

## Supporting Information for

### Rationally Designed Micropores within a Metal-Organic Framework for Selective Sorption of Gas Molecules

Banglin Chen,<sup>\*,†</sup> Shengqian Ma,<sup>‡</sup> Fatima Zapata,<sup>†</sup> Frank R. Fronczek,<sup>||</sup> Emil B. Lobkovsky,<sup>⊥</sup> and Hong-Cai Zhou<sup>‡</sup>

<sup>†</sup>Department of Chemistry, University of Texas-Pan American, Edinburg, TX 78541-2999, USA. Email: [banglin@utpa.edu](mailto:banglin@utpa.edu)

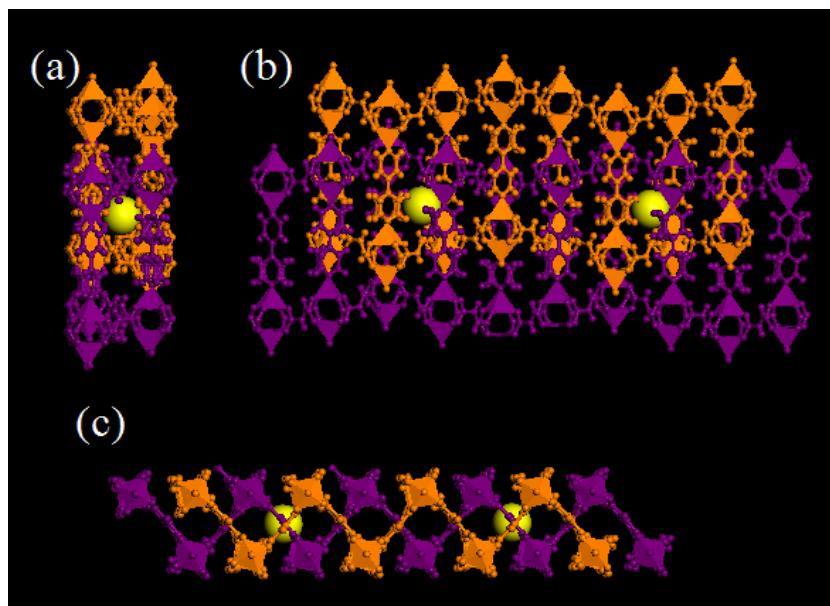
<sup>‡</sup>Department of Chemistry and Biochemistry, Miami University, Oxford, OH 45056

<sup>||</sup> Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA

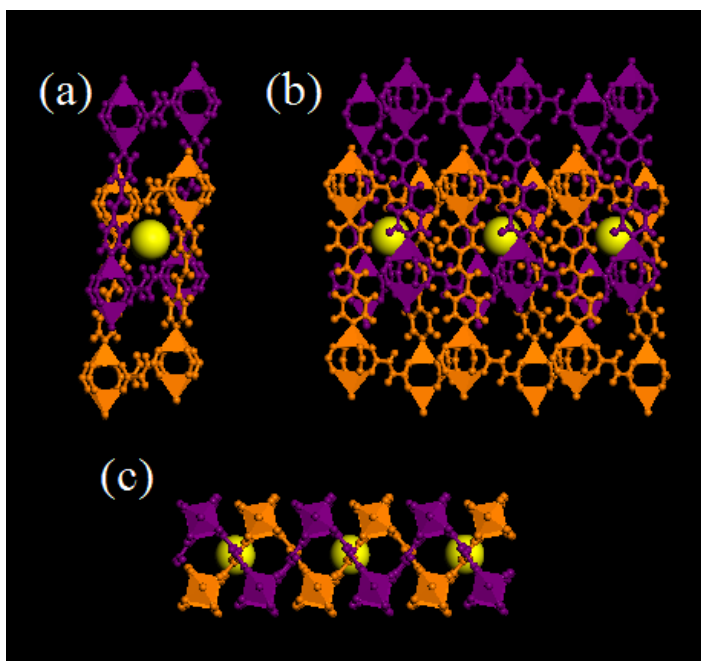
<sup>⊥</sup>Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301

**Single-crystal X-ray Crystallographic data:** Crystal data for MOF 1: Cu(FMA)(Pyz)<sub>0.5</sub>, T = 110 K, monoclinic, space group C2,  $a = 9.7192(19)$ ,  $b = 11.769(2)$ ,  $c = 7.2656(15)$  Å,  $\beta = 119.02(3)^\circ$ ,  $V = 726.8(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $d_{calc} = 1.989$  g/cm<sup>3</sup> and  $\mu(\text{Mo K}\alpha) = 2.973$  mm<sup>-1</sup>,  $2\theta_{max} = 51.60^\circ$ . Total number of reflections 1214 ( $R_{int} = 0.0996$ ),  $R_1 = 0.0528$  (1098 reflections with  $I > 2\sigma(I)$ ),  $wR2$  (all data) = 0.1382, GOF = 1.015 and 55 parameters. Crystal data for MOF 2: Cu<sub>2</sub>(FMA)<sub>2</sub>(4,4'-Bipy)·(H<sub>2</sub>O)<sub>0.5</sub>, T = 173 K, orthorhombic, space group Pnna,  $a = 23.275(5)$ ,  $b = 12.580(3)$ ,  $c = 14.073(3)$  Å,  $V = 4120.6(14)$  Å<sup>3</sup>,  $Z = 8$ ,  $d_{calc} = 1.681$  g/cm<sup>3</sup> and  $\mu(\text{Mo K}\alpha) = 2.115$  mm<sup>-1</sup>,  $2\theta_{max} = 65.16^\circ$ . Total number of reflections 7484 ( $R_{int} = 0.0641$ ),  $R_1 = 0.0370$  (3835 reflections with  $I > 2\sigma(I)$ ),  $wR2$  (all data) = 0.1120, GOF = 1.021 and 345 parameters. Crystal data for MOF 3: Cu<sub>2</sub>(FMA)<sub>2</sub>(4,4'-Bpe)·(H<sub>2</sub>O), T = 110 K, monoclinic, space group C2/c,  $a = 16.360(3)$ ,  $b = 10.753(2)$ ,  $c = 13.595(2)$  Å,  $\beta = 105.302(11)^\circ$ ,  $V = 2306.8(7)$  Å<sup>3</sup>,  $Z = 4$ ,  $d_{calc} = 1.599$  g/cm<sup>3</sup> and  $\mu(\text{Mo K}\alpha) = 1.896$  mm<sup>-1</sup>,  $2\theta_{max} = 61.60^\circ$ . Total number of reflections 3614 ( $R_{int}$

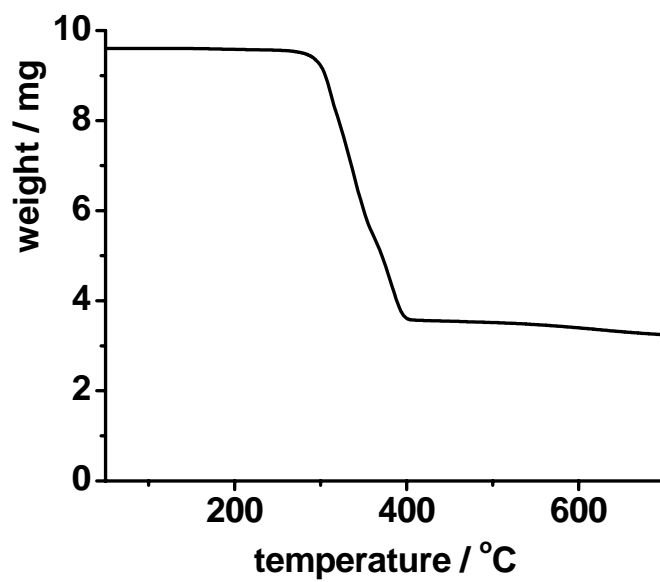
= 0.049),  $R_1 = 0.044$  (2327 reflections with  $I > 2\sigma(I)$ ),  $wR2$  (all data) = 0.092, GOF = 1.014 and 154 parameters. Crystal data for MOF **3a**:  $\text{Cu}(\text{FMA})(4,4'\text{-Bpe})_{0.5}$ ,  $T = 110$  K, monoclinic, space group  $C2/m$ ,  $a = 13.4864(9)$ ,  $b = 11.1000(8)$ ,  $c = 9.0925(7)$  Å,  $\beta = 120.335(3)^\circ$ ,  $V = 1174.78(15)$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $Z = 4$ ,  $d_{\text{calc}} = 1.519$  g/cm<sup>3</sup> and  $\mu(\text{Mo K}\alpha) = 1.855$  mm<sup>-1</sup>,  $2\theta_{\text{max}} = 68.58^\circ$ . Total number of independent reflections 2404 ( $R_{\text{int}} = 0.0352$ ),  $R_1 = 0.0324$ ,  $wR2$  (all data) = 0.0861, GOF = 1.077 and 113 parameters. Unit cells: MOF **3'** (re-hydrated MOF **3** from MOF **3a**),  $a = 16.348(3)$ ,  $b = 10.900(2)$ ,  $c = 13.515(3)$  Å,  $\beta = 105.226(12)^\circ$ ,  $V = 2323.7(8)$  Å<sup>3</sup> (195 K);  $a = 16.353(3)$ ,  $b = 11.062(3)$ ,  $c = 13.446(2)$  Å,  $\beta = 104.625(11)^\circ$ ,  $V = 2353.5(8)$  Å<sup>3</sup> (297K). MOF **3a**,  $a = 13.4864(9)$ ,  $b = 11.1000(8)$ ,  $c = 9.0925(7)$  Å,  $\beta = 120.335(3)^\circ$ ,  $V = 1174.78(15)$  (3) Å<sup>3</sup> (195 K).



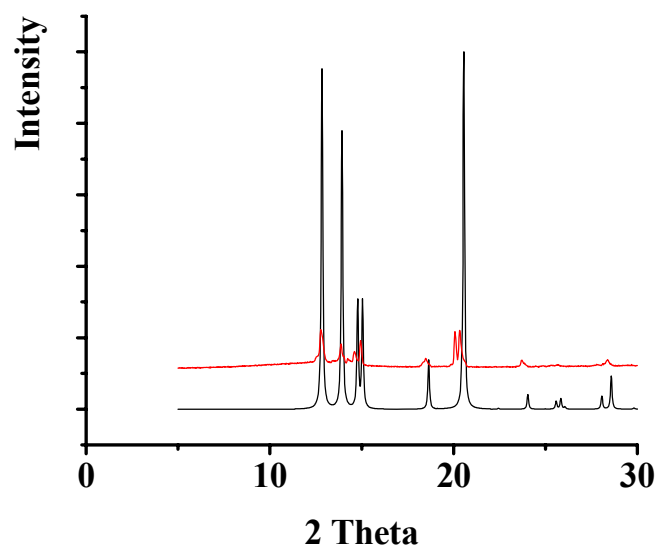
**Figure S1.** Crystal structure of MOF **2** showing pore cavities of about 3.6 Å interconnected by small pore window of about 1.4 x 1.8 Å, viewed along  $a$  (a),  $b$  (b) and  $c$  (c) axis, respectively.



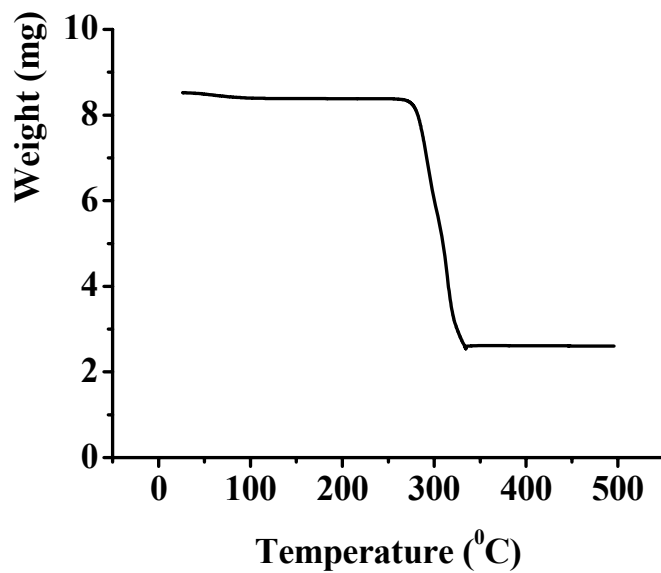
**Figure S2.** Crystal structure of MOF 3 showing pore cavities of about 3.6 Å interconnected by small pore window of about 2.0 x 3.2 Å, viewed along *b* (a), *c* (b) and *a* (c) axis, respectively.



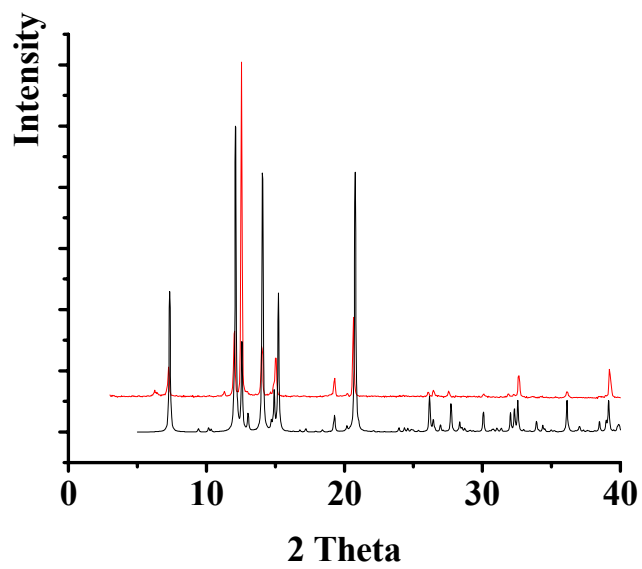
**Figure S3.** TGA plot of MOF 1



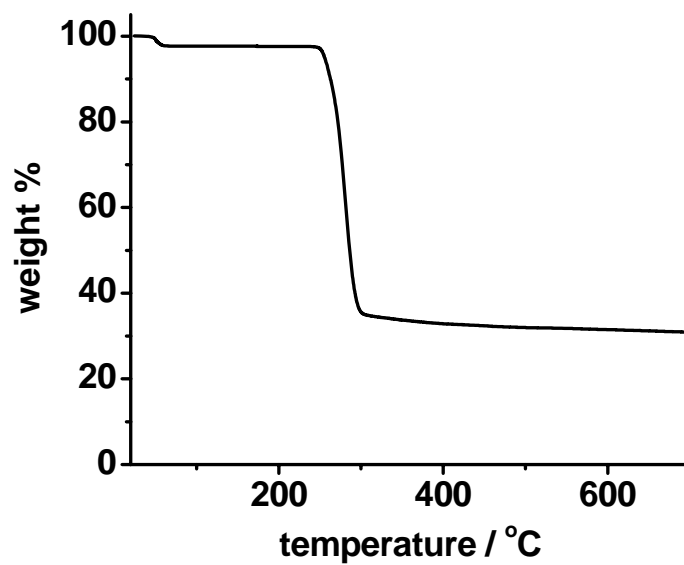
**Figure S4.** Powder X-ray diffraction (PXRD) patterns of simulated (black) and as-synthesized MOF 1 (red).



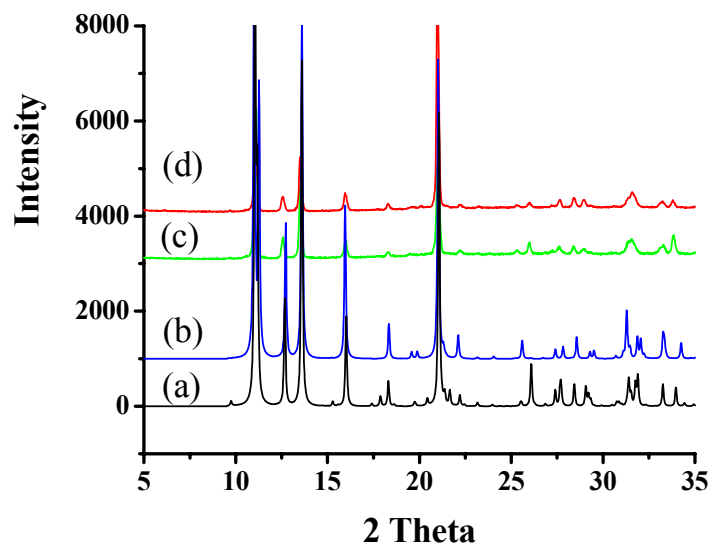
**Figure S5.** TGA plot of MOF 2



**Figure S6.** Powder X-ray diffraction (PXRD) patterns of simulated (black) and as-synthesized MOF 2 (red).



**Figure S7.** TGA plot of MOF 3



**Figure S8.** Powder X-ray diffraction (PXRD) patterns of (a) simulated MOF **3**, (b) simulated MOF **3a**, (c) dehydrated MOF **3** (**3a**) and (d) regenerated MOF **3** (the unit cells of simulated **3** and **3a** are based on those at room temperature and 195 K, respectively).