

Using a new Zr-based Metal-organic Framework to contort dimeric complexes

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Inspired by metalloenzymes in Nature, chemists have designed metal catalysts for applications in small molecule conversions and to access new chemical products. Many metalloenzymes incorporate multiple metals in a pocket that cooperate to favour substrate binding, increase turnover frequency or product selectivity.[1] With the aim of replicating this metal cooperativity in synthetic systems, binuclear complexes or small metal clusters, have been studied.[2] Metal-organic Frameworks (MOFs)[3] are open pore networks that can be tailored to site isolate and stabilise reactive metal complexes, and provide structural insight into their properties by single-crystal X-ray diffraction (SCXRD).[4] The inherent crystallinity of MOFs and the ability to incorporate secondary metals by post-synthetic metalation (PSMet)[5] has allowed “matrix isolation” and detailed structure elucidation of unprecedented, often highly reactive, organometallic species trapped inside the pores.[6] However, the characterization of small metal clusters in MOFs is rare[7] due to the challenge of synthesizing MOFs with a high density of coordinating groups that are close enough to allow the accommodation of small metal clusters.

Herein, we report a thermally and chemically stable zirconium-based Metal-organic Framework (MOF, University of Adelaide Material-1001, UAM-1001) (Fig. 1c) with a high density of free bis-pyrazolyl units (Fig. 1a) that can support mono- and binuclear metal complexes. The precursor MOF, UAM-1000 (Fig. 1b), has a high degree of structural flexibility but post synthetic modification with a bracing linker, biphenyl-4,4'-dicarboxylic acid (BPDC), partially rigidifies the MOF (UAM-1001). This allows “matrix isolation” and detailed structural elucidation of post-synthetically added dimeric complexes bound within a tetradentate binding site formed by two linkers. Dimeric species $[\text{Co}_2\text{Cl}_4]$, $[\text{Cu}_2\text{Cl}_4]$, $[\text{Ni}_2\text{Cl}_3(\text{H}_2\text{O})_2]\text{Cl}$ and $[\text{Rh}_2(\text{CO})_3\text{Cl}_2]$ (Fig. 1d) were successfully isolated in UAM-1001 and characterized by single-crystal X-ray diffraction (SCXRD). Comparison of the UAM-1001 “isolated” species with similar complexes in the solid state reveals that UAM-1001 can significantly distort the structures and enforce notably shorter metal-metal distances.

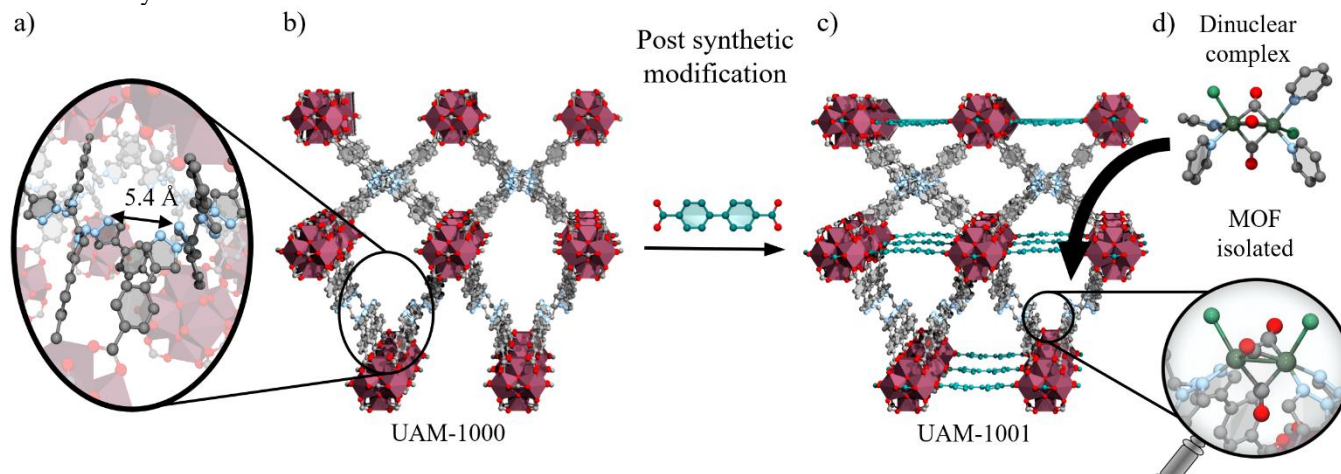


Figure 1. Synthesis and structural representations of UAM-1001. a) An enlargement of the node region of the framework UAM-1000 showing the proximity of adjacent bis-pyrazolyl units. b) Perspective view of the SCXRD structure of UAM-1000 material along the a/b axis (tetragonal unit cell). c) Perspective view of the SCXRD structure of UAM-1001 material along the a/b axis (tetragonal unit cell). d) Representation of the SCXRD structure of (top) molecular complex $[\text{Rh}_2(\text{CO})_3\text{Cl}_2]$ and (bottom) $[\text{Rh}_2(\text{CO})_3\text{Cl}_2]$ isolated in UAM-1001.

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