

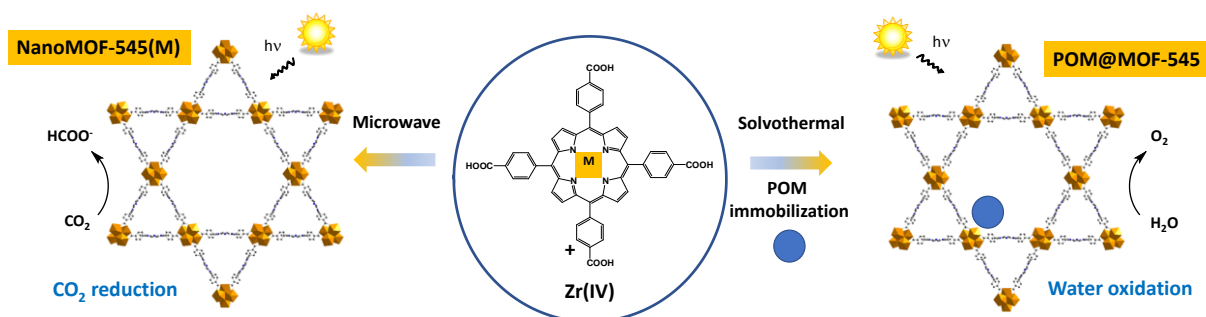
# Porphyrin-based metal-organic frameworks: from synthesis to characterization and applications in photocatalysis

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Porphyrins are a family of molecules which exhibit versatile functionalities and properties allowing a variety of applications in biomimetic catalysis, electro- or photocatalysis and biomedicine. They possess several key features that make them particularly attractive in the field of photocatalysis: i) strong visible-light absorption, ii) long-lived excited states, iii) high triplet quantum yield, iv) possible modulation of their redox, photophysical, and catalytic properties via their metalation. In a photocatalytic system, they can thus play the role of photosensitizer and/or molecular catalyst. The last few years have seen huge growing interest in the use of these active molecules in the synthesis of porous solids for photocatalytic purposes since their immobilization may bring increased chemical stability and tunable selectivities while allowing easier recyclability when compared to homogenous photocatalysis conditions. In this context, the development of porphyrin-based Metal-Organic Frameworks (MOFs), using porphyrins as linkers, and their derived composites containing additional guest species in their pores, appears particularly attractive as it can lead to multifunctional materials. [1]

In this presentation, our contribution in the field of porphyrin-based MOFs will be described in the larger context of other researches carried in the field. Firstly, we evidenced the structure-directing role of the  $PW_{12}O_{40}^{3-}$  polyoxometalate (POM) in porphyrin-based MOF synthesis whereby it promotes the formation of the kinetic topology versus the thermodynamic one. [2a] Secondly, we combined the metalation of the porphyrin linkers and the synthesis under micro-wave conditions of nanosized (150-200 nm) materials to reach one of the highest formate productions reported so far for the photocatalytic reduction of  $CO_2$  under visible light irradiation with a MOF-based catalyst. [2b] Finally, in the context of the photocatalytic oxidation of water, we immobilized a sandwich-type Co-containing POM in the hexagonal channels of the Zr(IV) porphyrinic MOF-545 hybrid framework. This noble-metal free composite exhibits a high photocatalytic activity and good stability for visible-light-driven water oxidation. [2c] This work was further extended to the shaping in thin films of the POM@MOF-545 composite on ITO supports using electrophoretic or drop-casting methods. [2d]



Synthetic strategies leading to MOF-545 derivatives for CO<sub>2</sub> reduction or water oxidation

## REFERENCES

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