Master in Molecular Nanoscience and Nanotechnology
Master dissertation defense
September 15th, 2025. SS6 Seminar

10:00 Manuel Redondo Marcilla
Synthesis of core@shell Nanostructures based on Prussian Blue Analogues over Plasmonic and Piezoelectric cores

10:30 Susana Ochando Pariente
Polyoxometalate-intercalated layered double hydroxide materials as water oxidation catalysts

11:00 Carme Umbert Bonet
Towards Multivariate HOFs Based On Tetrathiafulvalene and Nickel Bis(dithiolene) Derivatives

11:30 Pause

12:00 Nerea Menargues Sanz Agustí
Tuning Flexibility in Zeolitic Imidazolate Frameworks: Gate-Opening Modulation through Mixed-Linker and Mixed-Metal Strategies

12:30 Carla Alonso Ripoll
Development of novel antimicrobial communication systems based on the application of mesoporous silica nanodevices

13:00 Carlos Sánchez García
Design and characterization of flavin adenine dinucleotide-functionalized core-shell upconversion nanoparticles

Synthesis of core@shell Nanostructures based on Prussian Blue Analogues over Plasmonic and Piezoelectric cores

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MOLECULAR SCIENCE
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Master in Molecular Nanoscience and Nanotechnology

Manuel Redondo Marcilla

Thesis supervised by

Dr. Roger Sanchis Gual

University of Valencia, September 2025

ABSTRACT

In the last decades, nanotechnology has significantly increased the interest in hybrid nanomaterials. These materials two (or more) nanoparticles in a complementary manner, giving rise to enhanced performance or the emergence of new properties. In this context, Prussian Blue and its Analogues (PB and PBAs) have attracted great interest due to their structural versatility, tunable properties, and ease of integration with other materials at the nanoscale. Their open lattice structure allows for chemical composition modifications, enabling the adjustment of their properties.

Thus, in this master's thesis, we developed synthetic protocols based on colloidal chemistry for the controlled growth of PB and PBA shells over two types of inorganic cores: plasmonic gold nanoparticles and piezoelectric $BaTiO_3$ nanoparticles. In this way, this approach enabled the synthesis and characterization of well-defined core@shell that ensure intimate interfacial contact between the core and the shell, a critical aspect to enable the emergence of new or enhanced properties.

Thus, the project's objective is first to establish reliable synthetic routes for these hybrid nanostructures, and secondly, to pave the way for future studies aimed at exploring their multifunctional properties and potential synergistic effects.

MASTER IN MOLECULAR NANOSCIENCE AND NANOTECHNOLOGY

MASTER'S DEGREE THESIS

POLYOXOMETALATE-INTERCALATED LAYERED DOUBLE HYDROXIDE MATERIALS AS WATER OXIDATION CATALYSTS.

Author: Susana Ochando Pariente

Tutor: Dr. Joaquín Soriano López

September 2025

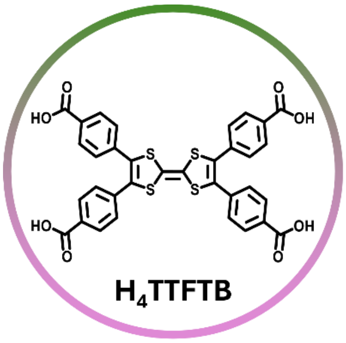
Abstract

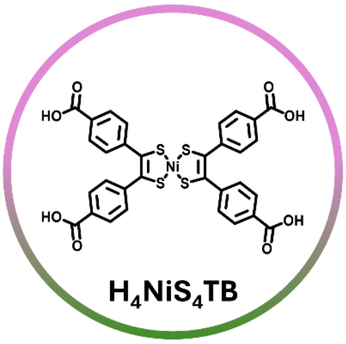
This work investigates strategies to improve the oxygen evolution reaction (OER), a key process for clean energy technologies such as water electrolysis, which is central to green hydrogen production and solar energy storage. Given the limitations of noble metal catalysts, the study focuses on NiFe layered double hydroxides (NiFe-LDHs) and cobalt-based polyoxometalates (Co-POMs), combining them through the intercalation of Co_4-POM and Co_2Fe_2-POM into the interlayer space of NiFe-LDH. The resulting hybrids were synthesized and characterized by multiple techniques, confirming uniform intercalation, partial loss of crystallinity, and interlayer expansion. Stability tests showed that at pH 8 the POMs remained intact, while at pH 14 significant hydrolytic decomposition occurred, with leaching of W and P and retention of Co as CoO_x species. Electrochemical tests revealed that at pH 8 no substantial improvement in OER activity was achieved compared to that of the NiFe-LDH alone, likely due to blockage of active LDH sites by POMs. In contrast, at pH 14 the NiFe-Co_4_W hybrid exhibited enhanced activity compared to pristine NiFe-LDH, with lower Ni oxidation potentials and Tafel slopes near 60 mV dec^{-1}, indicating the second electron transfer as the rate-limiting step. Mass-normalized activity confirmed superior performance of NiFe-Co_4_W, although ECSA-normalized activity decreased, suggesting the creation of new active sites rather than improvement of existing ones. Overall, the intercalation of POMs into LDHs yields promising hybrid catalysts for OER, with performance strongly dependent on pH and synthesis conditions. Despite POM decomposition at high pH, the resulting Co-derived species appear to induce favorable electronic modifications in NiFe-LDH, enhancing charge transfer and catalytic activity. Future work should explore other POMs and alternative host matrices to improve stability under alkaline conditions.

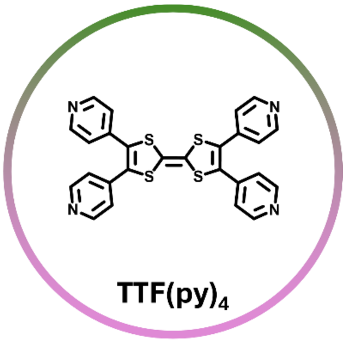
Master in Molecular Nanoscience and Nanotechnology

Master's Degree Thesis

Towards Multivariate HOFs Based On Tetrathiafulvalene and Nickel Bis(dithiolene) Derivatives


H_4TTFTB


H_4NiS_4TB


$TTF(py)_4$

Author:

Carme Umbert Bonet

Tutor:

Guillermo Mínguez Espallargas

Academic year 2024-2025

ABSTRACT

In recent years, Metal-Organic Frameworks (MOFs) have been extensively explored for a wide range of applications. However, their limited processability often restricts integration into practical devices. Hydrogen-bonded Organic Frameworks (HOFs) have emerged as a promising alternative: they self-assemble via hydrogen bonding, are solution-processable, and can be recrystallized with ease, while retaining the chemical versatility of MOFs. Careful selection of the building blocks enables tunable functionalities, giving access to multifunctional porous materials.

Recently, HOFs based on tetrathiafulvalene (TTF) derivatives have been reported. These building blocks exhibit excellent electron-donating ability and reversible oxidation processes, endowing many of the resulting materials with semiconductive properties. In parallel, a range of multifunctional MOFs has been constructed using an analogue of TTF, the nickel bis(dithiolene) complex (NiS_4), which acts as an electron acceptor. However, to date no HOFs incorporating NiS_4 have been reported.

To address this gap, we present a detailed study of the nickel bis(dithiolene-dibenzoic acid) complex (**H_4NiS_4TB**), encompassing its synthesis, electrochemical characterization, and assembly into a novel HOF, **HOF-WATER**, obtained by solvothermal crystallization. Single-crystal X-ray diffraction revealed a material build from porous sheets stabilized by weak intermolecular interactions. Further characterization was limited by challenges in obtaining a phase-pure crystalline sample.

To further advance the development of semiconductive HOFs, two TTF-based ligands – tetrathiafulvalene tetrabenzoic acid (**H_4TTFTB**) and tetra(4-pyridyl)tetrathiafulvalene (**$TTF(py)_4$**) – were synthesized and characterized. Mixed-ligand HOFs combining **H_4NiS_4TB** with these electron-donor ligands were then targeted. Crystallization attempts were undertaken as a first step towards promoting charge transfer interactions and establishing an alternative strategy, beyond conventional doping, for accessing semiconducting frameworks.

Tuning Flexibility in Multivariate Zeolitic Imidazolate Frameworks:

Gate-Opening Modulation through Mixed-Linker and Mixed-Metal Strategies

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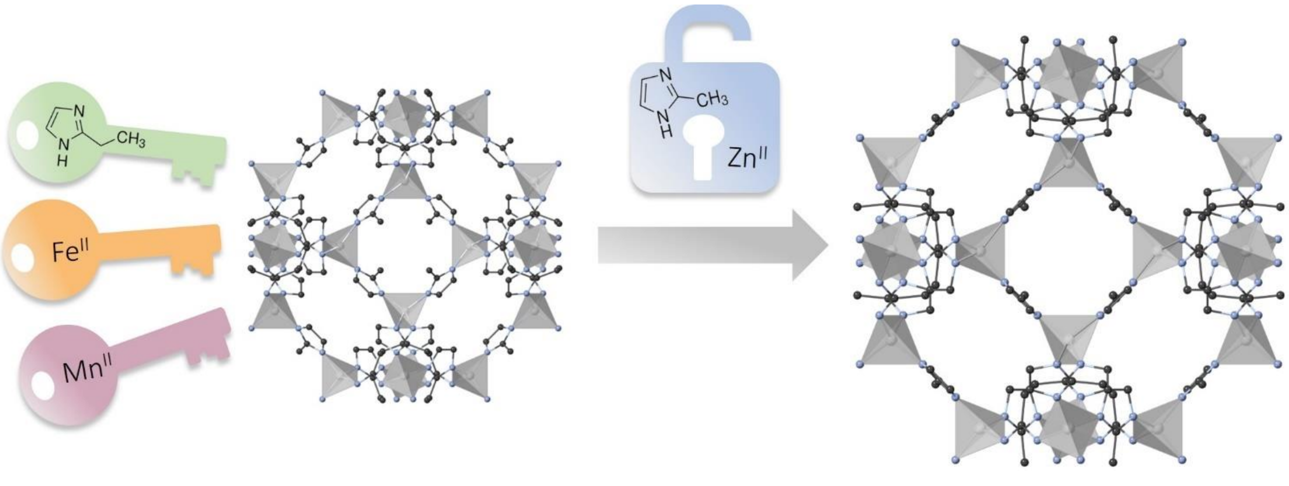

Presented by: **Nerea Menargues Sanz**
Supervised by: **Prof. Guillermo Mínguez Espallargas**
Dr. Luis León Alcaide

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Abstract

Zeolitic imidazolate frameworks (ZIFs) are highly tunable porous materials whose structural dynamics, such as the gate-opening effect, strongly influence gas adsorption. In this work, we explore a multivariate approach to modulate ZIF behaviour by varying linkers and metal centres within the same lattice. Specifically, we study Zn^{II}-based frameworks with partial substitution of 2-methylimidazole (mim) by 2-ethylimidazole (eim), and mim-coordinated mixed-metal systems including Zn^{II}/Fe^{II}, Zn^{II}/Mn^{II}, and Fe^{II}/Mn^{II} combinations. Comprehensive analysis using PXRD, NMR, SEM, elemental mapping, TGA and N_2 adsorption has been carried out, ensuring a complete chemical and structural characterization of the different materials. This Master's Thesis aims to demonstrate that even minor incorporations of a secondary building unit can precisely modulate framework flexibility, adsorption capacity, and gate-opening behaviour. These results show that multivariate design is an effective way to control ZIF properties, offering a flexible platform to tune adsorptive behaviour and structural dynamics in the sodalite (**sod**) topology, with potential uses in gas separation, catalysis, and other fields.

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Master in Molecular Nanoscience and Nanotechnology

Master Thesis:

Development of novel antimicrobial communication systems based on the application of mesoporous silica nanodevices

Carla Alonso Ripoll

Supervised by Ángela Morellá Aucejo
and Mónica Giménez Marqués

2024-2025

Abstract

The development of antimicrobial communication systems represents a promising approach in the fields of biomedicine and bioremediation. In this context, a key strategy for establishing such communication is the use of nanotechnology, which allows the design of hybrid systems loaded with active molecules and capable of controlling their release with precision.

In this work, we propose a nanotechnology-based system to establish a communication system between *Lactobacillus rhamnosus*, which is a probiotic bacterium, and the pathogenic bacterium *Helicobacter pylori*. To achieve this communication, mesoporous silica nanoparticles are used as carriers, loaded with metronidazole —a classic antibiotic used to treat *Helicobacter pylori* infections— and functionalized on their surface with a benzimidazole-cyclodextrin inclusion complex, which acts as a pH-responsive molecular gate. Under neutral conditions, the gate remains closed, preventing premature drug release. However, acid production by *Lactobacillus rhamnosus* induces local acidification, triggering gate opening and the controlled release of metronidazole.

This proof of concept demonstrates that effective antimicrobial communication can be established between a beneficial probiotic bacterium and a pathogenic bacterium using nanodevices. Additionally, this innovative approach holds potential to improve treatment efficacy, reduce side effects, and minimize the development of antimicrobial resistance.

Final master's thesis titled:

Design and characterization of flavin adenine dinucleotide-functionalized core-shell upconversion nanoparticles

Submitted as partial requirement for the Master's Degree in Molecular Nanoscience and Nanotechnology

By Carlos Sánchez García

Supervisors:

Dr. Laura Francés Soriano

Prof. Julia Pérez Prieto

Abstract

Upconversion nanoparticles (UCNPs) can convert near-infrared (NIR) light into higher-energy emission, offering opportunities for bioimaging and photodynamic therapy (PDT). Yet, their low quantum yield remains a limitation. In this work, we synthesized ultrabright core–shell β-$NaYF_4:Yb^{3+},Tm^{3+}@NaYF_4:Gd^{3+}$ UCNPs and functionalized them with flavin adenine dinucleotide (FAD), a photosensitizer for singlet oxygen ($^1O_2$) production. The core–shell design enhanced luminescence intensity and lifetime compared to core-only nanoparticles. Surface modification with FAD was confirmed by TEM, FTIR, ζ-potential, and photoluminescence measurements, which also revealed efficient energy transfer from UCNPs to FAD. NIR-triggered $^1O_2$ generation was evaluated using ABDA as a probe. The nanohybrids successfully produced $^1O_2$, although with lower efficiency than anticipated, likely due to FAD photoinstability and limited intersystem crossing. These results demonstrate the potential of FAD-functionalized UCNPs as NIR-activated nanohybrids for PDT, while also highlighting the need for improved photosensitizer stability and optimized donor–acceptor interactions to maximize therapeutic performance.