Final dissemination workshop of the MOF2H2 Project

Photoactive MOFs and Nanomaterials for Solar Fuel Production

MOF2H2

TUESDAY 31 MARCH 2026
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POSTER SESSION

BOOK OF ABSTRACTS

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Poster presented by Sanchari DASGUPTA

Dual-Photon-Driven Hydrogen Evolution over Copper-Based Photocatalysts under Visible and Near-Infrared Light

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While recent studies have explored the dynamic restructuring of Cu centers in metal–organic frameworks (MOFs) for photocatalysis, their electronic excitation processes remain poorly understood.[1-2] In recent study (***Nat. Comm. 2026***) we investigated the light-driven behavior of a Cu-metalated UiO-66-$(COOH)_2$ framework (Fig. 1A) under various irradiation conditions, using complementary operando techniques. Gas-phase photocatalytic dehydrogenation of formic acid (FAc) under ambient conditions was employed as a model reaction. Notably, a photocatalytic logic-gate behavior was observed for the first time (Fig. 1B). The MOF remained inactive (OFF) under either visible (390-720 nm) or near-infrared (NIR, >700 nm) irradiation alone, but exhibited a high H_2 evolution rate (6.1 mmol g^{-1} h^{-1}) when both irradiations sources were applied simultaneously (ON state). Operando FTIR and XAS analyses revealed that dual irradiations were required to induce restructuring of impregnated Cu^{2+} sites within the framework, leading to the formation of active Cu^0/Cu^+ binary center responsible for FAc dehydrogenation. Furthermore, XAS results indicated that visible and NIR irradiation selectively promote distinct photo-reduction pathways, generating Cu^+ and Cu^0 species, respectively, from the pristine Cu^{2+}. A cascade mechanism involving alternating visible and NIR excitation cycles was demonstrated, in which both types of photons were essential for forming the active Cu^0/Cu^+ species and maintaining the dynamic photocatalytic redox cycle for H_2 production. This dual-photon-driven logic-gate behavior is not unique to the MOF system, but is also observed in a reference Cu^0/Cu_2O photocatalyst. Overall, these findings provide new insights into multi-wavelength photocatalysis in metal-semiconductor systems and suggest new strategies for designing efficient photocatalysts for hydrogen generation.

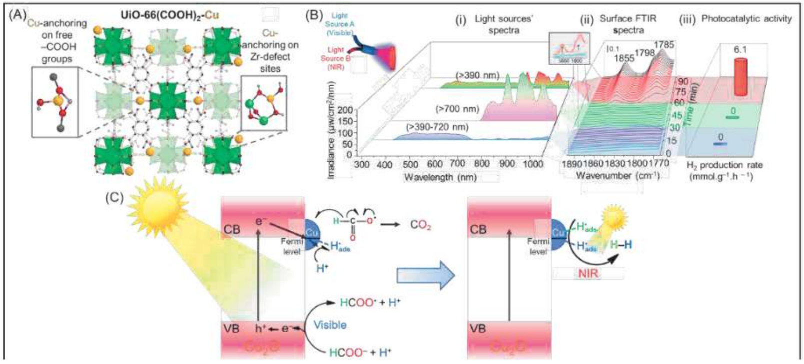

***Figure 1**. (A) Structure of UiO-66-$(COOH)_2$ MOF and potential anchoring sites for Cu (II). (B) (i) Light sources irradiation spectra (inset left: light irradiation on pellet photocatalyst) (ii) operando FTIR surface spectra in the anhydride region during reaction under various irradiation condition (inset: spectra at steady state: under visible (blue), NIR (green) and visible+NIR (red)), (iii) corresponding H_2 production at the steady state. (C) Schematic representation of CO_2 and H_2 formation under simultaneous visible and NIR irradiation.*

References

[1] Hamoud *et al.*, *J. Am. Chem. Soc.* 144 (2022) 16433-16446. [2] Hamoud et al., *ACS Catal.* 13 (2023), 16266-16278.

Acknowledgements

The European Union under the Grant Agreement #101084131 (MOF2H2 project) is acknowledged for funding.

Dual-photon–driven hydrogen evolution in copper-based photocatalysts under near-infrared and visible light

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Antony Beauvois[4], Valerie Briois[4], Christian Serre[3], Mohamad Hmadeh[2], Marco Daturi[1], Mohamad El-Roz[1*]

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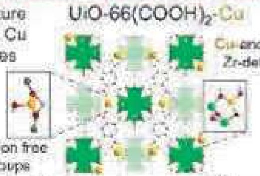
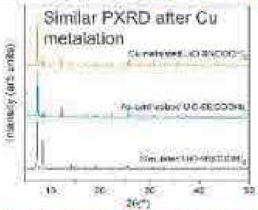
We investigate the light-induced activity of the Cu-metalated metal–organic framework (MOF), UiO-66(COOH)$_2$-Cu using gas-phase formic acid (FAc) dehydrogenation at ambient conditions as a model reaction. The material shows photocatalytic logic-gate behavior: it remains inactive (*OFF*) under visible (>390–720 nm) or near-infrared (>700 nm) light alone, while H_2 is produced (6.1 mmol·g^{-1}·h^{-1}) when both are applied. Operando FTIR and X-ray absorption spectroscopy reveal that dual irradiations drive the restructuring of the coordinated Cu^{2+}/Cu^{+} into active Cu^{0}/Cu^{+} binary redox centers, enabling the photocatalytic reaction. Similar behavior was also observed in a Cu^{0}/Cu$_2$O reference system, highlighting a generalized approach towards dual-photon-driven photocatalysis.

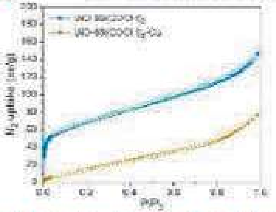
Characterization: UiO-66(COOH)$_2$ and UiO-66(COOH)$_2$-Cu

Crystal structure and Possible Cu anchoring sites



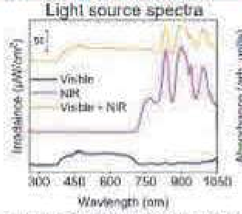
Similar octahedral morphology after Cu metalation

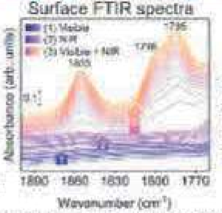


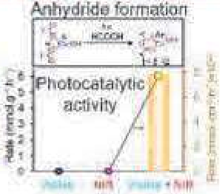


Upon post-synthetic Cu metalation, surface area and pore volume decreased from 239 to 32 m^2/g, and 0.22 to 0.11 cm^3/g, respectively.

Evidencing the restructuring by monitoring the anhydride formation

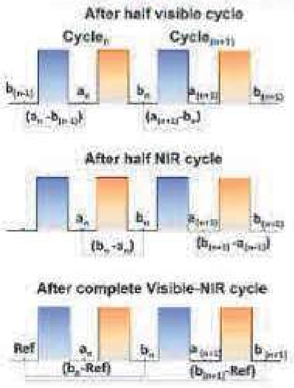




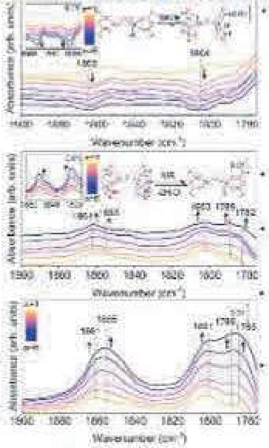


- No detectable anhydride formation and activity under visible and NIR irradiation alone
- High anhydride formation and 6.1 mmol·g^{-1}·h^{-1} H_2 production under both irradiation, also demonstrating a structural restructuring

Tracking anhydride formation under periodic irradiations

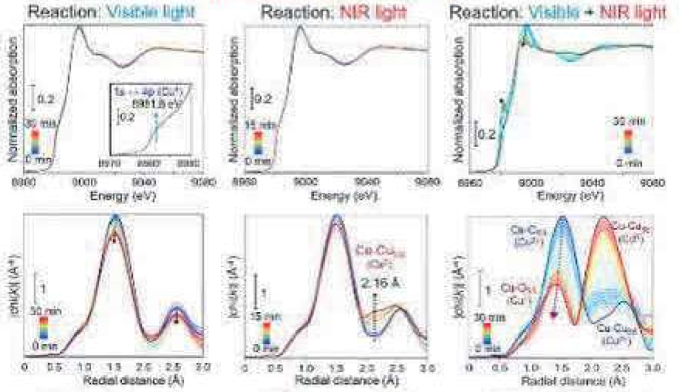


n: Cycles number, **Ref**: Spectrum after activation
Spectrum after **a**: visible **b**: NIR irradiation



- Slight decrease in anhydride bands (1900–1870 cm^{-1}) under visible light, suggesting partial hydration of anhydride in the presence of water vapor probably produced during the Cu(OH) condensation
- Increase in the anhydride bands after each NIR irradiation cycle
- Anhydride formation rate is 2.5 times greater than hydration reaction
- Successive alternating cycles of visible and NIR irradiations facilitated surface evolution
- **Strongly evidence: cascade nature**, visible-light initiates the restructuring, and NIR promotes its progression

Operando XAS analysis

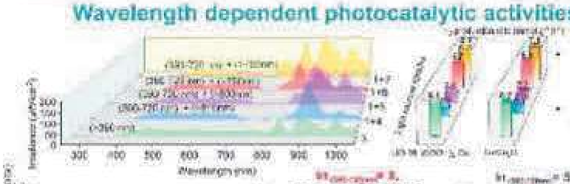


Visible light promotes initial Cu^{+} formation

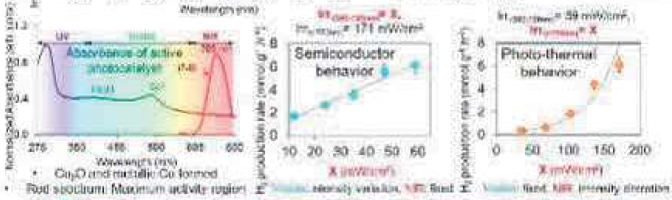
NIR promotes initial Cu^{0} formation

Visible + NIR promotes high Cu^{+}/Cu^{0} formation

Wavelength dependent photocatalytic activities

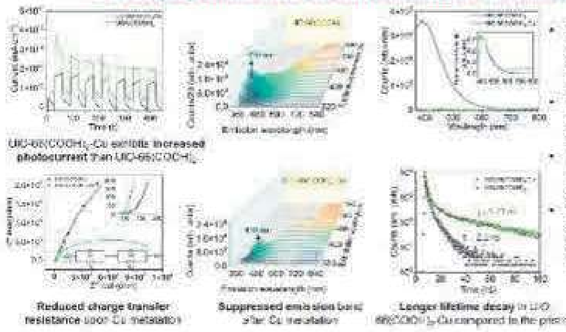


- Irradiation wavelength-dependent H_2 production
- Maximum activity: **visible light + NIR (between 800-750 nm)**



- Cu$_2$O and metallic Cu formed
- Red spectrum: Maximum activity region

Photophysical and electrochemical characterizations


UiO-66(COOH)$_2$-Cu exhibits increased photocurrent than UiO-66(COOH)$_2$

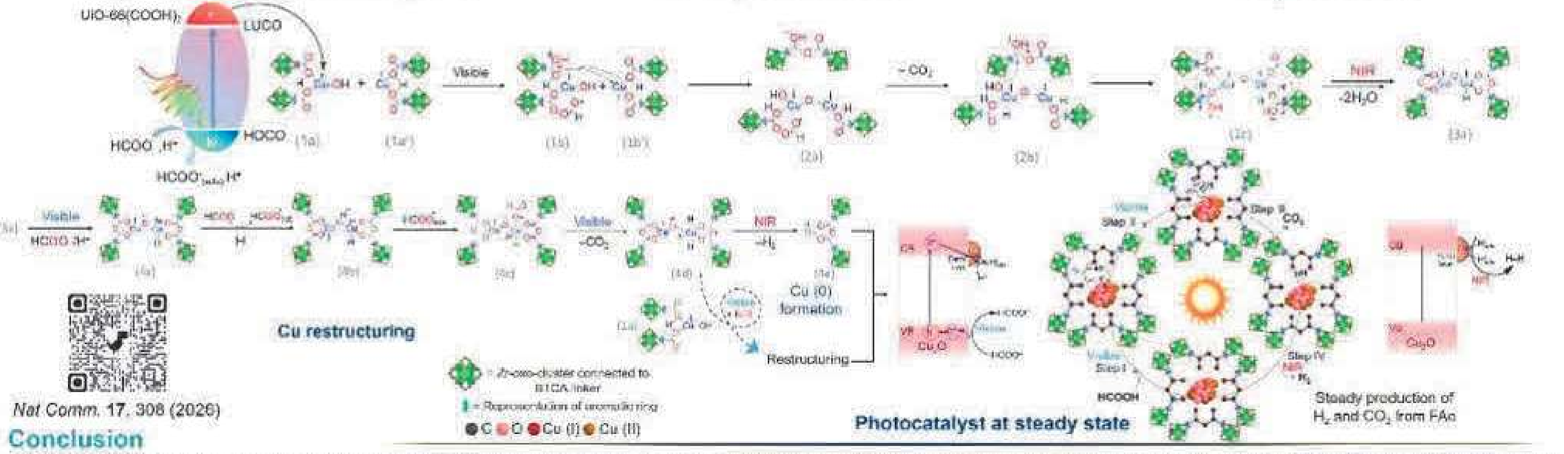
Reduced charge transfer resistance upon Cu metalation

Suppressed emission band after Cu metalation

Longer lifetime decay in UiO-66(COOH)$_2$-Cu compared to the pristine

- Enhanced photocurrent than pristine MOF indicates better charge separation efficiency upon Cu metalation
- Possible charge transfer from the UiO-66(COOH)$_2$ framework to the Cu center
- This promotes metalated Cu restructuring under visible light
- Longer lifetime decay suggests enhanced charge carrier separation attributed to possible charge transfer

Proposed photocatalytic mechanism



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Conclusion

Photocatalytic logic-gate behavior for H_2 production from FAc was observed. Charge transfer within framework induces metalated Cu restructuring. Visible and NIR initiates the restructuring of coordinated Cu^{2+} into Cu^{+} and Cu^{0} formation, respectively. Therefore, cascade double-photon irradiations are required for catalyst activation and H_2 production.

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Enhanced Photocatalytic Overall Water Splitting via Conductive Polymer Integration in Ti-MOF MIP-177-LT

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Keywords: *Metal-Organic Frameworks (MOF), photocatalysis, overall water splitting, Polymer*

Green production of H_2 through photocatalytic water dissociation into H_2 and O_2 is currently one of the most attractive processes for hydrogen generation, particularly due to its intrinsic sustainable nature.[1] Titanium-based metal-organic frameworks are particularly attractive due to their stability and photoactive Ti-oxo clusters[2] and the MOF2H2 project appears as a game changer in the sustainable production of hydrogen from water through photocatalytic overall water splitting (OWS).[3] Among them, MIP-177-LT has demonstrated promising activity for photocatalytic hydrogen evolution from water.[4] However, its performance remains limited by inefficient charge separation and transport.

Herein, we report a polymerization strategy to incorporate an aniline-derived polymer within the pores of MIP-177-LT, forming a hybrid conductive MOF composite. Structural characterization by PXRD confirms retention of crystallinity, while porosity measurements indicate partial pore filling. FTIR and UV-Vis spectroscopy evidence the formation of the polymer, with a loading of 8-10 wt% as determined by thermogravimetric analysis. Electron microscopy reveals preserved morphology of the parent framework.

Under light irradiation, the composite exhibits efficient overall water splitting with simultaneous H_2 and O_2 evolution in a near-stoichiometric ratio (∼2:1), confirming true photocatalytic activity without sacrificial agents. The enhanced performance is attributed to improved charge separation and transport enabled by the integrated polymer, highlighting a viable strategy to overcome intrinsic limitations of Ti-MOF photocatalysts.

References

[1] P. J. Calvo, Kazunari Domen et al. *Global Challenges*, **2024**, *8*, 2400122.

[2] S. Navalón, A. Dhakshinamoorthy and H. García. *Chem. Rev*. **2023**, *123*, 445–490.

[3] “MOF2H2: Game Changer for Water Splitting.” *mof2h2.eu*, Copyright © 2025 MOF2H2

[4] A. G. Baldovi, C. Serre, H. Garcia et al. *Energy Environ. Sci.*, **2023**,*16*, 167-177.

Acknowledgments:

The European Union under the Grant Agreement #101084131 (MOF2H2 project) is acknowledged for funding.

Mechanistic Insights into the *In-Situ* Restructuring of Coordinated Copper in Post-Metalated MOFs for Photocatalysis

*Zahraa Abou Khalil‡,[1] Karen Hannouche‡,[2] **Akashdeep Nath**,[1] Nisrine Assaad,[3] Leen Farhat,[2] Georges Mouchaham,[3] Dong Fan,[4] Oleg Lebedev,[5] Antony Beauvois,[6] Ali Youssef,[1] Valerie Briois,[6] Guillaume Clet,[1] Guillaume Maurin,[4] Christian Serre,[3] Marco Daturi,[1] Mohamad Hmadeh,[2] Mohamad El-Roz*[1]*

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Defect engineering and metal coordination in MOFs are key to enhancing photocatalytic activity and stability. Recently, we reported (*J. Am. Chem. Soc*. **2025**, *147*, 48331-48351) multivariate UiO-66 (MTV-UiO-66) frameworks with tunable BDC:BTCA linker ratios (x:y) (Figure 1A), followed by Cu post-metalation to investigate the role of free carboxylate groups in Cu coordination and *in-situ* restructuring during photocatalytic formic acid (FAc) dehydrogenation. *Operando* FTIR and XAS allowed real-time tracking of structural evolution in MTV-UiO-66-Cu and oxidation state changes at Cu centers under reaction conditions. FAc conversion enhanced with increasing BTCA content, from 1.2 to 5 mmol·g^{-1}·h^{-1} for UiO-66-Cu (12:0) to (0:12) (Figure 1B). *Operando* FTIR identified anhydride bridge formation between coordinated carboxylates of adjacent ligands (Figure 1C), evidenced by a characteristic 1855 cm^{-1} band attributed to symmetric anhydride stretching, whose intensity scaled linearly with BTCA fraction (Figure 1D) and catalytic activity (Figure 1E) at steady state. XAS revealed that coordinated Cu^{2+} species undergo *in-situ* transformation to Cu^{+} and Cu^{0} under simulated solar irradiation and FAc exposure (Figure 1F). These results emphasize the influence of linker composition and dynamic metal coordination on photocatalytic performance, providing a pathway for light-driven formation of metal clusters within MOFs. Overall, this study highlights the role of metal coordination and *in-situ* restructuring in governing photocatalysis and proposes a photochemical strategy for nano-synthesizing MOF-embedded metal-clusters.

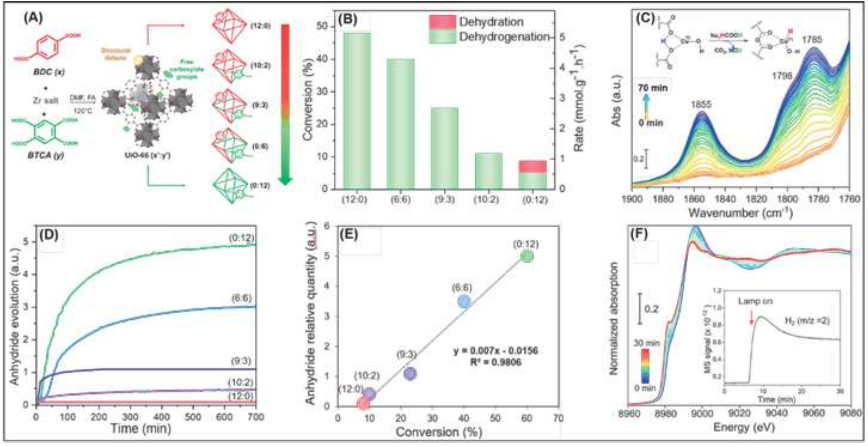

***Figure 1**. (A) Schematic illustration of MTV-UiO-66 derivatives, (B) Photocatalytic performance of different samples in FAc reforming, (C) IR spectra (1900-1700 cm^{-1}) of (0:12) sample and (D) anhydride band area evolution vs.time of the various samples, (E) Correlation of steady-state anhydride band area with the activity, and (F) Time-resolved Cu-XANES and H_2 evolution (inset) during FAc dehydrogenation under visible light ($\lambda \geq$ 390 nm).*

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Mechanistic Insights into the *In-Situ* Restructuring of Coordinated Copper in Post-Metalated MOFs for Photocatalysis

Zahraa Abou Khalil[1], **Akashdeep Nath**[1], Karen Hannouche[2], Leen Farhat[2], Georges Mouchaham[3], Antony Beauvois[4], Ali Youssef[1], Dong Fan[3], Nisrine Assaad[3], Oleg Lebedev[4], Marco Daturi[1], Guillaume Maurin[3], Mohamad Hmadeh[2], Mohamad El-Roz[1*]

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We studied Cu^{2+}-postmetalated UiO-66-$(COOH)_x$ derivates known as UiO-66-$(COOH)_x$-Cu and its in-situ restructuring during photocatalytic formic acid (FAc) dehydrogenation under simulated solar light. Multivariate UiO-66 derivatives with varied linker ratios (BDC:BTCA, x:y) were synthesized and post-metalated with Cu to examine how linker composition affects Cu coordination and therefore its restructuring. The results demonstrate that photocatalytic activity increased with decreasing BDC:BTCA ratio. *Operando* FTIR and XAS confirm the *in-situ* Cu^{2+} restructuring, initially bound to free carboxylates, into Cu^+ and Cu^0. DFT calculations revealed that the spatial arrangement of carboxylates influences Cu coordination stability and therefore the restructuring process.

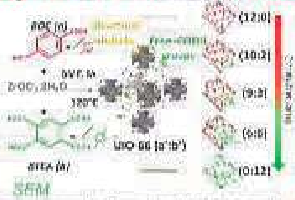
Experimental: FTIR and XAS *operando* analysis

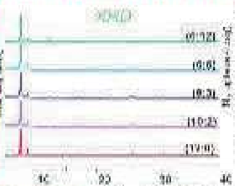
Simultaneous analysis of the photocatalyst surface (FTIR/XAS) and the gas phase (FTIR, GC, MS) under reaction conditions. Reaction conditions : [FAc] = 2600 ppm in Argon flow (25 cc/min) at 25 °C under visible light (λ > 360 nm).

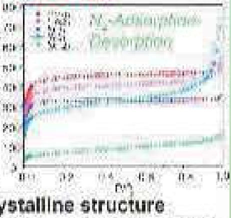
FTIR operando setup and reactor

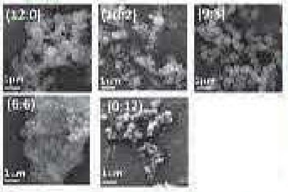
Operando XAS reactor (developed by Soleil synchrotron)

Synthesis and characterization of UiO-66$(COOH)_x$







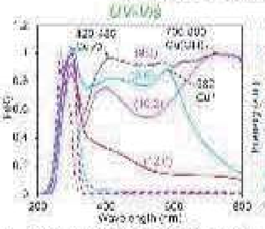


- **Highly crystalline structure**
- **Relatively high surface area** (240-1800 m²/g)
- **BDC/BTCA linkers' ratio validated by ¹H-NMR**
- **Similar hexagonal morphology** and similar Cu content (6-8 wt.%) for various samples

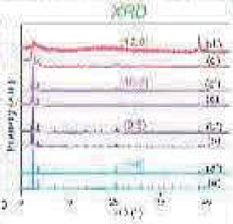
Evidencing the in-situ restructuring of UiO-66$(COOH)_x$-Cu under reaction conditions

Characterization of the catalyst before/after reaction

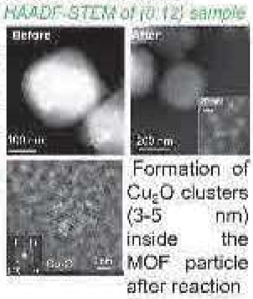
UV-Vis



XRD



HAADF-STEM of (0:12) sample

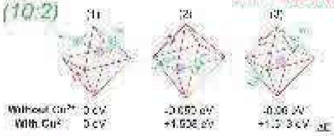


- Presence of Cu_2O and Cu^0 after reaction
- Formation of $Cu(OH)_2$ due to air exposure

- Crystallinity is maintained after reaction except for (12:0)

Formation of Cu_2O clusters (3-5 nm) inside the MOF particle after reaction

DFT calculations

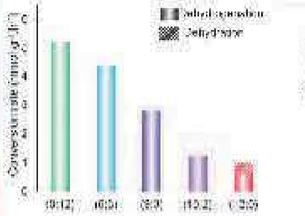


- Coordination of the Cu^{2+} with neighboring COOH groups lowers the system's E_{total} forming a highly stable tetra-coordinated Cu

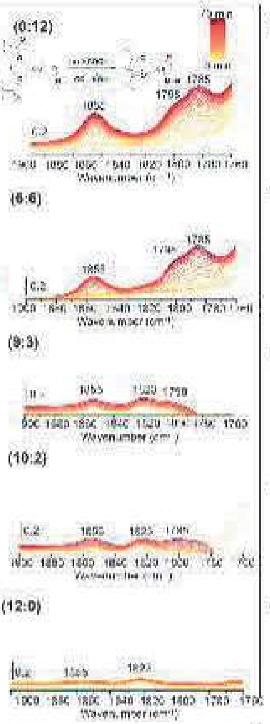
- Similar E_{total} before and after Cu^{2+}
- Different spatial distribution of BTCA doesn`t affect the stability of (9:3) structure

FAc dehydrogenation over UiO-66$(COOH)_x$-Cu

Performance at Steady state

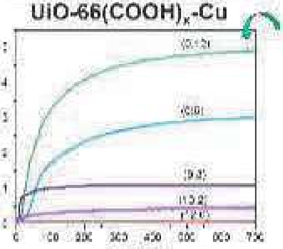


Surface analysis by FTIR

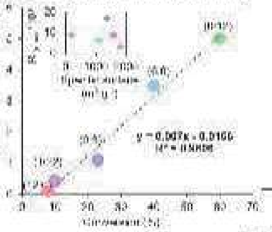


- **Decrease in activity of UiO-66-$(COO)_x$-Cu derivatives as the BTCA concentration decreases**
- **Formation of anhydride** (characteristic bands at 1900-1700 cm⁻¹) during the reaction
- **Proportional anhydride evolution with the BTCA** concentration
- **Linear relationship of activity and anhydride** concentration
- Independent rate of anhydride formation with the specific surface of the sample

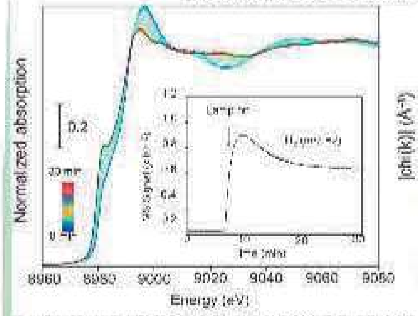
Anhydride evolution in UiO-66$(COOH)_x$-Cu

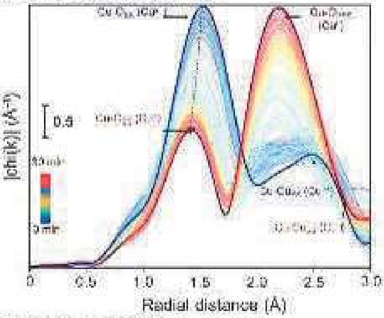


Anhydride vs. activity



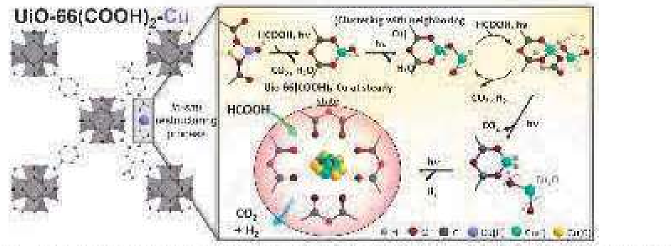
Operando XAS Analysis of (0:12) sample





- **Decrease of the pristine Cu^{2+} signals during the reaction**
- Shift of the Cu –Cu signal to 2.2 Å (Cu^0); shortening of the Cu–O bonds to 1.43 Å (Cu^+) ⟶ **restructuring of Cu^{2+} to Cu^+ and Cu^0 during FAc dehydrogenation** under simulated sunlight

Mechanism



Conclusions

UiO-66$(COOH)_x$-Cu derivatives were synthesized to study Cu restructuring during photocatalysis, showing that lower BDC:BTCA ratio enhances Cu^{2+} restructuring and therefore the photocatalytic dehydrogenation performance of FAc. *Operando* FTIR and XAS confirmed the *in-situ restructuring of* Cu^{2+} into Cu^+/Cu^0 under solar simulated sunlight. Also, DFT revealed that the (10:2) sample favors a stable tetra-coordinated Cu environment, boosting performance. However, decreasing the BDC:BTCA ratio (e.g. (9:3) sample) shows no significant impact on Cu^{2+} coordination. In summary, this study highlights how the use of MOFs' structural flexibility can drive the photocatalytic dehydrogenation of FAc as a prominent source of H_2 generation. Most importantly, it examines the in situ structural changes occurring within the Cu-metalated MOF structures, promoting the understanding of their mechanism of action, thus guiding the future design of potent catalysts for clean energy processes.

Acknowledgments : The authors thank **MOF2H2** (EU, 101084131), **MOFtoH2** (ANR 21 CE50 0022 01), and **DIM MaTeRE** (MOFPlasma Project) for financial support.

METAL-ORGANIC FRAMEWORK FOR HYDROGEN PRODUCTION BY PHOTOCATALYTIC OVERALL WATER SPLITTING

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Keywords: *metal-organic frameworks (MOF), photocatalysis, overall water splitting*

Non-sustainable, fossil fuel-dependent processes still account for most of the worldwide hydrogen (H_2) production.[1] Among alternatives, photocatalyzed water dissociation into H_2 and O_2 is particularly appealing owing to its intrinsic sustainable nature.[2] However, up till now reported catalysts for light-driven water splitting still do not meet the techno-economical requirements for industrial implementation as they suffer from either a lack of solar-to-hydrogen conversion (STH) efficiency and/or stability under operation, require complex synthesis processes and are in most cases inactive under visible light irradiation.[3]

Over the last few years, metal-organic frameworks (MOF) have drawn increasing interest as candidate catalysts, but most reported studies deal with either of the half reactions, i.e., the hydrogen and oxygen evolution reactions (HER and OER, respectively), thus requiring the use of sacrificial agents.[4] In this regard, the MOF2H2 project [5] is ambitious to be a game changer in producing hydrogen from water through a more sustainable process, the photocatalytic overall water splitting (OWS), using non-noble MOF-based catalysts.

This project relies, so far, on two main families of MOFs. Inspired by nature, a MOF made of a multicopper-based metalloligand reminiscent of the active site of certain reductive enzymes was first selected and found to be an efficient catalyst for photo-induced water splitting reactions. Besides, the specific $Ti_{12}O_{15}$-based MOFs[6] are also being explored. While the first studies demonstrated the high potential of these MOFs for HER and OWS,[7,8] deeper photophysical and photocatalytic investigations are on-going and driving the chemical modifications/optimization to reach higher performances.

In this communication, we will present the MOF2H2 project concept as a whole. A specific highlight will be shed on the most recent advances leading to ground-breaking results in terms of H_2 photo-induced production. Finally, our ongoing work directed at improving the MOF-based catalysts' performances will also be discussed.

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[6] S. Wang, T. Kitao et al. *Nat. Commun*., **2018**, 9, 1660.

[7] B. Chen, A. Mansouri et al. *Adv. Energy Mater.,* **2025**, 2500211.

[8] A. Kuila, V. Diez-Cabanes et al. *Small*, **2025**, 21, 2407273

Acknowledgments:

The European Union under the Grant Agreement #101084131 (MOF2H2 project) is acknowledged for funding.

METAL-ORGANIC FRAMEWORK FOR HYDROGEN PRODUCTION BY PHOTOCATALYTIC OVERALL WATER SPLITTING

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Vanessa Pimenta[a], Hermenegildo García[b], Sergio Navalón[b], Georges Mouchaham[a], Christian Serre[a]

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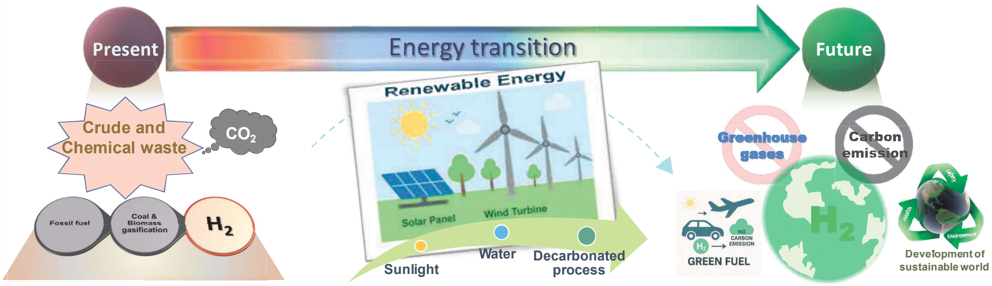
Motivation & Introduction

- ✓ **Sustainable energy harvesting via decarbonized process is becoming a global mandate**
- ✓ **Solar energy is a decentralized but inexhaustible natural energy resource**
- ✓ **'Sun + Water = Hydrogen: The equation for a greener planet'**

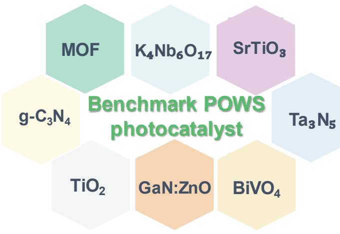


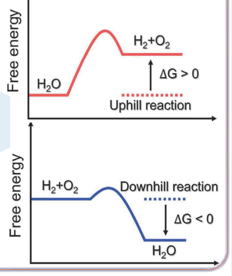
Photocatalytic overall H_2O splitting (POWS) can be a future sustainable energy vector

Water splitting (HER + OER): $2H_2O \rightarrow 2H_2 + O_2$, $\Delta G° = +237.2$ kJ/mol

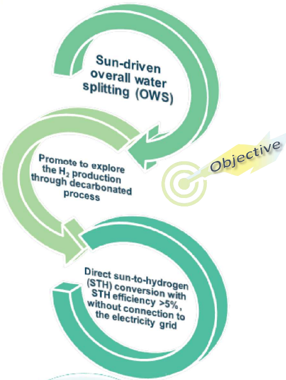
Reduction (HER): $2H^+ + 2e^- \rightarrow H_2$ $E^o_{red} = 0.00\ V$

Oxidation (OER): $H_2O + 2h^+ \rightarrow \frac{1}{2}O_2 + 2H^+$, $E^o_{oxd} = -1.23\ V$

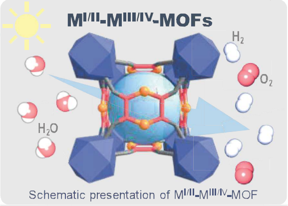




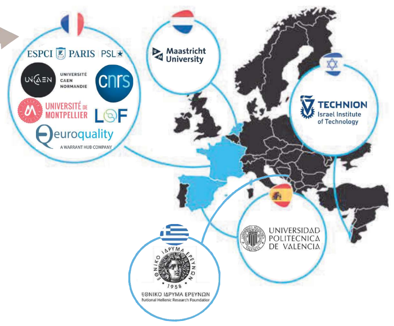
MOF-based photocatalysts for H_2 production



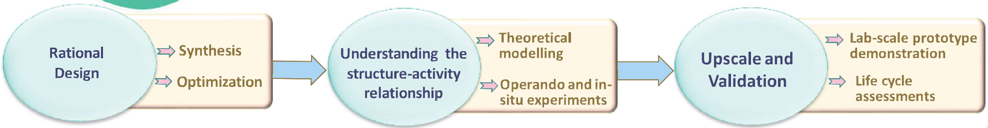
MOF2H2



Schematic presentation of $M^{I/II}$-$M^{III/IV}$-MOF

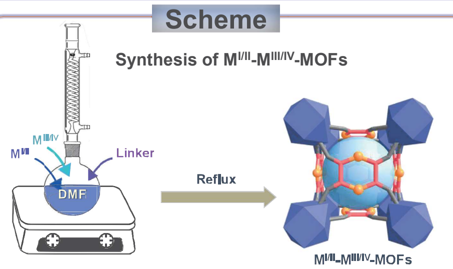


Protocols & Methodology

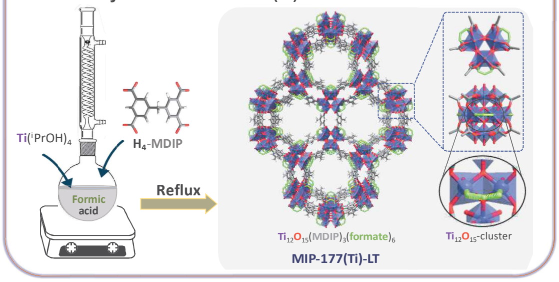


Scheme

Synthesis of $M^{I/II}$-$M^{III/IV}$-MOFs

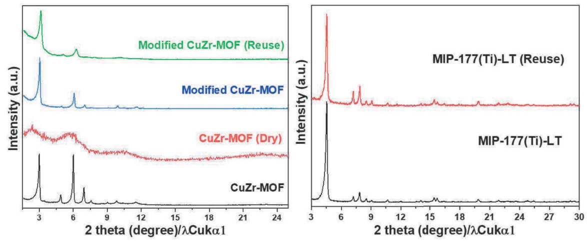


Synthesis of MIP-177(Ti)-LT

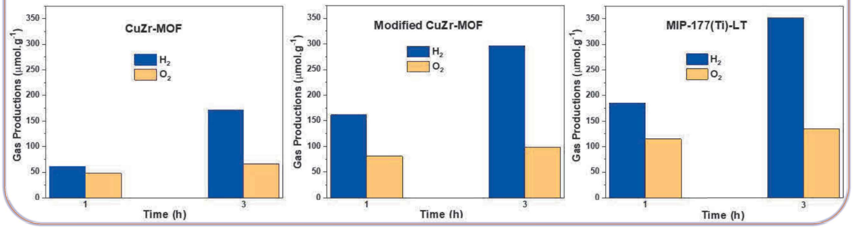


Results & Discussion

- ➢ CuZr-MOF can be synthesized on a gram-scale using a facile and fast synthesis approach.
- ➢ CuZr-MOF, on drying, loses crystallinity, but suitable chemical modifications can avoid the stability issue.
- ➢ MIP-177(Ti)-LT can be synthesized on a gram-scale using a reflux approach.



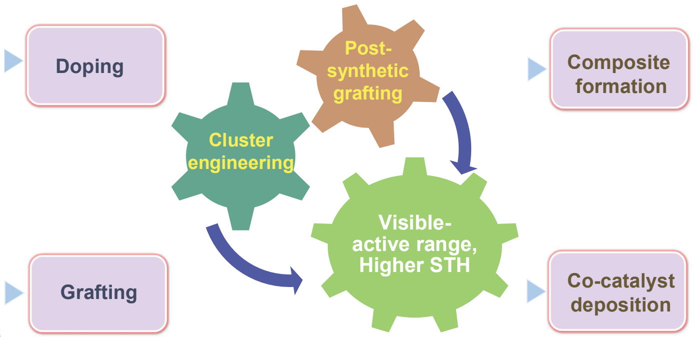
POWS Conditions
- 20mL H_2O
- 5mg Sample
- 100 mW/cm^2
- Xenon lamp.
- Filter 1.5



Future Plans

- ➢ To explore promising photoactive Ti MOFs.
- ➢ To explore the structural upgradation/modifications of $M^{I/II}$-$M^{III/IV}$-MOFs and MIP-177(Ti)-LT to achieve enhanced photoresponsive features and improved STH.
- ➢ To conduct the photophysical studies and advance material characterizations to outline the structure-activity relationships.

MOF structure modifications



Conclusion

- ➢ $M^{I/II}$-$M^{III/IV}$-MOF was synthesized via a facile synthesis approach.
- ➢ Suitable chemical modifications can avoid the stability issue and also improve the H_2 production rate.
- ➢ The structural modifications of MOF can lead to better efficiency.
- ➢ Photoactive Ti-MOFs other than MIP-177 are also being explored in this project.

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MOF-based catalysts for enhanced CO_2 conversion using non-thermal plasma-assisted methods

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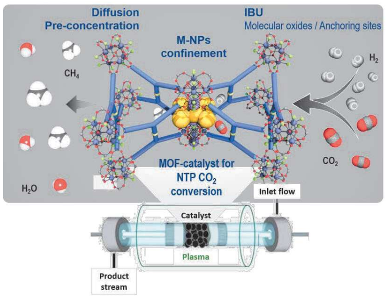
Since the Industrial Revolution, fossil fuel use has driven anthropogenic CO_2 emissions, causing pollutionandglobalwarming(IPCC). CO_2 capture and its conversion into fuels via catalytic hydrogenation (e.g., methane, methanol) is a promising strategy for sustainable energy valorization.

Thus, in MOFPlasma project, we are focusing on developing new hybrid catalysts to improve the conversion of CO_2 into CH_4 (i.e., selectivity, kinetics, productivity rate, lower temperature, pressure) by means of Non Thermal Plasma (NTP)-assisted catalysis [1]. This, combined to sustainable catalytic systems (higher stability /durability), is expected to enable a drastic decrease of the overall energy penalties, in comparison with conventional thermal hydrogenation [2,3]. This project specifically relies on the rational design of new Metal-Organic Framework (MOF)-based catalysts carefully loaded with catalytically active Ni-NPs.

Metal–organic framework materials, are a family of hybrid organic–inorganic crystalline porous solids, built-up of inorganic building units (IBU) (isolated or multinuclear metal ions) linked together by organic linkers (bridging ligands). The high and fine tunability of MOFs in terms of composition (organic ligand, inorganic moieties) and geometrical features (pore size and shape), make them appealing candidates for catalytic CO_2 conversion.

In this presentation, we will explain our strategy in designing MOF-based catalyst through eco-compatible methodologies (Figure1). We will also share some results obtained with our in-house developed catalysts.



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MOF-based catalysts for enhanced CO_2 conversion using non-thermal plasma-assisted methods

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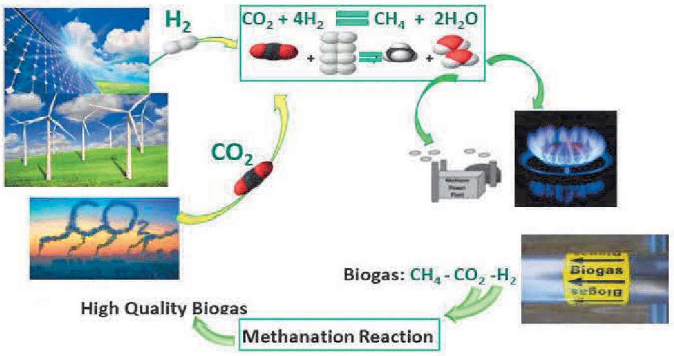
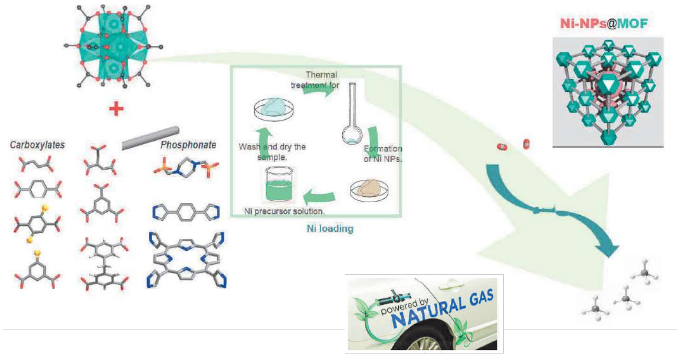
Introduction

Anthropogenic CO_2 emissions from fossil fuels necessitate innovative strategies for carbon capture and valorization. The MOFPlasma project pioneers hybrid catalysts combining Metal-Organic Frameworks (MOFs) and nickel nanoparticles (Ni-NPs) to convert CO_2 into methane (CH_4) via Non-Thermal Plasma (NTP)-assisted catalysis[2]. MOFs, with their tunable porosity and composition, provide tailored active sites, while NTP enhances reaction kinetics and energy efficiency under milder conditions (reduced temperature/pressure) compared to conventional thermal hydrogenation[1]. This approach prioritizes eco-friendly synthesis to ensure catalyst durability and sustainability. Preliminary results highlight improved CO_2 conversion rates, selectivity, and stability, aligning with goals to minimize energy penalties and advance circular carbon economies. By transforming CO_2 into high-energy-density fuels like methane, the project bridges environmental mitigation and renewable energy production, offering a scalable pathway for climate change solutions. The integration of MOF-Ni-NP composites with plasma technology underscores a novel, sustainable strategy to address global warming while promoting resource-efficient CO_2 utilization[3].

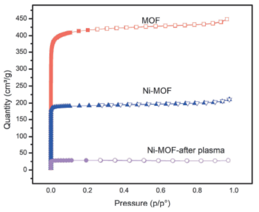
Sabatier Reaction or CO_2 methanation

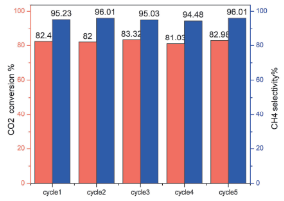


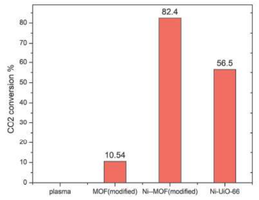
MOF Composite preparation

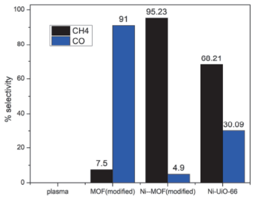


Main results







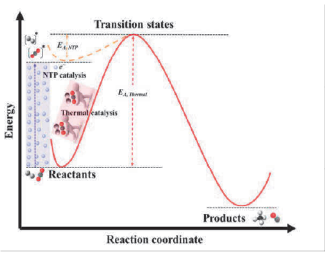


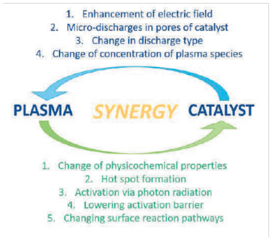
Acknowledgement

The authors acknowledge DIM MaTeRE for co-funding the MOFPlasma project.

Non-Thermal Plasma (NTP)

Promising alternative to conventional thermal catalysis





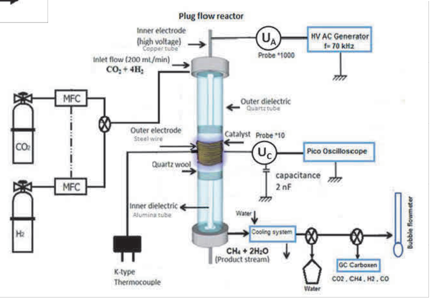
1. Enhancement of electric field
2. Micro-discharges in pores of catalyst
3. Change in discharge type
4. Change of concentration of plasma species

1. Change of physicochemical properties
2. Hot spot formation
3. Activation via photon radiation
4. Lowering activation barrier
5. Changing surface reaction pathways

- Low Temperature and Atmospheric pressure
- Dynamic equilibrium between oxidation and reduction of metal

activation energy
ca. 29 kJ mol^{-1} (NTP)
80 kJ mol^{-1}
(Thermalcatalysis)

Decrease the energy penalty



Conclusions & Perspectives

- MOF-Ni-NP hybrids enable efficient CO_2 methanation via plasma catalysis.
- Towards milder operational conditions reduce energy demands.
- Eco-friendly synthesis enhances catalyst stability and scalability.
- Preliminary data – *to be continued…*

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Photo-switchable copper-based MOFs for photocatalytic green Hydrogen production

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Abstract:

Producing green hydrogen (H_2) by photocatalysis, which uses sunlight, photocatalysts and water, is a promising solution for the energy transition. A new approach to enhance H_2 production is to promote interactions between confined water and the catalyst active sites, or to trigger the release of encapsulated reactants under external stimuli[1,2]. Azobenzene is a widely used photochromic molecule undergoing reversible E → Z isomerization under light and spontaneous Z → E relaxation in the dark, accompanied by a length change from 9 Å to 5.5 Å within the MOF structure[2]. Its nitrogen-substituted derivatives, azopyridines, can coordinate metal, offering the opportunity to develop photo switchable MOFs. In this project, we therefore designed a new copper azobipyridine iodine (Cu(AzoBiPy)(I)) MOF for photocatalytic H_2 generation. First characterization works demonstrated a crystalline structure in which copper is coordinated to AzoBiPy ligands thanks to the nitrogen from the aromatic cycle (Fig. 1). Coordination via the nitrogen of the azo bond appears also possible. This Cu(AzoBiPy)(I) MOF was then associated with TiO_2, by a physical mixing in EtOH, to form a composite material. Their photocatalytic H_2 production performance was evaluated in a water/triethanolamine mixture (3:1) with a 150 W mercury lamp. A production rate of 3.9 mmol/g/h was obtained after 4h with the ratio of (1:10).

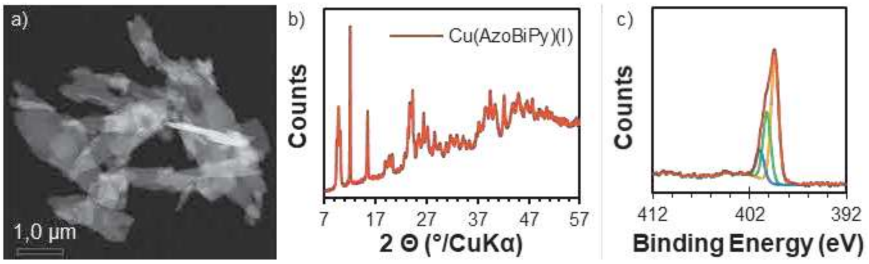

Figure 1. HAADF image (a), XRD pattern (b), and XPS N1s electronic binding energy spectra (c) of Cu(AzoBiPy)(I) MOF.

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Stacking Effects on the Opto-electronic Properties of 2D Perylene-Zn-porphyrin-based COFs

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Abstract:

Crystalline porous materials, such as Covalent Organic Frameworks (COFs), have emerged as promising candidates for photocatalytic and optoelectronic applications due to their tunable architecture and capacity to mitigate charge recombination. The incorporation of highly aromatic organic building blocks that promote self-assembly and columnar growth enables the formation of COFs with controlled layer thickness. However, the influence of interlayer stacking on the structural and optoelectronic behavior of these materials remains poorly understood. In this work, we combine experimental and theoretical approaches to elucidate the stacking-induced evolution of perylene–Zn–porphyrin COFs. Spectroscopic and microscopic analyses, supported by Density Functional Theory (DFT) calculations, reveal that self-assembly through AA stacking markedly modifies both geometry and electronic structure. The transition from non-planar 2D architectures to planar multilayered frameworks results in reduced band gaps, inversion of the frontier crystalline orbital delocalization, and a shift of absorption dominance toward the porphyrin units. These findings demonstrate that controlled layer stacking is a viable strategy to tailor the electronic and optical properties of stacked 2D COFs, paving the way for their integration into high-performance optoelectronic devices.

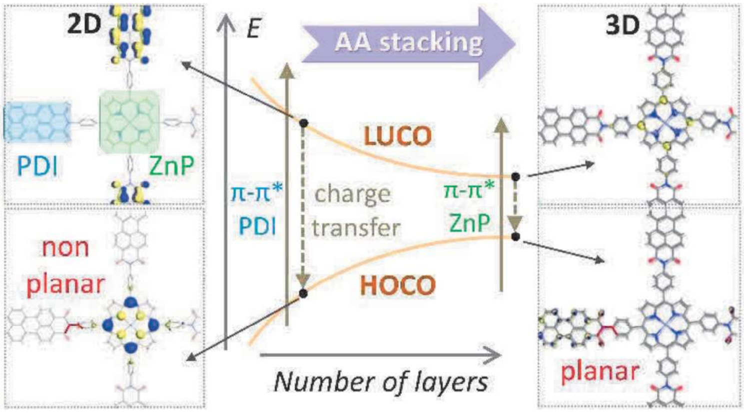

Figure 1. Scheme of the evolution of the opto-electronic properties of the perylene–Zn–porphyrin COFs due to the stacking of COF layers.

Stacking Effects on the Opto-electronic Properties of 2D Perylene-Zn-porphyrin-based COFs

V. Diez-Cabanes[1,2*] R. González-Gómez,[3] P. Farràs,[3] S. Aparicio,[1,2]

1 International Research Center in Critical Raw Materials for Advanced Industrial Technologies (ICCRAM), University of Burgos, 09001, Burgos, Spain
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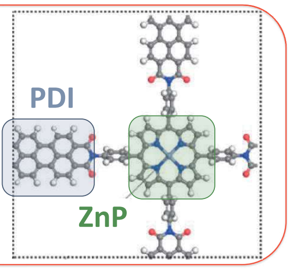
NADES4PFAS

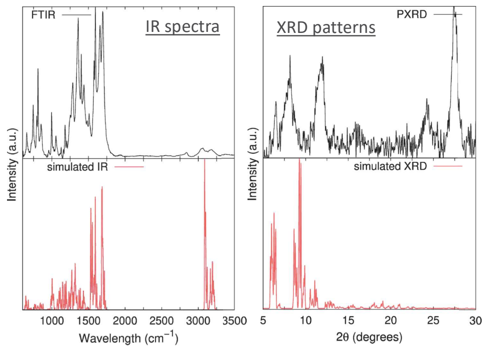
INTRODUCTION

Crystalline porous materials, such as Covalent Organic Frameworks (COFs), have emerged as promising candidates for photocatalytic and optoelectronic applications due to their tunable architecture and capacity to mitigate charge recombination. The incorporation of highly aromatic organic building blocks that promote self-assembly and columnar growth enables the formation of COFs with controlled layer thickness. However, the influence of interlayer stacking on the structural and optoelectronic behavior of these materials remains poorly understood. In this work, we combine experimental and theoretical approaches to elucidate the stacking-induced evolution of perylene–Zn–porphyrin COFs. Spectroscopic and microscopic analyses, supported by Density Functional Theory (DFT) calculations, reveal that self-assembly through AA stacking markedly modifies both geometry and electronic structure. The transition from non-planar 2D architectures to planar multilayered frameworks results in reduced band gaps, inversion of the frontier crystalline orbital delocalization, and a shift of absorption dominance toward the porphyrin units. These findings demonstrate that controlled layer stacking is a viable strategy to tailor the electronic and optical properties of stacked 2D COFs, paving the way for their integration into high-performance optoelectronic devices.



2-D COF PROPERTIES: EXPERIMENTS vs CALCULATIONS

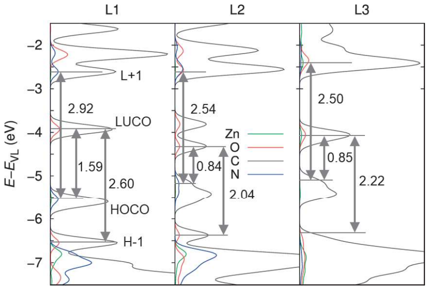
STRUCTURAL PROPERTIES



The remarkable agreement between the experimental (top) and simulated (bottom) IR spectra and XRD patterns, especially in the high frequency regions (υ > 1500 cm^{-1}) of the IR spectrum , and the XRD patterns located at 6-10º, validated the suitability of our COF monolayer model (L1) to reproduce the structural features of the PDI-ZnP COFs.

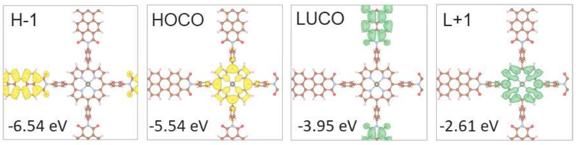
ELECTRONIC STRUCTURE

Projected Density of States (PDOS)

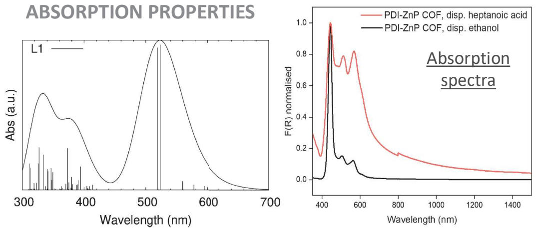


HOCO is mainly localized on the porphyrin moiety, the LUCO is predominantly located in the PDI region, thus leading in principle to a marked ZnP-to-PDI charge transfer (CT) character. The resulting HOCO-LUCO gap was equal to 1.59 eV. Energy gaps of the two COF components, in the case of PDI it corresponded to the H-1→LUCO gap with an estimated value of 2.60 eV, whereas for ZnP it corresponded to the HOCO→L+1 gap with a value amounting to 2.92 eV.

Frontier crystalline orbital (CO) shapes



ABSORPTION PROPERTIES



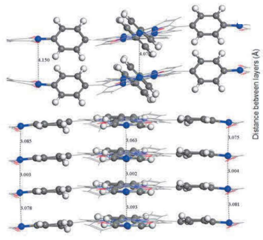
The overall shape of the experimental (right) absorption spectrum is well reproduced by the simulated spectra of the monolayer (L1) (left panel).

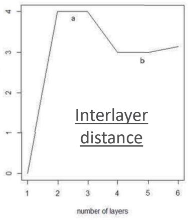
Both spectra are dominated by three main absorption bands, the first one (located at 523 nm) is attributed to the PDI π→π* transitions, being again in perfect agreement with the PDI absorption bands observed at 520 nm in previous studies.[2] The higher energy bands centered at 373 and 323 nm are related to PDI and ZnP transitions.

STACKING EFFECTS IN MULTILAYERED COFs

STRUCTURAL PROPERTIES

The Figure on the right represents the evolution of the COF structures due to the stacking of layers, with the lateral view of L2 and L4 multilayered systems.

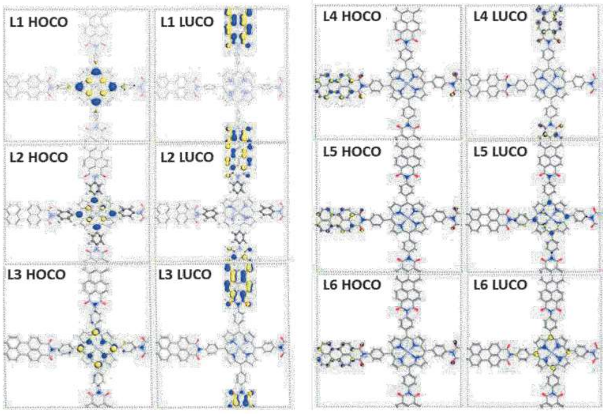




For the two- or three-stacked layers, the benzene linkers are rotated out of the COF original plane, increasing the distance between layers up to approximately 4 Å. However, when increasing up to four layers the large number of available degrees of freedom decreases, thus promoting the formation of a globally flat structure and shrinks the interlayer COF distances to 3.1 Å.

ELECTRONIC STRUCTURE

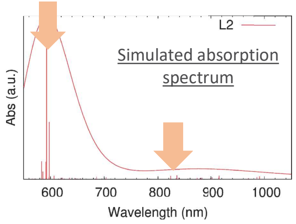
Frontier CO shapes



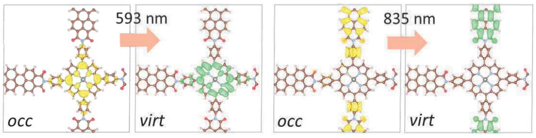
From 1 to 3 stacked layers, HOCO is predominantly located in the ZnP region, while LUCO is localized within the PDI units. When the number of stacked layers increases to 4 both HOCO and LUCO are now located in the PDI zone. Lastly, from 5 layers onwards, HOCO and LUCO exchange their positions with respect to the cases with fewer layers, *i.e.*, HOCO moves to the PDI area, while LUCO is delocalized along the ZnP region.

ABSORPTION PROPERTIES

L2 simulated spectrum showed that the lowest energy bright absorption bands corresponded to PDI π→π* transitions located at 835 nm, followed in energy by the ZnP π→π* transitions located at 593 nm, thus demonstrating that stacking leads to a pronounced enhancement of porphyrin-dominated absorption bands.



Main occupied-to-virtual CO transitions



CONCLUSIONS

Herein, a joint theoretical and experimental study of a novel Zn-porphyrin-perylene based COF displaying stacked structures due to columnar growth was carried out. The 2D-COF exhibited low inter-node planarity, a marked VIS absorption associated to the perylene group, a pronounced porphyrin-to-perylene CT behavior, and strong thermal stability. Then, the few layer models (2-3) revealed that the columnar growth of the COF layers is mainly governed by AA stacking interactions, within large interlayer distances due to the torsion of the benzene linkers. However, when a fourth PDI-ZnP-COF layer is added, steric impediment results in a globally planar layered structure where COF layers are closely packed with enhanced interlayer orbital overlap, which translated to a band gap reduction, exchange of HOCO and LUCO positions on perylene and porphyrin fragments, respectively; thus interchanging the CT directionality towards the porphyrin, and to an absorption dominated by the porphyrin group. To sum up, the results demonstrated the potential of stacking COFs combining functional building blocks to finely tune their structural and opto-electronic properties, thus being able to target multiple functions.

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[2] *J. Polym. Sci. Part A Polym. Chem.* **2009**, *47*, 6280–6291

ACKNOWLEDGEMENTS

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Agencia Estatal de Investigación - PID2022-142405OB-I00

Systematic Preparation of Processable Dispersions of Electroactive Covalent Organic Framework Nanosheets by Exfoliation

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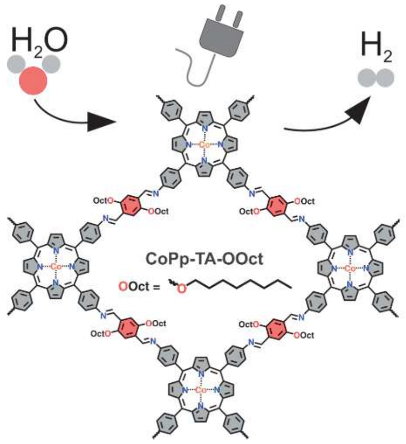
Abstract:



A series of covalent organic frameworks constructed from 5,10,15,20-tetrakis(4-aminophenyl)porphinato]cobalt(II) and the functionalized benzene dialdehydes 2,5-dihydroxyterephthalaldehyde (TA-OH), 2,5-dihexoxyterephthalaldehyde (TA-OHex), and 2,5-dioctoxyterephthalaldehyde (TA-OOct) was prepared by solvothermal synthesis. Previous studies showed, that attachment of side chains to the COFs backbone can facilitate the solvent-assisted exfoliation.[1] Within this contribution, we present the use of time-dependent UV-Vis spectroscopy to rationalize the choice of solvent for the exfoliation procedure. From the time dependent extinction in the UV-Vis spectra, the colloidal stability of the nanosheets can be determined on the one hand and on the other hand the non-resonant region provides insights into the agglomeration of nanosheets within solution. This analysis reveals that isopropanol is the most suitable solvent for the exfoliation procedure. Statistical analysis of the atomic force micrographs of the exfoliated fraction deposited on freshly cleaved mica verifies that we obtain thin nanosheets with an average thickness of 20-25 nm. These sheets form stable dispersions, which can be used to align the obtained COF-Nanosheets on graphene modified carbon paper via the Langmuir-Blodgett method. The modified carbon paper can be used as an electrode for the elechtrochemical synthesis of hydrogen from H_2O under alkaline conditions.

References

[1] A. De, A. Schneemann, *et al.* Chemistry of Materials, 35 (2023) 3911 – 3922.

Anodic electrocatalysts based on group VI transition metals for water oxidation and hydrogen generation

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[2]Institut de Chimie Moléculaire et des Matériaux d'Orsay, ICMMO, CNRS, Paris-Saclay University, 17 avenue des sciences, 91400 Orsay, France
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To accelerate the transition to sustainable energy, this research project aims to make green hydrogen production more **economical** and **viable** by developing alternative electrocatalysts for **proton exchange membrane (PEM) water electrolysers**. Currently, these electrolysers rely on expensive and **rare precious metals** such as **platinum** and **iridium**. Our project aims at replacing them by abundant element-based catalysts, using **oxo-metallate matrices** doped with **active catalytic units** (**cobalt** for the oxygen evolution reaction and **$\{Mo_3S_4\}$** for the hydrogen evolution reaction). This approach exploits the stability and advantageous electrochemical properties of oxo-metallate matrices in an acidic medium, paving the way for **more accessible and competitive green hydrogen production.** [1,2]

Why using Hydrogen?

- **Decarbonization of industry**

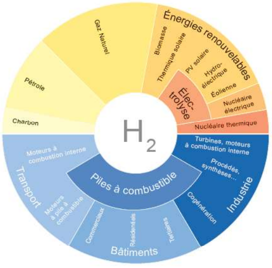
H_2 is massively used in industry

- **Renewable energy storage**

Conversion of electricity produced from renewable ressources into chemical energy (H_2) in a reversible manner

- **Mobility**

Hydrogen as a fuel for electric vehicles (heavy mobility)



Water electrolysis, how does it work?

Water electrolysis reaction:

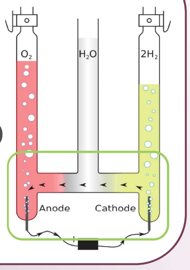
$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)}$$

Cathode: Hydrogen Evolution Reaction **(HER)**

$$2H^+ + 2e^- \rightarrow \mathbf{H_{2(g)}}$$

Anode: Oxygen Evolution Reaction **(OER)**

$$2H_2O_{(l)} \rightarrow \mathbf{O_{2(g)}} + 4H^+ + 4e^-$$



What is a PEM water electrolyzer [3] ?

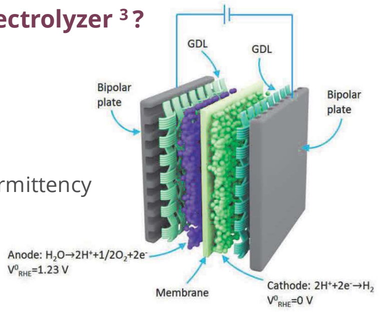
➢High purity of H_2 (99,999%)

Green Hydrogen

➢Compatible with power intermittency

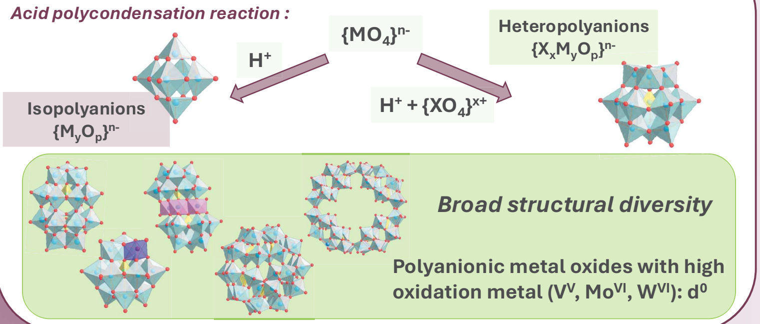
➢Acidic media, pH < 1

➢Electrocatalysts: **IrO_2**, **Pt/C**



➔ Materials stable at pH < 1

What is a PolyOxoMetalate (POM) ?



Acid polycondensation reaction :

$\{MO_4\}^{n-}$

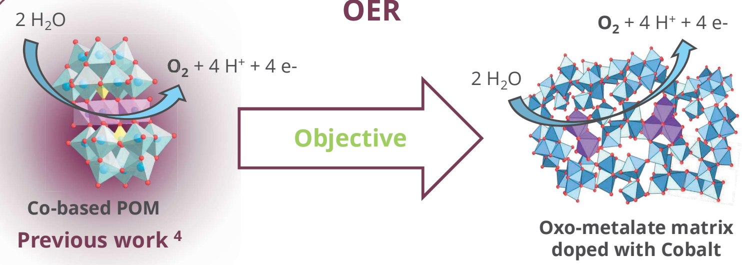
H^+ → Isopolyanions $\{M_yO_p\}^{n-}$

$H^+ + \{XO_4\}^{x+}$ → Heteropolyanions $\{X_xM_yO_p\}^{n-}$

Broad structural diversity

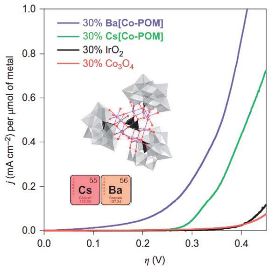
Polyanionic metal oxides with high oxidation metal (V^V, Mo^{VI}, W^{VI}): d^0

OER

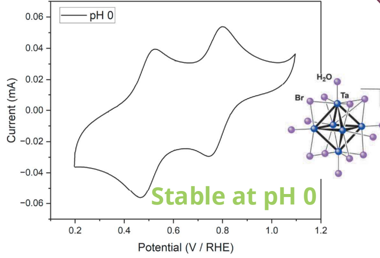


Co-based POM
Previous work [4]

Oxo-metalate matrix doped with Cobalt

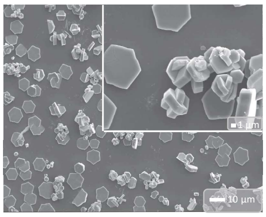


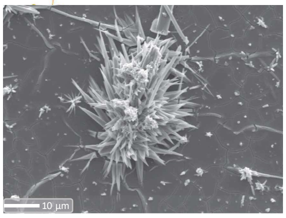
Linear Sweep Voltammetry of {Co-POM}/CP blend [5] in H_2SO_4 , 1M.

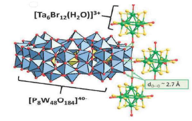


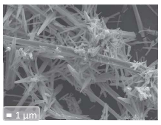
Cyclic Voltammetry of $\{Ta_6Br_{12}(H_2O)_6\}^{2+}$, 1mM in $HClO_4$, 1M.

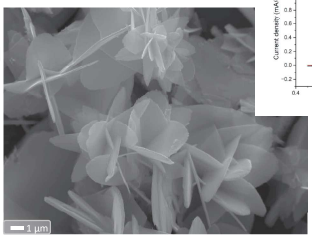
Cluster – POM interaction [6] ➔ Electrocrystalisation

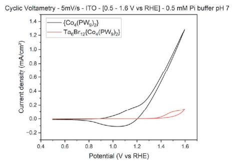


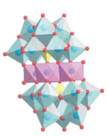












What's next?

Extend the fundamental knowledge to cobalt-based POM

Stability and electrochemical activity for OER

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Tuning the Metal Node Composition of Metal Organic Framework for Solar-Driven Hydrogen Evolution

Sanchari Dasgupta[1], Ashish Kumar Kar[1], Georges Mouchaham[1], Christian Serre[1]

[1] *Institut des matériaux poreux de Paris, Ecole normale supérieure, ESPCI Paris, CNRS, PSL University.75005 Paris, France.*

Abstract:

Harvesting renewable energy is very important to mitigate the growing demand for fossil fuels, and hydrogen is one of the most promising solutions for that purpose. Presently, the hydrogen production technologies in industries are mostly carbon-intensive. The carbon-free process, electrolysis, is a greener approach to producing hydrogen, but the upscaling demands a high cost. To overcome these limitations, photocatalytic hydrogen generation is one of the sustainable methods.[1]

The development of economically affordable hydrogen production by photocatalysis depends on several factors. The strategic design of the photocatalyst plays a crucial role in this purpose. The most important aspects for designing a catalyst are their (i) ability to absorb in the visible range with efficient charge separation, (ii) appreciable lifetimes of charge carriers, and (iii) the proper alignments of conduction and valence bands.[2]

Among the variety of photocatalysts explored to date, metal-organic frameworks (MOFs) with tunable band alignments and band gaps secure a promising position for photocatalytic hydrogen production. In the context of the MOF2H2, our objective is to obtain a stable MOF-based photocatalyst for solar-driven hydrogen production.

In this stage, a titanium MOF, comprising a $Ti_{12}O_{15}$ inorganic building unit and a tetracarboxylate organic linker, has been selected because of its high stability and photoactivity, which will have a positive impact on the photocatalysis.[3,4] Transitional metal ions with various compositions have been doped into the metal nodes to explore their effect on the band gap and photocatalytic activity. A correlation between the amount of doped metal ion and photocatalytic activity has been explored thereafter.

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Tuning the Metal Node Composition of Metal Organic Framework for Solar-Driven Hydrogen Evolution

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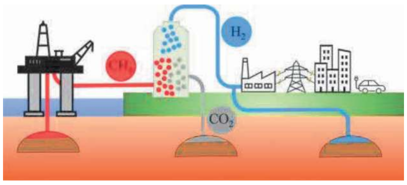
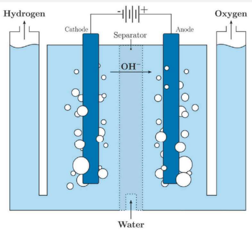
State of Art

Carbon Intense Method



Industrial Process

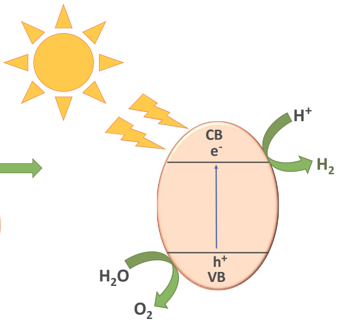
Electrolysis



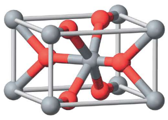
Green H_2

Solution

Photocatalytic Hydrogen Generation



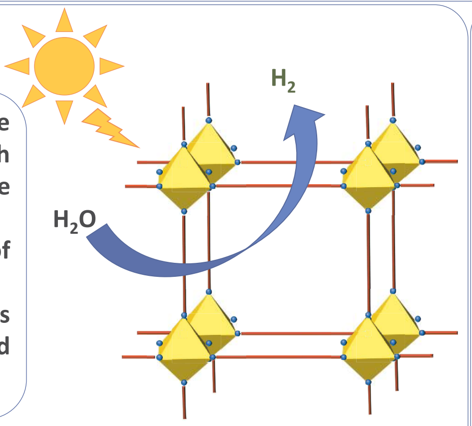
One of the most efficient benchmark photocatalyst reported so far



Absorbs in the UV-region only

Objective

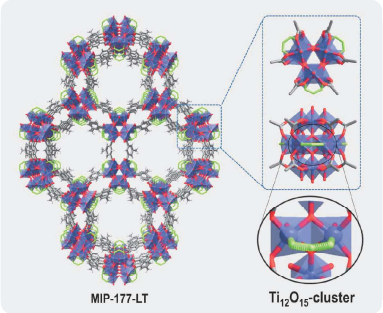
- Ability to absorb in the visible range with efficient charge separation,
- Appreciable lifetimes of charge carriers,
- The proper alignments of conduction and valence bands.



Metal Organic Frameworks(MOFs)

Selection of MOF

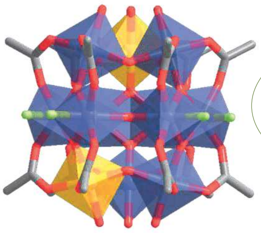
MIP-177(LT): (MIP: Materials from Institute of porous solids of Paris, LT: Low Temperature)



High stability and photoactivity

Positive impact on the photocatalysis

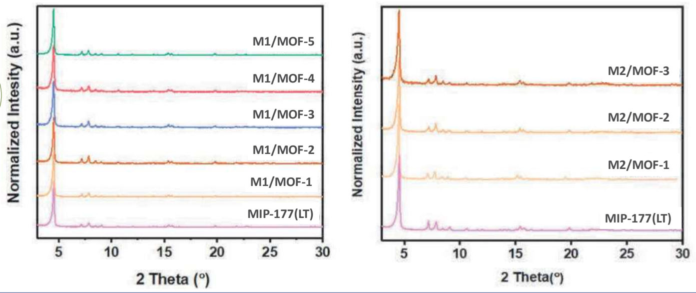
Modification to MIP-177(LT): Doping of metal ion to the inorganic building unit of MOF



$Ti_{(12-x)}M_xO_{15}$-cluster

Transitional Metal
Metal 1(M1)
Metal 2 (M2)

PXRD



EDX Analysis

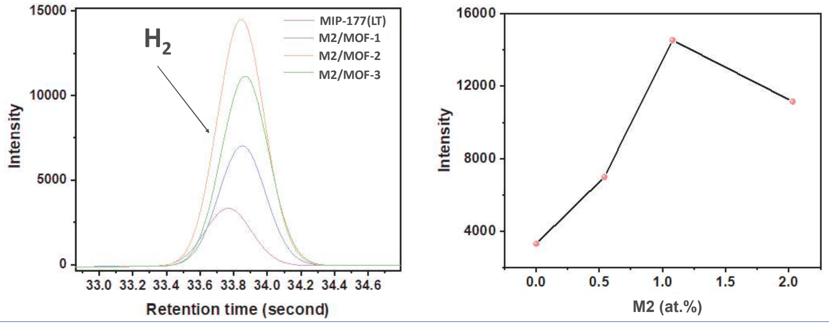
At.% of doped metal considering Ti

- M1: 1-25 at.%
- M2: 0.5-3 at.%

Hydrogen Evolution Reaction

EDX Results	Atomic%	
	M2	Ti
MIP-177(LT)	00	100
M2/MOF-1	0.54±0.2	99.46±0.2
M2/MOF-2	1.08±0.45	98.92±0.45
M2/MOF-3	2.03±0.86	97.97±0.86

Micro-GC Result



Conclusions

- Two different transitional metal ions have been doped successfully to MIP-177(LT).
- The hydrogen evolution reaction has been studied using M2 doped MIP-177(LT). It has been observed that ca. 1 at.% showed the highest oxygen evolution.
- The correlation between hydrogen evolution and M2 doping follows a bell-shaped pattern.

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THANK YOU

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