



**XI MEDITERRANEAN ORGANIC CHEMISTRY MEETING**  
ELCHE (ALICANTE) 16<sup>TH</sup> - 18<sup>TH</sup> OCTOBER 2024



Edificio Valona (Universidad Miguel Hernández-ELCHE)



**October 16<sup>th</sup> – 18<sup>th</sup>, 2024 – Elche (Alicante)**

<https://xireqomed.umh.es/>

*XI Reunión de Química Orgánica del Mediterráneo (XI REQOMED 2024)*

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# 1. WELCOME

It is a great pleasure to announce the XI Mediterranean Organic Chemistry Meeting (XI REQOMED), which pretends to be a scientific congress focused on the presentation and discussion of research works concerning any theoretical and practical aspects in the Organic Chemistry area. Participation is open to organic chemists and for scientists from other related research fields, coming from every Mediterranean country.

The meeting will be held in Elche, Spain, 16<sup>th</sup>-18<sup>th</sup> October, 2024.

Elche, the city of the Lady, has many charms to reveal and that is reason enough for you to come visit us. You have the possibility to enjoy our history, culture, festivals and natural spaces. 9 kilometers of natural beaches. Three sites listed in the different categories of UNESCO's World Heritage lists, the Historic Palm Grove, the Mystery Play of Elche and the Pusol School Museum. Enjoy with your partner, with your friends, alone, or with the family... endless experiences await you. Discover the Mediterranean Oasis!

Previous REQOMED meetings:

I REQOMED, Alicante, 2002  
II REQOMED, Almería, 2004  
III REQOMED, Castellón, 2006  
IV REQOMED, Girona, 2008  
V REQOMED, Cádiz, 2011  
VI REQOMED, Granada, 2013  
VII REQOMED, Málaga, 2015  
VIII REQOMED, Mallorca, 2017  
IX REQOMED, Murcia, 2019  
X REQOMED, Valencia, 2022

## 2. COMMITTEES

### 2.1. ORGANIZING COMMITTEE

Dr. Ángela Sastre Santos (President UMH)

Dr. Fernando Fernández Lázaro (UMH)

Dr. Luis Martín Gomis (UMH)

Dr. José Miguel Sansano (President UA)

Dr. Francisco Foubelo (UA)

Dr. Gracia Retamosa (UA)

### 2.2. SCIENTIFIC COMMITTEE

Prof. Ángela Sastre Santos, Universidad Miguel Hernández, Spain.

Prof. José Miguel Sansano, Universidad de Alicante, Spain.

Prof. María Consuelo Jiménez Molero, Universitat Politècnica de València, Spain.

Prof. Ezequiel Pérez de Inestrosa, Universidad de Málaga, Spain.

Prof. Géraldine. Masson, Institut de Chimie des Substances Naturelles, CNRS, Paris, France

Prof. Maurizio Prato, Universidad de Trieste, Italy.

Prof. Eva Hevia, Universität Bern, Switzerland.

Prof. Luis Echegoyen, ICIQ's distinguished researcher, Spain.

# 3. SPONSORS



# 4. PROGRAMME

WEDNESDAY OCTOBER 16<sup>th</sup>

VALONA BUILDING

13:00-16:00 h	Registration
16:00-16:15 h	Opening Ceremony
	Session 1a: Chair: Prof. Ángela Sastre
16:15-17:00 h	PL-1. Prof. Avelino Corma: "MOLECULAR CONFINEMENT AND CHEMICAL REACTIVITY"
17:00-17:30 h	IL-1. Prof. Emilio Palomares: "THE CONTACT MAKES THE DEVICE: MOLECULES THAT RULE THE SOLAR CELLS EFFICIENCY"
17:30-18:00 h	IL-2. Prof. Luis Martín: "SILICON PHTHALOCYANINES AS ORGANIC LINKERS FOR SURFACE-SUPPORTED METAL-ORGANIC FRAMEWORK MATERIALS"
	Session 1b: Chair: Prof. Consuelo Jiménez
18:15-18:30 h	OP-1. Javier Ortiz: "SYNTHESIS AND CHARACTERIZATION OF PHTHALOCYANINES AS HOLE TRANSPORTING MATERIALS IN PEROVSKITE SOLAR CELLS"
18:30-18:45 h	OP-2. Ana Sirvent: "CYCLOPROPANOLS AS HYDROXYALLYLATION AGENTS FOR THE DIASTERESELECTIVE ADDITION TO N-TERT-BUTANESULFINYL IMINES"
18:45-19:00 h	OP-3. Elias A. Romero-Cavagnaro: "SELECTIVE Rh-CATALYZED CYCLO-ISOMERIZATION/DIELS-ALDER CASCADE REACTIONS INVOLVING 1,6-ALLENYNES"
19:00-19:45 h	PL-2. Prof. Eva Hevia: "TAILORING SODIUM ORGANOMETALLIC REAGENTS FOR ARENE FUNCTIONALISATION AND CATALYSIS"
20:00 h	WELCOME COCKTAIL (VALONA BUILDING)

THURSDAY OCTOBER 17<sup>th</sup>

VALONA BUILDING

	Session 2a: Chair: Prof. José M. Sansano
9:00-9:45 h	PL-3. Prof. Géraldine Masson: "COMBINED ASYMMETRIC AND PHOTOREDOX CATALYSIS FOR THE EFFICIENT SYNTHESIS OF CHIRAL AMINES"
9:45-10:15 h	IL-3. Prof. Consuelo Jiménez: "PHOTOACTIVE ASSEMBLIES OF ORGANIC COMPOUNDS AND BIOMOLECULES: DRUG-PROTEIN SYSTEMS"

10:15-10:45 h	<b>IL-4. Prof. Montserrat Diéguez:</b> <i>“SYNERGISTIC APPROACHES TO CATALYST DESIGN FOR ASYMMETRIC HYDROGENATION. FROM BENCHMARK TO ELUSIVE SUBSTRATES”</i>
10:45-11:00 h	<b>OP-4. María González-Marcos:</b> <i>“DIASTERESELECTIVE SYNTHESIS OF SPIROOXINDOLO PYRROLIZIDINES AND PROLINES VIA 1,3-DIPOLAR CYCLOADDITION USING CHIRAL ACRYLATES: A MULTICOMPONENT REACTION”</i>
11:00-11:30 h	COFFEE BREAK AND POSTER SESSION
	<b>Session 2b: Chair: Prof. Montserrat Diéguez</b>
11:30-12:00 h	<b>IL-5. Prof. Antonio Vargas:</b> <i>“NANOSIZED CARBOHYDRATE COATED METAL ORGANIC FRAMEWORKS (MOF) AS DRUG CARRIERS”</i>
12:00-12:30 h	<b>IL-6. Prof. Nishant Singh:</b> <i>“HIERARCHICAL SELF-ASSEMBLIES FROM PHASE SEPARATED DROPLETS”</i>
12:30-12:45 h	<b>OP-5. Ana M<sup>a</sup>. Gutiérrez-Vilchez:</b> <i>“MIMICKING EARLY PHOTOSYNTHETIC EVENTS: ELECTRON AND CHARGE TRANSFER IN PERYLENE-DIIMIDE-BASED CONJUGATES”</i>
12:45-13:00 h	<b>OP-6. María Biosca:</b> <i>“TAILOR-MADE LIGANDS FOR THE PALLADIUM CATALYZED ASYMMETRIC ALLYLIC SUBSTITUTION”</i>
13:00-13:15 h	<b>OP-7. Manuel A. Ortuño:</b> <i>“COMPUTATIONAL MECHANISM OF FORMAL (4+2) CYCLOADDITION BETWEEN AMIDES AND DIENES VIA C-H BOND ACTIVATION”</i>
13:15-13:30 h	<b>OP-8. José L. Esquivel:</b> <i>“STUDY OF NOVEL ANION-INDUCED SUPRAMOLECULAR POLYMERS BASED ON TRIAZOLIUM AND SQUARAMIDE RECEPTORS”</i>
13:30-15:00 h	<b>XI REQOMED PHOTO AND LUNCH (VALONA BUILDING)</b>
	<b>Session 3a: Chair: Prof. Luis Martín</b>
15:00-15:30 h	<b>IL-7. Prof. Francisco A. Macías:</b> <i>“CAN NATURAL PRODUCTS LEAD THE NEXT AGRICULTURAL REVOLUTION?”</i>
15:30-16:00 h	<b>IL-8. Prof. Anna Pla:</b> <i>“EXPLORING THE USE OF Rh-CATALYZED CYCLIZATION REACTIONS FOR THE FUNCTIONALIZATION OF FULLERENES”</i>
16:00-16:15 h	<b>OP-9. Raúl Pérez-Ruiz:</b> <i>“FORMATION OF C(sp<sup>2</sup>)-B(s) BONDS MEDIATED BY VISIBLE LIGHT”</i>
16:15-16:30 h	<b>OP-10. Llorenç Rubert:</b> <i>“TWO-DIMENSIONAL SUPRAMOLECULAR POLYMORPHISM IN CYANINE H- AND J-AGGREGATES”</i>
16:30-17:00 h	COFFEE BREAK AND POSTER SESSION
	<b>Session 3b: Chair: Prof. Ezequiel Pérez</b>
17:00-17:30 h	<b>IL-9. Prof. Albert Granados:</b> <i>“ACCESSING NEW CHEMICAL SPACE IN ORGANOFLUORINE CHEMISTRY SETTINGS VIA PHOTOINDUCED SINGLE ELECTRON TRANSFER”</i>
17:30-18:00 h	<b>IL-10. Prof. Luis Álvarez de Cienfuegos:</b> <i>“SHORT PEPTIDE SUPRAMOLECULAR HYDROGELS AS A MEDIA TO OBTAIN COMPOSITE MATERIALS”</i>



18:00-18:15 h	<b>OP-11. Yolanda Vida:</b> <i>"DENDRIMERIC-ANTIGENS - SILICA PARTICLE BASED NANOCOMPOSITES FOR SPECIFIC IGS RECOGNITION"</i>
18:15-18:30 h	<b>OP-12. María Medel:</b> <i>"ENGINEERING POLYPEPTIDE-BASED NANOCONJUGATES FOR ENHANCED THERANOSTIC THERAPIES"</i>
18:30-18:45 h	<b>OP-13. David Curiel:</b> <i>"ROBUST MICROPOROUS HYDROGEN-BONDED ORGANIC FRAMEWORK FOR SELECTIVE CO<sub>2</sub> SORPTION"</i>
18:45-19:00 h	<b>OP-14. Aicha Anouar:</b> <i>"NANOSIZED COPPER STABILIZED ON TERNARY P, N, S-DOPED GRAPHENE FROM CHITOSAN SHELLFISH WASTE: PREPARATION AND CATALYSIS OF SINGLE AND DOUBLE A3-TYPE AMINE COUPLING"</i>
19:00-19:45 h	<b>PL-4. Prof. Nazario Martín:</b> <i>"MOLECULAR NANOGRAFENES: THE SEARCH FOR ENANTIOSELECTIVITY"</i>
19:45-20:00 h	<b>TRIBUTE TO PROF. MIGUEL ÁNGEL ALARIO</b> Nazario Martín (Chair: Ángela Sastre)

21:00 h	CONFERENCE DINNER (RESTAURANTE LA TAULA DEL MILENIO) POSTER AWARDS
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## FRIDAY OCTOBER 18<sup>th</sup>

## ELS ARENALS BUILDING

	<b>Session 4a: Chair: Prof. Francisco Foubelo</b>
9:00-9:45 h	<b>PL-5. Prof. Maurizio Prato:</b> <i>"WATER OXIDATION BY ORGANIC-INORGANIC SUPRAMOLECULAR 'QUANTASOMES'"</i>
9:45-10:15 h	<b>IL-11. Prof. Ezequiel Pérez:</b> <i>"THE USE OF DENDRIMERS AND FLUORESCENT LABELS FOR BIOMEDICAL APPLICATIONS"</i>
10:15-10:45 h	<b>IL-12. Prof. Patricia Remón:</b> <i>"DITHIENYLETHENE PHOTOSWITCHES APPLIED TO LIGHT-CONTROLLED SUPRAMOLECULAR CHEMISTRY"</i>
10:45-11:00 h	<b>OP-15. Carmen Rotger:</b> <i>"FLUORESCENT DERIVATIVES OF POLYAMINO SQUARAMIDE POLYMERS (PASQUA): UNVEILING CELL INTERNALIZATION AND MOLECULAR TRANSPORT MECHANISM"</i>
	<b>Session 4b: Chair: Prof. Antonio Vargas</b>
11:00-11:30 h	<b>IL-13. Prof. M<sup>a</sup>. de Gracia Retamosa:</b> <i>"ASYMMETRIC [3+2] AND [4+2] CYCLOADDITION REACTIONS AS USEFUL TOOL TO OBTAIN HETERO AND SPIROCYCLIC ADDUCTS"</i>
11:30-11:45 h	<b>OP-16. Laura Cerezo:</b> <i>"PROBIOTIC-BASED LIVING MATERIAL AS AN ALTERNATIVE TO TREATING CARBAPENEM RESISTANT BACTERIAL INFECTIONS"</i>
11:45-12:30 h	COFFEE BREAK



12:30-13:00 h	<b>IL-14. Prof. M. Nieves Piña:</b> <i>"FROM SUPRAMOLECULAR CHEMISTRY TO THE DESIGN OF NEW FUNCTIONAL NANOMATERIALS FOR A CLEANER WORLD"</i>
13:00-13:15 h	<b>OP-17. Albert Artigas:</b> <i>"CATALYTIC SYNTHESIS OF CONTORTED CHIRAL PICENE TRIMERS"</i>
13:15-13:30 h	<b>OP-18. Miriam Mas-Montoya:</b> <i>"THE ROLE OF HYDROGEN BONDING IN 7-AZAINDOLE-BASED ORGANIC SEMICONDUCTORS EVALUATED IN OPTOELECTRONIC DEVICES"</i>
13:30-15:00 h	<b>LUNCH (ELS ARENALS BUILDING)</b>
	<b>Session 5a: Chair: Prof. M<sup>a</sup>. de Gracia Retamosa</b>
15:00-15:30 h	<b>IL-15. Prof. Carmen Ramírez de Arellano:</b> <i>"CATALYTIC POCKET PARAMETRIZATION IN SCORPIONATE DERIVATIVES FOR THE DESIGN OF ACTIVE METAL CENTRES"</i>
15:30-16:00 h	<b>IL-16. Prof. Alberto Martínez-Cuezva:</b> <i>"THE MECHANICAL BOND AS A POWERFUL TOOL FOR CONTROLLING REACTIONS IN [2]ROTAXANES"</i>
16:00-16:15 h	<b>OP-19. Jan Deska:</b> <i>"EXPLOITING NON-NATURAL BIOCATALYSIS METHDOLOGIES AS TOOLS IN ORGANIC SYNTHESIS"</i>
16:15-16:30 h	<b>OP-20. María A. Lirola-Manzano:</b> <i>"ANAESTHETIC AND ANTICANCER DRUGS COMPLEXATION BY CYCLODEXTRINS APPENDED WITH PHOSPHONIC ACID GROUPS ON THEIR PRIMARY FACES"</i>
16:30-16:45 h	<b>OP-21. Aitor Maestro:</b> <i>"GENERAL AND VERSATILE SYNTHESIS OF HIGHLY RECYCLABLE CHIRAL PHOSPHORIC ACID ORGANOCATALYSTS"</i>
16:45-17:00 h	<b>OP-22. Mario Inclán:</b> <i>"SYNTHETIC AOLLOSTERIC SYSTEMS AS NOVEL BIOMEDICAL TOOLS"</i>
17:00-17:30 h	<b>COFFEE BREAK</b>
	<b>Session 5b: Chair: Prof. Fernando Fernández-Lázaro</b>
17:30-18:15 h	<b>PL-6. Prof. Luis Echegoyen:</b> <i>"FULLERENE CAGES TO STABILIZE UNUSUAL ACTINIDE CLUSTERS INSIDE AND FOR ENHANCED SOLAR CELL EFFICIENCIES AND ELECTROCATALYTIC APPLICATIONS"</i>
18:15-18:30 h	<b>Closing ceremony</b>

## 5. PLENARY LECTURES (PL)

**PL1-6**

Avelino Corma<sup>1</sup>

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Enzymes are catalysts characterized by operating at low temperatures with high activity and selectivity. The excellent catalytic properties of enzymes are associated to the presence of well-defined uniform active sites and, specially, to the presence of “pockets” in where the reaction occurs. It is in these “pockets” or “cavities” in where the active sites are located and the transition state of the reaction is formed and stabilized by weak long-range interactions, resulting in a decrease of the enthalpy of reaction. Meanwhile the weak interactions, together with the relatively low reaction temperatures, result in small entropy factors, and low Gibbs free energy of activation.

It is clear that the enzyme’s behaviour can be an excellent model for designing not only molecular but also solid catalysts.

We will show that in the case of molecular catalysts it is possible to prepare multisite catalysts, containing acid and base sites or Lewis and Bronsted acid sites within the adequate distance and configuration to stabilize the reaction transition state. Longer range type of interaction can also be considered with these catalysts to achieve additional activity and selectivity effects.

We will also present how to introduce well-defined homogeneous active sites in the case of solid catalysts, going from “isolated” to clusters of few atoms as the active catalytic centre.

Then, by introducing those active sites into well-defined cavities and pores of the solid, one can take advantage of the molecular confinement of the reaction transition state and its stabilization by long range weak interactions. It is possible then to approach the catalytic behaviour of enzymes with solid catalysts. On those bases, we have synthesized crystalline porous materials with well-defined homogeneous active sites, and cavities that match the transition state of a pre-established reaction. To do that, we have synthesized organic structure directing agents (OSDA) that mimic potential transition states of given reactions. Thus, solid catalysts have been obtained by hydrothermal synthesis that show excellent activities and selectivities for the pre-established reactions. We will show how these catalysts decrease the enthalpy of activation, and also decrease the entropy of activation in a manner that the final results is a decrease of the free energy of activation, in an analogous way as it occurs with enzymatic catalysts.

Will present that the combination of the above concept and directed Machine Learning, can predict the catalyst structure required for better performing a given catalytic reaction.

## TAILORING SODIUM ORGANOMETALLIC REAGENTS FOR ARENE FUNCTIONALISATION AND CATALYSIS

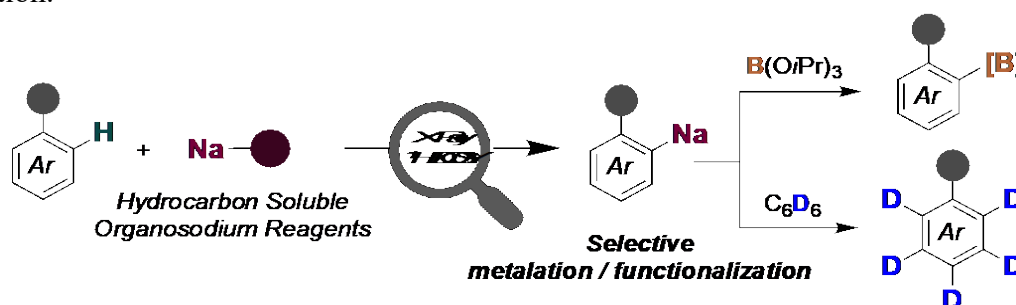
**Eva Hevia<sup>1</sup>**

<sup>1</sup>*Department of Chemistry, Biochemistry and Pharmacy, University of Bern. Freiestrasse 3, 3012 Bern (Switzerland)*

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Organosodium compounds have attracted the attention of the scientific community in recent years as an alternative to widely used organolithium reagents.<sup>[1]</sup> Lithium alkyls and amides reside at the front of organometallic synthesis as key players in countless transformations, owing to their availability, substantial stability and solubility in hydrocarbon solvents.<sup>[2]</sup> However, these desirable traits are often pitfalls of heavier alkali-metal organometallics, meaning that their applications have remained underexplored. While recent reports have hinted at the untapped potential of these reagents,<sup>[3]</sup> the constitution of the organometallic intermediates that operate in these reactions has been overlooked, missing an opportunity to tackle their high reactivity and improve their poor solubility.

Filling this gap in the knowledge, the preparation of organosodium compounds soluble in hydrocarbon solvents and the isolation and characterization of reactive sodium organometallic intermediates have allowed the development of new protocols for the functionalisation of organic molecules. Our efforts have been focused on selective deprotonative metalation reactions of synthetically attractive arenes, providing access to the selective functionalization of these scaffolds, including the borylation<sup>4</sup> and the perdeuteration of aromatic scaffolds,<sup>[5]</sup> alkene isomerisation,<sup>[6]</sup> and the arylation of toluene derivatives via selective benzylic metalation.<sup>[7]</sup>



[1] De, P. B.; Asako, S.; Ilies, L.; *Synthesis* **2021**, 53, 3180–3192.

[2] *Lithium Compounds in Organic Synthesis – From Fundamentals to Applications*, (Eds.: Luisi, R. and Capriati, V.), Wiley-VCH, Weinheim 2014

[3] a) Asako, S.; Kodera, M.; Nakajima, H.; Takai, K.; *Adv. Synth. Catal.* **2019**, 361, 3120–3123. b) Asako, S.; Nakajima, H.; Takai, K.; *Nat Catal* **2019**, 2, 297–303.

[4] a) Bole, L. J.; Tortajada, A.; Hevia, E.; *Angew. Chem. Int. Ed.* **2022**, 61, e202204262. b) Anderson, D. E.; Tortajada, A.; Hevia, E.; *Angew. Chem. Int. Ed.* **2024**, 63, e202313556.

[5] Tortajada, A.; Hevia, E.; *J. Am. Chem. Soc.* **2022**, 144, 20237–20242.

[6] Tortajada, A.; Righetti, G. L.; McGinley, A.; Mu, M.; García-Melchor, M.; Hevia, E. *Angew. Chem. Int. Ed.* **2024**, 63, e202407262.

[7] Anderson, D. E.; Tortajada, A.; Hevia, E.; *Angew. Chem. Int. Ed.* **2023**, 62, e202218498.

## COMBINED ASYMMETRIC AND PHOTOREDOX CATALYSIS FOR THE EFFICIENT SYNTHESIS OF CHIRAL AMINES

PL3

**Géraldine Masson**<sup>1,2</sup>

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<sup>2</sup> *HitCat, Seqens-CNRS joint laboratory, Seqens'Lab, Porcheville, France E-mail: [geraldine.masson@cnrs.fr](mailto:geraldine.masson@cnrs.fr)*

Nitrogen-activated carbon-carbon double bonds offer significant potential for constructing a diverse array of nitrogen-containing products. To expand the utility of these substrates, our research focused on exploring the reactivity of promising enamide derivatives.

We developed innovative methods for the  $\alpha,\beta$ -difunctionalization of enamides using a synergistic two-step strategy combining asymmetric organocatalysis with photoredox catalysis. A key aspect of our approach involved employing thiol as a transient reaction partner, which played a crucial role in ensuring the success of these processes and enabling the synthesis of a diverse range of enantioenriched  $\alpha,\beta$ -substituted amines.<sup>[1]</sup>

Moreover, we successfully implemented stereoselective and enantioselective photocatalytic processes for synthesizing both  $\alpha$ - and  $\beta$ -chiral amines. In these methods, amino acids proved to be ideal linchpins, facilitating selective transformations and achieving high enantioselectivity.<sup>[2,3]</sup>

This lecture will highlight our contributions, emphasizing their applications in synthesizing biologically active natural and synthetic compounds.

[1] Bouchet, Y. D.; Varlet, T.; Masson, G. *Acc. Chem. Res.* **2022**, *55*, 3265.

[2] Serafino, A.; Pierre, H.; Le Vaillant, F.; Boutet, J.; Guillamot, G.; Neuville, L.; Masson, G. *Org. Lett.* **2023**, *25*, 9249

[3] Ma, W.-Y.; Leone, M.; Derat, E.; Retailleau, P.; Reddy, C. R.; Neuville, L.; Masson, G. *Angew. Chem. Int. Ed.* **2024**, e202408154.

**Nazario Martín**<sup>1,2</sup>

<sup>1</sup> Dpto de Química Orgánica, Facultad de Química, Universidad Complutense, E-28040; Madrid, Spain.

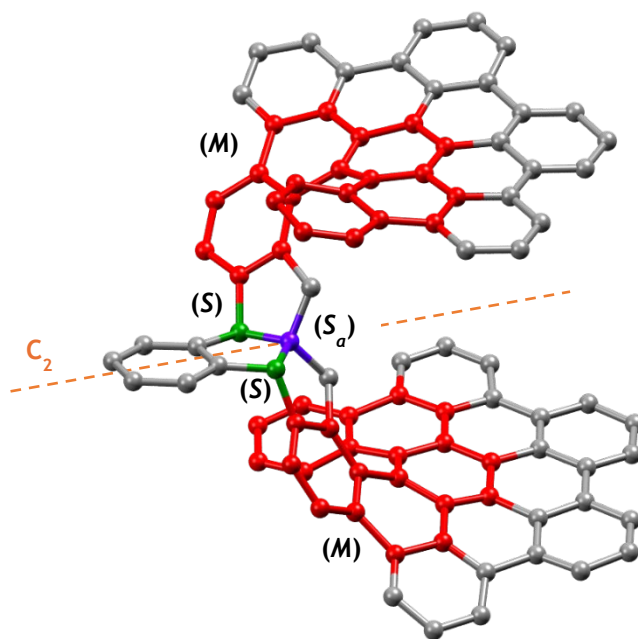
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Nanographenes (NGs) have usually been synthesized following a top-down approach by “cutting” a graphene sheet into smaller fragments using chemical or physical methods. Although this methodology starts from readily accessible bulk materials and it is easily scalable, it does not allow a fine control of the properties due to the polydispersion in sizes and shapes of the final material. In contrast, the bottom-up approach in which NGs are grown up from smaller chemical entities using solution-phase benchtop organic synthesis, leads to monodisperse molecules with a precise control on the size and shape, exhibiting fine-tuned optoelectronic properties.

Thus, taking advantage of the versatility that provides the set of organic reactions available, and the selectivity of these transformations depending on the reaction conditions, a large number of molecular NGs have been synthesized by design in the recent years. An example of this control is the introduction of out-of-plane defects at will, namely curvature, helicity, or strain, resulting in the presence of chirality as an additional and remarkable structural control.

Along the last recent years, we have carried out the synthesis and unveiled the properties of a variety of molecular nanographenes in the search for new chiroptical and optoelectronic properties in all-carbon materials. [1-4] In this presentation some recent and amazing NGs stemming from our research group, with special emphasis on the search for enantioselectivity, will be presented and discussed.[5]



[1] J. M. Fernández-García, P. J. Evans, S. Filippone, M. A. Herranz, N. Martín, “Chiral Molecular Carbon Nanostructures”, *Acc. Chem. Res.* **2019**, 52, 1565-1574.

[2] P. J. Evans, et al., *Angew. Chem. Int. Ed.* **2018**, 57, 6774 –6779.

[3] Z. Zhou, J. M. Fernández-García, et al. *Angew. Chem. Int. Ed.* **2022**, 61, e20211574.

[4] Patricia Izquierdo-García, et al. *J. Am. Chem. Soc.* **2023**, 145, 11599-11610.

[5] M. Buendía-Mateos, et al. *Nat. Synth.* **2024**, 3, 545-553.

# WATER OXIDATION BY ORGANIC-INORGANIC SUPRAMOLECULAR “QUANTASOMES”

PL5

**Maurizio Prato**<sup>1,2</sup>

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Among the most innovative strategies in the energy transition, photo-electrocatalytic splitting of water for the production of "green hydrogen" plays a key role, as it provides an ideal energy carrier, obtained from renewable and circular resources and whose production and combustion fuels the H<sub>2</sub>O/O<sub>2</sub> cycle, activated by sunlight. Currently, hydrogen production is mainly obtained from fossil sources, and in particular from natural gas, through thermochemical processes (reforming/pyrolysis) that generate quantities of carbon dioxide with high environmental impact. The perfect mechanisms of the leaf, realized in an artificial environment, allows for the production of hydrogen as a solar fuel, an ideal solution for sustainable development. In particular, a new catalytic system, based on the combination of perylene bisimides and polyoxometalates, arranged in a hierarchical assembly, offers new opportunities for the biomimetic splitting of water.

During this talk, we will discuss the latest results obtained in our laboratories on this exciting topic.

[1] Sartorel, A., Carraro, M., Toma, F. M., Prato, M., Bonchio, M. Shaping the beating heart of artificial photosynthesis: oxygenic metal oxide nano-clusters. *Energy Environ. Sci.* 5, 5592 (2012);

[2] Toma, F. M.; Prato, M.; Bonchio, M. et al. Efficient water oxidation at carbon nanotube–polyoxometalate electrocatalytic interfaces. *Nature Chemistry* 2, 826-831 (2010).

[3] Bonchio, M.; Sartorel, A.; Prato, M. et al. Hierarchical organization of perylene bisimides and polyoxometalates for photo-assisted water oxidation. *Nature Chemistry* 11, 146-153 (2019).

[4] Gobbato T.; Rigodanza F.; Benazzi, E.; Prato, M.; Bonchio M. et al. *J. Am. Chem. Soc.* 144, 14021-14025 (2022).



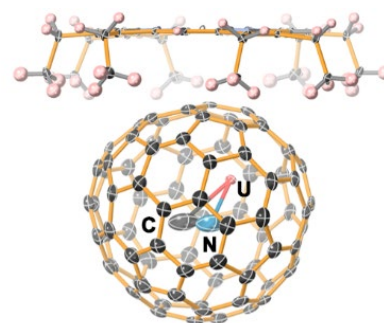
# FULLERENE CAGES TO STABILIZE UNUSUAL ACTINIDE CLUSTERS INSIDE AND FOR ENHANCED SOLAR CELL EFFICIENCIES AND ELECTROCATALYTIC APPLICATIONS

**Luis Echegoyen**<sup>1</sup>

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Because of their unique structures, variable isomeric compositions and tunable electronic properties, fullerenes have found multiple uses and applications in different fields: as electron acceptors and transporters, as structural building blocks, and as molecular containers to stabilize unique clusters inside, among many others.



In this presentation I will describe unique endohedral structures formed by incorporating actinide elements and never before observed actinide clusters inside the fullerene cages, by serving as stabilizing agents for these species, which cannot otherwise be prepared outside of the carbon structures.<sup>[1]</sup> I will also highlight the work that we have recently done with: 1) fullerene derivatives that act as electron extracting compounds from perovskite layers in solar cells<sup>[2]</sup>, 2) fullertubes (C<sub>90</sub> C<sub>96</sub> and C<sub>100</sub>) for electrocatalytic Oxygen Reduction Reaction (ORR)<sup>[3]</sup>, and 4) functionalized empty and endohedral fullerenes for HER.<sup>[4]</sup>

Finally, very recent results using Nd endohedral compounds as electron extracting layers in inverted perovskite solar cells showed remarkable photovoltaic performance, with a champion device exhibiting a 26.78% PCE and a certified PCE of 26.13%. In addition, the unencapsulated devices retained ~82% of the initial PCE after 2500 hours of continuous 1-sun maximum power point operation at 65°C. These results will also be presented.

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 b) *JACS* **2023**, *145*, 6710;  
 c) *JACS* **2023***145*, 5645;  
 d) *Nat. Commun.*,**2022**, *13*, 7192;  
 e) *Nat. Commun.***2018**, *9*, 2753;  
 f) *JACS* **2018**, *140*, 3907;  
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## 6. INVITED LECTURES (IL)

**IL1-16**

## THE CONTACT MAKES THE DEVICE: MOLECULES THAT RULE THE SOLAR CELLS EFFICIENCY

IL1

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Silicon solar cells have dominated the science and market for solar cells. Their efficiency was boosted after the passivation of their surface and minimised charge losses at the interface, allowing better contacts to extract the photoelectrical current.

In molecular solar cells, either organic or hybrid perovskite-based photoactive layers, selective contacts are paramount to obtain high efficiency. In the latter case, using self-assembled molecules is a must to push the solar cell efficiency up to 24% (under standard solar irradiation conditions). Our group pioneered the design and synthesis of self-assembled molecules (SAMs) in perovskite solar cells and has focused on studying the relationship between the SAMs' molecular structure and device function. I will discuss the latest advances in SAMs for perovskite solar cells and how far we can achieve the maximum theoretical limit in perovskite solar cells and tandem devices.

# SILICON PHTHALOCYANINES AS ORGANIC LINKERS FOR SURFACE-SUPPORTED METAL-ORGANIC FRAMEWORK MATERIALS

IL2

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Phthalocyanines, synthetic analogues of porphyrin compounds, have received significant attention due to their unique electronic properties and diverse applications. Silicon phthalocyanines, with two additional axial valences, offer distinct advantages, including their tunable electronic properties and compatibility with various axial functional groups.[1]

Metal-organic frameworks (MOFs) are crystalline porous materials constructed from metal ions or clusters connected by organic linkers, while surface-supported MOFs (SurMOFs) offer additional benefits, such as enhanced stability and integration with existing technologies. These materials have emerged as promising candidates for applications in photovoltaics, LEDs and transistor-related applications.[2]

In this presentation, we will introduce a series of ditopic silicon phthalocyanines (Figure 1), specifically designed to serve as organic linkers for SurMOF materials. These phthalocyanines incorporate functional groups that facilitate their attachment to surfaces and promote the formation of well-defined MOF structures in combination con Zn ions. [3] We will discuss the design principles behind these molecules and present experimental results demonstrating their effectiveness as linkers. Our findings highlight the potential of silicon phthalocyanines to enable the facile synthesis of high-performance SurMOF materials with diverse applications.

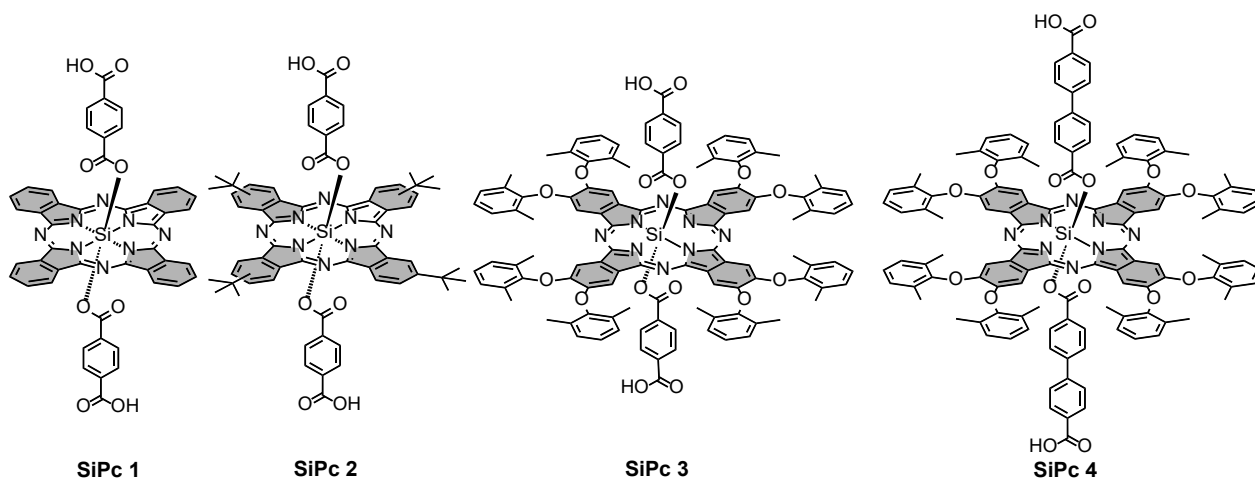


Figure 1. Chemical structure of ditopic SiPc linkers for SurMOF materials.

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The use of proteins as hosts can significantly alter the photoreactivity of encapsulated drugs, as the properties of their singlet and triplet excited states are highly dependent on the surrounding environment. This dependency opens the possibility of exploring drug excited states as probes for studying compartmentalized microenvironments within drug-protein supramolecular systems. Additionally, proteins can provide essential benefits to the guest, such as protection against oxygen and other external reagents, enforcing conformational restrictions within binding pockets, and influencing the stereochemical outcomes of reactions. [1]

Furthermore, certain drugs, when exposed to light, can undergo photochemical reactions that modify their structure and reactivity. These transformations may generate reactive species that covalently bind to proteins, altering their function and potentially causing adverse effects. A notable consequence of this photochemical binding is the development of photoallergies, where the modified drug-protein complex triggers immune responses in sensitive individuals. On the other hand, *in vitro* drug-protein photobinding techniques can serve as valuable tools for mapping protein binding sites, offering insights into protein-ligand interactions. [2]

In this presentation, we will show how the use of photoactivatable drug probes encapsulated within proteins can provide useful (bio)chemical information. By examining these interactions, it is possible to gain a deeper understanding of the underlying mechanisms and explore their implications for drug design and therapeutic applications. [1,3]

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# SYNERGISTIC APPROACHES TO CATALYST DESIGN FOR ASYMMETRIC HYDROGENATION. FROM BENCHMARK TO ELUSIVE SUBSTRATES

IL4

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Nowadays, a large list of pharmaceutical formulations, agrochemicals and fine chemicals are manufactured using chiral chemicals. One of the most powerful methods for producing enantiomerically pure products is the catalytic asymmetric hydrogenation (AH) of olefins.[1] This process is 100% atom economical and has been successfully used to produce single enantiomer intermediates, particularly in the pharmaceutical industry. However, to fully exploit its application there is still a constant need to expand the range of substrates to synthesize the most diverse chiral molecules. The finding of a catalyst that could work for new substrate types is hampered because of the lack of data, since most of the catalytic systems have only been tested using benchmark substrates. To limit time-consuming catalyst design is highly desirable to identify catalyst with a broad substrate scope. So, in this context I will present several examples that will illustrate different ways to integrate theoretical calculations into the catalyst design (from guiding it to predictive models going through in silico-based catalyst optimization) for the synthesis of elusive chiral synthons.[2] I will also discuss how to improve the chemical sustainability of the process with the development of practical continuous flow versions through the use of immobilized versions of the catalysts.

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# NANOSIZED CARBOHYDRATE COATED METAL ORGANIC FRAMEWORKS (MOF) AS DRUG CARRIERS

IL5

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Nanosized metal-organic frameworks (nanoMOFs) are highly porous and biodegradable materials that have emerged as promising drug nanocarriers. A key challenge is their surface functionalization to avoid recognition and clearance by the innate immune system while enabling specific molecular targeting. We present several approaches[1,2] for their coating with tetraethylene glycol, polyethylene glycol, and mannose residues based on carbohydrate scaffolds. These approaches involve organic solvent-free self-assembly on the nanoMOFs of building blocks based on  $\beta$ -cyclodextrin, cyclodextrin polymers and co-polymers of dextran derivatized with the desired functional moieties along with multiple phosphate or phosphonate groups to anchor to surface of the nanoparticles. The carbohydrate-based coatings effectively imparted a "stealth" effect, significantly reducing macrophage internalization in vitro, providing new perspectives for biomedical applications. In addition, mannose-coated nanoMOFs displayed a remarkably enhanced binding affinity towards a specific mannose receptor, such as Concanavalin A, while maintaining reduced macrophage internalization.

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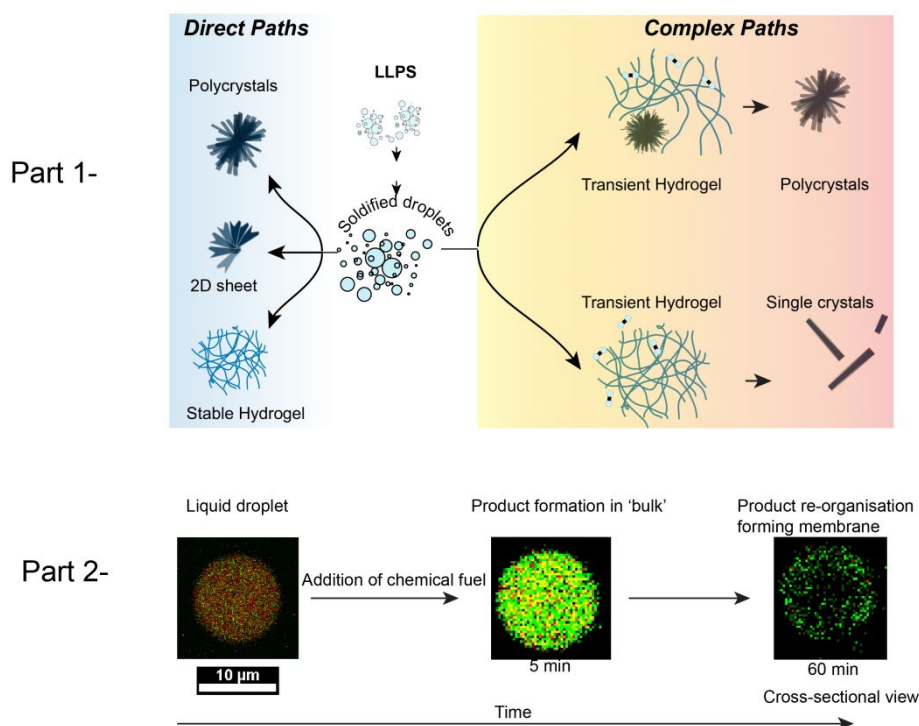
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The talk will show the use of disordered phase separated droplets as self-assembly tools to create higher order intricate self-assembled structures. The first part of the talk will deal with pathway complexity allowing simple coacervates to evolve into transient hydrogels, stable kinetic hydrogels, single crystals and poly-crystals. I will show how controlling initial conditions can allow the same monomers to assemble in uniquely different ways giving complex microscopic and macroscopic material outcomes (Fig. 1, Part 1) [1]. In the second part of the talk I will show a new class of small molecules which can form complex coacervates with a range of counter polyelectrolytes. These de novo molecules can react within these protocells to transform them from membrane-less droplets to membranous compartments and complex 3D superstructures (Fig. 1, Part 2) [2].



**Figure 1:** Schematics of the two parts planned to be discussed in the proposed talk.

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Parasitic weeds pose a significant threat to agricultural productivity, requiring the development of sustainable control methods. The use of traditional herbicides has led to the emergence of resistant weed varieties, highlighting the urgent need for environmentally friendly and effective alternatives. Allelopathy offers promising avenues of exploration, such as the honeypot strategy [1], which has been the focus of some of our ongoing research in this area. A primary approach involved the discovery of bioactive metabolites produced by host plants (biocommunicators), leading to the identification and study of promising compounds isolated from host species, such as strigolactones, sesquiterpene lactones or  $\alpha$ -tomatine. This involved the development of a simple and reliable UHPLC-MS/MS method for the simultaneous analysis of strigolactones in exudates and extracts. This method was tested with limits of quantification ranging from 0.05 to 0.96  $\mu\text{g/L}$ . A second approach focused on the synthesis of parasitic plant stimulants as strigolactone mimics and analogs. Encouraging results were obtained by adding a butenolide ring to phthalimides, isolated sesquiterpene lactones and diterpenoids as starting materials, and by optimising previously reported synthetic strategies [2]. The isolated and synthesised compounds showed stimulating activity in bioassays with seeds from different *Orobanche* and *Phelipanche* species. In addition, a selection of the most promising compounds was encapsulated and showed favourable results in bioassays. These results present novel structures with the potential to serve as active ingredients in natural product-based pre-emergence herbicides, thereby stimulating further exploration and research into their efficacy and applicability.

*Keywords:* Parasitic weeds, honeypot strategy, strigolactones, organic synthesis, encapsulations.

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Fullerenes, particularly their functionalized derivatives, have garnered significant interest since their discovery due to their unique properties and exceptional characteristics. These qualities make them highly attractive for applications in fields such as biomedicine<sup>[1]</sup> and photovoltaic energy.<sup>[2]</sup> Despite substantial advancements in fullerene functionalization, there remains a critical goal: to master the selectivity of these processes and synthesize novel topological derivatives with promising applications. One promising, albeit less explored, approach involves transition metal catalysed or promoted cyclizations.<sup>[3]</sup> This method offers an efficient alternative to traditional thermally activated or radical-driven processes for synthesizing fullerene derivatives fused with carbo- and heterocyclic rings of varying sizes and functionality.

Our research group, leveraging extensive experience in the transition metal-catalyzed cyclizations, has developed innovative methods for the functionalization of fullerenes. Notably, we have employed a rhodium-catalyzed [2+2+2] cycloaddition reaction between 1,6-diynes and C<sub>60</sub><sup>[4]</sup> or C<sub>70</sub><sup>[5]</sup> enabling the synthesis of new open-cage fullerene derivatives. Some of the derivatives have demonstrated to be good electron transport materials in perovskite solar cells<sup>[6]</sup> and have proven to be efficient photoinduced reactive oxygen species generators capable of cleaving DNA.<sup>[7]</sup> Additionally, we have developed new methodologies involving the transition-metal catalysed cyclization of 1,5-bisallenenes,<sup>[8]</sup> 1,6-enynes<sup>[9]</sup> or 1,6-allenynes.<sup>[10]</sup> These processes generate reactive dienes *in situ*, which efficiently undergo Diels-Alder reactions with fullerenes, yielding a diverse array of novel fullerene derivatives with 6,5-, 6,7- and 6,6-membered ring fusions. The mechanism of the novel processes has been investigated through experiments and computational studies revealing unprecedented cycloisomerization reactivity.

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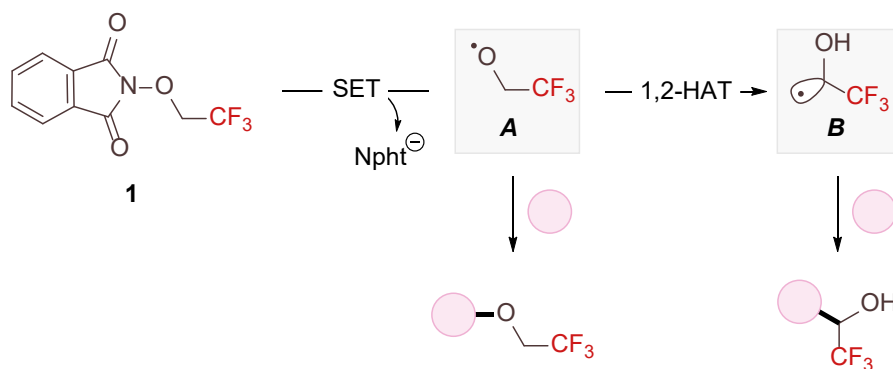
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Many organic reactions are driven by two-electron processes. While these processes are effective for numerous transformations, they often encounter limitations such as harsh reaction conditions and sensitivity to functional groups. These challenges are fundamentally linked to the mechanisms of two-electron processes, making certain reactions difficult to be accomplished. Single-electron transfer (SET) mechanisms offer a promising alternative to overcome these limitations.

In this context, *N*-trifluoroethoxyphthalimide (**1**) has emerged as an efficient redox-active ether reagent in organic synthesis under photoredox conditions. Through a SET process, reagent **1** is reduced to its radical anion, which undergoes  $\beta$ -scission to form an oxygen-centered radical (**A**). This radical can further undergo intramolecular 1,2-hydrogen atom transfer (1,2-HAT), yielding a synthetically valuable carbon-centered radical (**B**).<sup>1</sup> Remarkably, utilization of radical synthon **A** in organic synthesis is unknown.

Our group has developed photoredox conditions to generate, manipulate, and utilize both radicals **A** and **B**. This lecture focuses on alkene difunctionalization reactions, enabling the formation of carbon-carbon<sup>2</sup> and carbon-oxygen<sup>3</sup> bonds through the direct incorporation of these radicals into diverse synthetic transformations.



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Short-peptide supramolecular hydrogels containing aromatic fluorenylmethoxycarbonyl (Fmoc) protecting group are extremely versatile materials with remarkable bio- and technological applications [1,2]. These peptides can self-assemble under the application of different stimuli, such as solvent or pH switch, addition of salts, or enzymatic reactions. This can be exploited to induce gelation under biocompatible conditions and can be used to modulate the macroscopic and mechanical properties of the resulting gels offering an extra degree of versatility. addition, control over the stimulus-induced transition is also crucial to obtain composite or hybrid hydrogels made by the combination of several organic compounds or mixtures of organic and inorganic/metallic substrates [3,4].

In this communication the ability of these gels to obtain composite materials will be summarized. In particular, the use of these gels for protein crystallization will be commented as well as for the crystallization of other inorganic materials [5]. Details about protocols, advantages as well as applications/properties of the resulting composite materials will be commented.

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Dendrimers that are modified through their peripheral groups have been employed for many biomedical purposes. Diagnosis via specific interactions with target proteins is one of the objectives that has been given more attention.

We have been developing different methodologies for the detection of immunoglobulins, as an in vitro method for the diagnosis of allergic reactions to drugs.

Specific cell interactions of surfaces grafted dendrimers have been applied to the study of cell adhesion. We have studied also the application of dendrimer-based uneven nanopatterns to evaluate the local RGD surface density effects on cell adhesion, as bioactive substrates to evaluate the impact of the RGD local surface density on the chondrogenic induction of adult human mesenchymal stem cells.

For these purposes, we have required the development of new dendrimeric models. Monitoring these interactions is mainly necessary in order to assess their operability. Fluorescence imaging has become an indispensable tool for modern biomedical research and pre-clinical studies. For many biomedical applications, optimal excitation and emission wavelengths extend from far-red to near infra-red (650–900 nm), which allow greater tissue penetration, lower biotoxicity, and reduced autofluorescence compared to shorter wavelengths. We explain here our contributions to develop one- and two-photon fluorescent chromophores that can be useful for biomedical applications, their rational design, spectroscopic studies and photophysical characterization. The implementation of these fluorescent labels by assembling to molecules of biological interest, their assay in human samples and their validation in cell image is also reported.

The implementation of these fluorescent labels by assembling to molecules of biological interest, their assay in human samples and their validation in cell image is also reported.

In this way, their inclusion on dendrimeric structures generates new tools that represents an excellent basis for new NIR probes able to cross biological barriers, with good fluorescence properties, low-toxicity and high photostability.

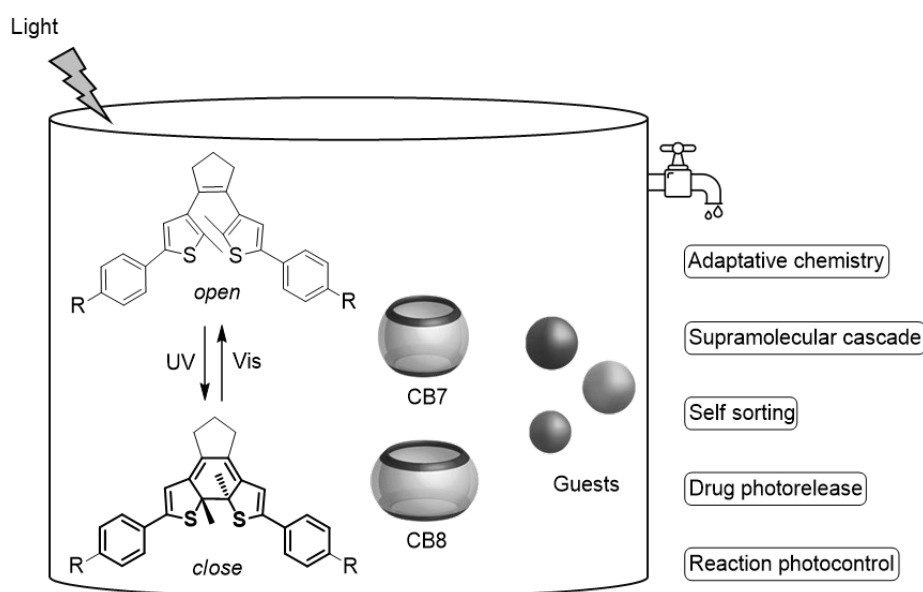


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Light is an attractive tool that enables the challenging goal of having spatiotemporal control, difficult to achieve with other chemical methods. The quest to use light as the primary and even sole tool to control molecular systems is therefore highly attractive. Due to its versatility, light can be used in various fields to photo-regulate supramolecular systems, the activity of prodrugs, reactions, material properties, Information Technology, etc.

In this talk, we will explore light as a sole controller of supramolecular systems based on cucurbiturils and different organic guests by using photochromic molecules as transmitters or “translators” of this photonic input to the supramolecular language [1][2]. Among the numerous families available nowadays, we focus on the modifiable and multifaceted dithienylethene photoswitches to achieve our goals [3].



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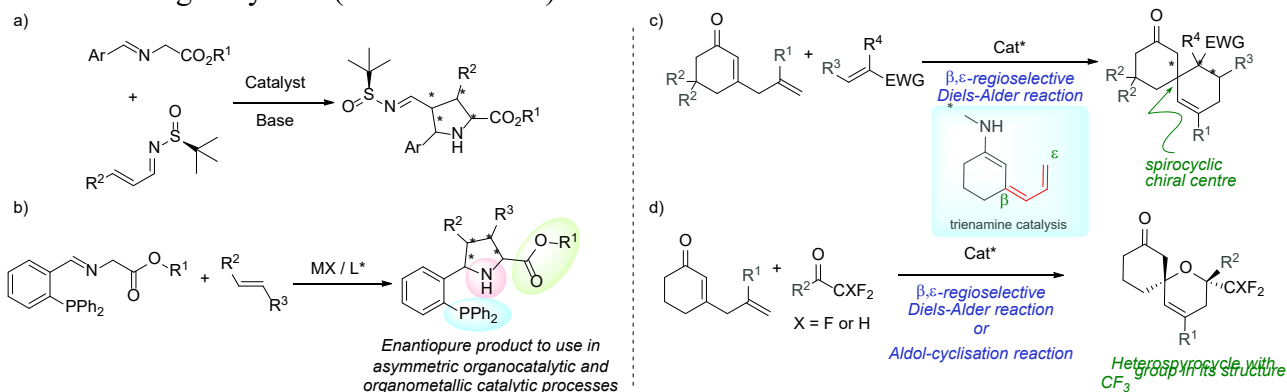
ASYMMETRIC [3+2] AND [4+2] CYCLOADDITION REACTIONS AS USEFUL TOOL TO OBTAIN HETERO AND SPIROCYCLIC ADDUCTS

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Inter- and intramolecular cyclization reactions are present in a lot of synthetic processes<sup>1</sup> as well as in the biosynthesis of natural products, for this reason it has enhanced the design of methodologies to obtain new drugs and compounds with different applications<sup>2</sup>. The enantioselective carbocyclization reactions allow to generate one or more stereocenters in only one step by C-C bonds formation. These processes allow to access natural products and/or biologically active molecules. The cycloaddition reactions are, until now, the most used methodologies to perform any type of synthesis. These reactions allow to generate complex and conformationally rigid organic skeletons which are very difficult to obtain using other methodologies. The [3 + 2]<sup>3</sup> and the [4 + 2]<sup>4</sup> cycloadditions are the most efficient reactions, specially in their asymmetric versions. The versatility of these processes and the tolerance of using diverse functional groups allows the synthesis of numerous biologically active molecules. Recently, we have developed diastereoselective and enantioselective metal catalyzed [3 + 2] cycloadditions and enantioselective organocatalyzed Diels-Alder reactions. The first mentioned have been carried out in two different approaches, on the one hand using chiral 1-azadienes as dipolarophile containing the *N*-tert-butanesulfinylimine group as electron-withdrawing group (Scheme a)<sup>5</sup> and on the other hand employing substituted 2-(diphenylphosphanyl)phenyl iminoesters as 1,3-dipolar precursors (Scheme b). The organocatalyzed Diels-Alder reactions have been performed using cyclic 2,5-dienones and a wide variety of dienophiles to achieve chiral spirocyclics with two or three stereogenic centres with moderate to excellent diastereomeric and enantiomeric excesses and good yields (Scheme c and d).<sup>6</sup>



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# FROM SUPRAMOLECULAR CHEMISTRY TO THE DESIGN OF NEW FUNCTIONAL NANOMATERIALS FOR A CLEANER WORLD

IL14

M. Nieves Piña<sup>1</sup>

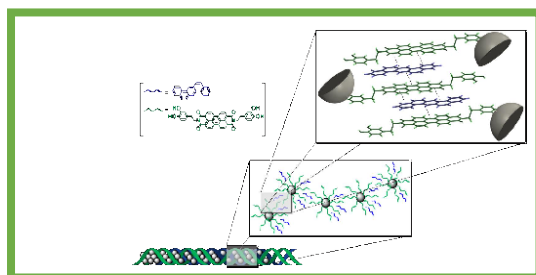
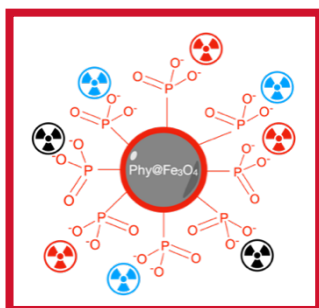
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The knowledge acquired after years of experimental and computational study of the behaviour of different supramolecular systems has led to their use in the development of new hybrid nanomaterials capable of interacting with a multitude of analytes of interest. Initially, the base chosen for the new nanoparticles was magnetite because it is affordable, easy to manipulate, functional and biocompatible. In addition, its magnetism provides a great advantage since it allows its separation from the medium by the action of a magnet. These new nanomaterials are synthesized by microwaves, obtaining them in a more efficient, simple, fast and economical way [1].

Thus, these new materials have demonstrated a great capacity to capture in aqueous media heavy metal cations, such as  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Au}^{3+}$  and  $\text{Ag}^+$  [2], radioactive cations such as  $\text{Sr}^{2+}$  or  $\text{Y}^{3+}$  [3], Polycyclic Aromatic Hydrocarbons (PAH) [4], all of them with high distribution constants, and also Volatile Organic Compounds (VOC) in air samples, with retention percentages of 100% [5]. The absence of solvent in the air samples also allows their computational study.

The search for new interactions that could improve the capture capacity of these materials led to the theoretical-experimental study of the interaction between gold and silver nanoparticles with different Volatile Organic Compounds (VOC). This study demonstrated that regium-pi interactions can be used to design materials that capture these compounds [6].

Currently, the group is working on the modification organic moieties to functionalize the nanoparticle to obtain new materials capable of selectively capturing other analytes.

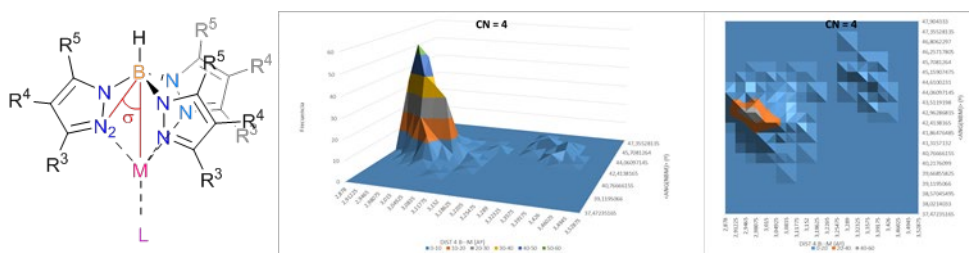


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Polypyrazolylborate scorpionate metal derivatives provide an important source for active catalytic centres.[1] The restriction of the coordination ability of the metal can force precise catalytic pathways. Furthermore, scorpionate ligand decoration allows the modulation of electronic and steric properties of the metal centre. Understanding the influence of the ligand decoration in the catalytic pocket geometry could improve the design of active metal centres although very limited work in this sense has been carried [2]. We here present a thorough study of metal centre geometry for this type of complexes based on the numerous structures deposited in the CSD.[3]. We have successfully parametrized the catalytic pocket scaffold and studied the influence of the metal, the coordination index and the ligand decoration. The studies show interesting tendencies that allow the design of optimized active catalytic centres. First conclusive catalytic activity results obtained in the group show the critical influence of the catalytic pocket in the reaction pathway.



Heat plot for B···M distance *versus* scorpionate ligand grip ( $\sigma$ ).

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## THE MECHANICAL BOND AS A POWERFUL TOOL FOR CONTROLLING REACTIONS IN [2]ROTAXANES

IL16

**Alberto Martínez Cuezva, Jesús de María Pérez, Carmen López-Leonardo, Mateo Alajarin, Adrián Saura-Sanmartín, Marta Marín-Luna, Aurelia Pastor, José Berná**

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The synthesis of mechanical interlocked molecules has received increased attention over the last decades, with the mechanical bond inferring particular properties to these systems.<sup>1</sup> Within the wide range of potential applications (mechanical work in motors or molecular machines,<sup>2</sup> catalysis,<sup>3</sup> etc), different research groups have focused their efforts on the study of the chemical reactivity of interlocked molecules. In general, the kinetic stabilization of the functional groups located in the inner of the sterically crowded macrocyclic counterpart is observed.

Herein we describe our efforts on the selective control of the reactivity of hydrogen-bonded rotaxanes due to the presence of the mechanical bond. Unprecedented effects of the mechanical bond on several processes are detected: protection of the final products against decomposition (quantitative yields), modulation of the reaction rate and control of the diastereo- and enantioselectivities.<sup>4</sup>

*Acknowledgments: This research was supported by the Spanish Ministry of Science and Innovation (PID2020-113686GB-I00/MCIN/AEI/10.13039/501100011033) and Fundacion Seneca-CARM (Project 21907/PI/22).*

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## 7. ORAL PRESENTATIONS (OP)

**OP1-22**

# SYNTHESIS AND CHARACTERIZATION OF PHTHALOCYANINES AS HOLE TRANSPORTING MATERIALS IN PEROVSKITE SOLAR CELLS

OP1

Javier Ortiz,<sup>1</sup> Adrián Hernández,<sup>1</sup> Jorge Follana-Berná,<sup>1</sup> Peng Huang,<sup>2</sup> Naveen Harindu Hemasiri,<sup>2</sup> Sanrama Kazim,<sup>2,3</sup> Luis Lezama,<sup>4</sup> Shahzada Ahmad,<sup>2,3</sup> Ángela Sastre-Santos<sup>1</sup>

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Perovskite solar cells could be a viable alternative to silicon cells if the necessary stability could be achieved under real-world operating conditions. The hole-transporting material (HTM) is an essential component of the cell and can help stabilize the device. The current reference compound, Spiro-OMeTAD, is expensive and a good conductor only when doped with Li-TFSI or *tert*-butylpyridine. Unfortunately, these dopants accelerate the degradation of the perovskite layer and decrease the lifetime of solar cells. There is a need for new, more stable and cheaper materials that do not require dopants to achieve good performance and long-term stability.[1]

Phthalocyanines are good p-type semiconductors, very stable and easy to prepare. Their physical and electronic properties can be tuned by varying the substituents at the peripheral positions and the central metal ion. [2] In this presentation, a new family of metallophthalocyanines (MPcs) substituted with bis(4-methoxyphenyl)amino groups will be presented (Figure 1). [3] Their HOMO-LUMO levels are suitable for use as hole-transporting materials in perovskite solar cells. Furthermore, their high solubility allows the deposition of thin films by solutions compatible with the perovskite layer. It has been studied how the number of substituents, the incorporation of fluorine atoms and the identity of the central metal ion affect photovoltaic properties.

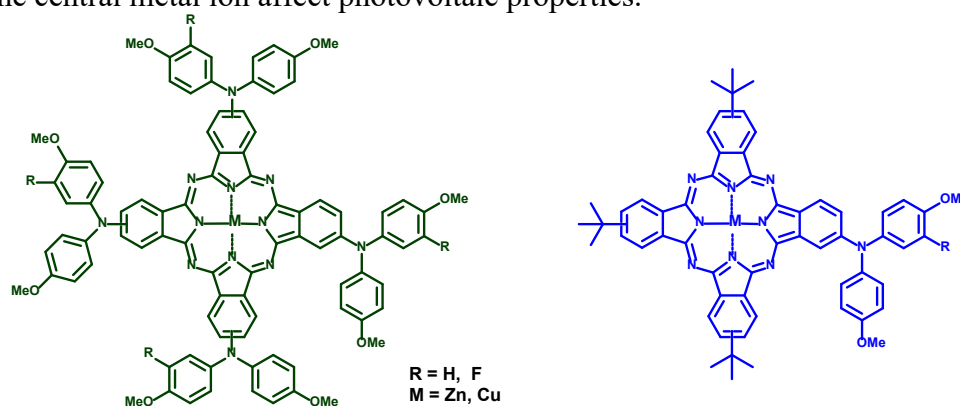


Figure 1. Different MPcs structures as HTMs in PSCs.

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# CYCLOPROPANOLS AS HYDROXYALLYLATION AGENTS FOR THE DIASTEREOSELECTIVE ADDITION TO *N*-*TERT*-BUTANESULFINYL IMINES

OP2

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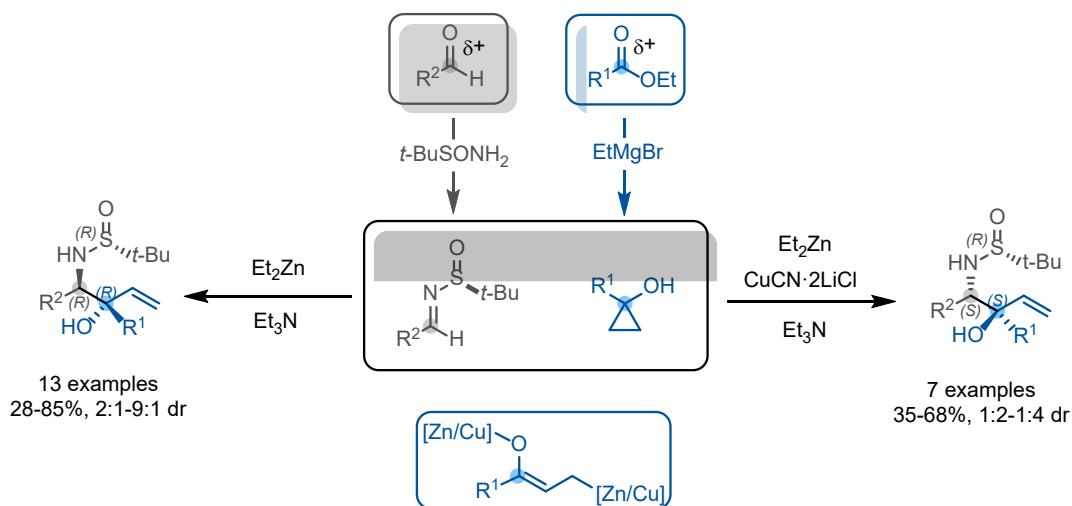
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The diastereoselective allylation of *N*-*tert*-butanesulfinyl imines has been widely studied.[1] This transformation yields enantioenriched homoallyl amine derivatives, that are intermediates of great interest in organic synthesis.[2] In this work, we have explored the stereoselective hydroxyallylation of these chiral sulfinyl imines.[3] The method is based in the generation of enolized zinc homoenolates from cyclopropanols, that can act as oxallyl nucleophiles and attack in a stereoselective manner the imine, favoring the *anti*-isomers.[4]

When Et<sub>2</sub>Zn and Et<sub>3</sub>N were used for the generation of the organozinc compound, the addition of the enolized homoenolate occurred selectively through the *Si*-face of the imines with *R*-configuration at the sulfur atom. On the other hand, when CuCN·2LiCl was used as an additive, it was possible to switch the selectivity of the attack to the imine.



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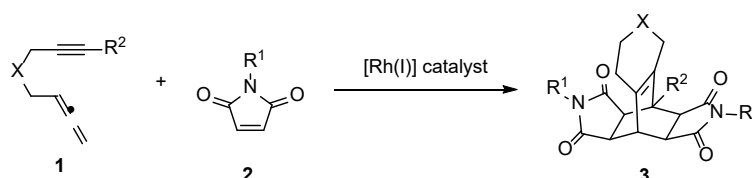
**Elias A. Romero-Cavagnaro,<sup>1</sup> Cristina Castanyer,<sup>1</sup> Anna Pla-Quintana,<sup>1</sup> Anna Roglans<sup>1</sup>**

<sup>1</sup>*Institut de Química Computacional i Catàlisi (IQCC) and Department of Chemistry. Universitat de Girona (UdG), C/Maria Aurèlia Capmany 69, 17003, Girona, Catalonia, Spain.*

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Transition-metal-catalyzed cyclization reactions have become a focal point in modern synthetic organic chemistry due to their ability to form multiple bonds and/or stereogenic centers in a single step with non-activated C-C unsaturated substrates, such as alkynes, allenes, and alkenes, thereby achieving ideal atom economy.[1] Among these, the use of allenes introduces unique unsaturation patterns, offering a rich landscape for novel cyclic compound formation, although controlling selectivity becomes more challenging.[2] To modulate and control the selectivity of the cycloisomerization reactions the most efficient strategy entails the fine tuning of the catalytic system and the reaction medium.[3]

Herein, we disclose our more recent efforts on the development of a novel cycloisomerization process entailing a rhodium-catalyzed cyclization cascade of 1,6-allenynes and maleimide derivatives for the efficient production of polycyclic *N*-based heterocycles. By modulating the catalytic system we have been able to generate a highly reactive vinylallene intermediate through a rhodium-catalyzed cycloisomerization of 1,6-allenynes, and by modulating the reaction medium this intermediate undergoes a double Diels-Alder cycloaddition with maleimide derivatives in a perfect cascade process resulting in bicyclo[2.2.2]oct-7-ene derivatives. (Scheme 1) Our findings highlight the versatility and efficiency of this transition metal-catalyzed cascade reaction allowing precise control over chemo- and diastereoselectivity. This approach not only simplifies the synthesis of complex polycyclic structures but also enhances our understanding of selectivity in cyclization reactions.



**Scheme 1.** General reaction between 1,6-allenynes and maleimide derivatives

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# DIASTEREOSELECTIVE SYNTHESIS OF SPIROOXINDOLO PYRROLIZIDINES AND PROLINES VIA 1,3-DIPOLAR CYCLOADDITION USING CHIRAL ACRYLATES: A MULTICOMPONENT REACTION

OP4

**M. González-Marcos,<sup>1</sup> F. Foubelo,<sup>1</sup> M. G. Retamosa,<sup>1</sup> J. M. Sansano<sup>1</sup>**

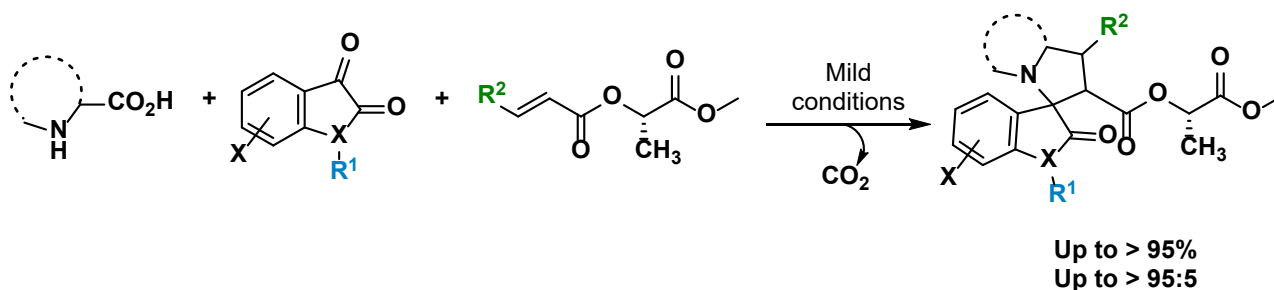
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The synthesis of spirocyclic, drug-like compounds has garnered significant attention in the scientific community due to their broad applicability in biomedical sciences and their potential for interacting with various biomolecules<sup>[1]</sup>. Among these, the spirooxindole pyrrolidine framework is a critical structural component in many naturally occurring alkaloids<sup>[2]</sup> and pharmaceutical molecules, known for their diverse inhibitory properties, including antitumor, antimicrobial, anti-HIV, antiviral, and anticancer activities<sup>[3]</sup>. Isatins and their derivatives are commonly employed as starting precursors for the synthesis of these compounds.

One of the most studied methods for constructing racemic spirooxindoles involves the 1,3-dipolar cycloaddition of azomethine ylides, generated in situ via the decarboxylative condensation of isatins and  $\alpha$ -amino acids with olefins. However, a review of the literature reveals that most approaches focus little on the diastereoselective production of spirooxindole alkaloids.

In this study, we successfully developed a diastereoselective synthesis of spirooxindole pyrrolizidines and prolines via 1,3-dipolar cycloaddition, using isatins, *L*-proline or sarcosine, and chiral acrylates derived from (*S*)-methyl lactate under mild conditions. The study explored the impact of various substituents on the isatins and olefins, yielding the corresponding products with high diastereomeric ratios and excellent yields. These compounds show promise as candidates for investigating antiviral activity, particularly against SARS-CoV-2.



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## Acknowledgements

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# MIMICKING EARLY PHOTOSYNTHETIC EVENTS: ELECTRON AND CHARGE TRANSFER IN PERYLENE-DIIMIDE-BASED CONJUGATES

OP5

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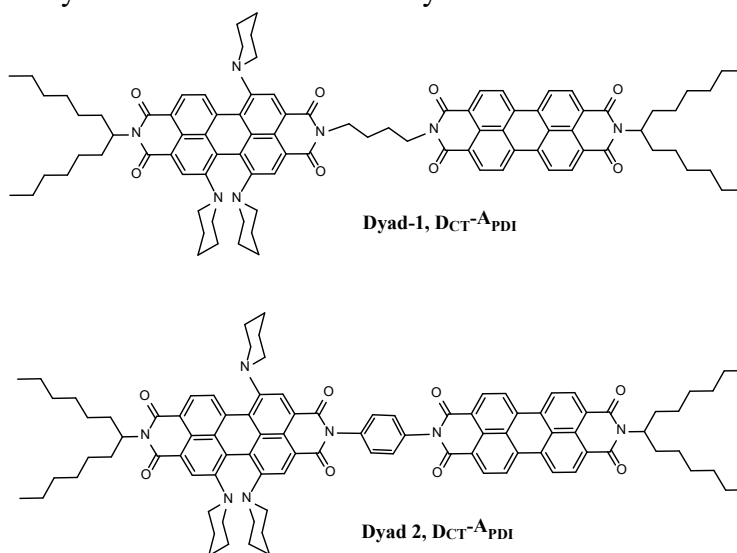
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Fundamental discoveries in charge and electron transfer (CT, ET) in chemical and biological systems propel scientific and technological advancements [1]. It is believed that in plant and bacterial photosynthesis, the primary donor, a chlorophyll or bacteriochlorophyll dimer, forms an initial excited symmetry breaking charge transfer state ( $^1\text{CT}^*$ ) upon photoexcitation which subsequently promotes sequential ET events [2]. Various molecular and supramolecular systems have been synthesized and characterized to mimic the functions of photosynthesis.

In this study we synthesize two only PDI-containing dyads and explore the mechanisms of CT and ET under external stimuli such as light and heat. We demonstrated the former photochemical event using an excited charge transfer molecule as a donor. An electron-deficient perylene-diimide (PDI) was functionalized with three electron-rich piperidine entities at the bay positions [3], resulting in a far-red emitting charge transfer molecule ( $\text{D}_{\text{CT}}$ ). This molecule was then covalently linked to another PDI ( $\text{A}_{\text{PDI}}$ ) with no substituents at the bay position, creating wide-band capturing  $\text{D}_{\text{CT}}\text{-A}_{\text{PDI}}$  conjugates.

After the investigation of the photodynamics and redox properties of these conjugates, the results show that photoinduced electron transfer initiated by the singlet excited charge transfer state as against a regular locally excited state is successfully established.



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Optically active alkene-substituted frameworks are important building blocks in enantioselective synthetic chemistry. The presence of a double bond makes these molecules highly versatile for the construction of more complex natural and biologically relevant products. In this sense, Pd-catalyzed asymmetric allylic substitution reaction offer a simple and efficient approach to forming chiral C–X bonds (where X= C, N, O, Scheme 1), and therefore is considered a valuable method for synthesizing these compounds.[1] This reaction is particularly advantageous due to its mild conditions and wide functional group tolerance.

Our research group has made significant contributions in this field through the development of an improved class of ligands. We have demonstrated that incorporating biaryl-phosphite moieties into ligand design offers substantial advantages, effectively addressing key limitations such as low reaction rates, high substrate specificity, and limited nucleophile scope.[2] These air-stable and easily accessible ligands provide excellent enantioselectivities (ee's up to 99%) across a broad range of both hindered and unhindered substrates with a diverse array of nucleophiles, including C-, O- and N-based nucleophiles. Through a combination of density functional theory (DFT) calculations and experimental studies, we have elucidated the key factors governing the high enantioselectivity observed in these reactions.

Additionally, the potential application of allylic substitution using functionalized malonates has been demonstrated by the practical synthesis of complex tricyclic compounds.[3] These compounds, containing multiple functional groups and stereogenic centers, were obtained with excellent diastereo- and enantioselectivities. The synthetic routes employed straightforward sequences that includes allylic substitution followed by Pauson-Khand reactions or Pt- and Au-catalyzed cycloisomerization reactions.

**Scheme 1.** General example of Pd-catalyzed asymmetric allylic substitution.

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# COMPUTATIONAL MECHANISM OF FORMAL (4+2) CYCLOADDITION BETWEEN AMIDES AND DIENES VIA C–H BOND ACTIVATION

OP7

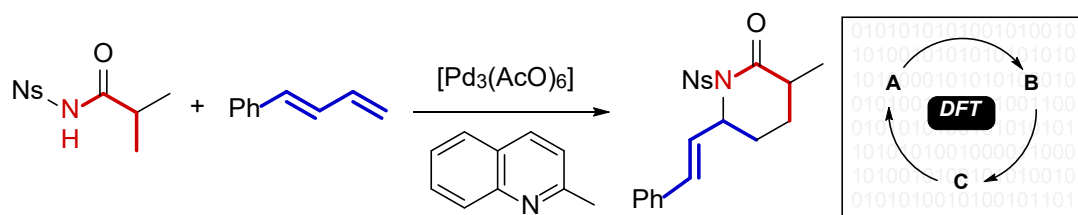
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Transition-metal-catalyzed activation and functionalization of C–H bonds has become a powerful tool in organic chemistry. While processes that activate substrates with C(sp<sup>2</sup>) atoms are widespread, those involving C(sp<sup>3</sup>) atoms are less common and more challenging [1]. In this context, some of us reported the Pd-catalyzed activation of alkyl amides coupled with dienes to form cycloadducts [2]. This system provided good yields and scope, although the detailed reaction mechanism is still unknown. To address this issue, we turn to computational chemistry (DFT) to simulate the catalytic process at atomic level.

Here we report the coupling between the nosyl secondary alkyl amide and the phenyl diene shown below, using [Pd<sub>3</sub>(AcO)<sub>6</sub>] as precursor and quinaldine as ligand. After an initial study on Pd speciation, we computed a feasible reaction mechanism to form the product, which involves (i) C–H bond activation, (ii) ligand exchange, (iii) insertion, and (iv) reductive elimination. We found that this particular N-based ligand plays a key role in both dissociating the initial Pd trimer and promoting the insertion step.



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# STUDY OF NOVEL ANION-INDUCED SUPRAMOLECULAR POLYMERS BASED ON TRIAZOLIUM AND SQUARAMIDE RECEPTORS

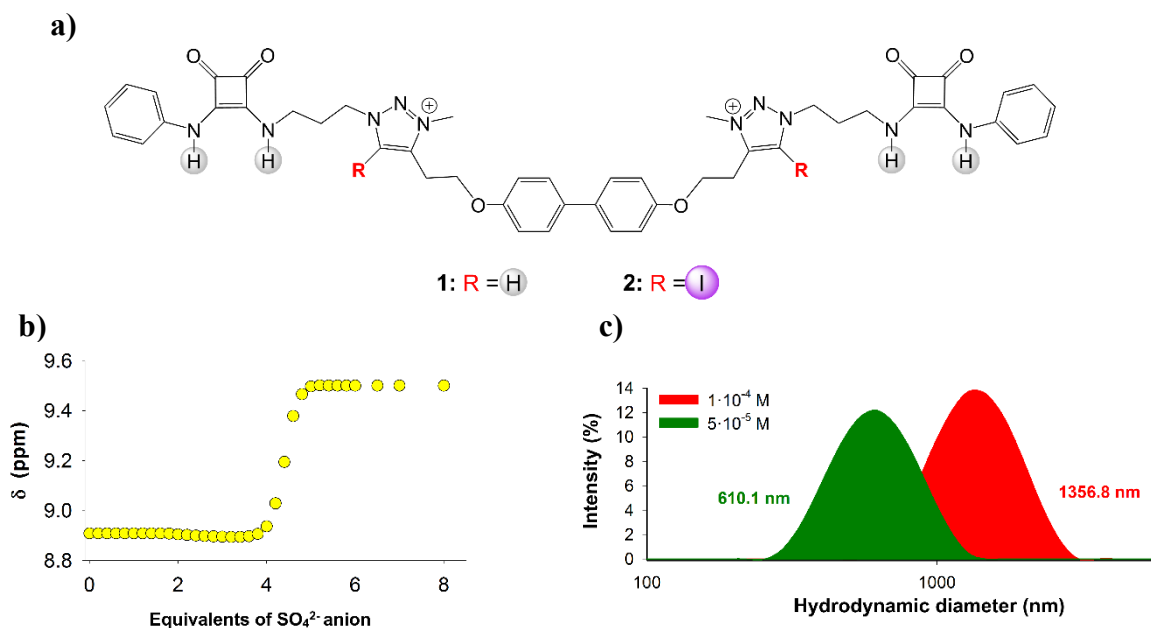
OP8

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In the past decades, anion recognition has been a significant well-established field within the supramolecular chemistry of anions [1]. However, anion-induced supramolecular polymers remain largely unexplored. These kinds of polymers are formed through the self-assembly of molecules, stabilized by reversible non-covalent interactions such as hydrogen and halogen bonding [2, 3].

In this work, we present the synthesis of two anion receptors bearing a central 4,4'-biphenyl group connected on each side to triazolium or iodo-triazolium groups, and squaramide groups acting as anion binding sites (Fig. 1a). Subsequently, a comparative study of novel supramolecular structures was carried out to evaluate the key role of anions in the formation of classical anion-receptor complexes versus supramolecular polymers in solution. The addition of increasing amounts of  $\text{SO}_4^{2-}$  anions into solutions of receptors **1** and **2** in  $\text{DMSO}-d_6$ , respectively, did not promote any shifts in the  $^1\text{H}$  NMR spectra, after 4.0 and 6.0 equivalents were added, significant downfield shifts were induced by the anions, suggesting the formation of supramolecular polymers (Fig. 1b and 1c). All of these supramolecular structures were studied by  $^1\text{H}$ -NMR, UV-Vis spectroscopy, Dynamic Light Scattering (DLS) and DOSY experiments.



**Figure 1.** a) Chemical Structure of the receptors, b)  $^1\text{H}$  NMR titration profiles for **1** during the addition of  $\text{SO}_4^{2-}$  anions. c) DLS results obtained for receptor **2** in presence of  $\text{SO}_4^{2-}$  anions.

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We have witnessed during the last 15 years the great evolution that visible-light photoredox catalysis has experienced as a powerful tool in organic synthesis and formation of new compounds can be now tackle. In this context, generation of radical intermediates such as aryl radicals and their subsequent trapping by the appropriate nucleophile is nowadays one of the main strategies to obtain added-value products.<sup>1</sup> The use of mild conditions and “sometimes” metal-free photocatalysts encompasses this methodology into the green principles from an economical and environmental point of view.

Organoboron compounds, environmentally benign scaffolds, attract considerable interest not only in organic synthesis (they can be easily transformed into any other functional group) but also in other scientific areas of research, for example, as conjugated materials such as organic electronic applications and LEDs manufacturing or antimicrobial agents in medicinal chemistry.<sup>2</sup> On the other hand, organosulfur compounds have a key role in nature, and development of new strategies for C-S bonds formation is crucial not only in numerous organic reactions, but also in drug discovery.<sup>3</sup> This is particularly relevant in the synthesis of aryl sulfides, which are significant structural moieties. Moreover, C-S bonds are present in drugs employed for the treatment of different diseases, such as cancer, HIV, and Alzheimer’s malady.<sup>4</sup>

Therefore, exploration of new procedures for their construction under milder conditions appears to be a challenge task. The question then arises whether production of new forming C(sp<sup>2</sup>)-heteroatom (B, S) bonds can be achieved by visible light as energy source. Herein, we wish to show our recent results on the borylation and thiolation of five-membered heteroarene halides.<sup>5</sup> Interestingly, the corresponding syntheses have followed a photocatalyst-free protocol. In the case of new boronic esters, an easy-to-use gel nanoreactor has been used which has permitted to enhance the production rate and to protect against oxygen poisoning. Regarding the new thioethers, a straightforward methodology involving an EDA complex formation has been successfully employed.

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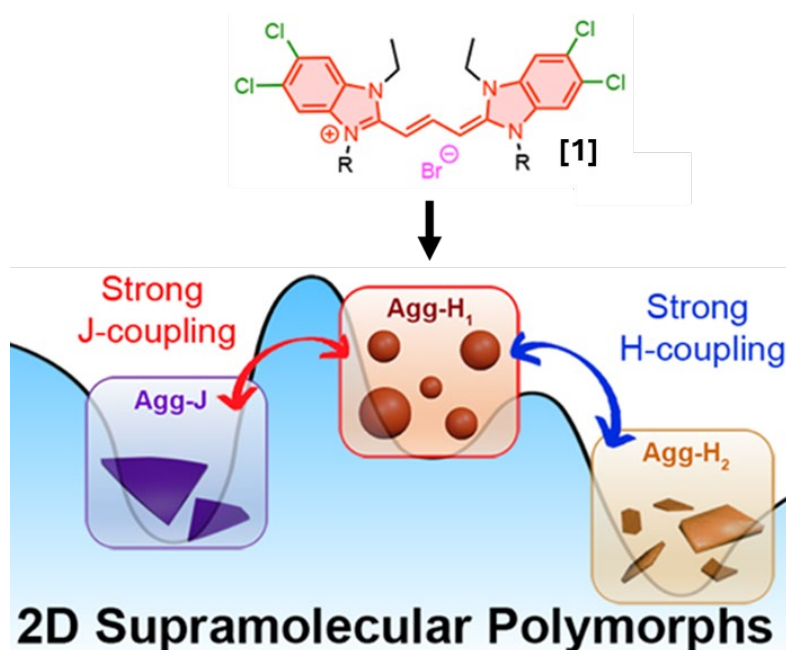
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Cyanines are a well-known class of dyes with a wide range of applications, from DNA or protein labeling to organic solar cells.<sup>[1]</sup> The self-assembly of cyanine dyes have been widely studied in in water where they tend to form nanotubular J-aggregates,<sup>[2]</sup> while relatively few examples of aggregation in organic solvents have been reported.<sup>[3]</sup> In this study, we developed a new cyanine dye (**1**), featuring two rod-like side groups, which can form two distinct two-dimensional (2D) supramolecular polymorphs in methylcyclohexane: an H-type aggregate (Agg-H<sub>2</sub>) and a J-type aggregate (Agg-J). These polymorphs were not formed through typical polymerization processes but instead resulted from the thermal transformation of a third, particle-like polymorph (Agg-H<sub>1</sub>).

The Agg-H<sub>2</sub> polymorph is reached upon cooling the Agg-H<sub>1</sub> solution by a reversible transition. On the other hand, Agg-J is accessed via a hidden pathway applying sonication and cooling to the Agg-H<sub>1</sub> solution. This is the first report of H- and J-type cyanine polymorphs that can be isolated as solid materials, resulting in two new 2D photoactive structures. This research introduces new strategies for designing 2D supramolecular assemblies using rod-like molecular groups and highlights the significance of pathway complexity and polymorph transitions in the development of novel photonic materials.



**Figure 1.** Scheme of the proposed energy landscape for the aggregation behavior of cyanine 1.

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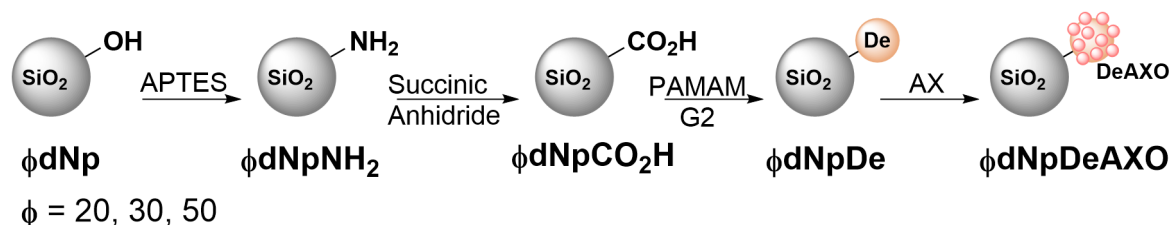
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A global health problem nowadays are drug hypersensitivity reactions. The drugs most commonly involved in these reactions are  $\beta$ -lactam antibiotics (BLs). However, diagnosis is complex and involves clinical history and *in vivo* methods (skin tests or drug challenge tests) which can be risky. To avoid drug challenge tests, the use of complementary *in vitro* methods is preferred, so accurate diagnostic methods are essential. Dendrimeric antigens (DeAns) consist of dendrimers decorated with multiple units of penicillin antigenic determinants. These conjugates have been shown to be a powerful tool for the diagnosis of penicillin allergy using *in vitro* immunoassays in which they are recognised by specific patient IgE [1-5].

Here, we present the use of improved nanoparticles with a biocompatible coating onto which DeAns have been anchored. These nanocomposites have the ability to be selectively recognised by certain antibodies involved in the allergic process, making them suitable for the *in vitro* detection of drug allergy. Immunoassays performed with these nanomaterials have resulted in improved sensitivity and specificity of known techniques, where the core of the Nps has been fundamental for viable application in hospital use.



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**INTRODUCTION:** Synthetic polypeptide-based nanomedicines represent highly versatile, advanced therapeutic platforms, with multiple examples currently under clinical evaluation and polypeptidic drugs (Vivagel® and Copaxone™) achieving market approval [1]. As a drug delivery component, imaging represents a crucial means of improving nanomedicine-based therapy by optimising patient stratification/treatment and accelerating the development/translation of personalised nanomedicines [2]. Theranostics combines therapeutic and diagnostic components into a single agent, providing real-time monitoring that can address remaining challenges in the field [2,3]. Introducing a porphyrin group can afford disease monitoring as part of theranostic approaches. Porphyrins and Phthalocyanines are robust organic compounds bearing interesting photophysical properties, such as their attractive absorption and emission [3], and have been used for various applications that include diagnostic (e.g., fluorescence or magnetic resonance imaging [4]) and therapeutic (through photodynamic effects [5]) uses.

**RESULTS AND DISCUSSION:** In this study, we exploited well-defined biodegradable polypeptide-based architectures prepared using N-carboxy anhydride ring-opening polymerised (NCA-ROP) [3,7] to obtain four-armed polyglutamic acid (PGA) constructs that self-assemble to yield stabilised supramolecular nanostructures with therapeutically-relevant properties [7]. Employing porphyrins and Phthalocyanines as a core supports intrinsic imaging properties due to their photovoltaic properties [6]. Deprotection steps ensured the complete removal of protecting groups without racemisation. This approach has obtained structures with different characteristics depending on the number of PGA units, going from cylindrical to spherical. They can be combined with imaging and photodynamic therapy using this characteristic because they also have different circulation times in the body and cell accumulation. Biological evaluation of these novel architectures has highlighted their robust imaging and photodynamic therapy potential.

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## ROBUST MICROPOROUS HYDROGEN-BONDED ORGANIC FRAMEWORK FOR SELECTIVE CO<sub>2</sub> SORPTION

OP13

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Reticular chemistry has become a hot topic along the last few decades due to the development of synthetic methods for the preparation porous materials such as Metal Organic Frameworks (MOFs) and Covalent Organic Frameworks (COFs).<sup>[1]</sup> The rich structural diversity of these reticular systems has led to the investigation of their application in areas as diverse as catalysis, sensing, electronics, batteries, drug delivery, biomedicine or gas separation and storage. Currently, these frameworks have become a promising alternative to traditional porous materials represented by polymers, active carbon or zeolites.

More recently a supramolecular approach for porous materials has emerged. This is based on the self-assembly of molecular tectons to build up Hydrogen-Bonded Organic Frameworks.<sup>[2]</sup> The weakness of hydrogen bonding, when compared to covalent or coordinate bonds, makes the investigation of HOFs a challenging target. In this regard, a precise design, considering the combination of rigid building blocks and adequately oriented hydrogen bonding sites, constitutes one of the essential principles for the growth of HOFs.

Our research about hydrogen-bonded azaphenes has proved the utility of 7-azaindole as a robust reciprocal hydrogen bonding motif. Accordingly, the integration of this unit into the  $\alpha$ -carboline skeleton and the synthesis of tetra( $\alpha$ -carbolin-6-yl)methane, TACM, has led to a crystalline microporous material with extraordinary thermal robustness. Moreover, the interpenetration of its diamonoid network defines monodimensional channels that bestow an interesting selectivity for CO<sub>2</sub> uptake on TACM-HOF.<sup>[3]</sup> This property highlights the potential of this material in the capture of pollutants related to the global warming and also in the separation of CO<sub>2</sub>/CH<sub>4</sub> mixtures for improving the quality of natural gas and biogas.

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**NANOSIZED COPPER STABILIZED ON TERNARY P, N, S-DOPED GRAPHENE FROM CHITOSAN SHELLFISH WASTE: PREPARATION AND CATALYSIS OF SINGLE AND DOUBLE A<sup>3</sup>-TYPE AMINE COUPLING**

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Heteroatom-doped carbons are typically obtained through multistep procedures, often requiring tedious post-grafting and/or harsh conditions to ultimately provide less-defined heterogeneous catalysts. We propose a simplified method to obtain heteroatom-doped carbons by modifying chitosan, an abundant marine waste, followed by its graphitization. This approach allows to produce a porous carbon material containing nitrogen, phosphorus, and sulfur, with tunable textural properties. Functional groups ensure exfoliation and dispersion of the sheets, while coordinating sites effectively stabilize the metal nanoclusters. Good catalytic activity has been observed for the synthesis of propargylamines, making this method a promising pathway for heterogeneous carbon-based catalysts.

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# FLUORESCENT DERIVATIVES OF POLYAMINO SQUARAMIDE POLYMERS (PASQUA): UNVEILING CELL INTERNALIZATION AND MOLECULAR TRANSPORT MECHANISM

OP15

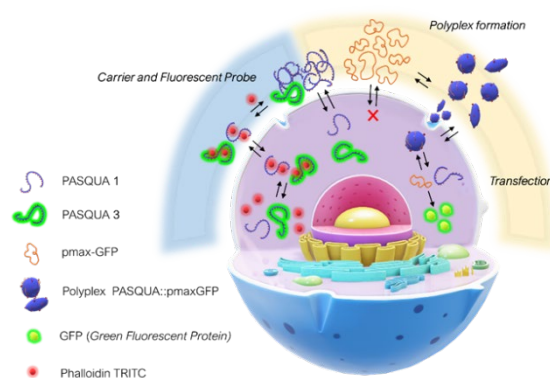
B. Galmés,<sup>1</sup> F. Olmo,<sup>2</sup> G. Ramis,<sup>1</sup> J. Kelly,<sup>2</sup> A. Costa,<sup>1</sup> C. Rotger<sup>1</sup>

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Gene delivery is a powerful technique with promising applications in fields such as molecular biology and medicine.<sup>1</sup> We have developed a family of synthetic polyaminosquaramide polymers (PASQUA) that demonstrate high efficiency in gene delivery across challenging biological environments.<sup>2</sup> To investigate the mechanisms of cellular internalization and molecular transport of these polymers, we synthesized fluorescent PASQUA derivatives. These derivatives retain the structural characteristics of the parent polymers to preserve their gene delivery capabilities.

In this study, we utilized two different fluorophores, BODIPY and coumarin linked to branched PASQUA. While BODIPY-PASQUA exhibits luminescence under all cellular conditions, the fluorescence of coumarin-PASQUA is pH-dependent, making it useful for studying intracellular trafficking. Both BODIPY-PASQUA and coumarin-PASQUA polymers efficiently internalize cells and deliver nucleic acids. Additionally, small anionic fluorescent cyclopeptides are also internalized in the presence of BODIPY-PASQUA.



**Figure 1.** PASQUA as fluorescent probe, carrier across the membrane and chemical gene vector

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## PROBIOTIC-BASED LIVING MATERIAL AS AN ALTERNATIVE TO TREATING CARBAPENEM RESISTANT BACTERIAL INFECTIONS

OP16

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The exponential increase of antibiotic-resistant bacteria has emerged as one of the most pressing and critical threats to global public health. In particular, carbapenem-resistant bacteria (CRB) attract special attention because carbapenem antibiotics are considered as the last resort treatments for multidrug-resistant bacteria [1]. In this study, we investigated the antimicrobial properties of probiotic cellulose (PC), which consists of dense cellulose nanofibers colonised by probiotic bacteria of the genus *Lactobacillus*, classified as GRAS (generally recognised as safe). This overcomes the fact that bacterial cellulose produced by *Komagataeibacter xylinus* itself has no antibacterial activity [2]. Different samples of PC loaded with *Lactobacillus fermentum* (*Lf*), *Lactobacillus plantarum* (*Lp*) and the mixture of both (*Lp+Lf*), were tested to fight against CRB, isolated from clinical samples from the Hospital Virgen de las Nieves (Granada). To test their efficacy, agar diffusion inhibition assays were performed in the medium favorable for pathogen growth. In conclusion, it was found that all the PC exhibited inhibition halos against the CRB tested. The effective inhibitory activity of PC against CRB is due to the encapsulation of the probiotics inside the cellulose membranes, since free *Lactobacillus* species (without BC) did not show inhibitory activity against any of the pathogenic strains tested (Fig1).

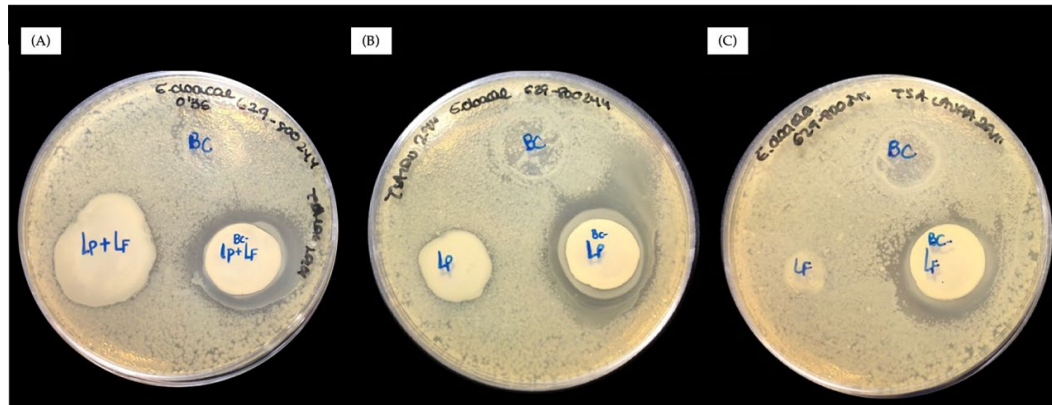


Fig1. PC and free *Lp+Lf* (A), *Lp* (B), and *Lf* (C) against CRB (*Enterobacter cloacae*), by agar diffusion tests on TSA plates.

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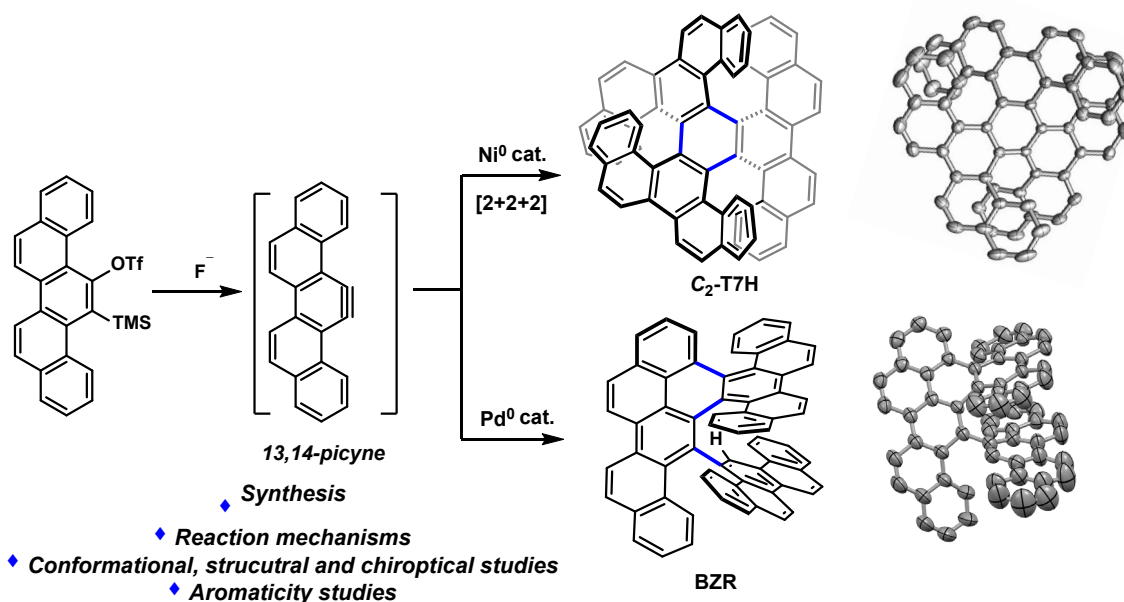
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A highly contorted polycyclic aromatic hydrocarbon (PAH) displaying three carbo[7]helicene moieties fused in a central six-membered ring (**C<sub>2</sub>-T7H**) was synthesized through the Ni<sup>0</sup>-catalyzed cyclotrimerization reaction of an aryne intermediate.<sup>1</sup> The reaction mechanism was studied in silico to explain the crucial role of the Ni catalyst to the reaction outcome and its diastereoselectivity. Additionally, the evaluation of the aromaticity in this triple carbo[7]helicene was analyzed utilizing magnetic and electronic criteria leading to important insights challenging the limitations of Clar's model of aromaticity. The conformational, structural and chiroptical properties of **C<sub>2</sub>-T7H** were also studied.<sup>2</sup> We observed that under certain Pd<sup>0</sup> catalysts, the same aryne intermediate trimerizes in a completely different manner to provide a trimeric molecule displaying a double carbo[5]helicene moiety and a stereogenic axis (**BZR**). This reaction product was further modified by the Scholl reaction. The conformational and chiroptical properties were again explored and the mechanism was studied both experimentally and by DFT calculations to explain that this dramatic change of reactivity requires the presence of trace amounts of water in the reaction medium.



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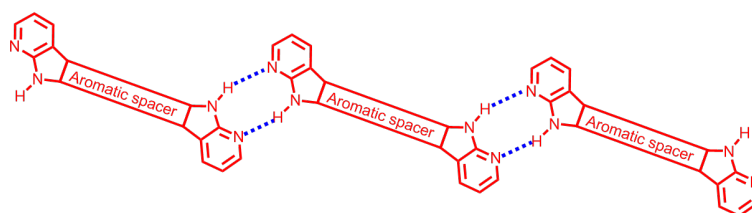
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The integration of organic semiconductors as active components of optoelectronic devices confers them very appealing technical features mainly related to lightness, flexibility, and ease of processing. Nevertheless, organic materials processed as solid thin films suffer from intrinsic disorder owing to the weak non-covalent intermolecular interactions that govern their organization [1]. Consequently, this has a detrimental effect on the charge transport properties.

With the aim of mitigating this shortcoming, different strategies have been explored from a molecular design perspective. In this regard, an interesting approach lies on the incorporation of functional groups that promote self-assembly through hydrogen bond interactions that enable certain control of the molecular arrangement in the solid state [2].

Herein, a series of fused polyheteroaromatic molecular materials integrating the 7-azaindole unit within the conjugated system itself is presented [3-6]. The material design has been conceived to set complementary hydrogen bonds between adjacent molecules. The influence of the hydrogen bond-directed self-assembly on the charge transport ability of novel hole transporting materials has been evaluated in organic field-effect transistors and hybrid photovoltaic devices.



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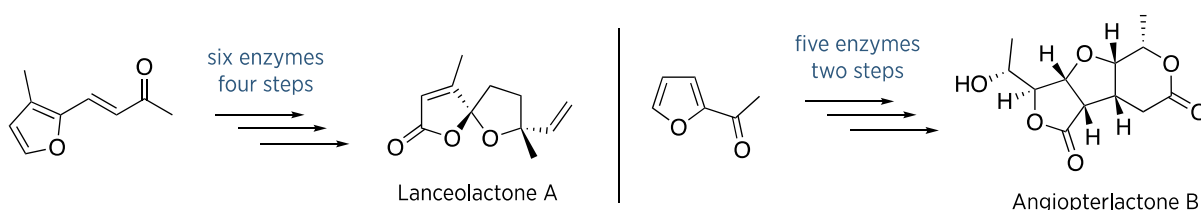
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Biocatalysis is increasingly gaining ground as powerful technique in the organic chemist's toolbox for the synthesis of well-defined building blocks. However, with regard to an even broader application of enzyme catalysts in classical synthetic chemistry, the lack of biosynthetic precedence for numerous synthetically relevant reactions and the consequent lack of biocatalysts to promote those reactions need to be considered a major drawback. Since many years, catalytic promiscuity, the enzymes' capability to catalyze fundamentally different chemical interconversions, has been in the scientific focus,<sup>[1]</sup> however, just recently entirely abiotic transformations came within reach by means of specialized, engineered protein catalysts.<sup>[2,3,4]</sup>

In our search of biological catalysts with abilities to address synthetically important reactions beyond the biosynthetic repertoire, a range of wild-type metalloenzymes was identified to be effective promoters in a variety of heterocyclic transformations.<sup>[5,6]</sup> This talk will highlight the synthetic potential resulting from the discovery of enzyme activities in abiotic processes. Focussing on furan oxidation biocatalysis, I will present the enzymatic method development and mechanistic deviations thereof,<sup>[7,8]</sup> implementations of the novel biocatalysis modules in tailor-made cellular factories for furan valorization chemistry,<sup>[9]</sup> and applications in natural product synthesis of complex polycyclic plant metabolites such as lanceolactone A<sup>[10]</sup> and angiopterlactone B.<sup>[11]</sup>



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# ANAESTHETIC AND ANTICANCER DRUGS COMPLEXATION BY CYCLODEXTRINS APPENDED WITH PHOSPHONIC ACID GROUPS ON THEIR PRIMARY FACES

OP20

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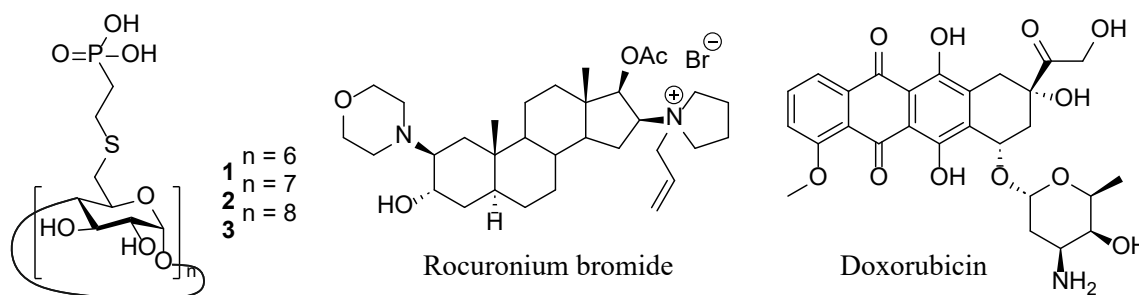
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Cyclodextrins (CDs) are water-soluble molecules composed of 6 ( $\alpha$ -), 7 ( $\beta$ -) or 8 ( $\gamma$ -CD) glucopyranoside units, which form a ring structure. This arrangement creates two openings of hydrophilic nature and different sizes, and a hydrophobic inner region, enabling CDs to host hydrophobic molecules in water solution. Their biocompatibility and low toxicity make CDs highly attractive for drug applications [1]. For instance, a  $\gamma$ -CD derivative decorated with 2-mercaptopropionic acid residues on its primary face (sugammadex, SGX) is widely used as a reversal agent for muscle relaxants, such as rocuronium and vecuronium [2], while the homologous  $\beta$ -CD derivative (subetadex, SBX) has been reported to enhance the solubility of certain anticancer drugs [3]. However, SGX-induced anaphylaxis is emerging as its usage is increased [4], probably due to the presence of carboxyl groups at the end of the branches [5]. Thus, we synthesized a series of CDs derivatives **1-3** featuring (2-mercaptoethyl)phosphonic acid residues, which were chosen for their bioisosteric similarity to phosphate groups commonly found in biological molecules [6].

The synthesis of such derivatives was carried out by reaction of periodinated  $\alpha$ -,  $\beta$ - and  $\gamma$ -CD with 2-(2-(diethoxyphosphoryl)ethyl)isothiuronium bromide, followed by ester hydrolysis. The resulting compounds were fully characterized by NMR, FT-IR and MALDI-MS. Their ability to form complexes with the anesthetic drugs rocuronium and vecuronium was assessed by isothermal titration calorimetry (ITC) and NMR spectroscopy. Interestingly,  $\gamma$ -CD derivative **3** showed binding constants in the same order of those reported for SGX, but with 2:1 (CD-drug) stoichiometry instead of 1:1. Additionally, the binding ability of the  $\beta$ -CD derivative **2** toward the anticancer drug doxorubicin (DOX) was studied using UV-Vis titration, showing a complexation behaviour similar to that described for SBX. Ongoing research is focused on studying the interactions of these derivatives with other anticancer drugs.



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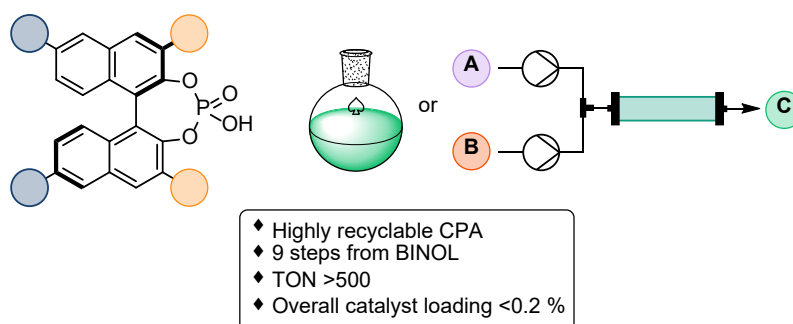
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Asymmetric organocatalysis has demonstrated high effectiveness in producing enantiomerically pure compounds since its introduction in the field around 20 years ago [1]. However, based on the limited applications of organocatalysis in industry and patent application processes in recent years [2], the scientific community is discouraged from applying asymmetric organocatalysis in large-scale production. In recent years, the development of recyclable organocatalysts has gained more attention in order to minimize the environmental effect and the overall cost of catalytic processes [3]. For the particular case of chiral phosphoric acids (CPA) [4], the current state-of-the-art requires up to 13 synthetic steps to access their recyclable analogues [5], making them less attractive than their homogeneous variants.

Here we report a general and concise approach to heterogeneous CPAs, which have shown high performance either in batch or continuous flow without observing catalyst degradation.



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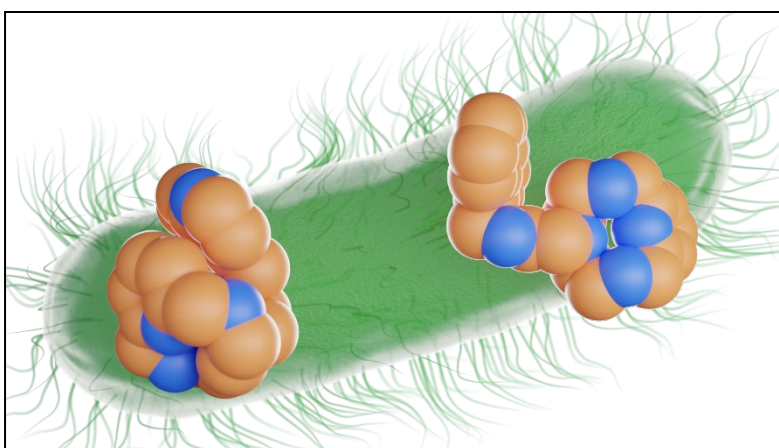
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Allosteric regulation is an important activity-modulation process in living systems. It takes place when a given substance (the effector) binds an enzyme and induces a conformational change that alters the activity of the protein.

At the dawn of medicinal chemistry, synthetic bioactive compounds were considered as rigid entities interacting with their biological target through a lock-and-key mechanism. Now, recent advances in experimental and computational techniques have given us insights into the “jiggling” nature of matter and the drastic conformational changes that molecules can experiment under different conditions. However, little importance has been given to the biomedical implications of this conformational changes.

Here we want to present a series of studies aimed at exploring how induced conformational changes can alter the activity of bioactive compounds, and how this “synthetic allosteric systems” can be exploited to develop advanced therapies, particularly in the fields of chemotherapeutic agents and antimicrobials.



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## 8. POSTERS (P)

**P1-29**



# SYNTHESIS OF PHTHALOCYANINE DERIVATIVES AS SELF-ASSEMBLED MOLECULES FOR EFFICIENT AND STABLE PEROVSKITE SOLAR CELLS

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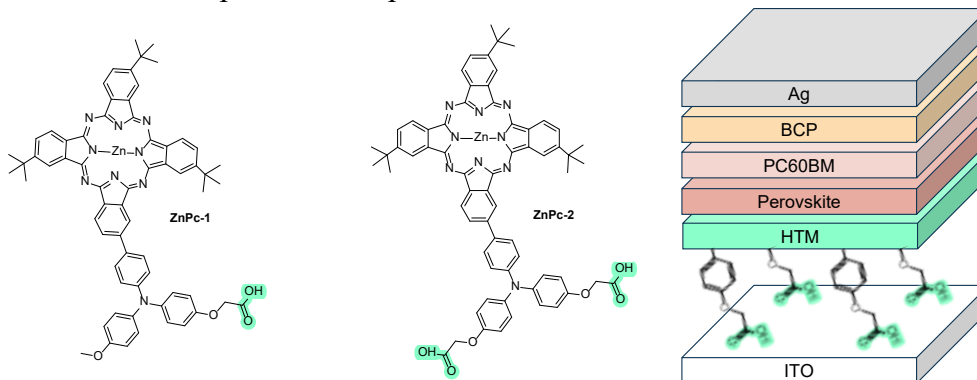
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Perovskite solar cells (PSCs) have emerged as a promising alternative to traditional silicon-based photovoltaics due to their low-cost fabrication and ease of preparation. Recent advancements have enabled PSCs to achieve power conversion efficiencies of up to 26.7% [1]. In conventional PSCs, the hole and electron transporting layers play a crucial role, and the use of self-assembled molecules (SAMs) has recently been explored due to their excellent selective properties [2]. Phthalocyanines (Pcs) offer a compelling solution, exhibiting both enhanced stability and potential for long-term economic viability as hole-transport materials [3].

In this study, we present the synthesis and characterization of two novel zinc phthalocyanines (ZnPcs) (Figure 1) as efficient, stable, and cost-effective hole transporting materials (HTMs) for PSCs. These ZnPcs are functionalized with three tert-butyl groups and a triphenylamine unit containing one or two carboxylic acid moieties. The molecular design provides suitable HOMO-LUMO levels and allows for solution-processable application across a range of PSC devices. We investigate how varying the number of anchoring groups in the phthalocyanine impacts the formation of SAMs and influences the photovoltaic performance of the PSCs.



**Figure 1.** Different ZnPcs structures as SAMs and the representation of the PSC device.

**Acknowledgments.** We want to thank the European Regional Development Fund “A way to make Europe” and the Spanish Ministerio de Ciencia e Innovación/Agencia Estatal de Investigación (PID2020-117855 RB-I00), and the Generalitat Valenciana (CIPROM/2021/059) for funding.

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# SYNTHESIS OF SUBSTITUTED PERYLENE-DIIMIDES AS SELF-ASSEMBLED MOLECULES FOR EFFICIENT AND STABLE PEROVSKITE SOLAR CELLS

P2

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Perylene-diimides (PDIs) are a very important family of dyes constituted by two fused naphthalene units. Their aromatic core can be functionalized in the *bay* and/or *ortho* positions, thus allowing the control of the optoelectronic properties of the PDI as a function of the nature of the introduced substituents [1]. Also, the *N*-imide positions are easily functionalized with different chains. Due to this synthetic versatility, PDIs can be applied in a wide variety of fields, being material chemistry one of the most important ones [2,3].

Perovskite solar cells have attracted the attention of researchers in recent years. In this type of device, self-assembled monolayers (SAMs) are employed as charge-selective contacts on ITO, being *p*-type hole-selective SAMs the most studied in this area, while the electron-selective SAMs have attracted less attention [4]. In this work, we will present the synthesis and photovoltaic studies on PDIs functionalized with carboxylic acid groups in the imide position that allows the anchoring of self-assembled monolayers in perovskite solar cells (see Figure 1). Photovoltaic studies show strong electron selectivity and excellent stability of devices, proving that PDIs are promising materials for electron selective SAMs [5].

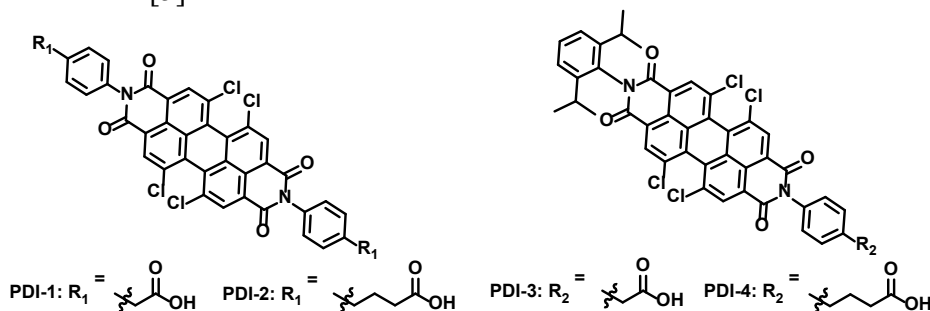


Figure 1: Different PDI structures used as SAMs

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## ENANTIOSELECTIVE [3+2] CYCLOADDITION REACTION OF ALDEHYDES WITH VINYLOGOUS ISOCYANOESTERS

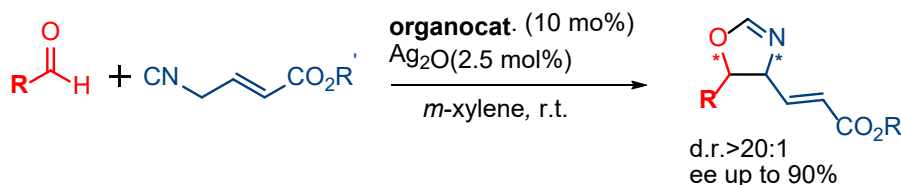
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$\alpha$ -Acidic isocyanides can be considered formal 1,3-dipoles due to the nucleophilic character of the deprotonated  $\alpha$  carbon and the presence of an empty orbital in the isocyanide group. This characteristic has been effectively utilized in the asymmetric synthesis of five-membered ring *aza*-heterocycles, including oxazolines, imidazolines and pyrrolidines [1]. These reactions require an electron-withdrawing group (e.g., carbonyl or sulfone) at the isocyanide  $\alpha$ -carbon to enhance hydrogen acidity, restricting the usable isocyanide-derivatives in asymmetric catalysis to  $\alpha$ -isocynoesters, isocynoamides and tosyl methyl isocyanide, thus limiting the broader application of the methodology.

On the other hand, the principle of vinylogy involves the transmission of electronic effects from a functional group in a molecule to a distant position through a system of conjugated double bonds. Vinylogous groups typically exhibit reactivity and chemical properties similar to those of the original functional group due to the propagation of electronic properties through the conjugated double bond system [2].

As a part of our research on asymmetric cycloaddition reactions with isocynoesters [3], we have synthesized vinylogous isocynoacetate derivatives and explored their potential in asymmetric catalysis. Herein, we present our preliminary results with aldehydes. The reaction provides isoxazolines bearing a conjugate ester chain in good yields, complete diastereoselectivity and high enantiomeric excesses.



**Acknowledgements:** Grant PID2020-116944GB-100 funded by MCIN/AEI/10.13039/501100011033 and by the “European Union Next Generation EU/PRTR”. Grant CIAICO/2021/147 funded by Conselleria d’Educació, Cultura, Universitats i Ocupació. C. G.-C. thanks the Generalitat Valencia for a Grisolia pre-doctoral grant.

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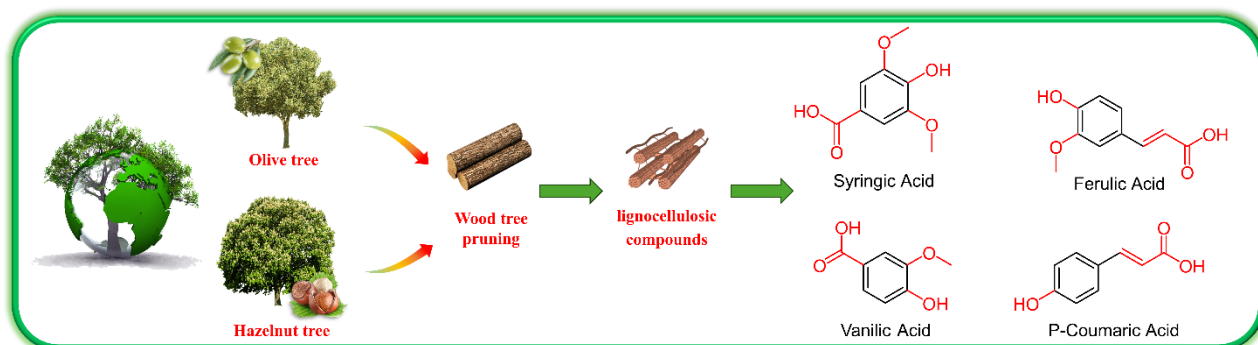
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Agricultural residues, such as olive and hazelnut tree prunings, represent an useful and renewable source of lignocellulosic biomass, offering the potential to recover high-value building blocks for sustainable chemicals and materials.<sup>1</sup> In this study, two complementary methods were employed to extract lignin, a phenolic-rich biopolymer, from these prunings. The first method utilized  $\gamma$ -valerolactone (GVL)<sup>1</sup>, an efficient and environmentally friendly solvent<sup>2</sup> known for its high lignin solubility, while the second method applied microwave-assisted<sup>3</sup> extraction using isopropanol, a fast and energy-efficient technique that enhances lignin recovery.

Despite the difference in yields, both extraction techniques provided lignin that was further purified through saponification and acidification processes<sup>4</sup> to isolate key phenolic building blocks. Characterization of these lignin-derived building blocks was performed using Nuclear Magnetic Resonance (1D and 2D-NMR) and High-Performance Liquid Chromatography (HPLC), revealing a complex mixture of phenolic compounds. The antioxidant capacity of the lignin extracts was also evaluated, showing significant potential for bioactive applications.

This research explores the potential of agricultural waste, specifically as a sustainable feedstock, for recovering lignin-derived building blocks through two innovative extraction techniques: GVL-based organosolv extraction and microwave-assisted isopropanol extraction. These recovered building blocks demonstrate significant antioxidant activity, presenting promising applications in the creation of bio-based antioxidants. This approach not only contributes to waste reduction but also supports the sustainable production of functional materials.



*"This study was carried out within the Agritech National Research Center and received funding from the European Union Next-GenerationEU (NATIONAL RECOVERY AND RESILIENCE PLAN (PNRR) – MISSION 4 COMPONENT 2, INVESTMENT 1.4 – DD 1032 17/06/2022, CN00000022). This manuscript reflects only the authors' views and opinions, neither the European Union nor the European Commission can be considered responsible for them."*

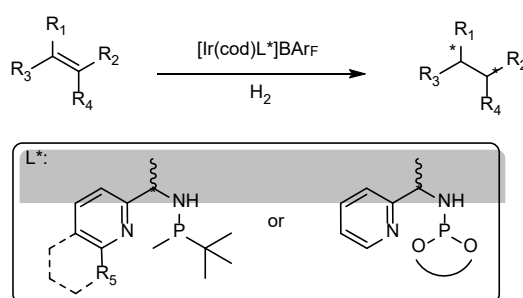
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Metal-catalyzed hydrogenation is among the most sustainable and efficient methods for producing pharmaceuticals, flavors, fragrances, and agrochemicals. Despite the significant advancements in asymmetric hydrogenation (AH) of olefins, several challenges remain unresolved. Most catalysts are effective for a narrow range of alkenes, requiring specific catalysts for each type of olefin to achieve optimal enantioselectivity. In this context, AH of chelating alkenes is a more established field, predominantly catalyzed by Ru- and Rh-diphosphine complexes. In contrast, AH of non-chelating olefins is far less developed and is typically catalyzed by Ir-P,N-based systems.[1] In this context, while P-oxazoline-based ligands have delivered excellent results, other ligand scaffolds containing different sp<sup>2</sup> N-donor groups have also shown promise. Among these, pyridine-based ligands have emerged as highly successful candidates due to their modularity, robustness, and ease of synthesis. Notably, Pfaltz and colleagues pioneered the development of pyridine-phosphinite ligands, which exhibit excellent enantioselectivities but are limited in substrate scope.[2] Building on these findings, our group further modified Pfaltz's ligands by replacing the phosphinite moiety with a phosphite group, allowing fine-tuning of ligand parameters for various substrate classes.[3] More recently, we have demonstrated that replacing phosphinite or phosphite groups with chiral aminophosphines further enhances catalytic performance.[4]

In light of these advances, we have developed a new family of P-stereogenic aminophosphine-pyridine ligands for the Ir-catalyzed asymmetric hydrogenation of olefins. These ligands combine the chiral aminophosphine moiety with Pfaltz's ligand scaffold. For comparison purposes and based on the previous successful phosphite-based ligands reported in the group, we also prepared a series of related phosphoramidite-pyridine ligands.



Scheme 1. New aminophosphine/phosphoramidite-pyridine-based ligands for iridium-catalyzed asymmetric hydrogenation of olefins

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## SYNTHESIS OF QUIRAL COUMARIN-SPIROCYCLIC COMPOUNDS VIA [4+2] CYCLOADDITION.

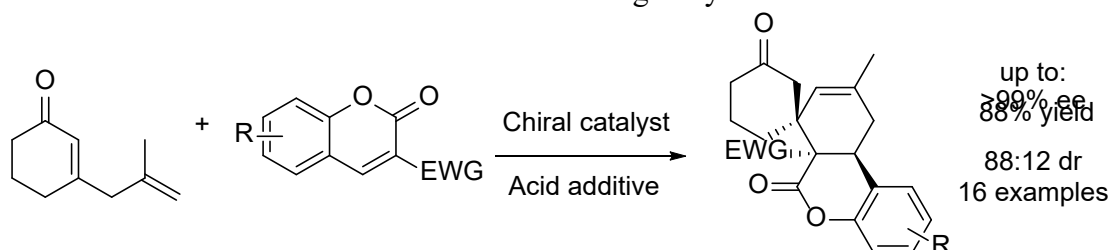
P6

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Coumarin derivative compounds possess several important characteristics that make them significant in various fields, including pharmaceuticals, agriculture and material science. For this reason, numerous methods and techniques have been developed for the synthesis of substituted coumarin.<sup>[1]</sup> On the other hand, spirocyclic frameworks are found not only in natural products and biologically active molecules, but have also been used as chiral ligands in organometallic complexes.<sup>[2]</sup> The enantioselective construction of spirocyclic moieties is still a challenge in organic chemistry. In addition, it has been previously reported in our group the use of organocatalyzed [4 + 2]  $\beta,\epsilon$ -regioselective reactions employing 2,5-dienones to generate chiral spirocyclic scaffolds.<sup>[3]</sup>

With this reactivity in mind, we have explored the reaction using coumarins as dienophiles with 2,5-dienones obtaining the chiral coumarin-spirocycles with three stereogenic centres with excellent diastereomeric and enantiomeric excesses and good yields.



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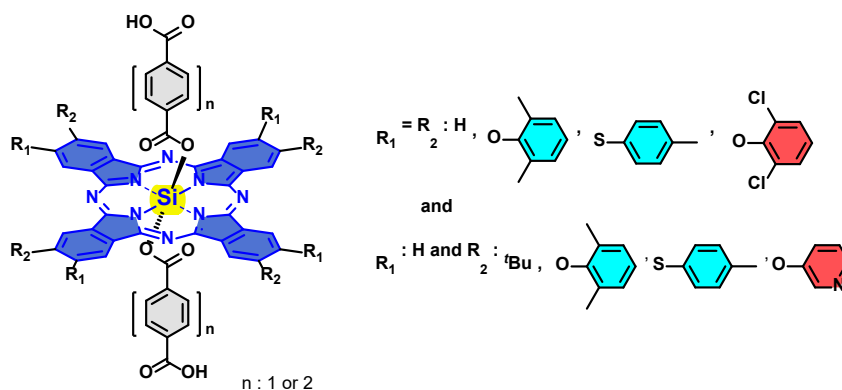
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Metal-organic frameworks (MOFs) are porous materials known for their extraordinarily stable crystalline structure. They have the ability to host guest molecules within their pores. These MOFs are composed of organic molecules acting as connectors, intricately linked with metallic compounds that serve as nodes. The bonding between these nodes and the organic molecules occurs through non-covalent interactions, providing distinctive strength and versatility to these materials.[1]

Phthalocyanines are highly versatile molecules that find application in the synthesis of MOFs. As a precedent, there are different silicon phthalocyanines (SiPc) axially functionalized with two COOH groups. [2,3] These may contain peripheral groups that modulate the properties of SiPc or not. These MOFs can be used for various purposes, such as studying quantum electrodynamic effects, capturing and storing gases, degrading contaminants in the environment, etc.

In the present study, the synthesis and characterization of various SiPc are addressed, proposed as candidates for the generation of MOFs. These SiPc exhibit a range of both axial and peripheral substituents, aimed at facilitating the formation of MOFs.[2,3] It is important to note that these molecules feature piridin or COOH groups in their axial positions, while also incorporating elements such as sulfur,[4] oxygen, and tert-butyl in their periphery, imparting a donor character to the molecule. Additionally, Cl groups are included, providing an acceptor character. These adaptations in the substituents are conceived to modify the inherent optical properties of the molecule.[5]



**Figure 1.** Silicon phthalocyanines for their application in MOFs.

**Acknowledgments.** We want to thank the European Regional Development Fund “A way to make Europe” and the Spanish Ministerio de Ciencia e Innovación/Agencia Estatal de Investigación (PID2020-117855 RB-I00) and the Generalitat Valenciana (CIPROM/2021/059 and MFA/2022/028) for funding.

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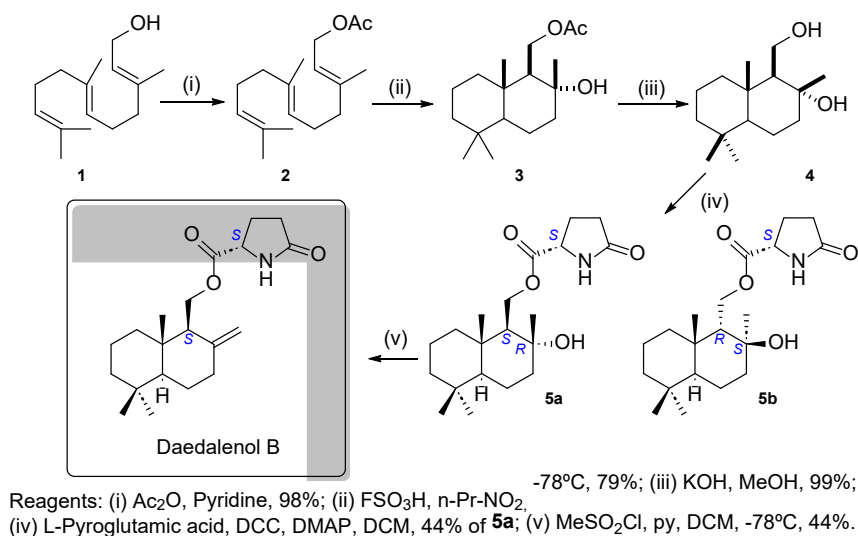


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Daedaleanol-B is a natural product isolated from cultures of the basidiomycete fungus *Daedalea incana* [1]. This fungus is a pathogen of trees and stored wood, exhibiting a brown rot in the attacked wood [2], a serious problem in wood producing areas of northern Europe, America and China. Metabolites from the genus *Daedalea* exhibit a wide variety of biological properties, such as anti-inflammatory activity, as well as effects against anti-CML, cytotoxicity, melanogenesis and tyrosinase inhibitory activity, among others [3].

In this study we have tried to address the lack of an efficient method for the preparation of this structure through two complementary pathways. We have achieved the enantioselective total synthesis of enantiomerically pure daedaleanol B using (+)-sclareolide as starting material in 4 steps (8% global yield). In addition, we have also developed a route for its preparation in only five steps starting from commercial (*E,E*)-farnesol. The last synthesis starts with an impressive diastereoselective cyclization in the presence of the superacid FSO<sub>3</sub>H (2→3). Saponification of 3 followed by selective esterification of 4 with enantiopure L-pyroglutamic acid gave 5 as a mixture of diastereomers. Careful chromatographic separation allowed us to undertake the dehydration of the tertiary OH in 5a thus obtaining the desired daedaleanol B together with the *endo* isomer in a (1:3) ratio, with a global yield of 15% (5 steps).



In conclusion, we have achieved the stereoselective synthesis of daedaleanol B from farnesol through a route which has two key steps: superacid mediated diastereoselective cyclization and a separation of diastereomeric pyroglutamic ester derivatives of drimenol (4). In addition, we have prepared two new analogs 5a and 5b, whose bioactivity is currently under examination.

**Acknowledgements:** We thank the financial support of University of Almería, Fondo Europeo de Desarrollo Regional (Project P\_FORT\_GRUPOS\_2023/88), and the Horizon 2020-Research and Innovation Framework Program of the European Commission (project 101022507 LAURELIN).

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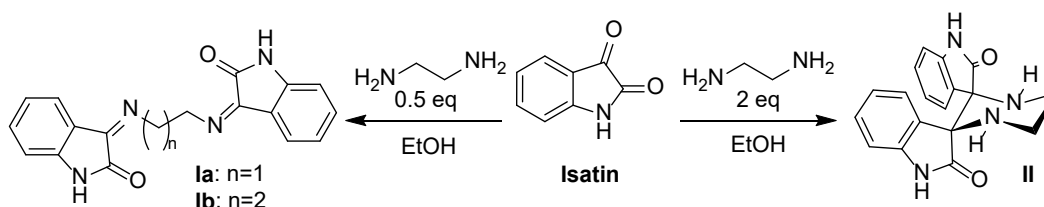
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There is a large number of natural products or synthetic drugs which have a spiro-fused 2-oxindole moiety (spirooxindoles). They exhibit a broad range of interesting biological activities, such as progesterone receptors modulators [1], MDM2-p53 interaction inhibitor [2] or antimalarial [3]. In recent decades, chemists have increased their efforts to develop new and efficient methodologies for the total synthesis of bioactive spirooxindole compounds as potential candidates for the treatment of various diseases. In addition to the challenges associated with the synthesis of complex spiro-polycycles, the intricacy of their structural elucidation must also be considered, as 1D and 2D RMN data analysis can be misleading since the spectroscopic data may be consistent with different structures. For this reason, single crystal X-ray diffraction studies are sometimes compulsory to ensure the structure.

Most common strategies to obtain spirooxindoles consist in cyclocondensation of isatin derivatives with different bis-nucleophiles, like those in the examples reported by Bergman et al., who described the formation of new 2:1 products in the reaction of isatin with methyl substituted ethylenediamines [4] when they were trying to synthesize diiminoisatin derivatives like **Ia** (Scheme 1) in a similar manner to the previously reported preparation of **Ib** by reaction of isatin with propan-1,3-diamine [5]. We have studied the reaction of isatin with ethylenediamine using different stoichiometries. Firstly, the reaction was carried out in a proportion of 1:0.5 eq isatin:ethylenediamine in refluxing ethanol. We could isolate the diimine **Ia** with a 66 % yield. However, when we repeated the reaction with a 1:2 isatin:ethylenediamine ratio in refluxing ethanol, the bis spiro oxindole **II** was formed (Scheme 1). To confirm the structure, the compound was crystallized in methanol and analyzed by single crystal X-ray diffraction.



Scheme 1. Synthesis of diiminoisatine **Ia** and spirooxindole **II**.

A mechanism proposal showing that the diamine acts also as reductant of some intermediates is also presented.

Acknowledgements: We thank the financial support of University of Almería, Fondo Europeo de Desarrollo Regional (Project P\_FORT\_GRUPOS\_2023/88), and the Horizon 2020-Research and Innovation Framework Program of the European Commission (project 101022507 LAURELIN).

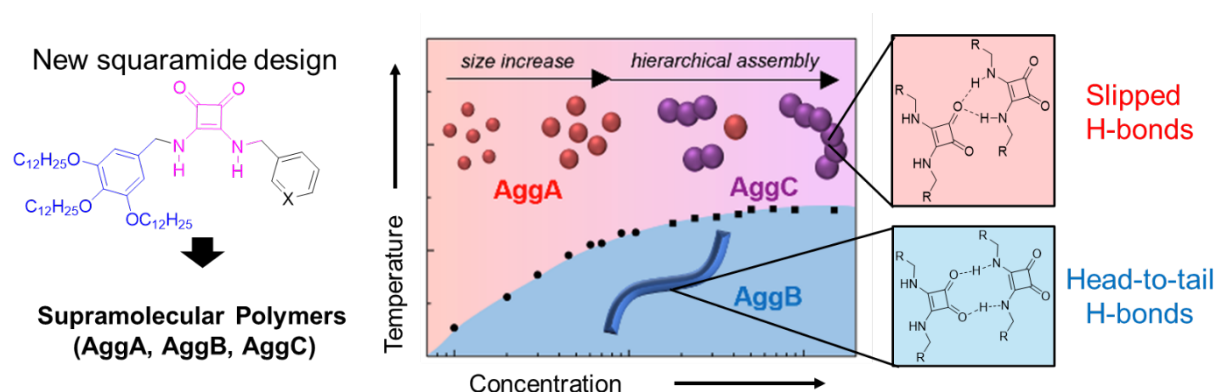
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Squaramides are a versatile class of compounds that have become increasingly significant in supramolecular chemistry due to their capacity to form multiple hydrogen bonds.<sup>[1]</sup> Recent studies have highlighted their applications in forming gels, liquid crystals, and supramolecular polymers. Our group previously reported different squaramide systems showing pathway complexity in self-assembly.<sup>[2-4]</sup>

In this work, two new squaramide-based monomers were designed, synthesized, and characterized, both capable of forming supramolecular polymers in methylcyclohexane (Figure 1). The new molecular design consists of a mono-dendronized squaramide bearing a benzyl or a methylpyridine group, respectively. These monomers exhibit self-assembly behavior through hydrogen bonding, forming distinct polymorphs depending on the concentration and temperature (Figure 1). The self-assembly behavior of the new squaramides was studied and characterized using UV/Vis spectroscopy and AFM. This study uncovers novel aspects of squaramide-based supramolecular polymers, which are of interest for the development of pathway complexity and stimuli-responsive systems



**Figure 1.** Chemical structure and diagram of the self-assembly profile of the newly designed squaramides

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# THADERPHOS: A NOVEL CHIRAL PHOSPHINE-PYRROLIDINE CATALYST TO ENANTIOSELECTIVE SYNTHESIS

P11

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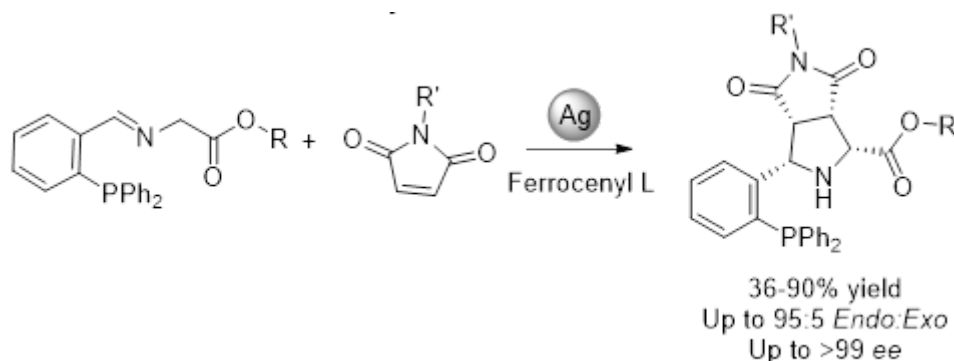
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The catalytic asymmetric 1,3-dipolar cycloaddition reaction is an important and efficient strategy to the enantioselective synthesis of proline derivatives. Proline-type heterocycles are extremely interesting compounds in many chemical areas.[1] Specifically, many different 1,3-dipolar products with a determined absolute configuration are using in numerous organocatalytic and organometallic catalytic process.[2]

On the other hand, phosphine groups are observed in many catalysts due their chemical properties.[3] Being a possible advantage to use phosphines with proline derivatives as asymmetric catalyst in different reactions, the objective of this project is obtained proline-type products with a phosphine group in their structure. Using phosphino-imino esters and alkenes as starting reactants, catalyzed by a silver salt and ferrocene-type ligand, the target molecule was obtaining with high diastereomeric ratio, moderate enantiomeric ratio and almost quantitative conversion.



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# MAGNETOTACTIC BACTERIA DECORATED WITH GOLD NANOPRISMS. A ROUTE TO NOVEL PHOTOTHERMAL AGENTS

P12

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Magnetotactic bacteria, with their unique ability to synthesize magnetic nanoparticles, offer a promising approach for biomedical applications,[1] as their natural magnetotaxis enables for their controlled navigation within the body. In addition to their native magnetic properties, magnetotactic bacteria themselves could represent a platform for integrating other metallic nanoparticles with different properties, giving them new functionalities and increasing their potential in biomedicine. However, this avenue has not been explored in depth.

Here, we report for the first time the functionalization of *Magnetospirillum gryphiswaldense* (MSR-1) with gold nanoprisms (MSR-AuNPR), giving MSR-AuNPR the ability to act as a novel photothermal agent. The attachment of AuNPR onto the outer surface of MSR-1 was achieved by two synthetic approaches:[2] i) MSR-1 was loaded with AuNPR to produce an MSR-AuNPR system, where AuNPR were arranged on a single layer of the bacterial surface; ii) exopolysaccharides (EPS) from different bacterial strains were loaded with AuNPR to produce EPS@AuNPR, which were subsequently incorporated onto the surface of MSR-1 to produce MSR-EPS@AuNPR systems (Fig 1).

The potential of MSR-AuNPR and MSR-EPS@AuNPR as photothermal therapy (PTT) agents was demonstrated during exposure to near-infrared (NIR) light. Bacterial viability was assessed and showed that MSR-1 remained viable after incorporation of AuNPR, particularly when AuNPR were pre-mixed with EPS of a Gram-negative bacterium, such as *Pseudomonas aeruginosa* (Pa).

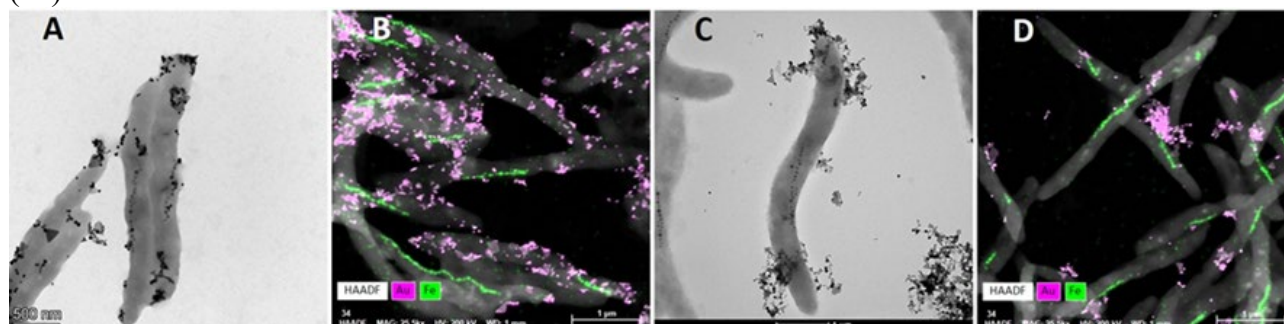


Figure 1. TEM and HAADF-STEM/EDX images (Au, pink; Fe, green) of the AuNPR-MSR-1 (A and B respectively). TEM and HAADF-STEM/EDX images (Au, pink; Fe, green) of the AuNPR-EPS-MSR-1 (C and D respectively).

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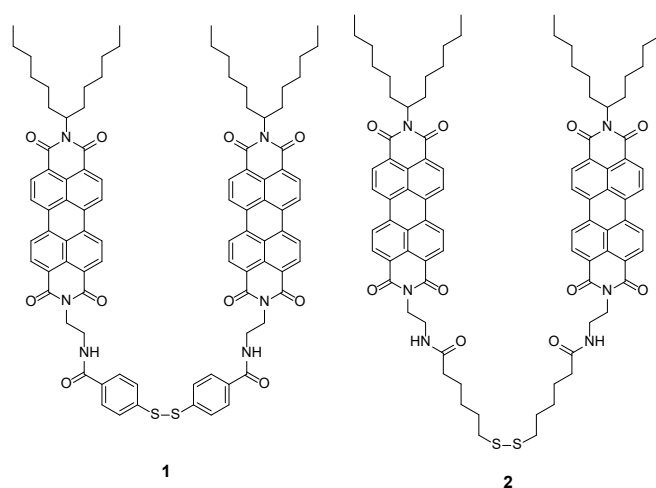


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Perylenediimides (PDIs) are highly versatile organic molecules. Their *bay* and *ortho* positions, as well as the *N*-imide positions, can be easily functionalized with different groups. These changes allow to control their properties, including the optoelectronic ones. As a consequence, PDIs can be applied in different research fields, being organic photovoltaics[1] or materials chemistry[2] the most important areas.

Quantum Dots (QDs) are promising models for artificial photosynthesis, being low cost materials that can efficiently transfer electrons. They are nanocrystals of semiconductor materials, and unlike other materials, the energy levels of their electrons will not remain continuous due to the phenomena of quantum confinement.[3] Moreover, the electronic properties of these materials can be controlled by changing their size. As the most used Qds only absorb in the visible, their performance as an artificial photosynthetic model could be enhanced if a near infrared-absorbing molecule, such as PDI, was attached to them, resulting in a structure that could maximize the absorption of the radiation.[4] Nevertheless, an adequate design of such materials requires a deep understanding of each component, including their interactions. The linking of PDIs to Qds could improve the efficiency of these materials, for this purpose a PDI dimers bearing a disulfide bridge have been synthesized (Figure 1), in order to evaluate the influence that anchoring PDI dimers would have on the photophysical properties of the material.



**Figure 1.** Structure of the synthesized PDI-Ar-S-S-Ar-PDI (1) and PDI-Alk-S-S-Alk-PDI (2).

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# FUNCTIONALIZATION OF DEXTRAN WITH ALENDRONATE, PEG AND SACCHARIDES FOR NMOFS SURFACE COATING

P14

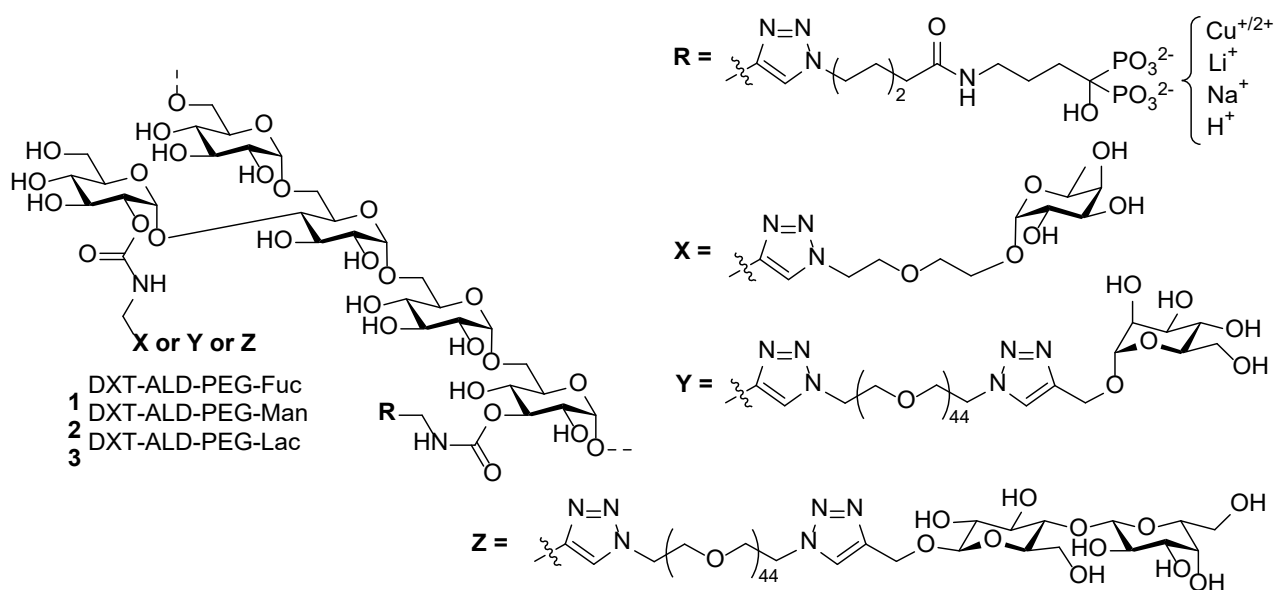
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Nanometric metal-organic frameworks (nMOFs), such as MIL-100(Fe), have emerged as promising materials for drug delivery due to their high capacity for loading various therapeutic agents of different nature [1]. However, nMOFs usually show low colloidal stability, as well as rapid clearance from bloodstream by immune cells. To address these limitations, surface functionalization is crucial to ensure proper biodistribution and reduce macrophage uptake. Our research group have employed dextran (DXT)-based copolymers functionalized with alendronate (ALD) and polyethylene glycol (PEG) as effective surface coating agents for nMOFs. Our results showed that ALD enables strong coordination of the DXT derivatives on the nMOFs surface, while PEG chains significantly reduce nanoparticle macrophage uptake [2].

In a further step, we decided to add mono- and disaccharide moieties at the end of PEG chains to impart biorecognition abilities to the resulting DXT conjugates. Lectins are overexpressed in some tumor cells or are present on bacterial membranes. Therefore, decorating nanoparticles with carbohydrates is an efficient approach to increase the local concentration of anticancer drugs near tumor cells or bacteria. This approach may facilitate selective cellular uptake through the specific binding interaction between the carbohydrate ligands on the nanoparticle and the particular lectin overexpressed on the target cells [3]. In addition, carbohydrates may also increase colloidal stability and could improve the 'stealth' effect towards the immune system.

In this regard, we have synthesized conjugates DXT-ALD-PEG-Fuc (**1**), DXT-ALD-PEG-Man (**2**), and DXT-ALD-PEG-Lac (**3**) using a strategy based on "click" chemistry reactions. Studies on their characterization and efficacy are currently in progress.



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The development of efficient catalysts for the electrochemical reduction of CO<sub>2</sub> to value-added products is a critical step towards addressing climate change and transitioning to a sustainable energy economy. Metalloporphyrins and metallophthalocyanines have emerged as promising candidates, exhibiting high selectivity for CO production and, in some cases, multielectron reduction to methanol or methane [1]. Immobilization of these catalysts on conductive supports, (such as carbon nanotubes), has been shown to enhance their performance and stability [2]. Latest studies have explored the role of catalyst design and reaction conditions in influencing the selectivity and efficiency of CO<sub>2</sub> reduction. Ligand modification and metal center selection have been employed to tailor the catalytic properties of molecular complexes. Electrocatalytic conversion of CO<sub>2</sub> to methanol was demonstrated on cobalt phthalocyanine (CoPc) [3]. A recent study on CoPc has shed light on the mechanism of CO<sub>2</sub> reduction, suggesting a crucial role for the phthalocyanine macrocycle in facilitating redox activity [4]. These findings open new avenues for optimizing catalyst design and improving the efficiency of electrocatalytic CO<sub>2</sub> reduction.

Here, we will present the synthesis and characterization of a novel cobalt pyridinoporphyrazine (Figure 1a) and cobalt phthalocyanines (Figure 1b), along with their performance as electrocatalyst for CO<sub>2</sub> reduction [5].

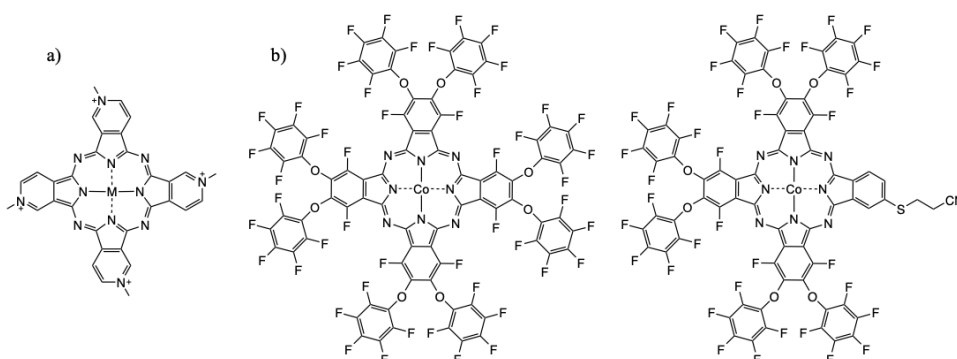


Figure 1. Chemical structures of a) cobalt pyridinoporphyrazine and b) cobalt phthalocyanines.

**Acknowledgments.** We want to thank the European Regional Development Fund “A way to make Europe” and the Spanish Ministerio de Ciencia e Innovación/Agencia Estatal de Investigación (PID2020-117855 RB-I00) and the Generalitat Valenciana (CIPROM/2021/059 and MFA/2022/028) for funding.

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Perylenediimides (PDIs) are semiconductor organic chromophores with great properties such as excellent thermal, chemical, and photochemical stabilities, high absorption coefficients, and fluorescence quantum yields close to unity [1]. These properties can be strategically modified by introducing different substituents into any of their functionalizable positions (imide, bay and/or ortho) through organic synthesis. This allows to prepare a wide variety of molecules with unique properties and, therefore, increases the range of applicability of PDIs [2].

Therefore, in this work, we summarize different synthetic routes to PDI derivatives through the functionalization of the imid, bay and/or ortho positions, with the aim of obtaining new types of PDIs with different properties and studying their application in fields such as medicinal chemistry, photophysics or materials science.



Figure 2: *PDIs with different substituents at bay positions.*

We acknowledge financial support from Grant PID2022-140315NB-I00 funded by MICIU/AEI/10.13039/501100011033 and by ERDF/EU.

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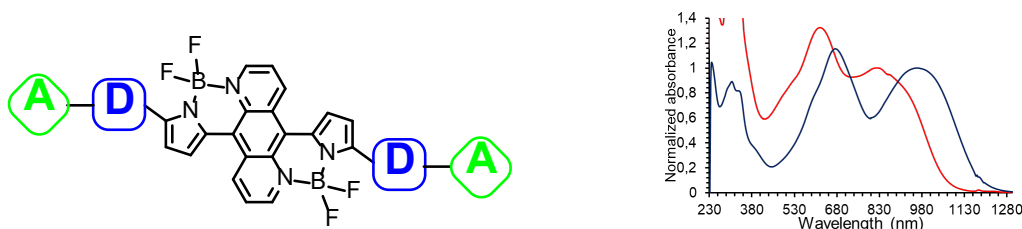
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The study of materials that are optically active in the near-infrared (NIR) region, specifically involving light absorption and/or emission beyond 780 nm, has garnered considerable attention due to their potential applications in areas such as photovoltaics, light-emitting devices, photonics, bioimaging, photothermal imaging, and photography [1,2,3].

Optical activity in the NIR requires certain structural design for the materials to show narrow band gaps. In this context, Organic Chemistry offers a significant advantage by enabling the modulation of the optoelectronic properties of molecules through a vast array of synthetic methods. Regarding the structure-property relationship for NIR-active materials, one effective strategy consists in the expansion of  $\pi$ -conjugated systems, where alternating electron-donor (D) and electron-acceptor (A) fragments promote intramolecular charge transfer processes, resulting in a bathochromic shift in the absorption spectra [4,5,6].

Following this approach, herein we present the synthesis and characterization of A-D-A'-D-A systems, incorporating innovative four-coordinate boron complexes as electron-acceptor building block (A'). Our design is based on a novel dipyrrolyl-1,5-diazaanthracene ligand for the integration of dinuclear boron complexes as A' core. Additionally, the  $\pi$ -expanded system is completed by attaching thiophene-based and indanone-based building blocks as D and A units, respectively. Spectroscopic analysis has demonstrated the suitability of this molecular design for reaching the NIR-II window (950-1700 nm). Consequently, these materials meet the requirements for potential exploration of the aforementioned applications.



**Figure 1.** A-D-A'-D-A conjugated system integrating a dinuclear boron complex as central electron acceptor unit (left) and absorption spectra of the synthesized materials (right).

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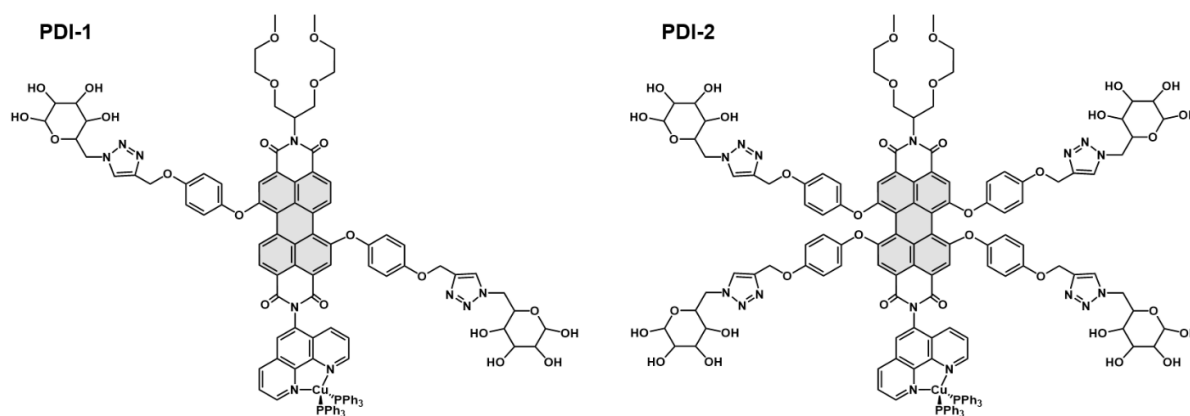
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Perylene-diimides (PDIs) have attracted considerable attention due to properties such as their thermal and photochemical stabilities, strong absorption of visible light, fluorescence quantum yields close to unity or high electronic mobility. In addition, their aromatic core can be functionalized in their bay and ortho positions, which allows to modify the optoelectronic properties of PDIs. Due to these properties, over the years they have been applied in different research fields such as organic solar cells, diagnosis and treatment of diseases or environmental applications [1].

In the field of biomedicine, the concept of photodynamic therapy (PDT) emerged around 1960, which consists of a non-invasive treatment with selective cytotoxic activity against cancer cells. PDT combines 3 main elements to carry out this process: the excitation of a photosensitizer, molecular oxygen and a light source [2]. Although the application of PDIs would be ideal in this field, they have a very low solubility in water, which hinders tasks such as distribution in biological fluids or internalization in cancer cells [3].

In this work, we will present two molecules (Figure 1) with an improved design containing oligo (ethylene glycol) chains in an imide position and galactose rings in the bay region to ensure both water solubilization of the compound and internalization through active transport processes, in addition to 1,10-phenanthroline on the other imide position, responsible for metal chelation.



**Figure 1.** Structure of perylene-diimide-galactose-phenanthroline conjugates.

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**Pablo Mestre, Axel J. Boulet, Antonio Caballero, Fabiola Zapata**

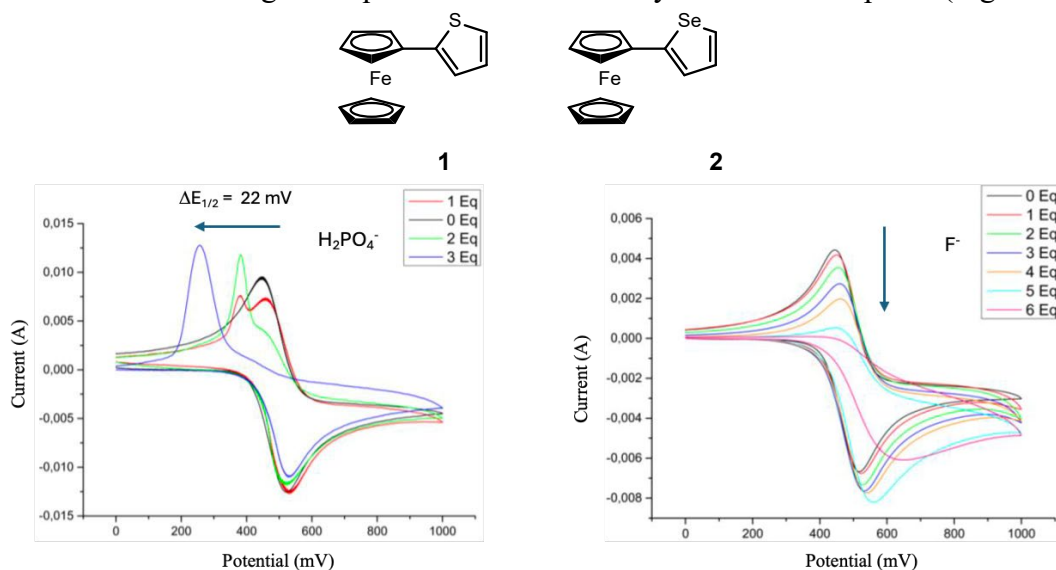
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Anion recognition has become one of the most important research fields in supramolecular chemistry due to the important role of the anions in biological systems and contamination of some environmental spaces. A few new chemosensors are being developed to detect and quantify those anionic species [1].

In the last years, new noncovalent interactions have emerged as strong alternatives to the widely known hydrogen bonding, such as the ion –  $\pi$ , halogen or chalcogen bonding interactions [2,3]. Electrochemical anion sensors are now emerging as solutions to avoid the instability of some organochalcogen compounds, making them easily synthesizable and very efficient in anion recognition [4].

We report here the synthesis and study of the anion sensing properties of two new chalcogen bonding (ChB) receptors **1** and **2** based on thiophene and selenophene units as anion binding sites and ferrocene moiety as an electrochemical response unit. (Figure 1 top). The evaluation of the sensing properties was realized by electrochemical techniques (OSWV and CV), UV-Vis and  $^1\text{HMRN}$  spectroscopy toward a set of different anions.

The addition of,  $\text{HP}_2\text{O}_7^{3-}$  and  $\text{F}^-$  anions to a solution of the different receptors, promoted significant and different changes in square wave voltammetry of the free receptors. (Figure 1 bottom).



**Figure 1.** Structure of receptors synthesized (top). CV of **1** in  $\text{CHCl}_3/\text{CH}_3\text{CN}$  in presence of  $\text{H}_2\text{PO}_4^-$  anions (left bottom) and **2** in  $\text{CHCl}_3/\text{CH}_3\text{CN}$  in presence of  $\text{F}^-$  anions (right bottom).

We acknowledge to the Ministerio de Ciencia e Innovación of Spain and FEDER project PID2020-113483GB-I00 and Fundación Séneca Región de Murcia (CARM) Project 21956/PI/22.

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# SYNTHESIS AND CHARACTERIZATION OF SPIRO-PHTHALOCYANINE DERIVATIVES AS HOLE TRANSPORTING MATERIALS IN PEROVSKITE SOLAR CELLS

P20

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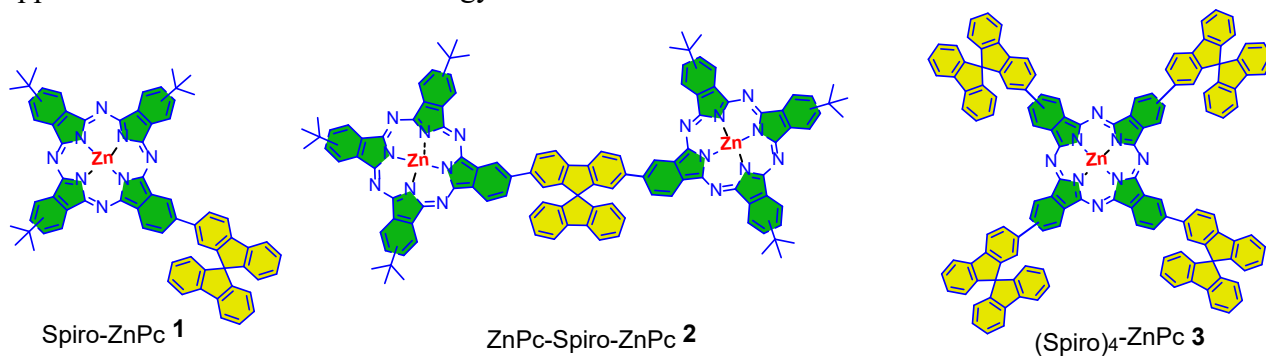
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Phthalocyanines (Pcs) have emerged as effective hole carriers, improving the efficiency and stability of PSCs. This is due to their tunable optoelectronic properties and remarkable photochemical and thermal stability.

Hole transporting layers (HTL) are essential components in standard perovskite solar cells (n-i-p PSCs). Their primary function is to block the passage of electrons while efficiently transporting holes to the corresponding electrode. Additionally, they protect the active layer from environmental factors such as humidity.

This study focuses on the synthesis and characterization of spiro-substituted ZnPcs, such as Spiro-ZnPc 1, ZnPc-Spiro-ZnPc 2, and (Spiro)<sub>4</sub>-ZnPc 3 (Figure 1). These compounds represent a new family of Pcs. The goal is to advance the understanding of their properties, paving the way for their application in the field of solar energy.



**Figure 1.** Spiro-ZnPcs molecules synthesized in this study.

**Acknowledgments.** We want to thank the European Regional Development Fund “A way to make Europe” and the Spanish Ministerio de Ciencia e Innovación/Agencia Estatal de Investigación (PID2020-117855 RB-I00), and the Generalitat Valenciana (CIPROM/2021/059) for funding.

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# SYNTHESIS OF TETRAPHENYLETHYLENE-BASED SILICON PHTHALOCYANINES AS AGGREGATION-INDUCED EMISSION PHOTOSENSITIZERS

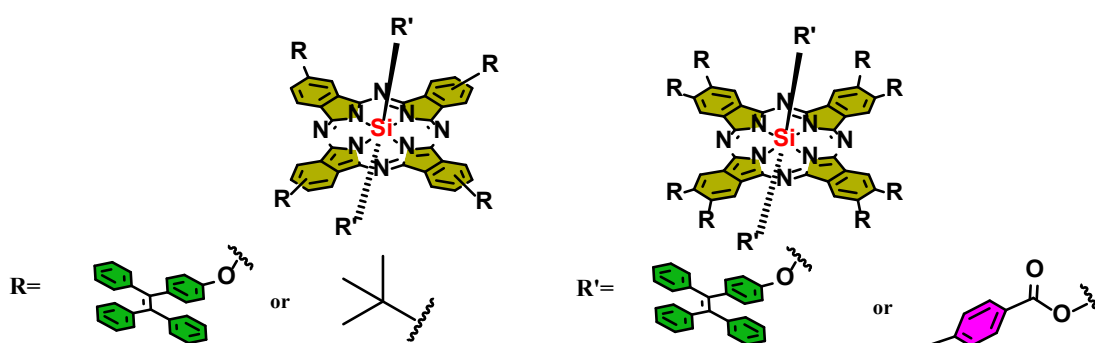
P21

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Aggregation-induced emission (AIE) is a phenomenon in which the molecules in an aggregation state possess stronger emission than in a single molecule [1]. AIE-active photosensitizers (PSs) are promising agents for use in antitumor photodynamic therapy (PDT) thanks to their advantages of aggregation-promoted photosensitizing properties and outstanding imaging ability. However, most of the synthesized PSs emit intensively in their dilute solution while their emission is intensely quenched when in aggregated form. This is explained by the formation of numerous exciplexes or excimers [2]. To overcome this quenching effect, various strategies such as attaching a much stronger solid-state fluorescence substituents like tetraphenylethylene (TPE) derivative, have been applied. Previous works have successfully conjugated some AIEgens to Pt prodrug for targeted PDT of cancer cells and long-term mitochondrial tracking [3].

Motivated by the AIE and energy transfer mechanism between TPE and PSs's core, herein we attached TPE functional groups at axial and peripheral positions of silicon phthalocyanines (Figure 1) to adjust their fluorescence abilities in the aggregation state. It was observed that the PSs in the molecular state (dissolved in THF) were moderately fluorescent, while in the aggregated form, obtained after the addition of different fractions of water (0-90%) to the THF solution, they became strongly fluorescent. The intensity and wavelength of AIEgens were readily tuned by varying the position of the substituent on the axial or peripheral position as well as the relative water fraction in the THF solution [4].



**Figure 1.** The synthesized silicon phthalocyanine molecules

**Acknowledgments.** We want to thank the European Regional Development Fund “A way to make Europe” and the Spanish Ministerio de Ciencia e Innovación/Agencia Estatal de Investigación (PID2020-117855 RB-I00), and the Generalitat Valenciana (CIPROM/2021/059) for funding.

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# SYNTHESIS OF METALLOPHTHALOCYANINES AS G-QUADRUPLEX DNA BINDERS AND THEIR APPLICATION AS PHOTSENSITIZERS

P22

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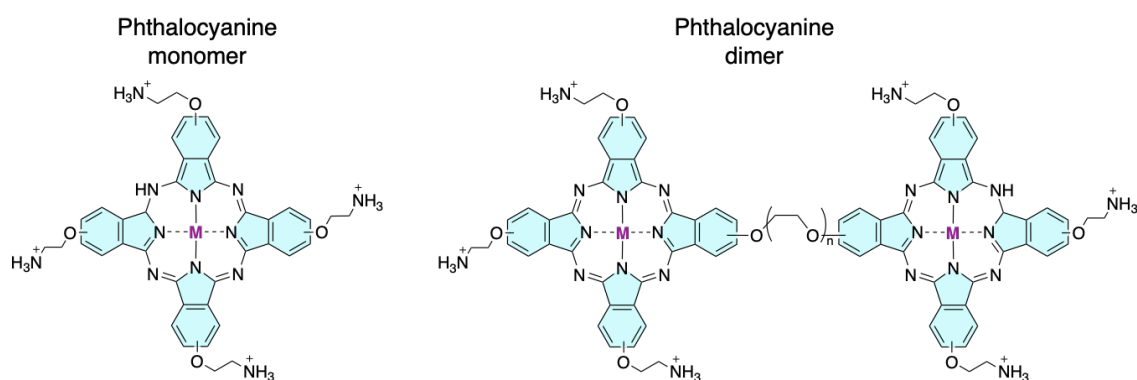
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G-quadruplexes (G4s) are non-canonical nucleic acid structures have emerged as molecular controlling gates of biological processes acting as epigenetic markers. Many putative G4 forming sequences have been identified in the human genome and evidence suggest their pivotal role in key biological processes, such as oncogene expression, telomere maintenance and chromosome stability.[1] In this regard, many G4 binders have been intensely studied as promising anticancer agents.

Most recently, an interesting approach to tackle cancer has emerged combining G4 binding and the photosensitization of the G4 ligand, which can then generate reactive oxygen species (ROS) and the resulting breakage of the G4 DNA/RNA structures and other nearby biomolecules. In this context, metallo-phthalocyanines have the suitable structure to interact via  $\pi$ - $\pi$  stacking with the external tetrads of G4s and the photophysical properties to act as photosensitizers in photodynamic therapy. [2,3]

Herein, we report the synthesis and characterisation of different ligands containing one or two metallophthalocyanines connected through an ethylenglicol linker, giving rise to two different topologies: monomeric and dimeric phthalocyanines, respectively (Figure 1). Their capacities for G4 binding have been assessed with a large number of biologically relevant G4 forming sequences by UV-Vis/fluorescence spectroscopies and FRET melting assays. Furthermore, the photosensitizing capacity has been studied in vitro, measuring the singlet oxygen generation upon irradiation.



**Figure 1.** Chemical structures of the metallophthalocyanines

**Acknowledgments.** We want to thank the European Regional Development Fund “A way to make Europe” and the Spanish Ministerio de Ciencia e Innovación/Agencia Estatal de Investigación (PID2020-117855 RB-I00), and the Generalitat Valenciana (CIPROM/2021/059) for funding.

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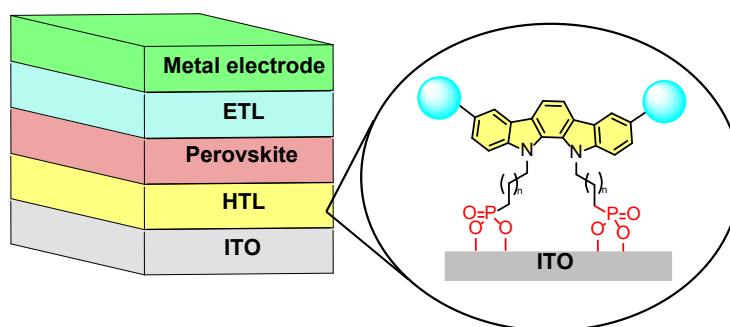
**José Manuel Ramón-Torres,<sup>1</sup> José G. Sánchez,<sup>2</sup> Miriam Más-Montoya<sup>1</sup>, Eugenia Martínez-Ferrero<sup>2</sup>, Emilio Palomares<sup>2</sup>, David Curiel<sup>1</sup>**

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Hybrid perovskite solar cells have become one of the most promising photovoltaic technologies nowadays. The incorporation of self-assembled monolayers (SAMs) as the hole transporting layers (HTLs) in these devices represents a successful strategy for optimizing the photovoltaic performance. [1] Amongst other benefits, SAMs can improve the energy-level alignment between the perovskite layer and the ITO electrode and assist in the defect passivation at the surface of the perovskite, contributing to the reduction of the undesired recombination processes. [2] As far as the molecular design is concerned, previous reports have shown that anchoring carbazole-based molecules onto the ITO surface can improve the efficiency of perovskite solar cells with an inverted (p-i-n) architecture. [3] Inspired by these results, in this contribution, we report a series of indolocarbazole derivatives that have been evaluated as hole selective SAM interlayers in perovskite solar cells (Figure 1). The expanded conjugation of the pentacyclic indolocarbazole, as well as the presence of two anchoring groups, are structural features that could contribute to the optimization of charge transport properties and stability of the SAM. Preliminary results show that our indolocarbazole molecules outperform the reference carbazole SAM. The effect of the alkyl chain length and the peripheral functionalization of the conjugated skeleton have been investigated, providing a deeper insight into the structure-property relationship of these novel indolocarbazole-based SAM in highly efficient perovskite solar cells.



**Figure 1.** Schematic representation of the indolocarbazole-based SAMs.

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# SYNTHESIS AND EVALUATION OF SiO<sub>2</sub> MICROPARTICLES BEARING ESSENTIAL OIL COMPONENTS FOR NON-THERMAL PASTEURIZATION OF LIQUID FOODS

P24

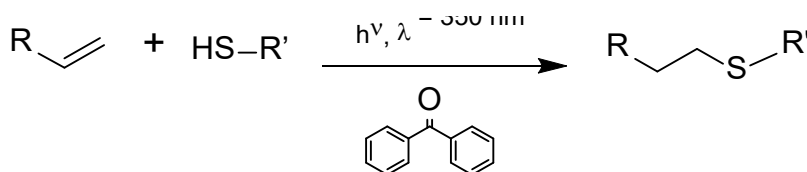
**Ainhoa C-Pacheco<sup>1</sup>, M. Consuelo Jiménez<sup>1</sup>, Raúl Pérez-Ruiz<sup>1</sup>, Oumaima Moumane<sup>2</sup>, Édgar Pérez-Esteve<sup>2</sup>, José Manuel Barat<sup>2</sup>**

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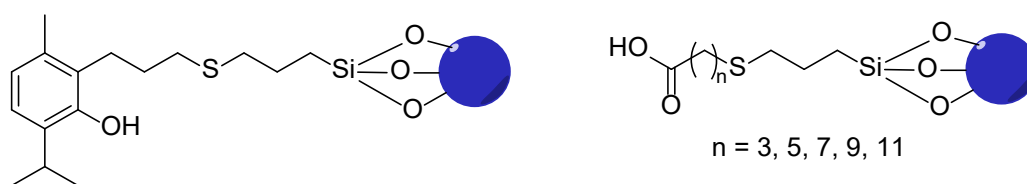
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Conventional food preservation technologies mainly involve heat treatments and/or the addition of chemical preservatives. Thermal processes, such as pasteurization, involve heating food, which results in nutrient loss, undesirable sensory changes, and a reduction in some functional properties. The aim of this work is to develop an alternative pasteurization method consisting of anchoring essential oil components with antimicrobial properties onto SiO<sub>2</sub> microparticles, which are subsequently used as a type of filter for liquid foods. This new methodology would prevent the damage to food caused by high temperatures [1].

For this purpose, derivatives of essential oil components (EOCs, such as thymol, carvacrol, or fatty acids) containing an olefin moiety will be coupled to 3-mercaptopropyltriethoxysilane (MPTES) through a photochemical thiol-ene click reaction using benzophenone as photocatalyst (Fig.1) [2]. The obtained EOC-MPTES was subsequently anchored to silica microparticles to afford the final support with antimicrobial properties (Fig. 2) [3]. The carvacrol-MPTES-SiO<sub>2</sub> microparticles displayed antibacterial activity when tested against *E. coli* K12.



**Fig 1.**



General scheme of the employed thiol-ene click reaction

**Fig 2.** Antimicrobials anchored to the silica microparticles (blue sphere). Left: thymol derivative; Right: fatty acids (4 to 12 carbon atoms) derivatives

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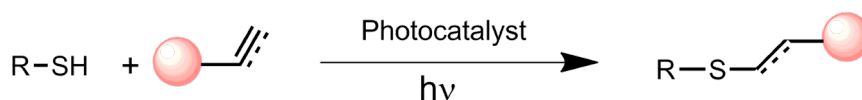
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The use of labeled proteins is a common and powerful technique in molecular biology, biochemistry, and cell biology for studying protein function, localization, interaction and dynamics. **Labeling proteins involves attaching** a detectable marker or tag to the protein of interest, allowing **the visualization or tracking of** its behavior in various biological contexts [1]. When proteins are labeled with fluorescent tags, it becomes possible to track their localization in live cells or tissues.

The reactions employed for amino acid modification within peptides and proteins differ widely in their site selectivity and functional group compatibility. **Chemical methods, such as click chemistry, have been widely used to label proteins at specific sites with different tags.** Ideally, these chemical reactions should work under mild conditions, be highly specific, and produce high yields [2].

Here, we propose the use of a **photocatalyzed thiol-ene reaction** for the modification of cysteine with different fluorophores. Once the reaction conditions for modifying this amino acid **are optimized**, modification of cysteine present in peptides or proteins will be attempted.

The two approaches presented here for cysteine labeling involve: a) selective irradiation of an organic photocatalyst (preferably with visible light), which mediates the coupling between cysteine and the fluorophore, and b) direct irradiation of a molecule that acts as both a photosensitizer and fluorophore simultaneously.



**Fig 1.** General scheme of the photochemical synthesis of [cysteine-fluorescent probe] adducts using the thiol-ene reaction.

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A mimetic system is a class of metalloprotein constituted by a simple metal complex able to reproduce, at least in part, the structure, properties, or function of the active centre of given enzymes. The superoxide dismutase (SOD) [1,2] family of enzymes is the first biological line of defence against reactive oxygen species (ROS) produced as a result of imbalances in oxygen metabolism but it's the family of catalase enzymes the ones that finish the cell detoxification process. ROS species are related to neuronal death processes in neurodegenerative disorders such as Alzheimer, Parkinson, and Huntington diseases.

In this work, we discuss the design, synthesis, and characterization of metal complexes of azamacrocyclic ligands with 1H-pyrazole aromatic spacers as SOD and catalase mimetics. We study their coordination with Cu (II) at different molar ratios and their applications as SOD and catalase or peroxidase mimetics using the McCord-Fridovich [2] enzymatic assay and the xylenol orange method. [3].

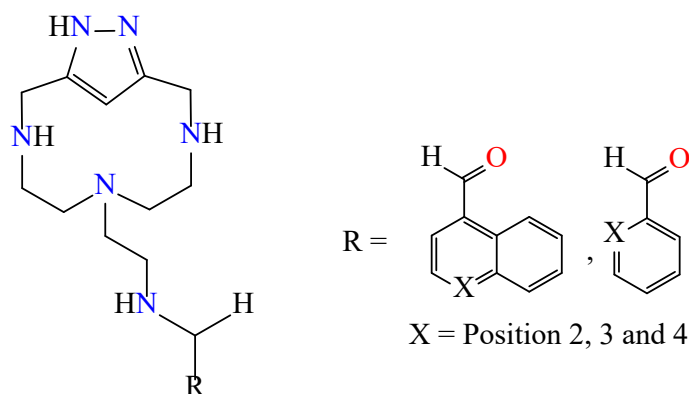


Figure 1. Azamacrocyclic ligands constituted by polyamine tris 2-(aminomethyl)amine linked to an 1H-pyrazole spacer; R= pyridine, quinolone.

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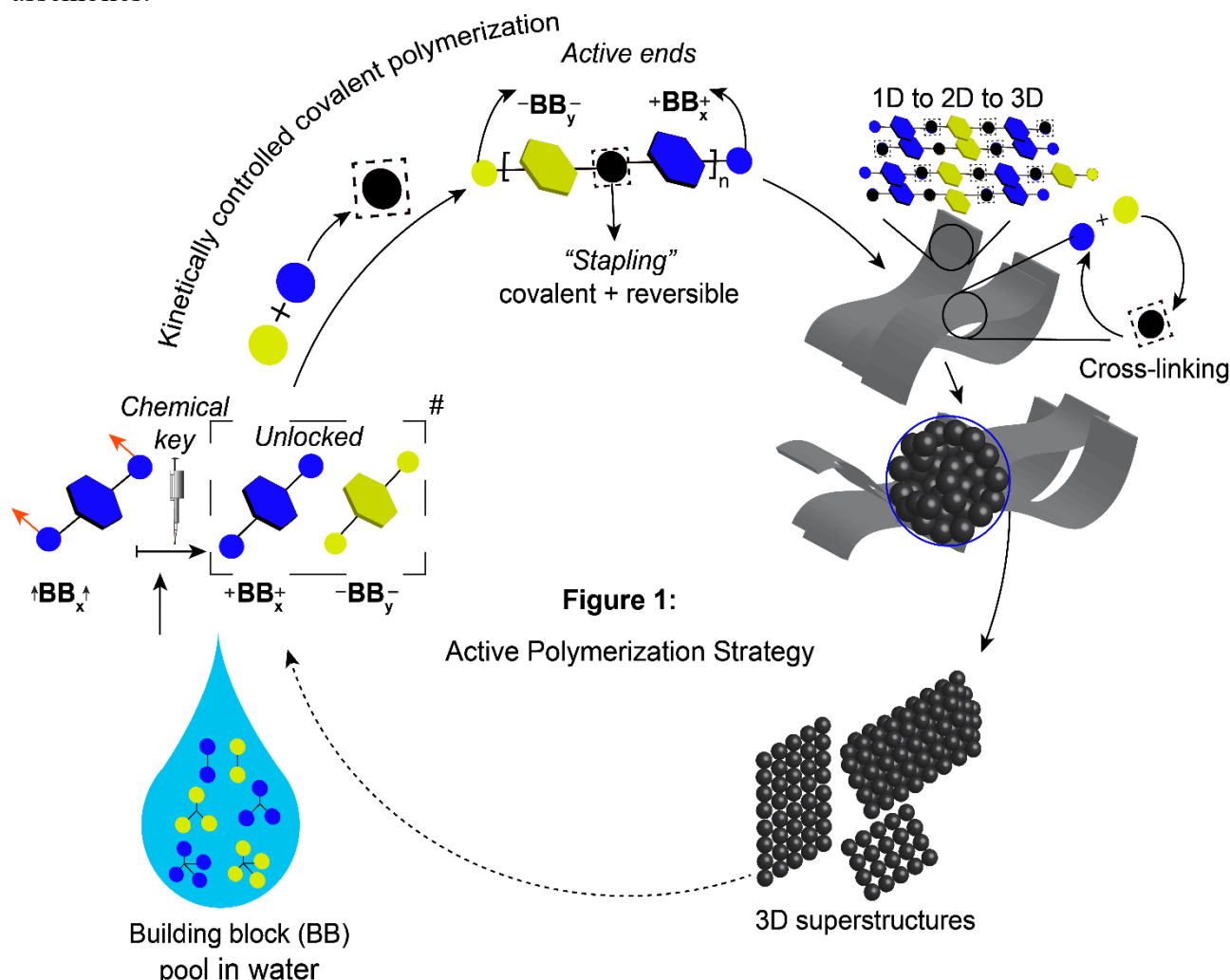
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Nature exploits self-assembling systems to generate multi-functional structures in a highly organized hierarchical manner [1,2]. Herein, we are creating higher-order assemblies that are made up of assemblies, also known as superstructures using small organic molecules in an aqueous environment. It was achieved by active polymerization of building blocks (aromatic compounds) by a kinetically controlled steady release of reactants from their water-soluble (functional group protected) to water-insoluble reactive form (deprotected) using fuels. [3] The reaction and self-assembly kinetics were optimized for uniform distribution of 3D self-assembly by tuning the fuels and reactants. In addition, the reversible nature of the linkages between building blocks and the hydrophobicity of the products (oligomers) also plays a crucial role in creating hierarchical assemblies.



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**SOLAR-ASSISTED CO<sub>2</sub> METHANATION VIA PHOTOCATALYTIC SABATIER REACTION BY CALCINED TITANIUM-BASED ORGANIC FRAMEWORK SUPPORTED RUOX NANOPARTICLES**

P28

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This study focuses on developing titanium oxide-based photocatalysts by calcining MIL-125(Ti)-NH<sub>2</sub>, decorated with RuOx nanoparticles (1 wt%), at temperatures between 350 and 650 °C. These materials were used for CO<sub>2</sub> methanation under simulated sunlight (45 mW/cm<sup>2</sup>), at temperatures below 200 °C and 1.5 atm pressure. The catalyst synthesized at 350 °C showed the highest activity, producing 4.73 mmol of CH<sub>4</sub> per gram after 22 hours, with quantum yields of 0.76%, 0.65%, and 0.54% at 400, 500, and 750 nm, respectively.

The performance was favorable compared to other MOF-based materials. Additional studies, including electrochemical impedance, electron spin resonance, and in situ FT-IR spectroscopy, provided insights into the photocatalytic process. The findings suggest that MOF-based materials can serve as precursors for efficient metal oxide photocatalysts for CO<sub>2</sub> methanation using sunlight.

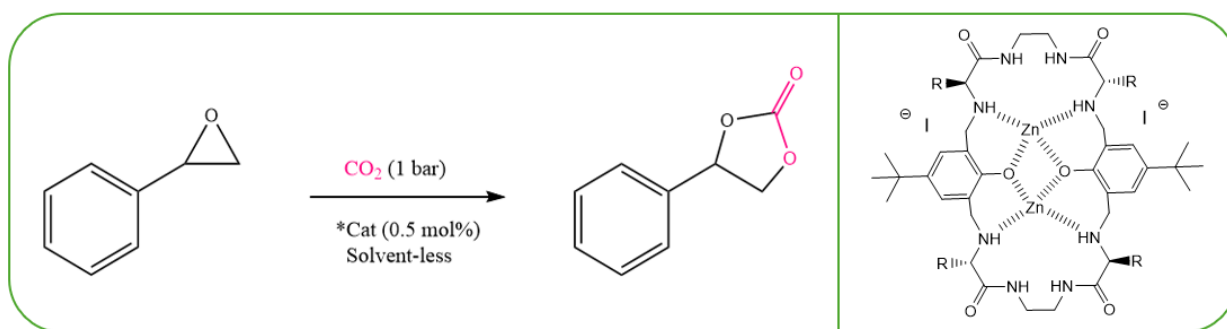
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In nature, enzymes can accelerate the rate of chemical reactions with high efficiency, achieving additionally a high selectivity. Carbonic anhydrase, with an active center consisting of a Zn<sup>2+</sup> cation coordinated with three imidazole rings, is one of the known enzymes that achieves a higher conversion rate (10<sup>6</sup> s<sup>-1</sup>) in the transformation of CO<sub>2</sub> [1]. Based on this premise, this project focuses on the synthesis of pseudo-peptidic macrocycles to obtain the corresponding Zn<sup>+2</sup> complexes capable of catalyzing the cycloaddition reaction of CO<sub>2</sub> to epoxides [2]. In this case, the synthesis of the macrocycle has been carried out using tyrosine as the starting amino acid, as the alcohol group attached to the aromatic ring will allow us to derivatize it by introducing a vinyl group that will enable, through polymerization, the production of the corresponding supported catalyst.



**Scheme 1.** On the left, the catalysed reaction of CO<sub>2</sub> cycloaddition to epoxides. On the right, structure of the macrocyclic catalyst (R group associated to the aminoacid side chain).

We have obtained a synthetic methodology for the preparation of vinyl monomers from tyrosine-derived pseudo-peptide macrocycles, suitable for subsequent polymerisation.

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