<Supporting Information>

# Isoreticular metal-organic frameworks based on a rhombic dodecahedral metal-organic polyhedron as a tertiary building unit

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Table S1. Crystal data and structure refinement for PMOF-4.

| | | |
|---|---|---|
| Empirical formula | $C_{312}\ H_{176}\ N_8\ O_{148}\ Zn_{28}$ | |
| Formula weight | 8234.97 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Cubic | |
| Space group | *Pm*-3*m* | |
| Unit cell dimensions | a = 32.366(5) Å | α = 90° |
| | b = 32.366(5) Å | β = 90° |
| | c = 32.366(5) Å | γ = 90° |
| Volume | 33906(8) $Å^3$ | |
| Z | 1 | |
| Density (calculated) | 0.403 $Mg/m^3$ | |
| Absorption coefficient | 0.509 $mm^{-1}$ | |
| F(000) | 4128 | |
| Crystal size | 0.25 x 0.15 x 0.15 $mm^3$ | |
| Theta range for data collection | 1.26 to 20.04° | |
| Index ranges | -31<=h<=31, -31<=k<=31, -27<=l<=31 | |
| Reflections collected | 93319 | |
| Independent reflections | 3136 [R(int) = 0.4530] | |
| Completeness to theta = 20.04° | 99.7 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9275 and 0.8832 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3136 / 232 / 114 | |
| Goodness-of-fit on $F^2$ | 1.693 | |
| Final R indices [I>2sigma(I)] | R1 = 0.2841, wR2 = 0.5272 | |
| R indices (all data) | R1 = 0.3461, wR2 = 0.5560 | |
| Largest diff. peak and hole | 1.473 and –1.321 $e \cdot Å^{-3}$ | |

Table S2. Crystal data and structure refinement for PMOF-5.

| | | |
|---|---|---|
| Empirical formula | $C_{288}\ H_{200}\ N_{32}\ O_{172}\ Zn_{28}$ | |
| Formula weight | 8691.16 | |
| Temperature | 100(2) K | |
| Wavelength | 1.00000 Å | |
| Crystal system | Cubic | |
| Space group | *Pm*-3 | |
| Unit cell dimensions | a = 31.102(4) Å | α = 90° |
| | b = 31.102(4) Å | β = 90° |
| | c = 31.102(4) Å | γ = 90° |
| Volume | 30086(6) $Å^3$ | |
| Z | 1 | |
| Density (calculated) | 0.480 $Mg/m^3$ | |
| Absorption coefficient | 0.864 $mm^{-1}$ | |
| F(000) | 4368 | |
| Crystal size | 0.20 x 0.10 x 0.10 $mm^3$ | |
| Theta range for data collection | 1.30 to 19.54° | |
| Index ranges | 0<=h<=20, -20<=k<=20, -20<=l<=20 | |
| Reflections collected | 18250 | |
| Independent reflections | 1748 [R(int) = 0.0929] | |
| Completeness to theta = 19.54° | 99.7 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9186 and 0.8462 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 1748 / 133 / 176 | |
| Goodness-of-fit on $F^2$ | 1.062 | |
| Final R indices [I>2sigma(I)] | R1 = 0.1101, wR2 = 0.2660 | |
| R indices (all data) | R1 = 0.1366, wR2 = 0.2876 | |
| Largest diff. peak and hole | 0.343 and –0.247 $e \cdot Å^{-3}$ | |

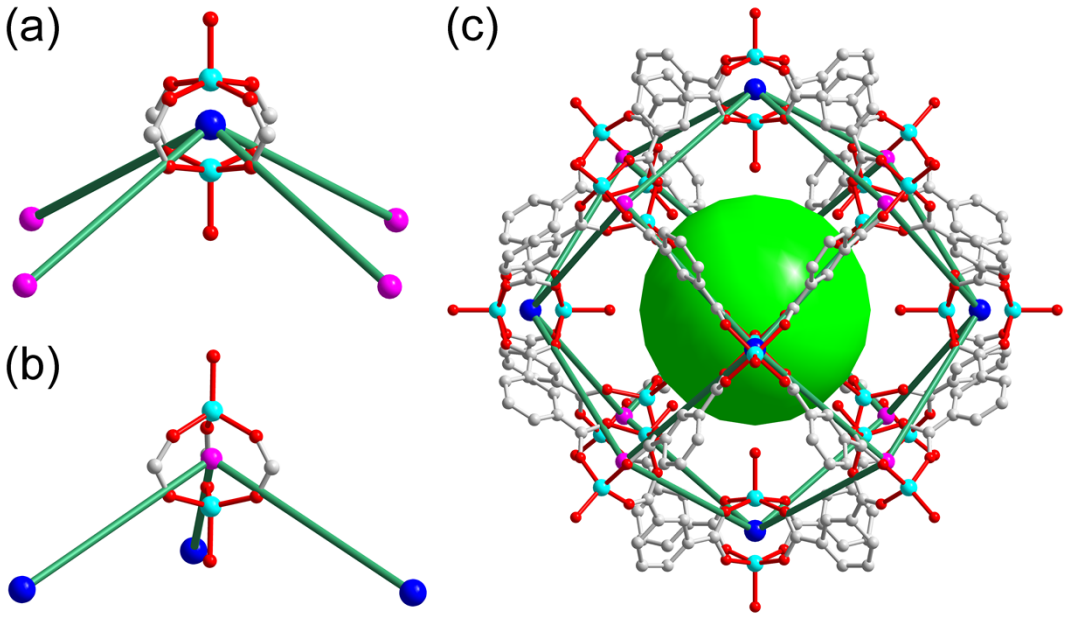


**Figure S1.** The SBUs and the TBU observed in PMOF-5. (a) A 4-c $[Zn_2(COO)_4(H_2O)_2]$ square paddle-wheel SBU, (b) a 3-c $[Zn_2(COO)_3(H_2O)_2]$ trigonal paddle-wheel SBU, and (c) a rhombic dodecahedral MOP as a TBU.

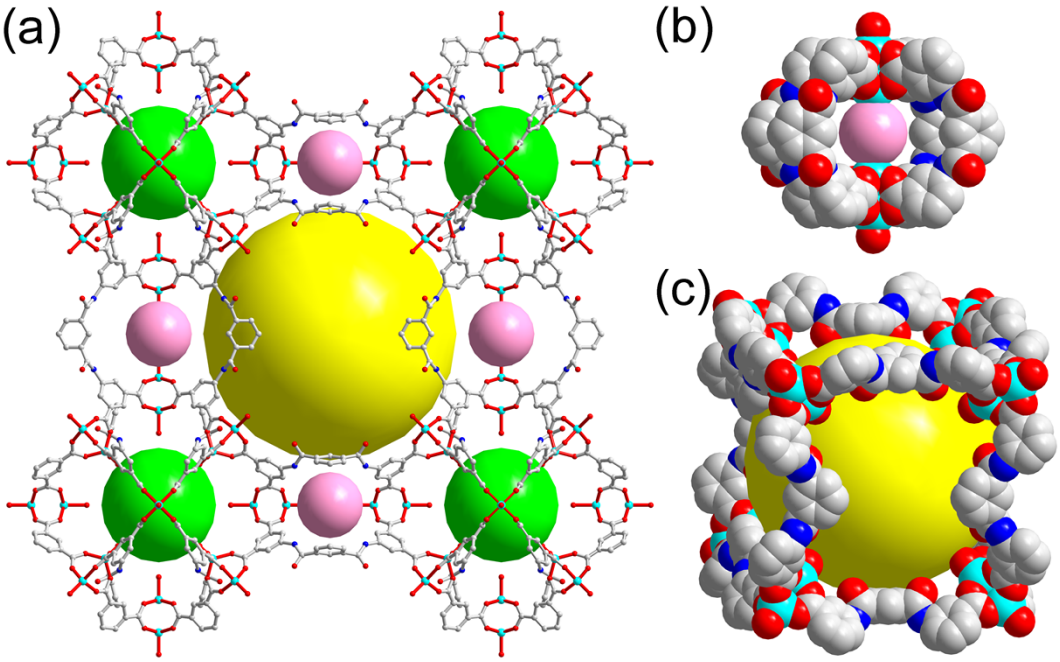


**Figure S2.** (a) Ball-and-stick packing diagram of PMOF-5 viewed along the crystallographic *c*-axis. (b) Space-filling diagram of the quadruple linkage between the MOPs. (c) Supercubic cage generated via the primitive cubic packing arrangement of the cuboctahedral MOPs. The cavities in the centers of the MOP, the quadruple linkage, and the supercube are represented by using green, pink, and yellow dummy balls.

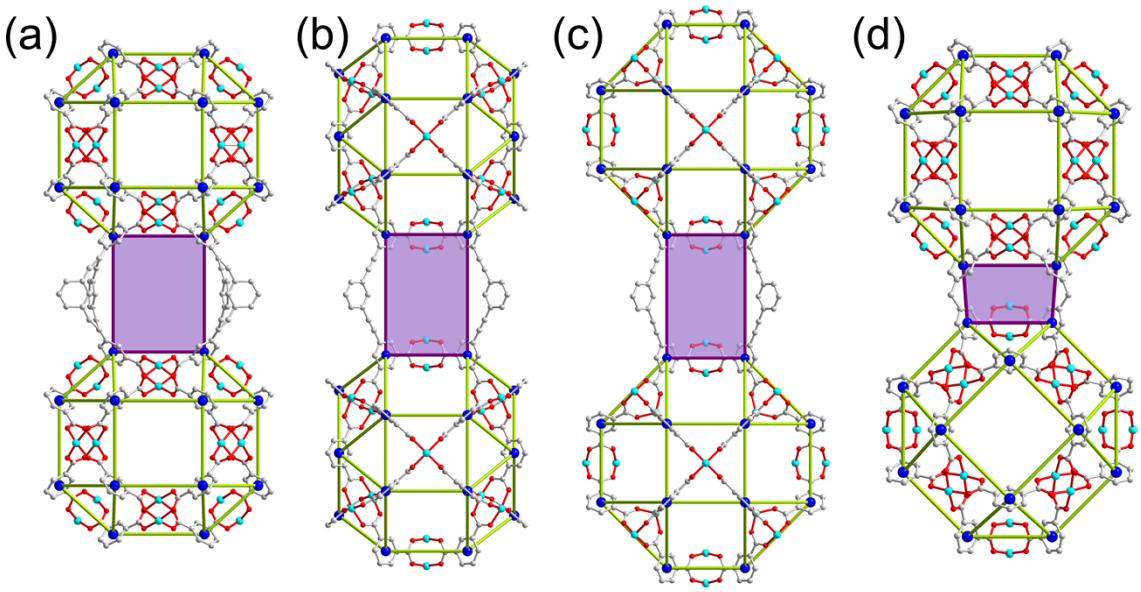


**Figure S3.** (a) An ***AA***-type quadruple linkage between the same two square faces of the cuboctahedral MOPs, (b) a ***BB***-type quadruple linkage between the same two square nodes of the cuboctahedral MOPs, (c) a ***bb***-type quadruple linkage between the same two square nodes of the rhombic dodecahedral MOPs and (d) an ***AB***-type quadruple linkage between the square face of the cuboctahedral MOP and the square node of the cuboctahedral MOP.

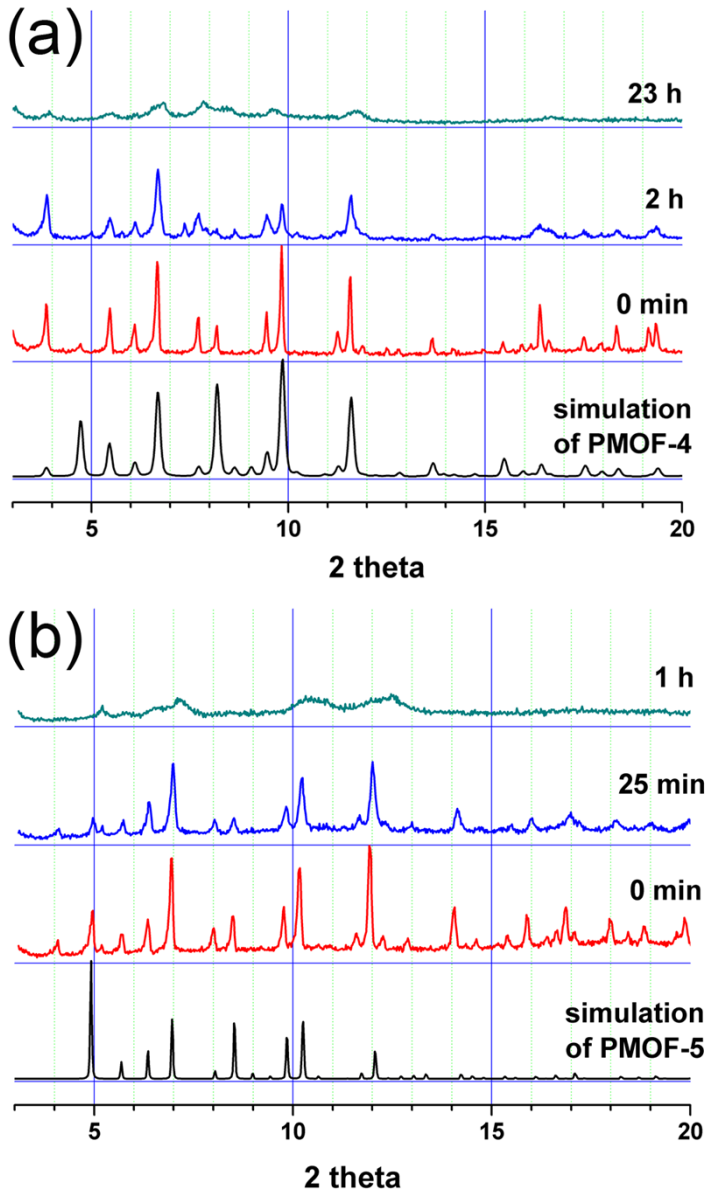


**Figure S4.** PXRD patterns of the as-synthesized samples of (a) PMOF-4 and (b) PMOF-5.

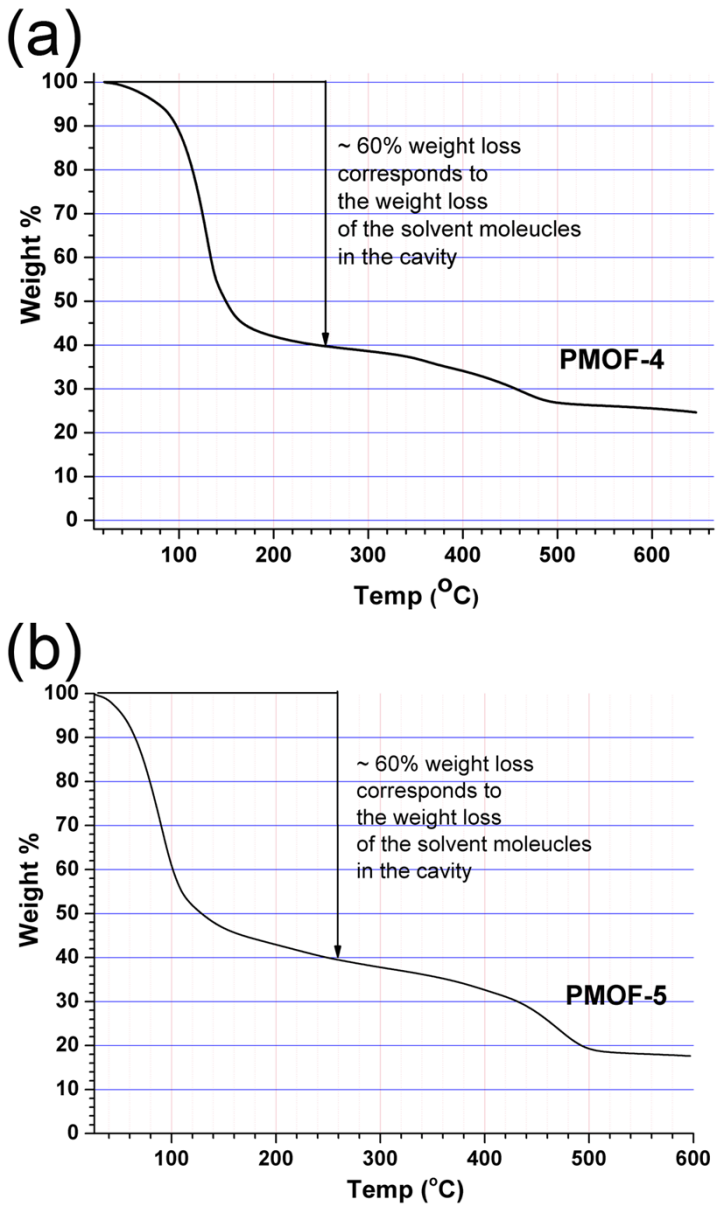


**Figure S5.** TGA plots of the as-synthesized samples of (a) PMOF-4 and (b) PMOF-5.