HORIZON 2020

# Defective Titanium Metal-Organic Frameworks

## Reporting

Project Information

**DefTiMOFs**

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Project website

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Project closed

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UNIVERSITAT DE VALENCIA
Spain

## Periodic Reporting for period 1 - DefTiMOFs (Defective Titanium Metal-Organic Frameworks)

**Reporting period:** 2019-05-13 to 2021-05-12

### Summary of the context and overall objectives of the project

Defect engineering of Metal-Organic Frameworks (MOFs) - hybrid porous compounds composed of metal ions or metal clusters linked by multidentate organic ligands – has recently acquired a tremendous interest since defects have direct implication in the material's properties, such as mechanical and thermal stability, photo-stimulation, transport and storage performance, chemical reactivity and porosity, and thus are strongly related with the material function and subsequent application. Despite defect engineering being a versatile tool to modify MOFs' properties, the synthetic control of defected MOFs is still a challenging goal and defect engineering of MOFs is mostly limited to Zr6-based MOFs.

Understanding the formation of defects at a molecular level and establishing a direct structure-function correlation is imperative for the application of defected MOFs. Elucidation of the type of defects, their concentration and spatial distribution within the framework at a molecular level is still a challenge for conventional characterization techniques and the handful of studies available are still limited to UiO-66 Zr6-MOFs derivatives.

Titanium-based MOFs - which are photoactive and have superior structural and chemical stability compared to other MOFs - are emerging in the literature, but their defect chemistry remains almost unexplored. Titanium has at the same time low cytotoxicity, a lower density than zirconium, and it is abundant. Importantly, TiO2 has been recently classified as a possible carcinogenic to humans by the International Agency for Research on Cancer, and its replacement in diverse applications might be achieved by the design of biocompatible Ti-MOFs.
The objective of DefTiMOFs is to establish fundamental synthetic platforms that guide defect engineering beyond Zr6-based UiO MOFs. By controlling defect chemistry at a molecular level, particle size and surface chemistry of Titanium MOFs during synthesis, DefTiMOFs aims to provide the base of knowledge to anticipate Ti-MOFs properties based on the synthetic conditions and to elucidate their defect-to-function correlation in the context of environmentally relevant applications such as sustainable energy (catalysis and photocatalysis) and water harvesting from air.

## Work performed from the beginning of the project to the end of the period covered by the report and main results achieved so far

DefTiMOFs has combined the novel concept of High-Throughput (HT) screening of coordination modulation conditions of Ti-MOFs with a set of novel characterisation techniques using synchrotron radiation and has elucidated the defect chemistry of Ti-MOFs, providing protocols for their synthetic control. Additionally, DefTiMOFs has studied the structure-to-function correlation of defected materials for applications of environmental relevance.

By using an HT approach this project has studied the role of several variables during the synthesis of Ti-MOFs and through the correlation of these variables with the resultant MOFs properties, DefTiMOFs has developed systematic methods to introduce structural defects in a series of highly stable functionalised Ti(IV)-MOFs in a controllable manner. Through thoughtful characterization of the resultant MOFs, the formation of short-range ordered missing clusters in certain MOFs' structures and under certain conditions has been identified.

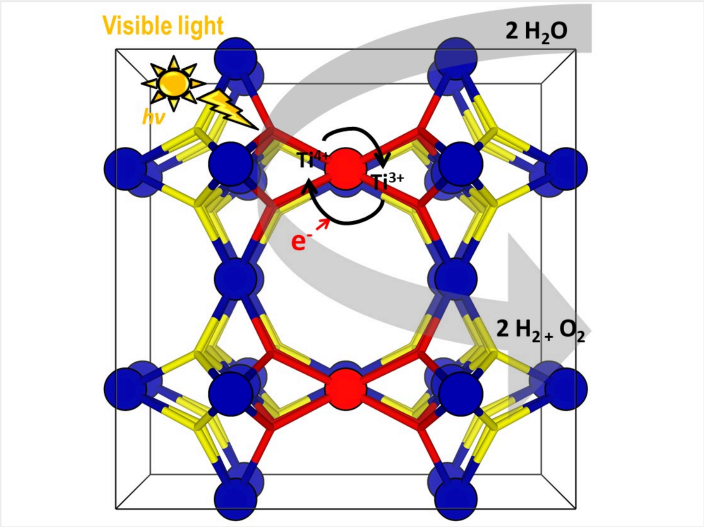
The materials' properties (crystallinity, size, morphology, modulator's incorporation, defectivity, porosity, stability and bandgap) have been rationalised with the synthetic conditions, providing knowledge to control the features of the materials such as size and defectivity.

Our published results show that the degree of defects (up to 40 molar per cent) can be tuned both by the modulator's choice and by fine-tuning the synthetic conditions such as linker to metal ratio or the modulator's concentration or acidity. The defective Ti-MOFs are highly crystalline and their defective nature is embodied in a drastic increase in porosity, with total pore volumes 1.5 times higher than the pristine MOF. Importantly, the porosity features are directly related to the synthetic conditions and the degree of incorporation of defects can be tuned by their modification, which will lead to the 'a la carte' syntheses of these defective Ti-MOFs with variable properties.
Understanding the chemical reactivity of these biocompatible Ti-MOFs as a function of the type of defects and their spatial distribution within the framework has been key for their successful application towards heterogeneous catalysis based on the combination of open vacant sites (missing and truncated linkers) working cooperatively with the modulators functionality and photocatalysis by tuning the bandgap through open metal sites and modulator´s incorporation, with a 5-fold increase in comparison to the pristine material. The MOFs' bandgap decreased with the incorporation of certain functionalised modulators as defect-compensating ligands. The performance of these defective Ti-MOFs as heterogeneous catalysts and as photocatalysts is related to their defective nature among other related properties.

Defective structures functionalised with hydrophobic modulators have been tested for water adsorption in conjunction with the defect-free MOF and analogue non-functionalised defective MOFs. Although water adsorption has been shifted through pore functionalization, the high mesoporosity of the MOFs results in hysteresis desorption behaviour is not ideal for water harvesting devices.

## Progress beyond the state of the art and expected potential impact (including the socio-economic impact and the wider societal implications of the project so far)

To the best of our knowledge, evidence of ordered missing clusters through common characterisation techniques has only been reported for Zr6 based MOFs, which together with their high tolerance to defects has made them the benchmark material regarding MOF's defect chemistry. We have developed versatile and reproducible controls for the controllable synthesis of defective Titanium MOFs structures with short-range ordered missing clusters, observable by common characterisation techniques. These results will be an important contribution to the field and a breakthrough for both defective and Titanium MOFs so that defect engineering can become a controllable tool for effective modulation of the structural and chemical properties of a broad range of materials.
The knowledge gained by this action will be applied to design and synthesise the next generation of defective Titanium MOFs with outstanding performance working towards new materials for sustainable energy (catalysis and photocatalysis) and water harvesting from air to provide low-cost, efficient water delivery systems of implementation in developing countries with limited access to drinkable water.



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