Supporting Information

A porous metal–organic framework based on Zn₆O₂ cluster: chemical steady, gas adsorption properties and solvatochromic behavior

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Experimental Details

All the chemicals used for synthesis are of analytical grade and commercially available. The luminescent spectra were recorded on WGY-10 spectrometer. IR absorption spectra of the complexes were recorded in the range of 400–4000 cm⁻¹ on a Nicolet (Impact 410) spectrometer with KBr pellets (5 mg of sample in 500 mg of KBr). C, H, and N analyses were carried out with a Perkin–Elmer 240C elemental analyzer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu–K α radiation ($\lambda = 1.5418$ Å), in which the X-ray tube was operated at 40 kV and 40 mA. Luminescent spectra were recorded with a SHIMAZU VF-320 X-ray fluorescence spectrophotometer at room temperature. The as-synthesized samples were characterized by thermogravimetric analysis (TGA) on a Perkin Elmer thermogravimetric analyzer Pyris 1 TGA up to 1023 K using a heating rate of 10 K min⁻¹ under N₂ atmosphere. High-resolution solid-state nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature on a Bruker DSX-400 spectrometer using a standard Bruker magic angle-spinning (MAS) probe with 4 mm (outside diameter) zirconia rotors.

Synthesis of H₃L:

H₃L was prepared by a similar literature method¹: To a round-bottomed flask equipped with a Dean-Stark trap were charged 3,5-dihydroxybenzoic acid (5 mmol), p-fluorobenzonitrile (10.8 mmol), and K₂CO₃ (22.5 mmol). Then, DMF (20 mL) was added into the flask under nitrogen. The reaction temperature was increased to 170 °C and the reaction was continued for 16 h. After cooling to room temperature, the mixture was poured into water and acidified with 1 M HCl (aq). The resulting precipitate was collected and charged in a round bottomed flask containing KOH (13 g, 0.2 mol), H₂O (50 mL), and ethanol (50 mL), and the mixture was refluxed overnight. After removal of ethanol by distillation, the mixture was cooled to room temperature and poured into water and acidified with concentrated HCl (aq). The resulting precipitate was collected (1.38 g, 70%). 1H NMR (DMSO-d₆, δ , ppm) 7.26 (4 H), 7.36 (2 H), 7.99 (4H).

Synthesis of 1

A mixture of Zn(NO₃)₂·6H₂O (33.4 mg, 0.1 mmol) and H₃L (39.4 mg, 0.1 mmol) was dissolved in 8 mL solution of DMF/H₂O (3:1, v/v). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (10 mL) under autogenous pressure and heated at 120 °C for 3 d, then cooled down to the room temperature at 1 0 C/min. A large quantity of pinky crystals [Zn₅(μ_{3} -OH)₄L₂]·7H₂O·DMF (1) were obtained, which were washed with mother liquid, and dried under ambient conditions (Yield: 69% based on Zn). Anal. Calcd for C₄₅H₄₇NO₂₈Zn₅: C, 39.25, H, 3.44, N, 1.02; found C, 40.17, H, 3.55, N, 1.09. IR (KBr, cm⁻¹): 3414(w), 3115(w), 2960(s), 1666(s), 1597(s), 1565(s), 1396(s), 1255(m), 1183(s), 1100(w), 839(w), 779(w), 665(m), 524(s).

Synthesis of 1'

MOF **1** was dipped in boiling ethanol for 12h, then MOF **1'** was obtained and dried under ambient conditions.

X-ray Data Collection and Structure Determinations.

X-ray crystallographic data of 1 and 1' were collected at room temperature using epoxy-coated crystals mounted on glass fiber. All measurements were made on a Bruker Apex Smart CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The structures of complexes 1 was solved by direct method, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least-squares procedures based on F^2 values.² The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. The distribution of peaks in the channels of 1 was chemically featureless to refine using conventional discrete-atom models. To resolve these issues, the contribution of the electron density by the remaining watermolecule was removed by the SQUEEZE routine in PLATON.³ The relevant crystallographic data are presented in Table S1, the selected bond lengths and angles are given in Tables S2-3, while hydrogen bonds table for 1 are given in Table S4 in Supporting Information,.

Gas adsorption of 1

Gas adsorption measurements were performed using an ASAP 2020 M gas adsorption analyzer. UHP-grade gases were used in measurements. The hydrogen sorption isotherms were collected in the pressure range from 10^{-4} to 850 mmHg at 77 K in a liquid nitrogen bath. The gas sorption experiments of CO₂ and CH₄ at 273 K was carried out in an ice-water bath.

As-synthesized sample of **1** was soaked in ethanol for 24 h, and the extract was discarded. Fresh ethanol was subsequently added, and the sample was allowed to stay in ethanol for an additional 24 h before ethanol was removed. Such a refilling and removal of ethanol recycle was repeated 4 times. Before adsorption measurement, the sample was further activated using the "outgas" function of the surface area analyzer for 12 hours at 150 ^oC. Finally, 79.5 mg sample was used for all gas adsorption measurements.

References

- 1. Matsumoto, K.; Higashihara, T.; Ueda, M. Macromolecules. 2008, 41, 7560.
- 2. SHELXTL NT Version 5.1. Program for Solution and Refinement of Crystal tructures. University of Gttingen: Germany: G. M. Sheldrick, 1997.
- 3. Spek, A. L., J Appl Crystallogr 2003, 36, 7-13.

Table S1. Crystallographic data and structure refinement details for 1 and 1'.

compound	1	1'
empirical formula	$C_{42}H_{30}O_{22}Zn_5$	C45H38O24Zn5
formula weight	1213.61	1291.68
crystal system	triclinic	triclinic
space group	$P\overline{1}$	$P\overline{1}$
<i>a</i> (Å)	6.3108(13)	6.3303(4)
<i>b</i> (Å)	12.639(3)	12.6819(8)
<i>c</i> (Å)	15.631(3)	15.6877(10)
α (deg)	95.723(3)	95.711(1)
β (deg)	99.878(4)	99.773(1)
γ (deg)	97.860(4)	97.973(1)
Ζ	1	1
$V(\text{\AA}^3)$	1207.0(4)	1219.33(13)
$D_{calcd}(g \text{ cm}^{-3})$	1.670	1.759
μ(Mo Ka)(mm ⁻¹)	2.528	2.513
<i>F</i> (000)	608.0	650.0
R(int)	0.0192	0.0117
observed data $[I > 2\sigma(I)]$	4182	4784
$R_1, wR_2 (I > 2\sigma(I))$	0.0423/ 0.1220	0.1498/0.0600
S	1.046	1.065

Complex 1					
O(1)-Zn(3) 1.9816(16)	O(1)-Zn(2) 2.0022(16)	O(1)-Zn(1) 2.0722(14)	O(2)-Zn(3) 1.9768(14)		
O(2)-Zn(2)#1 2.0137(15)	O(2)-Zn(1) 2.1805(16)	O(3)-Zn(2) 2.0615(18)	O(4)-Zn(3) 1.9059(19)		
O(6)-Zn(1)#2 2.0548(16)	O(7)-Zn(2)#3 2.1279(14)	O(7)-Zn(2)#4 2.4132(16)	O(9)-Zn(2)#5 2.1016(16)		
O(10)-Zn(3)#6		Zn(3)-O(1)-Zn(2)	118.13(8)		
1.9206(18)					
Zn(3)-O(1)-Zn(1)	94.07(6)	Zn(2)-O(1)-Zn(1)	120.45(7)		
Zn(3)-O(2)-Zn(2)#1	117.80(7)	Zn(3)-O(2)-Zn(1)	90.94(6)		
Zn(2)#1-O(2)-Zn(1)	120.87(7)	O(6)#3-Zn(1)-O(1)#9	84.96(6)		
O(6)#8-Zn(1)-O(1)#9	95.04(6)	O(6)#3-Zn(1)-O(2)#9	93.98(6)		
O(6)#8-Zn(1)-O(2)#9	86.02(6)	O(1)#9-Zn(1)-O(2)#9	83.03(6)		
O(1)-Zn(1)-O(2)#9	96.97(6)	O(1)-Zn(1)-Zn(3)#9	138.23(4)		
O(1)-Zn(2)-O(3)	94.58(7)	O(1)-Zn(2)-O(9)#5	85.20(6)		
O(1)-Zn(2)-O(7)#3	93.97(6)	O(2)-Zn(3)-O(1)	90.86(6)		
O(10)#6-Zn(3)-O(1)	109.97(7)	O(4)-Zn(3)-O(1)	109.05(8)		

Symmetry transformations used to generate equivalent atoms: #1 x-1, y, z, #2 x+1, y-1, z, #3 -x+1, -y+1, -z, #4 x, y-1, z, #5 -x+1, -y+2, -z+1, #6 -x, -y+2, -z+1, #8 x-1, y+1, z, #9 -x, -y+2, -z

Table S3.	Selected bond	lengths (Å)	and angles ((deg) for 1'.
			0	

Complex 1'					
O(1)-Zn(3) 1.997(4)	O(1)-Zn(2) 2.007(4)	O(1)-Zn(1) 2.081(4)	O(2)-Zn(3) 1.974(4)		
O(2)-Zn(2)#2 2.007(4)	O(2)-Zn(1) 2.200(4)	O(4)-Zn(3) 1.928(4)	O(6)-Zn(1)#3 2.078(4)		
O(7)-Zn(2)#4 2.132(4)	O(7)-Zn(2)#5 2.411(4)	O(10)-Zn(3)#7 1.935(4)			
O(6)#4-Zn(1)-O(1)	95.44(16)	O(6)#9-Zn(1)-O(1)	84.56(16)		
O(6)#9-Zn(1)-O(1)#10	95.44(16)	O(6)#4-Zn(1)-O(2)	85.91(15)		
O(1)-Zn(1)-O(2)	83.22(15)	O(1)#10-Zn(1)-O(2)	96.78(15)		
O(1)-Zn(2)-O(3)	94.93(16)	O(1)-Zn(2)-O(9)#6	85.15(16)		
O(3)-Zn(2)-O(9)#6	93.09(17)	O(3)-Zn(2)-O(7)#4	96.92(17)		
O(4)-Zn(3)-O(10)#7	113.04(18)	O(4)-Zn(3)-O(2)	118.14(18)		
O(4)-Zn(3)-O(1)	109.20(17)	O(2)-Zn(3)-O(1)	91.51(17)		

Symmetry transformations used to generate equivalent atoms: #1 -*x*+2, -*y*, -*z*+1, #2 *x*-1, *y*, *z*, #3 *x*+1, *y*-1, *z*, #4 -*x*+1, -*y*+1, -*z*, #5 *x*, *y*-1, *z*, #6 -*x*+1, -*y*+2, -*z*+1, #7 -*x*, -*y*+2, -*z*+1.

 D–H···A	D-H	Н…А	D…A	∠DHA
 O2-H2B…O9	0.850	2.389	2.973	126.37
O2-H2B…O7	0.850	2.422	2.837	110.78
O2-H2B…O3	0.850	2.605	3.048	113.69
O11-H11A…O12	0.850	1.976	2.427	112.12
O12-H12B…O11	0.850	1.495	2.295	155.39
O12-H12C…O6	0.850	2.88	3.199	104.21
O12'-H12E… O6	0.850	2.59	3.091	119.31

Table S4. Hydrogen bonds for 1.



Figure S1. The asymmetric unit of 1.



Figure S2. FT-IR spectroscopy of the compound 1.



Figure S3. Powder x-ray diffraction patterns of stimulated 1, as-made 1.



Figure S4. Views of the 1D chain structure based tetrahedron and octahedron along *b* axis.



Figure S5. $2 \times 2 \times 2$ supercell of **1** showing the pore structures with van der Waals surfaces (blue, toward the pore; gray, toward the framework).



Figure S6. Powder X-ray diffraction patterns of stimulated 1, the activated 1.



Figure S7. The curve of TGA of 1.



Figure S8. The curve of TGA of 1 with exchange with ethanol.



Figure S9. The curve of TGA of the activated 1.



Figure S10. FT-IR spectroscopy of the activated 1.



Figure S11. Powder X-ray diffraction patterns of **1** in hexane, acetonitrile, ethanol, DMF, toluene and water (from top to bottom) at room temperature for one week.



Figure S12. PXRD patterns of 1 treated with either acidic or basic condition at their boiling points for 12 h.



Figure S13.¹³C solid-state NMR spectra of 1.



Figure S14.¹³C solid-state NMR spectra of activated 1.



Figure S15. Solid-state H NMR spectra of 1 with treated by boiling water.

2,60K, D1=1s, different spectrum



Figure S16. Solid-state H NMR spectra of 1 with outgassing under vacuum.



Figure S17. N₂ sorption isotherms of 1 at 77 K



Figure S18. Gas sorption isotherms of MOF 1 for H_2 , CO_2 and CH_4 (a:Uptake amount, mmol/g, b: Uptake amount cm³/g).



Figure S19. Solid-state, room-temperature photoemission of H₃L



Figure. S20. Solid-state, room-temperature photoemission of 1.



Figure S21. The PL excitation (dashed) and emission spectrum (solid) of Na_3L and L in NaOH solution at room temperature.



Figure S22. Solid-state, room-temperature photoemission of evacuated 1.



Figure S23. Solvent-dependent emission spectra from a crystal of 1 soaked in water, DMF, ethanol, acetonitrile, hexane and toluene.