Construction of a trigonal bipyramidal cage-based metal-organic framework with hydrophilic pore surface *via* flexible tetrapodal ligands

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Supporting Information

1. Materials and instrumentations for physical property measurements.

All of the chemicals were purchased and used without further purification. The X-ray powder diffraction data were collected on a Panalytical X'pert Pro MPD diffractometer using graphite-monochromated CuKa radiation in the 2θ range of 5-50˚ with a step size of 0.05˚. TGA was carried out with a NETZSCH STA 449C instruments. The sample and reference (Al_2O_3) were enclosed in a platinum crucible and heated at a rate of 15˚/min from room temperature to 800°C under a nitrogen atmosphere. Elemental analyses (C, H, O and N) were determined using Perkin-Elmer 240C elemental analyzer. The IR spectrum was recorded on a Magna 750 FT-IR spectrometer as KBr pellets in the range of 4000–400 cm^{-1}. Vapor-phase adsorption isotherms were measured with the Intelligent Gravimetric Sorption Analyser IGA100B of Hiden Corporation. The samples were heated at 150°C (heating rate 2°C/min) under vacuum ~10^{-7} mbar (outgas rate 20mbar/min) for 12 hours before the analysis were started. The ASAP 2020 surface area analyzer was used to measure the N_2 and CO_2 isotherm in which the samples were heated at 150°C (heating rate 10°C/min) under vacuum ~ 10^{-5} mmHg.The NMR spectrum was measured on Nuclear Magnetic Resonance Spectrometer AVANCE III of Bruker Biospin Corporation

2. Preparation of $[Zn_4OX_{1.5}]\cdot 4DMA\cdot 10DEF\cdot 10H_2O$

The title compound was synthesized by the hydrothermal reactions of a mixture of $Zn(NO_3)_2\cdot 6H_2O$ (0.2mmol, 0.06g), H_4X (0.12g, 0.2 mmol) and 6 mL of DMA:DEF:H_2O=2:3:1 (volume ratio) sealed in an autoclave equipped with a Teflon liner (23 mL) at 80 ºC for 4 days, and then cooled to temperature. Colorless block single crystals of **1** were collected in a *ca* 86% yield based on H_4X. Elemental analysis for $C_{115.5}H_{202}N_{14}O_{43}Zn_4$, (2734) (%): Found. C=47.33, H=7.35, O=27.69, N=7.27; Calc. C=50.69, H=7.38, O=25.16, N=7.17. IR data (KBr, cm^{-1}): 3390(w), 1606 (s), 1403 (s), 1240(s), 1173 (m), 785 (m).

3. Crystal structure determination of 1.

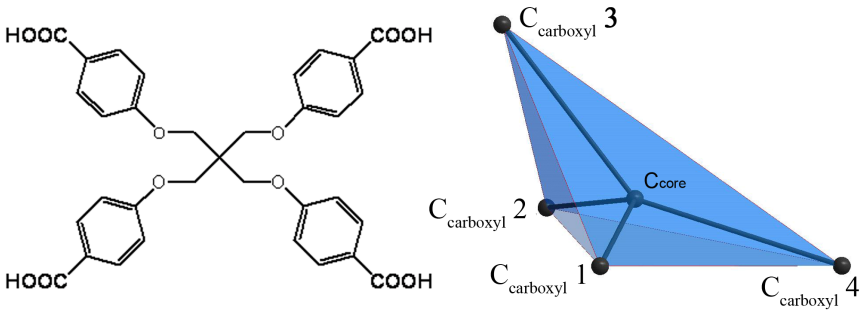
Crystal data for **[$Zn_4OX_{1.5}$]·4DMA·10DEF·10H_2O**, trigonal, $R\bar{3}c$, Mr = 2736, a = 26.918(4) Å, b = 26.918(4) Å, c = 86.67(2)Å, γ = 120°, V =54386(17) $Å^3$, Z = 12, D_{calcd} = 0.438g·cm^{-3} (removal of guest molecules). μ = 0.544 mm^{-1}, F(000) =7260, GOF = 1.038, A total of 130957 reflections were collected, 13777 of which were unique (R_{int} =0.0649). R_1/wR_2 = 0.0855/0.2446 for 219 parameters and 13777 reflections ($I>2\sigma(I)$). Measurement of **1** was conducted on a Saturn70 CCD diffractometer with graphite monochromated Mo–K radiation (λ=0.71073 Å) at 78 K. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares using the SHELXL–97 program package[1]. The positions of H atoms were generated geometrically. Nonhydrogen atoms were refined with anisotropic displacement parameters. Given that the refinement of the metal-organic coordination framework is essentially uninfluenced by the presence of the disordered solvent, the SQUEEZE routine in the PLATON software was applied to subtract the diffraction contribution from the solvent molecules[2]. **1** was immersed into DMSO(d_6) for 48h with out being dissolved, and than the ^{1}H NMR of the DMSO(d_6) were measured to confirm the components in the cavities of **1**. According to elemental analytic data, IR spectrum, TGA analysis and ^{1}H NMR, the solvent molecules were proposed to be approximately DMA:DEF:H_2O=4:10:10 per formula. CCDC-780176 for **1** contains the supplementary crystallographic for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

References:

1. G. M. Sheldrick, SHELXS 97, Program for Crystal Structure Solution; University of Göttingen: Göttingen, **1997**.
2. A. L. Spek, *Appl, J. Crystallogr.* 2003, **36**, 7.

4: Isotherms for N_2 and CO_2 sorption. The pore characteristics of **1** was characterized by N_2 and CO_2 adsorption. The Langmuir Surface Area of **1** was calculated to be 156.15 m^2/g (BET 90.11 m^2/g) based on the N_2 adsorption data collected at 78K. The DA (Dubinin-Astakhov) pore volume of **1** was calculated to be 0.31 cm^3/g based on the CO_2 adsorption data collected at 273K. The relative low adsorption capacities and surface area may result from the non-polority of adsorbates. However, the porosity of **1** can be still confirmed.

5. Supporting Figures



$C_{carboxyl}$**3**-C_{core}-$C_{carboxyl}$**1**	**90.93°**	$C_{carboxyl}$**4**-C_{core}-$C_{carboxyl}$**2**	**120.08°**
$C_{carboxyl}$**3**-C_{core}-$C_{carboxyl}$**2**	**85.20°**	$C_{carboxyl}$**4**-C_{core}-$C_{carboxyl}$**1**	**85.20°**
$C_{carboxyl}$**3**-C_{core}-$C_{carboxyl}$**4**	**141.63°**	$C_{carboxyl}$**2**-C_{core}-$C_{carboxyl}$**1**	**141.63°**

Scheme S1. Simplified representation of the geometry of the ligand in compound **1**.

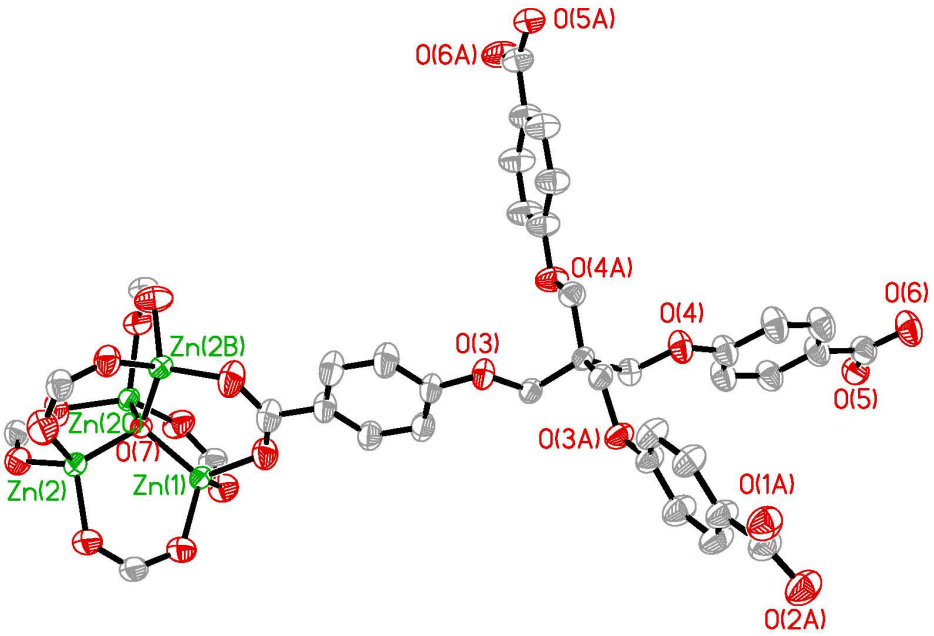


Figure S1. ORTEP drawing of the **1** and the Zn_4O cluster with thermal ellipsoids at 20% probability Symmetry code: A=1/3+y, x-1/3, 1/6-z; B=-y, x-y, z; C=-x+y, -x, z.

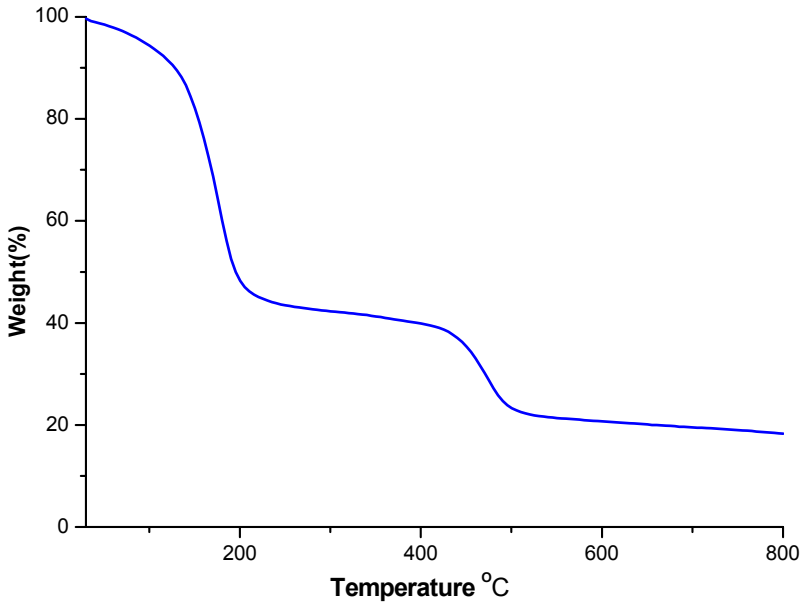


Figure S2. The TGA curve of complex **1** under a nitrogen flow

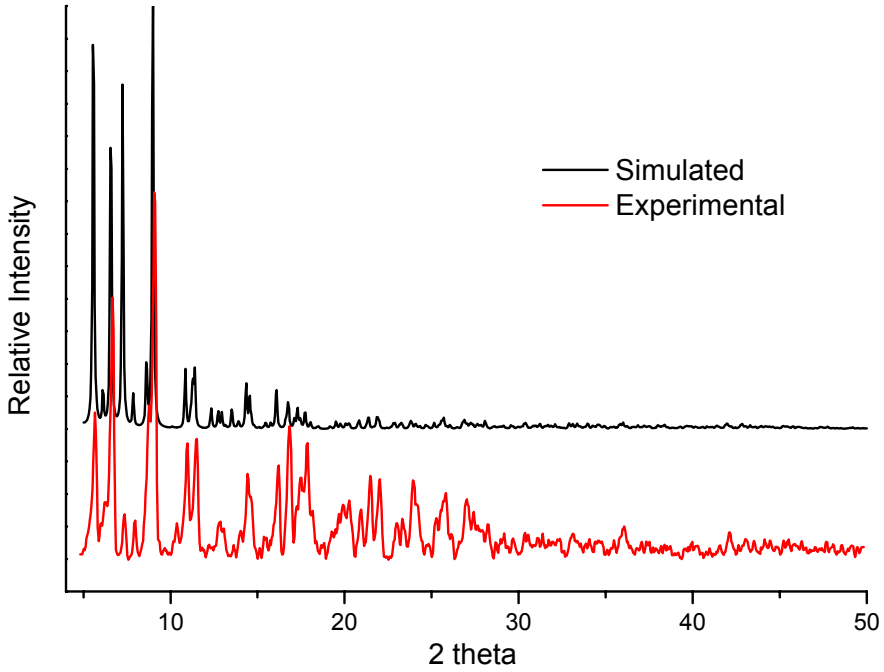


Figure S3. Simulated (black) and experimental (red) X-Ray powder diffraction patterns for **1.**

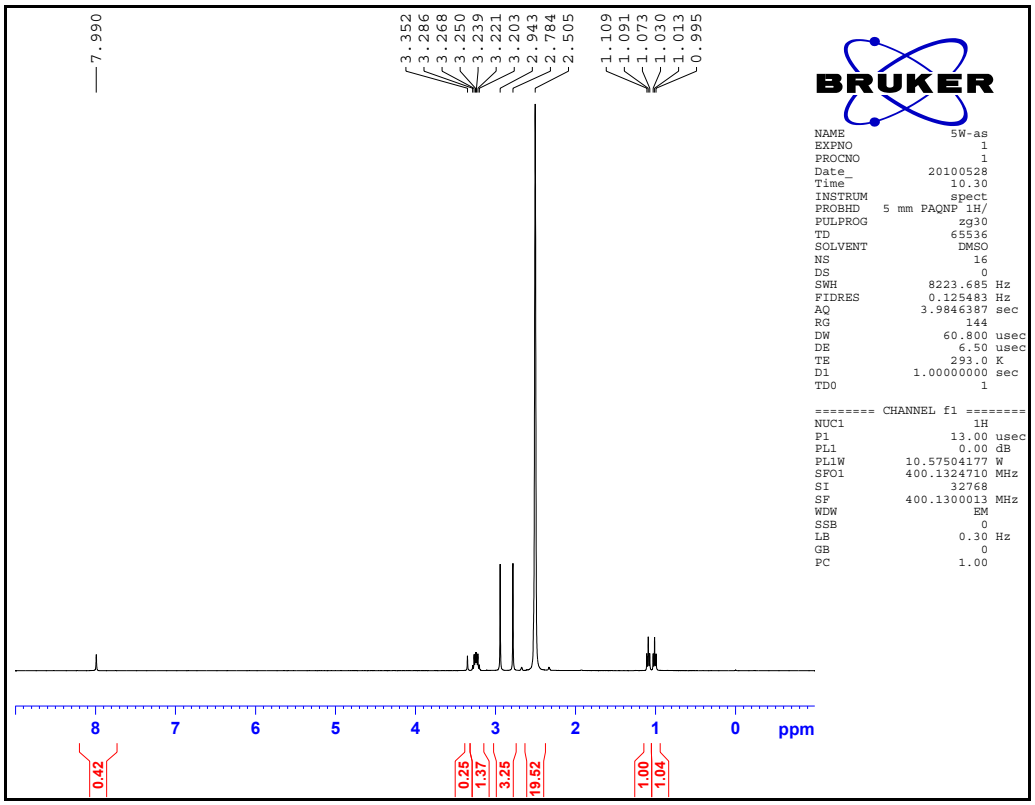


Figure S4. The ^{1}H NMR spectrum of solvents in the pores of compound **1 (**400 MHz, DMSO-d_6, 293 K).

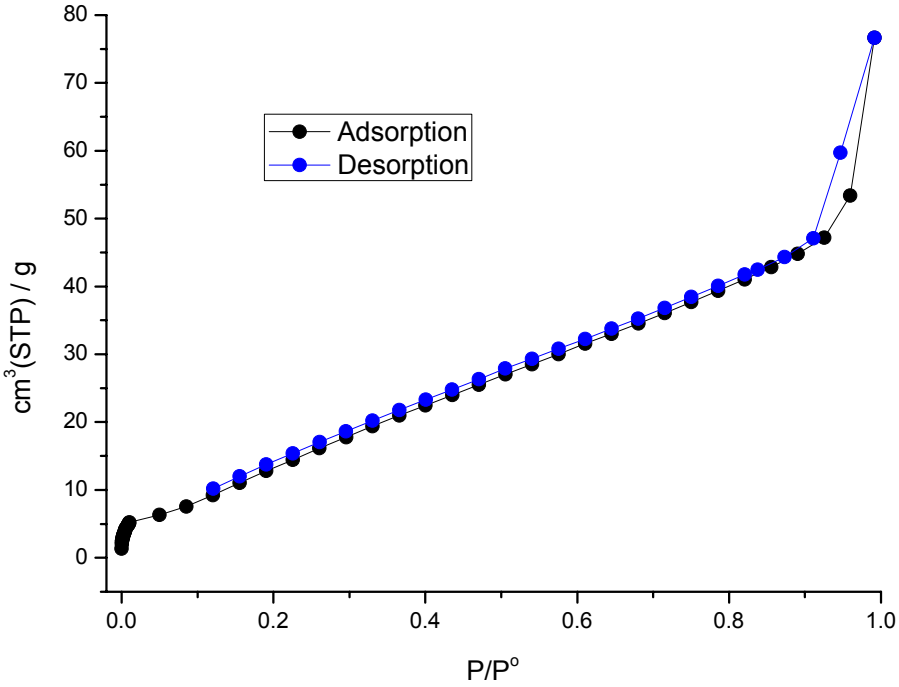


Figure S5. N_2 adsorption isotherms for **1.**

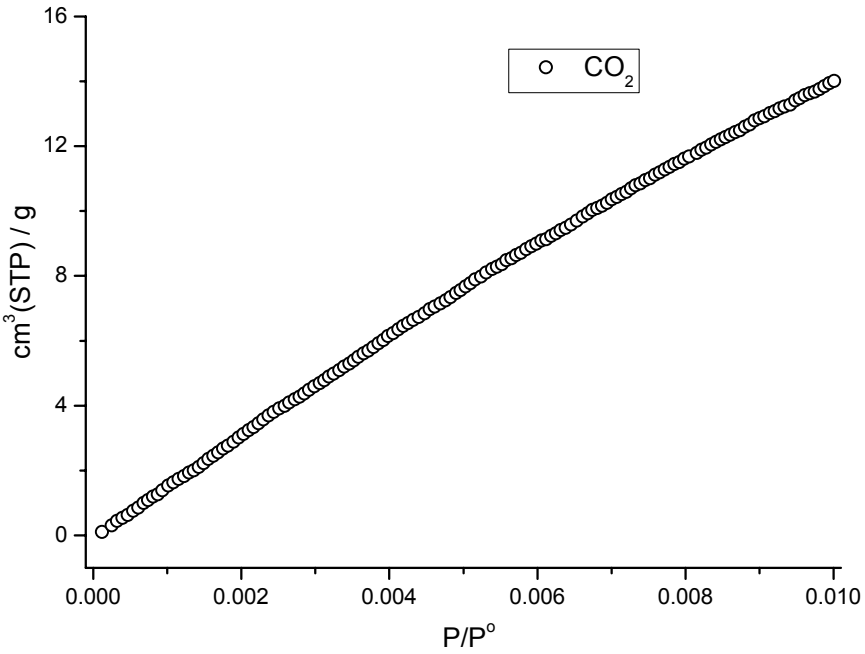


Figure S6. CO_2 adsorption isotherms for **1.**

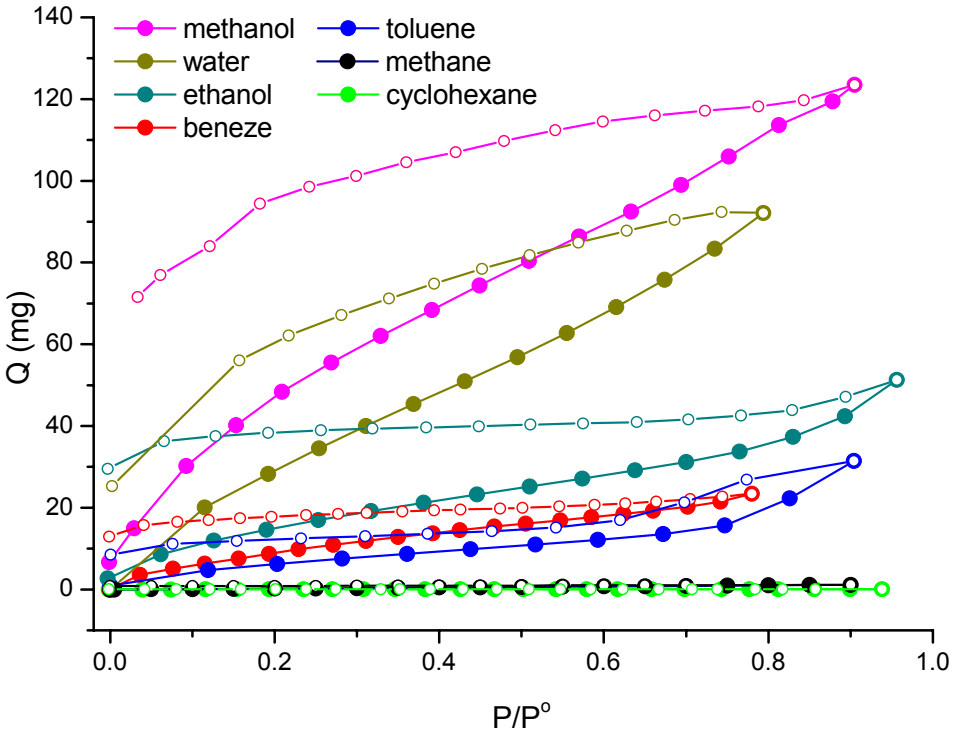


Figure S7. Sorption isotherms for each adsorbate in **1.** Filled circles represent adsorptions and open circles represent desorptions. P^o is the saturated vapor pressure at 298K. 149.99 millibars (methanol), 26.70 millibars (water), 74.92 millibars (ethanol), 99.78 millibars (benzene) 34.98 millibars (toluene), 120.36 millibars (cyclohexane). P^o is 1 bar for methane isotherm.

	Amount adsorbed(mg/g)	Molecular area($Å^2$)[a]	Molecule Dimensions($Å^3$)
methanol	123.5	18.0	3.8×4.2×5.0[b]
water	92.1	10.5	3.2×2.9×3.9
ethanol	51.2	23.1	4.2×4.3× 6.3[b]
toluene	31.4	55.3	6.6×4.0×8.3
benzene	23.4	48.2	6.6×7.3×3.3
methane	1.1	15.4	3.8×4.1×3.9
cyclohexane	0.07	47.5	7.2×6.6×4.9

Table S1. Sorption capacities and molecular sizes used in this study.

[a]The molecular area was calculated from the molecular weight and density of liquid at 298 K by eq: $areaLD(cm^2)=1.091(MW/N_a\rho)^{2/3}$ as ref 16a. [b] Molecule Dimension values are in reference 16b.