

Structural Characterization, Optical Properties and Photocatalytic Activity of MOF-5 and its Hydrolysis Products: Implications on their Excitation Mechanism.

Supporting Information

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Figure S1

XRD pattern of dry MOF-5. MOF-5 was obtained by centrifugation from the DMF suspension and extensively washed with CHCl_3 (Sintorgan, chromatographic grade) by centrifugation and redispersion cycles. Finally, the solid was dried in a vacuum-oven at 90°C , and stored in a desiccator.

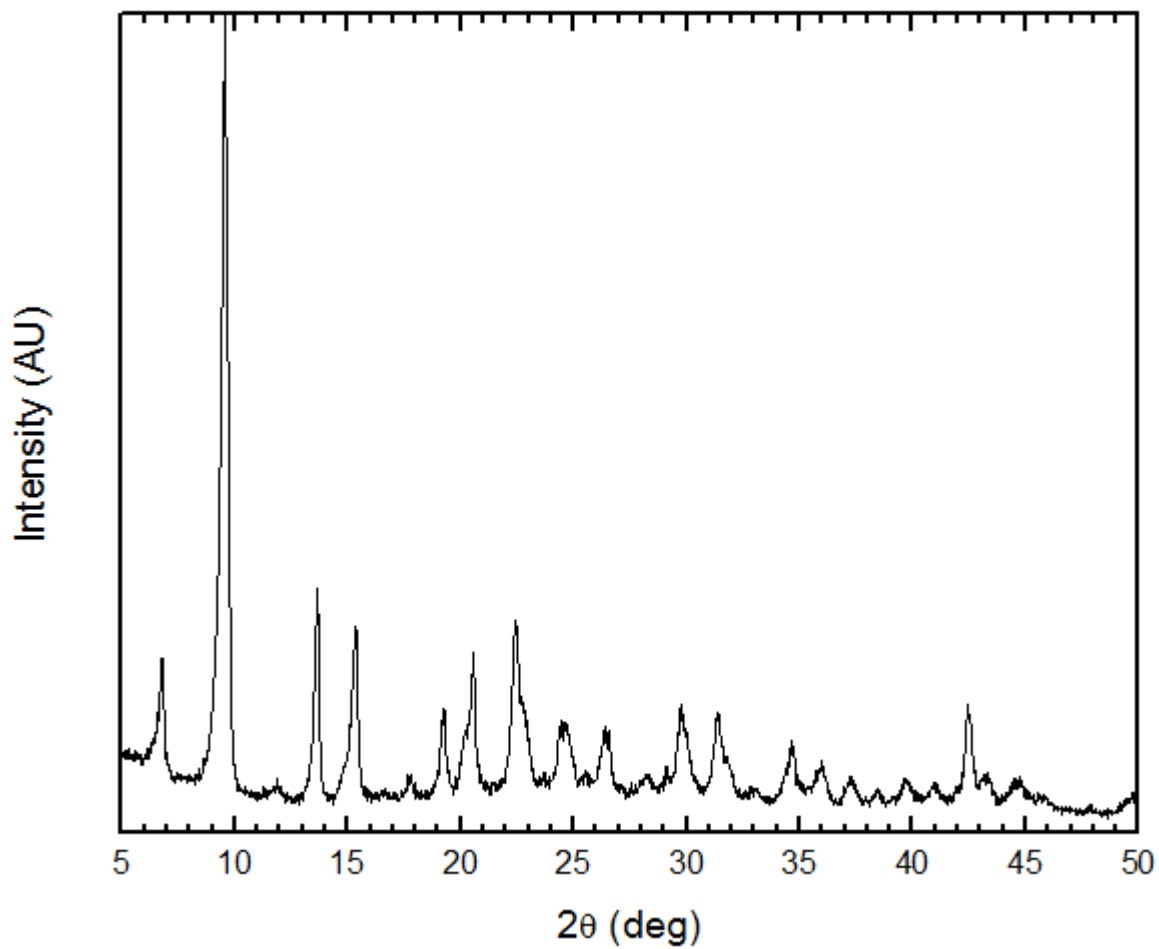
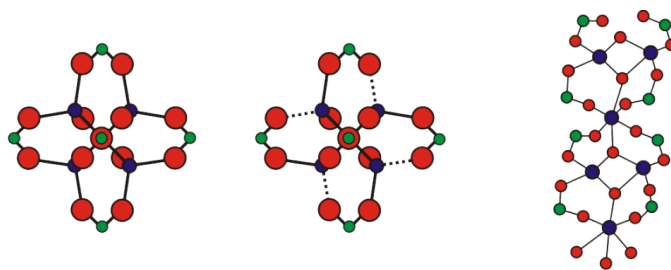
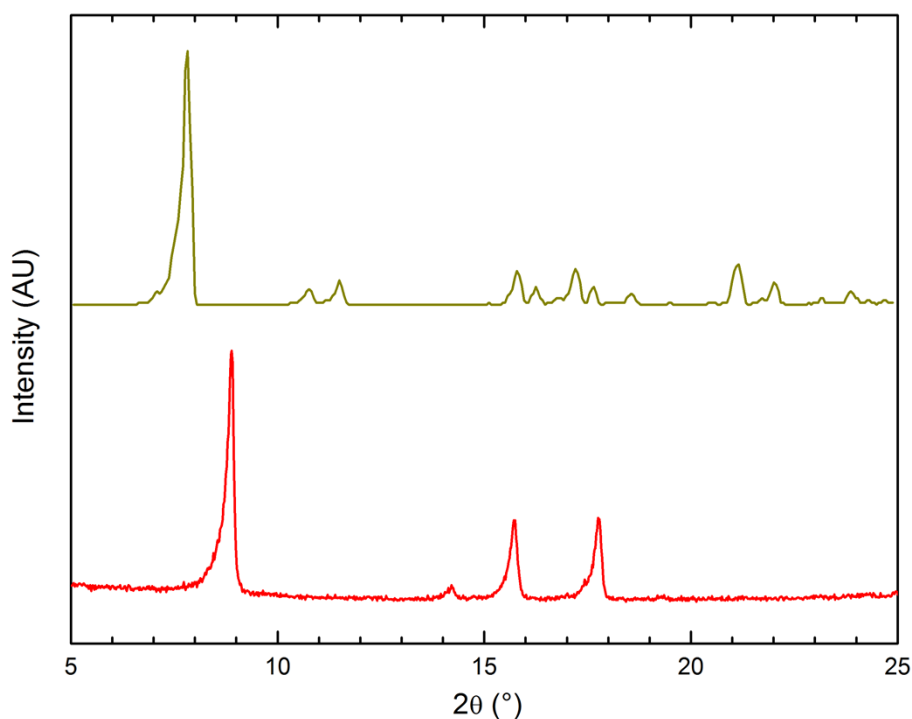


Figure S2

XRD patterns of MOF-69C (top, dark yellow, [Reference 1]) and MOF-5W (bottom, red). The structures of MOF-5, MOF-5W and MOF-69C clusters are compared below.



MOF-5 MOF-5W MOF-69C

Due to the noticeable differences between the metallic cluster morphologies, it is supposed that MOF-5 and MOF-69C cannot be in equilibrium at room temperature, as shown in S2 for MOF-5W and MOF-5. Thus, it is concluded that both phases are similar and that the main difference between them is the partial linkage of peripheral Zn-O bonds (see Scheme 1).

[1] Hausdorf, S.; Wagler, J.; Mossig, R.; Mertens, F. O. R. L. Proton and Water Activity-Controlled Structure Formation in Zinc Carboxylate-Based Metal Organic Frameworks. *J. Phys. Chem. A* **2008**, *112*, 7567-7576.

Figure S3

XRD patterns of MOF-5 (top, blue), MOF-5H (bottom, red), and the solid obtained after redispersion of MOF-5H in DMF at room temperature (middle, green). The easy interconversion between MOF-5 and MOF-5H suggest that changes in cluster morphology are unlikely.

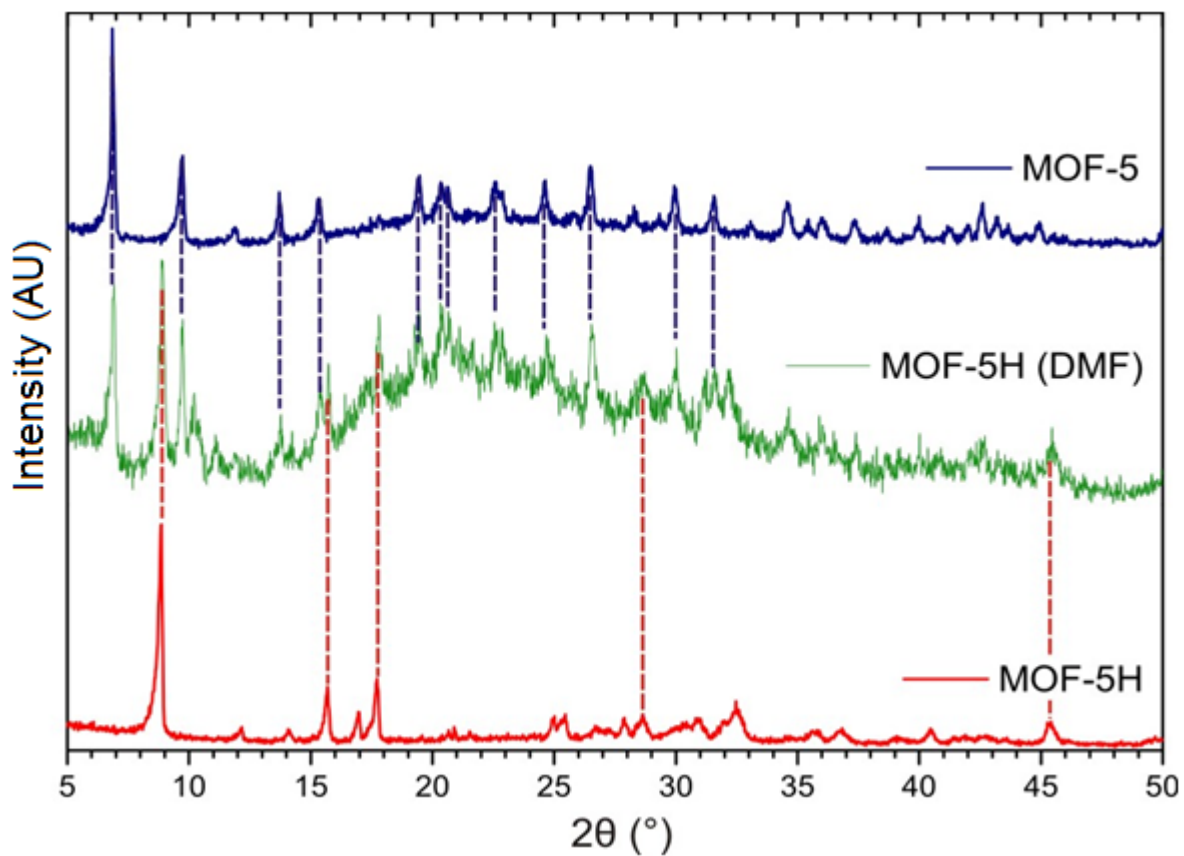
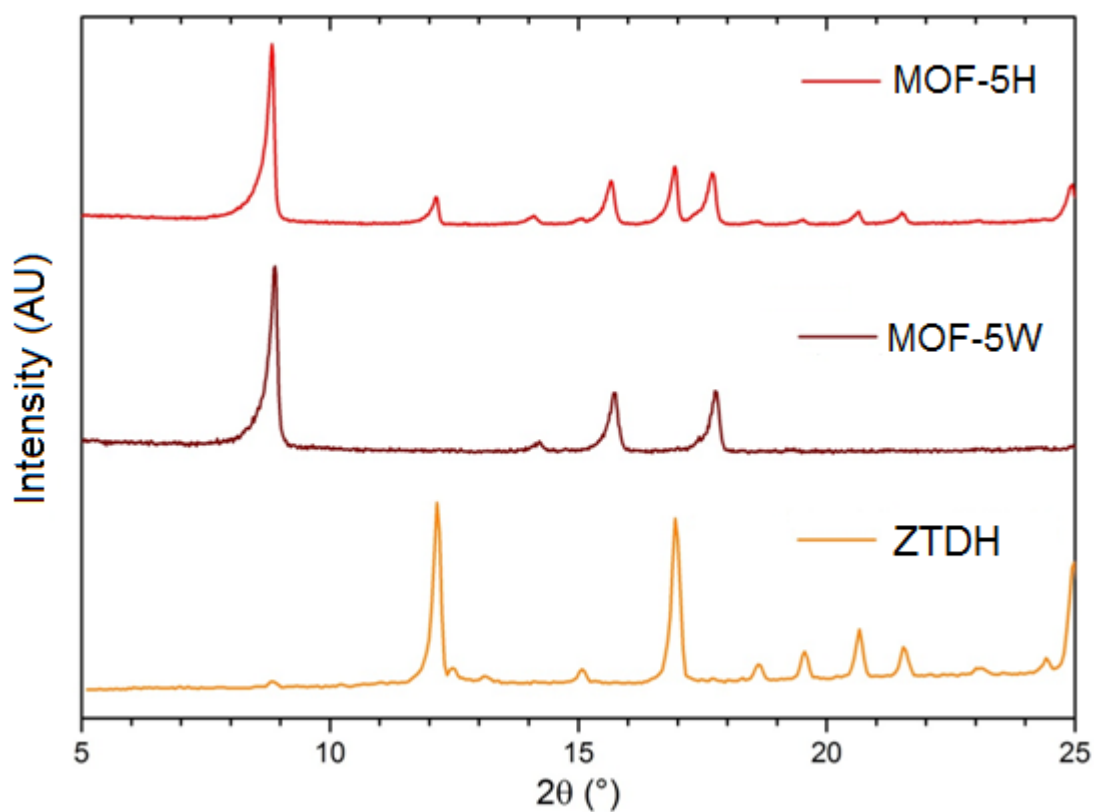


Figure S4

XRD patterns of MOF-5H, MOF-5W and ZTDH (from top to bottom), showing that MOF-5H is a mixture of MOF-5W and ZTDH. ZTDH was synthesized following the protocol proposed by Thirumurugan *et al* [Reference 2]: $\text{ZnSO}_4 \cdot 4 \text{H}_2\text{O}$ (1152 mg, Anedra), H_2BDC (664 mg, Aldrich), NaOH (320 mg, Anedra) and water (20 g) were mixed together in a closed recipient (molar ratios 1:1:2:278) and heated in a stove at 75°C during 72 h. The solid was washed twice with water and allowed to dry at room temperature in air.



[2] Thirumurugan, A.; Rao, C. N. R. 1,2-, 1,3- and 1,4-Benzenedicarboxylates of Cd and Zn of Different Dimensionalities: Process of Formation of the Three-Dimensional Structure. *J. Mater. Chem.* **2005**, *15*, 3852-3858.

Figure S5

FTIR spectra of MOF-5 and its hydrolysis products, MOF-5W and MOF-5H. Samples were prepared in the same way as for Raman analysis. It can be observed that the mode at 1435 cm^{-1} disappears after water exposure, in contrast with Raman results..

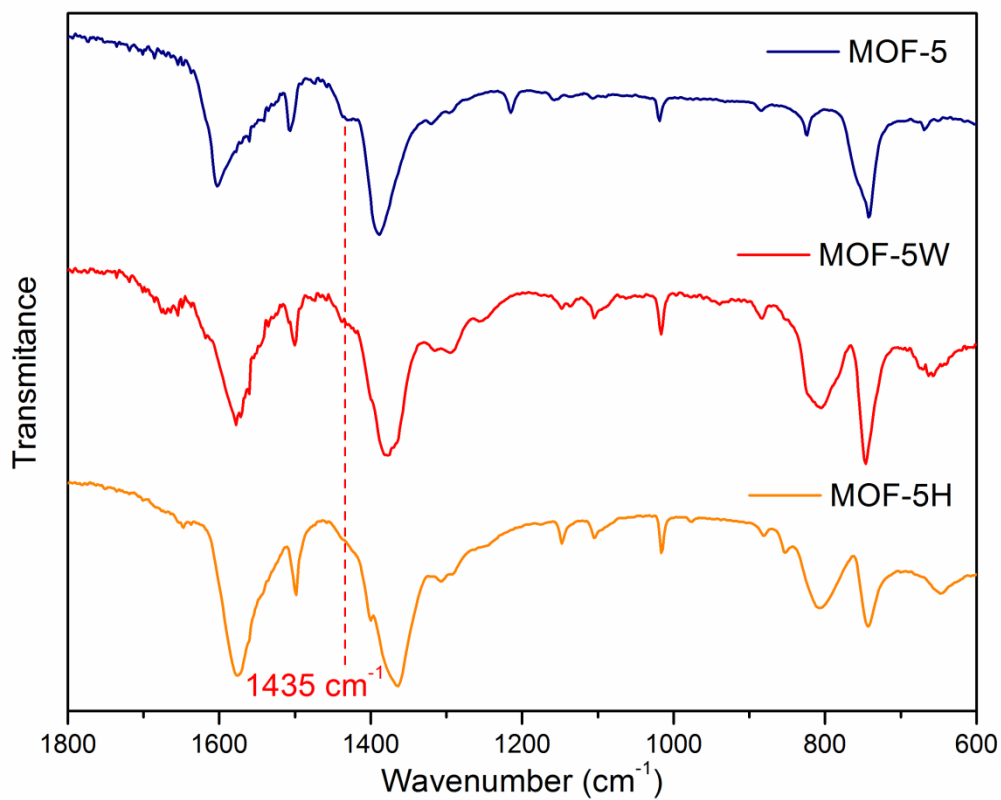


Figure S6

Absorption spectrum (1-R-T) of ZTDH. The inset shows the assessment of its optical bandgap. As discussed for MOF-5W, ZTDH is treated as an indirect semiconductor, due to the slow increment in the absorption.

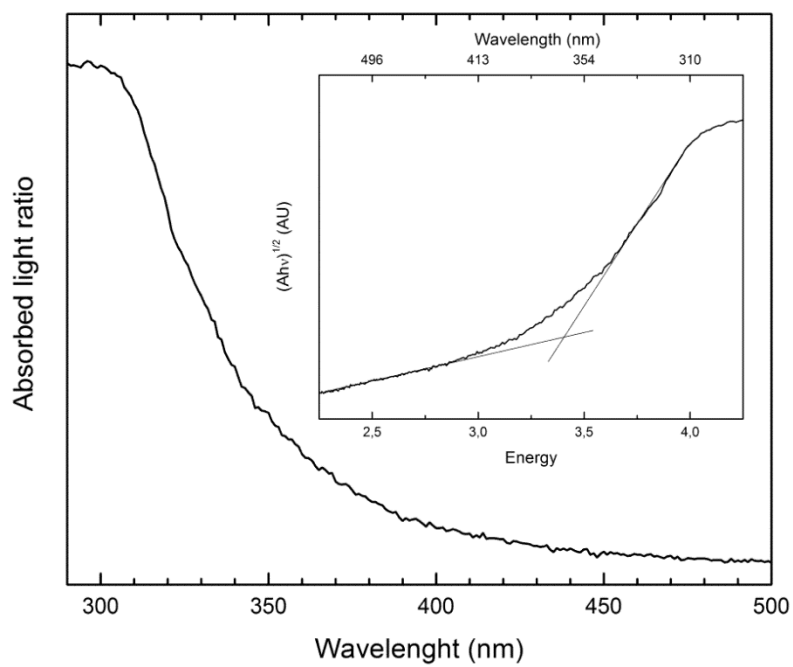


Figure S7

Absorption spectra of 60 mM (straight line) and 0.6 mM (dotted line) H₂BDC (orange) and Na₂BDC (blue) solutions (in DMF and H₂O, respectively).

