

Supporting Information for

**A Three-dimensional Metal-Organic Framework Based on a triazine
Derivative: Syntheses, Structure Analysis, and Sorption Studies**

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General Information. Commercially available reagents were used as received without further purification. Fourier transform infrared (FTIR) spectra were measured within the 4000-400cm⁻¹ wavenumber range using a Perkin-Elmer model 580B IR spectrophotometer with the KBr pellet technique. Elemental analyses (C,H,N) were carried out on a VarioEL analyzer. Thermogravimetric analysis (TGA) was performed on a SDT2960 analyzer (Shimadzu, Japan) up to 600 °C at a heating rate of 10 °C /min under N₂. A Micro meritics ASAP2020 surface area analyzer was used to measure gas sorption. The high pressure hydrogen storage was carried out by using computer-controlled gas reaction controller apparatus (Advanced Materials Corporation) and Hiden Isochema (IGA 001, Hiden Analytical Ltd) with ultrahigh-purity hydrogen (99.999% pure). NMR was collected on a Bruker 400MHz spectrometer. The powder X-ray diffraction (XRD) of the compound 1 was examined on a Rigaku-Dmax 2500 diffractometer using CuK α radiation (λ = 0.15405 nm).

Experimental

Synthesis of m-H₃TATB

2,4,6-tri-m-tolyl-s-triazine (1): At 0 °C, m-tolunitrile (6.03 ml) was added slowly to trifluoromethanesulfonic anhydride (18 ml) and water(3.3 ml). The mixture was stirred at room temperature for 24 h, poured on ice and neutralized with ammonia water. The precipitate was collected by filtration and then washed with water and acetone. Recrystallization in n-hexane gave the title compound as white crystals (4 g, yield: 70%).

¹H-NMR(CDCl₃, 400MHz) δ(ppm)=8.58(m, 6H), 7.47(t, J=8.0Hz, 3H), 7.42(d, J=7.2Hz, 3H), 2.53(s, 9H).

3,3',3''-s-triazine-2,4,6-triyltribenzoic acid (2): The title compound was synthesized from 2,4,6-tri-m-tolyl-s-triazine similarly as the reported procedure (Sun, D., Ma, S., Ke, Y., Collins, D. J. & Zhou, H.-C. *J. Am. Chem. Soc.* **128**, 3896-3897 (2006)).

¹H-NMR(DMSO-d₆, 400MHz) δ(ppm)=13.34(s, 3H), 9.22(s, 3H), 8.94(s, 3H), 8.27(s, 3H), 7.83(d, J=4.0Hz, 3H).

IR (cm⁻¹): 2874 (w), 2551 (w), 1693 (vs), 1608 (m), 1527 (vs), 1441 (m), 1357 (s), 1262 (vs), 1077 (m), 750 (s), 682 (vs).

Caution: Trifluoromethanesulfonic anhydride is highly corrosive, and it should be taken carefully.

Gas sorption Measurements.

A sample of **1** was soaked in methanol for 24 hours, and the extract was discarded. Fresh methanol was subsequently added, and the crystals were allowed to soak for another 24 hours to remove DMSO and H₂O solvates. The sample was then treated with dichloromethane similarly to remove methanol solvates. After the removal of dichloromethane by decanting, the sample was dried at room temperature. Before the measurement, the sample was dried again by using the “outgas” function of the surface area analyzer for 10 hours at 100 °C to remove all residue solvents in the channels. A sample of 62.5 mg was used for N₂ sorption measurement, and was maintained at 78K with liquid nitrogen. In the CO₂ storage measurement, high-purity carbon dioxide (99.99%) and a 60.0 mg sample were used. The measurement was maintained at 195 K with an acetone-dry ice bath. The CO₂ storage measurement was also maintained at 273 K with an ice bath for comparative study. In the hydrogen storage measurement, high-purity hydrogen (99.999%) and a 60.0 mg sample were used. The regulator and hoses were flushed with hydrogen before

connecting to the analyzer. The internal lines of the instrument were flushed three times by utilizing the “flushing lines” function of the program to ensure the purity of H₂. The measurement was maintained at 77 K with liquid nitrogen.

Table S1. Crystal data^a for **1**

Crystal	1.3DMSO.2H ₂ O
formula	C ₆₁ H ₅₉ Cu ₃ N ₇ S ₃ O ₁₉
Formula weight	1480.95
space group	I4 ₁ /a
T, K	200(2)
<i>a</i>	29.3618(6)
<i>b</i>	29.3618(6)
<i>c</i>	37.1534(14)
<i>α</i> (deg)	90
<i>β</i> (deg)	90
<i>γ</i> (deg)	90
<i>V</i>	32030.5(15)
<i>Z</i>	16
<i>D</i> _{calcd} (g cm ⁻³)	1.228
<i>F</i> (000)	12176
GOF on <i>F</i> ²	1.017
<i>R</i> ₁ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0938
w <i>R</i> ₂ ^c	0.2743

^a Obtained with graphite-monochromated Mo K_α (λ = 0.71073 Å) radiation.

^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^c $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$

References:

1. SAINT+, Bruker Analytical X-Ray Systems, Madison, WI, 2001.
2. Sheldrick, G. M., SHELX-97, Bruker Analytical X-Ray Systems, Madison, WI, 1997.

3. Spek, A. L., J. Appl. Crystallogr. 2003, 36, 7-13.

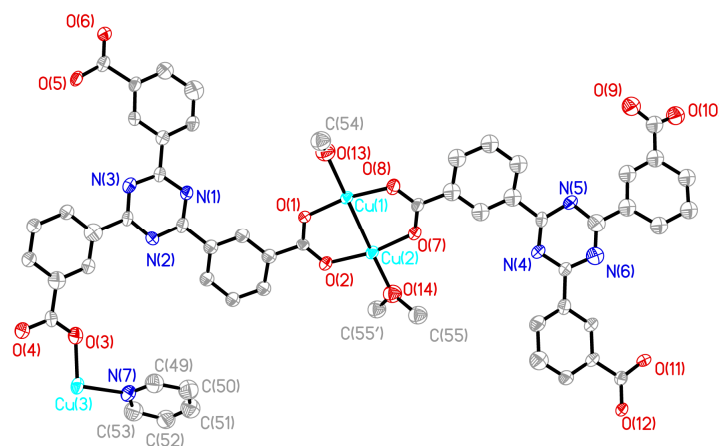


Figure S1. ORTEP plot of the unit for **1** (The axial ligands in **1** are pyridine and CH₃OH, and their molar ratio is 1:2).

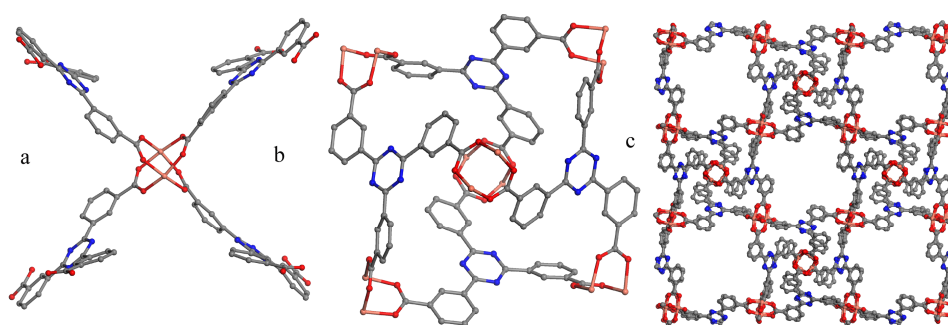


Figure S2. a) A paddlewheel SBU linked to four m-TATB ligands; axial ligands are omitted for clarity. b) A T_d-octahedral cage: the six SBUs (only half of each paddlewheel is shown) occupy all the corners, and the four m-TATB ligands cover every other face of an octahedron. c) A cuboctahedral net built from T_d-octahedral cages through corner-sharing.

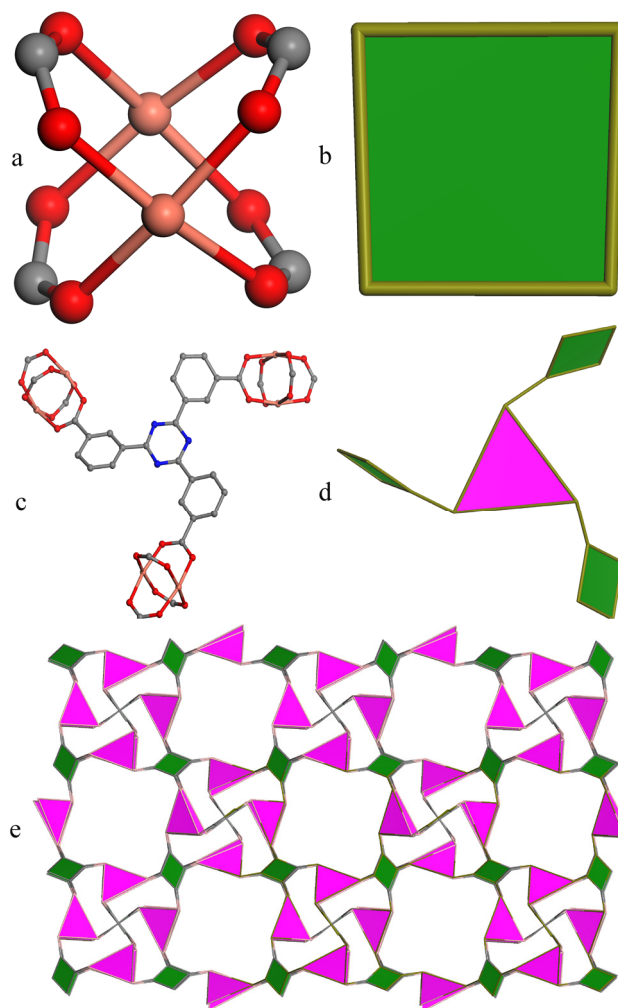


Figure S3. Illustrated for the topology of **1** (axial ligands are omitted for clarity, for atoms colors: Cu brick red, O red, N blue, C brown).

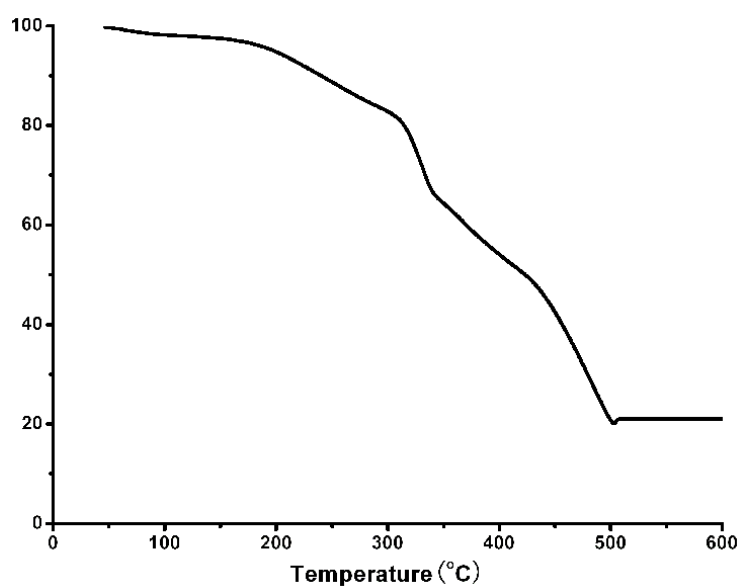


Figure S4. TGA for **1**·3DMSO·2H₂O

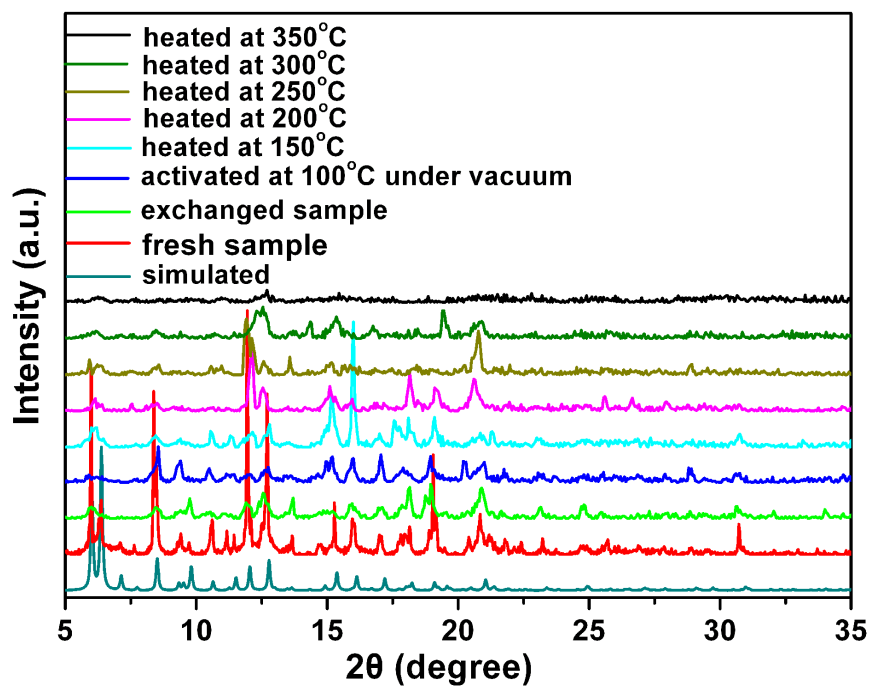


Figure S5. Powder XRD for 1.

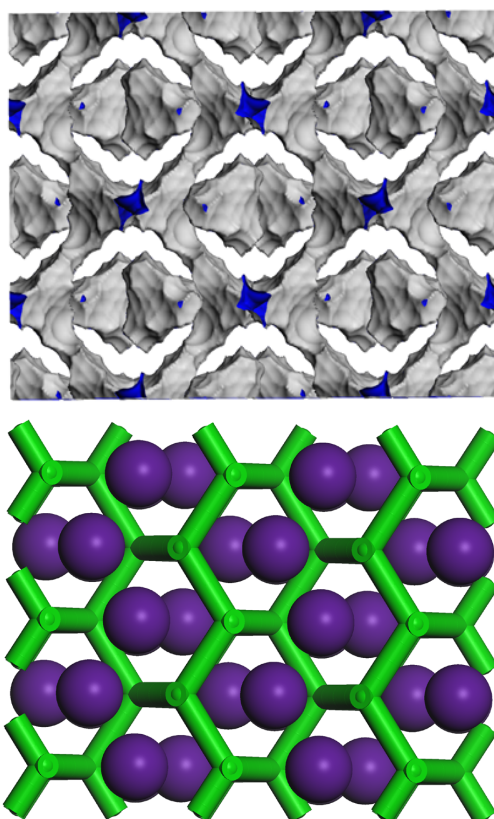


Figure S6. Two kinds of channels in 1

(The violet atoms represent the cavities, while the green connected bonds represent the 3D channels)

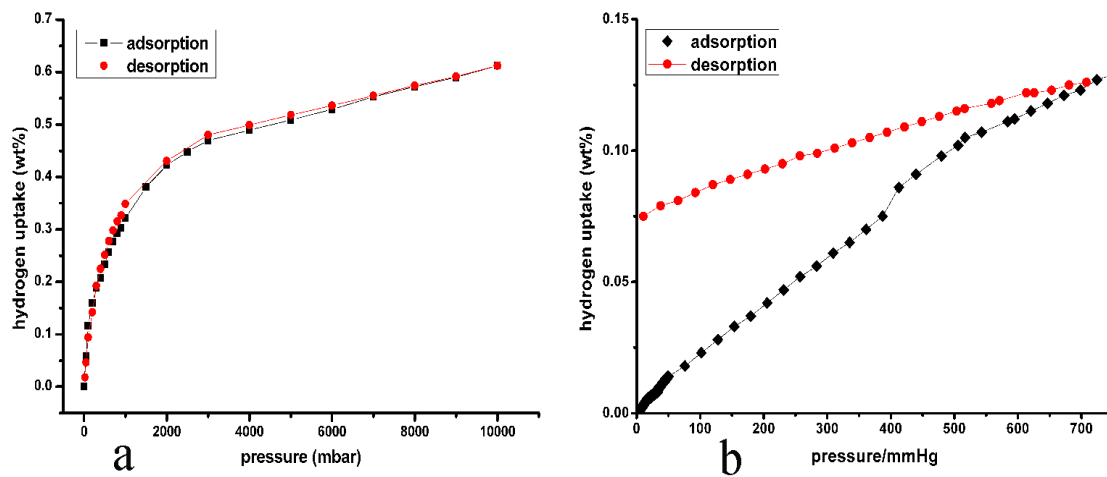


Figure S7. H₂ sorption isotherms for **1** (77 K): a) high pressure, b) low pressure.

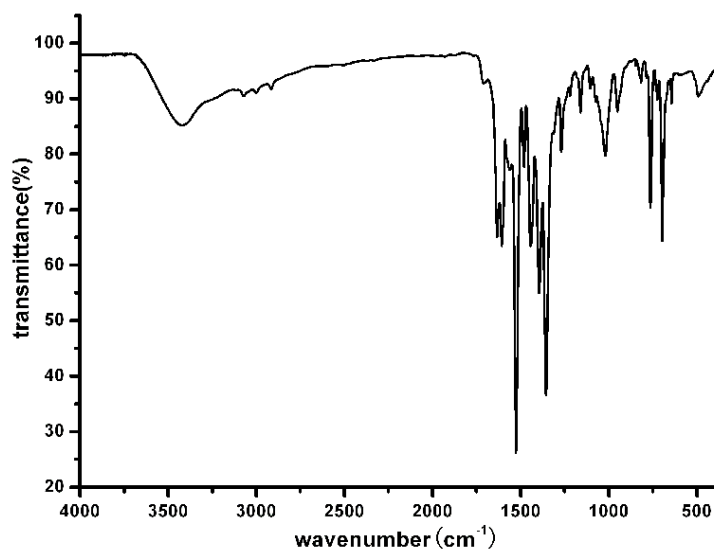


Figure S8. IR spectra of **1**