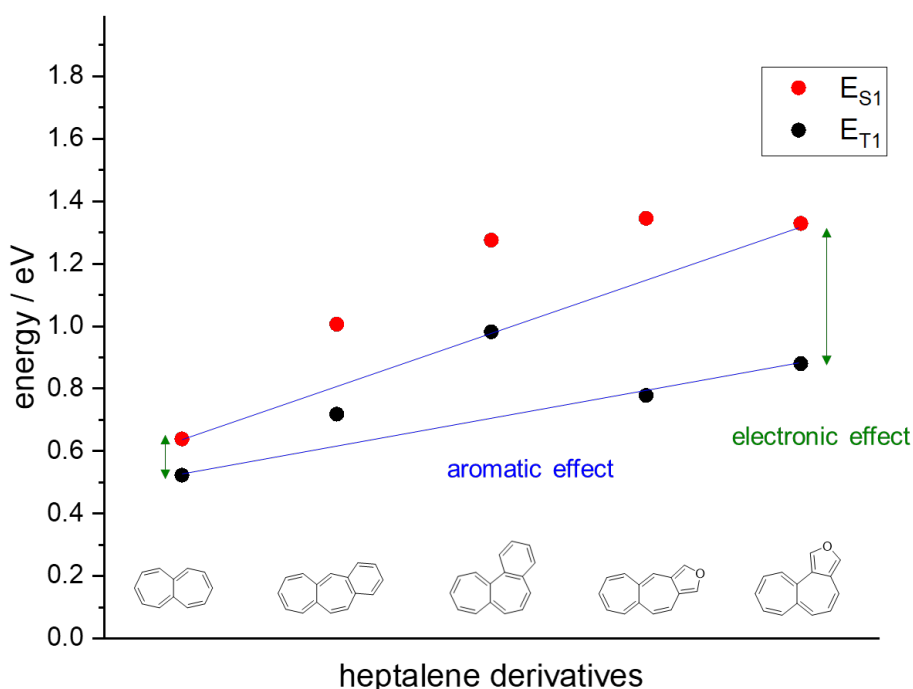


Figure 1. Singlet-triplet gap tuning via aromatic and electronic effects.

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New lamellar sulfur based materials (ITQ-75) with promising photocatalytic performances

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The consequences of humanity's strong dependence on fossil fuels are being felt now more than ever. The production of high value-added compounds through the photoreduction of CO₂ or the water photosplitting has been a viable option to mitigate the greenhouse gas effect and the energy demand. Metal oxides are the most studied materials as photocatalysts. However, the vast majority show high values for the optical band gap and can only absorb radiation in the UV region. Metal chalcogenides comprise a viable alternative to metal oxides, as they have a bandgap more suitable for solar radiation [1]. On the other hand, an open architecture is likely to reduce the electron-hole recombination rate since it reduces the average carrier path to reach the catalysts surface [2]. Recently, porous chalcogenides materials have received particular attention since they combine high surface area and crystallinity with semiconductor properties [2].

In this work, we report the development of a new ordered and structured sulfur-based material entitled ITQ-75 [3]. A hydrothermal synthesis under autogenous pressure was used to obtain the materials under study (see Figure 1). The synthesized materials, composed of Sn, Zn, and S, can be classified as laminar materials and are stable up to a temperature of 300°C. To reveal the surface area from an SDA-occluded material, different protocols were developed that would allow enhancing its accessibility without the removal of the

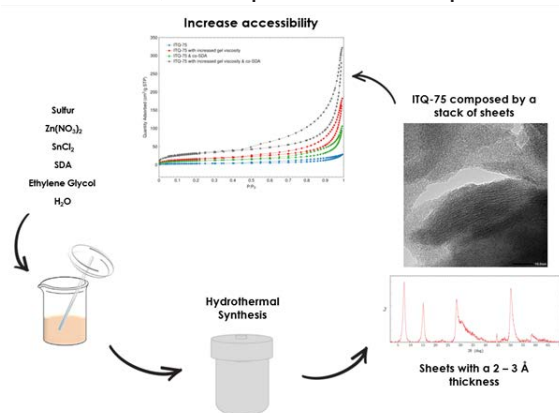


Figure 1. Synthesis procedure, based on hydrothermal synthesis, to obtain ITQ-75, as well as its diffraction pattern, an HRTEM image highlighting its laminar profile and N₂ physisorption isotherms showing its increased accessibility

SDA. To change the electronic properties of the obtained structure, a metal doping strategy has been carried out. After doping, it was observed the reduction of the bandgap value to 1,9 eV, the optimal value to use these materials in solar fuel

processes. Initial gas-phase photocatalytic tests show that these materials show promising photocatalytic performance. Therefore, the authors believe that the materials under study are promising photocatalysts, particularly in solar-to-fuel routes, that would help develop processes with high yields of conversion.

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Improvements in Mechanically Controllable Break Junctions Experimental Setup for atomic, molecular and two-dimensional conductors

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Abstract

The miniaturization of electronic devices has shown the necessity to investigate electronic behavior at the molecular level [1]. Experimental methods as Break-Junctions (BJ) are used to study of quantum transport in atomic, molecular and two-dimensional conductors. Two of the most common employed methodologies are the Scanning Tunneling Microscope in the Break-Junction configuration (STM-BJ) [2] and the Mechanically Controlled Break Junction (MCBJ) technique [3]. However, in the specific case of the MCBJ instrumentation, the developments have been very limited [4]. In this context, our research group have introduced some new improvements in the MCBJ approach. In this work, we want to report two significant advancements in our MCBJ experimental setup. Firstly, we developed an automated and motorized electrode rupture system, simplifying and controlling the initial process (see figure 1a). Secondly, we enhanced the substrates by introducing 3D-printable polylactic acid (PLA) substrates, reducing costs and streamlining production in a single step. To validate our system, we calibrated through atomic sized contacts of silver using manufactured electrodes. Our measurements of conductance versus relative displacement between electrodes (see figure 1b) are in good agreement with previous results [4]. Thanks to these improvements, we can state that we have a fully functional MCBJ experimental setup under ambient conditions with substantial improvements in the production of flexible substrates.

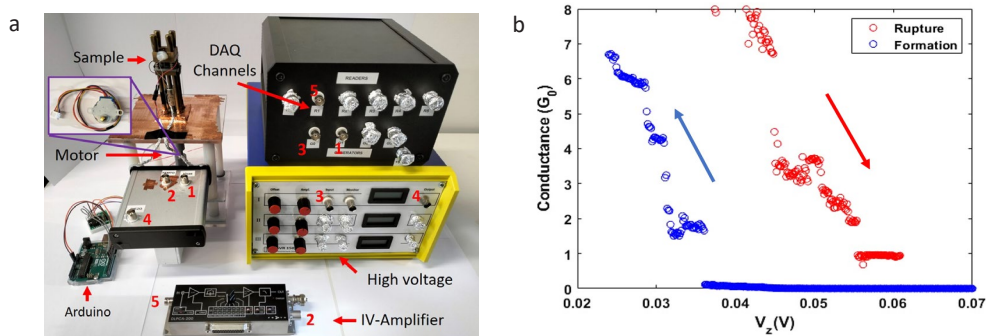


FIG 1. (a) MCBJ experimental setup, (b) Conductance measurement at room conditions of atomic-size contacts of silver.

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Exploring Electronic Transport in Atomic-Sized Contacts of Sn: Unveiling a Possible Scenario of Topological Insulator

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Theoretical studies using DFT applied to the α -Sn(111) [1] have revealed its nature as a topological insulator [2]. This implies that the surfaces of α -Sn(111) [1] must exclusively exhibit electronic transport along the material's edge, resulting in a conductance close to the conductance quantum ($G_0 = 2e^2/h$). In this study, we will apply the experimental procedure developed by C. Sabater *et al.* [3], where they demonstrated that Bi(111) bilayers were topological insulators using the Scanning Tunnelling Break Junctions (STM-BJ) technique. This discovery was based on the observation of stable conductance values at $1G_0$ for significant electrode separation distances, suggesting the presence of interconnected Bi(111) bilayers.

Our measurements of electrical transport using STM-BJ at 4K in Sn contacts have allowed us to observe values close to $1G_0$ for relatively large electrode spacings involving (4-6) atoms, as shown in Figure 1a. In Figure 1b, a histogram of typical conductances for tin is presented, where this behaviour of long plateaus in G_0 is also frequently observed. There are two plausible scenarios to explain this behaviour. The first possibility is that Sn is a topological insulator, or these $1G_0$ values may be due to monoatomic chains, as observed in materials like Au, Ir, or Pt [4]. However, future spectroscopic studies will reveal the mechanism that explains this behaviour.

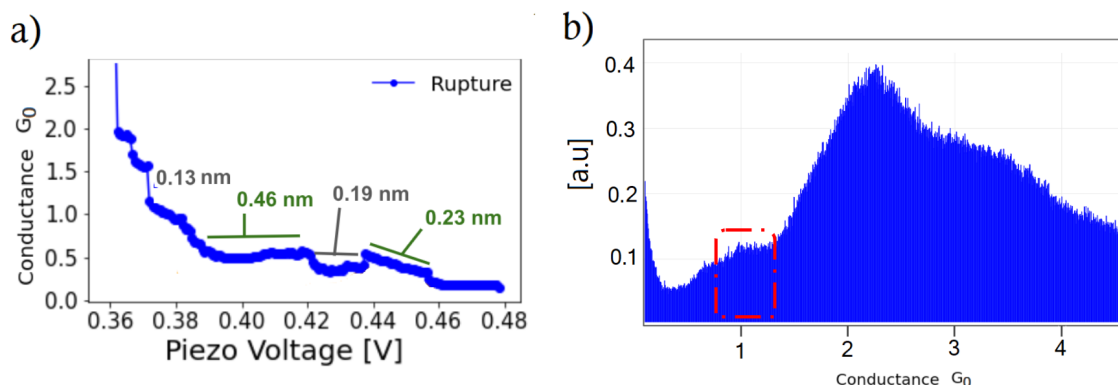


Figure 1. a) Conductance traces exhibiting plateaus with 6 atoms in Sn b) Histogram of conductance Sn obtained from traces exhibiting long plateaus.

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Electronic and spin transport of helicenes through ab initio calculations

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Helicenes are organic molecules characterized by their helical shape, which imparts chirality to them. This inherent symmetry property makes them intriguing candidates for the phenomenon known as CISS (Chiral Induced Spin Selectivity) [1]. Our research focuses on the electronic and spin transport properties of dithia[n]helicenes, where "dithia" indicates the presence of two thioether anchoring groups at the ends, and "n" denotes the number of benzene-like rings, in our case 7, 9, and 11 [2, 3]. Additionally, our study considers the topography, whether it's *exo* or *endo*, of the sulfur groups and of course chiralities involved P and M.

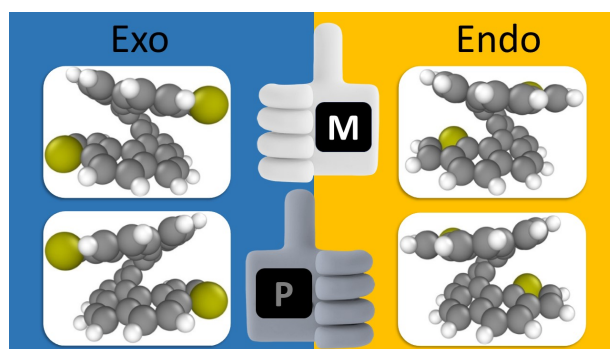


Figure 1: Illustration of the dithiahelicene[9] structure. The *exo* topologies are represented in the blue section, while the *endo* variants are depicted in the yellow region. At the upper portion, the white hand symbolizes the M chirality (right-handed) of the upper molecules. In contrast, the grey hand indicates the P chirality (left-handed) orientation of the molecules in the lower part.

Our calculations of electronic and spin transport are based on Density Functional Theory, utilizing the Non-Equilibrium Green's Functions (NEGF) approach. In this work, we present a comprehensive study of the spin and electronic transport properties in the various geometric configurations that dithia[n]helicenes can assume when trapped between two electrodes. Furthermore, we have enhanced our calculations through the utilization of optimization algorithms within DFT.

Moreover, our calculations have been carried out at a bias voltage different from 0, thereby breaking the time reversal symmetry condition, in conjunction with the implementation of spin-orbit coupling. These elements enable our results to shed light on how a single molecule can function as a spin filter.

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Sustainable processes to prepare N-doped activated carbons with high stability

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The development of double layer capacitors (EDLC) with improved energy density presents important challenges. One of the main challenges is obtaining high stability electrode materials. Therefore, it is necessary to implement methodologies for the synthesis of materials with high stability and with lower costs and higher sustainability. Regarding costs, it is important to modify the actual stabilization processes, which usually increase the cost of these materials and have high environmental impacts. One possibility is the use of other stabilization methods at softer conditions [1]. A previous study applied the LCA methodology to determine the environmental impacts of the different stages of a process to obtain nitrogen-functionalized activated carbons using biomass residues as a precursor [2]. This study revealed that the main sources of environmental impacts along the process chain come from the functionalization and washing steps [2]. In this work, we have studied the functionalization of activated carbons prepared from biomass residues with N-functional groups through a water-based methodology that reduces the environmental impacts of the process. Activated carbon was synthesized using almond shell residues as precursor. These activated carbons were functionalized by an organic reaction under mild conditions to introduce nitrogen functional groups [1]. Modifications of the process were made to avoid the use of pyridine and ethanol to minimize the environmental impacts of the process. The functionalization of a commercial activated carbon (YP50F) was also studied. The activated carbons were used as electrodes of EDLC in organic electrolyte. The stability of the supercapacitors was evaluated by 10000 galvanostatic charge-discharge cycles. The as-prepared activated carbons have a high BET surface area ($>1800 \text{ m}^2\text{g}^{-1}$). After the functionalization reaction, nitrogen contents between $\sim 2.0 \%$ and $\sim 1.0 \%$ are achieved. The activated carbons showed good electrochemical behavior as supercapacitor electrodes, showing the functionalized activated carbons higher retention of capacitance. It is important to highlight that the synthesis methodology used in this work allows the conversion of biomass residues into carbon materials with great potential for use as electrodes in supercapacitors and employing a process with reduced environmental impacts.

Acknowledgments

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FUNCTIONALIZATION OF 2D MATERIAL BY INTERCALATION.

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Alkali metals (AM) intercalate into graphite leading to the formation of AM-graphene layered materials (with AM = Li, Na, K, Rb, Cs). Intercalated species can modify the very electronic structure of **graphene** and consequently its electron mobility. Open question is how AM interact on graphene depending on the structure and coverage. We want to tackle this issue by first-principle calculations, in particular density functional theory, starting from a prototype system like K-graphene in different structural configurations and atomic percentages. Calculations are performed within first-principles **DFT** (density functional theory) under the local density approximation LDA. The **QUANTUM ESPRESSO** package is used to perform all calculations; codes in the package are based on density functional theory and on a plane wave/pseudopotential description of the electronic ground state and are ideally suited for structural optimizations (both at zero and at finite temperature), linear response calculations (phonons, elastic constants, dielectric and Raman tensors, etc.) and high-temperature molecular dynamics. Calculations for (2×2) and (4×4) pristine undoped graphene, and (2×2) and (4×4) K-adsorbed on graphene are performed with the same-sized hexagonal supercell. In particular, we analyze three different structural configurations: (i) K on one side, (ii) K on alternate sides, (iii) K between two graphene layers. The Brillouin zone is sampled with a 8×8×1 Γ centered k-point grid, and Gaussian smearing with a width of $\sigma = 0.01$ eV is used for the occupation of the electronic levels. The computational results predict a shift of the Dirac cone, which is qualitatively confirmed by UV photoelectron spectroscopy; the most significant observation is the progressive occupation of the π^* states shifted below the Fermi level E_F , upon K adsorption. Further analysis is currently under study.

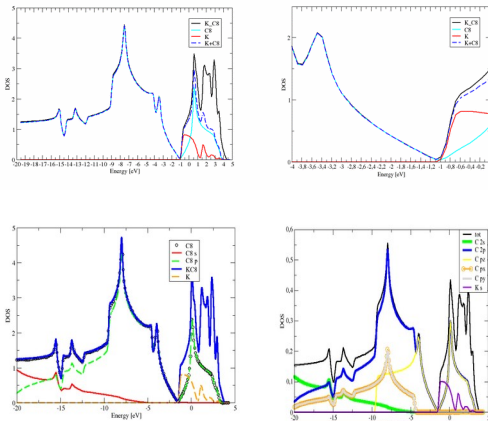


Figure 1. Top: The DOS (density of states) of the KC₈ system, on the left the full DOS and on the right a range of energy around the Fermi level. Bottom: The DOS of the KC₈ system and its partial densities of states s and p.

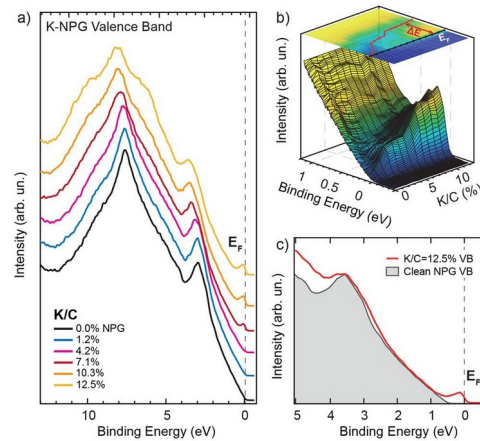


Figure 2. (a) UV photoemission spectral density of the K-NPG system as a function of K exposure (spectra vertically stacked for the sake of clarity). (b) Perspective 3D view of the spectral density evolution of the VB close to the Fermi level (black line) as a function of K dose; the Dirac point energy shift ΔE due to charge injection is reported as a red line in the top projection of the 3D perspective view. (c) Experimental spectral density of K-NPG at saturation coverage (red line) compared with clean NPG, shifted by -0.6 eV in spectral density (gray filled area).

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Two-Dimensional Materials for the Implementation of Hot-Carrier Solar Cells

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Conventional solar cells have a theoretical limiting efficiency of 40.7% and are based on the use of a single semiconductor material characterized by an energy gap. This leads to intrinsic losses due to transmission of low-energy photons and thermalization of hot-carriers. In this work, we present theoretical and experimental advances on the development of a different photovoltaic technology, the hot-carrier solar cell (HCSC), which has a limiting efficiency of 85.4%. The HCSC was proposed in 1982 by Ross and Nozik [1], but prototypes with high efficiency have not been fabricated yet because this technology demands materials with very specific properties. Its operation is based on the use of two elements. First, an absorber material, which may lack an energy gap (absorbing all photon energies) and that sustains a hot-carrier population. Second, two energy selective contacts (ESCs) that extract either electrons or holes with a constant energy, decreasing isentropically their temperature, and creating a voltage output.

Our work focuses on the theoretical and experimental study of ESCs. We show that the materials in these contacts should be excellent thermoelectric materials [3]. And from this result, our experimental study proves the validity of two-dimensional (2D) materials as promising ESC candidates for the HCSC.

To study theoretically realistic contacts where the conductivity has a finite value, we introduce a parameter called saturation particle current density. This parameter is infinite for idealized contacts, reducing the limiting efficiency when it diminishes. To describe the thermoelectric properties needed for the contacts to achieve high efficiency, we use the figure of merit ZT . We find that with lower energy differences between the contacts, we need materials with lower values of ZT facilitating the implementation of a realistic HCSC. To evaluate the thermoelectric properties of 2D materials, another figure of merit is experimentally analyzed: the power factor (PF). This parameter is measured for MoS_2 and it is found to increase with higher degree of substitutional doping and with lower thickness. These results will allow us to tune the properties of the materials to optimize the contacts.

In conclusion, with this work we gain a deeper understanding of the ESCs in the HCSC. Through the theoretical study, we prove that the contacts must have good thermoelectric properties and we calculate the optimum properties. The experimental results demonstrate the potential of 2D materials for the ESC implementation. However, to develop a high efficiency HCSC, it is necessary to study the properties of the absorbing material, to find 2D materials that allow the operation of this solar cell.

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Enhancing the absorption of two-dimensional material solar cells

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Solar cells of two-dimensional (2D) materials are promising for ultra-lightweight and flexible applications, but the performance of current prototypes is far below that the other technologies. The current record power conversion efficiency in 2D material solar cells is 5% [1] which is still far from the 21.07% achieved with perovskite cells [2] and the 29% obtained with silicon solar cells [3]. The reason for the low performance of 2D materials solar cells has been that the photovoltage was pinned to values of below 0.6 V. We have recently overcome this by demonstrating a photovoltage of 1 V in a substitutionally doped p-MoS₂/n-MoS₂ junction [4]. To reach high efficiencies the high voltage must now be combined with a high photocurrent. This work focusses on enhancing the photocurrent in MoS₂-based solar cells.

We have modelled an ultrathin MoS₂ absorber enclosed in different 1D optical cavities. We find for example that a 57 nm layer of MoS₂, sandwiched between two thin films of h-BN and a Ag back mirror as a rear reflector absorbs 89% of the photons in the 300-700 nm range of the AM1.5G spectrum [5]. We also find absorptance enhancements with respect to a material slab without additional layers for thin MoS₂ in the range of 1-9 nm due to the BN adlayers. Moreover, we propose scalable structures, such as a device deposited on an indium-tin oxide (ITO) combined with glass substrate and we find similar absorptances. The large absorptance is due to an enlargement of the zeroth Fabry-Perot interference mode, which causes high broadband absorption in these 2D material-based structures.

We have chosen a BN/MoS₂/Ag structure and implemented it experimentally. This included the development of a fast-transfer technique that prevents the sulphurisation of the Ag during the process. Our current record device has a short circuit density of 12 mA/cm² and an open circuit voltage of 0.6 V under a broadband illumination equivalent to 40 suns. We are currently making more tests using MoS₂ with heavier p-doping, which is expected to increase the photovoltage. This will result in a detailed understanding of the influences of doping level and material thickness on the device performance.

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Influence of the addition of different graphene nanoplatelets in polyurethane aerogels: study of thermal insulation and mechanical properties

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Aerogels are innovative materials presenting very low densities (80-300 kg/m³), high porosities (>80%), high specific surface area, and good thermal insulating properties¹. Although silica aerogels have gathered great attention by the scientific community for many years, currently, different materials are being used to manufacture aerogels, such as cellulose, chitin, or polyurethane. It has been demonstrated that polyurethane reach low thermal conductivity values and better mechanical strength than silica aerogels² which makes them suitable for various applications requiring these properties as is the case of thermal insulation.

However, these thermal and mechanical properties could be further improved. Due to the low density and small particle and pore sizes of these materials, infrared radiation barely suffers any absorption or scattering effects, which increases the total thermal conductivity. This problem could be overcome, for example, by including opacifiers that act as infrared radiation blockers. Additionally, these opacifiers can contribute to improvements in their mechanical properties³.

In this study, graphene nanoplatelets (GnPs) with different dimensions have been included into polyurethane aerogels with the aim of finding the optimum content and size for effectively reducing the total thermal conductivity, obtaining a reduction of 22% with respect to the non-opacified aerogel for a content of 3%wt of GnPs. Moreover, due to the addition of these opacifiers, an improvement in the mechanical properties have been achieved. Therefore, this work represents a straightforward strategy for effectively improving the performance of polyurethane aerogels non-explored before for this matrix.

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Sheathed Molecular Junctions for Unambiguous Determination of Charge-Transport Properties

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One of the alternatives to conventional silicon electronics is molecular electronics, which studies the application of molecules as components in electronic circuits [1]. In this field, the fabrication of unimolecular devices, where a single molecule can act as an individual component, is the final miniaturization objective. To reach this goal, many challenges are yet to be overcome, being one of them the low reproducibility of the conductance measurements of single molecules. For this purpose, an optimization of the molecule-substrate interphase needs to be achieved, and additionally, the avoidance of multimolecular junctions caused by intermolecular interactions.

Here, we describe the use of supramolecular host-guest complexation as a strategy to encapsulate a molecular wire and unambiguously measure its electrical properties [2]. A benchmark molecular wire, 4,4'-(1,4-phenylenebis(ethyne-2,1-diyl)) dianiline, is sheathed by an insulating cage, pillar[5]arene 1,4-diethoxy-2-ethyl-5-methylbenzene. The assembly of the 1:1 complex is probed by ¹H-NMR, whilst the capabilities of the molecular wire remain intact after complexation as demonstrated by XPS and AFM. By encapsulating the molecular wire, stacked dimers are prevented, and the true conductance of the individual molecule can be determined with greater accuracy and confidence, as demonstrated by using the STM-BJ technique (scanning tunnelling microscopy–break junction). This strategy allows new avenues for controlling single-molecule properties and demonstrates the capabilities of pillararenes to be used in the construction of arrays of encapsulated single-molecule functional units on large surfaces.

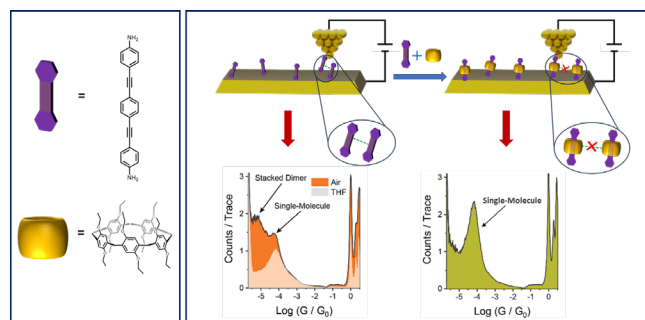


Figure 1: Scheme of the host-guest complexation and the effects on conductance measurements.

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NiRu supported on CeO₂ obtained by mechanochemical milling as catalyst for hydrogen production from ammonia

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The development of active and stable catalysts for carbon-free hydrogen production is a major goal in the power generation field, in order to limit the effects of climate change. Ammonia has emerged as one of the best choices among carbon-free hydrogen sources, alongside water, as it has a high hydrogen content and it is liquid at low pressure, which allows its easy storage and transportation. It is decomposed catalytically into hydrogen and nitrogen at moderate temperature, typically around 400 - 600 °C at 1 atm ($\text{NH}_{3(g)} \rightleftharpoons 1/2 \text{N}_{2(g)} + 3/2 \text{H}_{2(g)}$, known as ammonia decomposition). The on-site catalytic conversion of ammonia into hydrogen is an appealing method to supply proton exchange membrane fuel cells, which demand high-purity hydrogen [1].

We have recently developed a catalyst based on nickel (5 wt.%) with a small content of ruthenium (1 wt.%) supported on cerium oxide nanoparticles, which showed an excellent catalytic performance in long-term stability tests with respect to monometallic Ru/CeO₂ and Ni/CeO₂ [2]. We are currently exploring an alternative synthesis method, the mechanochemical milling (MM), to precisely control the formation of active sites based on specific properties of amorphous/crystalline interfaces. MM synthesis methods are highly attractive due to their low energy and time requirements, versatility, and scalability. Using different Ni and Ru precursors (acetate, chloride, or nitrate) interesting differences in terms of catalytic activity were observed. The catalyst prepared using nickel (II) nitrate hexahydrate and ruthenium (III) acetate showed the highest activity, achieving higher ammonia conversion rates than the catalyst prepared using the conventional impregnation method. Furthermore, a strong dependence of the catalytic activity on the milling conditions was observed, particularly on the order in which the metal precursors were added.

In-depth characterization of the NiRu/CeO₂ catalysts synthesized through MM using different precursors and milling conditions was conducted using X-ray diffraction and X-ray absorption spectroscopy (Synchrotron ALBA, NOTOS beamline). The oxidation state of Ni and Ru (XANES), their atomicity (EXAFS), and the atomic scale structural changes induced by the metals addition on ceria were analysed. In the samples prepared through MM, the presence of a small quantity of oxidized form of the metals was identified, suggesting that some of the precursors undergo oxidation during the MM process. Additionally, an increase of the reduced form of ceria, Ce(III), in all catalysts, compared to the support alone, has been identified, indicating a possible increase in the oxygen vacancies within the ceria structure.

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In-silico insights into the mechanism of formation of tin halide perovskite nanostructures

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Metal halide perovskite nanocrystals have emerged as a highly promising option for photoactive layers in solar cell devices, achieving impressive power conversion efficiencies of up to 25%. [1] Tin-based materials, known for their excellent charge carrier mobility and ideal band gaps for photovoltaic applications, have been suggested as the leading contenders to replace lead-based devices. [2] Notably, recent research has revealed that by using tin halide salts as precursors, it becomes possible to simultaneously generate 3D nanocrystals (ABX_3) and 2D nanosheets ($L_2A_{n-1}B_nX_{3n+1}$). [3] This breakthrough paves the way for synthesizing and characterizing materials with adjustable optical and electronic properties, contingent on both the nanocrystal particle size and the nanosheet dimensionality. [4]

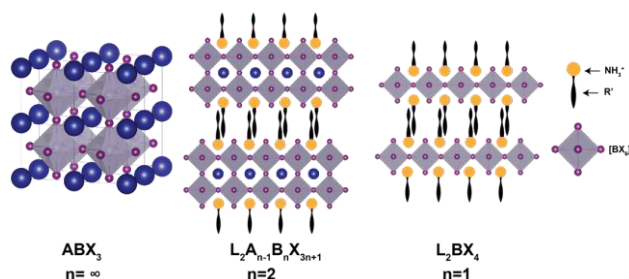


Figure 1. Perovskite nanostructures under investigation.

In our presentation, we introduce a theoretical and computational protocol aimed at elucidating the mechanisms underlying the formation of 2D nanosheets and 3D nanocrystals of tin halide perovskite nanostructures. Our approach integrates advanced density functional theory calculations with ab-initio molecular dynamics simulations. We particularly emphasize the interplay between dynamic disorder, [5] chemical composition, electronic characteristics, and the formation energy of these materials.

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Study of the thermoelectric effect in hydrogels synthesized from lignocellulosic biomass residue.

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Ionic thermoelectric materials have been garnering attention in recent years due to their possibilities for heat to electricity conversion purposes [1]. This study explores the potential of lignin-based hydrogels as ionic thermoelectric platforms made from clean and sustainable resources. The hydrogels were synthesized from a KOH solution, organosolv lignin and PEGDGE as the crosslinker. The thermoelectric properties of these hydrogels were investigated, with an emphasis on the Seebeck coefficient and electrical conductivity, with techniques such as FTIR and SEM being employed for further characterization. Large Seebeck coefficients in the range of 9 to 30.4 mV K⁻¹ were measured in the prepared samples, with electrical conductivities ranging from 0.3 to 5.9 S m⁻¹.

Thermoelectric characterization of the samples indicates that increased electrolyte concentration in the hydrogel increases the Seebeck coefficient, but only to a certain point, from where it starts decreasing, the same occurs when varying the amount of crosslinker in the sample. Similarly, electrical conductivity also increases with both KOH concentration and crosslinker ratio up to a certain point, but the subsequent decrease in electrical conductivity at higher concentrations or crosslinker ratios is drastically higher than the one observed for the Seebeck Coefficients. This is supported by the morphological characterization, which revealed a higher degree of crosslinking and a diminishment in porosity of the samples at higher KOH concentrations and crosslinker ratios, contributing to the observed decrease in Seebeck coefficient and electrical conductivity.

The power factor of the samples was calculated from the Seebeck coefficient and electrical conductivity measurements, obtaining values as high as 4187 $\mu\text{W m}^{-1} \text{K}^{-2}$, indicating the great potential these hydrogels have as future sustainable ionic thermoelectric platforms.

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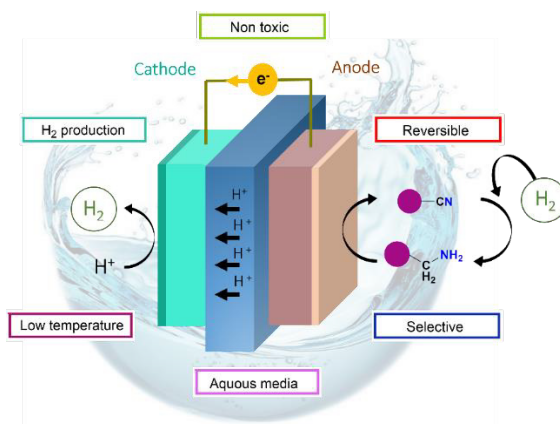
Room temperature hydrogen production via electro-dehydrogenation of amines into nitriles: Increasing the efficiency of Liquid Organic Hydrogen Carriers

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We describe the electrocatalytic dehydrogenation of primary amines and the catalytic hydrogenation of nitriles to store hydrogen in liquid form using Liquid Organic Hydrogen Carriers (LOHCs). Green, selective and soft method for the synthesis of nitriles in aqueous media without the use of harsh conditions has been developed. Additionally, molecular hydrogen as unique byproduct has been obtained. Moreover, the suggested method might be a solution to advance a reversible dehydrogenation/hydrogenation cycle for LOHCs industrial applications.



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Development Of Activated Carbons Derived From Chitosan For their Application As Electrodes In High-Durability Supercapacitors

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Supercapacitors are promising devices for energy storage due to their high power and lifetime [1], being an interesting alternative to mitigate current energy problems. One of the main challenges in their implementation is the development of appropriately modified materials for their use as electrodes. In this sense, N-containing activated carbons have generated great interest in these applications, since these functional groups improve their electrochemical behaviour [2]. In this work, activated carbons were prepared by chemical activation with H_3PO_4 from chitosan as precursor. High yield N-doped activated carbons were obtained because chitosan is a biomass that contains nitrogen in its structure. Supercapacitors were assembled in organic electrolyte using the prepared materials. The results show that these devices have excellent durability after 10000 charge-discharge cycles providing energy and power comparable to a commercial activated carbon (YP50F) used for this application. The synthesis methodology used is sustainable, straightforward and with high yield for the preparation of activated carbons with great potential for this application.

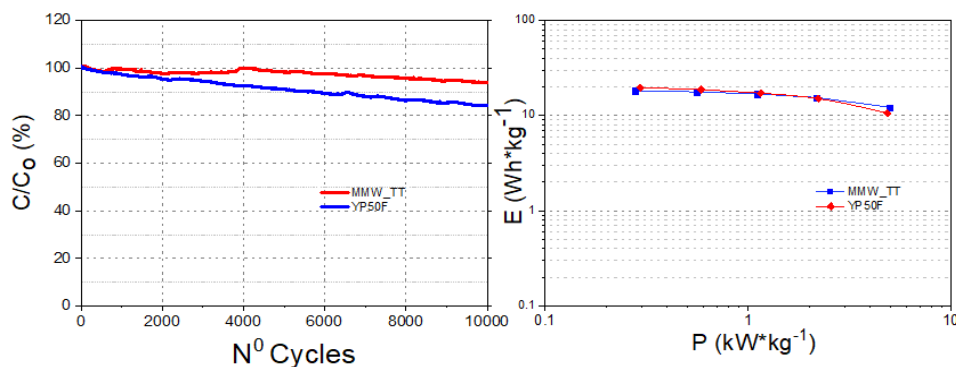


Figure 1. (a) Capacitance retention (%) vs number of cycles. (b) Ragone plot of symmetric capacitors at 2.5 V after durability test. Electrolyte: 1M TEMA-BF₄/PC.

Acknowledgments

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Oxygen vacancies in freestanding complex oxides by advanced electron microscopy

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In recent years, the field of 2D materials has grown exponentially to become a promising field for the next generation of devices and functional materials. Their reduced dimensionality enables the emergence of novel properties absent in the bulk, leading to exotic electronic, mechanical and topological effects. Recently, a new family of two-dimensional materials has been developed, consisting of freestanding membranes of complex oxides, which allow us to have advanced materials with simultaneous reduced dimensionality and strong electronic correlations [1]. In these systems, lattice point defects such as oxygen vacancies (Fig. 1) emerge as an aspect of high interest as they serve as a degree of freedom for controlling the advanced functionalities. It is of special interest their microscopic distribution, as small variations in concentration, even the presence of single vacancies, could lead to substantial changes in the macroscopic response. Therefore, probes capable of studying point defects with atomic resolution arise as an essential tool for the comprehension and control of emergent phenomena in these systems. However, the detection of single oxygen vacancies has yet remained elusive, challenging the advances in the field. In this work we propose a new method for the detection of point-like defects such as single-oxygen vacancies, that makes use of the new capabilities allowed by the 4D-STEM (4D-scanning transmission electron microscopy) technique [2]. Via experiment and simulation, we have studied the scattered intensity distribution of fully oxygenated columns and columns with a lack of oxygen, allowing us to identify the characteristic fingerprint of single-oxygen vacancies in the transmitted electronic beam. We propose a method based on virtual detector optimization that harnesses the beam intensity variations induced by single-oxygen vacancies to generate an imaging mode where the contrast between fully oxygenated and vacancy columns is enhanced. Although valid for any material, we illustrate the application of the technique in the case of single oxygen vacancies in SrTiO₃, the quintessential perovskite structure. The results show a significant increment in detectability, with sensibility to vacancy densities as low as 0.98% per column, improving the detection limits established by usual techniques in the field while maintaining atomic resolution.

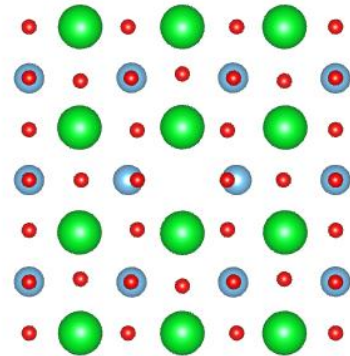


Figure 1. Calculated SrTiO₃ structural distortions caused by a single oxygen vacancy at the center. Green, blue and red atoms indicate Sr, Ti and O, respectively.

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***In operando* Characterization of the Ionic Conductivity Dependence on Liquid Transient Phase and Microstructure of Cold-Sintered Bi₂O₃-doped Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ Solid-State Electrolyte**

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A disruptive sintering technique, Cold Sintering Process (CSP), has been used to produce cold-sintered samples of Bi₂O₃-doped Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ (LATP) as solid-state electrolyte (SSE). An *in operando* impedance study has been performed to shed light on this sintering process [1]. In this work, Bi₂O₃ and 3M acetic acid solution sintering aids were synergistically added to LATP powders to sinter at low temperature. Effects of Transient Liquid Phase (TLP) content on the sintering behavior, phase composition, microstructure, and electrochemical properties were all investigated for a LATP doped with 2 wt.% Bi₂O₃ (optimal content) solid-state electrolyte (SSE). The data revealed that the final electrical properties, are defined by the following sintering parameters: Transient Liquid Phase (TLP) content, temperature, pressure, and dwell time.

Using acetic acid 3M as TLP, LATP-based samples can be cold-sintered at optimized sintering conditions of 150 °C and 700 MPa of uniaxial pressure for 90 min. The resultant SSE shows a high ionic conductivity (4.5·10⁻⁵ S cm⁻¹) at room temperature (RT) and relative density (~95%), which demonstrates the effectiveness of the low-temperature sintering process by optimizing the ionic conductivity of LATP-based SSE, also reducing preparation costs and CO₂ emissions [2].

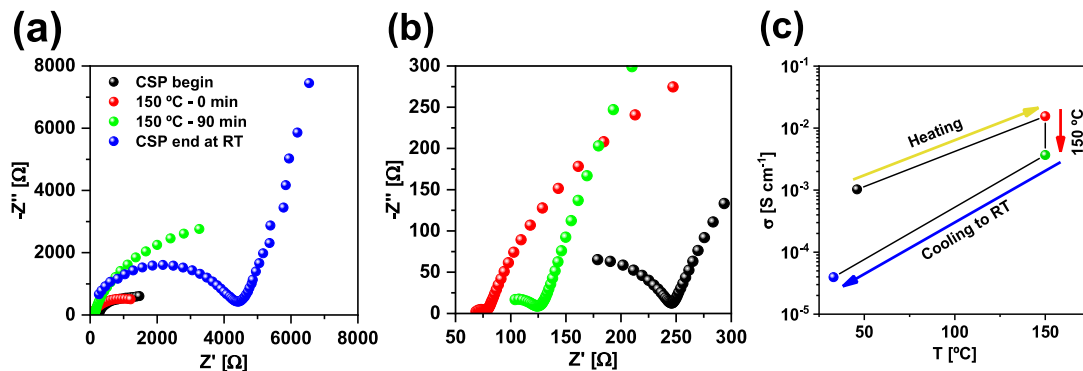


Figure 1. (a) Impedance spectra at different times of the CSP for a sample with 25 wt.% of TLP and 2 wt.% of Bi₂O₃, black dots refer to the first spectrum recorded at room temperature when the TLP is completely present in the sample. Red dots refer to the first spectrum recorded at maximum temperature (150 °C). Green dots denote the last spectrum at 150 °C and the blue dots represent the final spectrum at RT under pressure when CSP is completed. (b) Amplification of (a). (c) Ionic conductivity dependence on temperature along the CSP for a sample with 25 wt.% of TLP and 2 wt.% of Bi₂O₃.

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Introducing an ionic conductive matrix to the cold-sintered $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ -based composite solid electrolyte to enhance the electrical properties

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In this work, a Polymer-In-Ceramics (PIC) composite solid electrolyte based on $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) and $\text{PEO}_n\text{-LiTFSI}$ (poly(ethylene oxide) - lithium bis(trifluoromethanesulfonyl)imide) is obtained via Cold Sintering Process (CSP), at a temperature of 150 °C without any post-heat treatment, this is 900 °C below the traditional sintering temperature [1]. This novel study demonstrates the effect of the Transient Liquid Phase content (TLP) and the composition of the polymeric active filler on the final Composite Solid Electrolyte (CSE) properties, with the sintering process being monitored by in-operando Electrochemical Impedance Spectroscopy (EIS).

The highest ionic conductivity of $1.04 \cdot 10^{-4} \text{ S cm}^{-1}$ and a relative density above 98% are achieved at room temperature when the TLP content is 15 wt.% and the molar ratio (2:1), with the LATP content set in 90 wt.% [2]. Moreover, the activation energy for the lithium transport (E_a) is drastically reduced, from 0.388 eV (LATP ceramic electrolyte) to 0.298 eV (PIC electrolyte), with a lithium transference number (t_{Li^+}) close to 1. Therefore, this research work proposes a potential solid electrolyte to substitute the traditional liquid electrolytes.

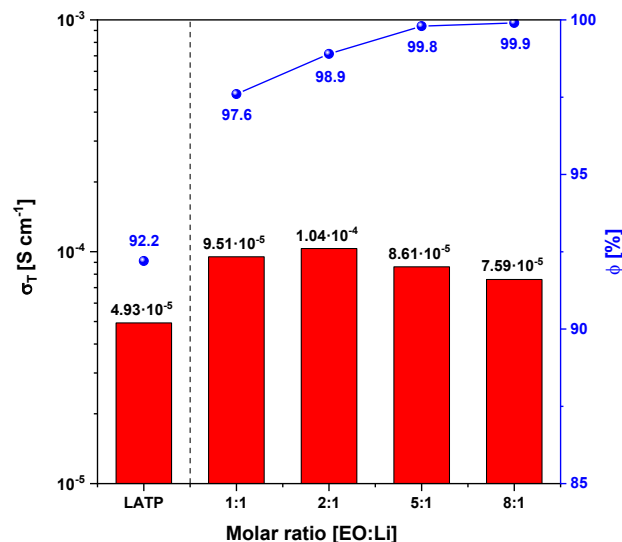


Figure 1. Total ionic conductivity of the Composite Solid Electrolytes (black) and relative density (blue) dependence on the composition of the polymer matrix employed as an electric dopant.

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Application of a Remote Sensing Platform using Luminescent Materials

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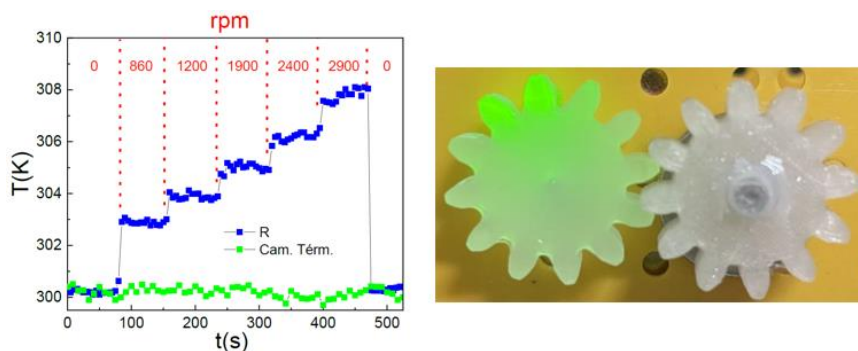
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In this work we have developed for the first time a multifunctional sensing platform that allows the optical detection of pressure (vacuum), temperature (both crucial parameters in materials science [1]) and excitation power density, using a sensor based on an upconversion inorganic material ($\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$) emitting in the visible range. This material has been used for the study or estimation of the temperature of a gear or mechanism capable of transmitting mechanical power in operation. To measure these parameters without contact, optical methods based on the luminescence of lanthanides, d-block metal ions and organic complexes are usually applied [2]. In order to develop this sensor, we used the relationship between temperature and luminescence intensity of thermally coupled levels (TCL) of Er^{3+} , namely the band intensity ratio (525 nm /550 nm) [3].



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Synthesis and Characterization of Colossal Dielectric Constant Materials for Energy Storage Devices

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Materials which have real part of permittivity i.e. $\epsilon' > 10^3$ are called Colossal dielectric constant materials (CDC) and these materials are important for the capacitive, microelectronics, compact & high-density devices for energy storage, and for the applications of high frequency devices [1].

Pristine ZnO, Gd_{0.005}Zn_{0.99}O and Gd_{0.01}Zn_{0.99}O materials were synthesized by employing solid state reaction method. Each composition has been sintered at high temperature of 1200°C, 1300°C and 1400°C. Lab & synchrotron base X-ray diffraction (XRD) studies shows single phase Wurtzite ZnO even when sintered at different temperatures. The Rietveld refinement analysis of the sintered samples of Gd_{0.005}Zn_{0.99}O and Gd_{0.01}Zn_{0.99}O composition shows that Gd is not sitting at Zn substitutional site, instead of this it is present in two different phases of Cubic (C-Gd₂O₃) & Monoclinic (M-Gd₂O₃) polymorphs of Gd₂O₃ in the ZnO host matrix. Field Emission Scanning Electron Microscopy (FESEM) of the Gd_{0.005}Zn_{0.99}O and Gd_{0.01}Zn_{0.99}O compositions further confirms the XRD results and reveal that Gd is not the part of ZnO grains and exist separately in the forms of lumps at or close to the grain boundaries. The confirmation of the presence of the Gd was also analyzed by Energy Dispersive X-ray spectrum (EDX) analysis. SEM results also demonstrate increase in porosity and grain growth with increase in sintering temperatures for every composition.

Room temperature impedance analysis suggests Gd_{0.005}Zn_{0.99}O composition sintered at 1400°C possess colossal dielectric constant (ϵ') with minimum tangent loss ($\tan\delta$) values. In addition, the Gd_{0.005}Zn_{0.99}O composition show highest values for permittivity both at high and low frequency ranges as compared to the other composition even that of pristine ZnO. This study showed that, relatively higher values of the ϵ' with stable & minimum $\tan\delta$ values within the wide frequency range makes the 1400°C sintered sample of Gd_{0.005}Zn_{0.99}O a potential candidate for practical applications, however further studies are still required.

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Study of the Sulfonation of Chitosan-based Composite Membranes containing fractionated Kraft and Organosolv Lignin for Fuel Cell Applications

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In recent years, the development of new high performance, environmentally friendly and low-cost polymer electrolytes has been of great importance for the advancement of proton exchange membrane fuel cells (PEMFCs). Chitosan-lignin composites are cheap biomaterials that can be derived from industrial waste products [1], [2] and exhibit interesting properties as polymer electrolytes [3]. However, the proton conductivity of chitosan shall be modified by ionic cross-linking via sulfonation [4].

This study aims to investigate the effect of sulfonation on the fuel cell performance of chitosan-based composite membranes containing fractionated kraft and organosolv lignin. In particular, their compartment in a H₂/O₂ fuel cell setup as well as the electron and proton conductivity are studied using dielectric thermal analysis (DETA). Complementary structural and thermal properties are analysed by Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA).

The sulfonated composites show the effective ionic cross-linking of the chains by incorporation of conductive sulfate groups. The sulfonated samples are more hydrophilic and absorb higher amounts of water. The increment in the proton conductivity and the power density demonstrates that these materials are competitive as fuel cell electrolytes.

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Single Ion Magnets based on anilato and ethylene glycol

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It is well known that two and three-dimensional materials with slow relaxation of the magnetization (single-ion magnets, SIM and single-molecule magnets, SMM) represent a very active field. [1-5]

Herein, we present two anilato-based coordination polymers based on Dy(III) and ethylene glycol (eg) with two different anilato-type ligands (dianions of the 3,6-disubstituted-2,5-dihydroxy-1,4-benzoquinone: $(C_6O_4X_2)^{2-}$, with $X = Cl$ and Br) and formulated as: $[Dy_2(C_6O_4Cl_2)_3(\mu\text{-eg-kO})(H_2O)_4]\cdot 2\text{eg}\cdot 4H_2O$ (**1**) and $[Dy_2(C_6O_4Br_2)_3(\text{eg-k}^2O,O^{\prime})_2(\text{eg-kO})(H_2O)]\cdot 2\text{eg}\cdot H_2O$ (**2**). Compound **1** has a 3D (4,6)-gon diamond net topology while **2** presents a 2D (3,6)-gon lattice with rectangular cavities with a brick wall disposition. Both compounds behave as single-ion-magnets (SIM). These results highlight the outstanding role of ethylene glycol, giving rise to a rich array of crystal structures and magnetic behaviours, such as zero-field and field-induced SIM.

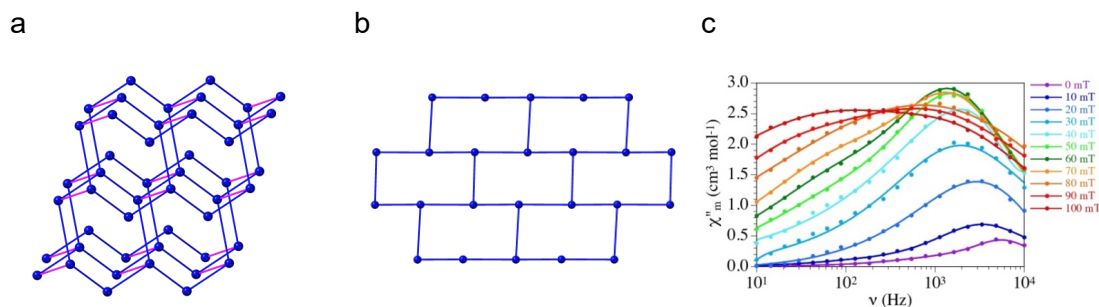


Figure 1: Schematic view of the 3D lattice for **1** (a) and 2D lattice for **2** (b). (c) Frequency dependence of the χ''_m signal at 2 K for compound **2** with different applied DC fields.

Acknowledgments

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A New two-Dimensional MOF with field induced Single Ion Magnet behaviour

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This work summarizes the research project about synthesising, characterising and studying the properties of a new two-dimensional (2D) metal-organic framework (MOF). For this purpose, we used Dy(III) as lanthanoid ion, the ligand chloranilato ($C_6O_4Cl_2^{2-}$ = dianion of the 3,6-dichloro,2,5-dihydroxy-1,4 benzoquinone) and formamide (fma) as co-ligand. In such wise, we have prepared $[Dy_2(C_6O_4Cl_2)_3(fma)_6] \cdot 4fma \cdot 2H_2O$ (Figure 1), which is the first Dy^{III}-containing MOF with fma and chloranilato.[1-2] The formation of neutral (6,3)-gon 2D networks and the nona-coordination of the lanthanoid ion are some interesting aspects of the compound obtained. In this case, the type of synthesis has a key role in the formed structure. In addition, this coordination complex has very interesting magnetic properties. It is a field-induced single-ion magnet (SIM) since it shows a slow relaxation of the magnetization only when a DC magnetic field is applied.

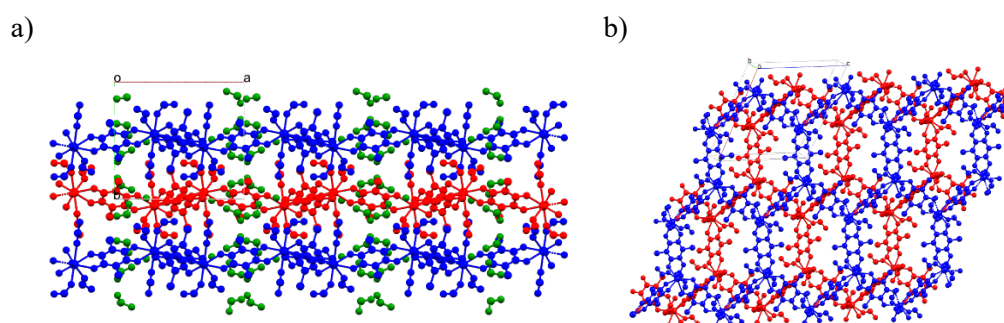


Figure 1. a) side view of three consecutive layers showing the formamide and water molecules located in the hexagonal channels (in green). b) Top view of two consecutive layers showing the alternating disposition.

Acknowledgments

This study forms part of the Advanced Materials program and was supported by the Spanish MCIN with funding from European Union NextGeneration EU (PRTR- C17.I1) and the Generalitat Valenciana (project MFA-2022-057). We also thank the projects CIPROM-2022-60, financed by the Generalitat Valenciana and PID2021-125907NB-I00, financed by MCIN/AEI/10.13039/50110 0 011033/FEDER, UE.

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Moisture-induced formation of perovskite nanocomposite for heterogeneous photocatalysis

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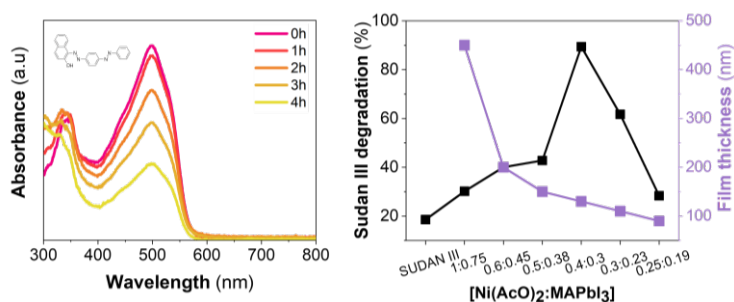
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Lead-halide perovskite nanoparticles are a very promising family of materials due to their optoelectronic properties and chemical versatility [1]. Despite the appealing characteristics of perovskite nanocrystals, traditional fabrication strategies such as heat-up, precipitation or bulk-to-nano approaches continue to present challenges in the development of functional thin-films using these materials. In this regard, in-situ approaches emerge as a promising alternative for the straightforward preparation of perovskite-based materials, offering cost-effectiveness and requiring less demanding conditions [2] [3]. Among the large number of applications for lead-halide perovskite materials, photocatalysis represents a less explored alternative with outstanding potential, showing great progress in photocatalytic degradation of organic dyes, which are one of the main sources of water pollution, asserting themselves as a strong option to move forward the perovskite-based photocatalysis research field.

In this context, we present a two-step annealing-free and antisolvent-free process to synthesize MAPbI₃ nanocrystals embedded in a Ni(AcO)₂ matrix only using humidity as driven force for the crystallization. This method allows us to obtain stable and functional thin-films capable of degrading organic dyes such as Sudan III under visible light. We firmly believe that this synthesis approach could serve as a groundwork for the future preparation of perovskite-based photocatalytic materials.



UV-vis absorption (left) and degradation (right) of Sudan III solution with the presence of Ni(AcO)₂-MAPbI₃ nanocomposite under visible light irradiation.

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Perovskite Thin-Film Single Crystal for a High Performance and Long Endurance Memristor

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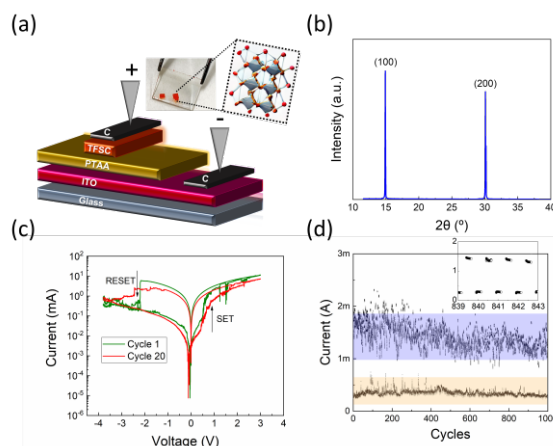
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Metal halide perovskites exhibit electronic and ionic characteristics suitable for memristors. However, polycrystalline thin film perovskite memristors often suffer from reliability issues due to grain boundaries, while bulk single crystal perovskite memristors struggle to achieve high ON/OFF ratios. In this study, we introduce a single crystal memristive device utilizing a wide band gap perovskite, MAPbBr₃, in a thin-film configuration. This thin-film single crystal overcomes these challenges, exhibiting a remarkable ON/OFF ratio of up to 10² and endurance of 10³ cycles, representing one of the highest reported values to date. This exceptional stability enables us to analyse the electroforming process and ON state through impedance spectroscopy, providing insights into the underlying operational mechanism. To the best of our knowledge, this is the first reported thin-film single crystal perovskite memristor device and the first time that the electroforming process has been recorded through impedance spectroscopy. Our device's outstanding stability and performance position it as a promising candidate for high-density data storage and neuromorphic applications.



Assembly and characterization of nanostructures for Molecular Electronic devices

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Electronic devices have become a central part of today's society, with an increasing need for more powerful, more compact, and importantly, more efficient devices. This can be achieved by reducing the size of each individual component of the device. However, the current technology, CMOS (Complementary Metal-Oxide-Semiconductor), is close to reaching its size limit. Molecular Electronics (ME) [1] poses itself as an alternative that would make it possible to continue the current trend of producing more advanced devices. This technology uses a bottom-up approach to produce arrangements of molecules that work as elements of an electronic circuit.

In this work, a compound from the family of curcuminoids [2] has been studied and characterized both at the air-water interface (Langmuir films) [3] and transferred onto solid supports (Langmuir-Blodgett), Figure 1. The main aim of this work was to fabricate highly ordered monolayers of the compound by finely controlling their formation, in order to produce conducting assemblies of molecular materials that could be used in large-area molecular electronic devices.

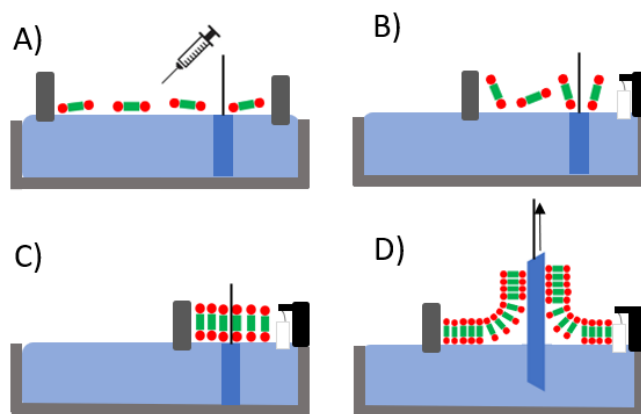


Figure 1. Scheme showing the working procedure of a Langmuir-Blodgett transference. A) Spreading of the solution onto the water subphase. B) Compression process. C) End of the compression process. D) Transference onto the desired substrate.

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ORGANIC POLYMERS BASED ON CURCUMINOIDS LINKERS

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Keywords: *curcumin derivatives, curcuminoids, phthalocyanines, coordination polymers, 2D molecular-based materials*

2D coordination polymers (2D-CPs) containing conjugated frameworks present interesting electronic properties with potential applications in areas such as optoelectronics and sensing, due to the conductivity, low dimensionality, high surface area and ordered arrangement of active sites in their structures^[1]. The use of conjugated and planar ligands, such as curcumin derivatives, the so-called curcuminoids (CCMoids), has been recently described for the construction of bioMOFs (Metal-Organic Frameworks)^[2] and 1D-3D CPs^[3]. This way, CCMoids have been used as organic linkers to bind to metal centers or clusters forming infinite structures^[2,3], due to the presence of three coordinative points in their structure (the β -diketone group and the aromatic ring substituents in lateral positions). Another exceptional family of organic systems are phthalocyanines (Pcs), which are planar macrocyclic structures, formed by four isoindole units connected by four nitrogen atoms, forming an inner ring with alternating carbon and nitrogen atoms. Peripheral modifications in these compounds increase the conjugation of the formed macrocycle and also allow their coordination with metals or other organic compounds, forming 2D coordinated and/or extended covalent structures^[1,4].

In this work we focus on the synthesis and characterization of 2D-CPs based on CCMoids and Pcs through the coordination with 3d-metal centers.

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Metal-Organic Frameworks in Nanomedicine: DNA Grafting as a Methodology for Building Colloidal & Structural Stability in Biorelevant Media.

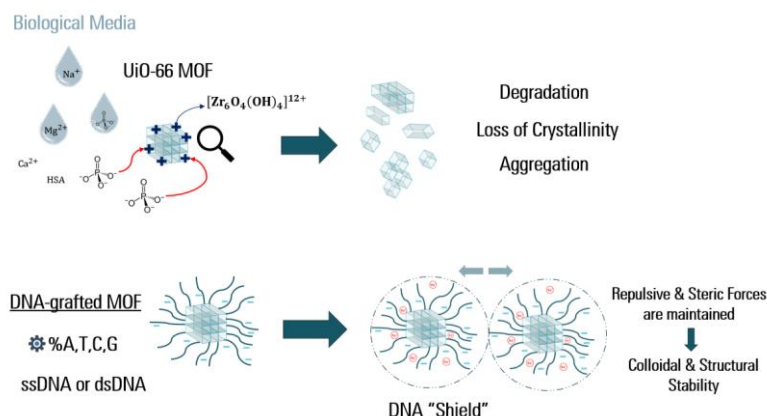
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Metal-organic frameworks (MOFs) constitute outstanding candidates among nanocarriers in medical imaging applications, due to their unique properties, including ultra-high surface area, permanent porosity, multifunctionality and facility in chemical modification. [1] However, MOF nanoparticles tend to decompose and aggregate rapidly in biological fluids, due to the presence of ionic species acting as competitors to the framework structure. [2] Post-synthetic functionalisation of the MOFs' surface with functional ligands, such as DNA oligonucleotides, is a promising option to prohibit unwanted interactions with the surrounding microenvironment and stabilize the nanoparticles. [1] In this present work, UiO66 was selected as an archetypal MOF to investigate the effect of DNA grafting on nanoparticle stability. UiO66 NPs were synthesised via the established solvothermal method, while DNA strands were self-assembled on UiO66 NPs' surface by metal-phosphate coordination bonding in a "salt-aging" process. We investigated the effect of DNA sequence composition (i.e., A₃₀, T₃₀, (CCT)₁₀, (GGT)₁₀) on nanoparticle stability by UV-Vis spectroscopy and Dynamic Light Scattering. Also, duplex-gated NPs were synthesised by hybridising the ssDNA-functionalized NPs with their complementary sequence. The duplex formation on UiO66 surface was identified by fluorescent indicator displacement and UV-melting assays. To evaluate colloidal stability, hydrodynamic size of all materials was monitored by time in a biological buffer. UiO66 NPs aggregated rapidly in the presence of phosphate ions and sedimented from the dispersant, while DNA motifs successfully reduced the aggregation rate according to the following order: (CCT)₁₀ < GC_{Duplex} < AT_{Duplex} < (GGT)₁₀ < T₃₀ < A₃₀ < Bare UiO66 NPs. Currently, we are fully characterising the novel systems by complementary techniques such as TEM, XRD, TGA, as well as internalization assays in cancer cell lines.



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MULTI-COMPONENT MATERIALS BASED ON MWW-TYPE ZEOLITES LAYERS AND MgAlCe HYDROTALCITES

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Designing and preparing new multi-component catalysts with specific properties and reactivity have become decisive in obtaining products with high industrial value using efficient and sustainable synthetic routes. For this purpose, the aim of this study is linking different components in the same structure to benefit from the advantages and physicochemical characteristics of each component and to generate new properties due to the synergy and cooperative effects established between them.

Lamellar materials are crucial to obtaining these multifunctional catalysts [1]. These types of materials are versatile in modifying their morphology and textural properties by altering the order and spatial arrangement of the individual sheets that form them. Likewise, their composition and reactivity can be changed by including organic or inorganic compounds on the surface and interlamellar space [2].

Mg-Al oxides are one of the most widely used solids in catalysis. It is due to their number of basic sites, high thermal resistance, and high specific surface area. In addition, Mg-Al layered double oxides (MgAl-LDH) are usually modified by the incorporation of a third atom. This could be improving the catalytic properties, modifying the acid-base sites [3].

In this study, different multi-component materials have been prepared from MWW-type zeolitic layers. Considering its silicoaluminate nature and using the appropriate synthesis conditions, it was possible to prepare in situ nanometric sub-domains of MgAlCe hydrotalcite-type on the surface and inside the semi-cavities and microporous channels present in the individual MWW layers, favoured by the tetrahedral units of aluminium present in the zeolitic structure.

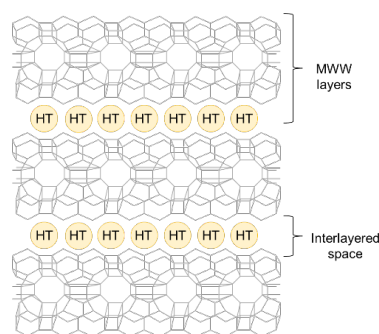


Figure 1. Scheme of the structure of materials.

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Study of the use of hydrogels as separators in microbial fuel cells

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Microbial fuel cells (MFCs) are devices capable of converting chemical energy stored in organic and inorganic molecules into electricity using bioelectrogenic microorganisms. One of the key elements in this technology is the ion exchange membrane, which plays an important role in the system, but its use limits the power output and increases the operating cost of the MFC [1]. Moreover, hydrogels are soft biocompatible materials that can bend due to an ionic gradient caused by an electric field. [2].

In this work, six different configurations of MFCs have been designed and tested to evaluate the viability of hydrogel as a separator element. Three MFCs have two chambers, called double compartment, and three other MFCs with air cathode, called air-breathing. The configurations studied were as follows: a) cation exchange membrane (Sterion[®]) assembled to the electrodes conforming a membrane-electrode assembly (MEA), b) using the same membrane but separate from the electrodes (distance between electrodes) and c) with hydrogel assembled to the electrodes (hydrogel as MEA). In double compartment MFCs, carbon cloths were used as anionic and cationic electrodes. In air-breathing MFCs, carbon cloths were used also as anionic electrodes and the cathode electrodes were made of carbon paper, on which surface was deposited a load of Pt 0.065 mg·cm⁻² to enhance the cathodic reduction reaction. The cells were fabricated by 3D printing.

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Additive manufacturing of YSZ scaffolds for bone tissue engineering by Fused Filament Fabrication (FFF)

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3 mol% yttria-stabilized zirconia (3-YSZ) is a well established material for bone-related applications, but it is studied on an ongoing basis because of two main drawbacks: its bioinert and its low-temperature degradation (LTD). However, no other oxide ceramic fits better the mechanical requirements for bone regeneration, placing 3-YSZ scaffolds as a promising solution for bone repairing. Scarce literature has been found in the additive manufacturing (AM) of 3-YSZ scaffolds, even less in Fused Filament Fabrication (FFF) [1], rated as the AM technique with the highest translational potential and the lowest cost of production [2]. Due to the limited availability of an adequate 3-YSZ filament on the market for FFF, the results presented involve the designing of a new 3-YSZ printable filament as a foundation for future incorporation of 2D materials, since it has been reported that some 2D materials can reduce LTD, enhance cell differentiation towards bone repairing and provide with antibacterial activity [3].

The challenges of designing a flexible filament with high ceramic load and of selecting the processing parameters will be discussed. Additionally, scaffolds with different architectures will be presented, with the goal of tailoring their mechanical properties in order to achieve a biomechanical-biofunctional balance. Compression tests were conducted to determine the mechanical properties for each architecture. As a result, the potential of these 3-YSZ scaffolds will be discussed through the lens of personalized medicine.

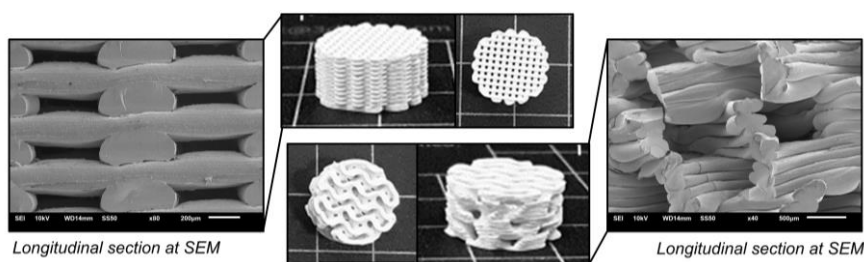


Figure 1. Examples of some of the 3- YSZ scaffolds with different architectures fabricated in this work through FFF.

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Real-time control of a hydrogel-based soft actuator with proprioception and self-healing capabilities

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Soft robotics has experienced a great growth in recent years, mainly due to the development of new smart soft materials [1]. Soft robots are desirable in many applications [2], from industrial tasks such as food manipulation to medical applications such as surgery and rehabilitation. One of the challenges to be solved in the field of soft robotics is the automatic control of soft actuators, mainly due to the infinite degrees of freedom and non-linearities of soft materials. In our work, a smart hydrogel is used to build a soft pneumatic bending actuator (Figure 1B), taking advantage of two properties of this material: its ionic conductivity, which confers proprioception, allowing it to measure its own curvature [3]; and its self-healing ability, which is a very desirable feature in the case of pneumatic actuators [4]. Our approach uses the first of these material properties as the feedback signal in a real-time closed-loop scheme (implemented in a CompactRIO from *National Instruments*®) to automatically control the actuator's curvature. Figure 1A shows the implemented control scheme, where a PID controller has been designed using an empirical model of the actuator's dynamics. This actuator and its control are currently used in the development of a soft glove for hand rehabilitation.

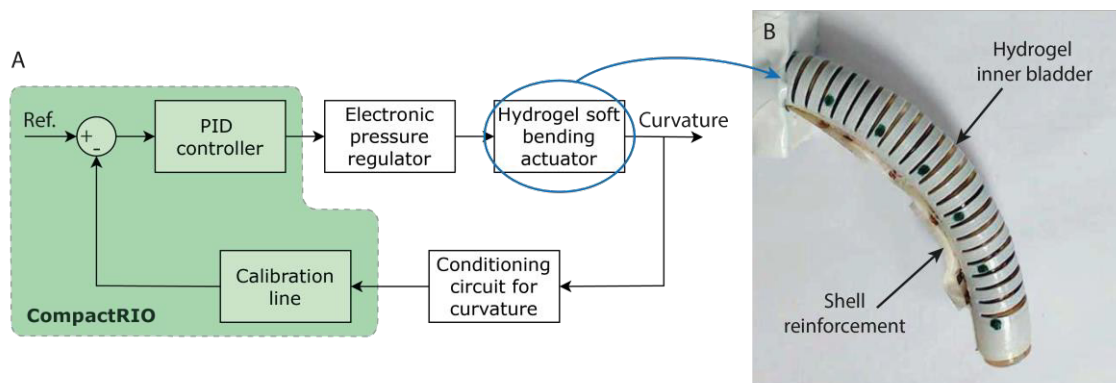


Figure 1. Closed-loop scheme control (A) for the curvature of our hydrogel soft bending actuator (B).

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Self-healing hydrogels for soft robotics.

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Materials normally used in soft robotics, such as polymers, elastomers, or hydrogels, can be easily damaged, for that reason, their lifetime, in most cases, is too short. This problem has led, in the last years, to the use of self-healing materials. This propriety can appear through different mechanisms, the most important are: i) encapsulation of self-healing agents, ii) metal-ligand coordination bonds, iii) reversible covalent bonds such as Diels-Alder reactions, iv) non-covalent bonds such as hydrogen bonds, ionic interactions, or hydrophobic interactions [1]. The objective of this work is to find hydrogels with autonomous self-healing and with good mechanical proprieties for soft robotic applications. The starting point is the SHAP hydrogel (Self-Healing AETA-based Polymer), this hydrogel was synthesized by photopolymerization of

(2-(Acryloyloxy)ethyl)trimethylammonium chloride (AETA) using N,N'-Methylenebisacrylamide (MBA) as the chemical crosslinker in water. The self-healing capacity of this hydrogel is given by the hydrogen bonds that form the water molecules inside the structure. [2] To improve this capacity, monomers with diverse charges were added to the SHAP chemical structure producing an additional electrostatic interaction between the different monomers, obtaining a self-healing of 90% (Fig. 1).

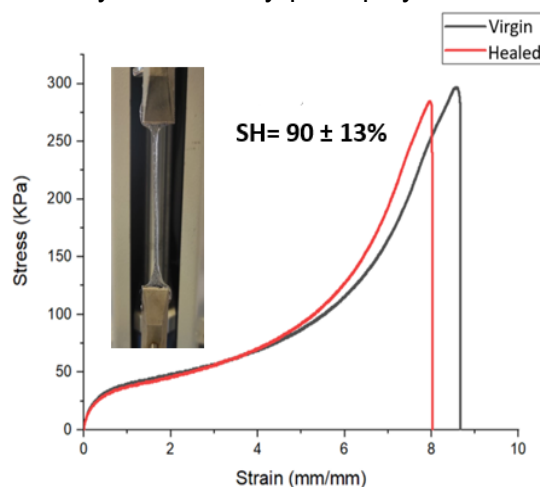


Figure 1. Strain-stress curve of the AETA-MAAc hydrogel.

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A Novel and Bioinspired Bilayer Hydrogel System for Engineering Assisted Reproductive Technologies

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In the realm of assisted reproductive technologies, oocyte *in vitro* maturation has surfaced as a promising alternative to address the limitations associated with conventional ovarian stimulation treatments. Nevertheless, existing *in vitro* maturation protocols suffer from a lack of standardization and often yield oocytes of subpar quality compared to their *in vivo* counterparts. In response to this challenge, innovative biomaterials, such as hydrogels, present distinct advantages in cell culture. They offer a three-dimensional cellular environment and facilitate easy tuning and assessment of mechanical properties, including hydrogel stiffness. This study introduces an inventive and reusable bilayer hydrogel system designed to accurately emulate the mechanical characteristics of the microenvironment surrounding oocyte maturation. The system consists of an outer layer crafted from either a 3D-printed synthetic polymer (2-vinyl-4,6-diamino-1,3,5-triazine) or a natural polymer (chitosan), paired with an inner layer composed of alginate. By faithfully replicating the mechanical properties of native tissue within a three-dimensional culture setting, this system substantially enhances oocyte quality and developmental potential, ultimately leading to successful embryo development. In summary, this groundbreaking system exhibits significant promise for future medical research and applications in cell culture. It represents a noteworthy advancement in assisted reproductive technologies, holding the potential to revolutionize this field.

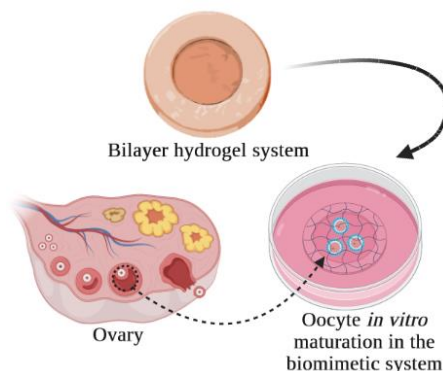


Figure 1. Development and application of a biomimetic system to enhance advanced assisted reproductive technologies, with a specific emphasis on oocyte *in vitro* maturation. This innovative and reusable design accurately mimics the mechanical properties of native tissue in a 3D-bioinspired cell culture environment, leading to successful embryo development.

Electroactive membranes for the stimulation of mesenchymal stem cells *in vitro*

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Therapies involving the use of mesenchymal stem cells (MSCs) hold great potential for bone regeneration purposes. However, challenges related to their expansion and differentiation *in vitro* hinder the translation from the bench to the clinic. An interesting approach which may improve some of these issues involves MSCs *in vitro* predifferentiation or commitment towards the osteogenic lineage. Some studies have addressed this matter by employing polymeric piezoelectric materials combined with magnetostrictive nanoparticles (NPs) to magnetoelectrically stimulate MSCs and thus mimic the natural piezoelectricity of bone tissue. However, given the small size of the NPs relative to the polymer matrix, it is proposed that NPs magnetostriction might not be the responsible for triggering piezoelectricity, but the magnetic movement of the NPs within the polymer matrix. To test this hypothesis, we developed membranes of piezoelectric poly (vinylidene fluoride) with magnetostrictive cobalt ferrite (PVDF-CFO) or magnetic iron (III) magnetite (PVDF-FE) nanoparticles.

Membranes were synthesized by non-solvent-induced phase separation (NIPS) and coated with 3-aminopropyltriethoxysilane (APTES) and tetraethoxysilane (TEOS) to decrease their hydrophobicity and provide them with functional groups for further collagen type I grafting. The microstructure of the membranes was studied by field emission scanning electron microscopy (FESEM) while the content of the electroactive crystal phases was assessed by Fourier-transformed infrared spectroscopy (FTIR). Cell culture of human MSCs on PVDF, PVDF-CFO and PVDF-FE membranes were performed to study adhesion after 24 hours by immunofluorescence, proliferation by total DNA quantification and osteogenic differentiation by colorimetric detection of alkaline phosphatase activity. Results suggested that after 24 hours of culture, the adhesion of cells on the membranes was lower than in the glass controls, displaying a more elongated shape. In terms of proliferation, cells expanded more rapidly on PVDF-FE membranes, but after 4 days the proliferation evened among substrates. Regarding osteogenic differentiation, alkaline phosphatase activity after 14 days was higher in the non-stimulated glass control condition, and no differences were found between PVDF-CFO and PVDF-FE membranes.

Sustainable 3D-printed supports modified with metal-organic frameworks for remediation of organic pollutants. A preliminary study

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The growing increase in industrial pollution has led to the presence of several organic pollutants in the environment, becoming a significant global threat. In fact, some of these compounds, are characterized by their high persistence and ability to bioaccumulate in the environment, pose a potential risk to human health and cause toxicity in aquatic life [1]. Then, there is a need to develop efficient methodologies for detecting and quantifying organic pollutants as well as their removal from environmental waters. In the last decade, the development of porous materials with high efficiency for environmental cleanup and remediation has attracted significant attention. Among them, metal-organic frameworks (MOFs), with tailorable porous architectures and tunable chemistry, have been demonstrated to be efficient adsorbents to decontaminate pollutants from the environment [2]. Nevertheless, despite their remarkable properties, most of them exhibit rigidity and are challenging to mold due to their powdered nature, which imposes restrictions on their practical applications. On the other hand, 3D-printing technology has attracted widespread attention in several fields due to its attractive advantages such as easy-handling, manufacturing complex shapes and customized designs at low cost [3].

In this communication, MOFs incorporated in sustainable 3D-printed structures are developed in order to retain organic pollutants (antibiotics and herbicides as target compounds) in water bodies. To this end, the fabrication of 3D-printed devices using fused deposition modelling (FDM) technique with sustainable filaments was carried out. Then, the post-printing solvothermal growth of MOFs onto the external surfaces of 3D-printed structures was optimized. Afterwards, the extraction performance of the resulting MOF@3D printed devices of organic pollutants was investigated.

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Transparent nanocellular high-performance polymers: production, structure, and properties.

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The use of polymers in both industry and science has revolutionised many aspects of modern life. Because of their great advantages such as lightness, strength, flexibility, and their ability to be moulded into a wide variety of shapes, among others, they are widely used in everyday life. However, the use of commodity plastics in demanding sectors, is limited by their low working temperature.

High-performance polymers (HPPs) have emerged to overcome this problem. HPPs are macromolecular materials designed with exceptional structures and properties, which can operate at temperatures up to 200 °C and outperform conventional polymers in terms of strength, stiffness, and other key characteristics. These polymers find applications in fields such as aerospace, automotive and high-performance electronic devices.

The inclusion of nanometric pores below 50 nm into commodity polymers allows to provide these materials with new or improved properties, such as weight reduction, thermal insulation, mechanical properties improvement while keeping the transparent character of the solid. However, this strategy has been barely used in HPPs.

This work aims to incorporate cells below 50 nm into HPPs, in particular, polyetherimide (PEI), and to establish a first relationship between the production parameters, the obtained cellular structure and its properties, in particular its transparency.

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Nanoporous polymers based on nanostructured polystyrene blends: Fabrication and application to vacuum insulation panels

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More than 40 % of global energy is consumed in the residential sector. Heating and cooling buildings is one of the main energy demanding activities in our planet and it is only expected to grow, thus increasing the associated emissions. The best way to reduce the energy use is to develop new insulators more efficient than the ones we have nowadays. Vacuum insulation panels (VIPs) are one of the most promising high performance thermal insulators which can be a solution for highly reducing energy consumption in buildings [1]. These panels are produced applying vacuum to an encapsulated micro- or nano- porous material (core of the panel). By removing the air from the porous structure, thermal conductivity can be reduced up to ten times. In this work we explore the possibility of producing a nanoporous polymer with specific characteristics which can serve as a new type of core material for this kind of panel.

It has been proved that nanoporous or nanocellular polymers can be produced using nanostructured polymer blends with CO₂-philic regions based on block-copolymers [2]. In this study, a tri-block copolymer polystyrene-poly(butyl acrylate)-polystyrene (SAS) was blended by extrusion with polystyrene (PS) to produce nanostructured PS/SAS blends. These blends were foamed by a two-step gas dissolution foaming process at different saturation pressures, with CO₂ as the foaming agent.

It has been proved that tuning the concentration of SAS, along with the pressure and temperature conditions in the gas dissolution foaming process, we can obtain cellular materials with pore sizes in the nanoscale with a high level of interconnectivity among the pores. These structures seem to be quite promising to the intended application of producing VIPs and a super-insulation performance is expected.

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Development and characterization of new biofoams using microwave radiation

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Natural rubber latex foams (NRLFs) are flexible foams that are used in comfort products such as mattresses and pillows [1]. The chemistry participating in the synthesis of NRLFs needs the use of vulcanizing agents, such as sulfur, to cross-link the polymeric matrix, and thus, promote the stability of the solid phase of the foams [2]. Therefore, in spite of the bioderived character of natural latex, the final foam is not easily degradable. Nowadays, the industrial and academic interest on looking for more sustainable alternatives encourages the development of new synthesis routes for these foams. In this work, we develop fully biobased NRLFs using egg white powder and corn starch as stabilizer. Egg white protein is usually used in edible foams as foaming agent and the low cost, abundance and biodegradability of the starch make them perfect additives to develop biofoams [3]. The foams are produced by a two-stage foaming process based on a previous aeration of the liquid blend followed by dehydration via microwave radiation, which is able to promote rapid heating and water evaporation saving more energy than the conventional heating methods [4].

The density and the main structural parameters of both liquid and solid foams are studied to understand the effect of the additives in the stabilization mechanisms involved in the synthesis of these foams.

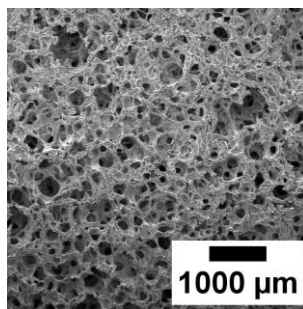


Figure 1. SEM micrograph of a NRLF developed through this lab-route.

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PMMA/acetone gels for the production of completely interconnected PMMA thick membranes: The role of different polymerization methods in structure

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Microcellular and nanocellular polymers are biphasic materials with micro or nanometric pores dispersed in the solid polymer. These materials offer unique combination of properties such as weigh reduction, good thermal insulation, and high surface-to-volume ratio. For this reason, they find applications in construction, packaging, and automotive sectors.

When the gas phase is interconnected, these cellular polymers expand their range of applications. On the one hand, they can be used for filtering or catalytic processes, combine the small pore size with an interconnected structure would allow for filtering out harmful particles. On the other hand, they could be used as the core materials for Vacuum Insulation Panels (VIPs), where material with excellent thermal insulation and an interconnected is required to provide the vacuum, so achieving energy efficiency and emission reduction as an eco-friendly solution.

The production of open-pore micro and nanocellular materials have been mainly limited to thin membranes. However, the production of thick interconnected micro- and nanocellular polymers faces several obstacles or drawbacks, such as a lengthy and energy-intensive production process, the need to use a second phase to produce lower open-cell structures, or post-processing of the materials.

To address these challenges, this study proposes the fabrication of open-cell microcellular materials from polymethylmethacrylate (PMMA)/acetone gels through the gas dissolution foaming process, an environmentally friendly process [2]. This results in a 90% reduction in cycle time and energy consumption [3] and thicker cellular samples in which high opened-cell structures are naturally exposed. Different polymerization methods are evaluated allowing the control on the molecular weight leading to tailor the final cellular structure.

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Enantioselective separation through chiral nanoporous polymers

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Since Thalidomide tragedy in 1960s, synthesis of enantiopure compounds have become essential, in order to prevent undesirable consequences. Thereafter, pharmaceutical and chemical industries have faced problems to overcome the inconveniences of different separation techniques, complex and expensive, in order to separate and purify enantiomeric mixtures. Regarding this topic, an alternative way of separating racemic mixtures has been developed using columnar liquid crystals (CLCs) as a tool to obtain polymeric materials, allowing the distinction between enantiomers.

In this project, CLCs are prepared from discotic supramolecular complexes, based on a central template and three acids in their periphery, which contain photopolymerizable units [1], as coumarins [2] or double bonds [3], and chiral centres, which boost supramolecular chirality in the final material. After obtention of columnar stacking, the mesophase is photopolymerized, giving rise a polymeric material, which undergoes an acid treatment, getting so the chiral nanoporous polymer. With these materials, adsorption experiments of different enantiomers are carried out by UV-Vis over time.

This way, we have developed a new strategy for chiral separation, which can be tuned depending on the characteristics and properties of the racemic mixtures to be separated.

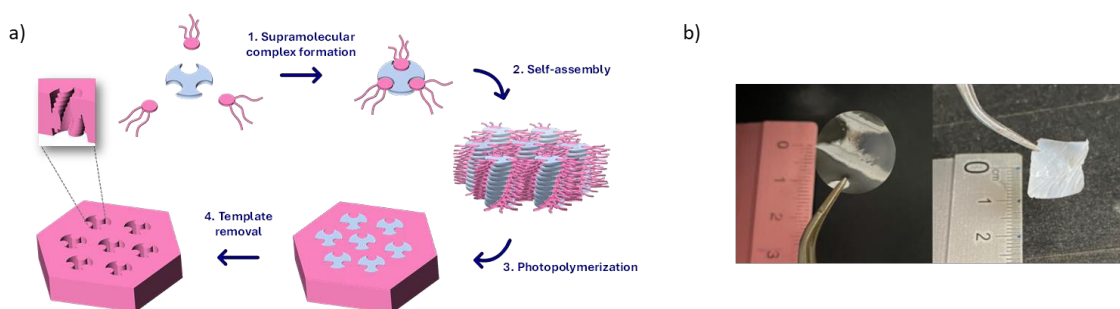


Figure 1: a) Schematic representation of chiral nanoporous materials obtention and b) chiral nanoporous materials.

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Di-block *bent-core* amphiphiles: An approach to functional supramolecular materials.

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V-shaped or *bent-core* molecules [1] have emerged as highly innovative structures for the development of new functional supramolecular materials. Their compact and polar packing allows them to induce unique liquid crystal phases and properties including supramolecular chirality, ferroelectricity, and nonlinear optical activity among others, from achiral molecules. In recent years, amphiphilic *bent-core* compounds have proven to be useful building blocks for a wide variety of supramolecular (thermotropic and lyotropic liquid crystals, nanoaggregates, and gels) and functional materials (chirality, ion conduction, etc...) [2] of technological interest.

Based on recent results of CLIP research group, the design, synthesis, and characterization (NMR, FTIR, etc.) of new tetraethylene glycol-decorated *bent-core* amphiphiles (bearing three different linkers X: -COO-, —, -N=N-) and its lithium and sodium complexes were carried out. In order to assess their potential as functional supramolecular materials (e.g., *bent-core* liquid crystal-based electrolytes and ferroelectric materials) (Figure 1), their characterization (POM, DSC, TGA, XRD, SEM, TEM), as well as their structure-property study were performed.

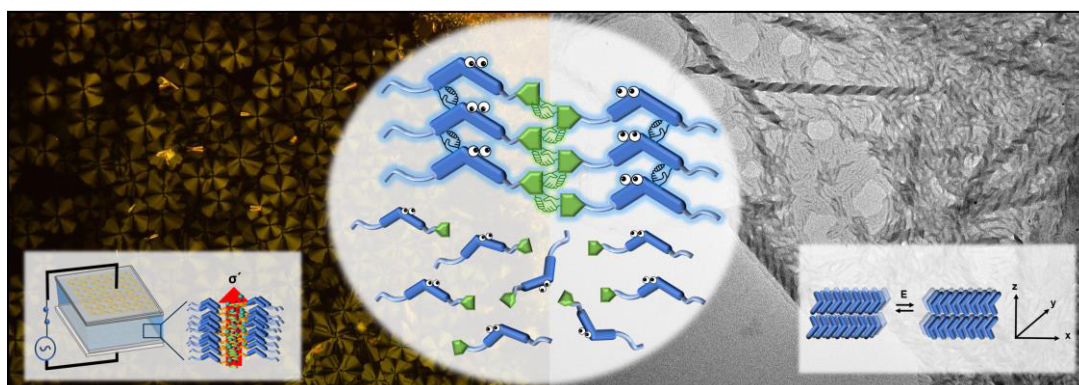


Figure 1. Supramolecular functional materials based on *bent-core* amphiphile molecules.

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