

## Probing Open Metal Sites in High Valence Metal-Organic Frameworks by *in-situ* Single Crystal X-ray Diffraction

Qi Wang<sup>1</sup>, Shuai Yuan<sup>1</sup>, Junsheng Qin<sup>1</sup>, Wenmiao Chen<sup>1</sup>, Hongcai Zhou<sup>1,2</sup>

<sup>1</sup>Department of Chemistry, Texas A&M University, College Station, TX, 77843

<sup>2</sup>Department of Materials Science & Engineering, Texas A&M University, College Station, TX, 77843

Email Contact: qiwang.chem@gmail.com

The crystallographic characterization of framework–guest interactions in metal–organic frameworks enables the location of guest binding sites and provides meaningful information on the nature of these interactions, allowing the correlation of structure with adsorption behavior. Herein, techniques developed for *in situ* single-crystal X-ray diffraction experiments on porous crystals have enabled the direct observation of CO<sub>2</sub> adsorption in the open metal site of Fe<sub>3-x</sub>M<sub>x</sub>O clusters (X=0, 1, 2) in PCN-250. PCN-250 is a metal–organic framework that can possess trivalent and bivalent metals in the cluster.<sup>1</sup> The single crystal samples were characterized before and after activation in N<sub>2</sub> at 423 K and after CO<sub>2</sub> adsorption. Interestingly, the CO<sub>2</sub> binding is stronger to the bivalent metals than to the trivalent metals, indicating orbital interaction plays a bigger role in the gas-open metal site interaction than the static electric force. To the best of our knowledge, this work is the first single-crystal structure determination of a trivalent metal–CO<sub>2</sub> interaction and the first crystallographically characterized open metal site for trivalent metals.

1. D. Feng, K. Wang, Z. Wei, Y.-P. Chen, C. M. Simon, R. K. Arvapally, R. L. Martin, M. Bosch, T.-F. Liu, S. Fordham, D. Yuan, M. A. Omary, M. Haranczyk, B. Smit and H.-C. Zhou, *Nature Communications*, 2014, **5**, 5723.