

Supporting Information

Construction of a Metal-organic Framework by Octuple Intercatenation of Discrete Icosahedral Coordination Cages

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Materials and Measurements

All solvents and reagents of analytical grade were used as received without prior purification. H₃BTTC ligand was synthesized according to the literatures.¹ IR spectra were recorded with a Thermo Scientific Nicolet 5700 FT-IR spectrophotometer with KBr pellets in the 400–4000 cm⁻¹ region. Elemental analyses for C, H and N were performed on a CHN-O-Rapid analyzer and an Elementar Vario MICRO analyzer. Thermogravimetric analyses were carried out on a TA Instruments SDT-Q600 simultaneous DTA-TGA under N₂ with a heating rate of 5°C/min. Powder X-ray diffraction (PXRD) data were recorded on Siemens Bruker D5000 X-ray Powder Diffractometer.

Preparation of compound **1**, Pb₁₃(BTTC)₈(OH)₂(H₂O)₄·9H₂O·3DMA

A mixture of H₃BTTC (40 mg 1.06×10⁻⁴ mol), Pb(NO₃)₂ (80 mg, 2.4×10⁻⁴ mol) and HBF₄ (40% aqueous, 5 drops) in 15 mL of dimethylacetamide (DMA) was fully stirred at room temperature for 30 min, sealed in a 25 mL Teflon-lined autoclave and heated at 100 °C for 72 h. The autoclave was slowly cooled (10 °C h⁻¹) to ambient temperature. The resultant yellow cubic crystals were isolated, washed with dichloromethane (DCM) and dried in air (40 mg, 42.6% yield based on H₃BTTC).

IR selected data (KBr, cm⁻¹) 3430 (m, br, H₂O), 1591 (s, carbonyl vibration of DMA), 1501 (s, carbonyl vibration of BTTC³⁻ ligand), 1379 (s) 1331 (s), 1097 (m), 1070 (m), 831 (m), 788 (s), 734 (m), 700 (m), 445 (m). Elemental analysis (% calc/found: C 25.47/25.76, H 1.28/1.54, N 0.68/0.95).

X-ray crystallography

The crystallographic data collections for **1** were carried out on a Bruker Smart Apex II CCD area-detector diffractometer with graphite-monochromated Mo *K*α radiation (λ = 0.71073 Å) at 298(2) K using the ω-scan technique. The diffraction data were integrated using the SAINT program,² which was also used for the intensity corrections for the Lorentz and polarization effects. A semi-empirical absorption correction was applied using the SADABS program.³ The structure of **1** was solved by direct methods and all the non-hydrogen atoms were refined anisotropically on *F*² by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package.⁴

All the hydrogen atoms except those with H₂O and OH were generated geometrically and refined isotropically using the riding model. In the asymmetric unit of **1**, there are disorders of S1/C8-H and S2/C3-H, which are site disorders and refined with the ‘part’ order. The DMA and H₂O solvent molecules of **1** are highly disordered, and attempts to locate and refine the solvent peaks were unsuccessful. Contributions to scattering due to these solvent molecules were removed using the SQUEEZE routine of PLATON structures were then refined again using the data generated.⁵ The details of the crystal parameters, data collection and refinements for the complexes are summarized in **Table S1**.

Table S1 Crystal data and structure refinements for **1**

Compound	1
Empirical formula	C ₁₃₂ H ₇₉ N ₃ O ₆₆ Pb ₁₃ S ₂₄
Formula weight	6225.890
<i>T</i> (K)	298(2)
Crystal system	Cubic
Space group	<i>Fd-3c</i> (No.228)
<i>a</i> (Å)	40.110(5)
<i>b</i> (Å)	40.110(5)
<i>c</i> (Å)	40.110(5)
<i>α</i> (°)	90
<i>β</i> (°)	90
<i>γ</i> (°)	90
<i>V</i> (Å ³)	64528(13)
<i>Z</i>	16
<i>D_c</i> (g.cm ⁻³)	2.563
<i>F</i> (000)	45920
<i>θ</i> range/°	1.4-27.6
Reflections collected	188415
Unique reflections	3124
Goof	1.09
<i>R</i> ₁ ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0504
<i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.1463

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR_2 = \sqrt{\sum w(|F_o|^2 - |F_c|^2)|^2} / \sum w(F_o)^2$ ^{1/2},
where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$.

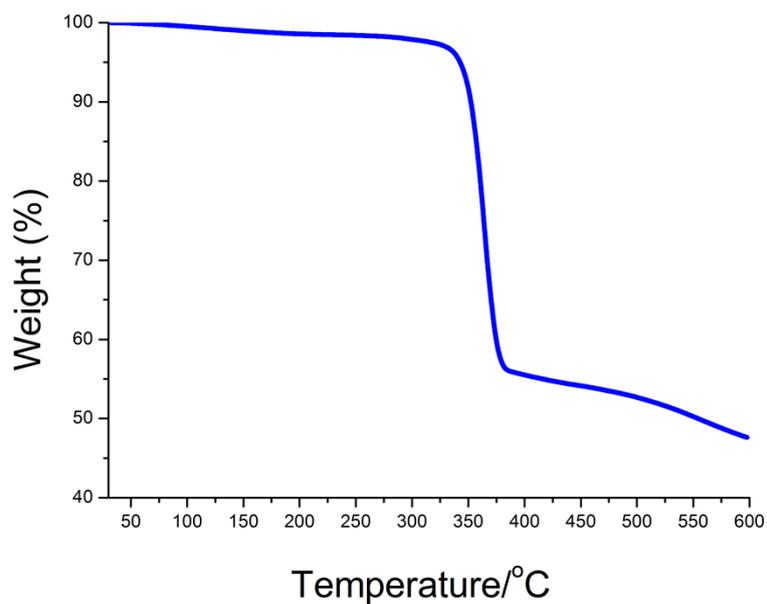


Fig. S1 TGA Curve of **1**.

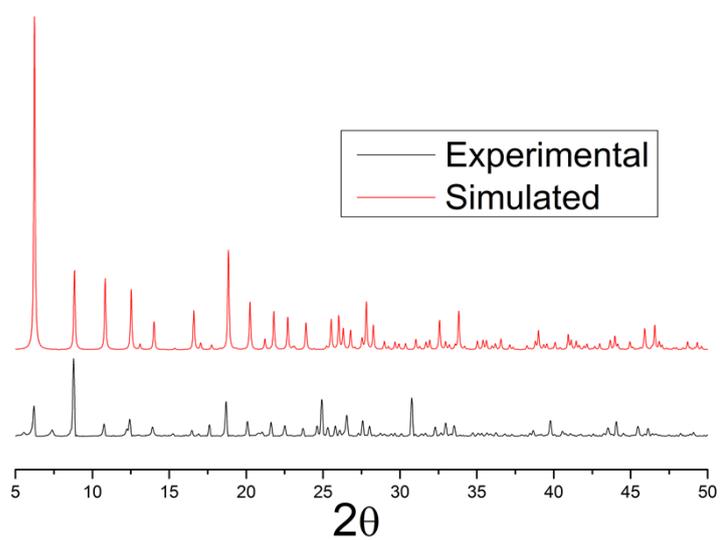


Fig. S2 Comparison between the experimental PXRD pattern of **1** and the simulated PXRD pattern



Fig.S3 Asymmetric unit of **1** (hydrogen atoms not shown)

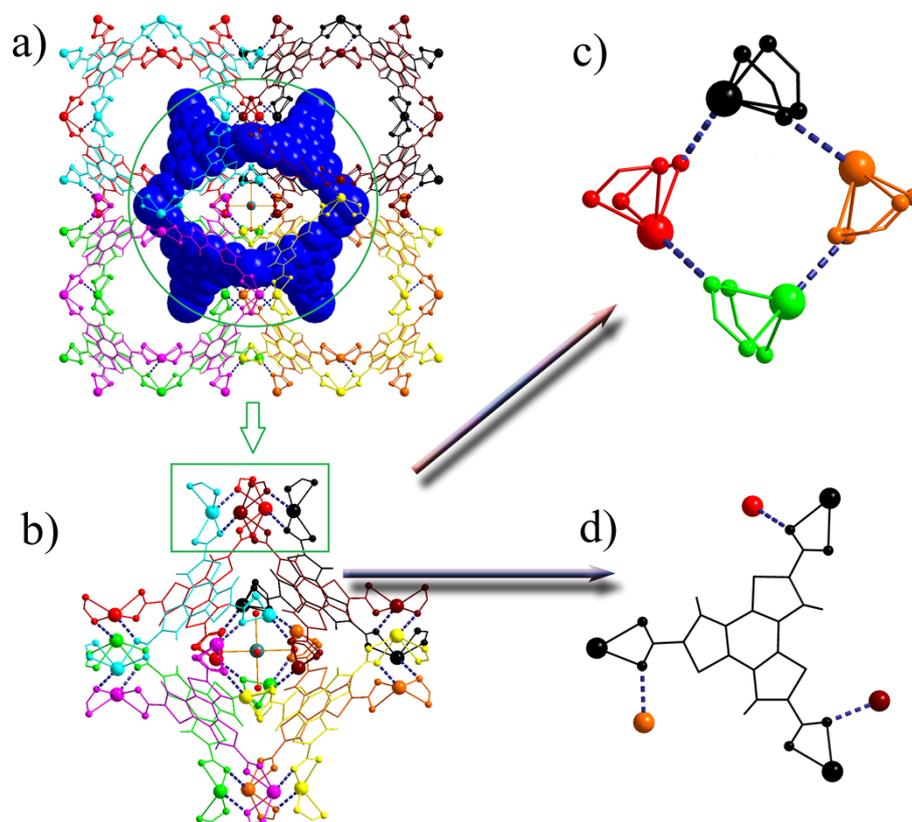


Fig.S4 **a)** Weak Pb-O interactions (highlighted by dashed lines) between coordination cages. **b)** Truncated-octahedral coordination cage encompassing a $[\text{Pb}(\text{OH})_2(\text{H}_2\text{O})_4]$ octahedron at its center. **c)** View of $\text{Pb}_4(\text{CO}_2)_8$ cluster structure. **d)** View of coordination mode of BTTC ligand.

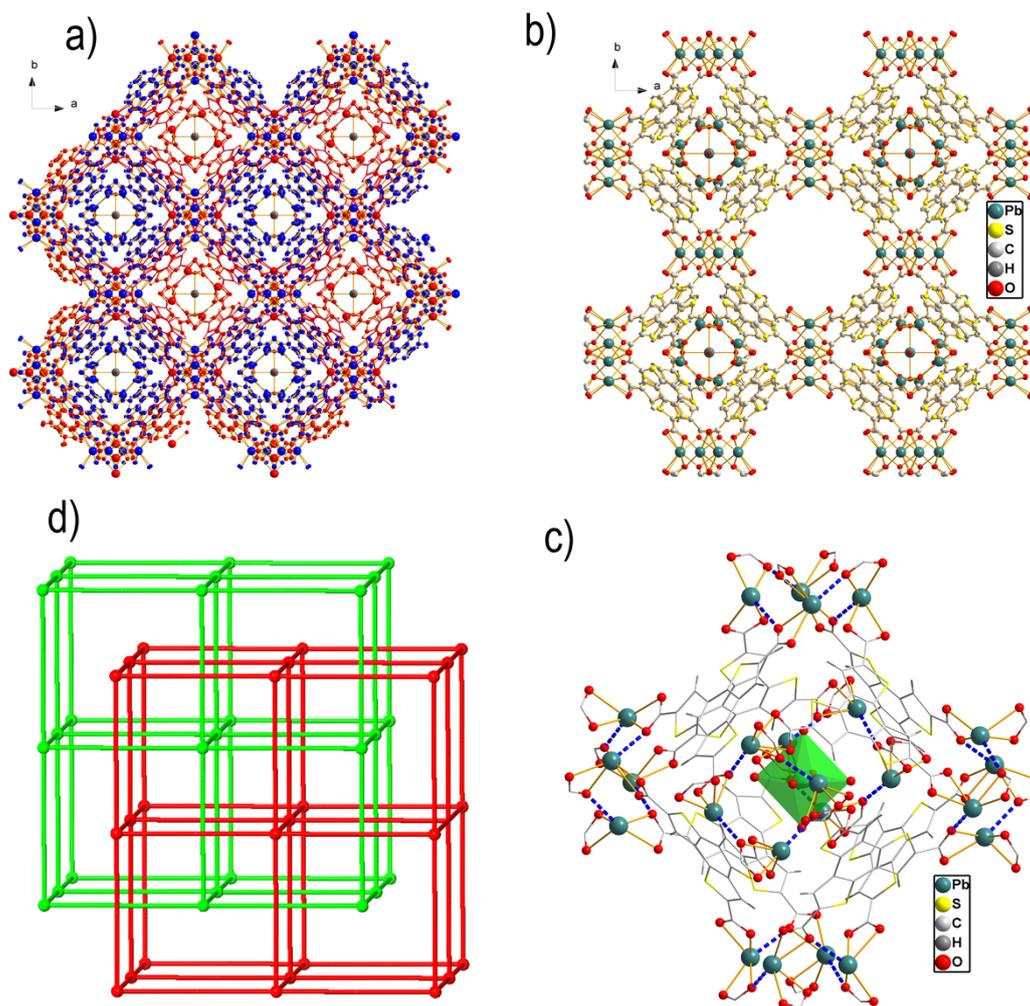


Fig. S5 **a)** Two identical and independent 3-D MOFs (highlighted by blue and red color) interpenetrating each other in **1**. **b)** Single 3-D MOF with truncated octahedral coordination cage as six-connected node. **c)** Highlight of truncated octahedral coordination cage (blue dotted lines represent secondary Pb-O bonds and green polyhedra represents $\text{Pb}(\text{OH})_2(\text{H}_2\text{O})_4$ octahedron. **d)** Topological showing of the interpenetrated structure of **1**.

References

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