

1st Iberian Symposium on Functional Organic Polymers

May 11th-12th, 2023, Aveiro, Portugal



Book of Abstracts

WELCOME MESSAGE

Dear Colleagues and Friends,

It is a great pleasure to invite you to attend the **1st Iberian Symposium on Functional Organic Polymers** (ISFOP2023) which will be held in the **11th and 12th of May 2023 at the University of Aveiro**. We also invite you to enjoy the Art Nouveau architecture and gorgeous canal boats in the beautiful city of Aveiro.

The Symposium will focus on the design and synthesis of **a wide range of functional organic polymers** including electroactive, chiral, porous (POPs, COFs) and bio-inspired polymeric materials. The symposium will also explore the fascinating properties of organic polymers and their processing towards **energy, electronics, biomedical or environmental applications**. Some of the topics covered by the symposium will be: **organic batteries, organic thermoelectrics, tissue engineering, chiral polymers and Covalent Organic Frameworks (COFs)**. This symposium will also serve to stimulate collaboration between research groups from Spain and Portugal.

We already have an exciting lineup of invited talks:

- **Thomas Bein** (LMU)
- **Daniele Mantione**(Polymat)
- **Rebeca Marcilla** (IMDEA Energy)
- **Josep Puigmartí-Luis** (UB)
- **Ester Vázquez** (UCLM/IRICA)
- **João Mano** (U. Aveiro/CICECO)
- **Mariano Campoy-Quiles** (ICMAB-CSIC)
- **Laura Salonen** (U. Vigo/CINBIO)
- **Carmen Freire** (U. Aveiro/CICECO)
- **Félix Zamora** (UAM)
- **Ana Rita C. Duarte** (UNL)
- **Félix Freire** (USC-CIQUS)
- **Nagore Ortiz-Vitoriano** (CIC EnergiGUNE)
- **Aurelio Mateo-Alonso** (Polymat)

The programme will further include **oral and poster presentations**, in a good balance while promoting mostly the interaction between scientists.

We very much look forward to welcoming you in Aveiro.

COMMITTEES

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GENERAL INFORMATION

Registration

The registration fee includes:

- Admission to all the Meeting's scientific sessions
- Conference materials
- Lunches (both days)
- Coffee Break(s)

Poster and oral presentations (technical information)

Oral Presentations

Participants giving an oral presentation are strongly encouraged to send the presentation at least one day before the beginning of the conference so it can be uploaded into the available computer in the room. Each participant will have the chance to test his/her presentation before the beginning of each session.

An Apple Macintosh with Keynote and the latest version of Microsoft Office will be available so all presentation formats can easily be used. Presentations in PDF can also be used. A laser pointer will also be available to each presenter.

Please note:

Plenary Lectures will have a total duration of 30 minutes (25 + 5 for discussion) while normal presentations are of 15 minutes (12 + 3 for discussion).

Posters

We would like to encourage the participants with an accepted communication as a poster to mount them during the registration period. Materials to fix the posters will be provided at the registration desk.

Please note:

Posters should be printed with a maximum dimension of 90 x 110 cm (width x height) and preferably in paper.

Official language

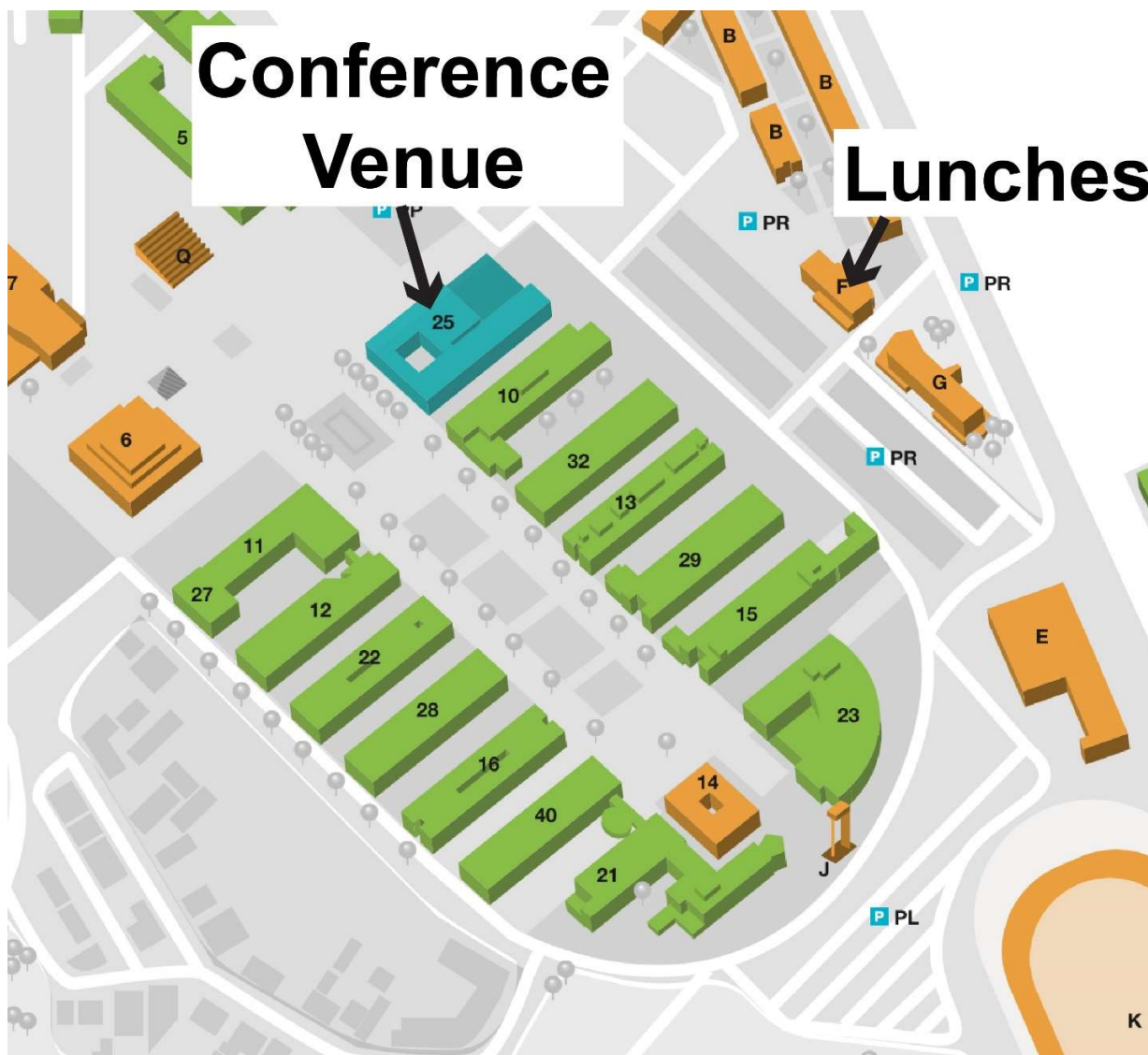
The official language of the Workshop is English. No simultaneous translation will be provided.

Badges and Security

It is essential that you wear your personal badge at all times while in the Workshop venue and during all the Events, as it is the official entrance pass to scientific sessions and other activities.

VENUE MAP

The 1st Iberian Symposium on Functional Organic Polymers will be held at the University of Aveiro, at **Auditório Renato Araújo at the Rectory building (building number 25 in the map)**



Reach the university campus from Aveiro train station

Aveiro railway station is located at about 15 minutes walking distance or 5 minutes taxi ride from the University Campus or 10 minutes bus (line 4) which departs from outside the railway station.

Reach the university campus by car

From the north using the A1 motorway or from the east using the A25: Take the A1 motorway headed to Lisbon. Exit the A1 in the direction of Aveiro and take the A25. There are two exits to the city from the A25, first "Aveiro-Norte" and some kilometers further on, the "Aveiro" exit. This second exit is the best for reaching the University of Aveiro campus.

From the south using the A1 motorway: Take the A1 motorway in the direction of Porto, exit the motorway at "Aveiro-Sul/Águeda" (exit 15) and follow the EN235 road directly to the University Campus. From the south, using the A8 and A17 motorways: Exit the motorway at "Aveiro-Sul" and follow the EN235 road directly to the University campus.

SCIENTIFIC PROGRAMM

Time	Thursday (11 th of May 2023)
8h30-9h00	Registration
9h00-9h15	Opening Session
	Organic polymers for energy S1 (Chair: M. Souto)
9h15-9h45	R. Marcilla: "Redox-Active Polymers for Sustainable Batteries"
9h45-10h15	D. Mantione: "Innovative polymers for electronic and ionic conductive materials"
10h15-10h45	N. Ortiz-Vitoriano: "Highly Performing Gel Biopolymer Electrolytes Based on Naturally Occurring Agarose for Primary Zinc-air Batteries"
10h45-11h15	Coffee break + poster session
	Organic polymers for energy S2 (Chair: F.A. Paz)
11h15-11h45	M. Campoy-Quiles: "Photovoltaics <i>à la carte</i> enabled by high throughput screening of organic semiconductors"
11h45-12h00	A. Mavrandonakis: "Insights into the Redox Properties of Organic Molecules by Computational Modelling"
12h00-12h15	P. Navalpotro: "Towards Totally Aqueous Membrane-Free Redox Flow Batteries with Organic Active Species"
12h15-12h30	A.C.Baptista: "Cellulose-based energy storage devices"
12h30-12h45	M. Culebras: "Layered nanocomposites based on conducting polymer nanoparticles for thermoelectric applications"
12h45-13h00	P. Barbosa: "Algae biomaterials: future building blocks for energy storage and conversion technologies"
13h00-15h00	Lunch + poster session
	Organic polymers for biomedical applications S1 (Chair: J. Borges)
15h00-15h30	J. F. Mano: "Macromolecular design of natural-origin functional hydrogels for biomedical applications"
15h30-16h00	E. Vázquez: "Smart soft materials in drug release and soft robotics"
16h00-16h30	A.R.C. Duarte: "Applications of natural deep eutectic systems in polymer engineering"
16h30-17h00	Coffee break + poster session
	Organic polymers for biomedical applications S2 (Chair: F. Figueira)
17h00-17h30	C.S.R. Freire: "Nanocellulose and protein amyloid fibrils: Reshaping old biopolymers"
17h30-17h45	J.M.M. Rodrigues: "Leveraging Chemical Modifications of Laminarin to Develop Bioinspired Tunable Biomaterials for Biomedical Applications"
17h45-18h00	I. San-Millán: "Hydrogels based on chitosan for tissue engineering applications"
18h00-18h15	E. Gabirondo: "Naturally occurring catalyst for high temperature polymerizations"

SCIENTIFIC PROGRAMM

Time	Friday (12 th of May 2023)
	Porous organic and chiral polymers S1 (Chair: M. Souto)
9h00-9h30	T. Bein: "Controlling Optoelectronic Processes in Covalent Organic Frameworks"
9h30-10h00	F. Zamora: "Processability studies on imine-based Covalent Organic Frameworks"
10h30-11h00	J. Puigmartí-Luis: "Functional materials by design via microfluidic technologies"
10h30-11h00	Coffee break + poster session
	Porous organic and chiral polymers S2 (Chair: M. Melle-Franco)
11h00-11h30	A. Mateo-Alonso: "Merging Distorted Nanographenes with Framework Materials"
11h30-12h00	L. Salonen: "Strategies for Tailoring Covalent Organic Frameworks towards Catalysis and Capture of Water Pollutants"
12h00-12h30	F. Freire: "Stimuli-Responsive Helical Polymers"
12h30-12h45	M. Sardo: "Assessing the dynamics of adsorbed CO ₂ species in Covalent Organic Frameworks via solid-state NMR methods"
12h45-13h00	M. Fumanal: "Optimizing the thermodynamics and kinetics of the triplet-pair dissociation in donor-acceptor copolymers for intramolecular singlet fission"
13h00-13h15	J.L. Segura: "Covalent Organic Frameworks as Platforms for the Construction of Electrocatalytic Materials"
13h15-13h30	K. Strutyński: "Prediction of COF structure from ab-initio methods"
13h30	Closing Ceremony + Lunch

INSTITUTIONAL SUPPORT



SPONSORS



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Plenary Sessions



Redox-active Polymers for Sustainable Batteries

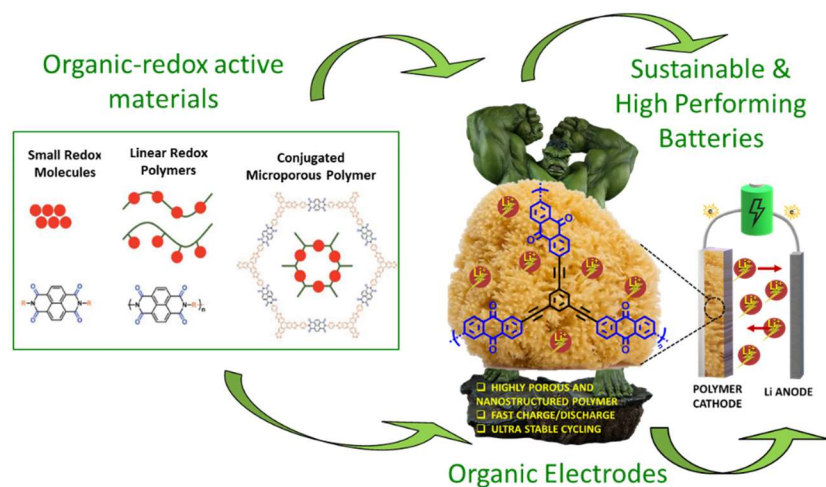
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The expected growth over the next few years in the battery sector is huge, with approximately 7 million tons of new batteries manufactured per year. This growth is mainly triggered by the deployment of the electric vehicle and by the energy storage coupled to wind and photovoltaic generation. However, the massive development of the sector could become an environmental problem since most commercial batteries are based on inorganic materials such as lithium, nickel and cobalt in lithium-ion batteries or vanadium in flow batteries. These materials are scarce, their production in some cases is not sustainable and some are even toxic. In this context, the replacement of these materials by organic compounds based on elements as abundant as C-H-O-N has become a very promising alternative [1].

In this talk, I will focus on exposing the enormous structural and synthetic possibilities of redox-type polymers and their application in different types of batteries. I will present an overview of the efforts of my group to develop more sustainable batteries using redox-active polymer electrodes. First, I will introduce the different polymer structures (linear, porous, nanoparticles) containing redox active functionalities (quinones, phenazines, etc) that we have developed in the last years. Among the huge variety of redox-active polymers, I will present our recent research on Conjugated Microporous Polymers that combine extended π -conjugation with inherent 3D microporosity, large specific surface area and high stability. Then, I will focus on the electrochemical properties of different polymer chemistries & structures in different electrolytes and their potential application in several battery technologies including Li-ion [2,3], multivalent [4], aqueous [5], all-polymer [6], etc).



Acknowledgements

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References

- [1] Kim, J., Kim, Y., Yoo, J. et al. Organic batteries for a greener rechargeable world. *Nat Rev Mater* (2022).
- [2] R. Marcilla et al., *Advanced Functional Materials*, (2020), **30**, 6, 1908074
- [3] R. Marcilla et al., *ACS Energy Letters*. (2020), **5**, 2945–2953.
- [4] N. Patil et al., *Adv.Ener.Mat*, (2021), 11 (26), 2100939,.
- [5] R. Marcilla et al., *Materials Today Energy*, (2022), **27**, 101014.
- [6] N. Patil et al., *J.Mater.Chem.A*, (2021), 9, 505 - 514.



Innovative polymers for electronic and ionic conductive materials

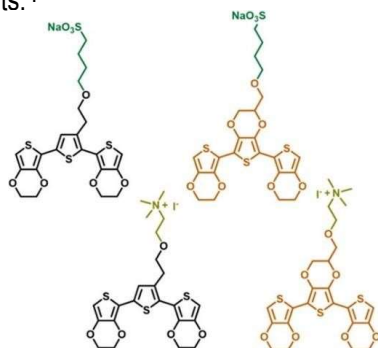
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Conductive polymers are the base materials for a large palette of devices and present a massive part of the nowadays literature. Among them, we can differentiate two types of conductivity: electronic and ionic.

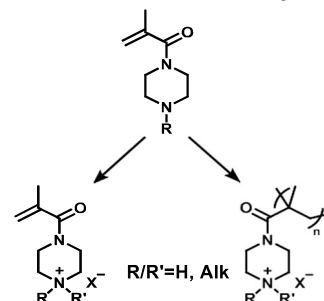
Electronic conductivity

The most known is PEDOT poly(3,4-ethylenedioxythiophene), with its formulation PEDOT:PSS, coupled with polystyrene sulfonate anion. This formulation, even if broadly studied in literature, misses structural variation and the possibility of decorating the closed-box of the polymerizable thiophene molecule. Moreover, the difficult variation of the chemical structure, usually, brings a highness of the oxidation potential, which is an important drawback. Thiophene derivative trimers are emerging in literature as extremely useful building blocks in order to compensate these two issues. The easy functionalization, mainly due to the increase of the possible functionalizable carbon atoms and to the possibility to use a combination of thiophene and EDOT, combine with a lowering of the oxidation potentials. These characteristics match them with a large variety of possible applications, like: self-doped conductive polymers, highly conductive materials, large variety of possible geometry like block-, alt- or graft- copolymers combinations, and, among them, the bio- and plant-systems represent one of the best outputs.¹



Ionic Conductivity

The field of ionic conductivity can touch different disciplines and aims, from the proton membrane to the gas separations, polyelectrolytes and solid polymer electrolytes for batteries or materials for bioelectronics. Usually, these materials are aimed to be soft solids with weak intermolecular interactions, that bear ionic coupled free to move. On the other hand, narrow ranges of temperature stability and highly disordered morphology, make the fine tune of the design of these structures tricky. Among the materials studied throughout the years, ionic liquids (ILs) have established themselves as one of the most versatile class of materials, and, poly(ionic liquids) one of the best approaches to their preparation. Piperazine structures represent a useful tool to the preparation of monomers with high possibilities of customization; in which the introduction of a polymerizable group will lead to the possibility to have self-standing materials easy tunable and easy synthesizable. The variation of the bearing groups over the nitrogen atom will include the possibility to have a proton, paving the way for proton exchange membranes, or alkyl groups, making the anion the main character of the migration.²



Acknowledgements

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References

- 1 Parker, D., et al.; Mater. Horizons 2021, 8 (12), 3295–3305. <https://doi.org/10.1039/D1MH01423D>
- 2 Gallastegui, A., et Al.; submitted



Highly Performing Gel Biopolymer Electrolytes Based on Naturally Occurring Agarose for Primary and Secondary Zinc-air Batteries

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Portable electronics in the very near future will require batteries with characteristics such as high energy density, flexibility, reliability, rechargeability, and safety at very low cost. In the development of systems with such requirements, rechargeable metal-air batteries arise as a promising alternative due to the use of non-flammable electrolytes and inexhaustible oxygen from air, providing a high theoretical energy density. In particular, zinc-air batteries (ZABs) have attracted the utmost attention due to the cheap materials involved, environmental friendliness, and safe operation. ZABs are based on abundant elements with excellent stability, high theoretical energy density (1350 Wh kg⁻¹) and theoretical cell voltage of 1.66 V. However, for their practical use, challenges such as low Zn utilization and lifetime for primary ZABs, short cycle life and low power density for secondary ZABs must be overcome. Among them, particularly the electrolyte system plays an essential role in the performance of primary as well as electrochemically rechargeable ZABs, because it is the medium for ionic migration.

In this talk, the development of gel biopolymer electrolytes based on the naturally occurring agarose polysaccharide, together with physicochemical characterizations and performance validation in zinc-air batteries (ZAB) will be discussed. The aim is to replace liquid electrolytes (adsorbed on a separator), and gels based on synthetic polymers with naturally derived materials for more sustainable energy storage solutions. Experimental data for main physical, chemical, and electrochemical properties, and lab-scale full cells under several testing conditions, are provided to demonstrate merits of the developed gels, and cell design details to be improved. Secondary ZABs using this gel give a range of performances, which are highly depending on cycling conditions/areal capacity, and cell design. However, interesting results are achieved at different conditions, with round-trip efficiency of 70%, high depth of discharge per cycle ≈7%, and 10-20 Wh kg_{cell}⁻¹ energy density per cycle.



Photovoltaics *à la carte* enabled by high throughput screening of organic semiconductors

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The change in energy paradigm towards sustainable sources implies the large scale deployment of highly efficient solar technologies. Novel technologies are needed for integration into buildings (lightweight, high incidence angle tolerance and neutral color), windows (semitransparency), greenhouses (complementary transmission with plant needs), infrastructure (robustness, integrability), wearables (lightweight, flexibility), indoor photovoltaics (high tolerance to low irradiances) as well as beyond photovoltaic farms (ever increasing efficiency). Polymer based photovoltaics are well suited for this huge challenge, as can be produced with the largest color pallet and transparency degree imaginable, as well as tunable flexibility, lightweight, etc. Indeed, there is an infinite number of molecules that can be synthesized to match our needs. The bottleneck, then, becomes how to identify and screen the best potential candidates and device structures for each application.

In this talk we will first describe a novel methodology for the fast evaluation of organic semiconductor systems for photovoltaics. The new approach is based on the fabrication of samples with gradients in the relevant parameters of interest that represent a large fraction of the corresponding parameter space. In particular, we fabricate gradients in thickness, microstructure, composition and apply hyperspectral imaging to correlate material and device properties. The method is up to 100 faster than conventional optimization protocols, uses less than 50 mg of each active layer material and generates hundreds to millions of data points per system [1,2].

We then will give three examples of the use of this machinery towards *à la carte* photovoltaics. The first one is in the search of new material combinations for in-door applications. As the spectrum of the indoor sources is different from the sun, material systems with wider band gap are required. We screen a large number of materials obtaining high V_{oc} ($>1.1V$) as well as high efficiencies (20% for indoor illumination). The second example is motivated by the need for photovoltaic technologies with high efficiency. We have described the large scale screening of materials for multijunction solar cells, in particular, in the spectral splitting configuration known as Rainbow solar cells. The high throughput technology enables the fast identification of matching systems which exhibit greater efficiency than the best single junction made with the given materials.

Last, we demonstrate that the self-consistent, generated big data is a perfect match to machine learning algorithms. As an example, the combinatorial evaluation of more than 15 donor/acceptor systems -which generates thousands of data points in the thickness/composition parameter space-, is coupled to machine learning algorithms. Trained algorithms can predict the composition for maximum efficiency, and even reproduce multi-maximum efficiency vs composition diagrams, from basic material inputs, such as energy levels and optical and electrical traits [1].

References

- [1] X. Rodríguez Martínez et al, *Ener. Environ. Sci.*, 14, 986-994 (2021)
- [2] A. Harillo-Baños et al, *Adv. Ener. Mater.*, 10, 1, 1902417 (2020)



Macromolecular design of natural-origin functional hydrogels for biomedical applications

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Different types of materials have been proposed in various biomedical areas, including tissue engineering and drug delivery systems. From the different sources of biomaterials, natural-based polymers have been proposed to produce matrices able to interact favourably with cells. Due to their hydrophilic nature and richness in chemically active groups, such polymers can be used to produce a variety of structures fabricated using aqueous-based or other environmental-favourable procedures. Examples are shown on the precise chemical modification of polysaccharides, human-derived proteins and the surface of cells and processing of devices into different sizes and shapes with structural and functional characteristics suitable to be used in tissue engineering and regenerative medicine applications. The macromolecular design of the systems may be used to produce special hydrogels with improved mechanical properties and with special functionalities, including capability to be used as bioinks for 3D bioprinting, or self-feeding ability of cells through the enzymatic degradation of glucose-based polysaccharides. Distinct strategies involving bioinspired approaches and nano/micro-technologies will be shown to prepare hybrid soft systems containing cells, in the form of microparticles, microgels or liquified capsules, that could give rise to biomedical devices using bottom-up strategies.



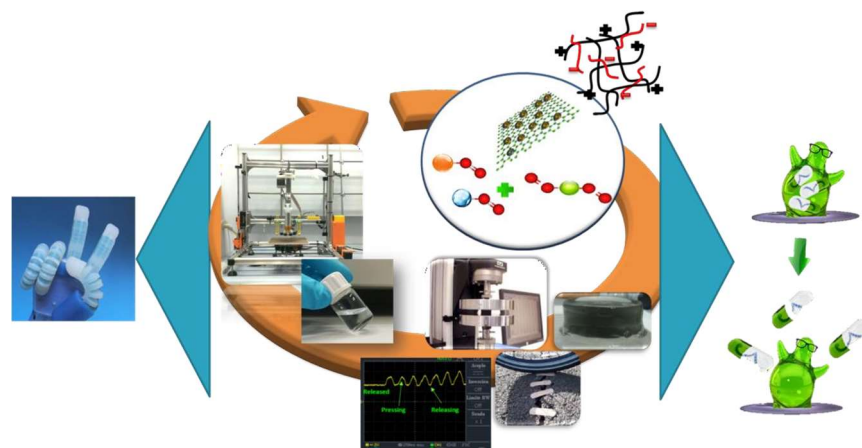
Smart soft materials in drug release and soft robotics

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The synthesis of different hydrophilic polymeric networks, by in situ radical polymerization in the presence of graphene derivatives, gives rise to three-dimensional soft structures. The role of the nanomaterial within the polymer network is primarily intended for reinforcing (i.e., increasing the stiffness and toughness). However, we have shown that the presence of graphene¹ can also enhance features such as biocompatibility and sensing,² giving rise to truly hybrid composites.³ In this talk, we will discuss the development of these polymeric networks as smart soft materials that emulate the mechanical properties of living tissues, as well as their ability to self-heal.⁴ In addition, their response to different stimuli, such as electric and magnetic fields, and the possibility of preparation following 3D printing methodologies, paves the way for applications in two large and currently highly relevant fields: drug release⁵ and soft robotics.⁶



Acknowledgments

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References

1. J. M. González-Domínguez, V. León, M. I. Lucío, M. Prato and E. Vázquez. Production of ready-to-use few-layer graphene in aqueous suspensions *Nature Protocols*, 2018, **13**, 495.
2. C. Martín, S. Merino, J. M. González-Domínguez, R. Rauti, L. Ballerini, M. Prato, E. Vázquez, *Scientific Reports*, 2017, **7** (1), 10942.
3. C. Martín, A. Martín-Pacheco, A. Naranjo, A. Criado, S. Merino, E. Díez-Barra, M. A. Herrero, E. Vázquez, *Nanoscale*, 2019, **11**, 4822.
4. A. Naranjo, C. Martín, A. López-Díaz, A. Martín-Pacheco, A. M. Rodríguez, F. J. Patiño, M. A. Herrero, A. S. Vázquez, E. Vázquez, *Applied Materials Today*, 2020, 100806.
5. J. Leganés, A. M. Rodríguez, M. A. Arranz, C. A. Castillo-Sarmiento, I. Ballesteros-Yáñez, A. S. Migallón, S. Merino, E. Vázquez, *Materials Today Chemistry*, 2022, **23**, 100702.
6. A. López-Díaz, A. Martín-Pacheco, A. M. Rodríguez, M. A. Herrero, A. S. Vázquez, E. Vázquez, *Adv. Func. Mater.*, 2020, 2004417.



Applications of natural deep eutectic systems in polymer engineering

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In the current scenario of a worldwide quest for sustainable and “greener” alternatives for current applications, in the past two decades the number of reports on Deep Eutectic Systems (DES) applicability in various situations has rapidly grown. The tailor-made versatility of these eutectics, meaning in practical terms a wide range of chemical and physical properties, has turned them into significant tools in the development of green and sustainable technologies. For this purpose, their use in polymeric applications has been growing and expanding to new areas of development. The present communication presents the progress in the field of DES applied to polymer science and engineering, namely recent applications of DES in extraction and modification, and the early developments on the formulation of DES–polymer products. In this sense, our group has explored DES for the extraction of collagen from blue shark skins which were subsequently processed to render different aerogel structures. This work demonstrated that the presence of DES as solvent allows the preparation of a lightweight, with a sponge-like structure, with high specific area and pore volume. In parallel to this work, we have investigated the possibility to produce injectable hydrogels, formed *in situ* by enzymatically crosslinking hydrolyzed collagen. DES, as it has been proved in previous studies, is able to promote an increase in thermal and structural stability of enzymes, in particular of horseradish peroxidase (HRP), improving its activity. Hence, HRP was selected to mediate this crosslinking reaction. One of the possible applications of these gels is regenerative medicine. The hydrogel preparation, gelation time, long term stability and mechanical properties were investigated. Moreover, the feasibility of using these gels as drug delivery systems was assessed by studying the compatibility of several non-steroidal anti-inflammatory agents (NSAID's) with the DES of interest. Within the same line of research, we have we developed other DES-based gels, with enhanced lubricating properties, and integrating an NSAID, with improved solubility (≥ 5 times), for local action. Their rheology was characterized in terms of viscoelastic properties (crossover frequency, G' and G'' at walking or running frequencies, temperature dependency, and response to loading forces (shear-rate profile)) and the gels' biocompatibility was also evaluated *in vitro* with a chondrogenic cell line. The results support the preparation of biocompatible formulations with potential to be used in regenerative medicine. In summary, the combination of DES and polymers is highly promising in the development of new and 'greener' materials. However, there is many questions that remain unanswered and open the doors for future research in this field.

Acknowledgements

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Nanocellulose and protein amyloid fibrils: Reshaping old biopolymers

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Polysaccharides and proteins play important roles in living organisms and are gaining increasing relevance on the fabrication of sustainable biopolymeric materials. In particular, the unveiling of biopolymeric nanofibrils, e.g., nanocellulose fibrils and protein amyloid fibrils, opens the possibility to widen the potential of these conventional biopolymers, because of their unique set of properties, namely high aspect ratio and specific surface area, ease of modification, high mechanical strength and thermal stability, renewability, biodegradability, and biological functions (particular for protein fibrils).¹

In this communication, a brief description of the preparation methodologies and characteristics of cellulosic nanofibrils, namely nanofibrillated cellulose (NFC), bacterial nanocellulose (BNC), and protein amyloid nanofibrils, and the recent trends on their use as versatile biopolymeric nanostructures for the design of high-performance nanomaterials (e.g., membranes, films, hydrogels, coatings and patches) for different applications are discussed (Figure 1).

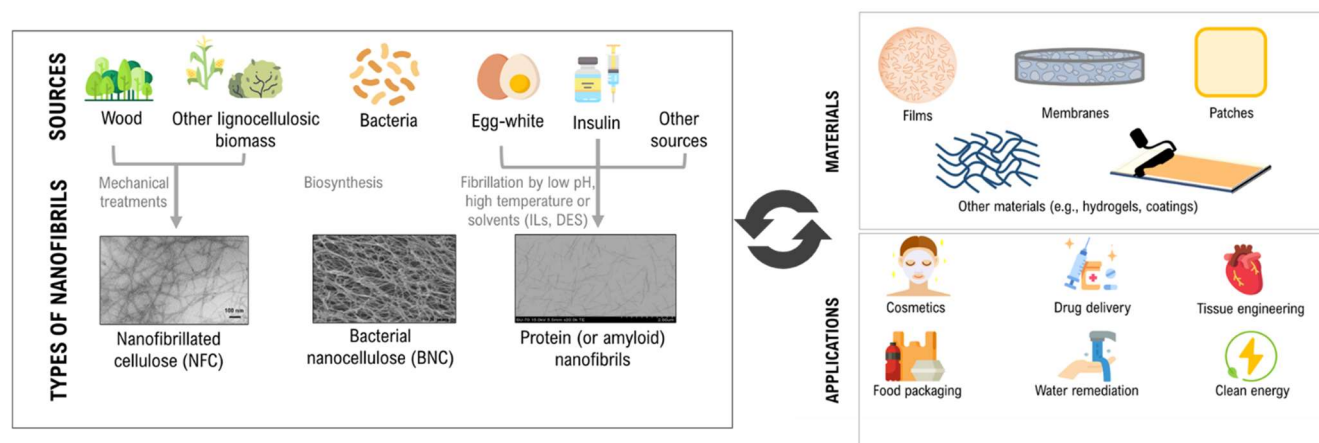


Figure 1: Scheme illustrating the outline of this communication (adapted from Silva *et al.* ¹)

Acknowledgements

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References

- 1- A. Q.C. Silva, A. J.D. Silvestre, C. Vilela and C. S.R. Freire, *Front. Bioeng. Biotechnol.*, 2022, **10**, 1059097



Controlling Optoelectronic Processes in Covalent Organic Frameworks

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Photoactive molecular building blocks can be spatially integrated into the crystalline lattice of covalent organic frameworks (COFs), allowing us to create models for organic bulk heterojunctions, chemical sensors and porous electrodes for photoelectrochemical systems. In this presentation, we will address means of controlling the morphology and packing order of COFs in thin films [1] and with spatially locked-in building blocks.[2]

We will discuss different strategies aimed at creating electroactive networks capable of light-induced charge transfer. For example, we have developed a COF containing stacked thienothiophene-based building blocks acting as electron donors with a 3 nm open pore system, which show light-induced charge transfer to an intercalated fullerene acceptor phase.[3] Contrasting this approach, we have designed a COF integrated heterojunction consisting of alternating columns of stacked donor and acceptor molecules, promoting the photo-induced generation of mobile charge carriers inside the COF network.[4] Additional synthetic efforts have led to several COFs integrating extended chromophores capable of efficient harvesting of visible and near infrared light, for example [5].

Extending newly developed thin film growth methodology to a solvent-stable oriented 2D COF photoabsorber structure, we have established the capability of COF films to serve in photoelectrochemical water splitting systems.[6] The detailed mechanism of excited state dynamics in light-harvesting conjugated COFs has been revealed by means of transient absorption spectroscopy.[7] Many optoelectronic applications of COFs depend on significant electrical conductivity. Here, Wurster-type structural motifs are attractive building blocks for imparting high conductivity in the corresponding COFs.[8] Finally, COF films can also act as ultrafast solvatochromic chemical sensors [9], as photodetectors [10], and show very efficient electrochromic response.[11] Ongoing work focuses on the design of ultra-large pore donor-acceptor COFs with extended light-harvesting abilities, and extends the structural paradigm of COFs to novel 3D conjugated frameworks. The great structural diversity and morphological precision that can be achieved with COFs make these materials intriguing model systems for organic optoelectronic materials.

References

1. Medina et al., *J. Am. Chem. Soc.* 2015, *137*, 1016.
2. Ascherl et al., *Nature Chem.* 2016, *8*, 310.
3. Dogru et al., *Angew. Chem. Int. Ed.* 2013, *52*, 2920.
4. Calik et al., *J. Am. Chem. Soc.* 2014, *136*, 17802.
5. Keller et al., *J. Am. Chem. Soc.* 2017, *139*, 8194.
6. Sick et al., *J. Am. Chem. Soc.* 2018, *140*, 2085.
7. Jakowetz et al., *J. Am. Chem. Soc.* 2019, *141*, 11565.
8. Rotter et al., *Chem. Sci.* 2020, *11*, 12843.
9. Ascherl et al., *Nature Commun.* 2018, *9*, 3802.
10. Bag et al., *J. Am. Chem. Soc.* 2023, *145*, 1649.
11. Bessinger et al., *J. Am. Chem. Soc.* 2021, *143*, 7351.



Processability studies on imine-based covalent organic frameworks

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Covalent Organic Frameworks (COFs) provided new organic polymers with controlled mesoporosity and structural order. They are formed by condensation reactions of organic molecules leading to the formation of dynamic imine bonds. Imine-based COF show higher chemical stability, porosity, and crystallinity than those previously reported, e.g., boronate ester-based COFs [1]. While the chemical design, thermal and chemical stability have been the subject of much research, COF processability is still little developed. This is a fundamental aspect of many COF applications.

This talk revises the most recent progress concerning the synthesis of imine-based COFs that enable their processability [2]. The focus of my discussion will be 3D printing of imine-based COFs [3] and imine-based COF gels' formation and their transformation into aerogels and films to form functional centimeters-long membranes [4,5]. Finally, I will show our recent results in processes based on dynamic chemistry that allow the formation of new imine-based gel and aerogel COFs.

References

- [1] J. L. Segura, M. J. Mancheno, F. Zamora, *Chem. Soc. Rev.* 2016, 45, 5635-5671.
- [2] D. Rodríguez-San-Miguel, F. Zamora. *Chem. Soc. Rev.*, 2019, 48, 4375-4386.
- [3] C. Franco, D. Rodríguez-San-Miguel, et al. *J. Am. Chem. Soc.* 2020, 142, 3540-3547.
- [4] J. Á. Martín-Illán, et al. *Angew. Chem. Int. Ed.* 2021, 60, 13969–13977.
- [5] J. Á. Martín-Illán, et al. *Adv. Sci.* 2022, 2104643.



Functional materials by design via microfluidic technologies

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Self-assembly has long been used to control covalent and non-covalent interactions where molecular design has been the major driving force to achieve a desired outcome. Like in nature, a full control over self-assembly processes could lead to rationalized structure-property correlations, a long-time sought in chemistry, physics and materials science. However, the pathways followed and the mechanisms underlying the formation of supramolecular aggregates are still a major challenge for the scientific community. Accordingly, the elucidation of nucleation and growth mechanisms will be highly required to push supramolecular chemistry to the next level, where access to nature inspired functions will be accomplished. In this contribution, I will present how reaction-diffusion (RD) conditions established within microfluidic devices can be used to uncover pathway complexity as well as to trigger pathway selection. Specifically, I will show that microfluidic RD conditions provide an unprecedented kinetic control over self-assembly processes; for example, enabling the isolation of well-defined kinetically trapped states as well as unprecedented metastable materials. This research provides a new tool to study and understand supramolecular chemistry, and opens up new avenues for the engineering of advanced functional assemblies and systems.

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Merging Distorted Nanographenes with Framework Materials

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Nanographenes –polycyclic aromatic hydrocarbons that extend over 1 nm– can adopt a broad range of non-planar conformations that challenge the perception of aromatic systems as rigid and flat structures. Such distorted structures are the result of the steric strain induced by overcrowding or congestion in key positions of the aromatic core. Distorted nanographenes have shown enhanced solubility and unique optoelectronic and chiroptical properties as an effect of their distorted molecular structure. Our group has pioneered the introduction of distorted nanographenes in framework materials.¹⁻⁵ This merge offers new possibilities in the design monomers with symmetries that deviate from standard graphitic geometries, and in turn, in the design of 2D and 3D covalent organic frameworks with unprecedented architectures and properties. The most recent advances of these distorted framework materials including synthetic routes, optoelectronic properties, self-organising properties, and potential applications will be discussed.

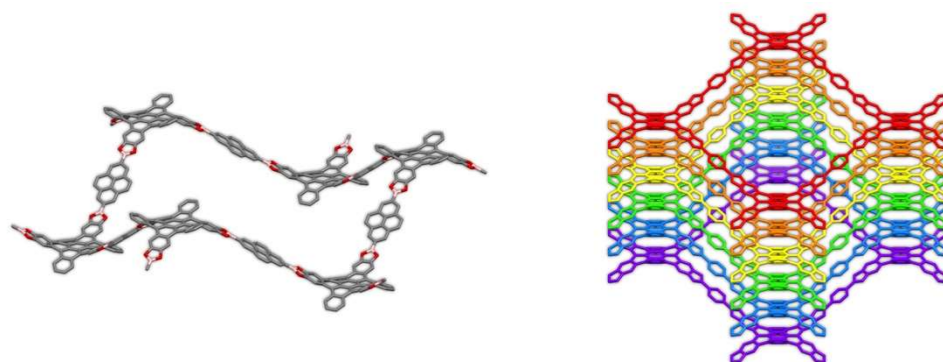


Figure 1: Examples of covalent organic frameworks with distorted nanographene nodes

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References

1. A. B. Marco, D. Cortizo-Lacalle, I. Perez-Miqueo, G. Valenti, A. Boni, J. Plas, S. De Feyter, F. Paolucci, M. Montes, A. Khlobystov, M. Melle-Franco and A. Mateo-Alonso *Angew. Chem. Int. Ed.*, 2017, **56**, 6946-6951.
2. M. Martínez-Abadía, C.T. Stoppiello, K. Strutyński, B. Lerma-Berlanga, C. Martí-Gastaldo, A. Saeki, M. Melle-Franco, A.N. Khlobystov and A. Mateo-Alonso *J. Am. Chem. Soc.* 2019, **141**, 14403-14410.
3. M. Martínez-Abadía, K. Strutyński, B. Lerma-Berlanga, C. T. Stoppiello, A. N. Khlobystov, C. Martí-Gastaldo, A. Saeki, M. Melle-Franco, and A. Mateo-Alonso *Angew. Chem. Int. Ed.*, 2021, **60**, 9941–9946.
4. A. Riaño, K. Strutyński, M. Liu, C. T. Stoppiello, B. Lerma-Berlanga, A. Saeki, C. Martí-Gastaldo, A. N. Khlobystov, G. Valenti, F. Paolucci, M. Melle-Franco, and A. Mateo-Alonso, *Angew. Chem. Int. Ed.*, 2022, **61**, e202113657.
5. E. De Bolòs, M. Martínez-Abadía, F. Hernández-Culebras, A. Haymaker, K. Swain, K. Strutyński, B. L. Weare, J. Castells-Gil, N. M. Padial, C. Martí-Gastaldo, A. N. Khlobystov, A. Saeki, M. Melle-Franco, B. L. Nannenga and A. Mateo-Alonso, *J. Am. Chem. Soc.*, 2022, **144**, 15443-15450.



Strategies for Tailoring Covalent Organic Frameworks towards Catalysis and Capture of Water Pollutants

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Molecular framework materials allow for the precise placement of building blocks in a crystalline matrix, which is highly advantageous in tailoring materials towards a specific purpose. Covalent organic frameworks (COFs) are a member of this class of materials, which, with their crystalline, highly ordered, and porous nature, are receiving increasing interest for various applications.

In this talk, synthetic approaches to obtain crystalline, functionalized COFs will be discussed.^{1,2} Different strategies to furnish the materials with catalytic activity will be presented, as well as our results on the stability of COFs under catalytically relevant conditions (Figure 1).^{3,4} On the other hand, key aspects on the design and synthesis of COFs for contaminant capture will be considered,⁵ such as the effect of COF pore surface functionalization on the adsorption of toxins.⁶

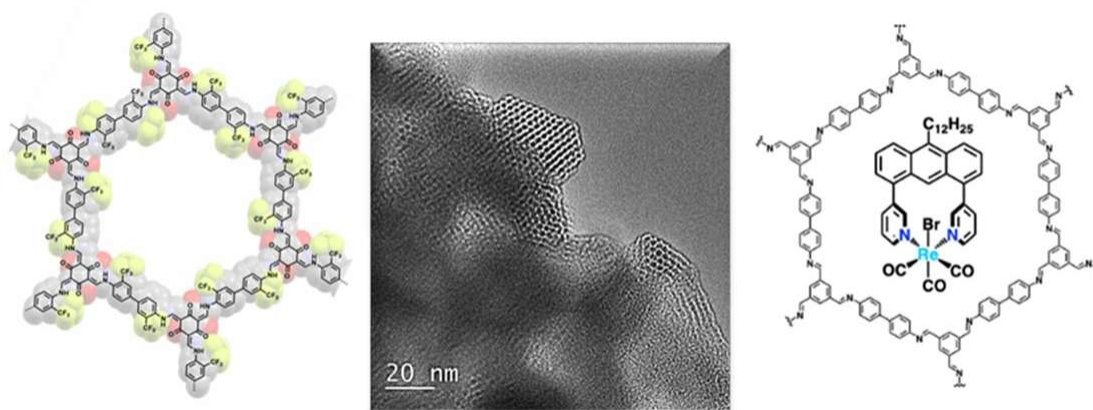


Figure 1: Fluorinated COF for efficient capture of water contaminants (left), highly crystalline hexagonal boronic ester COF (middle), and scheme of imine COF with homogeneous Re catalyst embedded (right).

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References

- 1 L. M. Salonen, D. D. Medina, E. Carbó-Argibay, M. G. Goesten, L. Mafra, N. Guldris, J. M. Rotter, D. G. Stroppa and C. Rodríguez-Abreu, *Chem. Commun.*, 2016, **52**, 7986–7989.
- 2 S. P. S. Fernandes, L. Frey, K. M. Cid-Seara, O. Oliveira, C. Rodríguez-Abreu, Yu. V. Kolen'ko, N. Guldris, E. Carbó-Argibay, A. M. S. Silva, D. D. Medina and L. M. Salonen, *Microporous Mesoporous Mater.*, 2022, **343**, 112162.
- 3 S. T. Goralski, K. M. Cid-Seara, J. J. Jarju, L. Rodríguez-Lorenzo, A. P. LaGrow, M. J. Rose and L. M. Salonen, *Chem. Commun.*, 2022, **58**, 12074–12077.
- 4 J. J. Jarju, A. M. Díez, L. Frey, V. Sousa, L. P. L. Gonçalves, D. D. Medina, O. I. Lebedev, Yu. V. Kolen'ko and L. M. Salonen, *Mater. Today Chem.*, 2022, **26**, 101032.
- 5 S. P. S. Fernandes, V. Romero, B. Espiña and L. M. Salonen, *Chem. Eur. J.*, 2019, **25**, 6461–6473.
- 6 S. P. S. Fernandes, P. Kovář, M. Pšenička, A. M. S. Silva, L. M. Salonen and B. Espiña, *ACS Appl. Mater. Interfaces*, 2021, **13**, 15053–15063.

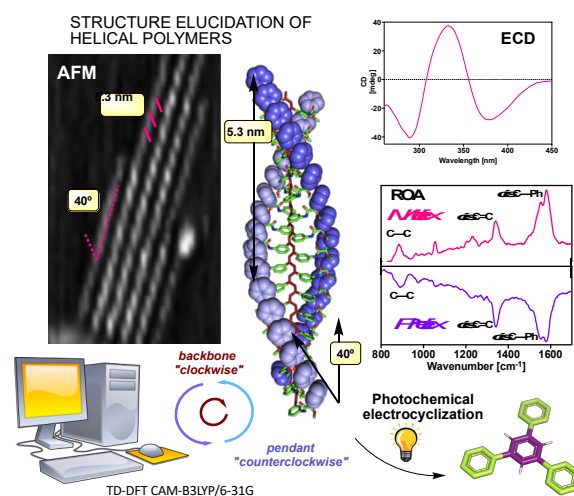


Stimuli-Responsive Helical Polymers

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Dynamic helical polymers have attracted the attention of the scientific community during the last decades due to their stimuli responsive properties and the functionality attributed to the helical scaffold.¹ Thus, while helical sense and elongation of dynamic helical polymers can be altered by their interaction with external stimuli, the helical scaffolds adopted by the polymers are responsible of their applications in different fields such as asymmetric synthesis, chiral recognition, or chiral stationary phases in HPLC.¹ Importantly, to create a dynamic helical polymer with a good performance in certain applications it is necessary to know its secondary structure, which also allows establishing a structure/function relationship in this kind of materials.² To obtain an approximated 3D structure of a helical polymer such as a poly(phenylacetylene), a combination of the information obtained from different structural techniques —UV-vis, circular dichroism (CD), vibrational circular dichroism (VCD), Raman, Raman optical activity (ROA), differential scanning calorimetry (DSC) and atomic force microscopy (AFM)— is needed. This fact is due to the complexity of the helical scaffolds found in PPAs, which are made by two coaxial helices: an internal helix described by the polyene backbone and an external one described by the pendants, which, depending on the stereoregularity of the polyene backbone, can rotate in the same (*cis-cisoidal*) or opposite directions (*cis-transoidal*).³⁻⁴ Herein, I will show how to elucidate the secondary structure of a helical polymer by solving the information puzzle obtain from different techniques. Moreover, the knowledge of the secondary structure will allow to control other structural parameters such as the dynamic behavior and stimuli responsive properties.⁵



Scheme 1: Secondary structure elucidation of helical polymers

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References

- 1) E. Yashima, N. Ousaka, D. Taura, K. Shimomura, T. Ikai, K. Maeda, *Chem. Rev.*, 2016, **116**, 13752-13990.
- 2) F. Rey-Tarrio, S. Guisán-Ceinos, J. M. Cuerva, D. Miguel, M. Ribagorda, E. Quiñoá, F. Freire, *Angew. Chem. Int. Ed.* 2022, **61**, e202207623.
- 3) J. J. Tarrío, R. Rodríguez, B. Fernández, E. Quiñoá, F. Freire, *Angew. Chem. Int. Ed.*, 2022, **61**, e202115070.
- 4) F. Rey-Tarrio, R. Rodríguez, E. Quiñoá, R. Riguera, F. Freire, *Angew. Chem. Int. Ed.*, 2021, **60**, 8095-8103.
- 5) Z. Fernández, B. Fernández, E. Quiñoá, F. Freire. *J. Am. Chem. Soc.* 2021, **143**, 49, 20962–20969.

ORAL PRESENTATIONS



Insights into the Redox Properties of Organic Molecules by Computational Modelling

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Identification of new redox compounds is essential for the design of new improved batteries. During the last few years there has been an increased interest in the field of organic electrode materials (OEMs) and organic-based redox flow batteries (ORFBs), because of their structural diversity, widespread availability, flexibility, low-toxicity and recyclability. For both battery technologies, there is significant interest in transition to organic molecules that are typically comprised of earth-abundant elements, and thus, their cost and availability is less constrained by the production and reserves of rare elements. Contrary to metals, organics can be synthesized in a sustainable fashion using green chemistry routes, opening the possibility of infinite structures with tuned redox properties, multiple oxidation states and improved solubility by means of rational synthetic design.

High-throughput computational screening offers the possibility of unraveling the reduction mechanisms of electrode materials and exploring thousands of molecules for desirable properties without the need for experimental trial and error. Phenazines, quinones and imides are an emerging family of organic compounds in electrochemical energy storage applications, because of their multi-redox activity, low-toxicity and structural diversity. Here, we report on the modelling activities carried out in our group towards the accelerated discovery of Phenazine-based electrolytes for ORFBs and to identify the reduction mechanism of catecholate- and imide-based polymers in the presence of metal salts in aqueous electrolytes.^{1, 2, 3} The DFT results provide key insights into their structure–activity properties that guide the design and tuning of new molecules for electrochemical energy storage.

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References

1. C. de la Cruz, A. Molina, N. Patil, E. Ventosa, R. Marcilla, A. Mavrandonakis, *Sustainable Energy & Fuels*, 2020, **4**, 5513-5521.
2. N. Patil, A. Mavrandonakis, C. Jerome, C. Detrembleur, J. Palma, R. Marcilla, *ACS Applied Energy Materials*, 2019, **2**, 3035-3041.
3. N. Patil, A. Mavrandonakis, C. Jérôme, C. Detrembleur, N. Casado, D. Mecerreyes, J. Palma, R. Marcilla, *Journal of Materials Chemistry A*, 2021, **9**, 505-514.



Towards Totally Aqueous Membrane-Free Redox Flow Batteries with Organic Active Species

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Redox Flow Batteries (RFB) have been recognized as a suitable technology for the integration of renewable energies into the electricity grids due to their ability to decouple power and energy. However, their wide-spread implementation is limited by some obstacles related to components such as: low abundance, toxicity and high cost of vanadium redox species, and the poor-performing and expensive ion exchange membranes used to separate catholyte and anolyte compartments. In order to face these drawbacks, a new approach of membrane-free battery was proposed based on immiscible/biphasic electrolytes and organic redox species^{1,2}. In this talk, we will show the last results of an aqueous membrane-free flow battery (without any type of separator) (Figure 1) in which the vanadium species are replaced by cheap and abundant organic redox molecules that can be specifically designed to exhibit high solubility, adequate redox potentials and suitable partition coefficient between the two electrolytes. The flow battery reactor, which is the first example based on biphasic aqueous electrolytes, demonstrated a stable performance over 250 cycles with a high capacity utilization (98%)³. In addition, new and critical aspects such as the inherent self-discharge, the new cell reactor and future opportunities of this innovative technology will be also discussed.⁴

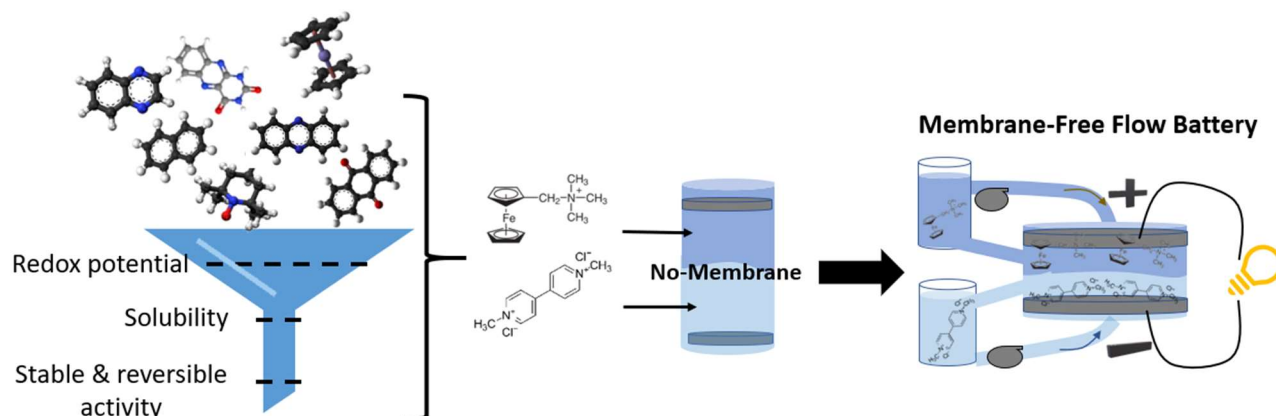


Figure 1: Membrane-free Flow battery scheme with organic active species selection

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References

- 1 P. Navalpotro, J. Palma, M. Anderson and R. Marcilla, *Angew. Chemie - Int. Ed.*, 2017, **56**, 12460–12465.
- 2 P. Navalpotro, N. Sierra, C. Trujillo, I. Montes, J. Palma and R. Marcilla, *ACS Appl. Mater. Interfaces*, 2018, **10**, 41246–41256.
- 3 I. Montes, R. Marcilla, J. Palma, E. Ventosa, M. Vera, M. Sánchez Sanz, S.E. Ibañez, IMDEA Energy Pat. WO2021209585A1, 2020
- 4 P. Navalpotro, S.E. Ibañez, E. Pedraza, R. Marcilla. *Energy Storage Mater.*, 2023, <https://doi.org/10.1016/j.ensm.2023.01.033>



Cellulose-based energy storage devices

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In recent years, the interest in the integration of electronics into textiles and clothing has increased significantly, adding advanced functionalities to conventional textiles. The process of embedding electronic functionalities into fibres, yarns and fabrics is now a demand in developing innovative smart textile-based systems¹. To date power supply of electronic textiles devices has been done by conventional batteries, which besides having low durability, are heavy and difficult to directly integrate into a textile. This work focus on the development of 1D cellulose-based supercapacitors able to use an artificial sweat solution as the electrolyte to evaluate its applicability to sport textiles. The inner and outer electrodes consist of a carbon-based thread functionalized with a conductive polymer (polypyrrole) which improves the electrochemical performances of the supercapacitor². The inner electrode is coated with electrospun cellulose acetate fibres, as the separator, and the outer electrode is twisted around it (Figure 1a). The electrochemical performance and stability of symmetrical supercapacitors were evaluated under several mechanical deformations and demonstrated a high capacitance retention (Figure 1b-c).

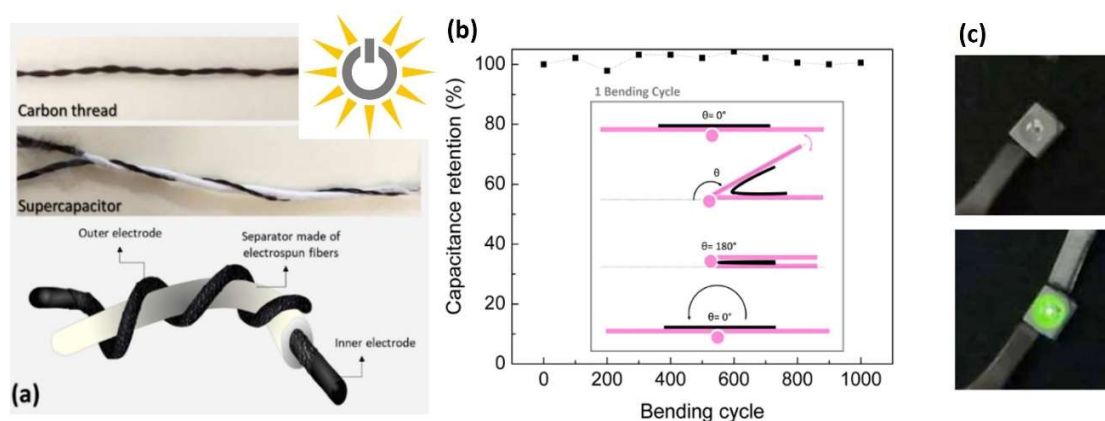


Figure 1: Wire-based supercapacitors were fabricated with the outer electrode in a twisted configuration as indicated in (a). The flexibility of the wire-based supercapacitor was tested by repeatedly bending it from 0° up to 180° for 1000 cycles (b). After each set of 100 bending cycles, the CV performance was evaluated to determine the capacitance retention. The devices were connected either in series or in a combination of series and parallel followed by charge/discharge measurements and demonstrated to provide enough power to turn on a green LED (c).

Acknowledgements

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References

1. A. Rafique, I. Ferreira, G. Abbas and AC. Baptista, Nano-Micro Letters, 2023, 15, 40
2. N. Lima, AC. Baptista, BMM. Faustino, S. Taborda, A. Marques, and I. Ferreira, Scientific Reports 2020, 10 (1) 1-9



Layered nanocomposites based on conducting polymer nanoparticles for thermoelectric applications

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Thermoelectricity has become a very interesting topic in the framework of energy harvesting. Historically, inorganic materials have dominated the thermoelectric applications. However, organic and hybrid semiconductors such as: conducting polymers and nanocomposites based on carbon materials (CNTs or graphene) are now considered promising candidates for the next generation of thermoelectric materials. Their thermoelectric efficiency, measured by the dimensionless figure of merit ZT ($ZT = S^2\sigma T/\kappa$ where S , σ and κ are the Seebeck coefficient, the electrical and thermal conductivities, respectively) has been improved several orders of magnitude, with values currently very close to the inorganic materials. In addition, conducting polymers and nanocomposites based on carbon materials present several advantages over inorganic materials such as: renewable raw materials, lack of toxicity, low cost of production and etc. Single wall carbon nanotubes (SWCNTs) and double wall carbon nanotubes (DWCNTs) are widely used for producing thermoelectric nanocomposites due to their good electric properties. However, processing this type of nanostructures into homogenous films is challenging due to problems related to the stability in water based suspensions and dispensability in polymer matrices. Therefore, Layer-by-layer (LbL) assembly has been gaining attention as one of the most promising techniques to develop nanostructured materials being possible to combine different materials such as conducting polymer nanoparticles and carbon nanostructures by electrostatic interactions in thin films. This method showed excellent results in terms of thermoelectric efficiency (see Power Factor values in Figure 1) being possible to increase the electrical conductivity and the Seebeck coefficient simultaneously.

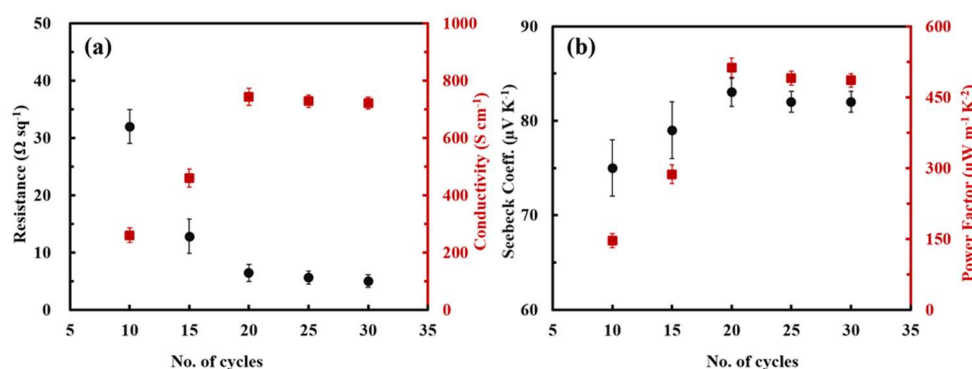


Figure 1: (a) Sheet resistance, (b) electrical conductivity, (c) Seebeck coefficient, and (d) power factor of PEDOT:NP/DWNT-PEDOT:PSS as a number of bilayers deposited on a PET substrate

Acknowledgements

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References

1. M. Culebras, Y.-y. Byun, J. Jang, A. Serafin, M. N. Collins, Y. T. Park and C. Cho, *Applied Surface Science*, 2023, **615**, 156432.



Algae biomaterials: future building blocks for energy storage and conversion technologies

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The development of new, more eco-friendly materials is essential to reduce greenhouse gas emissions and comply with the 2030 Agenda for Sustainable Development to combat climate change. Therefore, bio-based and biodegradable polymers are major players to design innovative eco-friendly materials with customizable properties and performance. Cost-effective and eco-friendly polymer electrolytes based on proteins and polysaccharides can become a promising substitute for synthetic polymers (e.g. Nafion®) for use in electrochemical devices involving energy generation and storage.

Silk fibroin (SF), present in the cocoons of the domestic silkworm *Bombyx mori*, is a crystalline protein responsible for the outstanding tensile properties of silk and has been extensively evaluated in biomedical fields due to its biocompatibility.¹ However, the functional properties of SF may make it suitable for applications outside this field, namely where ionic transport properties are required. Recently, marine resources from algae biomass have attracted attention due to their capacity to produce high-value components, such as proteins, polysaccharides, phenolic compounds, pigments, among others. Because of the chemical diversity and unique properties, these bioactive components have been the subject of intensive research and are widely used in food and cosmetics industries.² Algae compounds also represent promising eco-friendly and biodegradable alternatives to conventional polymer electrolytes.

The objective of this work is to develop electrolytes consisting of SF and algae bioactive compounds for electrochemical energy devices (fuel cells, batteries, electrochromic, among others). These materials were mixed to form flexible, transparent and free-standing films, where SF provides the necessary mechanical and hydrolytic stability and the algal extracts (phycocyanin, fucoidan, phlorotannins) provide the ionic conductivity, since they contain protogenic groups, e.g., sulphate, carboxyl and phenolic hydroxyl groups that enable proton motion. These membranes were extensively characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), dynamic water vapour sorption measurements (DVS), dynamic mechanical analysis (DMA), and ionic conductivity under variable temperature and relative humidity (RH). Preliminary results reveal good levels of ionic conductivity obtained at high temperature (94°C) and RH (98%) for SF membranes with phycocyanin ($3.3 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$), where the increase in conductivity is pronounced at lower RH (~5 orders of magnitude compared with pure SF).

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References

- 1 R. F. P. Pereira, M. M. Silva and V. De Zea Bermudez, *Macromol. Mater. Eng.*, 2015, **300**, 1171–1198.
- 2 Katarzyna Chojnacka, P. P. Wiczorek, G. Schroeder and I. Michalak, Eds., *Algae Biomass: Characteristics and Applications: Towards Algae-based Products*, Springer, 2018.



Leveraging Chemical Modifications of Laminarin to Develop Bioinspired Tunable Biomaterials for Biomedical Applications

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The marine environment is an extraordinary source of marine living resources from which a plethora of natural molecules and materials with specific and astonishing biological and chemical features can be readily extracted from. Among them, marine-origin biopolymers find widespread use in a wide array of biomedical applications, including in tissue engineering and regenerative medicine, as well as in targeted and sustained drug delivery.¹ Moreover, the marine environment also encompasses an enormous number of invertebrate organisms glued to wet surfaces due to particularly adhesives. These adhesives are secreted by marine sessile organisms, such as mussels, barnacles, and marine tubular worms, and adhere effectively and strongly to almost any underwater surface.² Through the combination of active biomolecules present in these organisms and taking the advantage of the use of marine polysaccharides due their desirable biological and physicochemical properties, including i) biocompatibility, ii) biodegradability, and iii) versatility in modification, is possible to develop ground-breaking biomaterials for biomedical applications.^{1,2}

Here we will focus on the development of straightforward and selective chemical methodologies to be applied in Laminarin (LAM),³⁻⁵ a natural origin polysaccharide from brown algae, modifying its chemical backbone structure, for further conjugation with different small molecules, such as active –functional or –catechol groups (Figure 1). Novel derivatives were prepared and used to produce several LAM-based biomaterials with potential for tissue regeneration purposes. Diverse chemical modification steps for the insertion of functional groups, such as –allyl, –alkyl, –azide, –methacroyl and –catechol groups, are reported. Characterization techniques of the derivatives (¹H NMR, FTIR, UV-Vis and SEM) and the final properties of the develop biomaterials (microparticles, hydrogels, cryogels and thin films) will be presented and discussed.

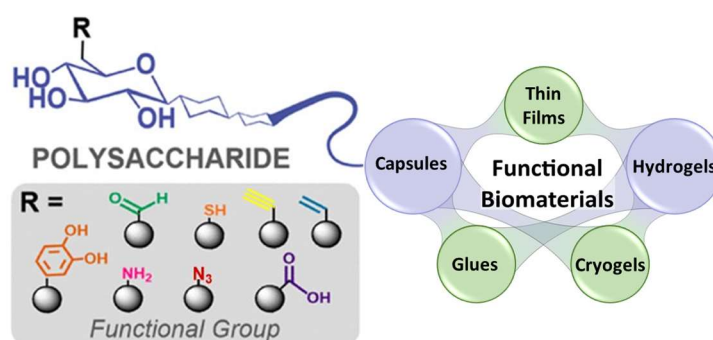


Figure 1: Chemical modifications of LAM polysaccharide

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References

- [1] Sacramento, M.M.A., Borges, J., Correia, F.J.S., Calado, R., Rodrigues, J.M.M., Patricio, S.G., Mano, J.F., *Front. Bioeng. Biotechnol.*, **2022**, *10*, 1041102
- [2] Zhang, W., Wang, R., Sun, Z.M., Zhu, X., Zhao, Q., Zhang T., Cholewinski A., Yang, F.K., Zhao B., Pinnaratip R., Forooshani, P.K., Lee, B.P., *Chem. Soc. Rev.*, **2020**, *49*, 433.
- [3] Castanheira, E.J., Correia, T.R., Rodrigues, J.M.M., Mano, J.F., *Bull. Chem. Soc. Jpn.*, **2020**, *93*, 713.
- [4] Costa, A. M. S., Rodrigues, J. M. M., Pérez-Madrigal, M. M., Dove, A. P. and Mano, J. F., *J. Am. Chem. Soc.*, **2020**, *142*, 19689.
- [5] Monteiro, L.P.G., Borges, J., Rodrigues, J.M.M., Mano, J.F., *Mar. Drugs*, **2023**, *21*, 92.



Hydrogels based on chitosan for tissue engineering applications

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Traditional 2D cultures present some disadvantages when they try to simulate the real behavior of living tissues. Cell shape is flat and elongated since the cells can only grow into a monolayer on the plate, cell-cell interactions are poor, cells experiment polarized forces that affect its proliferation and differentiation process... Therefore, 3D cultures have emerged as potential candidates to solve those problems. In particular,

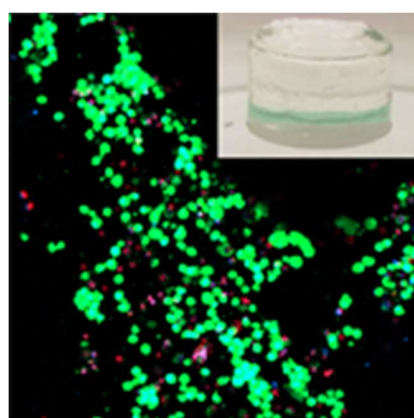


Figure 1: SH-SY5Y cells seeded into chitosan hydrogels during the live-dead experiment. Propidium iodide staining for dead cells in red, calcein-AM for living cells in green, and Hoechst 33342 for nuclear staining in blue.

hydrogels are ideal scaffolds because of their ability to mimic the highly hydrated environment of the extracellular matrix and their porous structure allows the diffusion of nutrients and oxygen required for the cells. Moreover, hydrogel properties can be tuned easily by changing the nature of the polymer that forms the structure or the amount of crosslinker employed. Besides all these advantages, some hydrogels can be considered smart materials, capable of generating a response to environmental stimuli such as changes in pH, temperature, magnetic fields...¹

In this work, we highlight the synthesis and characterization of new chitosan-based hydrogels as suitable scaffolds with potential applications for tissue engineering. Chitosan is a partially deacetylated form of chitin and it occupies a distinct position amongst other biomaterials due to its abundance, versatility, biocompatibility and antimicrobial properties.² Our research takes advantage of the synergic effect of biocompatibility provided by the natural polymer with the mechanical strength offered by the synthetic polymer of

polyacrylamide. Besides, the addition of nanomaterials such as graphene and superparamagnetic iron oxide nanoparticles (SPIONS) allows us to create new materials with different physicochemical and biological properties that have been fully characterized (mechanical properties, swelling degree, magnetic response, etc.). Previous studies show that the presence of graphene inside the structure of the hydrogel can improve cell adhesion and the formation of mature and active neuronal synaptic networks.³ Magnetic nanoparticles in the matrix afford us to obtain a magnetic response when an external magnetic field is applied. This property can be used to modify the release profile of different biomolecules such as growth factors or drugs loaded in the scaffold.⁴ Live-dead assays (Figure 1) have been carried out to test the cytocompatibility of the hydrogels as a first step to keep working in the future on the biological response produced by the different scaffolds during the cell differentiation process.

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References

1. C. Jensen, Y. Teng, *Frontiers in Molecular Biosciences*, 2020, **7**, 33
2. S. Sayyar, E. Murray, B. C. Thompson, J. Chung, D. L. Officer, S. Gambhir, G. M. Spinks, G. G. Wallace, *Journal of Materials Chemistry B*, 2015, **3** (3), 481-490
3. C. Martín, S. Merino, J. M. González-Domínguez, R. Rauti, L. Ballerini, M. Prato, E. Vázquez, *Scientific Reports*, 2017, **7** (1), 10942
4. J. Leganés, A. M. Rodríguez, M. A. Arranz, C. A. Castillo-Sarmiento, I. Ballesteros-Yañez, A. S. Migallón, S. Merino, E. Vázquez, *Materials Today Chemistry*, 2022, **23**, 100702



Naturally occurring catalyst for high temperature polymerizations

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Organocatalysis emerged as a good alternative to metal-based catalyst, due to its reduced environmental cost, versatility, high selectivity and possibility of purification or recovery of the catalyst from the final polymer, however, it still raises some concerns related to their relatively high toxicity.¹ In order to overcome this issue nature could be taken as a reference, as many reactions take place with the help of aminoacids and their derivatives in plants and animals. Nature offers a broad range of compounds that could work as catalyst, as they catalyze living processes in plants and animals. Moreover, some of these compounds have shown strong catalytic performance without sacrificing their non-toxic behavior. For instance, Guo et al. have found that by using a saccharin based catalytic system the ROP of L-LA could be promoted.² While several naturally occurring catalyst have been investigated, as far as we are aware none of them have shown to be competitive in terms of performance with other non-natural organocatalysts. Moreover, it should be noted down that in none of the cases the catalytic system is based on sulfonic acids which to date have shown to be much more competitive to perform the polymerizations at elevated temperatures. Among the biocompounds with a sulfonic group in its structure, we pay our attention to taurine (2-aminoethanesulfonic acid). This compound is present in the tissues of humans and animals, showing its high biocompatibility.³

In this work, we investigate the use of taurine, a naturally occurring abundant and biocompatible catalyst, for the high temperature polymerization of cyclic esters (Figure 1).

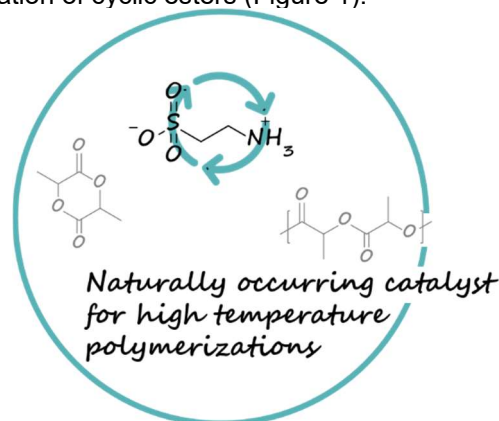


Figure 1: Taurine for the ROP of L-lactide.

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References

- 1 A. Bossion, K. V. Heifferon, L. Meabe, N. Zivic, D. Taton, J. L. Hedrick, T. E. Long and H. Sardon, *Prog. Polym. Sci.*, 2019, **90**, 164–210.
- 2 F. Wei, H. Zhu, Z. Li, H. Wang, Y. Zhu, L. Zhang, Z. Yao, Z. Luo, C. Zhang and K. Guo, *Adv. Synth. Catal.*, 2019, **361**, 1335–1347.
- 3 T. Bouckenoghe, C. Remacle and B. Reusens, *Curr. Opin. Clin. Nutr. Metab. Care*, 2006, **9**, 728–733.



Assessing the dynamics of adsorbed CO₂ species in Covalent Organic Frameworks via solid-state NMR methods

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Carbon dioxide emissions are known to be the major culprit of global warming, reaching a historic high of 36.3 gigatonnes in 2021. CO₂ removal and long-term storage technologies are part of the solution to tackle this crucial environmental challenge. The decades-old industrial technology based on liquid amines suffers from several limitations such as poor chemical stability and high regeneration energy requirements. Hence, the development of solid porous materials able to selectively capture CO₂ is a desirable alternative that is attracting great interest both in academic and industrial communities due to its potential to mitigate atmospheric CO₂ concentrations. Although mesoporous materials such as zeolites and activated carbons were already tested in pilot plants,^{1,2} the potential of covalent organic frameworks (COFs) as alternative sorbents has not been fully explored with few available studies in the literature.^{3,4} However, to fully develop the potential of heterogeneous sorbents for CO₂ capture, atomic-scale studies are essential to stimulate progress in the design of better CO₂-adsorbents by elucidating gas-sorption surface mechanisms. In addition to conventional techniques, such as volumetric and gravimetric gas adsorption, the use of spectroscopic techniques, in particular solid-state NMR, are a great asset due to their potential to shed light into structural details of distinct materials' surfaces, including the identification,⁵ quantification and characterization of the dynamics^{6,7} of confined chemisorbed and physisorbed CO₂ species. In this work, we undertake for the first-time a thorough solid-state NMR analysis of weakly interacting (physisorbed) CO₂ molecules in 2D hexagonal COFs (COF-42 and TpPA) combining ¹³C MultiCP and longitudinal relaxation times (T₁) NMR measurements. These methods were used to quantitatively distinguish physisorbed CO₂ species with overlapping NMR signals, confirming the presence of ¹³CO₂ molecules with three different relaxation time scales (ranging from microseconds to seconds). This observation strongly supports the existence of up to two and three physisorbed CO₂ species, with different molecular motional regimes, under dry and moist conditions, respectively. Our approach takes advantage from using adsorbed ¹³C-labelled CO₂ as probe molecules and quantitative cross-polarization magic-angle spinning to study both physi- and chemisorbed CO₂ species, showing that water not only induces the formation of bicarbonate species, as shown before in silica sorbents,^{8,9} but also changes the dynamics of physisorbed CO₂ inside the pores. The complex nature of physisorbed CO₂ in the presence and absence of water is revealed, shedding light on what fractions of weakly interacting CO₂ are affected upon exposure to moisture. This work extends the current knowledge on CO₂ sorption mechanisms providing new clues towards CO₂ sorbent optimization.

Acknowledgements

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References

- 1 S. Krishnamurthy, V. R. Rao, S. Guntuka, P. Sharratt, R. Haghpanah, A. Rajendran, M. Amanullah, I. A. Karimi and S. Farooq, *AIChE Journal*, 2014, **60**, 1830–1842.
- 2 P. A. Webley, *Adsorption*, 2014, **20**, 225–231.
- 3 K. Gottschling, L. Stegbauer, G. Savasci, N. A. Prisco, Z. J. Berkson, C. Ochsenfeld, B. F. Chmelka and B. v. Lotsch, *Chemistry of Materials*, 2019, **31**, 1946–1955.
- 4 H. Lyu, O. I. Chen, N. Hanikel, M. I. Hossain, R. W. Flaig, X. Pei, A. Amin, M. D. Doherty, R. K. Impastato, T. G. Glover, D. R. Moore and O. M. Yaghi, *J Am Chem Soc*, 2022, **4**, jacs.1c13368.
- 5 L. Mafra, T. Čendak, S. Schneider, P. v. Wiper, J. Pires, J. R. B. Gomes and M. L. Pinto, *J. Am. Chem. Soc.*, 2017, **139**, 389–408.
- 6 R. Fonseca, R. Vieira, M. Sardo, I. Marin-Montesinos and L. Mafra, *The Journal of Physical Chemistry C*, 2022, **126**, 12582–12591.
- 7 R. Vieira, I. Marin-Montesinos, J. Pereira, R. Fonseca, M. Ilkaeva, M. Sardo and L. Mafra, *J. Phys. Chem. C*, 2021, **125**, 14797–14806.
- 8 M. Pacheco, M. Bordinhos, M. Sardo, R. Afonso, J. R. B. Gomes, L. Mafra and M. L. Pinto, *Chemical Engineering Journal*, 2022, **443**, 136271.
- 9 M. Sardo, R. Afonso, J. Jůžkóv, M. Pacheco, M. Bordinhos, M. L. Pinto, J. R. B. Gomes and L. Mafra, *J Mater Chem A Mater*, 2021, **9**, 5542–5555.



Optimizing the thermodynamics and kinetics of the triplet-pair dissociation in donor-acceptor copolymers for intramolecular singlet fission

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Singlet fission (SF) is a two-step process in which a singlet (S_1) splits into two triplets ($2T_1$) throughout the so-called correlated triplet-pair (1TT) state (see Figure 1). Intramolecular SF (iSF) materials, such as oligomers and donor-acceptor (D-A) copolymers in particular,^{1,2} have attracted growing interest as they can be implemented in single junction solar cells and boost their power conversion efficiency beyond the Shockly–Queisser 33% limit up to 45%. In this context, previous work has been devoted to establishing molecular design rules³⁻⁵ and determining the mechanism that optimizes the S_1 -to- 1TT splitting process in these systems.⁶⁻⁷ These consist in appropriate *energetics*, $E(S_1) > E(2T_1)$, and *D-A coupling*, which can be achieved with well-balanced charge-transfer (CT) and local contributions.³⁻⁷ Still, their practical implementation in photovoltaic applications directly depends on their ability to go beyond the 1TT intermediate and generate free triplets ($2T_1$), which mechanism remains poorly understood. Traditionally, the 1TT binding energy is considered the minimal energy required for the separation of the triplet-pair state and is usually evaluated as the 5TT - 1TT vertical energy difference. In this work,⁸ we show that considering the 1TT binding energy is not enough to anticipate favourable intramolecular triplet-triplet dissociation rates in D-A copolymers. First, we show that both *thermodynamics* and *kinetics* play a crucial role in the intramolecular triplet-pair separation process. Second, we discuss whether it is possible and how to optimize both features simultaneously, and finally, we propose a simple model based on sequential T_1 potentials to rationalize and predict their behaviour. Overall, these results provide a better understanding of the intramolecular 1TT dissociation process in D-A copolymers and establish a new paradigm for the development of novel iSF active materials.

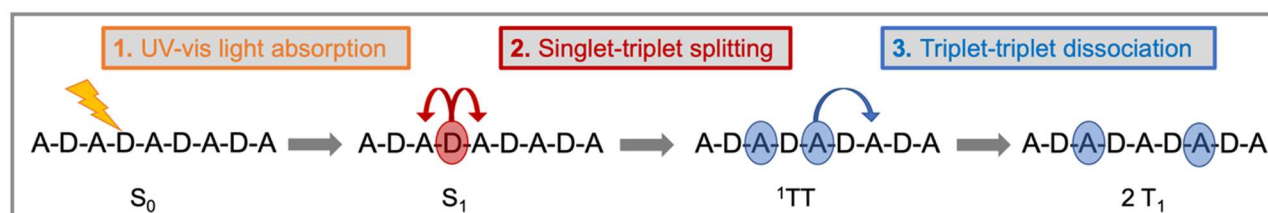


Figure 1: Schematic representation of the intramolecular singlet fission (iSF) steps in donor-acceptor (D-A) copolymers. First, UV-vis light absorption promotes S_0 to S_1 , characterized by strong D-to-A charge-transfer (CT) sideways. Second, S_1 decays via a spin-allowed process towards the triplet-pair state 1TT , localized in adjacent A. Third, the 1TT state spatially dissociates and become two independent T_1 triplets.

Acknowledgements

This work has received support from EPFL and funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant awarded to M. F. Participation to this conference has been funded by the Ramon y Cajal research program awarded to M. F.

References

1. E. Busby, J. Xia, Q. Wu, J. Low, R. Song, J. Miller, X. Zhu, L. Campos, M. Sfeir, *Nat. Mater.* 2015, **14**, 426.
2. J. Hu, K. Xu, L. Shen, Q. Wu, G. He, J.-Y. Wang, J. Pei, J. Xia, M. Sfeir, *Nat. Commun.* 2018, **9**, 2999.
3. J. T. Blaskovits, M. Fumanal, S. Vela and C. Corminboeuf, *Chem. Mater.* 2020, **32**, 6515-6524.
4. J. T. Blaskovits, M. Fumanal, S. Vela, R. Fabregat and C. Corminboeuf, *Chem. Mater.* 2021, **33**, 2567-2575.
5. J. T. Blaskovits, M. Fumanal, S. Vela, Y. Cho and C. Corminboeuf, *Chem. Commun.* 2022, **58**, 1338-1341.
6. M. Fumanal and C. Corminboeuf, *J. Phys. Chem. Lett.* 2020, **11**, 9788-9794.
7. M. Fumanal and C. Corminboeuf, *J. Phys. Chem. Lett.* 2021, **12**, 7270-7277.
8. M. Fumanal and C. Corminboeuf, *Chem. Mater.* 2022, **34**, 4115-4121.



Covalent Organic Frameworks as Platforms for the Construction of Electrocatalytic Materials

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Covalent organic frameworks (COFs) comprise an emerging class of materials based on the atomically precise organization of organic subunits into two- or three-dimensional porous crystalline structures connected by strong covalent bonds with predictable control over composition and topology.¹

In our research group we are dealing with the synthesis of COFs based on imine² and/or imide linkages³ by using both de novo synthesis and post-synthetic approaches.⁴ We are especially interested in the development of photo and electroactive COFs for energy-related applications including charge storage⁵ and catalysis.⁶ In this communication I will present our contribution for the development of functional COFs highlighting our most recent results in electrocatalytic applications.

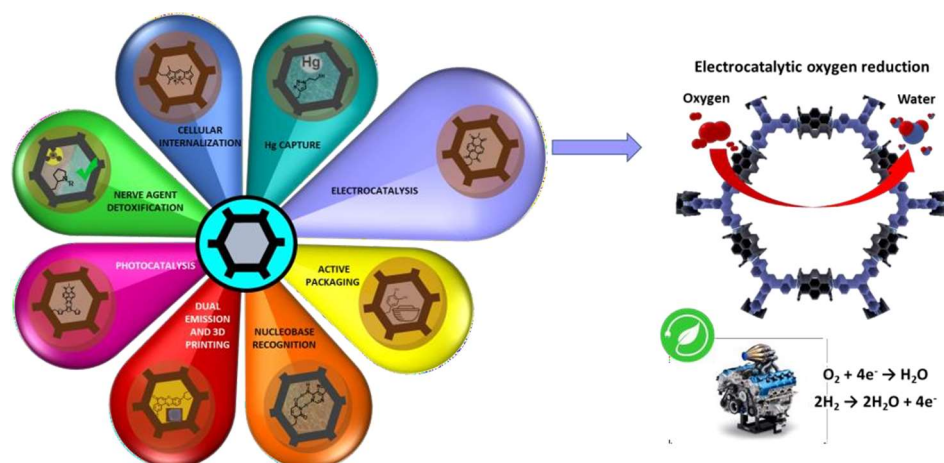


Figure 1: Applications of functional COFs synthesized in our research group highlighting electrocatalytic applications

Acknowledgements

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References

1. A.P. Citi, A.I. Benin, N.W. Ockwig, M. O'Keeffe, A.J. Matzger, O.M. Yaghi, O. M., *Science* 2005, 310, 1166.
2. J.L. Segura, M.J. Mancheño, F. Zamora, *Chem. Soc. Rev.* 2016, 45, 5635.
3. S. Royuela, E. Martínez, M. Arrieta, J.I. Martínez, M.M. Ramos, F. Zamora, E. Lorenzo, J.L. Segura, *Chem. Commun.*, 2020, 56, 1267.
4. a) J.L. Segura, S. Royuela, M.M. Ramos, *Chem. Soc. Rev.* 2019, 48, 3903; b) 5. L. Meri-Bofi, S. Royuela, F. Zamora, M.L. Ruiz-Gonzalez, J.L. Segura, R. Muñoz-Olivas, M.J. Mancheño, *J. Mater. Chem. A* 2017, 5, 17973; c) 6. S. Royuela, E. García-Garrido, M. Martín Arroyo, M.J. Mancheño, M.M. Ramos, D. González-Rodríguez, A. Somoza, F. Zamora, J.L. Segura, *Chem. Commun.*, 2018, 54, 8729; d) 7. S. Royuela, J. Almarza, M.J. Mancheño, J.C. Pérez-Flores, E.G. Michel, M.M. Ramos, F. Zamora, P. Ocón, J.L. Segura, *Chem. Eur. J.* 2019, 25, 12394; e) P. García-Arroyo, M.P. Arrieta, D. García-García, R. Cuervo-Rodríguez, V. Fombuena, M.J. Mancheño, J. L. Segura, *Polymer*, 2020, 196, 122466; f) J. A. Martín-Illán, S. Royuela, M. M. Ramos, J. L. Segura, F. Zamora, *Chem. Eur. J.* 2020, 26, 6495; g) M. Martínez-Fernández, R. Gavara, S. Royuela, L. Fernández-Ecija, J. I. Martínez, F. Zamora, J. L. Segura, *J. Mat. Chem. A*, 2022, 10, 4634;
5. S. Royuela, J. Almarza, M.J. Mancheño, J. C. Pérez-Flores, E. G. Michel, M. M. Ramos, F. Zamora, P. Ocón, J. L. Segura, *Chem. Eur. J.* 2019, 25, 12394
6. a) V. Briega-Martos, A. Ferre-Vilaplana, A. de la Peña, J.L. Segura, F. Zamora, J.M. Feliu, E. Herrero, *ACS Catal.* 2017, 7, 1015; b) M.J. Alonso-Navarro, J. Barrio, S. Royuela, N. Karjule, M.M. Ramos, J.I. Martínez, M. Shalom, J.L. Segura, *RSC Advances*, 2021, 11, 2701. c) M. Martínez-Fernández, E. Martínez-Periñán, S. Royuela, J.I. Martínez, F. Zamora, E. Lorenzo, José L. Segura, *Appl. Mater. Today*, 2022, 26, 101384; d) P. García-Arroyo, E. Martínez-Periñán, J. J. Cabrera-Trujillo, E. Salagre, E. G. Michel, J. I. Martínez, E. Lorenzo, José L. Segura, *Nano Research* 2022, 15, 3907. e) Martínez-Fernández, E. Martínez-Periñán, J. I. Martínez, M. Gordo-Lozano, F. Zamora, J. L. Segura, E. Lorenzo, *ACS Sustainable Chem. Eng.* 2023, 11, 1763.

Prediction of COF structure from ab-initio methods

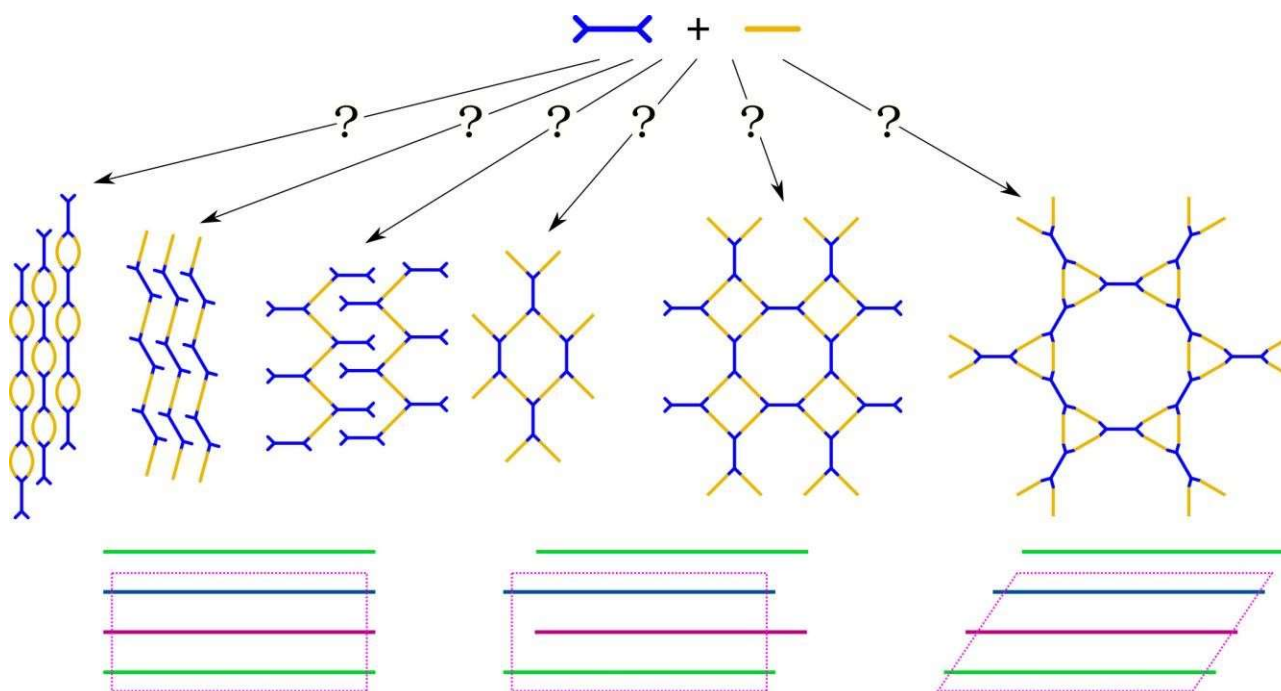


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Covalent Organic Frameworks (COFs) have shown a lot of potential as materials for gas separation and storage, liquid filtration and purification, heterogeneous catalysis, energy conversion, sensing, electronics, and storage applications.^{1–4} COFs can be built from very diverse building blocks, and assume different networks and symmetries (Scheme 1). Moreover, usually they are sizeable structures composed from tens/hundreds of atoms or exhibit large unit cells. For those reasons predicting their structure by ab-initio methods is problematic. We explore common problems with theoretical study of COFs and illustrate possible solutions with examples we encountered working on this topic.



Scheme 1: Possible Covalent Organic Frameworks build from simple building blocks.

Acknowledgements

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References

- 1 K. T. Tan, S. Ghosh, Z. Wang, F. Wen, D. Rodríguez-San-Miguel, J. Feng, N. Huang, W. Wang, F. Zamora, X. Feng, A. Thomas and D. Jiang, *Nat Rev Methods Primers*, 2023, **3**, 1–19.
- 2 X. Chen, K. Geng, R. Liu, K. T. Tan, Y. Gong, Z. Li, S. Tao, Q. Jiang and D. Jiang, *Angewandte Chemie International Edition*, 2020, **59**, 5050–5091.
- 3 M. Souto, K. Strutyński, M. Melle-Franco and J. Rocha, *Chemistry – A European Journal*, 2020, **26**, 10912–10935.
- 4 K. Geng, T. He, R. Liu, S. Dalapati, K. T. Tan, Z. Li, S. Tao, Y. Gong, Q. Jiang and D. Jiang, *Chem. Rev.*, 2020, **120**, 8814–8933.

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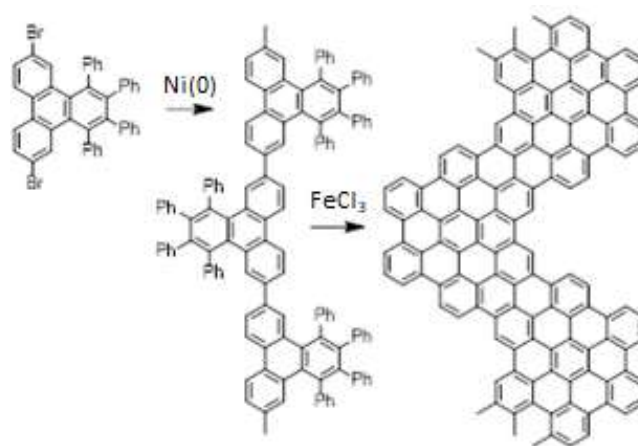
In-solution synthesis of well-defined graphene nanoribbons

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Graphene nanoribbons (GNRs) have unique electronic and mechanical properties that make them promising materials for improved electronic devices. An important feature of these materials is that the properties strongly depends on the size and shape, and therefore the development of synthetic methods to obtain well-defined GNRs by bottom-up approaches is particularly important.¹ For example, on-surface synthesis has been widely used for the preparation of GNRs, however, this methodology can limit the scalability of the final product.² There are several alternative solution-based bottom-up approaches that employs Suzuki cross couplings, Yamamoto couplings, or [4+2] cycloadditions among other reactions, combined with a final cyclodehydrogenation step to obtain GNRs in larger amounts.^{3,4,5} In this work, we explore the use of the Yamamoto coupling of dihalosubstituted precursors to obtain GNRs by solution chemistry (Scheme 1). We show that this methodology allows for precise control over the size and shape of the GNRs, and can be scaled up for large-scale production. This solution-based approach to prepare GNRs has the potential to significantly advance in the field of carbon-based nanoelectronics and paves the way for the development of novel electronic devices.



Scheme 1: Synthesis in solution of chevron graphene nanoribbons (GNRs).

Acknowledgements

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References

- [1] Z. Hao, H. Zhang, Z. Ruan, C. Yan, J. Liu, J. Cai, *ChemNanoMat.*, 2020, **6**, 493-515
- [2] Z. Chen, A. Narita and K. Müllen, *Adv. Mater.*, 2020, **32**, 2001893-2001919.
- [3] X. Yang, X. Dou, A. Rouhanipour, L. Zhi, H. J. Räder, K. Müllen, *J. Am. Chem. Soc.*, 2008, **130**, 4216-4217.
- [4] T. H. Vo, M. Shekhirev, D. A. Kunkel, M. D. Morton, E. Berglund, L. Kong, P. M. Wilson, P. A. Dowben, A. Enders, A. Sinitskii, *Nat. Commun.*, 2014, **5**, 3189-3197.
- [5] W. Niu, S. Sopp, A. Lodi, A. Gee, F. Kong, T. Pei, P. Gehring, J. Nägele, C. S. Lau, J. Ma, J. Liu, A. Narita, J. Mol, M. Burghard, K. Müllen, Y. Mai, X. Feng, L. Bogani, *Nat. Mater.*, 2023, **22**, 180-185.



Thermoelectric properties of cellulose/lignin hydrogels

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Lignocellulosic biomass from agriculture and forestry has shown enormous potential for high-value products in multiple sectors¹. Both lignin and cellulose are the main components of lignocellulosic biomass. Lignin shows a phenolic molecular structure that can be crosslinked with hydrophilic molecules to produce hydrogels. In addition, the combination of lignin and cellulose for producing hydrogels results in a myriad of possibilities in terms of controlling mechanical, swelling and morphological aspects of the final hydrogel. The presence of hydroxyl groups in both polymers allows to easily obtain an extensive three-dimensional network that can be functionalized for the targeted application. Cellulose/lignin hydrogels can be ideal platforms for ionic diffusion under temperature gradients to produce energy through the thermoelectric-effect. For this purpose, different electrolytes were infiltrated in the hydrogels to determine their thermoelectric properties. These results are very promising due to the fact that the Seebeck can be optimized increasing the salt concentration. This indicates the enormous potential of hydrogels to be used as ionic thermoelectric systems to obtain energy from waste heat.

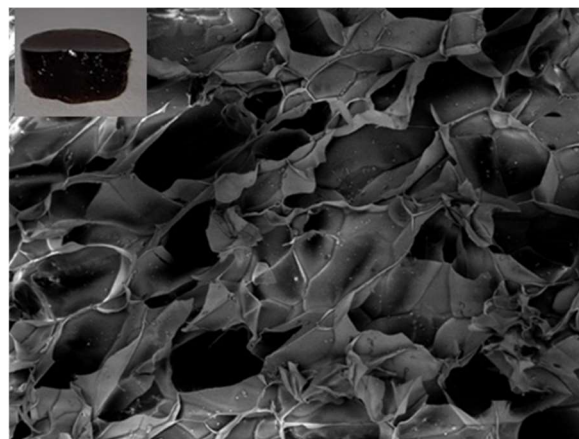


Figure 1: SEM image of Cellulose/lignin hydrogel.

Acknowledgements

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References

1. M. Culebras, A. Barrett, M. Pishnamazi, G. M. Walker and M. N. Collins, *ACS Sustainable Chemistry & Engineering*, 2021.



Development of polar phases in ferroelectric poly(vinylidene fluoride) (PVDF) nanoparticles

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Ferroelectric polymer nanoparticles of poly(vinylidene fluoride) (PVDF) were prepared by dialysis nanoprecipitation. Particles with mean diameter of 230 nm show piezoelectric response as observed by Piezoresponse Force Microscopy (PFM). The origin of this ferroelectric behavior has been attributed to the presence of ferroelectrically active crystalline phases of PVDF in the nanoparticles (mainly β and γ phases) as demonstrated by differential scanning calorimetry (DSC) and temperature dependent Fourier transform infrared spectroscopy (FTIR) and X ray diffraction. The combination of the preparation method and temperature treatment can provide a method for tuning the ferroelectricity in PVDF homopolymer nanoparticles.

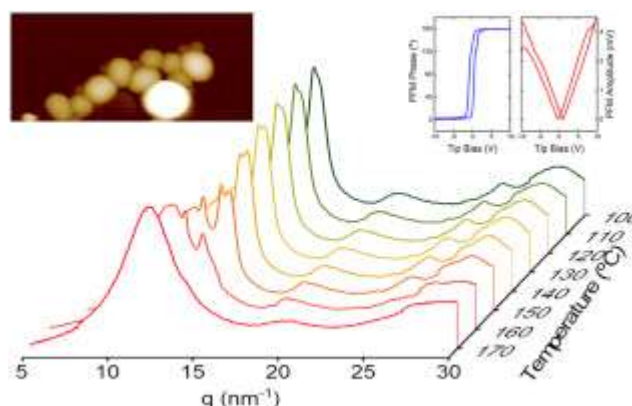


Figure 1: Nanoparticle X ray diffraction patterns as a function of temperature. Hysteresis cycles and morphology of the nanoparticles

Acknowledgements

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References

1 E. Gutiérrez-Fernández, J. Sena-Fernández, E. Rebollar, T. A. Ezquerra, F. J. Hermoso-Pinilla, M. Sanz, O. Gálvez and A. Nogales, *Polymer*, 2023, **264**, 125540.



Direct C-H arylation of dithiophene-tetrathiafulvalene

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Tetrathiafulvalene (TTF) and its derivatives are electron-donor and redox-active molecules that received a lot of attention in the field of molecular electronics [1]. The synthesis of arylated TTF derivatives allowed the formation of TTF-based extended structures such as metal-organic frameworks (MOFs), and covalent organic frameworks (COFs) [2]. Because of its high charge carrier mobility, dithiophene-tetrathiafulvalene (DT-TTF) derivative, attracted a lot of attention as an active material for organic field-effect transistors (OFETs) [3,4]. However, the direct functionalization of DT-TTF building blocks to tune its electronic structure has not yet been reported. Herein, we describe the direct C-H arylation of DT-TTF (1) to synthesize derivatives bearing different electron-donor or electron-withdrawing functional groups in order to modify its electrical structure (Fig. 1). Finally, the formation of DT-TTF-tetrabenzoic acid (H₄DT-TTFTB, 5) 2D self-assembled networks were also studied using scanning tunneling microscopy (STM).

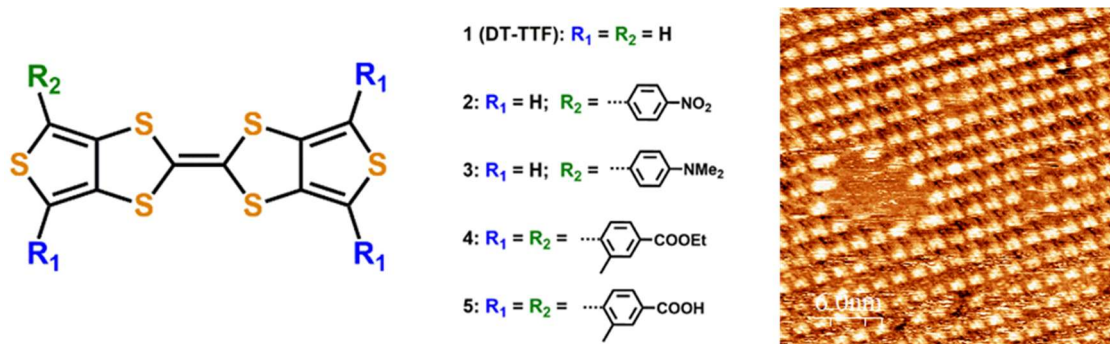


Figure 1: a) Molecular structures of arylated DT-TTF derivatives and b) STM image of physisorbed monolayer of **5** on HOPG.

Acknowledgements

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References

- [1] N. Martn, *Chem. Commun.*, 2013, **49**, 7025–7.
- [2] M. Souto, K. Strutynski, M. Melle-Franco and J. Rocha, *Chem. Eur. J.*, 2020, **26**, 10912–10935.
- [3] M. Mas-Torrent, M. Durkut, P. Hadley, X. Ribas and C. Rovira, *J. Am. Chem. Soc.*, 2004, **126**, 984–985.
- [4] R. Pfattner, S. T. Bromley, C. Rovira and M. Mas-Torrent, *Adv. Funct. Mater.*, 2016, **26**, 2256–2275.



Covalent organic framework photocatalysts for efficient degradation of waterborne pollutants

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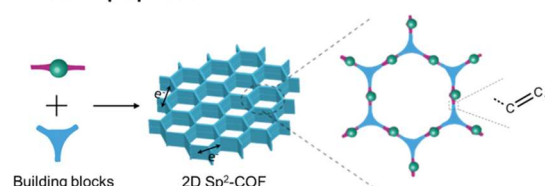
Intensive anthropogenic activities have increased the concentration of persistent and highly toxic organic pollutants in freshwater, threatening the well-being of humans and sustainability of the ecosystem.¹ The currently used water/wastewater treatments, e.g. coagulation-flocculation, flotation and membrane filtration, are expensive and ineffective against these pollutants.²

Recently, photocatalysis has shown great potential in water remediation, being clean, eco-friendly, low-cost, and enabling the degradation of waterborne pollutants into harmless substances under sunlight irradiation. However, current photocatalysts suffer from low visible light absorption and rapid charge recombination, so new materials with tailor-made properties are required.³

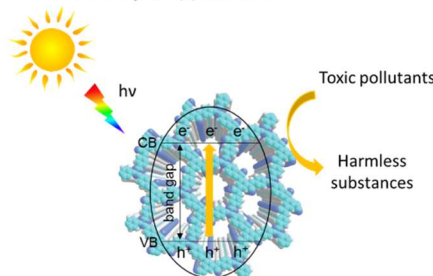
Recently emerged sp^2 -carbon-conjugated COFs show great potential as high-performance photocatalysts, due to their unparalleled characteristics, including exceptional chemical and thermal stability even under harsh conditions, high crystallinity, ordered 1D π -columns and continuous π -electron delocalization over the 2D lattice. These features, along with their large surface areas, give access to superior visible light absorption, fast mobility of charge carriers, rapid mass transport and high accessibility to the photoactive sites, crucial for high photocatalytic efficiencies.⁴

The present work describes the synthesis of a novel sp^2 -carbon-linked COF. Characterization of the material regarding its crystallinity (powder X-ray diffraction), textural properties (nitrogen adsorption/desorption), thermal stability (thermogravimetric analysis), connectivity (infrared spectroscopy) and optical properties will be shown. Photocatalytic studies of the degradation of methyl orange (MO) as model compound will also be presented. The effect of key factors will be investigated, such as photocatalyst dosage, MO initial concentration, irradiation time, and light wavelength.

1. Material preparation



2. Photocatalytic application



Scheme 1: General representation of sp^2 -carbon-linked COFs and application as photocatalyst.

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References

1. C. J. Vörösmarty, P. B. McIntyre, M. O. Gessner, D. Dudgeon, A. Prusevich, P. Green, S. Glidden, S. E. Bunn, C. A. Sullivan, C. R. Liermann and P. M. Davies, *Nature*, 2010, **467**, 555-561.
2. V. Romero, S. P. S. Fernandes, P. Kovář, M. Pšenička, Y. V. Kolen'ko, L. M. Salonen and B. Espiña, *Microporous and Mesoporous Materials*, 2020, **307**, 110523.
3. T. Banerjee, F. Podjaski, J. Kröger, B. P. Biswal and B. V. Lotsch, *Nature Reviews Materials*, 2021, **6**, 168-190.
4. S. Xu, M. Richter and X. Feng, *Accounts of Materials Research*, 2021, **2**, 252-265.



In-situ synthesis of polythiophene in a polyurethane matrix

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Organic electronics has been attracting an increasing attention of the energy materials community over the past decade. Conductive polymers have become the focus of many investigations due to their low cost, flexibility, easy chemical modification, nontoxicity, light weight, and versatility in a wide range of applications. However, one of the main challenges of conductive polymers is their processability since, due to the rigidity of the aromatic backbone and the stacking force between molecules, the solubility of conductive polymers is compromised.¹ The *in-situ* polymerization allows obtaining materials based on conductive polymers and insulating polymeric matrices, for example, by mixing the host polymeric matrix with monomers, precursors of the conductive polymer, that in presence of an initiator polymerize. An interpenetrating polymeric network (IPN) is obtained formed by at least a polymer synthesized in the presence of another one to form a cross-linked network where the two polymers are mixed at the molecular level.

In this work, we report the *in-situ* synthesis of polythiophene (PT) in presence of two oxidants salts, silver perchlorate (AgClO_4) and copper (II) perchlorate ($\text{Cu}(\text{ClO}_4)_2$), embedded in a polyurethane (PU) matrix to form an IPN conducting polymer.² The reaction is very fast and is carried out in solid state during the thermal annealing after spin-coating. In this method, the thiophene polymerization, and doping reaction occur simultaneously within a host matrix (Figure 1). The presence of Ag nanoparticles (NPs) significantly improves the electrical properties of the resulting IPN film. A complete understanding of the polymerization process is provided to optimize the conducting and thermoelectric properties. This approach allows us to design hybrid nanocomposite materials with high flexibility in terms of compositions and morphology and the possibility of optimizing and tuning the electrical properties of the final film. In addition, the complete procedure is industrially scalable for large-area printing, representing a good opportunity for the industry to produce the next generation of conductive materials and devices at a reduced cost.

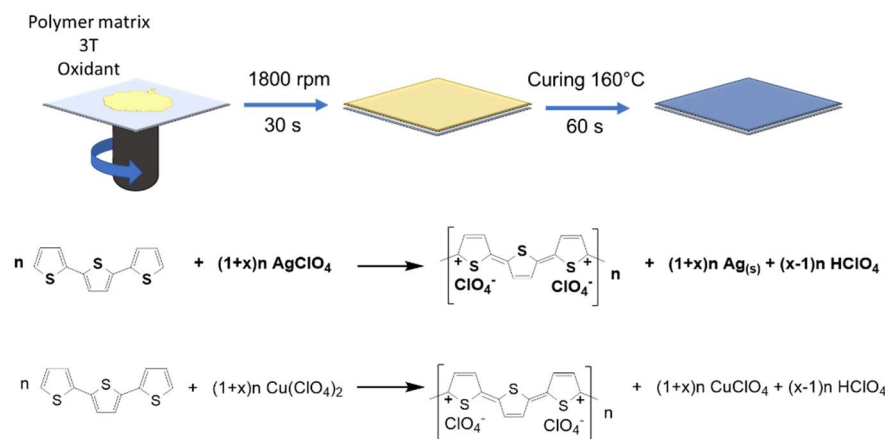


Figure 1: Synthesis procedure of polythiophene films in a polyurethane matrix and oxidative polymerization of terthiophene by AgClO_4 and $\text{Cu}(\text{ClO}_4)_2$.

Acknowledgements

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References

- 1 Y. Yang, H. Deng and Q. Fu, *Mater. Chem. Front.*, 2020, **4**, 3130–3152.
- 2 J. F. Serrano-Claumarchirant, A. S.-D. Silva, J. F. Sánchez-Royo, M. Culebras, A. Cantarero, C. M. Gómez and R. Abargues, *ACS Appl. Energy Mater.*, 2022, **5**, 11067–11076.



Soft free-standing multilayered membranes made of marine-origin polysaccharides for controlled therapeutics delivery

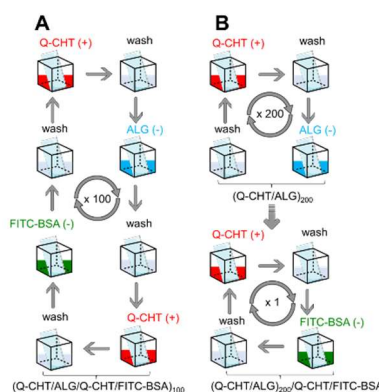
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The Layer-by-Layer (LbL) assembly technology has been widely used to functionalize surfaces and engineer robust architectures under mild conditions, with finely tuned properties and functions at nanoscale, by resorting to a myriad of building blocks exhibiting complementary intermolecular interactions.¹ In particular, chitosan (CHT), extracted from crustaceans' shells, and alginate (ALG), extracted from brown algae, are attractive marine-origin polysaccharides commonly used for the development of supramolecular multilayered assemblies due to their bioavailability, biocompatibility, biodegradability, non-cytotoxicity, non-immunogenic properties and opposite charge nature.^{2,3} However, the insolubility of CHT in physiological conditions limits the use of LbL structures with CHT in biological and biomedical applications.

In this work, we propose the development of free-standing membranes enclosing water-soluble quaternized CHT (Q-CHT) and ALG for the release of model hydrophobic drug molecules. To study the influence of the film structure in the release rate, two different free-standing membranes, having either the model drug fluorescein isothiocyanate-labeled bovine serum albumin (FITC-BSA) as an intrinsic building block [(Q-CHT/ALG/Q-CHT/FITC-BSA)₁₀₀] or added after the assembly of the membranes [(Q-CHT/ALG)₂₀₀/Q-CHT/FITC-BSA], have been produced (**Scheme 1**). The morphology, thickness, release rate and *in vitro* biocompatibility of both free-standing multilayered membranes towards human umbilical cord-mesenchymal stem cells was evaluated, compared, and will be discussed. We foresee that this work could open new avenues on the development of a wide array of CHT-based biomedical devices under physiological conditions for a multitude of bioapplications.



Scheme 1: Schematic overview of the preparation of the two set-ups of free-standing membranes: **(A)** (Q-CHT/ALG/Q-CHT/FITC-BSA)₁₀₀ and **(B)** (Q-CHT/ALG)₂₀₀/Q-CHT/FITC-BSA assembled onto poly(vinyl carbonate) substrates.

Acknowledgements

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References

- 1 J. Borges and J.F. Mano, *Chem. Rev.*, 2014, **114**, 8883-8942.
- 2 J.M. Silva, R.L. Reis and J.F. Mano, *Small*, 2016, **12**, 4308-4342.
- 3 N.I. Martins, M.P. Sousa, C.A. Custódio, V.C. Pinto, P.J. Sousa, G. Minas, F. Cleymand and J.F. Mano, *Acta Biomater.*, 2017, **57**, 313-323.



Processing of porous organic polymers as free-standing membranes using a dip-assisted Layer-by-Layer assembly methodology

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Covalent Organic Frameworks (COFs) are crystalline porous materials based on organic building blocks that have emerged in the past few years towards a wide range of applications including gas adsorption and separation, energy storage and biomedicine¹⁻³. In particular, TpPa-COF (based on 1,3,5-triformylphloroglucinol and phenylenediamine) has been receiving considerable attention due to its high chemical and thermal stability, as well as high sorption capacity³. However, this organic porous material is commonly synthesized as a powder, thus not enabling its full exploitation and use in practical applications.

This work aimed to process TpPa-COF as a free-standing membrane through the dip-assisted Layer-by-Layer (LbL) assembly methodology⁴. Free-standing membranes encompassing multilayers ranging from 10 to 250 bilayers were processed and characterized for their chemical, morphological and mechanical properties via attenuated total reflectance-Fourier transform infrared spectroscopy, powder X-ray diffraction, scanning electron microscopy and universal mechanical testing machine, respectively. The gathered results were compared with the ones obtained for TpPa-COF, in the powder form, obtained through solvothermal and microwave syntheses. The LbL assembly process resulted in a microporous membrane (pore size of 1.88 nm), with thickness of ca. 40 μm and homogenous surface morphology. Additionally, the powder TpPa-COF showed high thermal stability and selectivity towards CO₂ adsorption, with a total capacity of 102.48 cm³ g⁻¹ at 1 bar and 273 K, which makes it of special interest for gas separation applications when obtained as a membrane. Therefore, the developed free-standing multilayered membranes show great promise for being used in practical applications, including in gas sorption/separation and controlled drug/therapeutics delivery.

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References

- [1] S. Kandambeth, A. Mallick, B. Lukose, M. V. Mane, T. Heine and R. Banerjee, *J. Am. Chem. Soc.*, 2012, **134**, 19524–19527.
- [2] K. Geng, T. He, R. Liu, S. Dalapati, K. T. Tan, Z. Li, S. Tao, Y. Gong, Q. Jiang and D. Jiang, *Chem. Rev.*, 2020, **120**, 8814–8933.
- [3] H. Wei, S. Chai, N. Hu, Z. Yang, L. Wei and L. Wang, *Chem. Commun.*, 2015, **51**, 12178–12181.
- [4] J. Borges and J. F. Mano, *Chem. Rev.*, 2014, **114**, 8883–8942.



Unexpected solubility of non-functionalized TEMPO in aqueous solution and its application for redox flow batteries

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Redox flow batteries (RFB) are a unique type of batteries which allows decouple power and energy. Moreover, they exhibit other desirable features such as safety, design flexibility and, scalability. All these together make them promising candidates for large-scale energy storage applications¹. However, the all-vanadium and zinc-bromide RFB, which are the most mature technologies, use expensive and toxic electrolytes hindering their massive expansion into the market. Hence, in recent years, organic redox active compounds have been considered as sustainable alternative to replace the vanadium and bromide species due to their high availability, synthetic versatility, and lower cost. Among the large variety of reported organic molecules² the (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) has been widely used due to its good redox kinetics and excellent chemical and electrochemical stability³. However, due to the low solubility of TEMPO in water (≈ 70 mM) this molecule cannot be used in aqueous RFBs. Although with a proper chemical functionalization the solubility of TEMPO-derivatives increases, the long-term stability of the functionalized TEMPOs is usually worse than the pristine TEMPO⁴.

In our research, we report a different and simple approach to solubilize large amount of pristine TEMPO in aqueous solution. Our approach consists on modifying the properties of the supporting aqueous electrolyte to promote intimate interaction between supporting salt and pristine TEMPO. By doing that, we have demonstrated that the pristine TEMPO reaches an unprecedented solubility record (up to 5.6 M in presence of supporting electrolyte) that results in an unheard-of high theoretical volumetric capacity as high as 150 Ah/L_{catholyte}. This extraordinary solubility relies on the essential interaction of TEMPO with the supporting salts ions, as it was confirmed by molecular dynamics calculations.

Interestingly, the electrochemical performance of TEMPO in this supporting electrolyte was demonstrated to be excellent with a highly reversible redox reaction, outstanding kinetics ($k_0 = 0.018$ cm/s) and impressive long-term stability in symmetric RFB configuration (0.552%/day). Moreover, this new TEMPO catholyte was paired with a sulfonated viologen anolyte resulting in a RFB with a theoretical energy density of 22.15 Wh/L and an open-circuit voltage of 1.08 V. In addition, this hitherto unseen aqueous redox flow battery presents a very low capacity fading over cycling (0.60%/day and 0.048%/cycle). This work paves the way to the development of new redox electrolytes and broaden the opportunities of aqueous redox flow batteries.

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References

- 1 P. Alotto, M. Guarnieri and F. Moro, *Renew. Sustain. Energy Rev.*, 2014, **29**, 325–335.
- 2 K. Wedege, E. Dražević, D. Konya and A. Bienten, *Sci. Rep.*, 2016, **6**, 1–13.
- 3 Y. Liu, M.-A. Goulet, L. Tong, Y. Liu, Y. Ji, L. Wu, R. G. Gordon, M. J. Aziz, Z. Yang and T. Xu, *Chem*, 2019, **5**, 1861–1870.
- 4 W. Zhou, W. Liu, M. Qin, Z. Chen, J. Xu, J. Cao and J. Li, *RSC Adv.*, 2020, **10**, 21839–21844.
- 5 E. Pedraza, C. de la Cruz, A. Mavrandonakis, R. Rubio-Presa, R. Sanz, E. Ventosa, S.T. Shentilkumar*, P. Navalpotro*, R. Marcilla*. Submitted to *Joule* (Under revision).



A novel coarse-grain molecular dynamic simulation framework to unravel the impact of ionic liquids in TX-114 micellar solutions

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A novel coarse-grained molecular dynamics (CG-MD) framework based on the MARTINI force field was developed for TX-114 aqueous solutions and mixtures with Imidazolium-based $[C_n\text{mim}]\text{Cl}$ ($n= 10, 14$) or Phosphonium-based $[P_{4,4,4,14}]\text{Cl}$ ILs. The Pluronic TX-110 developed by Pizzirusso et al.⁴ was taken as a reference from which five EO groups were eliminated to resemble the TX-114 moiety. A CG-MD simulation for 0.15 %wt of TX-114 aqueous solution was run to validate the model, yielding a micellar aggregation number (67) in agreement with experiments (62-88).^{5,6} The CG-MD models for the $[C_{10}\text{mim}]\text{Cl}$, $[C_{14}\text{mim}]\text{Cl}$, $[P_{4,4,4,14}]\text{Cl}$ ILs and chloride anions were taken from the literature.⁷⁻⁹ A set of CG-MD simulations were performed for 3%wt TX-114 concentration in aqueous solution mixed with 2.5mM of $[C_{10}\text{mim}]\text{Cl}$, $[C_{14}\text{mim}]\text{Cl}$ or $[P_{4,4,4,14}]\text{Cl}$ to compare with the experimental trials.¹⁰ Simulations exhibited diverse TX-114 structures, from spherical to prolate shape or rod like vesicles depending on the IL. Simulations provided significant information regarding the initial stages of the cooperative TX-114 and ILs self-assembly. Figure 1 shows the simulation snapshots for the four tested solutions, indicating that addition of $[C_{10}\text{mim}]\text{Cl}$ promotes a sphere-to-rod transition. Conversely, small spherical vesicles were found with $[C_{14}\text{mim}]\text{Cl}$ where a quick formation of charged $[C_{14}\text{mim}]^+$ micelles hindered the absorption by early TX-114 aggregates. Addition of $[P_{4,4,4,14}]\text{Cl}$ yielded a prolate structure similar to the $[C_{10}\text{mim}]\text{Cl}$ mixture, indicating a greater impact of the stearic character of butyl groups compared with alkyl tail-tail interactions.

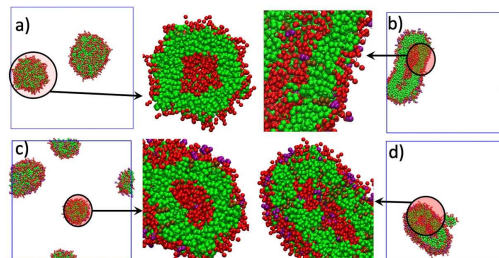


Figure 1: CG-MD simulations snapshots for a) 3 %wt. TX-114 aqueous solution and their mixtures with ionic liquids (IL): b) 2.5mM of $[C_{10}\text{mim}]\text{Cl}$, c) 2.5mM $[C_{14}\text{mim}]\text{Cl}$ and d) 2.5 mM $[P_{4,4,4,14}]\text{Cl}$. A detailed picture of the IL organization inside the TX-114 vesicles is shown for each system. The color code is as follows; the hydrophobic and hydrophilic regions of TX-114 moieties are in green and red, respectively. The ILs are colored in brown and purple for the alkyl chains and head groups, respectively. Water molecules and chlorides were removed for clarity.

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References

- (1) A. Pizzirusso, A. De Nicola and G. Milano, *J. Phys. Chem. B*, 2016, 120, 3821.
- (2) G. Komaromy-Hiller, N. Calkins, and R. von Wandruszka, *Langmuir*, 1996, 12, 916.
- (3) T. Sun, S. Gao, Q. Chen and X. Shen, *Colloids Surfaces A Physicochem. Eng. Asp.*, 2014, 456, 18.
- (4) N. Schaeffer, H. Passos, M. Gras, V. Mogilireddy, J. P. Leal, G. Pérez-Sánchez, J. R. B. Gomes, I. Billard, N. Papaiconomou and J. A. P. Coutinho, *Phys. Chem. Chem. Phys.*, 2018, 20, 9838.
- (5) E. A. Crespo, N. Schaeffer, J. A. P. Coutinho and G. Perez-Sanchez, *J. Colloid Interface Sci.*, 2020, 574, 324.
- (6) G. Pérez-Sánchez, F. A. Vicente, N. Schaeffer, I. S. Cardoso, S. P. M. Ventura, M. Jorge, and J. A. P. Coutinho, *J. Phys. Chem. B*, 124, 2020, 7046.
- (7) Cecília Naomi Nakamura, Nathalia V. Veríssimo, Fernanda Oliveira, Clarissa P. Frizzo, G. Pérez-Sánchez, João A. P. Coutinho, Jorge F. B. Pereira, and Valéria C. Santos-Ebinuma, manuscript under preparation.



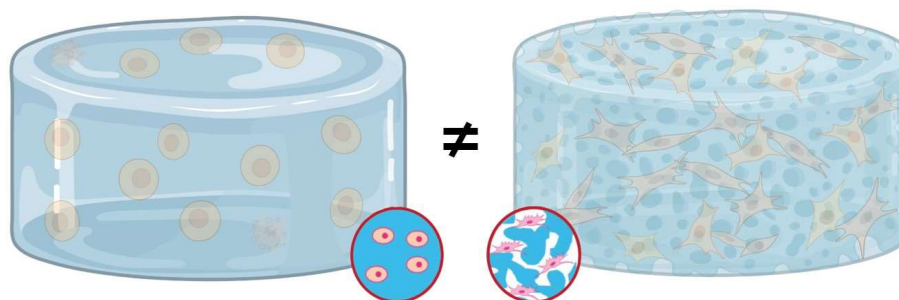
Production of Interconnected Microporous Methacrylated Gelatin Hydrogels by Aqueous Two-phase Enabled Emulsion Templating

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Collagen is a cell degradable, protein-based polymer that represents the main constituent of the extracellular matrix (ECM) where it provides support for the cells in the tissues, allowing their adhesion, proliferation and function. Gelatin is an easily obtainable version of denatured collagen that retains most of its organic properties. The addition of methacryloyl groups to gelatin, originating GelMA allows their photocrosslinking in aqueous solution into hydrogel scaffolds that can replicate the mechanical and biochemical properties of the ECM, supporting cell proliferation and their gradual development into functional organotypic tissues.^{1,2} The resulting hydrogels generally consist of nanoporous networks that limit cell motility, cell-cell interactions and the diffusion of nutrients, oxygen, and waste, thus limiting their potential in tissue engineering applications. Interconnected microporous hydrogels (IMPHs) are being increasingly explored to mitigate these issues as their cell scaled pores provide space for cell and medium movement.^{1,2} Emulsion templating is a simple and highly versatile technique to manufacture IMPHs based on the mixing of a pre-gel with an immiscible liquid porogen to form an emulsion where the porogen phase is volumetrically suspended throughout the pre-gel. Originally porogen phases consisted on organic solvents such as toluene or chloroform, but aqueous two-phase systems (ATPSs), based on immiscible aqueous biopolymer solutions, have been replacing them as greener and citocompatible alternatives allowing the inclusion of cells in the pre-gel, further simplifying the construction of the scaffolds.¹⁻³ Herein we explored, ATPS-enabled emulsion templating to produce porous Gelatin-methacrylate (GelMA) hydrogels through the use of Poly(ethylene oxide) (PEO) and dextran based porogens. Different volumetric fractions ranging from 30 to 50% were investigated. The obtained hydrogel constructs exhibit different microarchitectures and interconnected pores with sizes ranging from 10 to 50 μm . Overall, the PEO/dextran porogens were successfully leveraged to produce GelMA hydrogels with intrinsic cell adherent features that are to be further explored for tissue engineering and disease modelling applications in the foreseeable future.



Scheme 1: Schematic comparison of cells encapsulated in a bulk hydrogel (left) with cells encapsulated in an interconnected microporous hydrogel (right).

Acknowledgements

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References

- 1- GL. Ying, N. Jiang, S. Maharjan YX. Yin, RR Chai, X. Cao, JZ. Yang, AK. Miri, S. Hassan and YS. Zhang, *Adv. Mater.* 2018, 30(50).
- 2- S. Yi, Q. Liu, Z. Luo, JJ. He, HL. Ma, W. Li, D. Wang, C. Zhou, CE. Garciamendez, L. Hou, J. Zhang and YS. Zhang, *Small* 2022, 18(25).
- 3- XS. Qin, M. Wang, W. Li and YS. Zhang, *Regener. Eng. Transl. Med.* 2022 471–481.



Covalent organic frameworks supported on alumina for the capture of water contaminants

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Emerging contaminants are found in natural waters with increasing frequency, which not only affects aquatic ecosystems, but also directly impacts public health¹. Of particular concern are persistent contaminants that are not efficiently removed by wastewater treatment. Although dangerous, the concentration of these contaminants in water is usually low (ppb or ppt), which makes their detection through direct water analysis challenging. Therefore, there is a need for more efficient and selective methods to extract and pre-concentrate these pollutants.²

Covalent organic frameworks (COFs) are a class of crystalline porous materials that are formed by reversible covalent bonds³. The linker characteristics, such as size, symmetry, and connectivity, define the geometry of the resulting framework. Structural diversity, low density, high crystallinity with permanently uniform pore shape and size render them materials of high interest for adsorption applications, and therefore, COFs are increasingly explored efficient adsorbent materials for selective water pollutant capture.²

A challenge regarding their usage is that typically COFs are prepared in powder form, thus limiting their recovery and consequently their reusability. As a way to address this, we present herein the development of COFs supported on alumina pellets. The functionalization of the pellets will be described, as well as subsequent COF growth. Characterization of the materials was done using vibrational fingerprinting from the material organization (Raman spectroscopy), morphology (SEM) and textural properties (nitrogen adsorption). Finally, studies on the adsorption of water contaminants were carried out, comparing the adsorption of bulk and supported COFs.

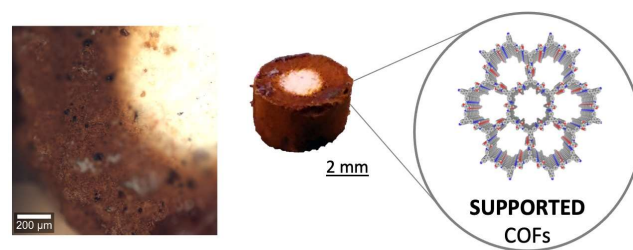


Figure 1: Supported covalent organic framework on an alumina pellet

Acknowledgements

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References

- 1 M. M. Khin, A. S. Nair, V. Jagadeesh Babu, R. Murugan and S. Ramakrishna, *Energy Environ. Sci.*, 2012, 5, 8075–8109.
- 2 S. P. S. Fernandes, V. Romero, B. Espiña and L. M. Salonen, *Chem. - A Eur. J.*, 2019, 25, 6461–6473.
- 3 M. S. Lohse and T. Bein, *Adv. Funct. Mater.*, 2018, 33, 1705553



3D C₆₀ fullerite clathrate

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Investigations of a new 3D C₆₀ polymer with clathrate structure were performed recurring to Density Functional Theory (DFT). Double 5/5 2+3 cycloaddition bonds are formed between each C₆₀ molecule and its twelve nearest neighbors in the face-centered cubic lattice. Remarkably, this bonding generates, on octahedral sites, new C₆₀ cages identical to the original ones, and on tetrahedral sites, distorted sodalite-like cages. The polymer's electronic and elastic properties were also evaluated via DFT simulations. Only twenty percent of its atoms are sp²-hybridized, leading to a narrow gap semiconducting behavior. Above the Fermi level there is a big density of states peak indicating that proper doping may yield the structure metallic and hence a possible high T_c superconductor. The new phase is likely to be prepared by applying high-pressure and high-temperature treatments of C₆₀.

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References

[1] J. Laranjeira, L. Marques, M. Melle-Franco, K. Strutynski and M. Barroso. Clathrate structure of polymerized fullerite C₆₀. Carbon 194 (2022) 291-302. <https://doi.org/10.1016/j.carbon.2022.03.055>



Self-Assembled Bioactive Colloidal Gels as Injectable Multi-Particle Platforms

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Comprised by nanosized building blocks capable of self-organizing into hierarchically complex 3D networks, colloidal gels constitute a highly attractive platform for biomedical applications.¹ Leveraging on intrinsic supramolecular mechanisms (e.g., Van der Waals forces, magnetic interactions, and electrostatic forces), these versatile platforms present attractive physicochemical properties, including self-healing, multimodal degradation, viscoelasticity or shear-thinning, that can be useful for potentiating advanced tissue engineering applications.^{2,3} Moreover, due to their superior drug delivery properties, including higher cargo load capacity, prolonged lifespan, and focalized delivery, colloidal gels constitute an attractive drug delivery system capable of overcoming the concerns regarding the rapid clearing of freely administrated nanotherapeutics.¹ Herein, colloidal gels were generated via electrostatically-driven self-assembly of oppositely charged nanoparticles of poly(D,L-lactide-co-glycolide)-polyethylenimine (PLGA-PEI) and zein-hyaluronan (zein-HA), produced via nanoprecipitation solvent evaporation technique (Figure 1). The resulting colloidal gels were exploited as versatile bioactive 3D platforms for focalized and autonomous release of bioactive Quercetin flavonoids to bioinstruct processes in macrophages. Overall, the generated fully nanostructured gels revealed autonomous multiparticle shedding, providing a focalized and efficient delivery of bioinstructive cues, capable of reducing key proinflammatory biomarkers (nitrite) in pro-inflammatory macrophages (Figure 1).

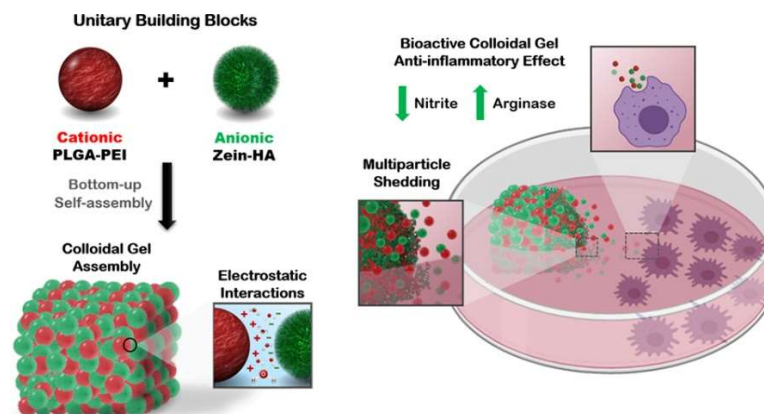


Figure 1: Illustration of bottom-up self-assembly process of nanosized colloidal gels with anti-inflammatory properties.

Acknowledgements

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References

- [1] B. Freitas, P. Lavrador, R. J. Almeida, V. M. Gaspar, J. F. Mano, *ACS Applied Materials & Interfaces* 2020, **12**, 31282-31291.
- [2] W. Gao, Y. Zhang, Q. Zhang, L. Zhang, *Annals of Biomedical Engineering* 2016, **44**, 2049-2061.
- [3] M. Diba, S. Spaans, K. Ning, B. D. Ippel, F. Yang, B. Loomans, P. Y. W. Dankers, S. C. G. Leeuwenburgh, *Advanced Materials Interfaces* 2018, **17**, 1-21.



Wood inspired biobased nanocomposite films for active packaging

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The intensive use and waste disposal of common petroleum-based plastics, with short lifetimes, like food packaging films or trash bags has been raising increasing concerns¹. On this basis, the concept of active biobased packaging arises as an eco-friendly alternative technology, contributing to the reduction of waste, while improving the safety and quality of the food^{2,3}.

In this context, the aim of the current work was to prepare functional wood inspired biopolymeric nanocomposite films by solvent casting of blends of beechwood xylans and lignosulfonates, reinforced with nanofibrillated cellulose, aiming at producing films with antioxidant and UV blocking properties and improved mechanical performance.

The optical properties, antioxidant activity, mechanical performance, thermal stability, and moisture uptake capacity of the obtained biobased films were assessed to demonstrate their potential for application for active packaging. All films presented good homogeneity, translucency, and thermal stability up to 153 °C. The incorporation of nanofibrillated cellulose into the xylan/lignosulfonates matrix provided good mechanical properties to the films (Young's modulus = 1.08 – 3.79 GPa and tensile strengths at break up = 12.75 – 14.02 MPa). The lignosulfonates imparted the films with antioxidant capacity (DPPH scavenging = 71.57 – 82.40 %) and UV protection (transmittances ≤ 18.6 % (200 – 400 nm)). These results, show the potential of using low-cost and eco-friendly resources for the development of sustainable active food packaging materials.



Figure 1: Schematic illustration of the preparation of the films.

Acknowledgements

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References

- 1 G. Fiorentino, M. Ripa and S. Ulgiati, *Biofuels, Bioprod. Biorefining*, 2017, **11**, 195–214.
- 2 C. Vilela, M. Kurek, Z. Hayouka, B. Röcker, S. Yildirim, M. D. C. Antunes, J. Nilsen-Nygaard, M. K. Pettersen and C. S. R. Freire, *Trends Food Sci. Technol.*, 2018, **80**, 212–222.
- 3 S. Yildirim, B. Röcker, M. K. Pettersen, J. Nilsen-Nygaard, Z. Ayhan, R. Rutkaite, T. Radusin, P. Suminska, B. Marcos and V. Coma, *Compr. Rev. Food Sci. Food Saf.*, 2018, **17**, 165–199.



Electrostatic-driven LbL assembly of neutral marine polysaccharides through chemical functionalization

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The Layer-by-Layer (LbL) assembly technique has emerged as a simple, cost-effective, and highly versatile technology for coating surfaces and fabricating multifunctional multilayered assemblies at the nanoscale¹. The intricate landscape of intermolecular interactions has been widely scrutinized over the years, with a particular emphasis on the role of electrostatic interactions between oppositely charged polyelectrolytes². Natural cationic and anionic polysaccharides have been widely studied in LbL assemblies, while neutral ones have been overlooked due to their low chemical versatility. Herein, we explore the potential of marine-origin neutral polysaccharides, namely laminarin (LAM) and pullulan (PUL) as building blocks in electrostatic-driven LbL assemblies for various biomedical applications. We present a novel approach to functionalize LAM and PUL with charged peptides (positively charged – K₆; negatively charged – D₆) through Cu(I)-catalyzed azide–alkyne cycloaddition to synthesize positively and negatively charged polysaccharide-peptide conjugates (Figure 1). The electrostatic-driven LbL build-up of either LAM-D₆/LAM-K₆ or PUL-D₆/PUL-K₆ multilayered thin films was monitored *in situ* by quartz crystal microbalance with dissipation monitoring, revealing the successful multilayered film growth and the enhanced stability of the PUL-based films. The construction of the PUL-peptide multilayered thin film was also assessed by scanning electron microscopy and its biocompatibility demonstrated *in vitro* towards L929 mouse fibroblasts. We anticipate that this work could enable the inclusion of any kind of small molecules in the multilayered assemblies, thus extending the usefulness of neutral polysaccharides and opening new avenues in the biomedical field, including in controlled drug/therapeutics delivery, tissue engineering and regenerative medicine strategies.

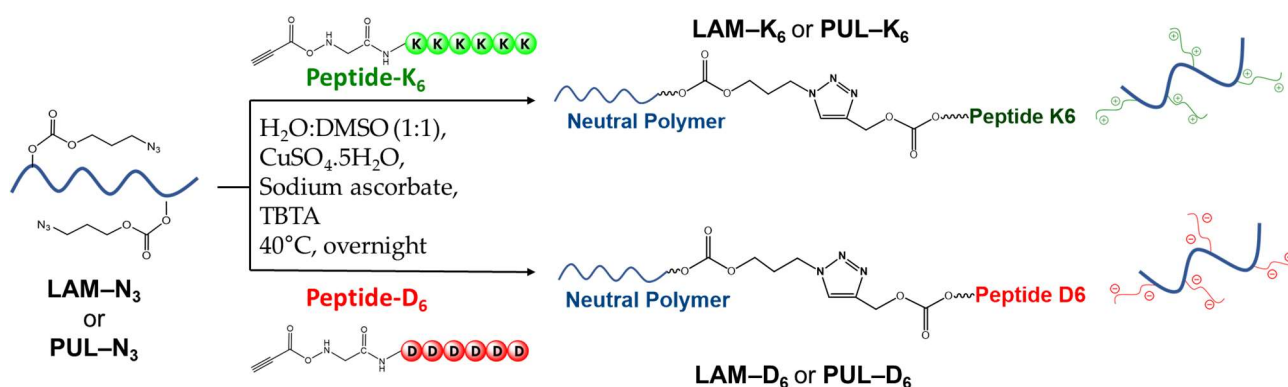


Figure 1 – Chemical route used to couple the charged peptides to the marine polysaccharide.

Acknowledgements

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials (UIDB/50011/2020, UIDP/50011/2020 and LA/P/0006/2020), financed by national funds through the FCT/MEC (PIDDAC) and in the scope of the projects COP2P (PTDC/QUIQOR/30771/2017 – POCI-01-0145-FEDER-30771) and SUPRASORT (PTDC/QUI-OUT/30658/2017 – CENTRO-01-0145-FEDER-030658). L.P.G.M., J.B. and J.M.M.R. gratefully acknowledge FCT for the individual PhD grant (2020.06767.BD) and individual researcher contracts (2020.00758.CEECIND and CEECIND/01363/2018), respectively.

References

- ¹ J.J. Richardson, M. Björnalm, F. Caruso, *Science* **2015**, *348*, aaa2491.
- ² J. Borges, J.F. Mano, *Chemical Reviews* **2014**, *114*, 8883.



Stimuli-responsive poly(phenylacetylene)s containing chiral allenes as pendants

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Helices are one of the most abundant structural motifs present in many macromolecules such as proteins, DNA, or polysaccharides and are directly related to the biological functions of these biomolecules. This strong structure/function relationship led the scientific community to look for novel materials that adopt helical structures. In this sense, poly(phenylacetylene)s (PPAs) are a good example of this due to the possibility of tuning their helical structure once the polymer is synthesized.¹ Furthermore, helix inversion in chiral dynamic helical polymers is usually achieved by a conformational change at the monomeric repeating unit (m.r.u.) induced by an external stimulus.^{2,3,4} Herein, we show a novel helix inversion mechanism produced in a PPA bearing a chiral and rigid m.r.u. group, via the activation/deactivation of a supramolecular interaction. In this work, we have prepared a PPA that bears a chiral allene as m.r.u. group. This chiral allene is conformationally locked, and therefore its substituents are located in a specific orientation, the largest being the one that commands the helical sense of the PPA. This command can be surpassed as long as supramolecular interactions are established between the other allenic substituents and appropriate external stimuli. In such case, a new helix induction command is produced, which results in the helix inversion of the PPA. Thus, this helix inversion effect, produced by a novel axial-to-helical communication mechanism, gives a new perspective to control the helix of chiral dynamic helical polymers.

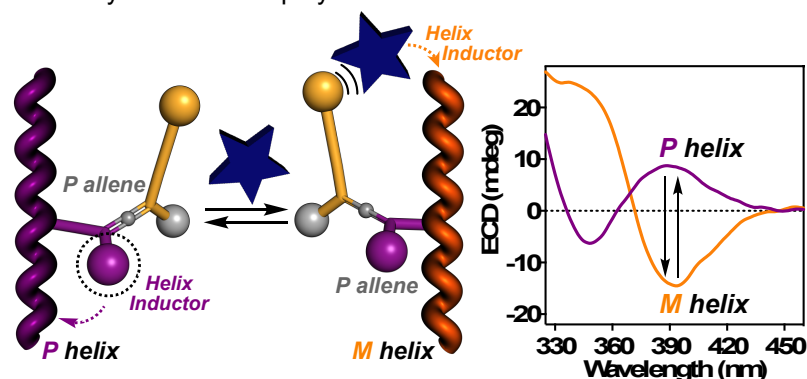


Figure 1: Conceptual view of the chiral information transmission mechanism from the allenic pendants to the polyene backbone through axial-to-helical communication.

References

1. F. Freire, E. Quiñoá, R. Riguera, *Chem. Rev.* **2016**, *116*, 1242-127.
2. Y. -Z. Ke, Y. Nagata, T. Yamada, M. Suginoe, *Angew. Chem., Int. Ed.* **2015**, *54*, 9333-9337.
3. R. Rodríguez, E. Suárez-Picado, E. Quiñoá, R. Riguera, F. Freire, *Angew. Chem., Int. Ed.* **2020**, *59*, 8616-8622.
4. Z. Fernández, B. Fernández, E. Quiñoá, R. Riguera, F. Freire, *Chem. Sci.* **2020**, *11*, 7182-7187.



Carrageenan-based Bioinks reinforced with Lysozyme Nanofibers for Extrusion Bioprinting

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Within the field of 3D bioprinting, the development of high performance bioinks with adequate mechanical and rheological properties and high cell viability, is still a major challenge. Among the several types of bioinks, hydrogels have been widely explored due to their similarities with the extracellular matrix (ECM) and tunable mechanical and rheological properties. Engineered hydrogel bioinks based on natural polymers, namely polysaccharides, are being widely explored.¹ Among them, κ -Carrageenan closely mimics the glycosaminoglycan structure of one of the most important constituents of native tissues ECM, and forms hydrogels via thermo and ionic gelation, rendering strong, but brittle hydrogels.² Currently, the development of nanocomposite bioinks has been broadly explored and the incorporation of bioactive nanofibrous materials into native hydrogel-based bioinks improves structural stability and shape fidelity during and after printing, as well as cell growth, proliferation, and differentiation. Considering this approach, protein nanofibers, viz. lysozyme nanofibers, have excellent properties in terms of mechanical strength and stability, in combination with antimicrobial and cell-adherent activities, and can be used as building nanoblocks for the design of novel nanocomposite bioinks.³

Herein, we explored the incorporation of lysozyme nanofibers into κ -Carrageenan based hydrogels for the development of advanced nanocomposite bioinks with improved rheological, mechanical, and biological performance. These bioinks were characterized in terms of physicochemical parameters, rheological behavior, and biological activity, to produce cell-laden analogues via extrusion bioprinting.

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References

- 1 M. C. Teixeira, N. S. Lameirinhas, J. P. F. Carvalho, A. J. D. Silvestre, C. Vilela and C. S. R. Freire, *Int. J. Mol. Sci.*, 2022, **23**, 6564.
- 2 S. M. Mihaila, A. K. Gaharwar, R. L. Reis, A. P. Marques, M. E. Gomes and A. Khademhosseini, *Adv. Healthc. Mater.*, 2013, **2**, 895–907.
- 3 M. C. Teixeira, N. S. Lameirinhas, J. P. F. Carvalho, B. F. A. Valente, J. Luís, L. Pires, H. Oliveira, M. Oliveira, A. J. D. Silvestre, C. Vilela and C. S. R. Freire, *Nanomaterials*, 2022, **12**, 2190.



Carbon Yarn Coated with PEDOT:PSS for Flexible Supercapacitors: Exploring Electro spray Process

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The growing demand for flexible electronic devices and electronic textiles (e-textiles) has motivated the exploration of alternative energy storage solutions such as textile-based supercapacitors. These devices can have a variety of configurations, being one of them the 1D configuration, which is the simplest while maintaining reliability in energy storage capabilities¹. Although there is much interest in the production of textile-based supercapacitors, this is not always an easy task and may require the use of complex and expensive fabrication techniques such as wet-spinning². In this study, we propose the use of electro spray (ES) as a facile deposition technique, for the fabrication of functionalized carbon yarn electrodes for fibre-shaped supercapacitors (FSCs). With this technique we can deposit, the highly conductive polymer, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), creating thin films composed of coalesced nanoparticles over the carbon yarns. Different deposition parameters were optimized using ES technique, such as flow rate, distance between the tip of the nozzle, and applied potential. With optimal deposition conditions, PEDOT:PSS functionalized carbon yarn electrodes, proved to be a reliable way to fabricate FSCs. These devices have shown excellent electrochemical performance with specific capacitance attaining 63 mFg⁻¹ and cyclic and bending stability showing remarkable results, with capacitance retention of 85 % after 1500 charge and discharge cycles.

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References

- 1 N. Lima, A. C. Baptista, B. M. M. Faustino, S. Taborda, A. Marques and I. Ferreira, *Sci. Rep.*, 2020, **10**, 1–9.
- 2 A. Rafique, I. Ferreira, G. Abbas and A. C. Baptista, *Recent Advances and Challenges Toward Application of Fibers and Textiles in Integrated Photovoltaic Energy Storage Devices*, Springer Nature Singapore, 2023, vol. 15.



Study of the thermoelectric effect in ionic membranes and 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 work aims to explore the viability of lignin-based ionic platforms as thermoelectric material made from clean and sustainable resources. The ionic platform was a hydrogel made of a solution of sodium hydroxide, organosolv lignin and PEGDGE as crosslinker. The samples were encapsulated between two electrodes to measure the properties of interest: Seebeck coefficient and electrical conductivity to determine their suitability for thermoelectric applications. Large Seebeck coefficients (in the range of 2-5 mV K⁻¹) were obtained in the prepared samples, and a positive correlation between the Seebeck coefficient and ion concentration embedded in the hydrogel was observed. The resulting hydrogel was found to be good from the mechanical point of view and stable at temperatures <100 °C, making it suitable for thermoelectric applications, for low-grade heat conversion. In addition, further characterization tests were performed on the samples with techniques such as FTIR, TGA and SEM.

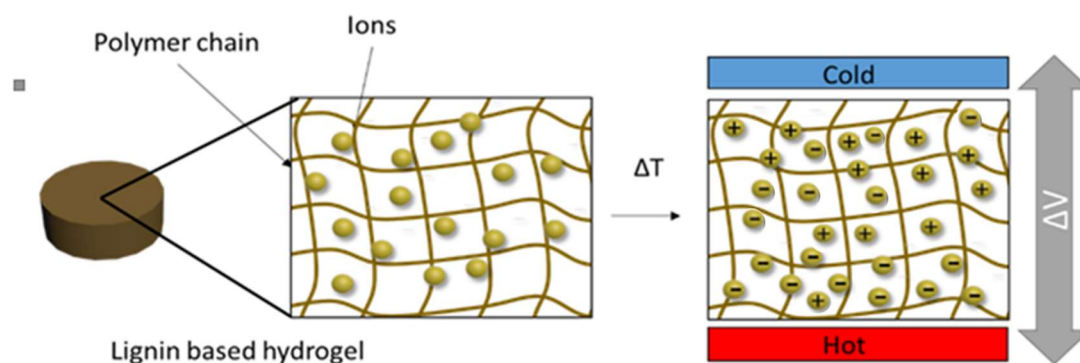


Figure 1: Lignin based hydrogel schematic and ion drift under the action of a temperature gradient

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References

1. Y. He, Q. Zhang, H. Cheng, Y. Liu, Y. Shu, Y. Geng, Y. Zheng, B. Qin, Y. Zhou and S. Chen, *The Journal of Physical Chemistry Letters*, 2022, **13**, 4621-4627.



Bottom-up design of functional bio-inspired polymeric materials: from *in silico* chemistry to their green production

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The antibody market is expected to reach EUR 218 billion at the end of this year, growing at an annual rate of ~12%.¹ However, the antibody production/purification has several limitations, such as the use of low-efficient isolation methods and low cost-effectiveness.² Moreover, the development of more sustainable functional materials and processes is needed to address environmental challenges, efficiency, scale-up and low cost. Molecular Imprinted Polymers (MIPs) are synthetic materials within specific affinity sites complementary in size, conformation and functionality to the target molecule. MIPs are significantly advantaged when compared to natural antibodies, since they use low-cost starting materials, are robust, stable under harsh conditions, have a long lifetime, and are easily stored. Herein, L-leucine (LEU)-MIPs are being developed as sustainable *bio-inspired* polymers from a bottom-up perspective. Firstly, rational design using quantum mechanics calculations and molecular modeling were performed to select the most appropriate functional monomers and understand their interactions with template (LEU). LEU-MIPs were synthesized by two different green approaches (Figure 1), supercritical carbon dioxide (scCO₂) technology and mechanochemistry (ball milling).³ MIP production under scCO₂ has a great potential on the development of high-value materials.⁴ ScCO₂ technology is non-toxic, non-flammable, scalable, has a very accessible critical point and is easily tuned by simply adjusting pressure and temperature.⁵ On the other hand, ball mill is an expanding technology that is also easily scalable, requires low-cost equipment and operates under solventless conditions.⁶ Both green technologies were effectively applied in the syntheses of LEU-MIPs, which were obtained as dry, free-flowing powders with yields up to 80%. The performance of the materials produced, were assessed by static binding tests using several concentrations of LEU (0.5 and 1.5 mg/mL) that revealed very promising results, with a maximum imprinting factor (*IF*) of 13 for the LEU-MIP synthesized in scCO₂, and an *IF* of 1.4 for the ball milled LEU-MIP. Both green technologies have been showing high potential in obtaining ready-to-use, stable and low-cost *bio-inspired* polymers with biorecognition ability for target biomolecule, able to compete with natural molecules and, envisaging a great potential for bio-applications including biopurification processes.



Figure 2: Green strategies for LEU-MIP development.

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References

- 1 Antibodies Market Size, Share, Trends, Growth & Outlook – 2033, <https://www.futuremarketinsights.com/reports/antibodies-market>, (accessed 25 January 2023).
- 2 M. Teufl, C.U. Zajc and M.W. Traxlmayr, *ACS Synth. Biol.*, 2022, **11**, 1030–1039.
- 3 A.I. Furtado, R. Viveiros, V.D.B. Bonifácio, A. Melo, T. Casimiro, *accepted in ACS Omega*, 2023.
- 4 CleanMIPTech, <https://sites.fct.unl.pt/clean-mip-tech/home>, (accessed 30 January 2023).
- 5 A.I. Furtado, R. Viveiros, T. Casimiro, *Methods mol. biol. (Clifton, N.J.)*, 2021, **2359**, 19–42.
- 6 J.L. Do. and T. Friščić, *ACS Cent. Sci.*, 2017, **3**, 13–19.



Three-component Synthesis of Pyrene-fused Azaacene Covalent Organic Frameworks

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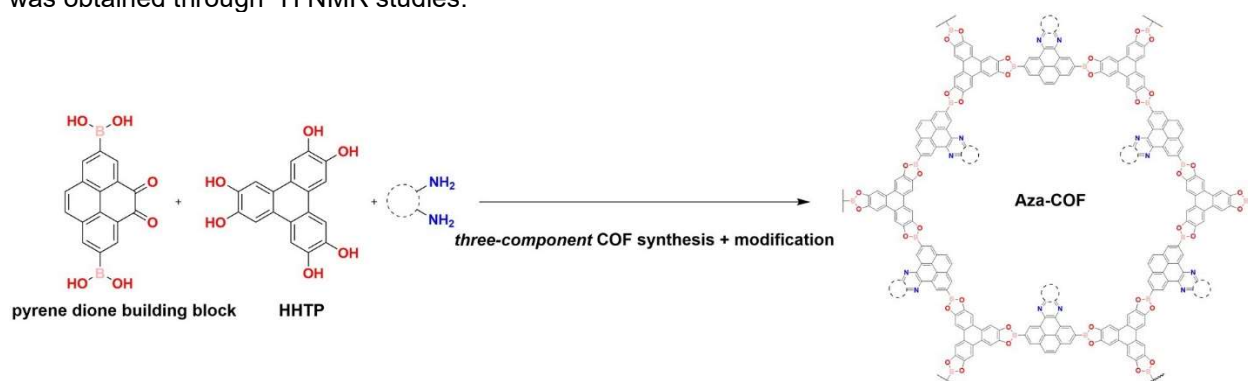
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Abstract: Covalent Organic Frameworks (COFs) are nanoporous materials formed by self-assembly of organic building blocks. Their characteristics such as high crystallinity and regular porosity make them attractive materials for numerous applications. Two main strategies are typically employed for the functionalization of COFs: the modification of the reacting building blocks with the desired functionalities, and post-synthetic modification, where the functionalization is performed in a different reaction step, after the synthesis and isolation of the COF. Both these strategies have some limitations, such as, for the former, possible solubility issues of the functionalized building block in the COF synthesis conditions as well as unfavorable stacking. For the latter, possible low stability of the framework under the reaction conditions together with low yield of post-synthetic modification are the most common.¹ Furthermore, incorporation of azaacenes moieties in COF structures can be advantageous considering their interesting photophysical properties mainly as light emitting materials.²

Herein, a novel approach for the formation of COFs containing extended aromatics is presented based on three-component synthesis, where building block and COF synthesis take place simultaneously at a similar time scale.³ Using fragmental building block components, namely pyrene dione diboronic acid as aggregation-inducing COF precursor and diamines extending functionalization units along with 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP), gave access to pyrene-fused azaacene, i.e., Aza-COF series with full conversion of the dione moiety (Scheme 1). Insight into the COF formation and reactivity of the building blocks was obtained through ¹H NMR studies.



Scheme 1: Schematic illustration of the three-component synthesis of the Aza-COF series using multiple diamines.

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References

- [1] a) J. L. Segura, S. Royuela, M. Mar Ramos, *Chem. Soc. Rev.*, 2019, **48**, 3903.; b) L. Frey, J. J. Jarju, L. M. Salonen, D. D. Medina, *New J. Chem.*, 2021, **45**, 14879.
 [2] J. P. Mora-Fuentes, I. Papadopoulos, D. Thiel, R. Álvarez-Boto, D. Cortizo-Lacalle, T. Clark, M. Melle-Franco, D. M. Guldi, A. Mateo-Alonso, *Angew. Chem. Int. Ed.*, 2020, **59**, 1113.
 [3] Under revision



Ab initio characterization of the polyvinylidene difluoride phases and their interaction with Carbon Nanotubes

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Polyvinylidene difluoride (PVDF) is a polymer with exceptional characteristics, such as its outstanding ferroelectric, piezoelectric and thermoelectric properties¹. Its high stability makes it biocompatible and suitable for several kinds of applications, as for example actuators, sensors, energy harvesting and energy storage. Nonetheless, the synthesis of the electroactive phases (Figure 1) of this polymer is still challenging, and can be enhanced by the addition of carbon nanotubes (CNT) into the polymer matrix². Here we present a DFT study on the properties and structures of the PVDF-CNT nanocomposites.

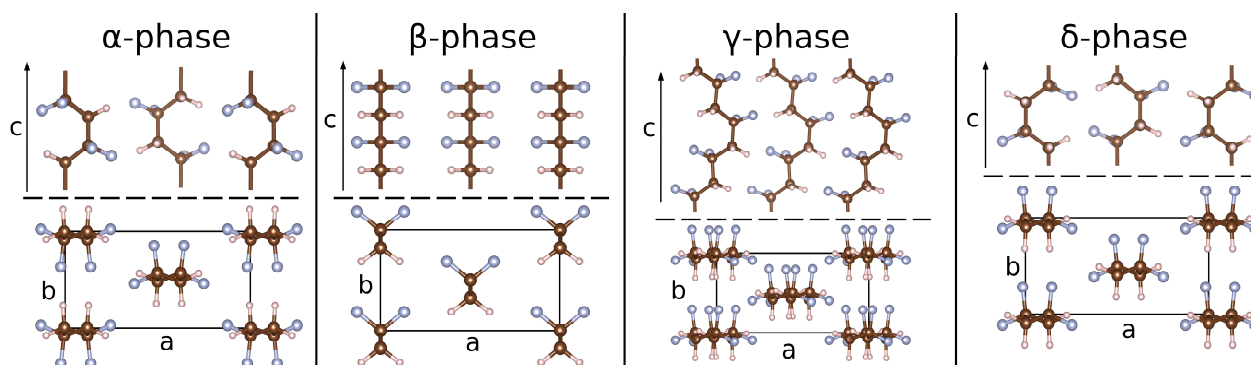


Figure 1: Views of the different phases of PVDF, being the β , γ and δ the electroactive ones.

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References

- (1) P. Martins, A. C. Lopes, and S. Lanceros-Mendez, *Prog. Polym. Sci.*, 2014, **39**, doi: 10.1016/j.progpolymsci.2013.07.006.
- (2) E. Kabir, M. Khatun, L. Nasrin, M. J. Raihan and M. Rahman, *J. Phys. D: Appl. Phys.*, 2017, **50**, doi: 10.1088/1361-6463/aa5f85.



Inter and intra molecular dynamics in poly(trimethylene 2,5-furanoate) as revealed by infrared and Broadband Dielectric Spectroscopies

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Infrared spectroscopy (IR) and Broadband Dielectric Spectroscopy (BDS) experiments have been performed in poly(trimethylene 2,5-furanoate)(PTF) and poly(trimethylene terephthalate)(PTT) below their glass transition temperatures. The BDS experiments reveal a richer inter-molecular dynamic for PTT as characterized by a multimodal β relaxation in contrast with the monomodal one exhibited by PTF. The evolution with temperature of comparable IR absorption bands is very similar for PTF and PTT and shows small shifts in wavenumbers towards lower values, with exception of the band related to the stretching mode of the carbonyl group. In addition, a significant difference appears in the shape of the bands associated with the $-C=O$ stretching. While for PTT the absorption feature is comprised of a single component, that for PTF exhibits several components suggesting the presence of hydrogen bonds. This effect may be responsible for the monomodal shape of the β relaxation of PTF since a higher degree of intramolecular coupling between the furan ring and the rest of the monomer is expected. Density Functional Theory (DFT) calculations support the experimental results revealing that as temperature increases an increment of the syn conformations of the 2,5-furandicarboxylic acid (FDCA) moiety is likely to occur in the amorphous state. The energy gain from more stable anti to less stable syn isomers can be compensated by the formation of hydrogen bonds between interchain FDCA moieties in syn conformations. This effect may cause additional hindrance to the intermolecular dynamics of the dielectric β relaxation. It is conceivable that the hindrance exhibited by PTF in both intra and inter-molecular dynamics may play a role in the reduction of gas diffusion and permeability of PTF in comparison with PTT.

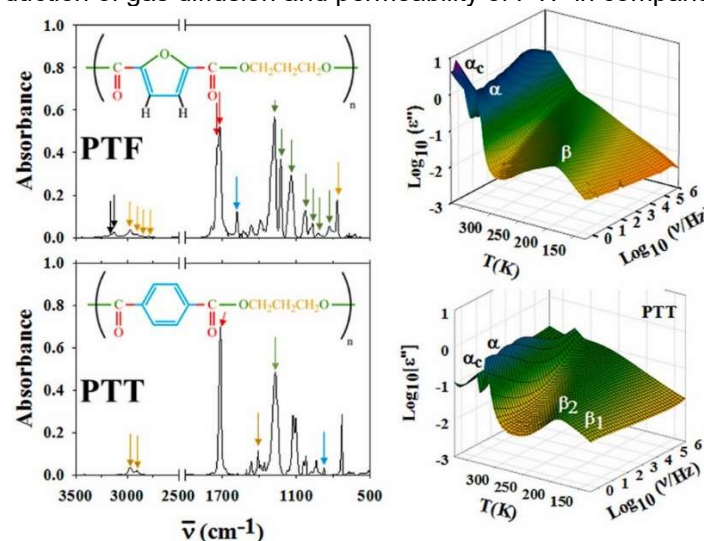


Figure 1: FTIR absorption spectra and dielectric loss data, ϵ'' , versus temperature (T) and frequency (ν) for PTF and PTT.

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References

1, O. Gálvez, O. Toledano, F. J. Hermoso, A. Linares, M. Sanz, E. Rebollar, A. Nogales, M. C. García-Gutiérrez, G. Santoro, I. Irska, S. Paszkiewicz, A. Szymczyk, T. A. Ezquerro, *Polymer*, 2023, **268**, 125699.



Redox-Active Tetrathiafulvalene-based Covalent Organic Frameworks as cathodes for lithium batteries

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Covalent organic frameworks (COFs) are an emerging class of crystalline porous materials constructed from organic building blocks linked by covalent bonds. Due to their great chemical and structural, COFs have received a lot of interest towards applications in gas sorption and separation, catalysis or sensing, among others.¹ More recently, 2D COFs have received particular interest for electronics,² optoelectronics,³ and energy related applications,⁴ due to the possibility of 2D π -conjugation. The intrinsic porosity of the COFs, combined with the electrical conductivity derived from the 2D π -conjugation can lead to exciting new electronic related applications, unattainable with either 1D polymers or inorganic 2D materials.⁵

Tetrathiafulvalene (TTF) and its derivatives are organic molecules with outstanding electron-donor and redox properties, making them the ideal candidates as building blocks for the preparation of redox-active COFs for electronic and energy-related applications.² Herein we present a new family of TTF-based COF with different building blocks, in order to study the influence of the spacer between the TTF moieties on the electrical conductivity. The neutral and doped TTF-based COFs were characterized by multiple spectroscopic techniques in order to fully understand the charge transport mechanisms occurring in these materials. Finally, some TTF-COFs were explored as organic cathodes for lithium batteries.

Acknowledgements

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References

- [1] K. Geng, T. He, R. Liu, S. Dalapati, K. T. Tan, Z. Li, S. Tao, Y. Gong, Q. Jiang and D. Jiang, *Chem. Rev.* **2020**, *120*, 8814.
- [2] M. Souto, K. Strutynski, M. Melle-Franco and J. Rocha, *Chem. Eur. J.* **2020**, *26*, 10912.
- [3] M. Souto, D. F. Perepichka, J. Mater. Chem. C. **2021**, *9*, 10668.
- [4] J. Rotter, R. Guntermann, M. Auth, A. Mähringer, A. Sperlich, V. Dyakonov, D. Medina and Thomas Bein, *Chem. Sci.* **2020**, *11*, 12843.
- [5] H. Ding, Y. Li, H. Hu, Y. Sun, J. Wang, C. Wang, C. Wang, G. Zhang, B. Wang, W. Xu and D. Zhang, *Chem. Eur. J.*, **2014**, *20*, 14614 – 14618.



Full Control of the Chiral Overpass Effect in Helical Polymers

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In helical polymers, helical sense induction is usually commanded by teleinduction mechanism, where the largest substituent of the chiral residue directly attached to the main chain is the one that commands the helical sense. In this work, different helical structures with different helical senses are induced in a helical polymer [poly-(phenylacetylene)] when the conformational composition of two different dihedral angles of a pendant group with more than two chiral residues is tamed. Thus, while the dihedral angle at chiral residue 1 [(*R*)- or (*S*)-alanine], attached to the backbone, produces an extended or bent conformation in the pendant resulting in two scaffolds with different stretching degree, the second dihedral angle at chiral residue 2 [(*R*)- or (*S*)-methoxyphenylacetamide] places the substituents of this chiral center in a different spatial orientation, originating opposite helical senses at the polymer that are induced through a total control of the “chiral overpass effect”.

Multi-State Chiral Overpass Induction: Control of Both Elongation and Handedness

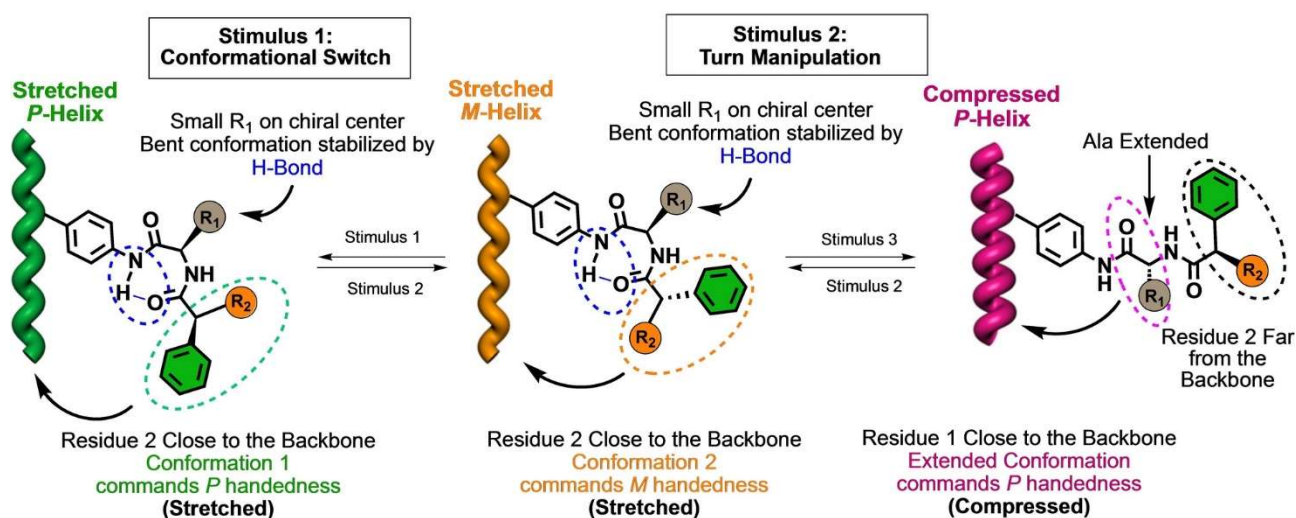


Figure 1: Conceptual representation of the total control of the chiral overpass

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References

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Redox-active Covalent Organic Frameworks as electrode materials for lithium-ion batteries

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Today the energy sector is still the main contributor towards global warming, raising the urgency for a faster transition from fossil fuels to cleaner energy sources. Due to the renewable's intermittent availability problem, there is an increased need for better, safer, and more sustainable energy storage solutions.¹ This communication focuses on the use of Covalent Organic Frameworks (COFs), a type of crystalline porous organic polymer, as electrode materials for lithium-ion batteries. First, the focus is centered on the synthesis and characterization of two different redox-active COFs, DAAQ-TFP-COF² and TTF-BT-COF.³ Afterwards, the synthesized materials were used as electrodes in coin-cell type lithium batteries.⁴ For that purpose, the electrode preparation process was optimized, and the batteries were manufactured and tested. Additionally, the electrodes based on DAAQ-TFP-COF were further studied using Scanning Kelvin Probe (SKP), a non-destructive and non-invasive technique that allows the study of the chemical surface's potential on a delimited sample area. Lastly, Soft X-ray Transmission Microscopy (TXM) measurements performed at ALBA's MISTRAL synchrotron beamline were used to study the homogeneity of the state of charge within the DAAQ-TFP-COF electrodes with DAAQ-TFP-COF as well as the lithiation process by using electrodes at a different state of charge and discharge and with different particle thickness. These results were useful to further uncover relations between covalent organic frameworks and their application as electrode materials for rechargeable batteries.

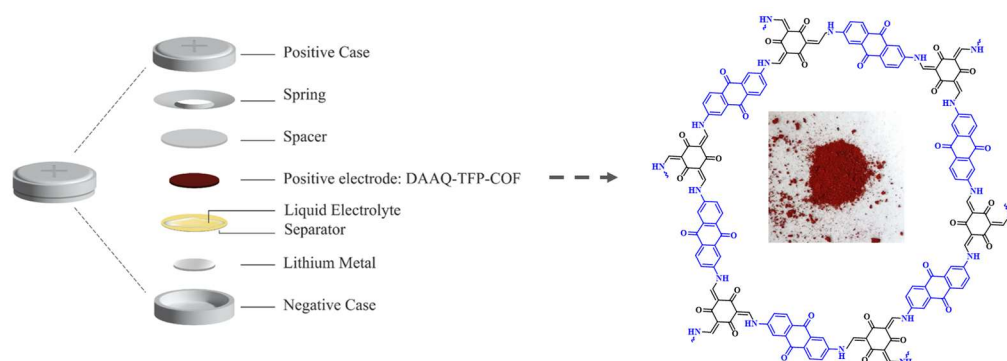


Figure 1: Schematic representation of the electrochemical half-cell assembly, as well as the representation of DAAQ-TFP-COF used as the positive electrode.

Acknowledgements

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References

- 1 Independent Evaluation Office (IEO) of the United Nations Development Programme (UNDP), *Evaluation of UNDP Support to Energy Access and Transition*, 2021.
- 2 C. R. Deblase, K. E. Silberstein, T. T. Truong, H. D. Abruña and W. R. Dichtel, *J Am Chem Soc*, 2013, **135**, 16821–16824.
- 3 J. N. Chang, Q. Li, J. W. Shi, M. Zhang, L. Zhang, S. Li, Y. Chen, S. L. Li and Y. Q. Lan, *Angewandte Chemie - International Edition*, 2023, DOI:10.1002/anie.202218868.
- 4 S. Wang, Q. Wang, P. Shao, Y. Han, X. Gao, L. Ma, S. Yuan, X. Ma, J. Zhou, X. Feng and B. Wang, *J Am Chem Soc*, 2017, **139**, 4258–4261.



Supramolecular hyaluronic acid-functionalized G-quadruplex based perfusable hydrogels for bioapplications

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DNA is not only one of the most intriguing macromolecules in nature but also an unprecedented building block to precisely assemble sophisticated supramolecular bionanostructures. Among them are the G-quadruplex which are noncanonical four-stranded structures that are formed in guanine-rich DNA sequences and serve multiple biological functions.¹⁻³ Herein, a novel dynamic hyaluronic acid (HA)-functionalized G-quadruplex hydrogel with self-healing, thermo-reversible, injectable and conductive properties was developed at physiological pH via hydrogen-bonding and π - π interactions between guanines coupled via dynamic boronate ester bonds to the 3-aminophenylboronic acid functionalized HA and stabilized by K⁺ ions, as demonstrated by a combined experimental-computational study. The well-known instability of the G-quadruplex structures was used to produce interconnected, size and shape tunable perfusable hollow microchannels embedded in virtually any kind of photocrosslinkable supporting matrices at physiological conditions (Figure 1). The microchannel-embedded 3D constructs showcased a higher number of viable cells than the 3D bulk constructs. Moreover, the cells migrated toward the perfusable microchannels, holding great promise for being use as artificial vessels for enabling the diffusion of nutrients and oxygen essential for cell survival. The versatility imparted by the proposed approach opens new avenues in drug delivery, tissue engineering and regenerative medicine.

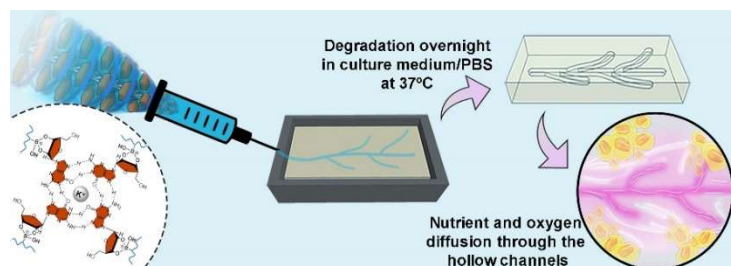


Figure 1. Schematic representation of bioengineered perfusable 3D constructs obtained by the supramolecular self-assembly of HA-functionalized G-quadruplex hydrogels as sacrificial materials.

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References

1. M. L. Bochman, K. Paeschke and V. A. Zakian, *Nat. Rev. Genet.*, 2012, **13**, 770-780.
2. R. Hänsel-Hertsch, M. Di Antonio and S. Balasubramanian, *Nat. Rev. Mol. Cell Biol.*, 2017, **18**, 279-284.
3. D. Varshney, J. Spiegel, K. Zyner, D. Tannahill and S. Balasubramanian, *Nat. Rev. Mol. Cell Biol.*, 2020, **21**, 459-474.



Polysaccharides-based hydrogel with cross-linked chitosan nanoparticles

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Polysaccharides, which have received much attention from the beginning and are still being investigated today, represent a diverse class of raw materials with enormous advantages over other materials for the preparation of hemostatic materials and drug delivery systems.

In the model of wound healing management, it is important to use drugs with antibiotic activity in hemostatic materials. Caraginan-based gels have been shown to have good biocompatibility and this hydrogel can support tissue repair. Moreover, the hydrogel may be useful for the delivery of biomolecules.

The konjac glucomannan forms a hydrogel, which has excellent antibacterial and hemostatic ability due to electrostatic and hydrophobic interactions between cell membrane and functional groups. Konjac glucomannan can confer anti-inflammatory effects to the hydrogel by activating macrophages.

Chitosan is a competitive candidate for hemostatic material and drug delivery systems. It is a polymer with antibacterial properties and the possibility of chemical modification. Chitosan can also form microspheres for drug delivery. The use of chitosan nanoparticles with a modified surface (functional groups) will make it possible to better distribute the particles in the matrix and possibly interact with the polysaccharide groups. This will allow the drugs to be released gradually.

We have proposed the creation of hydrogel materials with netted nanoparticles inside that can be used in healing wounds and haemostatics.

By the method of ionic gelation chitosan nanoparticles were obtained. Sodium tripolyphosphate was used for this purpose. The optimal ratio of chitosan and sodium tripolyphosphate was chosen to obtain nanoparticles [1]. Distribution of nanoparticles and lamellae from chitosan looks like a cross-linked 3-d structure (figure 1). Quercetin has been used as a drug with anti-inflammatory activity.

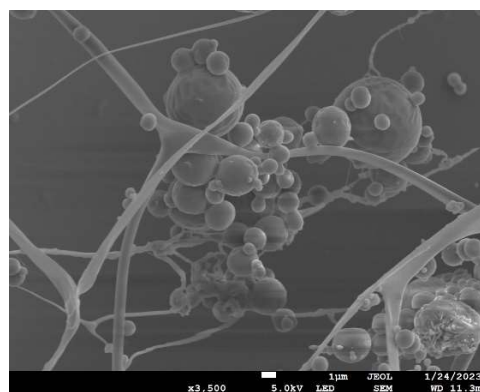


Figure 1: Chitosan nanoparticles

As the hydrogel matrix were used k-caraginan and conjac glucomannan [2]. Optimal concentrations for introducing nanoparticles into the hydrogel matrix were selected. Optimally, there should be a gradual release of nanoparticles with the drug. Therefore, it is important that the nanoparticles are bonded to each other and that the release does not occur immediately.

References

1. K. Vieira Jardim, J. L. Neves Siqueira, S. Nair Bão, A. Luis Parize, Journ. of Drug Del. Scien. and Tech., DOI: 10.1016/j.jddst.2022.103561
2. Y. Chen, C. Song, Y. Lv, X. Qian, Polymer, DOI: 10.1016/j.polymer.2019.121913

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Ionic Covalent Organic Frameworks for Energy and Environment purposes.

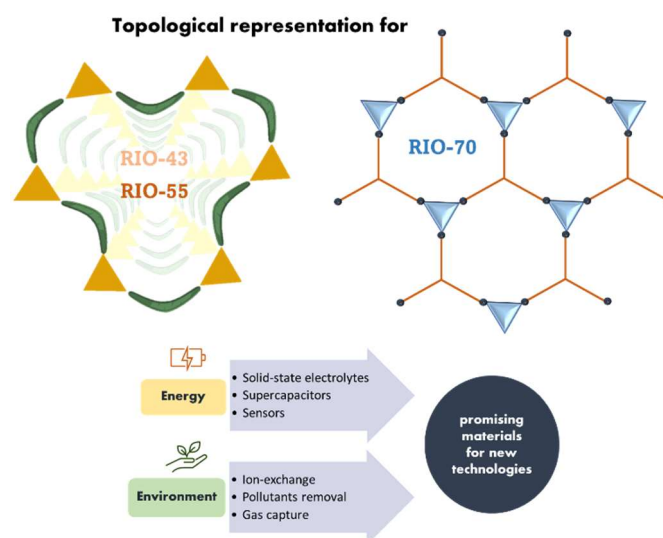
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Covalent Organic Frameworks (COFs) are an emergent class of nanoporous materials that have shown great versatility, involving applications as such as water treatment, gas capture, batteries, solar cells, catalysis, thermal insulation, etc.^{1,2}. Among the various subgroups for COFs, the ionic networks have presented a more attractive performance, mainly about ion exchange, electrical conductivity, more affinity with adsorbates (e.g.: metals and gases), etc.^{3,4} In this work, some ionic materials were developed from commercial dyes, carrying interesting physical-chemical properties. Called Reticular Innovative Organic compounds (RIOs), these porous structures are built through condensation reactions between aromatic amines and aldehyde groups^{5,6}. Thus, the dye-based RIO-43 (thionin acetate), RIO-55 (Bismarck brown Y), and RIO-70 (pararosaniline hydrochloride) were selected for this presentation, where their main characteristics and applications will be addressed, especially in the Energy and Environment areas, such as water purification, greenhouse gas capture, and electrical conductivity.



Scheme 1: A single representation of the different topologies for the ionic RIOs in this work and their potential applications.

Acknowledgments

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References

- (1) Yang, C.-H.; Chang, J.-S.; Lee, D.-J. Covalent Organic Framework EB-COF:Br as Adsorbent for Phosphorus (V) or Arsenic (V) Removal from Nearly Neutral Waters. *Chemosphere* **2020**, *253* (126736).
- (2) Xia, Z.; Zhao, Y.; Darling, S. B. Covalent Organic Frameworks for Water Treatment. *Adv Mater Interfaces* **2021**, *8* (1), 1–17.
- (3) Zou, J.; Fan, K.; Hu, W.; Wang, C. Perspectives of Ionic Covalent Frameworks for Rechargeable Batteries. *Coord Chem Rev* **2022**, *458*, 214431.
- (4) Liu, Z. W.; Han, B. H. Ionic Porous Organic Polymers for CO₂ Capture and Conversion. *Curr Opin Green Sustain Chem* **2019**, *16*, 20–25.
- (5) Freitas, S. K. S.; Oliveira, F. L.; Merlini, C.; Justo, E. P. S.; Gioda, A.; Esteves, P. M. Dye-Based Covalent Organic Networks (CONs). *Journal of Physics: Materials* **2020**.
- (6) Freitas, S. K. S.; Oliveira, F. L.; Dos Santos, T. C.; Hisse, D.; Merlini, C.; Machado, C.; Esteves, P. M. A Carbocationic Triarylmethane-Based Porous Covalent Organic Network. *Chem. Eur. J.* **2020**, *27*, 2342.

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