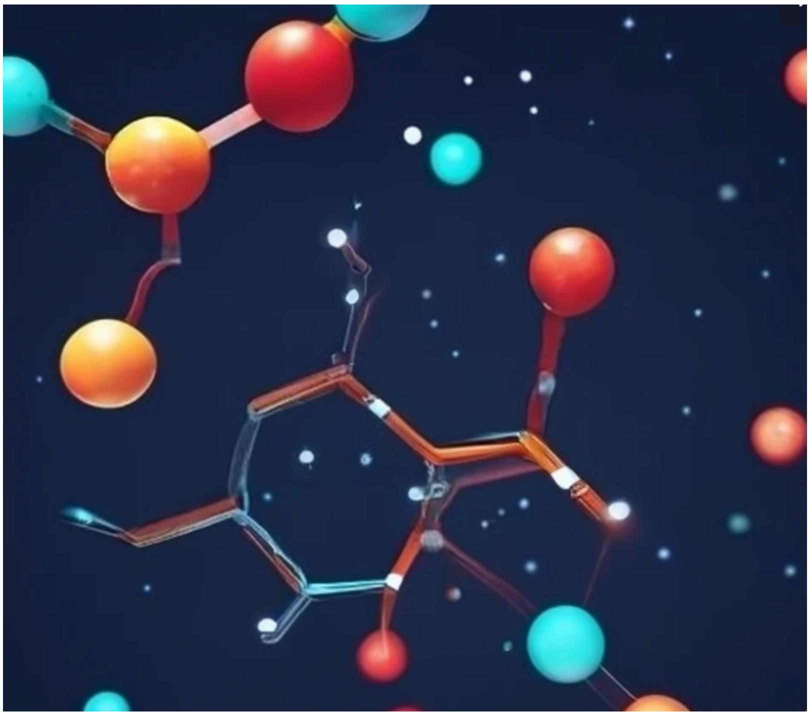
# Joint scientific days of GDR Solar Fuels and Photo Electro Stimulation



*2024, June 24-25-26 – Grenoble*

Chères et chers collègues,

Les GDR Solar Fuels et Photo-Electro-Stimulation (PES) sont très heureux de s'associer pour ces journées scientifiques organisées à Grenoble du 24 au 26 juin 2024.

Le GDR Solar Fuels rassemble les acteurs français dans le domaine de la production de carburants solaires, discipline transverse en plein essor. Il réunit des expertises en science des matériaux, chimie moléculaire et biochimie au travers de l'utilisation de concepts et d'approches communs (nanosciences, bio-inspiration, capture de lumière et conversion énergétique, catalyse, mécanismes réactionnels), et du partage de méthodologies et d'outils (électrochimie, photochimie, méthodes de caractérisation avancées et couplées, modélisation et simulation).

Le GDR PES, quant à lui, rassemble une large communauté scientifique autour des thématiques liées à la photoélectrochimie et à la commutation de propriétés optiques et électrochimiques de molécules et matériaux, avec un intérêt pour des applications entre autres dans la production et le stockage d'énergie.

Les liens entre ces deux communautés sont donc étroits et nous espérons que ces journées permettront de les renforcer et d'initier de nouveaux projets collaboratifs entre les membres des deux réseaux. Nous espérons aussi que vous apprécierez le programme scientifique concocté avec les organisateurs locaux qui, comme chaque année, donne l'opportunité à de jeunes chercheurs doctorants et post-doctorants de venir présenter leurs travaux de recherches. Nous vous souhaitons de très bonnes journées à Grenoble !

Valérie Keller, Directrice du GDR Solar Fuels
Fabien Miomandre, Directeur du GDR PES

Dear colleagues,

The French Solar Fuels and Photo-Electro-Stimulation (PES) networks are delighted to organize joint scientific days in Grenoble from June 24 to 26, 2024.

The Solar Fuels network brings together the French players in the field of solar fuels production, a fast-growing cross-disciplinary field. It gathers expertise in materials science, molecular chemistry and biochemistry through the use of common concepts and approaches (nanoscience, bio-inspiration, light capture and energy conversion, catalysis, reaction mechanisms), and the sharing of methodologies and tools (electrochemistry, photochemistry, advanced and coupled characterization methods, modeling and simulation).

The Photo-Electro-Stimulation network, on the other hand, brings together a broad scientific community around themes linked to photoelectrochemistry and the switching of optical and electrochemical properties of molecules and materials, with an interest in applications related to energy production and storage, among others.

The links between these two communities are therefore close, and we hope that these days will help to strengthen them and initiate new collaborative projects between members of the two networks. We also hope that you will enjoy the scientific program concocted with the local organizers which, as every year, gives young doctoral and post-doctoral researchers the opportunity to present their work. We wish you a great time in Grenoble!

Valérie Keller, Director of the French Solar Fuels network
Fabien Miomandre, Director of PES network

# *Many thanks to our sponsors and institutions*

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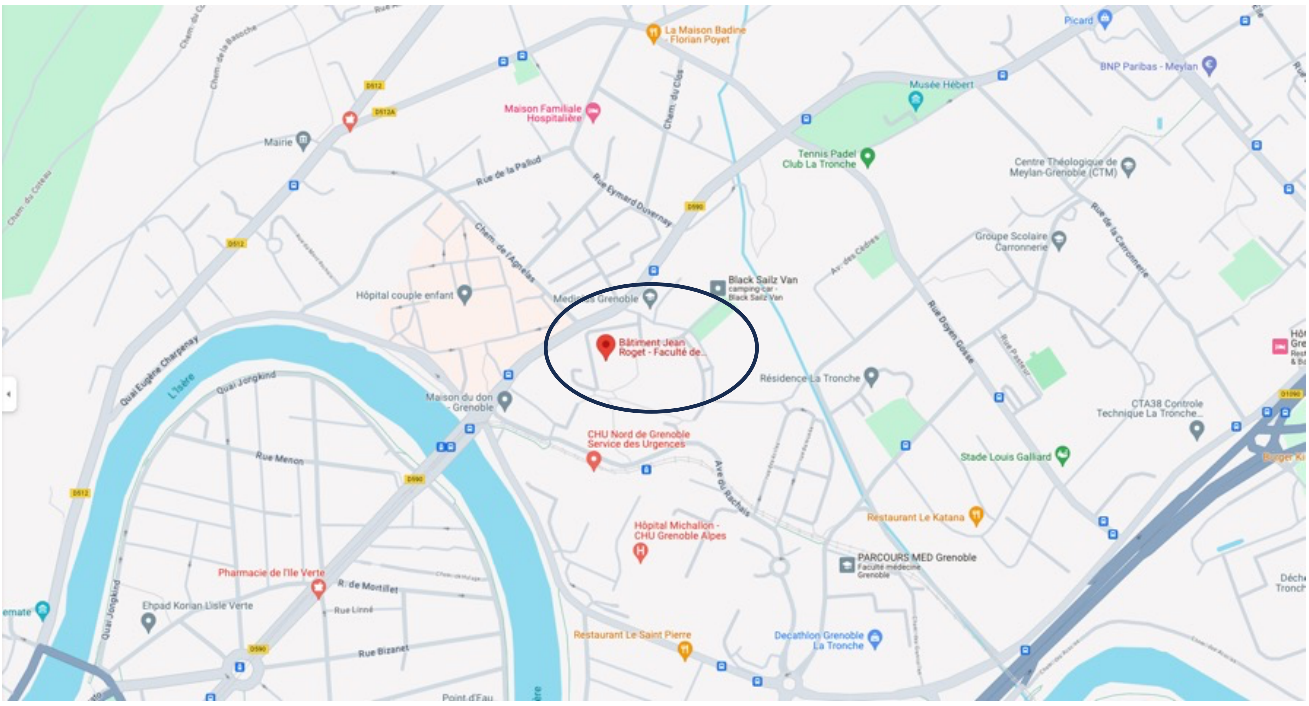
# *Location*

The GDR will take place on the health campus, in the "**Amphi inférieur Nord**" of the building **Jean ROGET**. The venue is easily accessible by tram (Line B, "La Tronche Hopital", "*Hopital Michallon*" or "Sablons" stops).

Adress: **Bâtiment Jean Roget - Faculté de Médecine & Pharmacie, 38700 La Tronche (or Place du commandant Nal)**



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**Venir en Voiture :** Itinéraire jusqu'au site de Jean Roget

**Venir en Tramway :** De la Gare de Grenoble au site Jean Roget

**Se garer :** - Parking de la faculté : accès par l'avenue des Maquis du Grésivaudan

- Parking Biopolis (recommandé) : 8 min à pied pour rejoindre le Bât. Jean Roget (voir itinéraire piéton sur le plan – – – –)

# *Joint scientific days of GDR Solar Fuels and Photo Electro Stimulation - 2024, June 24-25-26 - Grenoble*

## *Monday, 24th*

| | | | |
|---|---|---|---|
| 13:00-13:45 | **Arrival of participants - Reception** | | |
| 13:45-14:10 | **Opening speech** | | |
| 14:10-14:30 | C01 | Caitlín McMANUS | Electrochemical CO2 reduction by an immobilised molecular bimetallic catalyst |
| 14:30-14:50 | C02 | Jana MEHREZ | Stereochemical tunning of nickel based HER electro-catalysts |
| 14:50-15:10 | C03 | Si-Thanh DONG | Assessment of Ni-Mo-Fe based catalysts for solar hydrogen production |
| 15:10-15:30 | C04 | Daniel CRUZ | On the Photophysics of a Triazatriangulenium Carbocationic Dye for Solar Fuel Production |
| 15:30-15:50 | C05 | Julie DESCAMPS | Photoinduced electrochemiluminescence: a tool for imaging charge transfer at water-splitting photoanodes |
| 15:50-16:20 | **Coffee break** | | |
| 16:20-17:10 | IL1 | Oliver WENGER | Emergent photophysics and photochemistry of first-row transition metal complexes |
| 17:10-17:30 | C06 | Mahdi SAAD | Electrocatalytic Reduction of CO2 by Copper Molecular Catalysts |
| 17:30-17:50 | C07 | Vien-Duong QUACH | Abnormal copper coordination obtained by strong metal – Support interaction as a key for enhanced photocatalytic hydrogen generation |
| 17:50-18:10 | C08 | Geoffroy GUILLEMOT | Proton-coupled electron transfer to and from polyoxotungstates |
| 18:10-18:30 | C09 | Maxime VALAY | Communication orale sponsor Origalys |
| 18:30-22:00 | **Posters session and Cocktail - Dinner** | | |

## *Tuesday, 25th*

| | | | |
|---|---|---|---|
| 09:10-10:00 | IL2 | Christel LABERTY | Proton insertion vs. HER : Role of light? |
| 10:00-10:20 | C10 | Julian GUERRERO | Evaluating P-N Junction Configurations for Enhanced CO2 Reduction Using Cu(In,Ga)Se2 (CIGS) Based Photocathodes |
| 10:20-10:40 | C11 | Eliane KHOURY | Bimetallic platinum-copper/titanium dioxide photocatalysts for CO2 reduction with water |
| 10:40-11:10 | **Coffee break** | | |
| 11:10-11:30 | C12 | Laura OPDAM | A study of the role of a gas channel residue in the small molecule selectivity of CODH TC2 |
| 11:30-11:50 | C13 | Quentin STEMBAUER | Organic photosensitizers for photoelectrochemical cells based on semiconductor of delafossite structure for sustainable hydrogen production |
| 11:50-12:10 | C14 | Julie ANDREZ | Heptazine Chemistry Development for CCE Applications |
| 12:10-12:30 | C15 | Fatima MERHI | III-V Semiconductor-based photoelectrodes for the solar-driven production of green H2 |
| 12:30-14:30 | **Lunch** | | |
| 14:30-14:50 | C16 | Dana STANESCU | Efficient strategies to optimize hematite based photoanodes for efficient solar water splitting |
| 14:50-15:10 | C17 | Hong Phong DUONG | Improving synthesis of n-propanol from CO reduction by silver and copper nitride electrocatalyst |
| 15:10-15:30 | C18 | Claire BOURGUIGNON | Development of a novel push-pull organic dye for hydrogen production in dye-sensitized photoelectrochemical cells (DSPECs) |
| 15:30-15:50 | C19 | Denis FRATH | Photoredox-responsive and Conductive Supramolecular Materials |
| 15:50-16:40 | **Coffee break** | | |
| 16:40-17:00 | C20 | Zineb EL MOQAOUIL | Photocatalytic Deoxygenation of N-O and S-O bonds |
| 17:00-17:20 | C21 | Encarnacion TORRALBA | Photoelectrocatalytic CO2 reduction on bimetallic-decorated silicon photocathodes |
| 17:20-17:40 | C22 | Julien PERARD | Development of a CO2-biomethanation reactor for producing methane from green H2 |
| 17:40-18:35 | IL3 | Kevin SIVULA | Organic Semiconductors for Photoelectrochemical and Photocatalytic Water Splitting |
| 19:00-22:00 | **Dinner** | | |

## *Wednesday, 26th*

| | | | |
|---|---|---|---|
| 08:30-8:50 | C23 | Prescillia NICOLAS | Highly SHG active pyrimidine-based liquid crystal for 3D optical storage |
| 08:50-09:10 | C24 | Yutzil SEGURA-RAMIREZ | CO2 Electroreduction from Simulated Low-Concentrated CO2 Flue Gas Using Molecular Catalysts |
| 09:10-9:30 | C25 | Zahraa ABOU KHALIL | Insight in-situ restructuring of coordinated copper in UIO-66 derivatives during visible light driven hydrogen production from formic acid: an operando study |
| 09:30-9:50 | C26 | Thi-Hieu HOANG | Hydrogen-substituted graphdiyne combined with perovskites toward photocatalytic CO2 reduction |
| 09:50-10:20 | **Coffee break** | | |
| 10:20-11:10 | IL4 | Moritz KÜHNEL | The Oxygen dilemma in solar fuel generation |
| 11:10-11:30 | C27 | Rongning LIN | Artificial photosynthesis: molecular catalysts for water activation and oxidation |
| 11:30-11:50 | C28 | Irene SUAREZ ANTUNA | A Bio-inspired Heterodinuclear NiFe complex for photocatalytic H2 production |
| 11:50-12:10 | C29 | Riddhi KUMARI RIDDHI | Heterogenized molecular photocatalysis for CO2 to formic acid conversion using visible light |
| 12:10-12:30 | C30 | Cyrille COSTENTIN | Turnover Number in Photoinduced Molecular Catalysis of Hydrogen Evolution: a Benchmarking for Catalysts? |
| 12:30-12:40 | **Concluding ceremony** | | |
| 12:40-13:30 | **Packed lunches** | | |
| 14:00-16:00 | **GdR Solar Fuels - General Assembly** | | |

# Posters

| | | |
|---|---|---|
| **P01** | **Artero Vincent** | Solar fuels generators: integration at different levels and scales |
| **P02** | **Hsini Abdelghani** | Influence of Sr-doping on structural, optical and photocatalytic properties of synthesized Ca3(PO4)2 |
| **P03** | **Fabro Cesar Miguel** | Imidazolium modified nickel porphyrins: the role of electrostatics in hydrogen evolution catalysis |
| **P04** | **Dang Thi Huyen My** | Photocatalytic systems based on octahedral tungsten halide cluster and polyoxometalates for solar energy conversion |
| **P05** | **Laisne Lucas** | Optimise photoelectrochemical cell |
| **P06** | **Haurez Alix** | Electrocatalytic reduction of CO2 to methane by copper cluster immobilized on carbon nanotubes |
| **P07** | **Carino Christian** | Light-induced charge accumulation in polyoxometalate-photosensitizer dyads |
| **P08** | **Gomez-Mingot Mari** | Tuning electrocatalytic CO2 conversion by molecular surface electrode modification |
| **P09** | **Pham Duong Tuan** | Polymeric porphyrin-based material for the activation and reduction of COo2 |
| **P10** | **Kchour Assil** | Tailoring iron porphyrin catalysts for covalent attachment to semiconductor surfaces |
| **P11** | **Piccoli Alberto** | Electrochemical CO2 reduction with metal-pincer catalysts |
| **P12** | **Klement Bas** | Substituents effect on CO2 conversion to formate by [FeFe]-hydrogenase mimics |
| **P13** | **Hoang Huy Tu** | Electrochemical and spectroscopic characterization of iron phthalocyanines and their carbene species in homogeneous conc |
| **P14** | **Kovani Eleni** | Polyoxometalate-based artificial photosynthesis |
| **P15** | **Malano Giorgia** | ALD of ternary silicides as efficient catalysts for water photooxidation |
| **P16** | **Papadakis Michael** | Series of bis(thiosemicarbazone) catalysts for photocatalytic hydrogen evolution reaction |
| **P17** | **Maurel Vincent** | Hybrid CdSe/ZnS quantum dots-gold nanoparticles composites assembled by click chemistry: towards affordable and efficie |
| **P18** | **Haake Matthieu** | A macrocyclic cobalt-based molecular hybrid cathode for selective CO2-to- electroreduction |
| **P19** | **Chemineau Victor** | Development of an experimental set-up in operando conditions to study photoelectrochemical reactions by x-rays absorptio |
| **P20** | **Smith Olivier** | Noble-metal-free photocatalytic system for CO2 reduction in gas phase |
| **P21** | **Pascal Simon** | Design of coupled heptamethine-oxonol dyes |
| **P22** | **Righetti Claudio** | Exploring CODH for electrochemical CO2 reduction reaction and water-gas shift reaction |
| **P23** | **Defferrari Diego** | Improved synthesis of metal tetrabenzotriazaporphyrins to develop second coordination sphere catalysts |
| **P24** | **Da Mata Lazinski Le** | Hemiindigos as acetylcholinesterase inhibitors for photopharmacological applications |
| **P25** | **Desjonqueres Alix** | Proton-coupled electron transfer to and from polyoxotungstates |
| **P26** | **Moreaux Florian** | Optimization of molybdenum-sulfide based electrodes for catalytic hydrogen production under neutral conditions |
| **P27** | **Naciri Yassine** | The impact of metal deposition on graphdiyne-carbon nanotube hybrids for electrolytic hydrogen production |
| **P28** | **Gomez-Mingot Mari** | Encapsulation of polyoxometalates in MOF-545 for improving the photocatalytic CO2 reduction activity hydrogen hydrogen |
| **P29** | **Sibi Puthanagady Mariet** | Carbon isotope radiolabeling via photo-induced carbondioxide radical and formate salts. Insight into the mechanism |

# *Invited Lectures*

## IL1

### Prof. Oliver WENGER, University of Basel

***Emergent photophysics and photochemistry of first-row transition metal complexes***

## IL2

### Prof. Christel LABERTY-ROBERT, Sorbonne University, Paris

***Proton insertion vs. HER : Role of light?***

## IL3

### Prof. Kevin SIVULA, EPFL (Lausanne)

***Organic Semiconductors for Photoelectrochemical and Photocatalytic Water Splitting***

## IL4

### Prof. Dr Moritz F. KÜHNEL, University of Hohenheim

***The Oxygen dilemma in solar fuel generation***

Conference sponsored by

## C01

# Electrochemical $CO_2$ reduction by an immobilised molecular bimetallic catalyst

Caitilín McManus,[a,b] Carole Duboc*[a], Vincent Artero*[b]
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One possible technology for achieving chemical circularity is the utilisation of captured $CO_2$ as a feedstock. The electrochemical $CO_2$ reduction reaction ($eCO_2RR$) allows for the use of renewable energy to drive this valorisation of $CO_2$ into useful carbon building blocks.[1] The immobilisation of molecular catalysts onto carbon electrodes is promising strategy for combining the advantages of molecular catalysts with those of solid-state materials.[2] The molecular nature of the catalyst permits tunability and a wide range of spectroscopic techniques, while the heterogenized systems may be studied in aqueous conditions, free from diffusion limitations. This work studies the immobilisation of bimetallic transition metal complexes onto carbon nanotube electrode surfaces, using π-π stacking interactions. A cobalt homobimetallic earth abundant metal catalyst,[3] supported by a pyridyldiimine macrocyclic ligand, was first studied in organic media in the solution state and found to show low Faradaic efficiencies and poor selectivity for $CO_2$ reduction versus the competing proton reduction reaction. Immobilisation, *via* the appending of a polyaromatic pyrene moiety to the ligand, resulted in a marked improvement in both the overall Faradaic efficiency, as well as the product ratio of CO to $H_2$.

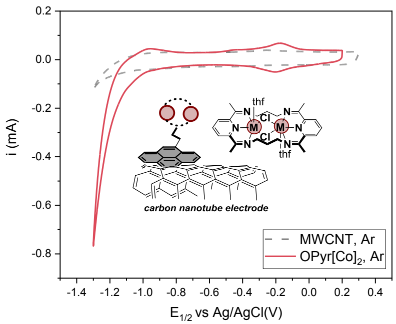

Figure 1. Cyclic voltammogram of the cobalt catalyst $OPyr[Co]_2$ immobilised on carbon nanotubes

## References.

[1] Y. Pei, H. Zhong, F. Jin, *Energy Sci Eng.* **2021**, 9, 1012–1032

[2] Tran, P. D.; Le Goff, A.; Heidkamp, J.; Jousselme, B.; Guillet, N.; Palacin, S.; Dau, H.; Fontecave, M.; Artero, V. *Angew. Chem., Int. Ed.* **2011**, *50*, 1371.

[3] F. L. M. Thierer, S. H. Brooks, A. B. Weberg, P. Cui, S. Zhang, M. R. Gau, B. C. Manor, P. J. Carroll, N. C. Tomson, *Inorg. Chem.* **2022**, *61*, 16, 6263–6280

## C02

# Stereochemical tunning of nickel based HER electro-catalysts

Jana Mehrez[a], Michael Papadakis[a], Renaud Hardré[a], Maylis Orio[a]

*Aix Marseille University, CNRS, Centrale Marseille, iSm2, Marseille, France.*

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Numerous challenges for the upcoming decades arise from the worldwide reliance on fossil fuels as energy carriers and raw materials for industrial products. The resources being finite, there is a great interest of the research community to find alternative sources. Hydrogen is regarded as an "ideal" fuel due to its abundance and considering it only emits water vapors as side-products during combustion. The new challenge is to generate hydrogen from renewable and sustainable resources. A first series of catalysts was designed from chemical tuning of the ligand.[1] Different substituents were placed in para position of the phenyl ring of the TSC ligand. Another series also was created to enhance the influence of substituent position.[2] The resulting electrocatalytic performances of the complexes indicated that the chemical nature of the substituent indeed influences the electrochemical and catalytic behavior of the system.[1][2] To get further into this key parameter, we are now investigating a new series of nickel based electro-catalysts with non-polar substituents (Figure 1). The resulting complexes were then evaluated for their capability to mediate electrocatalytic hydrogen evolution with the aim to establish structure-property relationships.

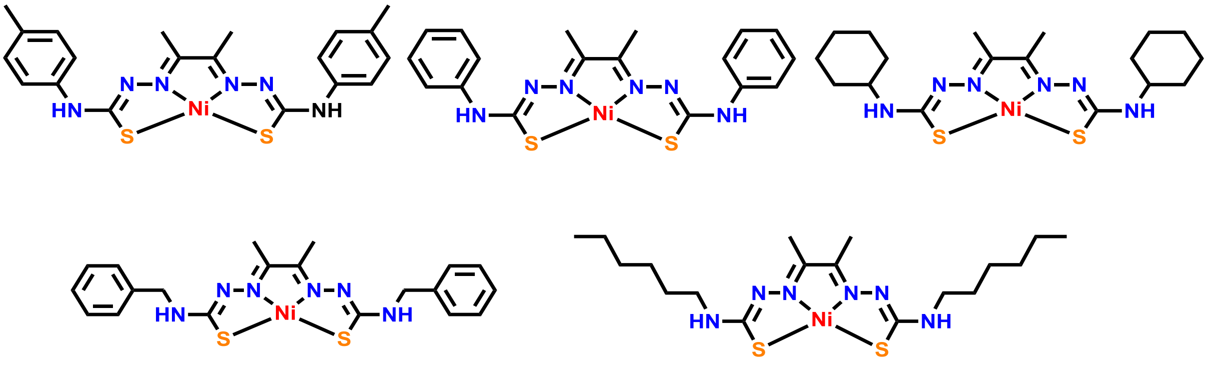

Figure 1: Series of Nickel complexes with non-polar substituents.

[1] M. Papadakis, A. Barrozo, T. Straistari, N. Queyriaux, A. Putri, J. Fize, M. Giorgi, M. Réglier, J. Massin, R. Hardré, M. Orio, *Dalton Trans.* **2020**, *49*, 5064.

[2] M. Papadakis, J. Mehrez, I. Wehrung, L. Delmotte, M. Giorgi, R. Hardré, M. Orio, Chem.Cat. Chem. 2024, accepted.

C03

# ASSESSMENT OF NI-MO-FE BASED CATALYSTS FOR SOLAR HYDROGEN PRODUCTION

Si-Thanh Dong,[a] Dmitry Kurchavov,[a] Nicolas Loones,[a] Frederique Donsanti,[a] Julian Guerrero[b], Muriel Bouttemy[c], Mirella Al-Katrib[a], Negar Naghavi*[a,b]

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Combining alkaline electrolyzers with solar photovoltaic can efficiently convert solar energy into clean hydrogen, offering a versatile means of energy storage and contributing to decarbonization efforts. However, the efficiency and durability of these systems depend highly on the optimization of the catalysts. Through meticulous catalyst design, we can maximize the performance of these configurations to advance the integration of photovoltaic systems in $H_2$ production. Commonly employed catalysts for alkaline electrolyzer include Ni, Mo, Fe, and their alloys.[1] Despite their abundance, these catalysts often exhibit inferior performance compared to their proton exchange membrane counterparts in terms of activity and stability. In this study, we address this limitation by developing stable and efficient NiMoFe-based catalysts using a sputtering deposition technique. We evaluated the performance of the thin-film catalysts in an original PV-alkaline electrolyzer system operating at 10 mA/cm² for both HER and OER. The relationship between the chemical composition of the thin-film catalysts and their catalytic activity has been conducted by combining in-situ Raman spectroscopy, X-ray absorption spectroscopy, and ex-situ XPS analysis. These results highlight the influence of the oxides and hydroxides formed under catalytic conditions on the electrode's activity and stability. Our results underscore the potential of our catalysts in enabling sustainable and efficient hydrogen production through solar-driven electrolysis.

## References.

[1] McCrory, C. C. L.; Jung, S.; Ferrer, I. M.; Chatman, S. M.; Peters, J. C.; Jaramillo, T. F. Benchmarking Hydrogen Evolving Reaction and Oxygen Evolving Reaction Electrocatalysts for Solar Water Splitting Devices. *J. Am. Chem. Soc.* **2015**, *137* (13), 4347–4357. https://doi.org/10.1021/ja510442p

[2] Kurchavov, D., Méndez-Medrano, M.G.; Loones, N.; Danieu, V.; Donsanti, F.; Al Katrib, M.; Bouttemy, M.; Naghavi, N.; A comparative study of Ni-Mo-Fe sputtered based catalysts for solar hydrogen fuel production, *J. Material Chemistry*, **under preparation**

### C04

# ON THE PHOTOPHYSICS OF A TRIAZATRIANGULENIUM CARBOCATIONIC DYE FOR SOLAR FUEL PRODUCTION

Daniel H. Cruz Neto,[a] My Dang Thi Huyen,[a] Daniel Peláez,[a] Jérôme Fortage,[b] Philippe Lainé,[c] Marie-Noëlle Collomb,[b] Thomas Pino[a], Minh-Huong Ha-Thi*[a]

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Light-driven catalytic systems for solar fuel production usually feature expensive, rare and environmentally-harmful photosensitizers based on 2nd or 3rd row transition metals due to their outstanding photophysical properties.[1,2] The development of robust photosensitizers based on abundant elements is required for the establishment of artificial photosynthetic systems compatible with real-world applications. Metal-free organic dyes are attractive alternatives and they have increasingly been used as substitutes to metal-based photosensitizers in photocatalytic reductions.[3] A triazatriangulenium carbocationic dye (TATA$^+$) has been shown to challenge the properties of the prototypical $[Ru(bpy)_3]^{2+}$ complex as a photosensitizer for light-driven $H_2$ evolution in aqueous acidic solution.[4] In this work, we investigate the photophysics of a similar TATA$^+$ dye (Figure 1) to scrutinize its abilities to sensitize electron accumulation reactions in inactive model systems and active biomimetic systems containing modified iron porphyrins as $CO_2$ reduction catalysts. Through nanosecond-resolved spectroscopy techniques, we show that TATA$^+$ can mediate charge accumulation in $CH_3CN:H_2O$ (6:4) mixtures in dual electron acceptors such as naphthalene diimide (NDI), and in active catalytic systems based on iron porphyrins, inducing catalysis and $CO_2$ reduction.

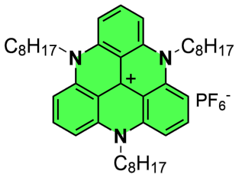

Figure 1. $[TATA(Oct)_3](PF_6)$ dye used as photosensitizer for solar fuel production.

## References.

[1] M. S. Lazorski, F. N. Castellano, Polyhedron **2014**, *82*, 57–70.
[2] C. Bruschi, X. Gui, O. Fuhr, W. Klopper, C. Bizzarri, Dalt. Trans. **2023**, *52*, 7809-7818.
[3] C.-F. Leung, T.-C. Lau. Energy Fuels **2021**, *35*, 18888–18899.
[4] R. Gueret, L. Poulard, M. Oshinowo, J. Chauvin, M. Dahmane, G. Dupeyre, P. P. Lainé, J. Fortage, M.-N. Collomb, ACS Catal. **2018**, *8*, 5, 3792–3802

## C05

# PHOTOINDUCED ELECTROCHEMILUMINESCENCE: A TOOL FOR IMAGING CHARGE TRANSFER AT WATER-SPLITTING PHOTOANODES

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Photoelectrochemistry at illuminated semiconductors (SCs) has promising applications in the field of energy conversion as the basis for artificial photosynthesis. In these systems, semiconductor photoelectrodes, often coated with protection and/or catalytic layers are immersed in a liquid electrolyte. Probing the local activity is essential for elucidating the operation of photoelectrodes. Due to the complexity of these interfaces, the photoelectrochemical reaction is not expected to occur at the same rate over the whole surface. ElectroChemiLuminescence (ECL) is a light emission process generated near an electrode by an electrochemical reaction. This is a very sensitive analytical technique widely used for medical diagnostics or clinical assays and it is currently progressing for microscopy and imaging.[1] We propose here a surface characterization method for photoelectrochemistry using Photoinduced ECL (PECL).[2-4] A series of photoactive *n*-Si partially covered by metal overlayers, relevant photoanodes in the frame of solar fuel generation, has also been investigated to spatially localize the charge transfer at SC/electrolyte interface with PECL using homogeneous IR front-illumination, allowing for precisely imaging the hole-driven heterogeneous photoelectrochemical reactivity.[5]

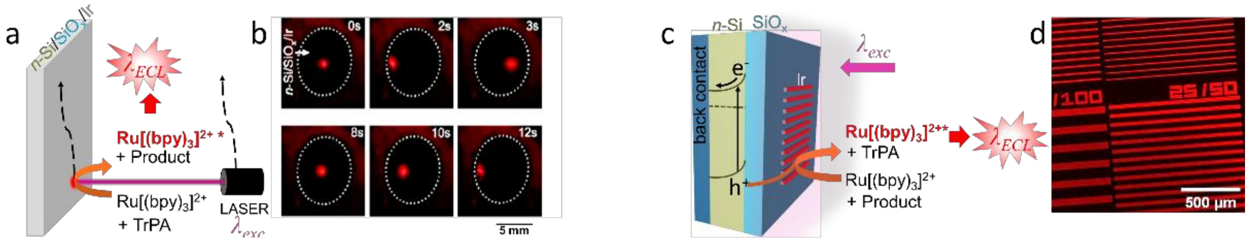

Figure 1. a) Scheme and b) pictures of the IR beam ($\lambda_{exc}$) that photo-induces ECL emission ($\lambda_{ECL}$). c) Scheme and d) microscopy imaging of ECL localized on Ir patterns.

## References.

[1] X. Gou, Z. Xing, C. Ma and J.-J. Zhu, Chem. Biomed. Imaging, **2023**, *1*, 414–433.
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## C06

# Electrocatalytic Reduction of $CO_2$ by Copper Molecular Catalysts

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Cu-based molecular complexes were shown to exclusively reduce $CO_2$ into C2 products such as ethylene, oxalate, or alcohols.[1-2] However, very few mechanistic information could be obtained from studies on Cu-based molecular complexes, in particular on the active catalytic species. Therefore, we focused our attention on studying two new binuclear Cu-based molecular complexes with a pyridine-based scaffold (Fig. 1-a) in order to characterize their active species for $CO_2$RR. To carry out this task, we have used electrochemical, and in situ UV-vis spectroelectrochemical approaches (Fig. 1-b, c). Catalytic properties (selectivity, TON, and FE) of all the catalysts were determined after electrocatalysis of $CO_2$ homogeneously in DMF and heterogeneously in $H_2O$ in order to have more insights on the effect of the ligand on these properties. Moreover, preliminary results indicate that these catalysts demonstrate better activity for photocatalytic $CO_2$ reduction compared to the most effective copper-based complexes reported to date.[3]

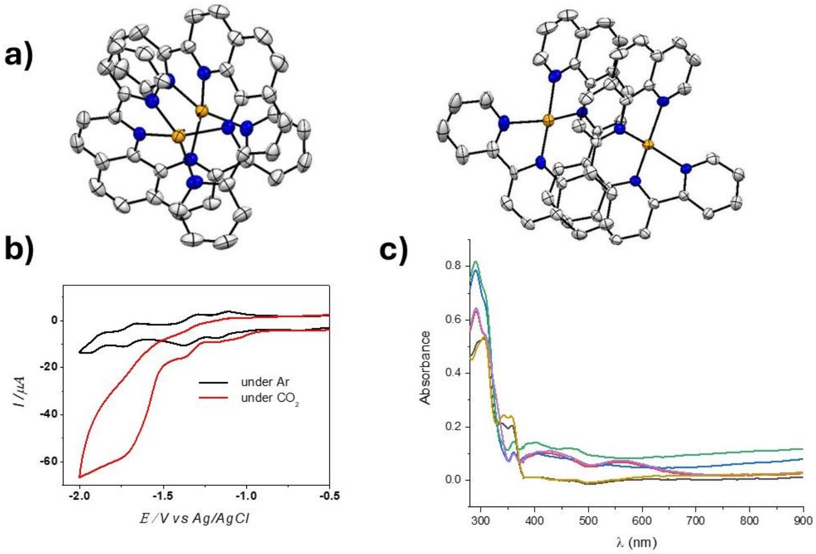

Fig.1: a) Crystal structures of two new Cu-catalysts; b) CVs of 1mM of Cu-catalyst in DMF under Ar vs $CO_2$; c) UV-vis spectra from in-situ spectroelectrochemistry

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C07

# ABNORMAL COPPER COORDINATION OBTAINED BY STRONG METAL – SUPPORT INTERACTION AS A KEY FOR ENHANCED PHOTOCATALYTIC HYDROGEN GENERATION

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Strong metal-support interaction (SMSI) is a pivotal strategy in thermal catalysis, while its application in photocatalysis leaves ample area for further development. A method inducing the SMSI between earth-abundant metals, such as copper, and $TiO_2$ at room temperature, hindering the agglomeration of copper species, remains rarely reported. In this work, we achieve SMSI construction of $TiO_2$ overlayer on Cu nanoparticles via a straightforward soft-chemistry method. The SMSI coverage is even stable after high-temperature treatment in air (500°C), as demonstrated by chemical mapping and surface analysis. The method is more accurate than thermal reduction since it produces metastable highly active anatase phase. Interestingly, the $TiO_2$ overlayer induces the formation of six-coordinated copper (II) species, which are surrounded by oxygen atoms, resulting in coexisted $CuO_2$ planes, monitored by high-resolution transmission electron microscopy and electron paramagnetic resonance spectroscopy. The stronger interfacial interaction by forming Ti-O-Cu bonding promotes charge carrier separation, leading to the production of twice as much $H_2$ than the low interfacial interaction within a conventional photoactive system wherein copper was decorated onto $TiO_2$. Our approach offers a rational design for SMSI materials in photocatalysis, extendable to other catalytic reactions.

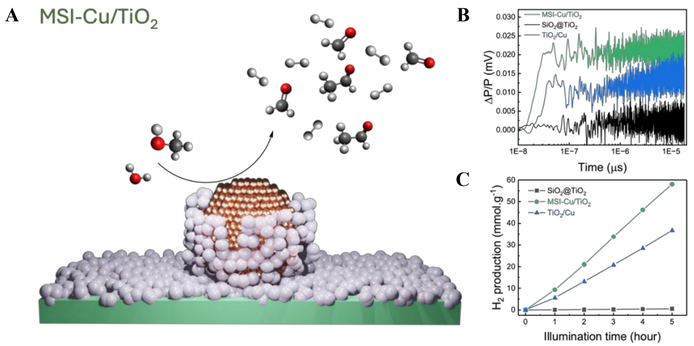

**Figure 1.** **(A)** Graphic illustration of photocatalytic $H_2$ production on SMSI-like $SiO_2@Cu@TiO_2$ nanostructure. **(B)** Charge carrier dynamics monitored by time-resolved microwave conductivity spectroscopy. **(C)** Photocatalytic $H_2$ production yield.

C08

# PROTON-COUPLED ELECTRON TRANSFER TO AND FROM POLOXOTUNGSTATES

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The accumulation of several reductive equivalents on a single–site is considered a key step towards the development of catalytic materials addressing environmental and energy challenges.[1] Due to their ability to behave as electron acceptors, polyoxometalates are ideal candidates in these areas, particularly in photocatalyzed hydrogen production.[2] Therefore, W and Mo derivatives of the Keggin and Wells–Dawson series have been widely employed in related studies but, to date, the mechanism leading to hydrogen evolution onto polyoxometalates remains rather undefined. We thus came interested in understanding how the addition of protons or dioxygen trigger the release of electrons from reduced polyoxotungstate hybrids (*Silox*POM) that we synthesized in our group (Fig. 1).[3] Our results and perspectives will be presented in this communication.

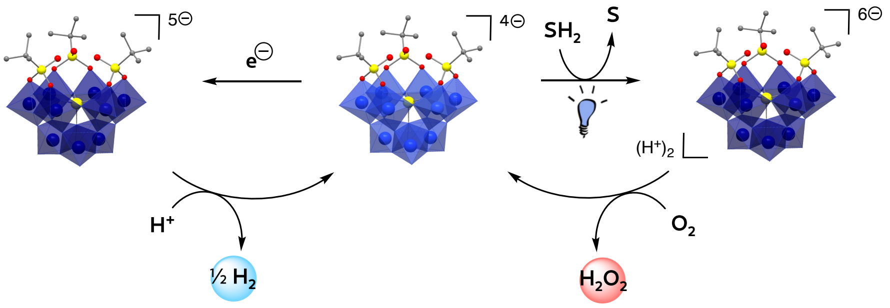

Figure 1. (left) spontaneous hydrogen release from reduced *Silox*POM upon protonation, and (right) hydrogen peroxide formation from aerobic solution of protonated / reduced cluster obtained by photo-oxidation of a suitable substrate $SH_2$.

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**C09**

# DIFFERENCE BETWEEN 2-POINT AND 4-POINT MEASUREMENT IN BATTERY STUDIES

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OrigaLys is a high-tech company based in Lyon who designs high quality and sustainable instruments in electrochemistry.

Our mission is also to communicate on the best practice in electrochemistry.

This work aims to show the difference between 2-electrode and 4-electrode measurements in electrochemical research, especially in energy storage. The 4-electrode configuration is used by most research without even knowing why it impacts their results.

Figure 1: the difference between a 2 and 4-electrode measure

In galvanostatic mode, the charge/discharge curves will differ between measurements with 2 and 4 electrodes. The Nyquist curve allows us to conclude that the resistance of the electrochemical cell is reduced with 4 electrodes.

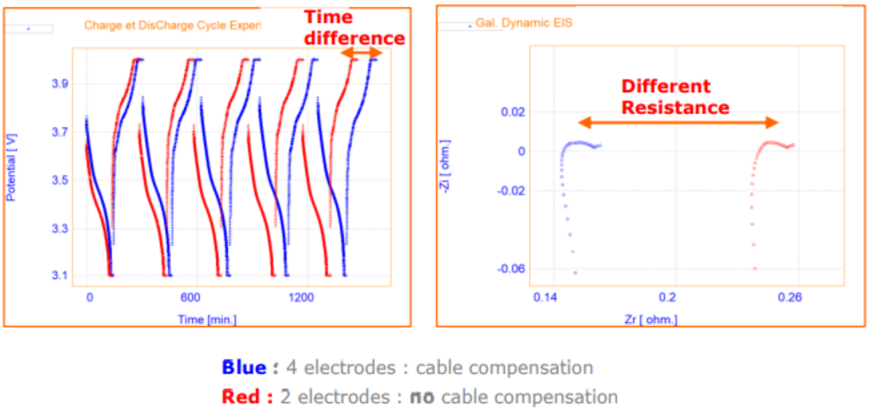

Figure 2: charge/discharge and impedance curves of Li-ion battery

We will also investigate in this presentation some key analysis in photovoltaic such as EIS, Mott-Schottky and IV characterization.

## C10

# Evaluating P-N Junction Configurations for Enhanced $CO_2$ Reduction Using $Cu(In,Ga)Se_2$ (CIGS) Based Photocathodes

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Photovoltaics absorbers materials are excellent candidates as photoelectrodes, as they yield high photocurrents by efficiently absorbing the majority of the visible light. However, these materials often lack the necessary energy to catalyse the $CO_2$ reduction reaction ($CO_2RR$) by themselves, requiring either high bias voltages or coupling with co-catalysts. In photovoltaics, the mechanism for charge carrier separation, facilitated by the p-n junction, generally surpasses the solid−liquid counterpart in terms of charge separation and electron transport, creating higher voltages. Based on this principle and to better understand the influence of p-n junctions on the photoelectrochemical (PEC) $CO_2RR$, we selected $Cu(In,Ga)Se_2$ (CIGS) materials as a representative model to be studied. We have assessed performance of both bare CIGS and CIGS/CdS p-n junction photocathodes for PEC $CO_2$ reduction. Additionally, we evaluated the impact on their performance of the addition of protectives metal oxides layers (such as $TiO_2$, NiO, $Al_2O_3$, $SnO_2$) and/or inorganic co-catalysts. These protective layers and nanostructured catalysts have been deposited either by Atomic layer deposition or photoelectrodeposition. The PEC activity of various CIGS based configurations was assessed and compared, results show that through appropriate interface engineering, remarkable efficiency can be achieved, demonstrating PEC reduction of $CO_2$-to-CO with selectivity up to 97% and current densities up to 8 $mA/cm^2$ at −1.3 V vs SCE. This study not only advances our understanding of the use of photovoltaic materials for PEC applications but also highlights the importance of appropriate interfacial engineering to achieve highly efficient photoelectrodes.

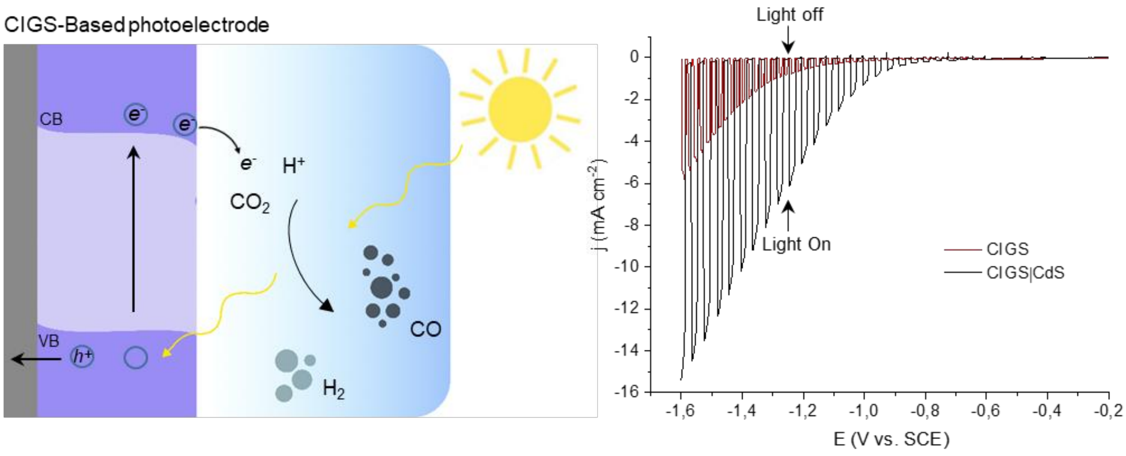

Figure 1. Schematic representation of a CIGS based photoelectrode during PEC CO2 reduction (left). Linear sweep voltammograms of CIGS and CIGS|CdS photoelectrodes (right) under chopped light illumination

C11

# BIMETALLIC PLATINUM-COPPER/TITANIUM DIOXIDE PHOTOCATALYSTS FOR $CO_2$ REDUCTION WITH WATER

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The high concentration of $CO_2$ in the atmosphere is a concerning environmental issue.[1] Photocatalytic $CO_2$ reduction using solar light appears as a way of synthesizing strategic solar fuels from $CO_2$ waste.[2] Plasmonic photocatalysts were synthesized by depositing bimetallic copper and platinum nanoparticles on titanium dioxide, either by chemical co-reduction of both metal precursors, or by sequential reduction of platinum salt followed by copper salt in an aqueous dispersion of the support. Under visible light illumination and a $CO_2/H_2O$ flow mixture, methane is produced with 100% selectivity, regardless of the synthesis route and the composition of the bimetallic photocatalyst. A synergistic effect is observed for the Cu0.2Pt0.8/$TiO_2$ composition, which exhibits a significantly higher average $CH_4$ production rate compared to the weighted average productions observed over the monometallic references (Figure 1).

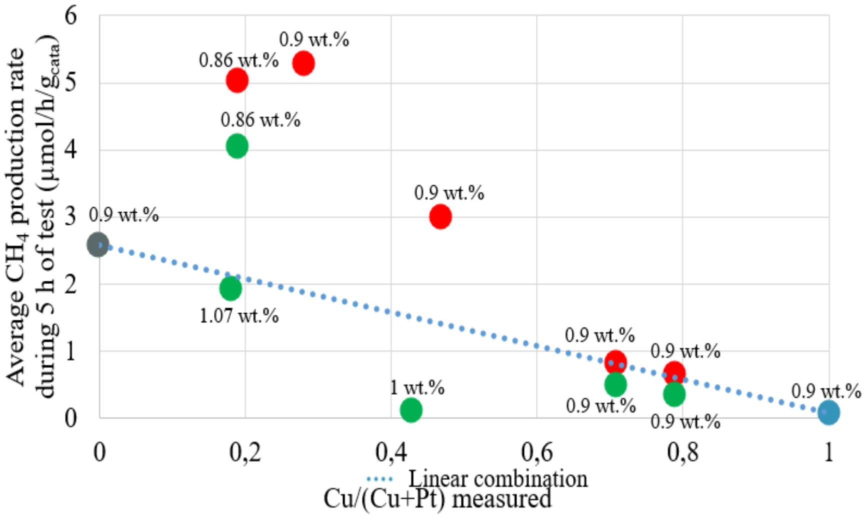

Figure 1. $CH_4$ production as a function of nominal copper content in the photocatalysts tested under visible irradiation λ > 400 nm (Grey: Pt, blue: Cu, red: simultaneous, green: sequential).

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C12

# A STUDY OF THE ROLE OF A GAS CHANNEL RESIDUE IN THE SMALL MOLECULE SELECTIVITY OF CODH TC2

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Carbon monoxide dehydrogenases (CODH) are metalloenzymes capable of performing the interconversion of CO and $CO_2$. In nature CODHs play an important role in carbon capture, removing approximately $10^8$ tons of CO from the atmosphere [1]. In industry their high turnover frequencies (TOF) make them interesting both for the removal of CO and of $CO_2$ from waste gasses so that they may be converted into fuels or valuable chemicals [2]. NiFe CODHs are, however, rather sensitive to oxygen exposure, which severely limits their applicability.

The active site in the NiFe CODHs is buried in the protein and gasses are transported to and from it using one ore multiple gas channels. These gas channels naturally govern the selectivity with which different gasses are imported into the active site and have not yet been well studied in NiFe CODHs. The gas channels have been mapped in CODH from *Desulfovibrio vulgaris* using crystallography in presence of high-pressure xenon to identify residues that are of importance to the channel [3]. Mutation studies on these residues can be employed to investigate their impact on the selectivity of the channel for its three relevant gasses (being CO, $CO_2$, and $O_2$) and with that their impact on the function of the enzyme. In the present study we present a series of variants of *Thermooccus sp AM*4 CODH 2 [4] which significantly impacted the Km for CO, the CO/$CO_2$ bias, and increased the resistance to oxygen.

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# ORGANIC PHOTOSENSITIZERS FOR PHOTOELECTROCHEMICAL CELLS BASED ON SEMICONDUCTOR OF DELAFOSSITE STRUCTURE FOR SUSTAINABLE HYDROGEN PRODUCTION

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**Keywords** : Green hydrogen; Photoelectrochemistry; Delafossite; Dyes; Solar energy

## Abstract

In the ongoing transition towards sustainable energy sources, dye-sensitized photoelectrochemical cells (DSPEC)[1] represent a promising technology for the development of renewable energies. DSPECs facilitate the production of green hydrogen through the solar-driven splitting of water molecules. These intricate systems are constructed using photoactive electrodes comprising p-type mesoporous semiconductors, onto which photosensitizers and water-splitting catalysts are immobilized. Specifically, the photocathodes in DSPECs traditionally incorporate nickel oxide as p-type semiconductor. However, inherent limitations such as low transparency and hole conductivity have prompted the exploration of alternative materials. Among these alternatives, some members of the delafossite family, namely $CuMO_2$, where M represents a trivalent cation exhibit promising features, including improved transparency and conductivity.

This presentation will provide a comprehensive overview of the advancements in my PhD project, focusing on three main areas: synthesis of organic photosensitizers, preparation of $CuMO_2$ particles, and formulation of inks for coating fluorine-doped tin oxide glass (FTO). To achieve this, new dyes with phosphonic acid anchors derived from P1 a well-described sensitizer for p-type dye-sensitized solar cells were synthesised and characterized.[2] Sub-micronic-sized $CuGaO_2$ particles were successfully synthesized from a hydrosolvothermal reaction technique, utilizing microwave irradiation at low temperatures. $CuGaO_2$ inks were formulated using ethyl cellulose and coated onto FTO glass, leading to greyish films that were further grafted with P1 photosensitizers as confirmed by the final orange coloration.

Having highlighted the key aspects of my PhD project, a closer examination of the results will be discussed.

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## Acknowledgments

This work was conducted as part of the Post-Petroleum Materials (PPM) project, funded by University of Bordeaux’s IdEx “Investments for the Future” program/GPR PPM.

## C14

# HEPTAZINE CHEMISTRY DEVELOPMENT FOR CCE APPLICATIONS

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The chemistry of heptazine compounds is tightly linked to the understanding of heptazine polymers (g-CN) (Figure 1), which have recently been highlighted for their unique chemical and photochemical performances [1]. These organic materials are low-cost, easy to synthesize, and have shown highly promising photoelectrochemical activity to promote HER, water oxidation and CO2RR [2-4]. Despite the high interest for heptazine-based materials, the heptazine chemistry remained mainly underexplored, notably owing to the challenging control of its derivative's reactivity. Despite the apparent versatility of this platform, the successful reactions to functionalize the heptazine core remained limited. This still developing chemistry explains the difficulty in obtaining and studying molecular models of g-CN. Such models would allow to better understand the structure/activity relationship of these materials. Our team explores the chemistry of heptazine derivatives and designs original methods to functionnalize them and thus opens the avenue for applications of these molecules in catalysis or photocatalysis.

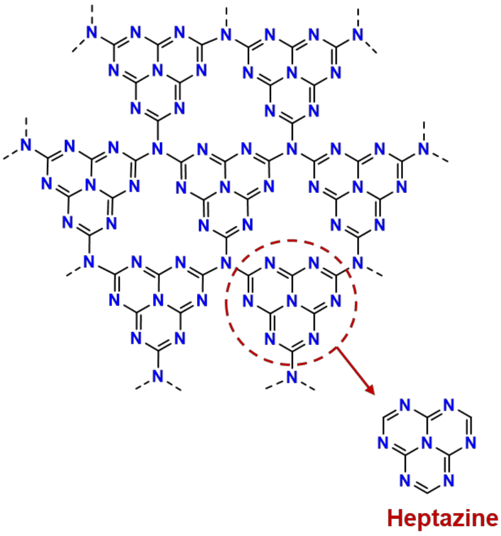

Figure 1. g-CN polymer and heptazine building block.

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C15

# III-V SEMICONDUCTOR-BASED PHOTOELECTRODES FOR THE SOLAR-DRIVEN PRODUCTION OF GREEN $H_2$

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Despite the availability of solar energy, the world's dependency on fossil fuels as a main energy source still accounts for 80% due to solar cell performance limitations.[1] Another problem is that sunlight is intermittent. One promising approach to solve this problem is the storage of solar energy into chemical bonds to be utilized whenever the sun is not directly available. In this context, decarbonized dihydrogen ($H_2$) can be generated by mimicking the plants' photosynthesis process through solar water splitting.[2,3] This pathway allows the conversion of clean and renewable energy. However, there remains an important challenge represented by reaching a high solar-to-$H_2$ (STH) conversion efficiency while maintaining a non-expensive technology.

III-V (GaAs, InP, GaN,…) semiconductors are known for their remarkable electronic properties that make them suitable candidates for solar water splitting. These materials exhibit a direct bandgap, high electron mobility, and high STH efficiency.[4] However, the major drawback is the instability of the III-V/liquid interfaces.[5] Based on the challenges stated above, we report in this work the preparation, modification and study of photoelectrodes composed of III-V thin films epitaxially grown on Si substrate for the aim of reaching a cost-effective, efficient, and robust photoelectrochemical (PEC) cell.

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C16

# EFFICIENT STRATEGIES TO OPTIMIZE HEMATITE BASED PHOTOANODES FOR EFFICIENT SOLAR WATER SPLITTING

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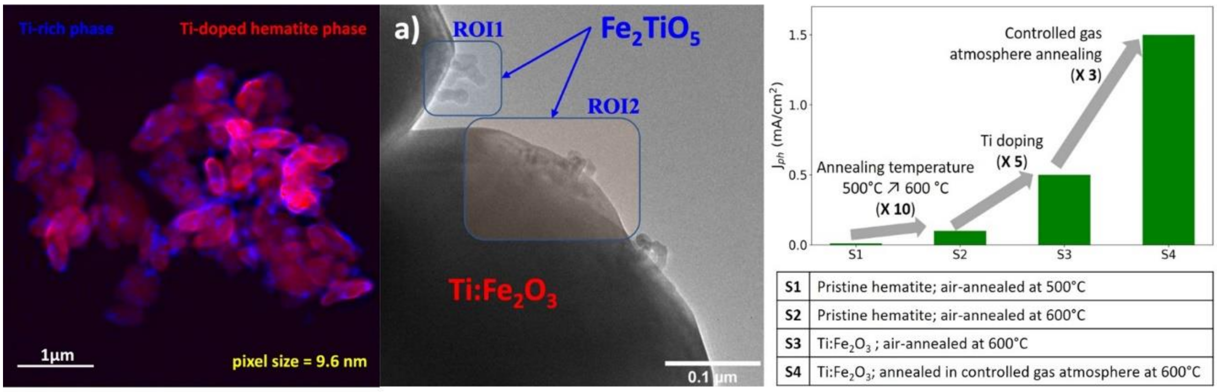
Pristine hematite (α-$Fe_2O_3$) is abundant and cheap, absorbs efficiently solar spectrum and has already attracted attention of researchers in the framework of $H_2$ production by solar water splitting[1]. But, in spite of all these benefits, it became disregarded for water splitting applications because of its poor photoelectrochemical (PEC) activity. Very short holes mean free path (≅ 4 nm) and a complex 4-steps oxygen evolution reaction are responsible for both strong electron-hole recombination and a sluggish water oxidation kinetics. Band engineering is thus employed to enhance hematite innate PEC activity. We demonstrate here that annealing Ti-doped hematite nanorods, synthesized by simple aqueous chemical growth (ACG)[2], under $N_2$ atmosphere leads to strongly enhanced photocurrent[3]. Combined nanoscale X-rays spectromicroscopy (STXM, spectro-ptychography, XPEEM) and transmission electron microscopy (TEM) reveal Ti-rich pseudo-brookite clusters at the surface of the hematite particles offering additional unoccupied states in the conduction band at the origin of this activity (Figure 1). Quantitative measurements of $H_2$ produced during more than 18 hours functioning using optimized photoanodes have demonstrated very good stability during the reaction.



| | |
|---|---|
| **S1** | Pristine hematite; air-annealed at 500°C |
| **S2** | Pristine hematite; air-annealed at 600°C |
| **S3** | $Ti:Fe_2O_3$ ; air-annealed at 600°C |
| **S4** | $Ti:Fe_2O_3$; annealed in controlled gas atmosphere at 600°C |

Figure 1: Typical spectro-ptychography STXM and STEM images[2]. Photocurrent evolution for different strategies employed to optimize hematite based photoanodes[1,2]

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## C17

# IMPROVING SYNTHESIS OF N-PROPANOL FROM CO REDUCTION BY SILVER AND COPPER NITRIDE ELECTROCATALYST

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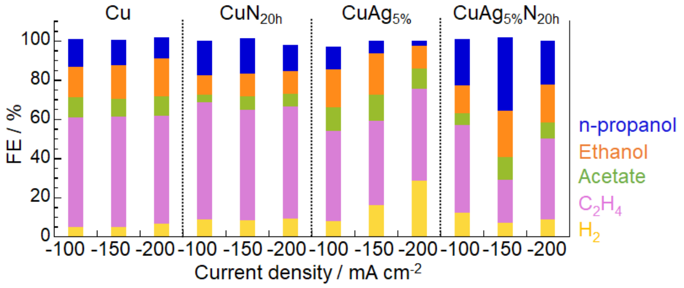
Electrochemical reduction of carbon monoxide (CO) has been known as a promising method to improve the $CO_2$ conversion thanks to its thermodynamic advantage to obtain better selectivity for valuable multi-carbon products such as ethylene, ethanol and n-propanol [1]. To date, various strategies about designing electrocatalysts for selective CO conversion like morphological modification, noble metal and heteroatom doping have been reported [2].. In this presentation, we will introduce a novel copper nitride combined with silver (CuAgN) electrocatalyst showing a high Faradaic Efficiency for CO reduction to n-propanol of 45% at an industrially relevant applied current density of 150 mA $cm^{-2}$ in the optimized reaction condition using an alkaline flow cell electrolyzer, CsOH 1.0 M electrolyte and CO flow rate of 10 ml $min^{-1}$. Via *in-situ* XRD and *in-situ* XANES characterizations, CuAgN catalyst was shown to comprise metallic Cu and Ag under the applied electrocatalytic condition. DFT calculation suggested that the enhancement of FE for n-propanol production was owing to the higher feasibility of $C_1$-$C_2$ coupling reactions on CuAg compared the bare Cu surface [3].



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C18

# Development of a novel push-pull organic dye for hydrogen production in dye-sensitized photoelectrochemical cells (DSPECs)

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In the context of climate change, an important research goal is to find sustainable alternatives to fossil fuels, typically solar fuels which are produced from a renewable energy source, the sun, and from abundant raw materials such as water and $CO_2$. Our group is working on the development of dye-sensitized mesoporous NiO photocathodes to convert sunlight into chemical energy, stored in bonds as in dihydrogen or carbon-based molecules [1][2]. These first published examples are very promising, but their efficiency still needs to be improved. In this sense, the field of dye-sensitized solar cells is a great source of inspiration for the design of novel strongly light-absorbing organic photosensitizers [3][4]. This work discusses the design, synthesis and optoelectronic characterizations of a new push-pull dye with a benzothiadiazole core, **pRK1**, and its integration into a functional dye-sensitized photocathode. The photoelectrochemical hydrogen production activity will be presented (Figure 1) in combination with a cobalt-based hydrogen-evolving catalyst in fully aqueous electrolyte [5].

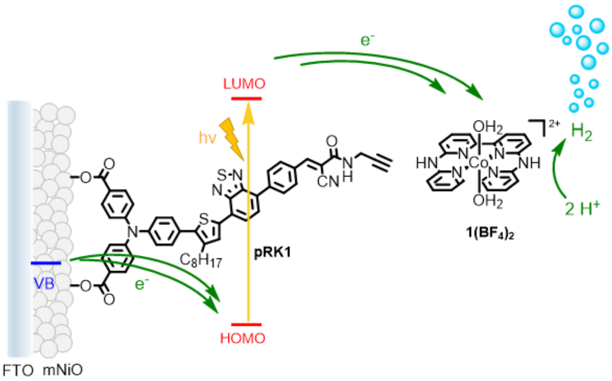

Figure 1. Working principle of the **pRK1**-sensitized photocathode with a cobalt catalyst in solution.

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C19

# PHOTOREDOX-RESPONSIVE AND CONDUCTIVE SUPRAMOLECULAR MATERIALS

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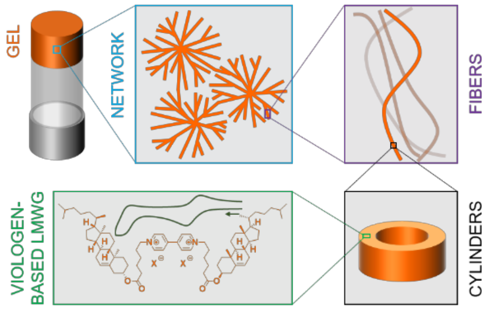
The key elements in the development of nanoscience are to observe, modify and control mater at the nanoscale. One strategy proposed to meet these immense challenges is to develop responsive molecular or supramolecular systems for which a structural reorganization is obtained in response to an external stimulation. Our research efforts in this field have led us to focus on molecular and supramolecular architectures involving viologens (4,4'-bipyridinium salts) as key electron-responsive building elements.[1] In particular, we have developed different strategies allowing to exploit the ability of viologen derivatives to form π-dimers in their reduced state to achieve a remote control over their organization within supramolecular assemblies. Among our recent achievements, we have reported a sol/gel transition triggered by light-irradiation of a viologen-based coordination polymer formed in the presence of Pd ions.[2]



We now report supramolecular gels obtained by self-assembly of a viologen gelator. These molecules have been shown to self-assemble in pentanol to form chiral hollow core-shell cylinders eventually yielding dendritic clusters inducing gelation. We also showed that the optical, rheological and electrical properties of the gels can be tuned by addition of ionic additives. Careful control of the formation of charge-transfer complexes between viologens and iodides have led to a robust, transparent, conductive and chiral gel.[3] Properties of this responsive material can be modulated when submitting it to electrical or light stimulation.

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**C20**

# PHOTOCATALYTIC DEOXYGENATION OF N-O AND S-O BONDS

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Modern human activities disrupt biochemical flows (e.g. C, N, S-cycles), leading to an accumulation in nature of harmful oxides (such as $CO_2$, $N_2O$, $SO_2$).[1] The development of selective and efficient interconversion pathways between the oxidation states of these elements, in particular the deoxygenation processes, appear to be mandatory. However, traditional deoxygenation reactions for *N*- and *S*-oxide derivatives often rely on thermochemical methods and sacrificial reducing agents.[2]

Here, we present recent advancements in our investigation of selective, sustainable, and energy-efficient processes for reducing N-O and S-O bonds using photocatalysis (Figure 1).[3] We explored the underlying mechanisms through a combination of techniques including time-resolved spectroscopy, photoaccumulation followed by IR/UV-Vis and DFT computations.

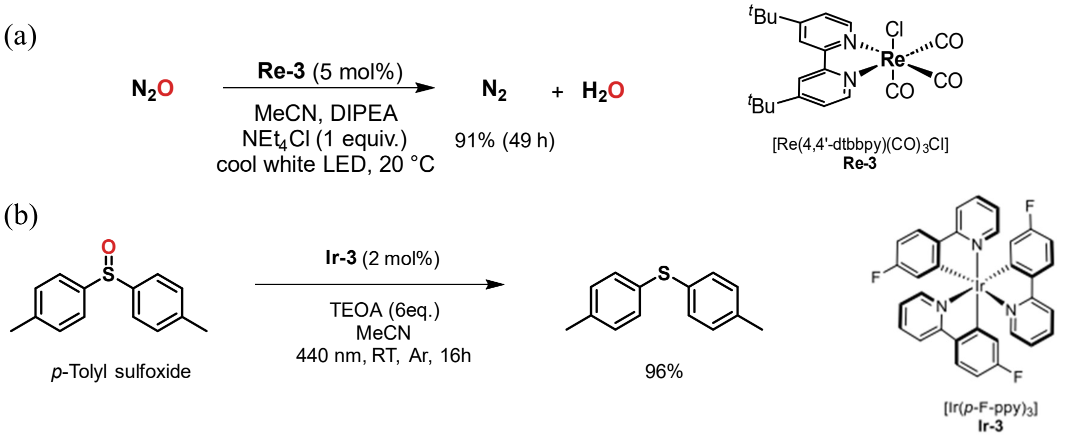

Figure 1. Photocatalytic deoxygenation of: $N_2O$ using Rhenium complexe (a), *p*-tolyl sulfoxide using Iridium complexe (b).

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# PHOTOELECTROCATALYTIC $CO_2$ REDUCTION ON BIMETALLIC-DECORATED SILICON PHOTOCATHODES

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The photoelectrochemical reduction of $CO_2$ (PEC-$CO_2$RR) using semiconductor materials is a promising energy conversion route to produce solar fuels (e.g., $CH_4$) [1]. A promising combination is the use of Silicon (Si), a photoelectrode material of choice, and bimetallic nano-electro-catalysts that can work in synergy to enhance the catalytic activity, by for example modifying the adsorption energy of key reaction intermediates [2]. Despite its interest, to date very little work has been devoted to the PEC-$CO_2$RR on Si photocathodes decorated with bimetallic catalysts, and even less when these are volumetric electrodes [3].

In this communication, we will show results on the synthesis of $Ag_xCu_{100-x}$ and $Pd_xCu_{100-x}$ decorated Si photocathodes and their application to PEC-$CO_2$ [4,5]. The synthesis is based on an original adaptation of metal-assisted chemical etching (MACE), and allows straightforward control of the bimetallic composition. With 3D Si photocathodes, a coverage over the whole length of the Si MPs (micropillars) is achieved, highlighting the suitability of the method for high aspect ratio structures. J-V characteristics measured under $CO_2$ and solar illumination show a photocurrent enhancement for SiMPs over flat Si due to lower reflectivity losses in the SiMPs array and the increased surface area in contact with the electrolyte. Long-term electrolysis coupled with stability tests show the synergy of the AgCu system to guide the selectivity towards high density energy products [6], but a significant disaggregation of the bimetallic nanoparticles. Equivalent studies with the PdCu system are ongoing.

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### C22

# *Development of a $CO_2$-biomethanation reactor for producing methane from green $H_2$*

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The Power-to-Methane processes enable the storage and transportation of environmentally-friendly methane, derived from renewable energy sources and various $CO_2$ inputs [1]. In nature, some microorganisms, namely methanogens, feed on $CO_2$ and $H_2$, producing methane through an ancient metabolic pathway known as methanogenesis under mild conditions. These microorganisms efficiently catalyze the Sabatier reaction ($4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$), utilizing $H_2$ and $CO_2$ as their sole energy and carbon sources. Our work focuses on the development of a biomethanation reactor to cultivate a pure culture of the mesophilic methanogen, *Methanococcus maripaludis*. We have engineered a modular, scalable, and cost-effective 2 L-bubble column bioreactor capable of operating efficiently and autonomously for extended periods under diverse conditions [2]. This device was selected as one of the three finalists in the EIC Horizon Prize "fuel from the sun" international competition (https://sunergy-initiative.eu/eic-horizon-prize-on-artificial-photosynthesis-2022), demonstrating its potential in green methane production from solar $H_2$ [3].

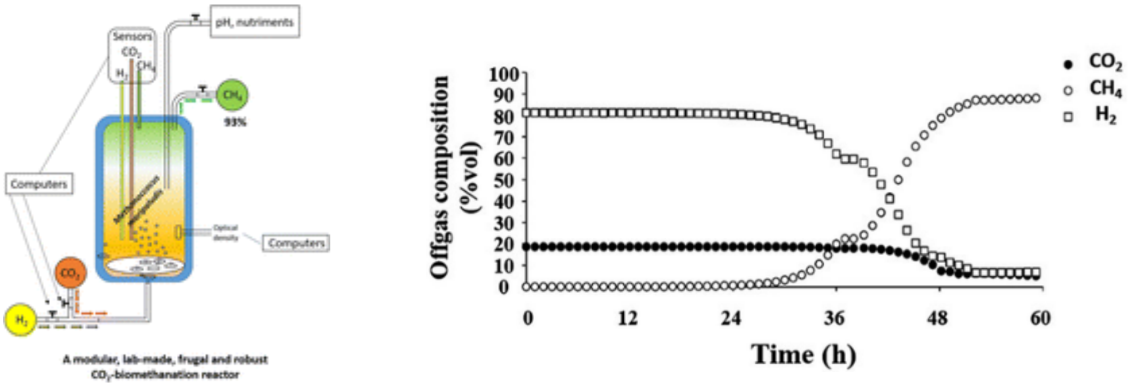

Figure 1
A/ Schematic view of the experimental setup. Gas, pH and reducing potential are continuously monitored. B/ Composition of the offgas during a 60-h experiment.

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C23

# HIGHLY SHG ACTIVE PYRIMIDINE-BASED LIQUID CRYSTAL FOR 3D OPTICAL STORAGE

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Strong effort have been made the last 50 years to increase significantly the optical storage capacity from 0.74 GB to 200 GB with Blu-ray technology. But optical data storage have reached his limits in the available memory density owing to their 2D nature. A smart way to further increase would be to use materials with nonlinear optical (NLO) properties allowing to store information in 3D[1]. The writing process will be the result of local irradiation which will induce a local disorganization and the reading process will be based on the second harmonic generation (SHG) contrast mapping between the ordered and the disordered areas.

SHG, a second order NLO phenomenon, requires molecules with a non-zero dipole moment. To preserve a good SHG signal in solid state, non-centrosymmetry must also be maintained at the macroscopic level within an ordered structure. This requirement is generally ensured by functionalising the compounds of interest using chiral chains.[2] The challenge here is to obtain a competitive SHG signal with a thin film composed of achiral dissymmetric molecules. For this purpose high conjugated pyrimidine-based compound functionalized with long carbon chain has been synthesized. Its thermal properties and photo-physical studies in solution and in solid state will be described and discussed. Also, first experiments of NLO writing will be presented.

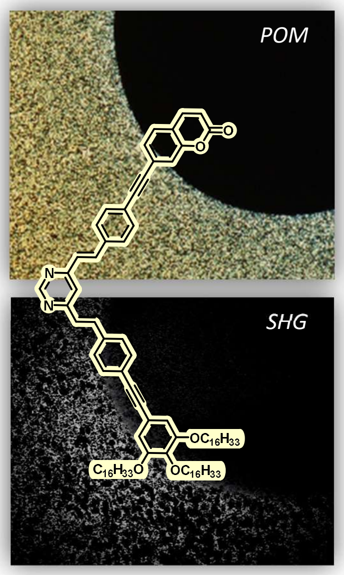

Figure 1. Structure of the compound of interest and images with a polarized optical microscope (top) and SHG contrast mapping (bottom) of an encoded film.

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C24

# $CO_2$ Electroreduction from Simulated Low-Concentrated $CO_2$ Flue Gas Using Molecular Catalysts

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Exhaust gases from industrial activities heavily contribute to increasing atmospheric $CO_2$. The electrochemical $CO_2$ reduction reaction ($CO_2RR$) represents a promising technology to convert $CO_2$ from these effluents into valuable chemicals. While the research for homogeneous and heterogeneous catalyst is vast and shows the development of high-efficient catalysts for the $CO_2RR$, most of the research conducted nowadays use 100% pure $CO_2$ as a reactant, despite the fact that industrial effluents contain low concentrations of $CO_2$ (10-20%).[1] This is done to avoid any side effect from low-concentrated $CO_2$ sources and from contaminants present in industrial flue gas, such as $O_2$, $NO_2$ and $SO_2$. Studies using heterogeneous catalysts have shown that the presence of such impurities cause catalyst surface modifications and competitive $CO_2$ reactions.[2] Our approach evaluates the use of selective molecular catalysts for direct $CO_2$ electroreduction under realistic gas feeding conditions, which is far from being studied and would avoid the need of highly energetic $CO_2$ condensation technologies used by industry.

Previous studies show that, imidazolium-based ionic liquids (IL), have a co-catalytic effect for $CO_2RR$ in the presence of a model molecular catalyst.[3] This ILs can be immobilized on the surface of carbon electrodes.[4] This approach, presented in this work, shows a high selectivity for formate production using a low concentrated $CO_2$ source (10% $CO_2$ concentration in a $N_2$ matrix). The use of a modified electrode reached a faradaic efficiency of 66% for formate production, compared to 19% using a bare-carbon electrode. Such effect is explained by the ability of immobilized imidazolium cations to interact with the molecular catalyst, favoring $CO_2$ conversion to formate, and by its electrostatic suppressing effect of the hydrogen evolution reaction. This concept can be applied in a series of electrochemical reactions where charged surface electrodes interact with polarizable reactants, intermediates, and/or products.

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## C25

# *INSIGHT IN-SITU* RESTRUCTURING OF COORDINATED COPPER IN UIO-66 DERIVATIES DURING VISIBLE LIGHT DRIVEN HYDROGEN PRODUCTION FROM FORMIC ACID: AN *OPERANDO* STUDY

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Formic acid (FAc) is considered one of the most potential liquid organic hydrogen carries (LOHCs). However, its (photo)catalytic dehydrogenation ($HCOOH \rightarrow CO_2+H_2$) tickles many challenges like low reaction selectivity, due to the dehydration pathway ($HCOOH \rightarrow CO+H_2O$), and/or low activity under moderate conditions. In this work, photocatalytic dehydrogenation of FAc was studied over different UiO-66 multivariate derivatives. Two sets of UiO-66's samples were investigated: the first by using different linkers ratio: BDC and Dicarb indicated as (x:y); and the second by considering other linkers such as BDC with ATC or BTC (fig.1A). Results reveal that a restructuring phenomenon takes place at the MOF's surface (fig. 1B). Operando-FTIR (fig.1C) demonstrates a concurrent formation of anhydride bridge between the coordinated carboxylate of neighboring ligands on UiO-66-Cu (x:y) structure simultaneously with the increase of its activity from 10 % with UiO-66-Cu (1:0) to reach 47% with UiO-66-Cu (0:1) (fig.1D). Furthermore, the activity of the sample proved to be directly related to the concentration of the Dicarb and the amount of anhydride formed (fig.1E).

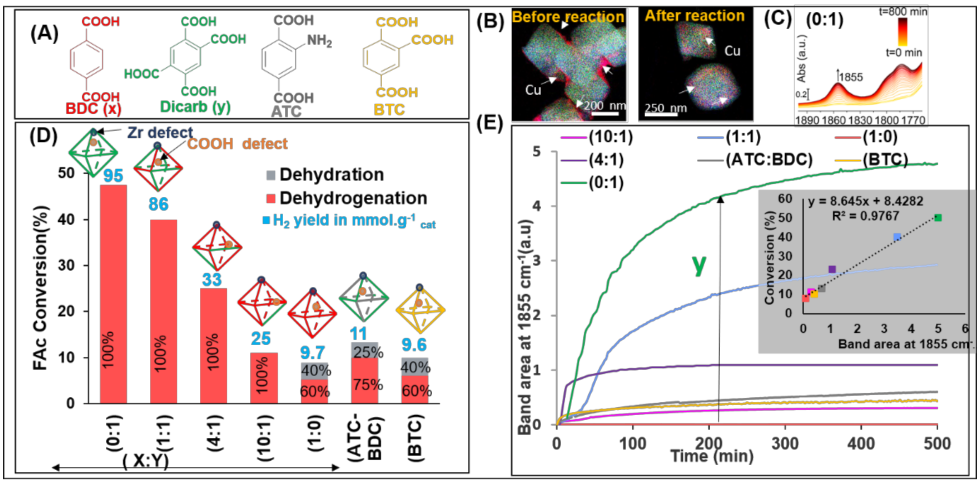

Fig.1 (A) Chemical structures of UiO-66'slinkers; (B) EDS-TEM mapping of UiO-66-Cu (0:1) before and after reaction; (C) Evolution of the IR spectra of UiO-66-Cu (0:1) in the anhydride vibration region during the reaction; (D) Performance of the various UiO-66-Cu (x:y) samples in FAc dehydrogenation under visible light at RT**;** (E) Evolution of the anhydride vibration band during the photocatalytic reforming of FAc of various samples. Insert: plot of the conversion vs the band area of anhydride at steady state. Nb.Unpublished results.

C26

# HYDROGEN-SUBSTITUTED GRAPHDIYNE COMBINED WITH PEROVSKITES TOWARD PHOTOCATALYTIC $CO_2$ REDUCTION

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In response to the urgent need for sustainable and clean energy sources for the upcoming generations, converting $CO_2$ into fuel or chemical feedstock compounds could reduce, in principle, fossil fuel consumption and climate-changing $CO_2$ emission. One strategy aims to convert solar light to chemical fuel through the reduction of CO2. In this context, photocatalysis involving light-irradiated catalysts offers both sustainable and relatively low-cost solutions to face the challenge. In this work, we investigate the $CO_2$ reduction under organic solution using H-substituted graphdiyne (HGDY) and perovskite composite. In situ growth of HGDY was performed under the presence of the perovskite, allowing the formation of the $Cs_4PbBr_6/CsPbBr_3$ junction in Pyridine. The material was characterized by XRD, TRPL, PL and TEM to shed the light on the electronic and morphological properties. The results enable defining the charge transfer mechanism and the electronic properties of the composite, which was proven to be suitable for $CO_2$ reduction reactions. Indeed, our funding shows that H-GDY was revealed to play a crucial role in preventing the dissolution of perovskites in an aqueous solution, reducing photogenerated charge recombination, and improving charge separation efficiency. The hybrid HGDY/perovskite exhibits good activity and selectivity toward the $CO_2$ conversion to CO and $CH_4$.

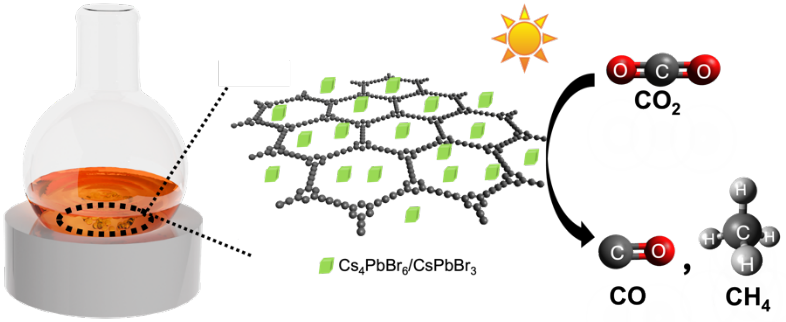

Figure 1. Scheme photocatalytic diagram of a heterostructure of $Cs_4PbBr_6/CsPbBr_3$@H-GDY composite for $CO_2$ reduction.

C27

# ARTIFICIAL PHOTOSYNTHESIS: MOLECULAR CATALYSTS FOR WATER ACTIVATION AND OXIDATION

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Photosystem II is the only enzyme that can capture sunlight to oxidize water to $O_2$. The formation of the O-O bond is argued proceed via two principal routes: a water nucleophilic attack (WNA) on a highly oxidized Mn=O species or the radical coupling of two manganese-oxyl radical species.[1],[2] An $Fe^{V}O$ species has recently been suggested to be involved in catalytic water oxidation. However, experimental support for this mechanism is yet to be delineated. Clarifying the mechanism of water oxidation is thus of fundamental importance to understanding how PSII operates and to develop cost-effective catalysts to drive the four-electron and four-proton oxidation of water. We found that an Fe porphyrin holding urea groups in the second coordination sphere can catalyze water oxidation chemically or electrochemically in acetonitrile with either water or hydroxide. We are able to stabilize and identify an $Fe^{V}O$, $Fe^{III}$-OOH and $Fe^{III}OO$- species by using UV-vis, spectroelectrochemistry EPR, IR and Raman spectra.

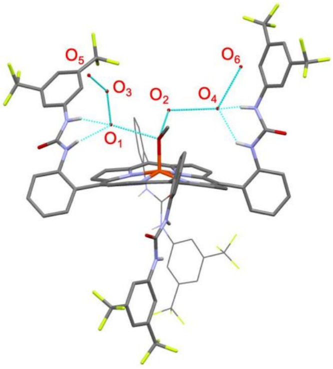

Figure 1. The X-ray crystal structure of FeTPP-Ur.[3]

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**C28**

# A Bio-inspired Heterodinuclear NiFe complex for photocatalytic $H_2$ production

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Hydrogen production is a promising solution for the storage of renewable energy. In nature, hydrogenases ([NiFe] and [FeFe]) can efficiently catalyse the reversible reduction of protons into $H_2$ thanks to the dinuclear {$MFeS_2$} clusters present in their active sites (M= Ni or Fe) (Figure 1).[1] In the context of photo-assisted processes, chemists have dedicated extensive efforts over decades to engineering catalysts that reproduce key features of the active site of hydrogenases.[2] However, despite the success in mimicking the [FeFe] hydrogenase, the design of photocatalytic systems inspired by the NiFe hydrogenase is still a challenge due to its heterodinuclear active site. To date, only a trinuclear $NiFe_2$ complex[3] and a dinuclear NiRu precatalyst[4] have been described, with no dinuclear NiFe photocatalyst reported.

Recently, the group has developed a [NiFe] hydrogenase mimic (NiFeCp, Figure 1) that is able to electrochemically reduce protons to $H_2$ in both organic and aqueous media.[5a-b] Encouraged by these results, we have evaluated the ability of this catalyst for $H_2$ photogeneration in the presence of $[Ir(PPy)_3]$ as molecular photosensitiser, BIH (1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[*d*]imidazole) as electron source and $Et_3NHBF_4$ as proton source. The remarkable catalytic activity (46200 TON in 25h) and unique dimer structure of NiFeCp operated in photocatalysis opens a broad research prospect in hydrogenases mimics for $H_2$ evolution.

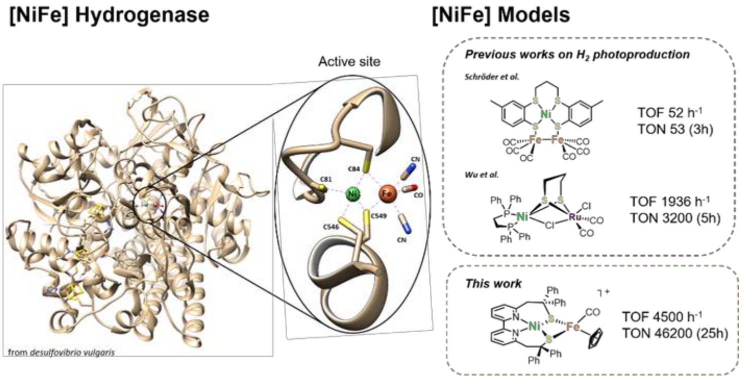

Figure 1: Schematic representation of the active site of the [NiFe] hydrogenase, the trinuclear $NiFe_2$ complex[3] and the dinuclear NiRu precatalyst[4] with their respective performance for photocatalytic $H_2$ production, as well as the NiFe complex described in this work.

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C29

# HETEROGENIZED MOLECULAR PHOTOCATALYSIS FOR $CO_2$ TO FORMIC ACID CONVERSION USING VISIBLE LIGHT

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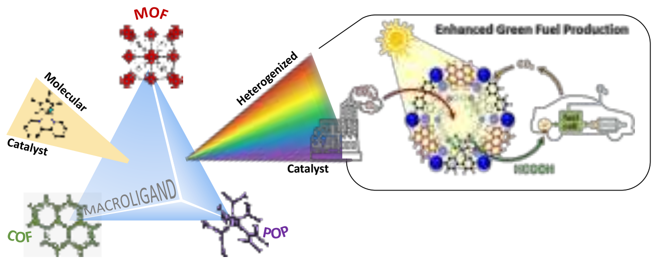
The incorporation of a homogeneous catalyst onto a molecularly defined porous solid support can help overcome various limitations associated with traditional homogeneous catalysts, including issues related to recyclability, stability, selectivity, and ease of product purification. On the other hand, visible-light photoredox catalysis has emerged as a powerful and sustainable alternative to harsh thermal conditions for chemical bond activation and forming reactions.[1] Merging the heterogenization of molecular catalysts with visible light photoredox catalysis can be crucial for bridging the gap between molecular and heterogeneous catalysis[2, 3] and at the same time can offer enhanced long-term productivity, eliminate the need for external photosensitizers, and promote a more sustainable catalytic process.

Herein, we discuss photoactive porous materials containing bipyridine moieties as macroligands.[4] for the immobilization of a rhodium-based molecular catalyst for visible-light-driven $CO_2$ reduction.[5] The immobilization of rhodium catalyst allows the visible light-mediated $CO_2$ photoreduction of a cumulative productivity of up to 8.3 grams of formic acid per gram of catalyst. The porous organic polymers enable these catalysts to achieve the same intrinsic productivity as the parent molecular complexes, without electronic or steric detrimental effects such as diffusion limitations, while also offering advantageous recycling capabilities. Therefore, the synthetic versatility of porous organic polymers, envisioned as porous macroligands, presents promising prospects for developing novel heterogeneous catalysts for more sustainable molecular catalytic processes.



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### C30

# Turnover Number in Photoinduced Molecular Catalysis of Hydrogen Evolution: a Benchmarking for Catalysts?

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Development of devices for production of $H_2$ using light and a sustainable source of electrons may require the design of molecular systems combining a molecular catalyst and a photosensitizer. Evaluation of the efficiency of hydrogen production is commonly performed in homogeneous solution with a sacrificial electron donor and the report of the maximal turnover number *vs* catalyst ($TON_{cat}^{lim}$). This figure of merit is dependent on deactivation pathways and does not by itself provide a benchmarking for catalysts. In particular, when the photosensitizer degradation is the primary source of limitation, a kinetic model (figure 1),[1] rationalizing literature data, shows that a decrease of the catalyst concentration leads to an increase of $TON_{cat}^{lim}$. It indicates that exceptionally high $TON_{cat}^{lim}$ obtained at very low catalyst concentration shall not be considered as an indication of an exceptional catalytic system. A systematic kinetic analysis is required to get a quantitative measure of the competitive pathways leading to $TON_{cat}^{lim}$ values and to provide keys for performance improvement.[2]

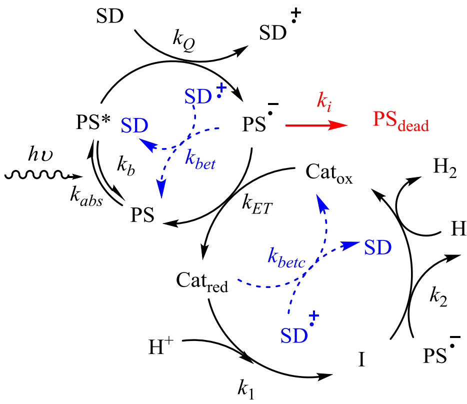

Figure 1. Homogeneous photoinduced catalysis of hydrogen evolution.

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P01

# SOLAR FUELS GENERATORS: INTEGRATION AT DIFFERENT LEVELS AND SCALES

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In this poster we will present our efforts to prepare a dye-sensitized PEC cell for syngas generation at the cm$^2$ scale [1] as well as a large scale (>300 cm$^2$) prototype for solar methane production based on PV + Electrolysis to produce $H_2$ and feed a bioreactor for running the Sabatier reaction [2].

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P02

# Influence of Sr-doping on structural, optical and photocatalytic properties of synthesized $Ca_3(PO_4)_2$

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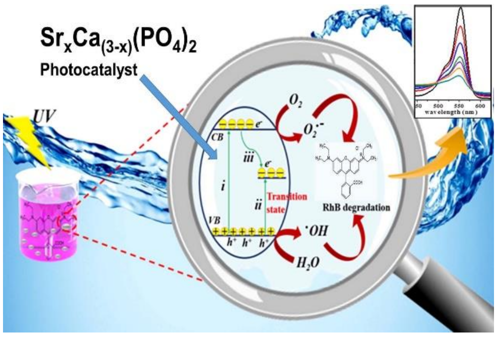
## Abstract



Well-crystallized $Ca_3(PO_4)_2$ doped and un-doped nano-particles with the maximum strontium content (40 wt% Sr) followed by calcination at 800 °C for 3 h were synthesized via facile co-precipitation method. DTA/TGA, X-ray diffraction (XRD), energy dispersive scanning electron microscopy (SEM/EDX), UV–vis diffuse reflectance spectrum (UV–vis DRS), Raman spectroscopy and photoluminescence (PL) techniques were used for material characterization. The (XRD) patterns of as-synthesized Sr-doped $Ca_3(PO_4)_2$ solid solution samples exhibited a systematic shift toward lower angles by possessing a single rhombohedral crystal structure without any secondary phases. The UV light driven photocatalytic activity was assessed for rhodamine B (RhB) degradation. The regeneration cycles indicated the higher stability of the photocatalyst to be effectively recycled up to four times without any considerable reduction in photocatalytic performance. Thus, these informations further provides us a scalable pathway to fabricate Sr doped $Ca_3(PO_4)_2$ and its consequent use as an efficient photocatalyst for rhodamine B (RhB) contaminated wastewater treatment.

***Keywords***: Sr-doped $Ca_3(PO_4)_2$, Solid solution, Structural properties, photocatalytic degradation

P03

# IMIDAZOLIUM MODIFIED NICKEL PORPHYRINS: THE ROLE OF ELECTROSTATICS IN HYDROGEN EVOLUTION CATALYSIS

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Hydrogen has been identified as one of the best choices for a green energy vector that can compensate for our society's ever-growing energy demands.[1] Currently, the most efficient systems of hydrogen production use platinum as a catalyst. However, due to its scarcity and high price, platinum remains an unattractive choice for the widespread use of hydrogen for energy. As such, efforts have been undertaken to develop a cheaper alternative.

Metalloporphyrins, inspired from enzymes found in nature, have been found to effectively catalyse hydrogen evolution reactions (HER), *i.e.,* the reduction of protons to hydrogen. In particular, nickel porphyrins have been reported to exhibit high performance in this application.[1,2] Additionally, improving catalyst performance via modifying the porphyrin ring to ameliorate efficiency and/or lower overpotential are ongoing points of research.

In this study, a series of nickel porphyrins were modified with imidazolium substituents as electrostatic actuators and were studied for their HER catalytic activity (Figure 1). Electrochemical characterization were done via cyclic voltammetry evaluating (i) the effect of the proton source, and (ii) the absence, presence, and positioning of the cationic groups on the porphyrin platform. Intermediates were followed through IR and UV-Vis spectroelectrochemistry to explore subtle mechanistic deviances in rationalizing catalysis.

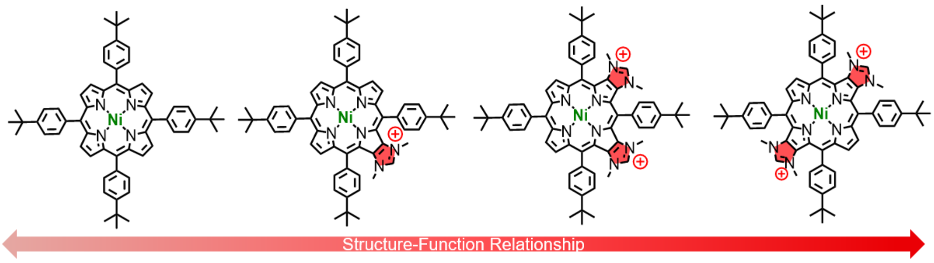

Figure 1. Structures of imidazolium modified nickel porphyrins evaluated for HER.

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# PHOTOCATALYTIC SYSTEMS BASED ON OCTAHEDRAL TUNGSTEN HALIDE CLUSTER AND POLYOXOMETALATES FOR SOLAR ENERGY CONVERSION

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One promising solution to the energy crisis is artificial photosynthesis (AP),[1] which mimics natural photosynthesis to convert solar energy into chemical energy carriers. However, a significant challenge in this field is the design of catalysts that are efficient, selective, recyclable, and free of noble metals. Octahedral transition-metal halide clusters made from earth-abundant elements are promising photosensitizers for their strong luminescence and long-lived triplet state.[2,3] On the other hand, polyoxometalates (POMs) are water-soluble metal-oxide discrete polyanions known for their ability to reversibly exchange many electrons (electrons reservoir)[3] making them attractive candidates for catalysis. In this study, we propose the photophysical investigation of novel systems for the production of hydrogen (HER) designed to function in water, involving the utilization of the octahedral tungsten halide cluster $[W_6I_8Cl_6]^{2-}$ as photosensitizer in conjunction with POMs such as $[PW_{12}O_{40}]^{3-}$, $[P_2W_{18}O_{62}]^{6-}$ as catalysts (Figure 1). A complete photophysical study was conducted on $[W_6I_8Cl_6]^{2-}$ cluster and POMs tandems using steady-state absorption and emission, time-resolved emission and nanosecond transient absorption spectroscopy. The spectroscopic characteristics of the charge-separated state obtained by transient absorption spectroscopy, complemented by spectro-electrochemical experiments demonstrate the photoinduced electron transfer from the excited cluster to POMs.

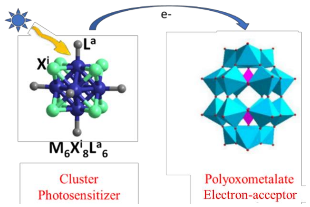

Figure 1. Photo-induced electron transfer from $[W_6I_8Cl_6]^{2-}$ to polyoxometalate

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P05

**Oral/Poster**

# OPTIMISE PHOTOELECTROCHEMICAL CELL

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Hydrogen production by solar water splitting using a photo-electrochemical (PEC) cell is considered the most promising way of storing large quantities of solar energy over long period.[1] Photoelectrode is the most important component of a PEC cell, so research has focused on the manufacture of high-performance, stable and scalable photoelectrodes. Although, at present, no material meets all these requirements[2], photoelectrodes based on metal oxide nearly reached their theoretical limits,[3] so it becomes important to understand how material properties, cell design and geometry influence overall system efficiency and stability. An essential tool for this is mathematical modelling and numerical simulation. The PROSPER-H2 project brings together the expertise of ENGIE's R&I department and five CEA laboratories in materials chemistry, electrochemistry, photocatalysis and solar thermal to develop a 0.1 $m^2$ PEC cell composed of photoelectrodes based on metal oxide and catalyst to reach 5% STH efficiency, with minimal environmental footprint and a scalable system. Our objective is to develop a model on COMSOL multiphysics® software, taking into account optical, electrochemical and hydrodynamic processes, in order to simulate system operation. To identify the best illumination mode and electrodes geometries for light harvesting as transparent, perforated or mesh electrodes, and optimize cell geometry such as neutral electrolyte thickness and distance between electrodes. Our methodology involves designing a PEC cell and set up a scale-up test bench capable of measuring operating current, voltage, temperature, and $O_2$ and $H_2$ flow rate produced. The experimental results obtained will enable us to correct and validate our model. By designing and optimizing a high-performance PEC cell, this project should increase the technology's level of maturity.

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**P06**

# Electrocatalytic reduction of $CO_2$ to methane by copper cluster immobilized on carbon nanotubes

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$CO_2$ reduction reaction ($CO_2$RR) is extensively studied as a means to use man-emitted $CO_2$ to store renewable energy into value-added fine chemicals and fuels.[1,2] Methane is one of the most interesting products from the $CO_2$RR as it is the main component of natural gas, accounting for a quarter of global electricity production, a market worth USD 4.3 billion a year.[3,4] $CO_2$RR using low-cost copper catalysts has shown great promise as a viable and scalable process for the industrial production of methane from renewable energies.

In this context, we reproduce previous results from the literature using a copper phthalocyanine (CuPc) deposited on multi-wall carbon nanotubes.[5] The molecular catalyst plays the role of a precursor for the generation of copper clusters that are highly active for the reduction of $CO_2$ into methane. A faradaic efficiency up to 55% was obtained at -1.15 V vs RHE, with a current density of - 13 mA cm$^{-2}$. Our journey in this research has highlighted key points to consider in order to implement this type of system on gas diffusion electrodes within membrane-electrode assemblies,[6] paving the way for scalable electrolysis on a larger scale.

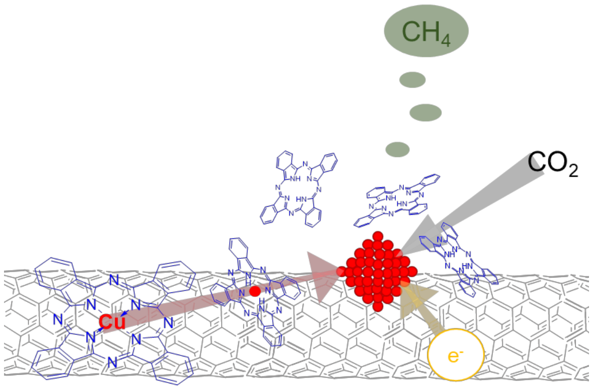

Figure 1: Scheme of the atomic agglomeration from CuPc for selective reduction of $CO_2$ to methane.

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P07

# LIGHT-INDUCED CHARGE ACCUMULATION IN POLYOXOMETALATE-PHOTOSENSITIZER DYADS

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Polyoxometalates (POMs) are relevant platforms for multi-functional artificial photosynthetic systems as they can act as electron reservoirs and their facile functionalization provides means to append visible-light-active organic/organometallic photosensitizers to form a donor-acceptor dyad.[1] Here, we present a series of hybrid dyads of a BODIPY dye tethered to organosilyl Keggin-and Dawson-type polyoxotungstates. Transient absorption measurements revealed that photoexcitation of such dyads induce a fast intramolecular charge transfer leading to a charge-separated state with lifetime of up to tens of nanoseconds.[2] More recently, we showed that steady-state illumination of the Dawson-BODIPY hybrids in the presence of triethylamine as a sacrificial donor and trifluoroacetic acid (TFA) allowed the quantitative accumulation of up to two electrons in the POM. The presence of acid dramatically increases the reduction potential of POMs and is crucial not only to promoting the charge-separation but also the accumulation of electrons.[3] We further pursued the preparation of POM-BODIPY hybrids bearing ancillary arms with a carboxyl end for grafting onto photocathode semiconductors like NiO. Preliminary results demonstrated the potential of the dyads as photocathode materials for dye-sensitized photoelectrochemical cells.

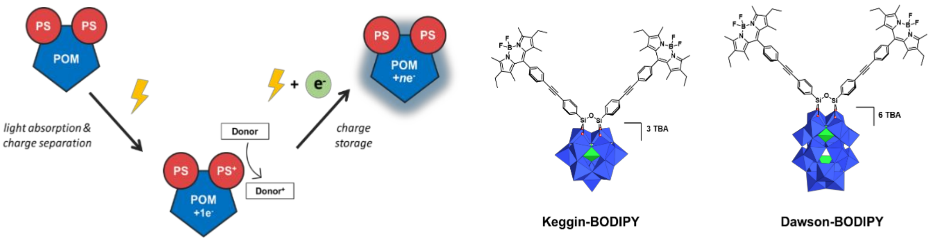

Figure 1. Photoinduced electron storage in POM-photosensitizer dyads in the presence of a sacrificial donor

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# TUNING ELECTROCATALYTIC CO2 CONVERSION BY MOLECULAR SURFACE ELECTRODE MODIFICATION

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The electrochemical $CO_2$ reduction reaction ($CO_2RR$) is highly influenced by the induced electric field at the electrode-electrolyte interface. Local electric fields (LEFs) can be applied for tuning any electrocatalytic reaction, for example, a higher concentration of cations likely accumulates at the interface leading to a more powerful LEF[1]. In the case of $CO_2RR$, the role of those cations is likely associated with the stabilization of negatively charged intermediates by favorable electrostatic interactions at the electrode-electrolyte interface[2]. Lately, there is a huge effort of research focused on identifying new stabilizing cationic species in the electrolyte, different from alkali metal cations, for heterogeneous $CO_2RR$[3]. We present here a novel electrolyte immobilization method to control the electric field at this interface by positively charging the electrode surface with an imidazolium cation organic layer that suppresses hydrogen evolution reaction (HER) and diminishes the operating cell voltage. This smart electrode surface is successfully scaled up for operating at industrially relevant conditions for two applications. The first using a flow cell configuration[4], where the $CO_2$ conversion to formate is catalyzed by a model molecular Rh complex in acidic aqueous solution with formate production rate of 4.6 $g_{HCOO-}$ $m^{-2}$ $min^{-1}$ at 100 mA $cm^{-2}$ [4]. In the second[5], by using Cu nanoparticles surface molecular modification to show a rather drastic change of selectivity, both in terms of $CO_2RR$ vs. HER and $C_{2+}$ (ethylene and ethanol) vs. $C_1$ products, at industrially relevant current densities (300 mA $cm^{-2}$) and at acidic pH (<1), actually mimicking a $K^+$ layer.

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P09

# POLYMERIC PORPHYRIN-BASED MATERIAL FOR THE ACTIVATION AND REDUCTION OF $CO_2$

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The electro- and photo-catalytic $CO_2$ reductions are promising approaches to overcome the global warming issue caused by this greenhouse gas. Iron porphyrin monomers have been well-known for their performance in electrochemical $CO_2$ reduction to CO. The modification of this iron porphyrin can produce novel catalysts with lower activation energy and higher selectivity. In this work, we synthesized new iron porphyrin dimers connected by a diacetylene function (see structure in Figure 1a). The dimers were characterized by NMR, IR and UV-Vis spectra. The electronic and photophysical properties of the dimers were studied using cyclic voltammetry, spectroelectrochemisty, photoaccumulation and laser flash photolysis. Then, their performances in both electrocatalytic and photocatalytic $CO_2$ reduction were investigated. Their activities will be compared with that of the commercially available iron tetraphenylporphyrin. Moreover, we will utilize the topochemical polymerization of diacetylene functional groups under UV irradiation[1] to afford polymeric iron porphyrin materials (Figure 1b). The potential synergy between two iron centers in a face-to-face disposition in the polymers will be investigated in the multiple electron $CO_2$ reduction. Our goal is to produce higher reduced forms than CO with C-C containing products, such as ethane and ethanol.

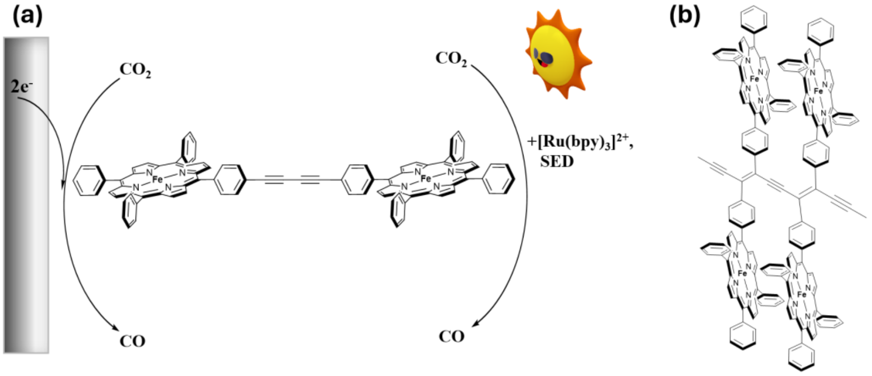

**Figure 1.** (a) Scheme for the electro- and photo-catalytic $CO_2$ reduction of iron porphyrin dimer. (b) Structure of the polymeric iron porphyrin.

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P10

# TAILORING IRON PORPHYRIN CATALYSTS FOR COVALENT ATTACHMENT TO SEMICONDUCTOR SURFACES

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With the pressing need to curb carbon dioxide ($CO_2$) emissions, utilizing waste CO2 as a sustainable non-fossil-based carbon source is increasingly crucial. Additionally, employing a renewable energy source for this conversion is imperative. A promising approach to realize this is through PhotoElectroChemistry (PEC), leveraging advancements in semiconductor photocathodes and molecular catalysts to create integrated hybrid devices capable of sunlight-driven $CO_2$ conversion.[1,2] In this study, we explore various covalent attachment methods by modifying the *meso* phenyl groups of iron tetraphenyl porphyrin catalysts (Figure 1). This investigation aims to elucidate the optimal orientation and packing of the catalyst on a semiconductor surface, leading to more efficient and stable hybrid assemblies.

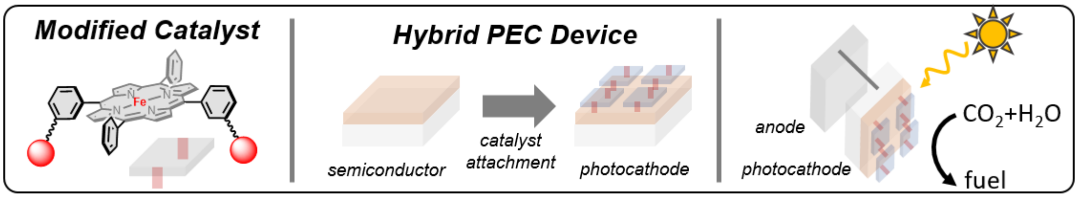

Figure 1. Modifying iron porphyrin catalyst towards covalent attachment on semiconductor surface for hybrid photoelectrochemical conversion of $CO_2$.

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P11

# ELECTROCHEMICAL $CO_2$ REDUCTION WITH METAL-PINCER CATALYSTS

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The conversion of carbon dioxide into chemical feedstocks and fuels is critical due to the increasing concentration of greenhouse gases in the atmosphere. A sustainable approach based on the use of *green energy* for the electrochemical reduction of $CO_2$, employing molecular catalysts based on non-noble transition metals is desirable.

The family of metal complexes studied by the group of Milstein, bearing pincer-type ligands (P/N-donor) proved great performances as thermal catalysts for the hydrogenation of $CO_2$. [1-2] We have thus explored the activity of the $Ni^{II}$ and $Fe^{II}$ complexes bearing a Milstein-type pincer ligand as electrocatalysts for $CO_2$ reduction (Figure 1). In this regard, only a few examples of pincer-supported (N/C-donor) nickel complexes are reported as $CO_2$RR homogeneous electrocatalysts, yet they lack selectivity. [3-5] Weak acids namely water, phenol and trifluoroacetic acid were tested as proton sources working in organic media (MeCN/DMF). Further analysis of the products formed, *via* gas cromatography, NMR and ion cromatography are currently ongoing. In parallel, mechanistic investigations are carried out to study the possible intermediates involved.

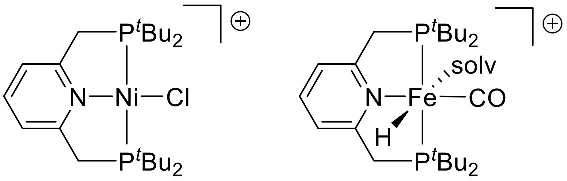

Figure 1. $Ni^{PNP}$ and $Fe^{PNP}$ studied in this work.

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P12

# Substituents effect on $CO_2$ conversion to formate by [FeFe]-hydrogenase mimics

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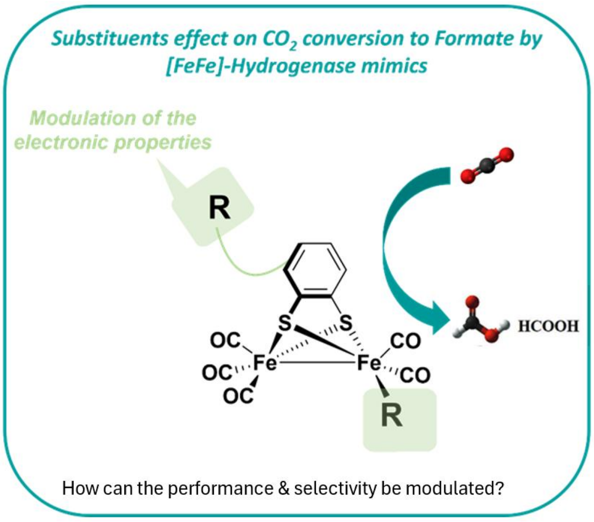
Tremendous efforts are currently devoted to convert intermittent renewable energy sources into storable chemical forms, for instance by catalyzing $CO_2$ electroreduction ($CO_2$RR) into valuable fuels and chemicals (CO, HCOOH, or $CH_3OH$).[1] A [FeFe]-hydrogenase model based on the bridging bdt ligand [(μ-bdt)-$Fe_2(CO)_6$] (bdt = benzene-1,2-dithiolate) has demonstrated electrochemical activity toward $CO_2$RR to formate with a faradaic efficiency of 71%.[1] In order to modulate the electronic properties of this model, substituents have been incorporated either on the bdt ligand or to replace one CO ligand. This strategy has proven successful as one of the mimics shows an improved $TOF_{max}$ value of 1225 $s^{-1}$ compared to 195 $s^{-1}$ found for [(μ-bdt)-$Fe_2(CO)_6$] .[1] Controlled potential electrolysis experiments on mercury pool electrode reveal a selectivity toward formate production with a faradaic efficiency up to 85%.



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P13

# Electrochemical and Spectroscopic Characterization of Iron Phthalocyanines and their Carbene Species in Homogeneous Condition

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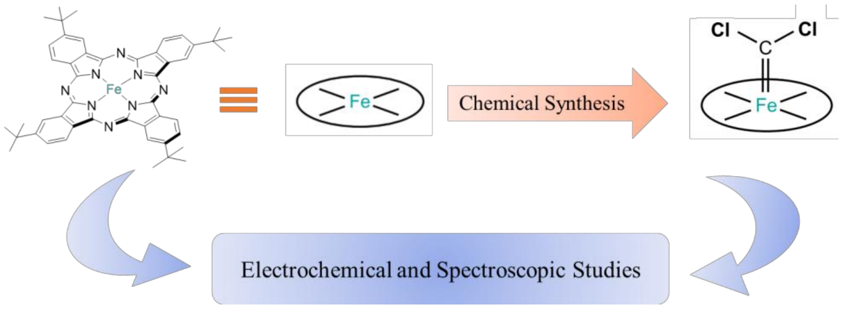
Phthalocyanine complexes of transition metals are well-known as promising catalysts for $CO_2$ electroreduction to $C_1$ products (CO, $CH_3OH$, and $CH_4$)[1-3] with high faradaic efficiency. The compounds with longer carbon chains such as ethylene, ethanol, acetone, *etc* are rarely obtained from the $CO_2$/CO reduction by molecular catalysts. Surprisingly, the previous study using iron phthalocyanine (FePc) loaded on carbon powder as a single-atom catalyst reported the detection of $C_{2+}$ hydrocarbons in the product mixture from $CO_2$ electrocatalytic reduction[4]. The key intermediate responsible for forming $C_{2+}$ products was predicted as iron carbene species FePc=$CH_2$ which could perform C–C coupling via CO insertion by theoretical calculation[5]. However, the mechanistic insights of this electrocatalytic system are lacking the direct evidence provided by *in-situ* spectro-electrochemical experiments and activity evaluations of iron carbene species.

In this poster presentation, the electrochemical properties of iron(II)-2,9,16,23-tetra(t-butyl) phthalocyanine (FePc*) investigated in homogeneous conditions will be presented. The UV-Vis and X-ray absorption spectro-electrochemical under Ar and $CO_2$ atmosphere will demonstrate the electronic structure, $CO_2$ binding, and catalysis of the reduced FePc*. Moreover, the chemical synthesis and characterization of iron carbene species will also be shown in order to investigate the $CO_2$ electrocatalytic mechanism.



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## P14

# POLYOXOMETALATE-BASED ARTIFICIAL PHOTOSYNTHESIS

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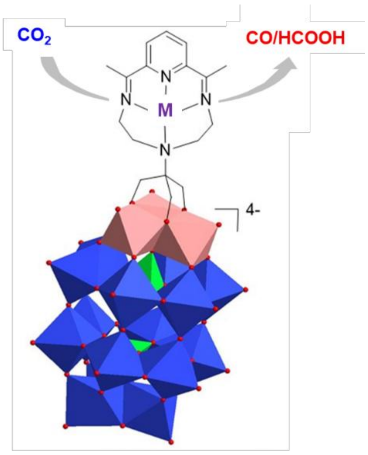
Addressing the imperative of sustainable energy solutions, this research delves into the pivotal role of solar energy as a prospective alternative to fossil fuels within developed countries. Despite its abundance, effective storage mechanisms are indispensable for harnessing solar energy at a scale comparable to traditional energy sources. This study explores the feasibility of leveraging chemical bonds to store intermittent solar energy, focusing on (photo)reduction reactions of molecules such as proton and carbon dioxide ($CO_2$) into valuable C1 chemicals[1]. However, efficient storage solutions for intermittent solar energy remain elusive.

Building upon previous advancements utilizing the V-W Dawson Polyoxometalate (POM) functionalized with a Cu-complex which could store up to three electrons,[2], this research aims at enhancing the catalytic properties of grafted complexes, replacing the Cu-Dipyridyl moiety with Co-complex and its Fe- or Ni-analogues[3,4], known for their proficiency in electro-reducing protons or $CO_2$[5]. The synthesis and characterization of triol-functionalized ligands grafted onto polyoxometalate surfaces (Fig) pave the way for investigating the catalytic potential of these novel hybrids, particularly in photo-/electrocatalytic processes. By elucidating the intricate mechanisms underlying the photo-induced electron transfer steps, this research contributes to the advancement of sustainable energy technologies.



$(TBA)_4[P_2V_3W_{15}O_{59}(TrisN_4)\{M\}]$

Fig.Structure of hybrid POM

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# ALD of Ternary Silicides as Efficient Catalysts for Water Photooxidation

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Silicon is a well-known semiconductor, whose abundance and stability make it the most widely used material in the electronics industry. Among all the applications, the position and the width of its band gap make it also suitable for photoelectrochemical devices, specifically for the water-splitting reaction. However, due to the poor stability and efficiency of silicon in aqueous solutions, protective and catalytic layers are necessary. Currently, Pt and $IrO_2$ are considered the best catalysts for HER and OER reactions, but they are rare and critical materials.[1] In this context, the research on affordable, abundant, and efficient catalytic materials has become crucial. Our group recently optimized the Atomic Layer Deposition (ALD) of $TiO_2$ as an efficient protective layer[2] and tested innovative ALD precursors for the synthesis of $NiO_x$, which shows good catalytic properties in alkaline media[3]. From the combination of these two non-critical materials, we obtained a new class of promising cost-effective co-catalysts for water photooxidation (figure 1a). The $Si/TiO_2/NiO_x$ system was annealed through rapid thermal processing in a reductive atmosphere, resulting in the formation of a chemically stable $Si_7Ti_4Ni_4$ alloy, in the shape of nanoparticles (figure 1b). A patent was filed for this development.[4] The nanostructured particles enhance the active surface area of the electrode and reduce the charge recombination rate, leading to a remarkable improvement in the onset potential of the oxygen evolution reaction (figure 1c).

However, the catalytic mechanism is not yet well understood and a photoelectrochemical activation of the catalyst is needed to improve the photoanode performance. Therefore, we are investigating different deposition combinations of the two oxide layers and trying to understand the correlation between the material structure and the photoelectrochemical results. From a preliminary analysis, an excess of Ni in the $Si_7Ti_4Ni_4$ synthesis brings an improvement in the photocurrent. However, the stability of the photocurrent over time and the onset potential need to be optimized. To improve them, a possible strategy might be to add a $SiO_x$ interlayer between the substrate and the catalyst. This would create a metal-insulator-semiconductor system, which can enhance the effective barrier height and the degree of band bending near the Si surface, and as a result, increase the photovoltage and reduce the overpotential.[5] Moreover, $SiO_x$ can play a role as a protective layer for Si from the alkaline electrolyte and therefore extend its lifetime.

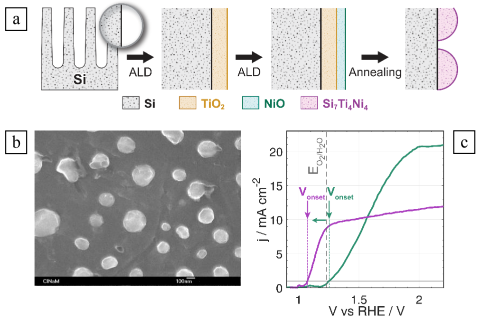

***Figure 1**: (a) Scheme of the synthesis process of $Si_7Ti_4Ni_4$, (b) SEM picture of the $Si_7Ti_4Ni_4$ nanoparticles on the silicon substrate, (c) Comparison between the first polarization of the CV of $nSi/Si_7Ti_4Ni_4$ (purple curve) and nSi/Ni (by PVD) (green curve), the dashed red line indicates the thermodynamic OER potential. $V_{onset}$ are indicated for $j = 1\ mA{\cdot}cm^{-2}$.*

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**P16**

# SERIES OF BIS(THIOSEMICARBAZONE) CATALYSTS FOR PHOTOCATALYTIC HYDROGEN EVOLUTION REACTION

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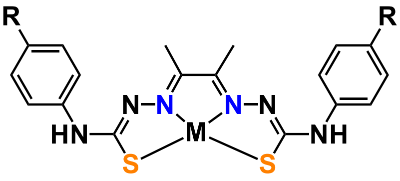
Over the past two centuries, the exponential consumption of fossil fuels has led to their depletion, necessitating a shift towards catalytic systems that generate environmentally friendly fuel sources. Hydrogen is abundant and is considered an “ideal” fuel since its combustion only releases water vapours into the environment. Recent endeavours focus on developing novel methods to harness hydrogen from renewable and sustainable resources.[1]

Photocatalytic hydrogen production is a crucial step towards this goal, given the abundance of sunlight as an energy source. Inexpensive, stable, and non-toxic carbon dots have been synthesized and utilized as photosensitizers in water in conjunction with a series of molecular nickel[2] and cobalt[3] catalysts. These complexes, based on thiosemicarbazone ligands, facilitate the transfer of electrons for the hydrogen evolution reaction (HER). Under visible light irradiation, nitrogen-doped carbon dots (NCdots) transfer photoexcited electrons to the catalyst, promoting hydrogen evolution activity. These novel molecular systems demonstrate high HER activity while utilizing inexpensive compounds free of noble metals.



**M= Ni or Co**

**R= -$OCH_3$, -$SCH_3$, -CN, -$N(CH_3)_2$**

Figure 1. Chemical Structure of Nickel and Cobalt complexes

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# P17

# HYBRID CDSE/ZNS QUANTUM DOTS-GOLD NANOPARTICLES COMPOSITES ASSEMBLED BY CLICK CHEMISTRY: TOWARDS AFFORDABLE AND EFFICIENT REDOX PHOTOCATALYSTS

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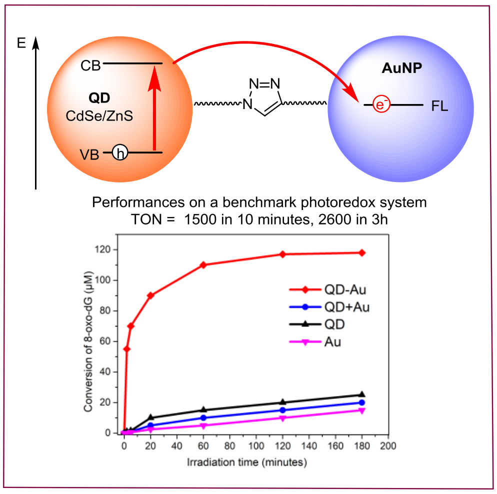
A new modular, easy-to-synthesize photocatalyst was prepared by assembling colloidal CdSe/ZnS quantum dots (QD) and gold nanoparticles (AuNP) via their ligands thanks to Copper-Catalyzed Azide to Alkyne Cycloaddition (CuAAC) click chemistry (see Figure). The resulting composite (QD-AuNP) photocatalyst was tested with a benchmark photoredox system previously reported by our group, for which QD alone acted as photocatalyst, but with a modest Quantum Yield (QY = 0.06%) and turnover number (TON = 350 in 3 hours) due to poor charge separation. After optimization, the QD-AuNP composites exhibited much improved photocatalytic performances: up to 5 times higher TON (2600 in 3 hours), and up to 24 times faster reaction in the first 10 minutes of visible irradiation[1]. Such an improvement is attributed to an efficient electron transfer from QD to AuNP in the photoexcited QD-AuNP composites, which ensures a much better charge separation than in QD alone.



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P18

# A MACROCYCLIC COBALT-BASED MOLECULAR HYBRID CATHODE FOR SELECTIVE $CO_2$-TO-CO ELECTROREDUCTION

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The preparation of molecular heterogeneous catalysts, so-called hybrid catalysts, stands as an attractive and promising alternative for electrochemical conversion of $CO_2$ into hydrocarbons and/or useful chemicals.[1] These hybrid catalysts combine the robustness of material-based heterogeneous catalysts with the ease of tuning of molecular structures.[2] In particular, cobalt-based ones have shown great promises for selective $CO_2$ conversion once incorporated into electrolyser devices.[3] Therefore, our group recently modified the ligand scaffold of a cobalt complex based on a tetraaza-macrocyclic ligand, known for promising activity for electrochemical $CO_2$ reduction under homogeneous organic conditions,[4] with a pyrene anchoring unit in order to allow its smooth immobilisation onto multi-walled carbon nanotube (MWCNT) based electrodes. Through catalyst loading control this new molecular hybrid cathode allows efficient $CO_2$-to-CO conversion in neutral fully aqueous conditions giving rise to large turnover number ($TON_{CO}$) up to $20 \times 10^3$ at reasonable overpotentials ($\eta$ = 450 mV) with faradaic efficiencies of above 95%. No obvious degradation of the molecular catalyst could be observed *post-operando* making of this Co based electrode a new benchmark for aqueous molecular electrocatalytic conversion of $CO_2$ to CO. Furthermore, electrochemical investigations and XAS analysis allowed gaining more insights into the chemical environment of the hybrid catalyst upon reduction and *post*-electrolysis.

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P19

# DEVELOPMENT OF AN EXPERIMENTAL SET-UP IN OPERANDO CONDITIONS TO STUDY PHOTOELECTROCHEMICAL REACTIONS BY X-RAYS ABSORPTION SPECTROSCOPY.

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Photocatalysis offers immense potential for transforming solar energy into useful chemical energy, paving the way for more sustainable and cleaner energy production. As part of the PEPR LUMA (light-matter interaction) program, the SOLEIL synchrotron acts as a platform. To this end, we are developing an experimental set-up to study materials and photoelectrochemical reactions using low- and high-energy X-ray absorption spectroscopy (XAS). This spectroscopic technique enables us to study the local and electronic structure of catalysts. The experimental set-up consists of a solar simulator connected to the back of the photoelectrochemical cell via an optical fiber, a gas chromatography system for analysis of the products generated, and a solvent circulation system. The solvent circulation system is adapted to isolate the experimental chamber when the pressure rises, thus avoiding significant contamination.

The photoelectrochemical cell (figure 1) has 2 compartments, enabling oxidation and reduction to be carried out in parallel. A special space is reserved for an Ag/AgCl reference electrode. The cell allows the use of different substrates such as glassy carbon, graphite or PET sheets with a conductive ITO coating. The cell is suitable for an experimental vacuum environment and is leak-free. This poster presents a description of the cell and initial experimental results from the set-up.

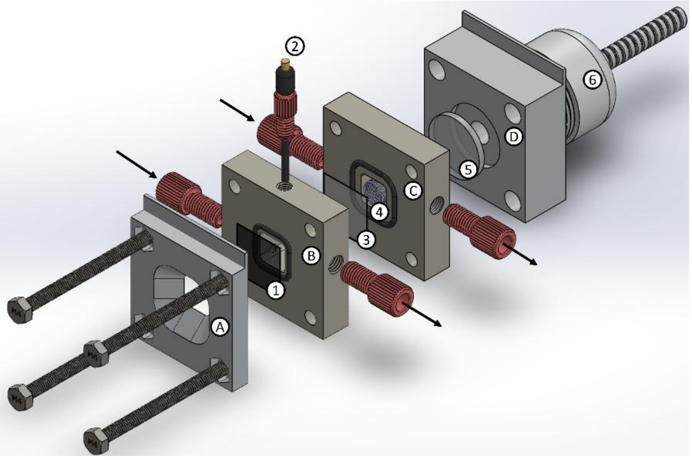

*Figure 1 : Exploded view of the photoelectrochemical cell for XAS measurements. (A) Aluminum front cover, (B) PEEK working electrode chamber, (C) PEEK counter electrode chamber, (D) Aluminum back-cover, (1) glassy carbon, (2) Ag/AgCl reference electrode, (3) Nafion membrane, (4) Spirale counter electrode (Ti), (5) Quartz window, (6) Illumination system (Optical fiber)*

P20

# NOBLE-METAL-FREE PHOTOCATALYTIC SYSTEM FOR $CO_2$ REDUCTION IN GAS PHASE

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Photoreduction of $CO_2$ into added-value chemicals appears as a promising path towards developing a carbon circular economy.[1] An ideal photocatalyst system would function in the absence of a sacrificial reagent, using only $H_2O$ as the source of protons and electrons.[2] In this project, Ni and Cu nanoparticles are synthesized by reduction of nitrate precursors on a semiconductor support (Figure 1). Cu is used in the hope of promoting the formation of $C_{2+}$ products, as well as offering the opportunity to exploit its plasmonic resonance for enhanced solar spectrum utilisation. Because we are working with non-noble metals, the oxidation states of the nanoparticles are relevant and are subsequently observed using $H_2$-TPR and XPS. The optical response of the system is studied with UV-Vis spectroscopy and the overall performance of the system is evaluated on a gas-phase photocatalytic setup.

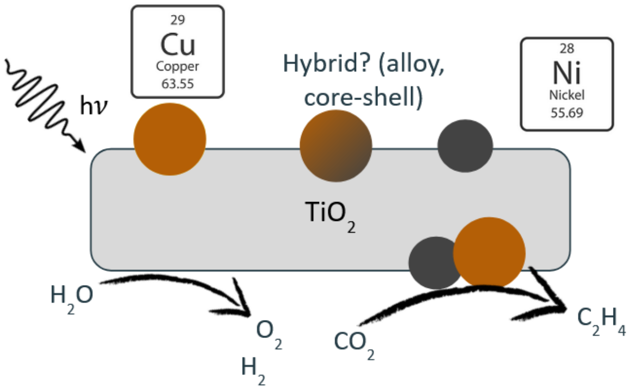

Figure 1. Photocatalyst system consisting of Ni and Cu nanoparticles on a semiconductor support (commercial $TiO_2$)

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## P21

# DESIGN OF COUPLED HEPTAMETHINE-OXONOL DYES

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Contemporary applications related to bio-photonics, energy conversion or optics may require near-infrared (NIR) dyes that can be tailored-made and obtained within few synthetic steps, with a view to maximize their potential production and for atom economy purposes. Nevertheless, the conception of NIR organic chromophores generally implies intricate molecular design and multi-step synthesis affording imposing conjugated architectures.

To aim at developing simple and efficient NIR dyes, we recently focused on a strategy based on the coupling of two cyanines subunits. Our latest endeavors highlighted the potential of coupled polymethines to readily design simple far-red-to-NIR dyes with zwitterionic or bis-cationic structures built around quinoidal (polycyclic) rings (Figure 1).[1–3] We recently developed a family of extended coupled polymethines based on heptamethine-oxonol chromophores featuring switching properties.[4]

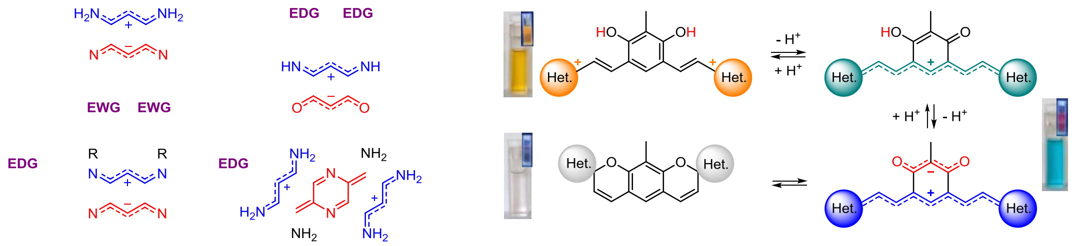

Figure 1. Recently designed Coupled Polymethine Dyes.

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P22

# EXPLORING CODH FOR ELECTROCHEMICAL $CO_2$ REDUCTION REACTION AND WATER-GAS SHIFT REACTION

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The utilization of CO is a central metabolic feature of several aerobic and anaerobic microorganisms. [NiFe]-Carbon monoxide dehydrogenase (CODH) catalyzes the reversible reduction of $CO_2$ to CO. It embodies an appealing biocatalyst due to its high activity, selectivity, and capacity to function under no harsh conditions with minimal overpotentials. Consequently, numerous investigations have explored CODHs for their potential in electrocatalytic $CO_2$ reduction reaction ($CO_2RR$)[1]. CODHs feature a complex multimetallic $NiFe_4S_4$ active site alongside additional FeS clusters involved in the electron transfer from the buried active site to the surface[2]. In this study, we present the stable immobilization of the thermophilic carbon monoxide dehydrogenase II (*Ch*CODH II) on non-covalently and covalently functionalized carbon nanotubes integrated in a gas-diffusion electrode[3]. Our immobilization strategies aim to precisely orientate the enzyme and optimize its capacity for direct ET with the electrode. The enzyme time stability and $O_2$ tolerance are also explored in experimental conditions (solvents, temperature, pH). We endeavor to integrate CODH into functional devices[4]. We get inspired by the in vivo multiprotein complex performing the biological water-gas shift reaction (WGSR)[5], and we aim to exploit this multiprotein complex in vitro. The $H^+/H_2$ and $CO_2/CO$ redox couples are both reversible at electrodes[6] modified – in our case – with a hydrogenases-mimic[7] and CODH. Finally, the electrochemical reversibility of the $CO_2/CO$ interconversion catalyzed by CODH opens avenues for performing the reverse WGSR (solar energy supply). The design of a biofunctionalized nanostructured electrode provides insights into its integration into novel biotechnological devices, offering promising pathways for sustainable energy conversion and carbon utilization strategies.

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P23

# IMPROVED SYNTHESIS OF METAL TETRABENZOTRIAZAPORPHYRINS TO DEVELOP SECOND COORDINATION SPHERE CATALYSTS

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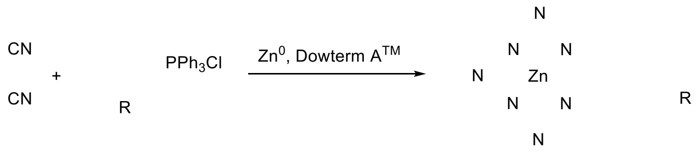
Tetrabenzotriazaporphyrins are hybrids macrocycles between porphyrin and phthalocyanine, differing from phthalocyanines by the presence of a methylene unit instead of a nitrogen atom in the *meso*-position. This feature offers the opportunity to introduce any moiety at the vicinity of the metal centre like with porphyrins.[1,2] Moreover, metal porphyrins and phthalocyanines display valuable catalytic properties for solar fuels production such as proton and $CO_2$ reduction.[3] However, the synthesis of tetrabenzotriazaporphyrins presents several challenges, including low yields, tedious purifications, and scaling up difficulties.[4] In this study, we propose a new methodology utilizing Dowterm A$^{TM}$ as a solvent. This innovation has enabled us to synthesize known compounds in higher yields and to access new molecules that were not achievable using other protocols. The simplified synthetic pathway is illustrated in Scheme 1. The benzonitrile is commercially available and the phosphonium salts are stable and easy to synthesize. The progress achieved through this work in synthesizing tetrabenzotriazaporphyrins and their complexes is pivotal, particularly when considering the catalytic properties of these molecules regarding $CO_2$ reduction. In this presentation, the scope, the limitations and some preliminary catalytic studies will be discussed.



Scheme 1. Synthesis of tetrabenzotriazaporphyrin metal complexes.

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**P24**

# HEMIINDIGOS AS ACETYLCHOLINESTERASE INHIBITORS FOR PHOTOPHARMACOLOGICAL APPLICATIONS

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Hemiindigos (HIs) represent an emerging class of molecular photoswitches that show close structural analogy with potent human acetylcholinesterase (*h*AChE) inhibitors, making them perfect candidates for the development of photoactivable anti-cholinergic drugs in the context of photopharmacology. When irradiated with light of appropriate wavelength, HIs can change their molecular geometry from the thermodynamically stable *Z*-isomer to the metastable *E*-isomer[1]. Expecting that AChE will be able to discriminate between the two isomers, we designed and synthesized a series of HIs structural analogs of AChE inhibitor donepezil (Figure 1), for which inhibitory activity over AChE before (isomer *Z*) and after illumination (photostationary state, PSS) was evaluated and compared. Our results showed that isomers Z and *E* did show differences in AChE inhibitory activity, with half-maximum inhibitory concentrations ($IC_{50}$) light/dark ratios reaching up to 3.9 (Figure 1). We equally performed photochemical/physical characterization for the synthesized HIs and observed that structural modifications at the A-ring and C-ring strongly influence these properties.

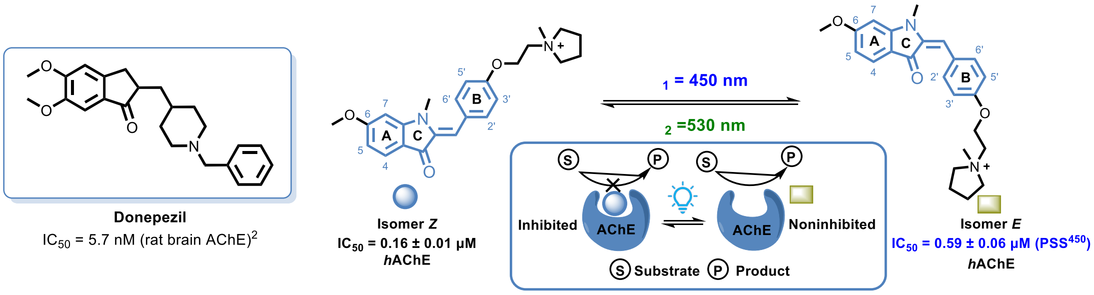

FIGURE 1: structures and biological activity of donepezil (left) and example of HI developed in this work (right).

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**P25**

# PROTON-COUPLED ELECTRON TRANSFER TO AND FROM POLOXOTUNGSTATES

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The accumulation of several reductive equivalents on a single–site is considered a key step towards the development of catalytic materials addressing environmental and energy challenges.[1] Due to their ability to behave as electron acceptors, polyoxometalates are ideal candidates in these areas, particularly in photocatalyzed hydrogen production.[2] Therefore, W and Mo derivatives of the Keggin and Wells–Dawson series have been widely employed in related studies but, to date, the mechanism leading to hydrogen evolution onto polyoxometalates remains rather undefined. We thus came interested in understanding how the addition of protons or dioxygen trigger the release of electrons from reduced polyoxotungstate hybrids (*Silox*POM) that we synthesized in our group (Fig. 1).[3] Our results and perspectives will be presented in this communication.

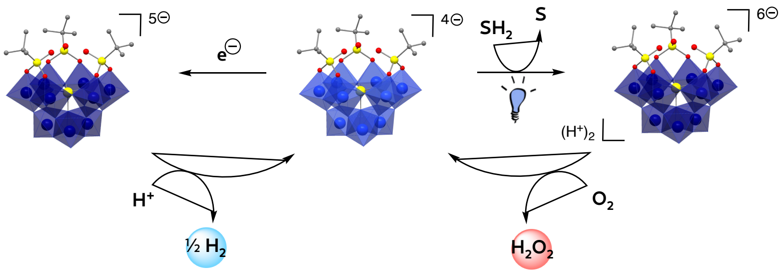

Figure 1. (left) spontaneous hydrogen release from reduced *Silox*POM upon protonation, and (right) hydrogen peroxide formation from aerobic solution of protonated / reduced cluster obtained by photo-oxidation of a suitable substrate $SH_2$.

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P26

# OPTIMIZATION OF MOLYBDENUM-SULFIDE BASED ELECTRODES FOR CATALYTIC HYDROGEN PRODUCTION UNDER NEUTRAL CONDITIONS

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In the quest for sustainable energy solutions, hydrogen production through photoelectrolysis of water stands out as a promising avenue.[1] The PROSPER-H2 industrial chair –an ANR project between ENGIE and the CEA within which this thesis takes place- aims to assemble and scale up a photoelectrochemical device. However, the current reliance on platinum-group metals catalysts used for electrochemical $H_2$ production presents challenges in terms of scalability and cost effectiveness.[2] To face this issue, the potential catalyst should avoid the use of critical metals and materials, thereby enhancing its viability.[3]

Our primary objective is to develop a noble metal-free catalyst for hydrogen evolution reaction and to subsequently deposit it onto either a cathode or a photocathode. In this study, we explore the utilization of amorphous molybdenum sulfide (a-$MoS_x$). The electrocatalytic properties of a-$MoS_x$ for hydrogen evolution reaction (HER) have been extensively investigated under acidic conditions in laboratory settings.[4] Another noteworthy aspect of this material is its versatility in implementation, as it can be prepared by wet synthesis and then formulated in inks, or directly electrodeposited onto the (photo)electrode support. To facilitate industrial and safer widespread deployment, we aim to transition from acidic to neutral electrolyte. Furthermore, we seek to optimize the catalyst deposition processes, either onto a cathode or photocathode, in order to enhance overall efficiency.

Electrochemistry data will be presented demonstrating differences in deposition methods and substrate nature.

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P27

# THE IMPACT OF METAL DEPOSITION ON GRAPHDIYNE-CARBON NANOTUBE HYBRIDS FOR ELECTROLYTIC HYDROGEN PRODUCTION

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Hydrogen ($H_2$) is regarded as an ideal alternative to traditional fossil fuels due to its high gravimetric energy density, earthabundance and carbon-free emission. Electrocatalytic water splitting is an important means to produce hydrogen on a large scale and at a low cost, and it is also considered to be one of the potential strategies to solve these two major social problems. Reasonable design of efficient and stable catalysts is a major problem in the current electrocatalytic hydrogen evolution reaction (HER).

Carbon nanotubes (CNTs) hold immense potential in the realm of electrocatalysis, heralded for their remarkable electrical conductivity, high surface area, and inherent stability. Their unique structural attributes make them highly desirable for facilitating catalytic reactions, including the HER. However, despite their promise, challenges persist in optimizing their performance and enhancing their catalytic activity to meet the demands of industrial-scale hydrogen production. Introducing graphdiyne (GDY), an emerging carbon allotrope with captivating properties that have begun to garner attention in the field of materials science and catalysis. With its exceptional electrical conductivity and robust chemical stability, GDY presents an intriguing complement to the prowess of CNTs in electrocatalytic applications. By combining these two materials, a novel hybrid emerges: graphdiyne-decorated carbon nanotubes (GYD-CNTs), poised to offer synergistic benefits that could revolutionize electrocatalysis for hydrogen production.

In this study, we delve into the exploration of GD-CNTs as catalysts for the HER, seeking to unravel the mechanisms underlying their enhanced catalytic activity. Through a comprehensive investigation encompassing experimental characterization, we aim to elucidate the intricacies of the catalytic behavior exhibited by this hybrid material. Moreover, our findings reveal that incorporating palladium (Pd) onto the GDY-CNTs yields superior results compared to gold (Au) incorporation. The Pd-decorated GDY-CNTs exhibit a low onset overpotential of 51 mV and a small Tafel slope of 71 mV per decade, showcasing comparable or even better performance than many reported nonprecious metal catalysts. This highlights the potential of GD-CNTs as efficient catalysts for sustainable hydrogen production, with palladium decoration offering particularly promising results.

**Acknowledgement**:

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## P28

# ENCAPSULATION OF POLYOXOMETALATES IN MOF-545 FOR IMPROVING THE PHOTOCATALYTIC $CO_2$ REDUCTION ACTIVITY

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Photocatalytic transformation of $CO_2$ into added-value carbon-based compounds (e.g., CO, $HCO_2H$, $CH_4$ …) is a promising approach to valorizing excess $CO_2$ in the atmosphere. Our group has previously focused on modifying metal-organic frameworks (MOFs) such as UiO-67 and MOF-545 to make better-performing heterogeneous photocatalysts for the transformation of $CO_2$ to formate ($HCO_2^{-}$).[1-3] Notably, we have reported that the polyoxometalate (POM) $[PW_{12}O_{40}]^{3-}$ ($PW_{12}$) can act as electron reservoir when encapsulated in Cp*Rh@UiO-67 to make a $[PW_{12}O_{40}]$,(Cp*Rh@UiO-67) composite material that is twice as active for formate production with respect its parent material.[2]

In this work, we further demonstrate the utility of this strategy by encapsulating either the $[SiW_{12}O_{40}]^{4-}$ ($SiW_{12}$) or the $[W_{10}O_{34}]^{4-}$ ($W_{10}$) POMs within MOF-545. Although the $SiW_{12}$@MOF-545 material was initially more sluggish than the parent material, both of the POM@MOF-545 composites were ultimately much more active than the parent MOF-545 for the production of formate (Fig. 1).

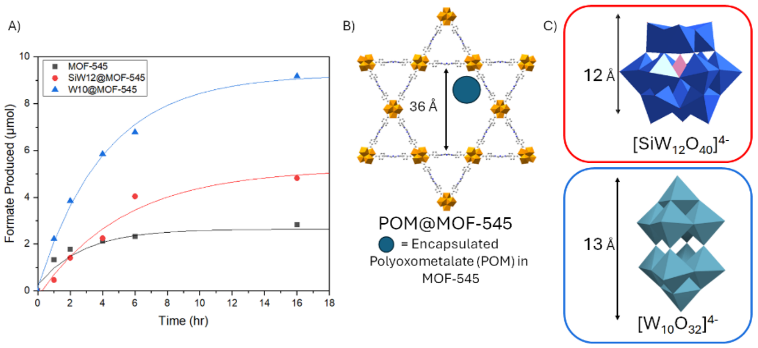

Figure 1. (A) Formate production for MOF-545 and the POM@MOF-545 materials over time (2 mg in 2 mL of $CH_3CN$/TEOA (20:1), solar simulator, 1 sun. (B) Representation of the POM@MOF-545 materials. (C) Structures of encapsulated POMs.

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# CARBON ISOTOPE RADIOLABELING VIA PHOTO-INDUCED CARBONDIOXIDE RADICAL AND FORMATE SALTS. INSIGHT INTO THE MECHANISM

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Being a major greenhouse gas, $CO_2$ has gained popularity among researchers to do its valorization by the common 2 electron reduction process. Owing to a high reduction potential ($E^0$= -2.21 V vs SCE), the single electron reduction rendering $CO_2^{\cdot -}$ (useful in imaging and drug discovery and development) is difficult to obtain via electrochemical process.

However, a new photocatalytic pathway to access this anion via formate salts, thiol and a photosensitizer, 4DPAIPN, has been studied where a dynamic isotopic equilibration between $CO_2$ and $CO_2^{\cdot -}$ is used to successfully achieve C-labeled compounds.[1] Our research aims to understand the mechanism involved in this reaction using spectroscopic techniques and photochemistry. We employed time-resolved photophysical studies to get insight into the initial steps of the photo redox process, the interaction of different substituents of the reaction mixture in the excited and ground state and capture transient species using nanosecond transient flash photolysis, FTIR spectroscopy and UV-Vis spectroscopy.

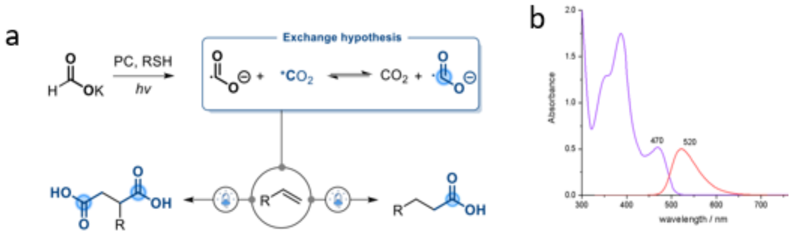

Figure 1a.) Photocatalytic reaction scheme b.) 4DPAIPN UV-Vis characterization

## References.

[1] Malandain A, Molins M, Hauwelle A, Talbot A, Loreau O, D'Anfray T, et al., J Am Chem Soc. Carbon Dioxide Radical Anion by Photoinduced Equilibration between Formate Salts and [11C, 13C, 14C]CO2: Application to Carbon Isotope Radiolabeling. 2023,145(30):16760–70.

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