

## Supporting Information

# An Unprecedented Twofold Interpenetrated Layered Metal–Organic Framework with a MoS<sub>2</sub>-H Topology

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## Experimental sections

### General procedures

All the reagents were purchased from commercial sources and were used without further purification. Elemental analysis (C, H, and N) was performed using a Thermo Scientific Flash 2000 elemental analyzer. Infrared spectra were recorded over the range 4000–600 cm<sup>-1</sup> using a Varian 670 FT-IR spectrophotometer. Powder X-ray diffraction (PXRD) data were recorded using a Rigaku D/M 2200T automated diffractometer at room temperature using a step size of

0.02°. Simulated PXRD patterns were calculated using the Material Studio software package<sup>S1</sup> employing single crystal data. Thermogravimetric analysis (TGA) was performed using a Q600 system in flowing N<sub>2</sub> at a heating rate of 6 °C min<sup>-1</sup> between ambient temperature and 600 °C. The 3,3',3''-[1,3,5-benzenetriyltris(carbonylimino)]trisbenzoic acid was prepared according to a literature procedure.<sup>S2</sup>

Preparation of [Zn<sub>4</sub>OL<sub>2</sub>]<sub>2</sub>·6DMA·7(dimethylamine), **1**: A 0.0700 g (0.123 mmol) amount of H<sub>3</sub>L in 2.5 mL DMA and a 0.0887 g (0.298 mmol) amount of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in 0.5 mL acetonitrile were mixed, sealed in a Pyrex tube, and heated at 120 °C for 4 d. After cooling to room temperature, the colorless block-shaped crystals formed were filtered, washed with DMA, and then dried in air. Yield = 0.0751 g, 66.9%. Elemental analysis of **1**: Calc. for [Zn<sub>4</sub>OL<sub>2</sub>]<sub>2</sub>(DMA)<sub>6</sub>(dimethylamine)<sub>7</sub> (Zn<sub>8</sub>C<sub>158</sub>H<sub>175</sub>N<sub>25</sub>O<sub>44</sub>, fw = 3651.31): C, 51.97; H, 4.83; N, 9.59 %. Found: C, 52.16; H, 4.39; N, 9.58 %. IR (KBr, cm<sup>-1</sup>): 3429, 3264, 3073, 2930, 1667, 1623, 1580, 1557, 1440, 1397, 1316, 1287, 1261, 1098, 768, and 674. The activated sample **1b** was obtained by evacuating crystals of **1** under vacuum at 100 °C for 12 h. Elemental analysis of **1b** exposed to air: Calc. for [Zn<sub>4</sub>OL<sub>2</sub>]<sub>2</sub>(DMA)<sub>6</sub>(H<sub>2</sub>O)<sub>4</sub> (Zn<sub>8</sub>C<sub>144</sub>H<sub>134</sub>N<sub>18</sub>O<sub>48</sub>, fw = 3407.78): C, 50.75; H, 3.96; N, 7.40 %. Found: C, 50.60; H, 4.29; N, 8.07 %.

### Crystallographic data collection and refinement of the structure

A crystal that was freshly harvested from the mother liquor was coated with paratone oil, and the diffraction data were collected at 173 K using a Siemens Smart CCD diffractometer with graphite monochromated Mo-*K*<sub>α</sub> radiation (λ = 0.71073 Å) using the SMART and SAINT software packages.<sup>S3</sup> Empirical absorption corrections were applied using the SADABS software package based upon Laue symmetry using equivalent reflections.<sup>S4</sup>

The crystal structure of **1** was resolved using a direct method and refined using full-matrix

least-squares calculations employing the SHELXTL-Plus (ver. 5.1) software package.<sup>S5</sup> A tetranuclear (Zn<sub>4</sub>O)L<sub>2</sub> unit on the crystallographic C<sub>3</sub> axis and a DMA molecule were identified as an asymmetric unit in the crystal structure. Three additional electron density sites around the metal centers probably corresponding to statistically disordered and partially identified solvent and/or dimethylamine molecules were found in the difference Fourier map but not included in the structural model.¶ All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2 (C and N) or 1.5 (C<sub>methyl</sub>), and their coordinates were allowed to ride on their respective atoms. The refinement converged to R<sub>1</sub> = 0.1334 and wR<sub>2</sub> = 0.3249 for 3192 reflections with I > 2σ(I). Structure refinement after modification of the data for the disordered solvent region (1500 Å<sup>3</sup>, 6.7% of the crystal volume) with the SQUEEZE routine of PLATON<sup>S6</sup> led to better refinement and data convergence. Refinement of the structure converged to a final R<sub>1</sub> = 0.1257 and wR<sub>2</sub> = 0.2593 for 3312 reflections with I > 2σ(I); R<sub>1</sub> = 0.1608 and wR<sub>2</sub> = 0.2772 for all reflections. The largest difference peak and hole were 1.512 and -1.966 e·Å<sup>-3</sup>, respectively.

A summary of the crystal and intensity data is given in Table S1. CCDC-826842 contains the supplementary crystallographic data. The data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK.

## References

S1. Materials Studio program, version 4.3, Accelrys, San Diego, CA, 2008.

S2. M. J. Prakash, Y. Zou, S. Hong, M. Park, M.-P. Ngoc Bui, G. H. Seong, M. S. Lah, *Inorg. Chem.* **2009**, *48*(4), 1281–1283.

S3. SMART and SAINT, Area Detector Software Package and SAX Area detector Integration Program; Bruker Analytical X-ray: Madison, WI, 1997.

S4. SADABS, Area Detector Absorption Correction Program; Bruker Analytical X-ray: Madison, WI, 1997.

S5. G. M. Sheldrick, SHELXTL–PLUS, Crystal Structure Analysis Package; Bruker Analytical X-ray, Madison, WI, 1997.

S6. PLATON program: Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, 194.

¶ Although the dimethylamine was not used as a reactant, it is well known that DMA can be hydrolyzed to dimethylamine during the solvothermal syntheses of MOFs. The EA data of the as-synthesized sample **1** can be better fitted using the formula containing dimethylamine than DMA or water for the sample.

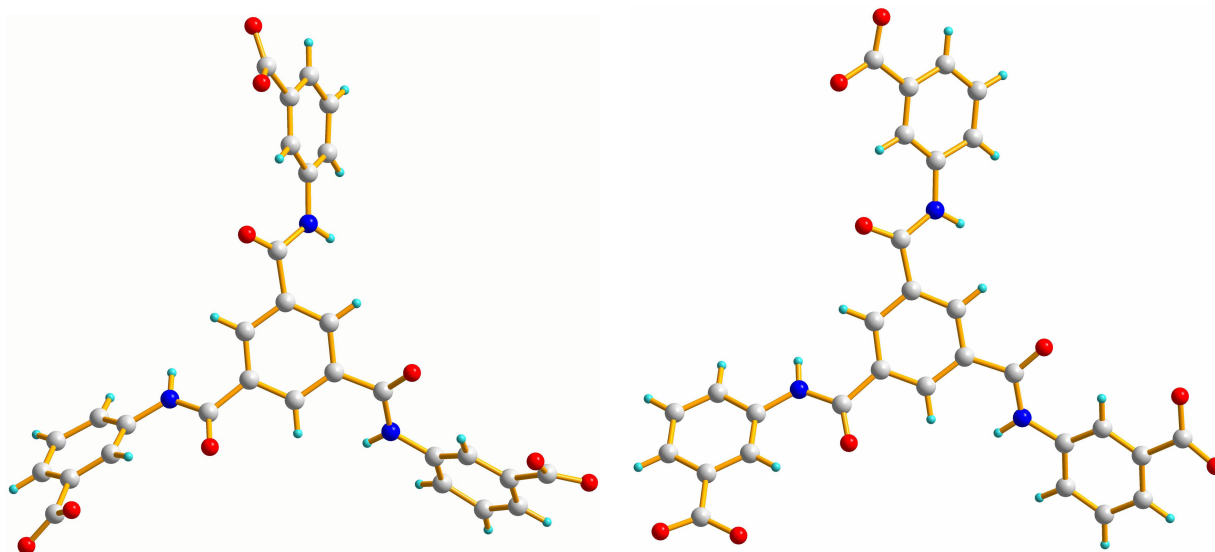
**Table S1.** Crystal data and structure refinement for **1**.

Empirical formula	C <sub>144</sub> H <sub>126</sub> N <sub>18</sub> O <sub>44</sub> Zn <sub>8</sub>	
Formula weight	3335.59	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Rhombohedral	
Space group	<i>R</i> -3 <i>c</i>	
Unit cell dimensions	a = 17.837(5) Å	α = 90°.
	b = 17.837(5) Å	β = 90°.
	c = 81.03(5) Å	γ = 120°.
Volume	22327(15) Å <sup>3</sup>	
Z	6	
Density (calculated)	1.488 Mg/m <sup>3</sup>	
Absorption coefficient	1.354 mm <sup>-1</sup>	
F(000)	10248	
Crystal size	0.18 x 0.18 x 0.16 mm <sup>3</sup>	
Theta range for data collection	1.66 to 25.15°.	
Index ranges	-19 ≤ h ≤ 21, -20 ≤ k ≤ 21, -94 ≤ l ≤ 96	
Reflections collected	34661	
Independent reflections	4408 [R(int) = 0.1134]	
Completeness to theta = 25.15°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8125 and 0.7926	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	4408 / 6 / 325	
Goodness-of-fit on F <sup>2</sup>	1.189	
Final R indices [I > 2σ(I)]	R1 = 0.1257, wR2 = 0.2593	
R indices (all data)	R1 = 0.1608, wR2 = 0.2772	
Largest diff. peak and hole	1.512 and -1.966 e·Å <sup>-3</sup>	

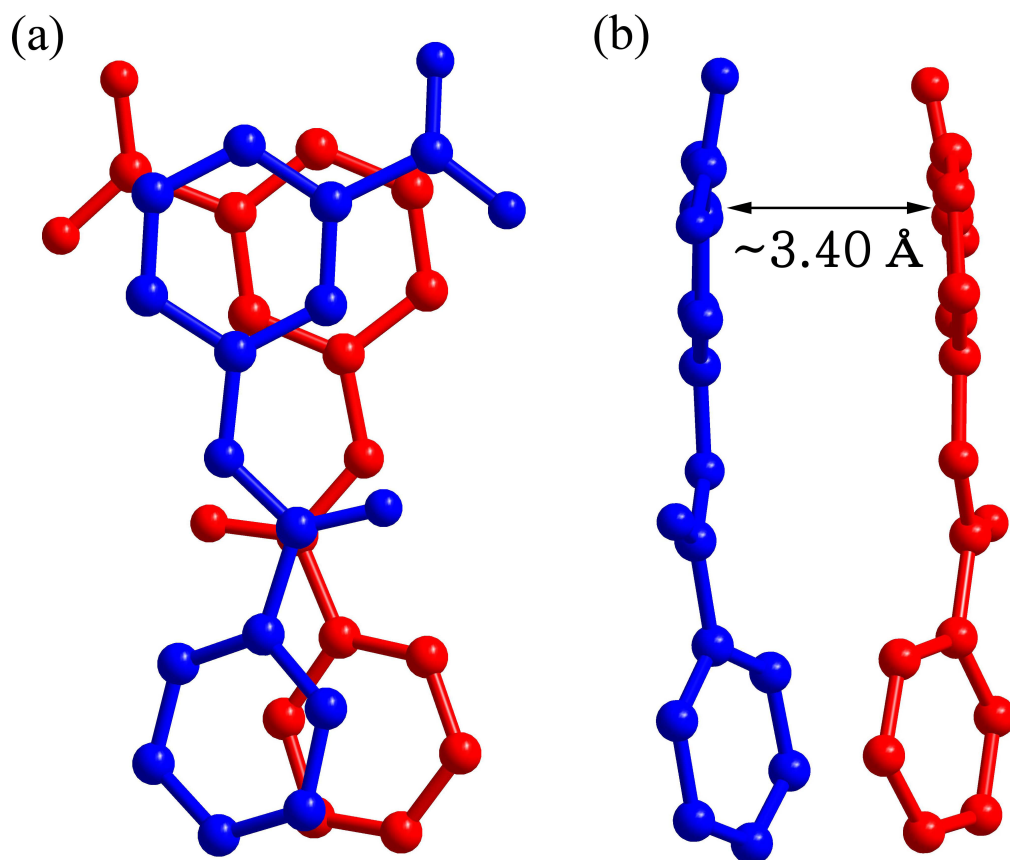
**Table S2.** Hydrogen bonds for **1** (Å and °).

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(1S)	0.88	1.91	2.776(12)	166.9
N(2)-H(2)...O(3)#1	0.88	2.16	2.882(11)	138.7

Symmetry transformations used to generate equivalent atoms: #1  $-x+4/3, -x+y+2/3, -z+1/6$

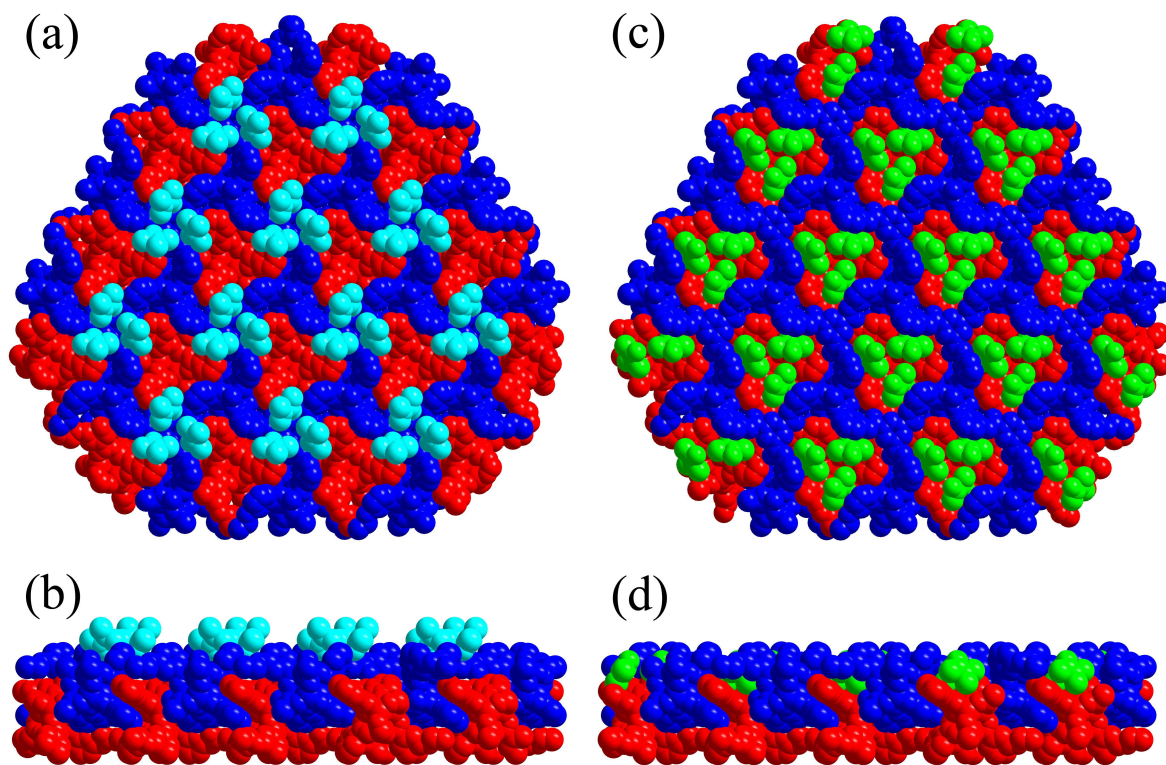


**Figure S1.** Ball-and-stick representation of the two ligands on the crystallographic  $C_3$  symmetry axes observed in **1**.

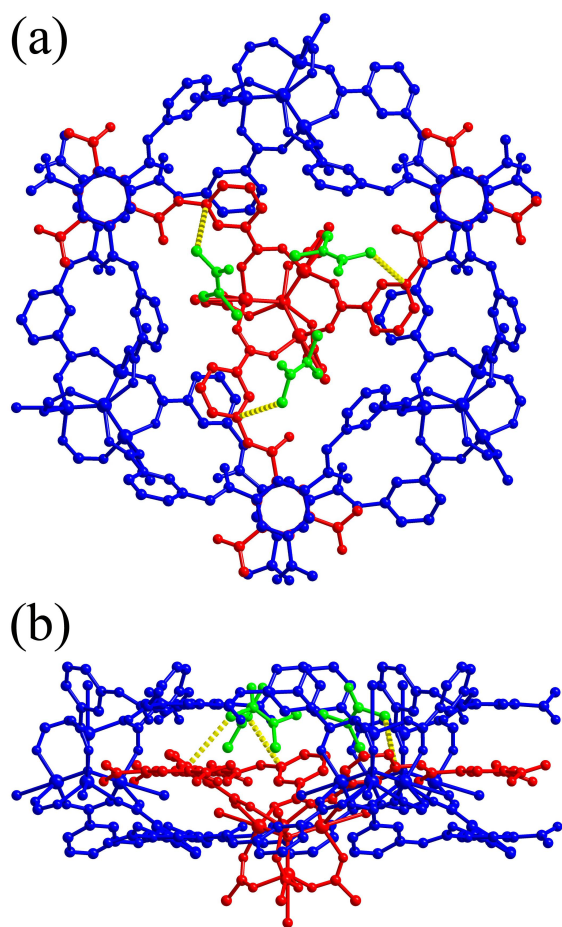


**Figure S2.** The face-to-face  $\pi$ - $\pi$  stacking interaction observed between the carboxyphenyl moieties of the interpenetrated layer in **1**. (a) Top view. (b) Side view. Only one arm of the ligand is shown for clarity.

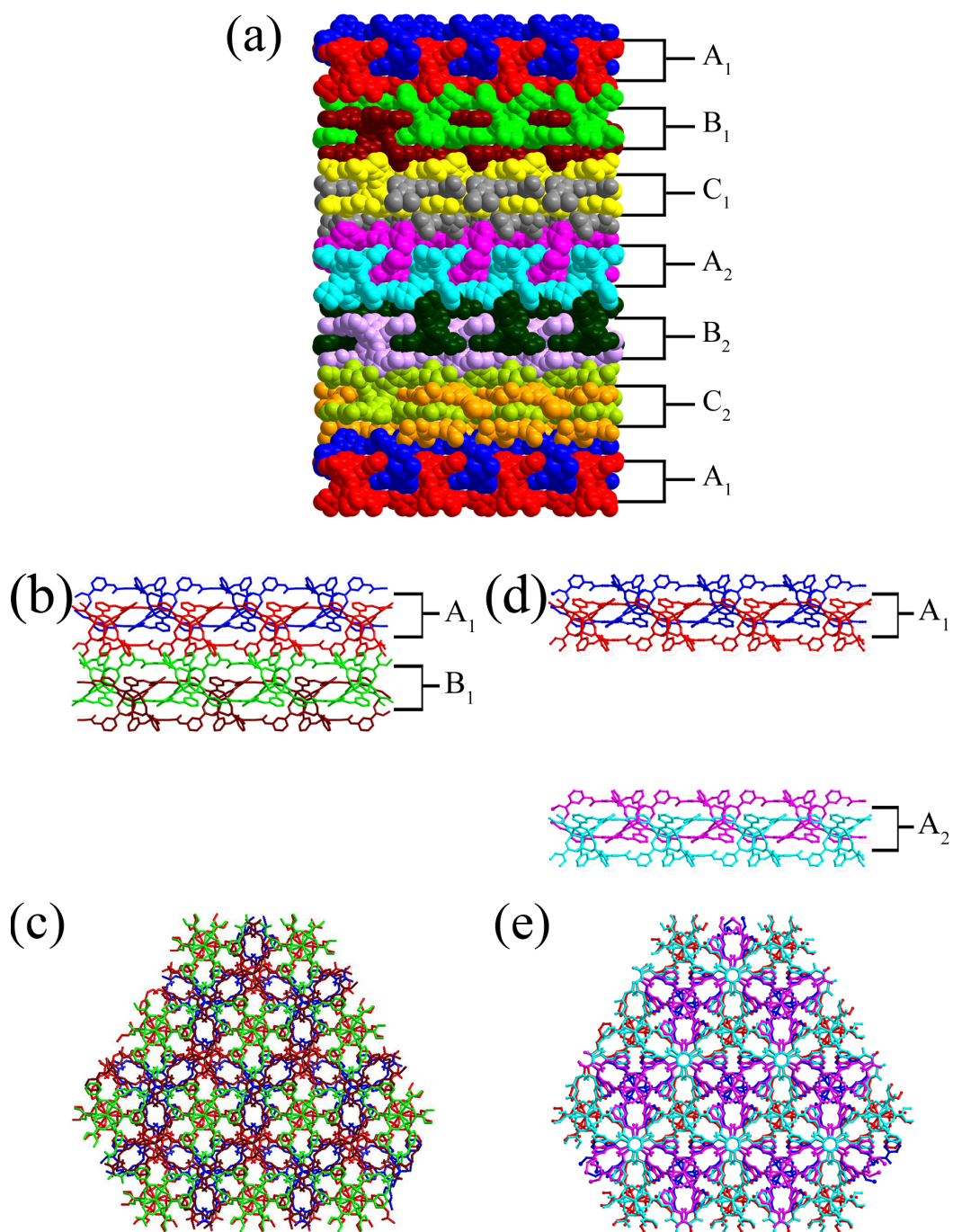




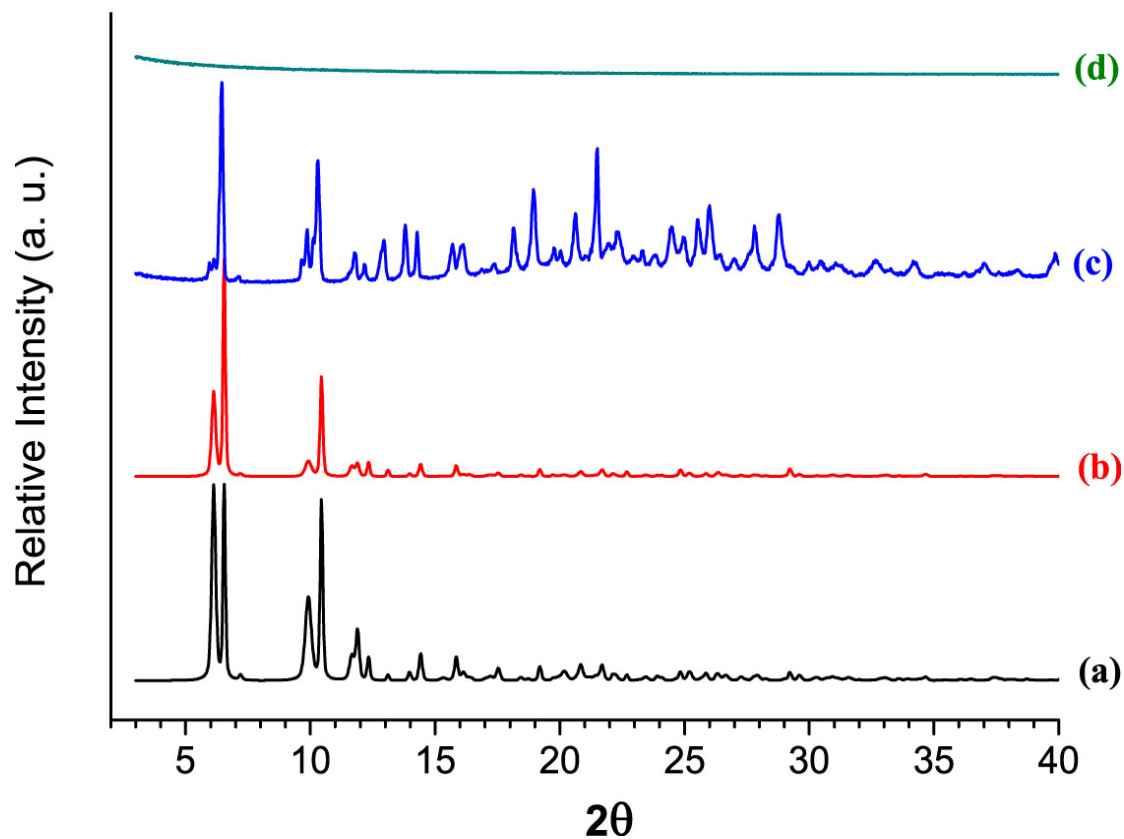
**Figure S3.** Space-filling representation of the interpenetrated 2D layer with the hydrogen bonded DMA molecules (shown in aqua) in (a) a top view and (b) a side view, and with DMA molecules interacting *via* C–H... $\pi$  interactions (shown in green) in (c) a top view and (d) a side view.



**Figure S4.** The DMA molecules (shown in green) in the pocket of the interpenetrated 2D layer interacting with the carboxyphenyl moieties *via* C–H... $\pi$  interactions (denoted by the yellow dotted lines) in **1**: (a) top view and (b) side view.



**Figure S5.** 3D packing diagrams of the interpenetrated 2D layers. (a) The layers packed in  $-(A_1B_1C_1A_2B_2C_2)_n-$  repeating order are shown along the crystallographic *b*-axis in a space-filling model.  $A_1$  and  $B_1$  two layers are shown along the crystallographic (b) *b*-axis and (c) *c*-axis in a ball-and-stick model.  $A_1$  and  $A_2$  two layers are shown along the crystallographic (d) *b*-axis and (e) *c*-axis.



**Figure S6.** PXRD patterns. (a) A simulated PXRD pattern from the single crystal structure of **1**, and (b) a simulated PXRD pattern with the  $[1\ 1\ 0]$  preferred orientation. PXRD patterns of (c) an as-synthesized sample, **1**, and (d) an activated sample, **1a**, prepared by vacuum-drying **1** at  $100^\circ\text{C}$  for 2 d.

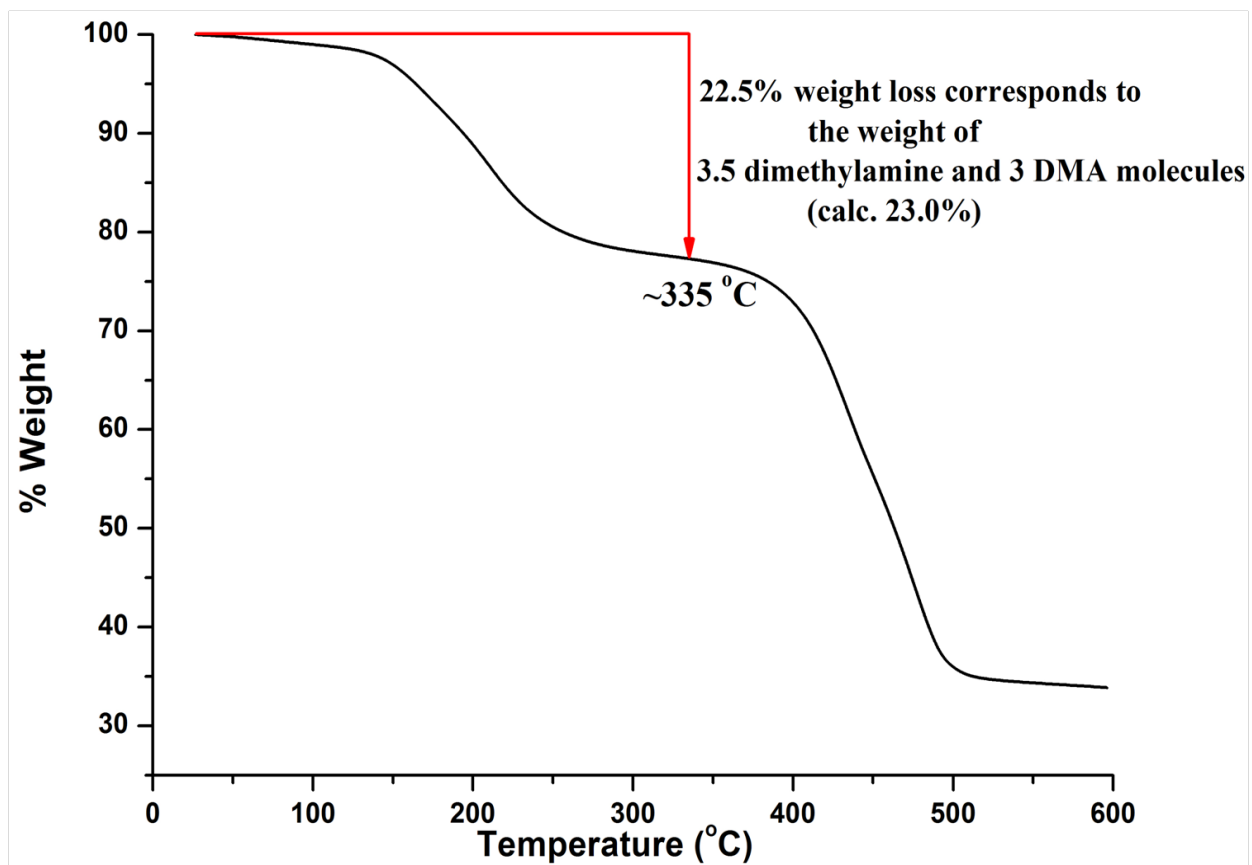


Figure S7. TGA of 1.