

## Electronic Supporting Information

# Large H<sub>2</sub> Storage Capacity of a New Polyhedron-based Metal–Organic Framework with High Thermal and Hygric Stability

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## General Procedures

All other reagents were purchased from commercial sources and were used without further purification. Elemental analyses were conducted at the Elemental Analysis Laboratory of the Korean Basic Science Institute, Korea. Mass spectral data were obtained on a Jeol JMS 700 (JEOL, Japan) high resolution mass spectrometer at the Korea Basic Science Institute (Daegu). Fourier Transform infrared (FTIR) spectra were recorded as KBr pellets with a Varian 1000 FTIR spectrophotometer (4000–400  $\text{cm}^{-1}$ ). Powder X-ray diffraction (PXRD) data was recorded using a Rigaku D/M 2200T automated diffractometer at room temperature with a step size of 0.02°. The variable temperature PXRD (VT-PXRD) measurements were carried using a Bruker D8 Advance system in air, and the sample was heated gradually from room temperature with a holding time of at least 30 min at each temperature. Thermogravimetric analysis (TGA) was performed using an STA-1000 system (Scinco Co. LTD, Korea) in air with a heating rate of 4  $^{\circ}\text{C min}^{-1}$  between ambient temperature and 550  $^{\circ}\text{C}$ .

**Preparation of 1,3,5-tris(3,5-dicarboxylphenylethynyl)benzene methyl ester:** A solution of triethylamine (40 mL) in anhydrous tetrahydrofuran (80 mL) was degassed by bubbling dry  $\text{N}_2$  for 30 min. A 4.895 g (15.29 mmol) sample of dimethyl-5-iodoisophthalate was added to the solution, followed by dichlorobis(triphenylphosphine)palladium(II) (0.175 g, 0.249 mmol) and copper(I) iodide (0.145 g, 0.761 mmol). The mixture was stirred at room temperature for 30 min, and then the solution of 1,3,5-triethynylbenzene (0.765 g, 5.09 mmol) in anhydrous THF (20 mL) was added to the solution drop-wise for 20 min while bubbling. The mixture was stirred for 16 h at room temperature. The yellow precipitate was separated by filtration, and the filtrate was dissolved in 50 mL dichloromethane. The organic phase was washed three times using 100 mL water and dried over anhydrous  $\text{MgSO}_4$ . The volatiles were removed by evaporation under reduced pressure, and the brown solid residue was

freeze-dried. Yield = 3.082 g, 83.3%. HRMS (FAB)  $m/z$  for  $C_{42}H_{31}O_{12}$  ( $[M + H]^+$ ), calcd: 727.1816; found: 727.1820.  $^1H$  NMR spectrum (300 MHz,  $CDCl_3$ ,  $\delta$  ppm): 8.68 (s, 3H), 8.40 (d, 6H), 7.74 (s, 3H), 3.40 (s, 18H).  $^{13}C$  NMR spectrum (75.42 MHz,  $CDCl_3$ ,  $\delta$  ppm): 165.69, 136.79, 134.88, 131.23, 130.67, 123.90, 123.77, 89.43, 89.03, 52.83. IR spectrum (KBr,  $cm^{-1}$ ): 3442, 2592, 1729, 1598, 1578, 1439, 1338, 1245, 1140, 1020, 1001, 912, 877, 754, 723.

**Preparation of 1,3,5-tris(3,5-dicarboxylphenylethynyl)benzene ( $H_6L$ ):** A 5.611 g (100 mmol) sample of potassium hydroxide was dissolved in 130 mL methanol. A 3.082 g (4.241 mmol) sample of 1,3,5-tris(3,5-dicarboxylphenylethynyl)benzene methyl ester was slowly added to the solution, and stirred for 5 h at 80 °C. The volatiles were removed by evaporation under reduced pressure. The residue was dissolved in 100 mL water, acidified to pH 2–3 using 1 N HCl, and stirred for 5 h. The precipitate was separated by filtration, washed with water, and freeze-dried. Yield = 2.423 g, 88.9%. HRMS (FAB)  $m/z$  for  $C_{36}H_{18}O_{12}$  ( $M^+$ ), calcd: 642.0798; found: 642.0798.  $^1H$  NMR spectrum (300 MHz,  $DMSO-d^6$ ,  $\delta$  ppm): 13.54 (s, 6H), 8.48 (d, 3H), 8.32 (s, 6H), 8.00 (s, 3H).  $^{13}C$  NMR spectrum (75.42 MHz,  $DMSO-d^6$ ,  $\delta$  ppm): 166.00, 135.64, 134.73, 132.55, 130.21, 123.27, 122.68, 89.21, 88.82, IR spectrum (KBr,  $cm^{-1}$ ): 3419, 3078, 1708, 1698, 1596, 1445, 1264, 1245, 1149, 1009, 913, 878, 757, 668.

**Preparation of  $[Zn_{24}L_8(H_2O)_{24}] \cdot xDMF \cdot yH_2O$ , **1**** (where x and y are the unidentified numbers of molecules of the solvent, *N,N'*-dimethylformamide (DMF), and water, respectively): A 0.4821 g (0.750 mmol) sample of  $H_6L$  was dissolved in 30 mL DMF, then a 0.7139 g (2.40 mmol) sample of  $Zn(NO_3)_2 \cdot 6H_2O$  was added, sealed in a 50 mL vial, and heated at 85 °C for 20 h. The colorless block-shaped crystals were filtered, washed with DMF, and then air-dried. Yield 0.413 g. IR (KBr,  $cm^{-1}$ ):

3420, 3074, 2932, 1660, 1632, 1590, 1495, 1428, 1384, 1302, 1255, 1158, 1104, 1061, 1013, 910, 866, 775, 721, 674, 527. The desolvated sample, **1a**, was prepared by repeatedly soaking and decanting **1** in DMF and methylene chloride for 3–4 days, then vacuum-drying overnight at an ambient temperature. Yield = 0.346 g, 40.2% (based on ligand). Elemental analysis data calcd for  $[\text{Zn}_{24}\text{L}_8(\text{H}_2\text{O})_{24}] \cdot 22\text{DMF} \cdot 35\text{H}_2\text{O}$ , **1a** ( $\text{C}_{348}\text{H}_{352}\text{N}_{20}\text{O}_{174}\text{Zn}_{24}$ , fw = 9331.98): C 45.56, H 3.97, N 3.48%; found: C 45.59, H 3.47, N 3.48%. IR (KBr,  $\text{cm}^{-1}$ ): 3393, 3078, 2927, 1702, 1656, 1619, 1584, 1562, 1431, 1383, 1370, 1303, 1253, 1107, 1012, 914, 877, 775, 724, 679, 532.

**Preparation of  $[\text{Cu}_{24}\text{L}_8(\text{H}_2\text{O})_{24}] \cdot 74\text{DMF} \cdot 56\text{H}_2\text{O}$ , **2**** (where x and y are the unidentified numbers of molecules of the solvent, *N,N'*-dimethylformamide (DMF), and water, respectively): A 0.0643 g (0.100 mmol) sample of  $\text{H}_6\text{L}$  was dissolved in 5 mL DMF. A 0.2791 g (1.200 mmol) sample of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and 0.30 mL 6M HCl solution was added to the solution and stirred for 1–2 min. The solution was sealed in a 10 mL vial, and heated at 70 °C for 2 days. Pale blue crystals were filtered, washed with DMF, and then exposed in air for several days. Yield = 0.140 g, 83.1% (based on ligand). Elemental analysis data for  $[\text{Cu}_{24}(\text{L})_8(\text{H}_2\text{O})_{24}] \cdot 74\text{DMF} \cdot 56\text{H}_2\text{O}$ , **2** ( $\text{C}_{510}\text{H}_{774}\text{N}_{74}\text{O}_{250}\text{Cu}_{24}$ , fw = 13476.21), calcd: C 45.49, H 5.79, N 7.70%; found: C 45.31, H 5.11, N 8.22%. IR (KBr,  $\text{cm}^{-1}$ ): 3420, 2930, 1661, 1587, 1431, 1378, 1301, 1255, 1156, 1100, 1013, 918, 878, 775, 735, 663, 535, 489, 413. The desolvated sample, **2a**, was prepared by repeatedly soaking and decanting **2** in DMF and methanol for 2 days for each solvent, vacuum-drying at 150 °C overnight, then exposing in air for several days. Yield = 0.079 g, 85% (based on ligand). Elemental analysis data calcd for  $[\text{Cu}_{24}\text{L}_8(\text{H}_2\text{O})_{24}] \cdot 24\text{H}_2\text{O}$ , **2a** ( $\text{C}_{288}\text{H}_{192}\text{O}_{144}\text{Cu}_{24}$ , fw = 7481.71): C 46.23, H 2.59%; found: C 46.02, H 2.42%. IR (KBr,  $\text{cm}^{-1}$ ): 3420, 3082, 2923, 2360, 2341, 1698, 1615, 1583, 1557, 1428, 1372, 1303, 1261, 1117, 1012, 914, 878, 771, 726, 678, 535.

## Crystallographic data collection and refinement of the structure

A single crystal of **1** was coated with paratone oil. The diffraction data were measured at 100 K with synchrotron radiation ( $\lambda = 0.77489 \text{ \AA}$ ) on a 4AMXW ADSC Quantum-210 detector with a Pt-coated Si double crystal monochromator at the Pohang Accelerator Laboratory, Korea. The ADSC Quantum-210  
5 ADX program<sup>S1</sup> was used for data collection, and HKL2000 (Ver. 0.98.698a)<sup>S2</sup> was used for cell refinement, reduction and absorption correction. A single crystal of **2** was coated with paratone oil. The diffraction data were measured with Mo K $\alpha$  radiation on a Bruker SMART CCD equipped with a graphite-crystal, incident-beam monochromator. The SMART and SAINT software packages<sup>S3</sup> were used for data collection and integration, respectively. The collected data were corrected for absorbance  
10 using SADABS<sup>S4</sup> based upon Laue symmetry using equivalent reflections.

Crystal structure analysis of  $[\text{Zn}_{24}\text{L}_8(\text{H}_2\text{O})_{24}]$ , **1**: A colorless block crystal,  $0.60 \times 0.40 \times 0.40 \text{ mm}^3$ ,  $\text{Zn}_{24}\text{C}_{288}\text{H}_{144}\text{O}_{120}$ ,  $M = 7092.91 \text{ g mol}^{-1}$ , cubic, space group  $Fm-3m$  (space group # 225),  $a = 42.854(5) \text{ \AA}$ ,  $V = 78\,699(16) \text{ \AA}^3$ ,  $T = 100(2) \text{ K}$ ,  $Z = 4$ ,  $\mu$  (synchrotron,  $\lambda = 0.77489 \text{ \AA}$ ) =  $0.752 \text{ mm}^{-1}$ , 147 398 reflections were collected, 4347 were unique [ $R_{\text{int}} = 0.0576$ ]. The crystal structure was solved by direct  
15 methods and refined by full-matrix least-squares calculations with the SHELXTL-PLUS software package.<sup>S5</sup> Two zinc and two ligated water sites with a quarter site occupancy, and 1/6 ligand unit, and one lattice water molecule in a crystallographic  $m-3m$  symmetry site were identified as an asymmetric unit. (The ligated water molecules could be partially identified solvent DMF molecules.) All nonhydrogen atoms were refined anisotropically; all hydrogen atoms except those attached to the  
20 ligated water molecules were assigned isotropic displacement coefficients  $U(\text{H}) = 1.2U$ , and their coordinates were allowed to ride on their respective atoms. The hydrogen atoms of the ligated water molecules were not included in the least-squares refinement. The refinement converged to a final  $R1 = 0.1123$ , and  $wR2 = 0.3703$  for 3655 reflections of  $I > 2\sigma(I)$ . The structure refinement was further

performed after modification of the data for electron density for the solvent cavity including a lattice solvent molecule (58 750 Å<sup>3</sup>, 74.7% (without ligated water: 59 607 Å<sup>3</sup>, 75.7%)) with the *SQUEEZE* routine of PLATON,<sup>S6</sup> which led to better refinement and data convergence. Refinement of the structure converged at a final  $R1 = 0.0653$ ,  $wR2 = 0.2344$  for 3890 reflections with  $I > 2\sigma(I)$ ,  $R1 = 0.0699$ ,  $wR2 = 0.2434$  for all 4347 reflections. The largest difference peak and hole were 0.380 and -0.528 e·Å<sup>-3</sup>, respectively.

Crystal structure analysis of [Cu<sub>24</sub>L<sub>8</sub>(H<sub>2</sub>O)<sub>24</sub>], **2**: A pale blue block crystal, 0.35 × 0.33 × 0.13 mm<sup>3</sup>, Cu<sub>24</sub>C<sub>288</sub>H<sub>144</sub>O<sub>120</sub>,  $M = 7048.99$  g mol<sup>-1</sup>, cubic, space group *Fm-3m* (space group # 225),  $a = 42.833(3)$  Å,  $V = 78\,583(10)$  Å<sup>3</sup>,  $T = 173(2)$  K,  $Z = 4$ ,  $\mu$  (Mo K $\alpha$ ,  $\lambda = 0.71073$  Å) = 0.670 mm<sup>-1</sup>, 95 044 reflections were collected, 3375 were unique [ $R_{\text{int}} = 0.1675$ ]. The crystal structure was solved by direct methods and refined by full-matrix least-squares calculations with the SHELXTL-PLUS software package.<sup>S5</sup> Two copper and two ligated water sites with a quarter site occupancy, and 1/6 ligand unit were identified as an asymmetric unit (The ligated water molecules could be partially identified solvent DMF molecules.). All nonhydrogen atoms were refined anisotropically; all hydrogen atoms except those attached to the ligated water molecules were assigned isotropic displacement coefficients  $U(\text{H}) = 1.2U$ , and their coordinates were allowed to ride on their respective atoms. The hydrogen atoms of the ligated water molecules were not included in the least-squares refinement. The refinement converged to a final  $R1 = 0.1737$ , and  $wR2 = 0.4664$  for 2826 reflections of  $I > 2\sigma(I)$ . The structure refinement was further performed after modification of the data for electron density for the solvent cavity (58 583 Å<sup>3</sup>, 74.6% (without ligated water: 58 583 Å<sup>3</sup>, 77.2%)) with the *SQUEEZE* routine of PLATON,<sup>S6</sup> which led to better refinement and data convergence. Refinement of the structure converged at a final  $R1 = 0.0944$ ,  $wR2 = 0.1721$  for 2860 reflections with  $I > 2\sigma(I)$ ,  $R1 = 0.1228$ ,  $wR2$

= 0.1846 for all 3375 reflections. The largest difference peak and hole were 0.488 and  $-1.679 \text{ e} \cdot \text{\AA}^{-3}$ , respectively.

A summary of the crystal and intensity data is given in Tables S1 and S2. CCDC 707996 and 722583 contain the supplementary crystallographic data for this paper. 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.

### Gas sorption measurements

**1a** for gas sorption measurement was prepared by presoaking in DMA for 2 days, in methylene chloride for a day, and then vacuum-drying overnight at ambient temperature. **2a** was prepared by presoaking in DMF for 2 weeks, in methanol for 2 days, and then vacuum-drying for 15 hours at 150 °C. The low-pressure gas sorption isotherms for **1a** and **2a** were measured with a BELSORP-mini II (BEL Japan, Inc.) in a standard volumetric technique up to 1 atm at 77 K and 87 K. A part of the N<sub>2</sub> sorption isotherm in the  $P/P_0$  range 0.0002–0.1111 was fitted to the BET equation to estimate the BET surface area and the Langmuir surface area calculation was performed using all data points. The high-pressure H<sub>2</sub> adsorption experiments were conducted using a volumetric sorption analyzer HPVA-100 (VTI Corporation) equipped with a rotary vane pump (DUO 5 M, PFEIFFER) and a turbomolecular drag pump (TMH 064/TMU 064, Pfeiffer). The sample holder consisted of a sample cell and tube equipped with a diaphragm valve (6LV-DSBW4, Swagelok). The two assemblies were connected via filter gasket (SS-4-VCR-2-.5M, Swagelok) and the materials of construction are all 316 stainless steel. Around 0.6 g of sample was transferred to the sample cell and outgassing was performed overnight at 180 °C for 6 h under a high vacuum ( $\sim 0.001 \text{ Pa}$ ). Upon completion of outgassing, the sample cell was

recharged with helium (99.999%) to measure the loading amount of the dehydrated sample, which was calculated from the weight difference between the blank and sample-loaded cell. The activation described above was then repeated, and gas sorption was performed. High purity hydrogen (99.999) obtained from Korea Gas Co. During the sorption measurements, the sample cell was immersed in a  
5 cryogenic dewar at 77 K. The total H<sub>2</sub> uptake was calculated using the following equation,<sup>S7</sup>

$$N_{\text{total}} = N_{\text{excess}} + (V_{\text{pore}} \times d_{\text{H}_2,\text{gas}} \times 100)$$

where  $N_{\text{total}}$  (wt%) is the total uptake amount of H<sub>2</sub>,  $N_{\text{excess}}$  (wt%) is the surface excess uptake amount of H<sub>2</sub>,  $V_{\text{pore}}$  (cm<sup>3</sup>/g) is the crystallographic pore volume, and  $d_{\text{H}_2,\text{gas}}$  (g/cm<sup>3</sup>) is the density of H<sub>2</sub> gas as a function of pressure at 77 K.<sup>S8</sup>

10

## References

S1 A. J. Arvai and C. Nielsen, ADSC Quantum-210 ADX Program, Area Detector System Corporation; Poway, CA, USA, **1983**.

S2 Z. Otwinowski and W. Minor, in *Methods in Enzymology*, ed. Carter, Jr., C. W.; Sweet, R. M.  
15 Academic Press: New York, 1997, **276**, part A, 307–326.

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

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

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



S6 A. L. Spek, Platon program. (Ver 1.08), *Acta Crystallogr., Sect. A*, 1990, **46**, 194–201.

S7 (a) S. S. Kaye, A. Dailly, O. M. Yaghi and J. R. Long, *J. Am. Chem. Soc.*, 2007, **129**, 14176–14177; (b) H. Furukawa, M. A. Miller and O. M. Yaghi, *J. Mater. Chem.*, 2007, **17**, 3197–3204.

S8 NIST Chemistry WebBook (Thermophysical Properties of Fluid Systems):

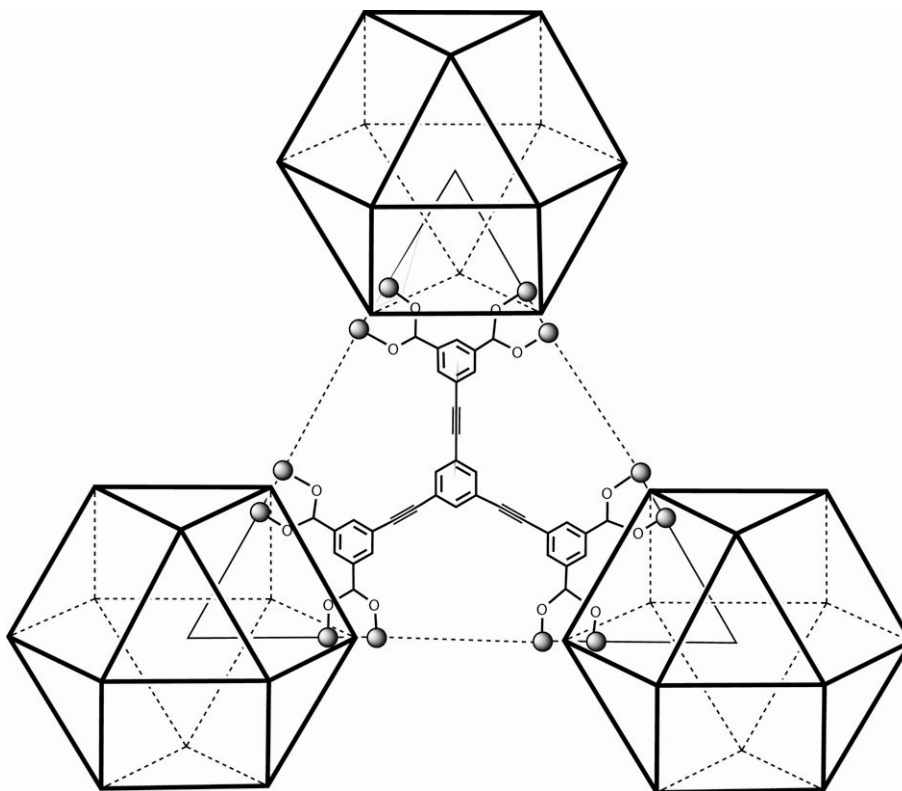
5 <http://webbook.nist.gov/chemistry/fluid/>.

Table S1. Crystal data and structure refinement for  $[\text{Zn}_{24}\text{L}_8(\text{H}_2\text{O})_{24}]$ , **1**.

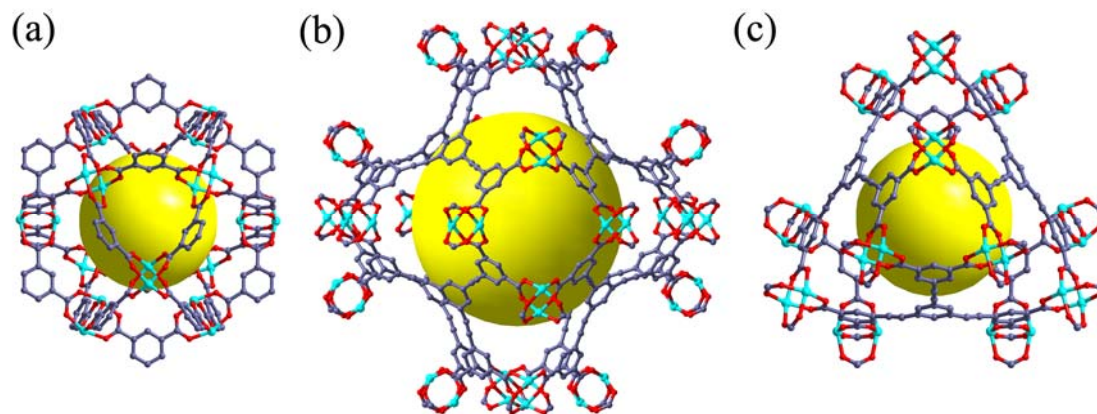
Empirical formula	$\text{C}_{288}\text{H}_{144}\text{O}_{120}\text{Zn}_{24}$	
Formula weight	7092.91	
5 Temperature	100(2) K	
Wavelength	0.77489 Å	
Crystal system	Cubic	
Space group	<i>Fm-3m</i>	
Unit cell dimensions	$a = 42.854(5)$ Å	$\alpha = 90^\circ$ .
10	$b = 42.854(5)$ Å	$\beta = 90^\circ$ .
	$c = 42.854(5)$ Å	$\gamma = 90^\circ$ .
Volume	$78699(16)$ Å <sup>3</sup>	
Z	4	
Density (calculated)	0.599 Mg/m <sup>3</sup>	
15 Absorption coefficient	0.752 mm <sup>-1</sup>	
F(000)	14368	
Crystal size	$0.60 \times 0.40 \times 0.40$ mm <sup>3</sup>	
Theta range for data collection	2.26 to 30.25°.	
Index ranges	$-55 \leq h \leq 55, -55 \leq k \leq 55, -55 \leq l \leq 55$	
20 Reflections collected	147398	
Independent reflections	4347 [R(int) = 0.0566]	
Completeness to theta = 30.25°	99.1%	
Absorption correction	Empirical	
Max. and min. transmission	0.7530 and 0.6611	
25 Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	4347 / 0 / 99	
Goodness-of-fit on F <sup>2</sup>	1.136	
Final R indices [I > 2σ(I)]	R1 = 0.0653, wR2 = 0.2344	
R indices (all data)	R1 = 0.0699, wR2 = 0.2434	
30 Extinction coefficient	0.00045(7)	
Largest diff. peak and hole	0.380 and -0.528 e.Å <sup>-3</sup>	

Table S2. Crystal data and structure refinement for [Cu<sub>24</sub>L<sub>8</sub>(H<sub>2</sub>O)<sub>24</sub>], **2**.

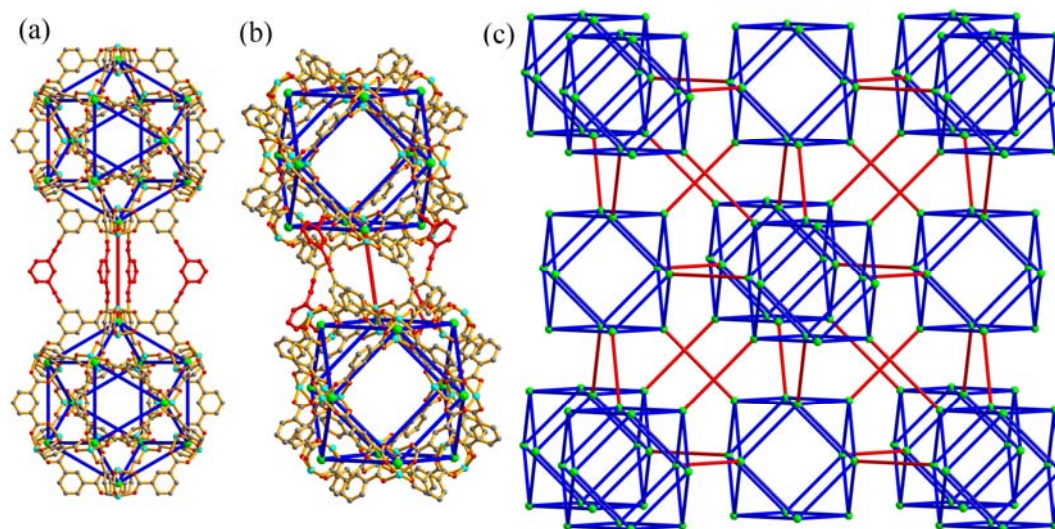
Empirical formula	C <sub>288</sub> H <sub>144</sub> O <sub>120</sub> Cu <sub>24</sub>	
Formula weight	7048.99	
5 Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	<i>Fm-3m</i>	
Unit cell dimensions	a = 42.833(3) Å	α = 90°.
10	b = 42.833(3) Å	β = 90°.
	c = 42.833(3) Å	γ = 90°.
Volume	78583(10) Å <sup>3</sup>	
Z	4	
Density (calculated)	0.596 Mg/m <sup>3</sup>	
15 Absorption coefficient	0.670 mm <sup>-1</sup>	
F(000)	14112	
Crystal size	0.35 × 0.33 × 0.13 mm <sup>3</sup>	
Theta range for data collection	1.58 to 24.99°.	
Index ranges	-50 ≤ h ≤ 34, -50 ≤ k ≤ 44, -50 ≤ l ≤ 50	
20 Reflections collected	95044	
Independent reflections	3375 [R(int) = 0.1675]	
Completeness to theta = 24.99°	99.7%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9180 and 0.7993	
25 Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	3375 / 2 / 103	
Goodness-of-fit on F <sup>2</sup>	1.273	
Final R indices [I > 2σ(I)]	R1 = 0.0944, wR2 = 0.1721	
R indices (all data)	R1 = 0.1228, wR2 = 0.1846	
30 Largest diff. peak and hole	0.488 and -1.679 e.Å <sup>-3</sup>	



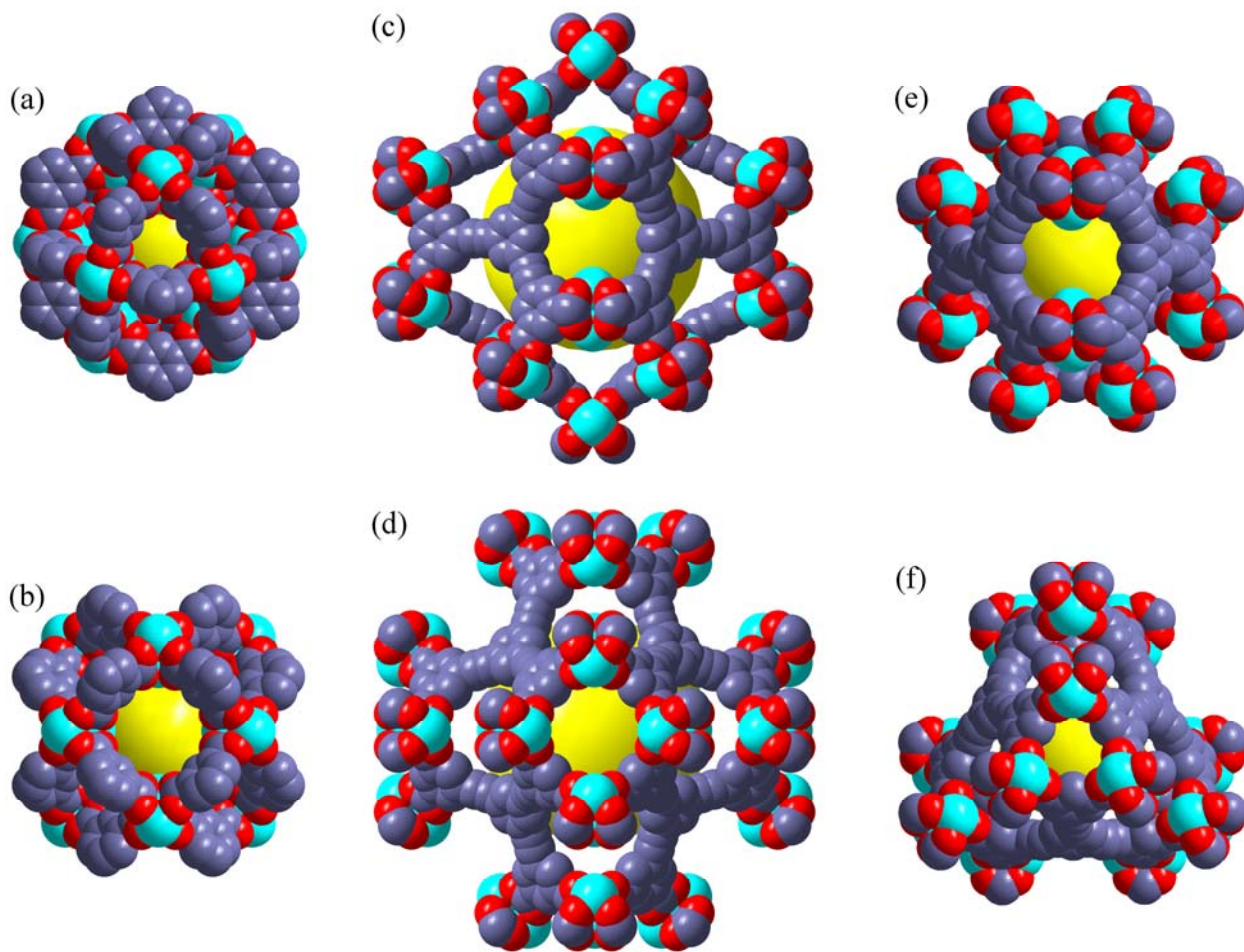
Scheme S1. A  $C_3$  symmetric ligand ( $L^{6-}$ ) with three bdc units interlinked via the 1,3,5-triethynylbenzene group and three schematic cuboctahedra,  $[(M_2)_{12}(bdc)_{24}]$ , where small gray balls represent either Zn(II) or Cu(II) ions.



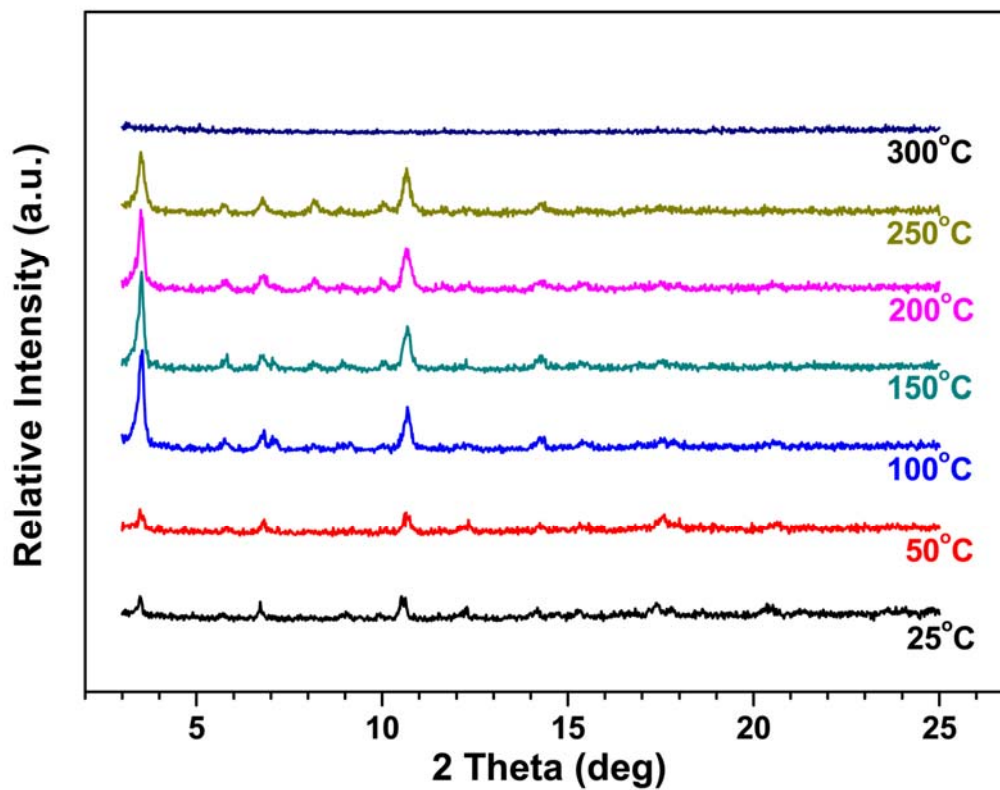
5 **Fig. S1** Ball-and-stick diagrams of three different kinds of metal–organic polyhedra observed in **1**. (a) Metal–organic cubooctahedron. (b) Superoctahedron. (c) Supertetrahedron. The yellow balls inside the cavities represent the dummy balls showing the approximate cavity sizes.



5 **Fig. S2** (a) Ball-and-stick diagram of two MOCs interconnected via quadruple covalent linkage, where the cyan ball depicts the Cu(II) ions in the paddle-wheel unit, the MOC is schematized using green balls and blue rods, and the quadruple covalent linkage is simplified using a red rod. (b) The diagram in (a) viewed in a slightly tilted direction. (c) The cubic close packing arrangement of the MOCs in **1** represented in a face-centered cubic lattice type arrangement.

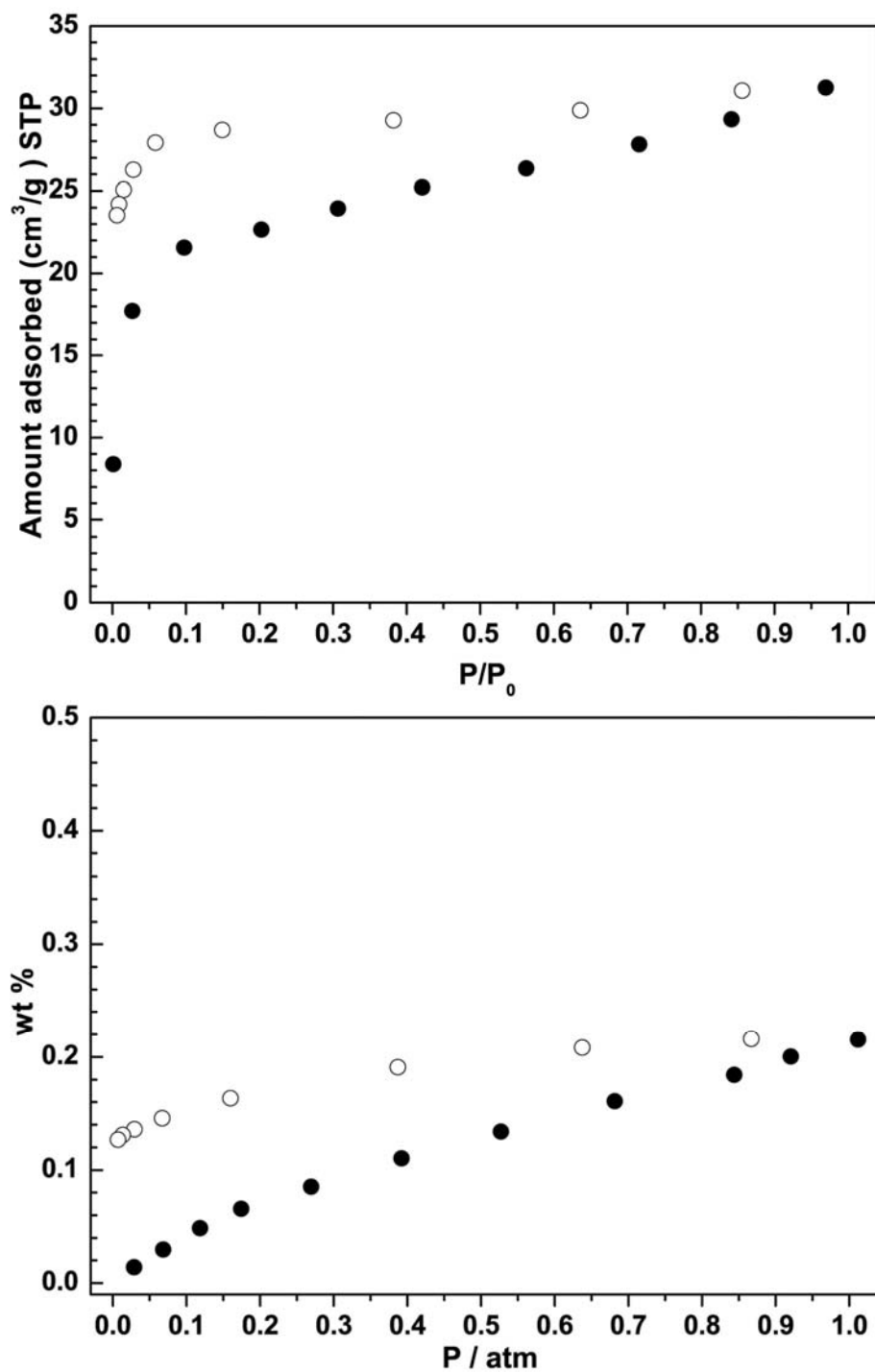


**Fig. S3** Three different windows in the MOF 1: (a) and (b) the MOC has two different types of windows,  $C_3$ -symmetric triangular and  $C_4$ -symmetric square windows; (c) and (d) the superoctahedron has  $C_2$ -symmetric rectangular and  $C_4$ -symmetric square windows; and (e) and (f) the supertetrahedron has  $C_2$ -symmetric rectangular and  $C_3$ -symmetric square windows.

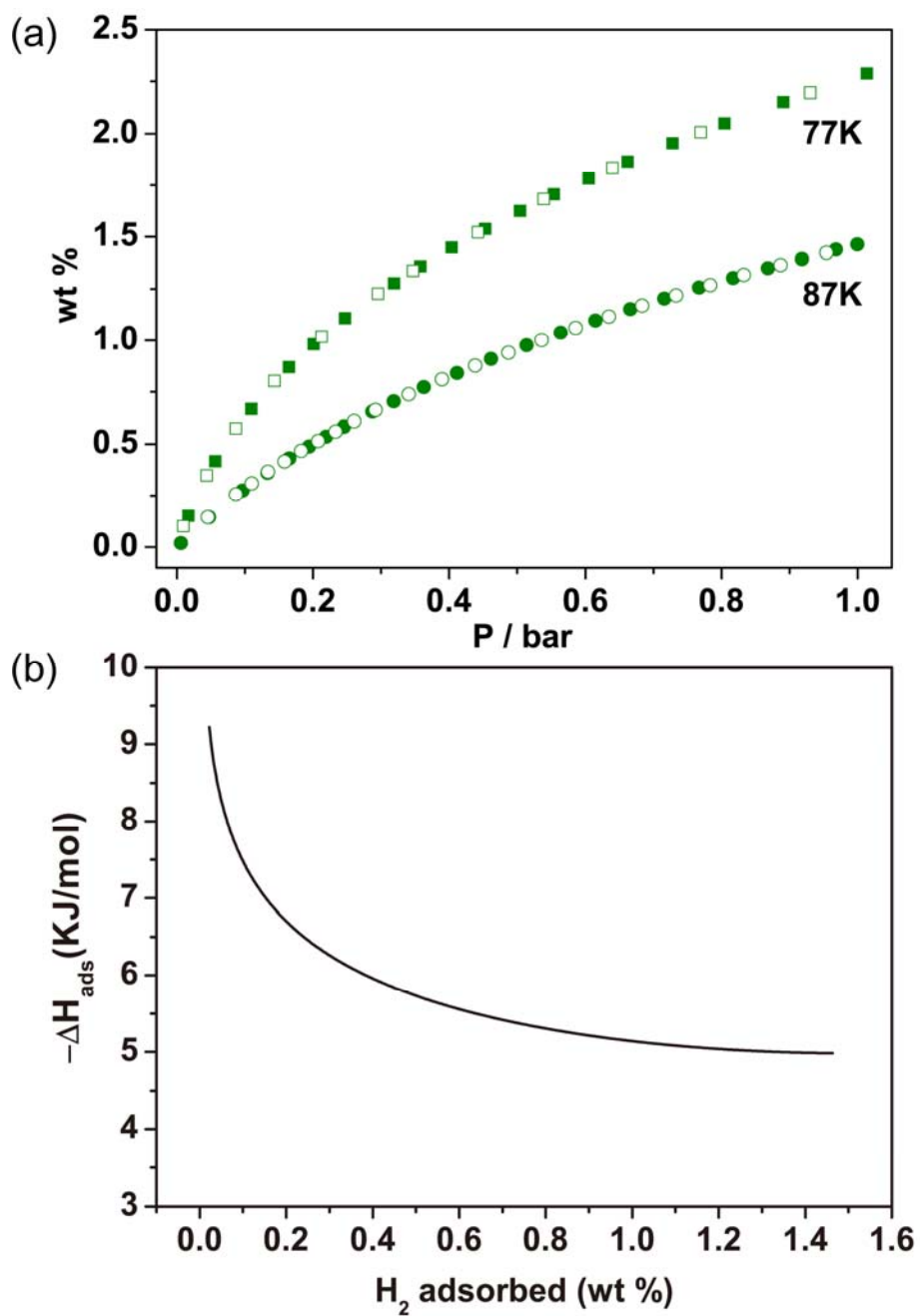


**Fig. S4** VT PXRD of the framework 2.

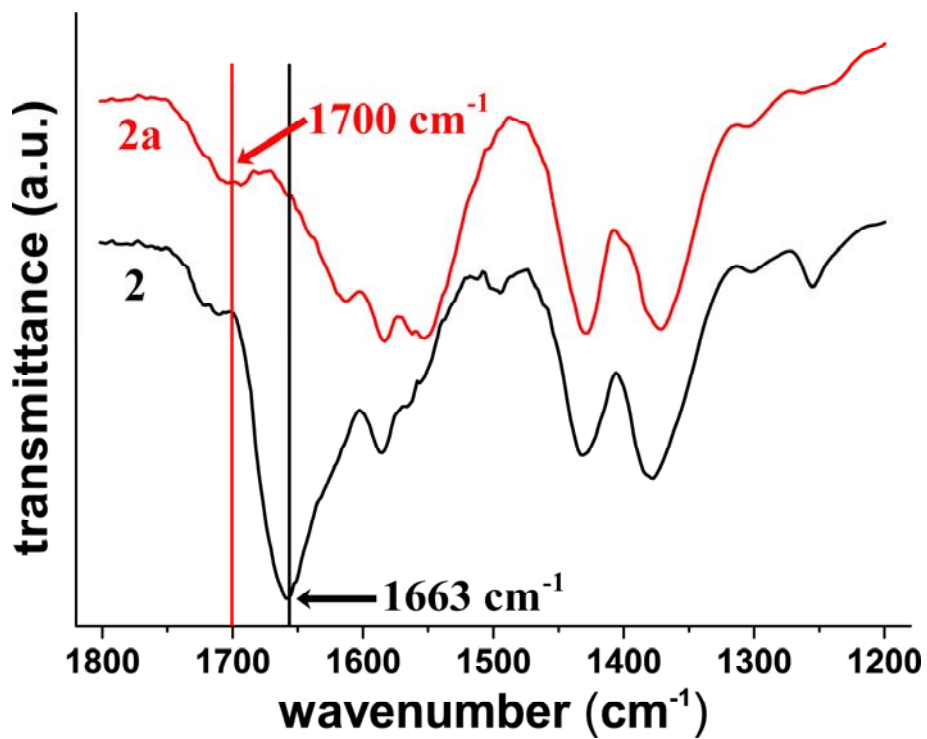




**Fig. S5** Isotherms on **1a** at 77 K for (a) N<sub>2</sub>, and for (b) H<sub>2</sub>.



**Fig. S6** (a) H<sub>2</sub> sorption isotherms on **2a** at 77 K and 87 K; (b) H<sub>2</sub> adsorption enthalpy on **2a**.



**Fig. S7** Comparison of the IR spectra of the frameworks, **2** and **2a**.