

Supplementary Information

A twofold interpenetrated (3,6)-connected metal–organic framework with rutile topology showing a large solvent cavity

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Experimental Sections

General Procedures.

All other reagents were purchased from commercial sources and used without further purification. ^1H and ^{13}C NMR spectra were recorded on VNMRS-600 (600 MHz) spectrometers with the residual solvent as the internal standard. The chemical shifts are listed in ppm on the δ scale. Elemental analyses (C, H, and N) were performed at the Elemental Analysis Laboratory of the Korean Institute of Basic Science and Central Research Facilities of Ulsan National Institute of Science & Technology. FT-IR spectra were recorded as KBr pellets with a Varian 1000 FT-IR spectrophotometer, using the reflectance technique (4000–400 cm^{-1}). Powder X-ray diffraction (PXRD) data were recorded using a Rigaku D/M 2200T automated diffractometer. Simulated PXRD patterns were calculated with the Material Studio program^{S1} using the single-crystal data. Nitrogen and hydrogen sorption isotherms were measured with a BELSORP-mini II (BEL Japan, Inc.) in a standard volumetric technique, at 77 K.

Crystallographic Data Collections and Refinements of Structure.

A crystal of **1** was coated with paratone oil and the diffraction data were measured at 100 K with synchrotron radiation on a 6B MX-I ADSC Quantum-210 detector with a silicon (111) double-crystal monochromator at the Pohang Accelerator Laboratory, Korea. The ADSC Quantum-210 ADX program (Ver. 1.92)^{S2} was used for data collection, and HKL2000 (Ver. 0.98.699)^{S3} was used for cell refinement, reduction, and absorption correction.

Crystal structure determination of $[(\text{Zn}_4\text{O})_2\text{L}_4(\text{DMF})_2(\text{H}_2\text{O})_3]$ ($\text{Zn}_8\text{C}_{126}\text{H}_{92}\text{N}_{14}\text{O}_{43}$, fw = 3013.10 $\text{g}\cdot\text{mol}^{-1}$), **1**. Monoclinic, space group $P2_1/c$, $a = 36.130(7)$, $b = 27.033(5)$, $c = 34.291(7)$ Å, $\alpha = 90.00^\circ$, $\beta = 108.81(3)^\circ$, $\gamma = 90.00^\circ$, $V = 31704(11)$ Å³, $T = 100(2)$ K, $Z = 4$, $\mu(\text{synchrotron}, \lambda = 0.75000 \text{ \AA}) = 0.632 \text{ mm}^{-1}$, 149 700 reflections were collected, 40

052 were unique [$R_{\text{int}} = 0.0811$]. The crystal structure was solved by direct methods and refined by full-matrix least-squares calculation with the SHELXTL-Plus (ver. 5.1) software package.^{S4} Eight zinc atoms, four ligands, three coordinated water molecules (some of the water molecules might be partially identified DMF molecules), and two partially identified coordinated DMF sites were found as an asymmetric unit in the crystal structure. In addition, 16 water molecules (some of the water molecules might be partially identified DMF molecules) at hydrogen-bonding distances from the ligands and four DMF sites (two of them are partially identified) were observed in the lattice. All non-hydrogen atoms, except for those of the solvent molecules, were refined anisotropically. Hydrogen atoms, except those attached to the solvent molecules, were assigned isotropic displacement coefficients of $U(\text{H}) = 1.2U(\text{C})$, and their coordinates were allowed to ride on their respective atoms. The hydrogen atoms attached to the solvent molecules were not included in the least-squares refinement. The geometries of one carboxylate group and the linking phenyl group of the ligand were restrained using the FLAT command of the SHELXTL-Plus software package. One coordinated DMF molecule with poor geometry was also refined with a geometry restraint using FLAT during the least-squares refinement. The distances and the angles of the bonds in some DMF solvent molecules were also restrained using DFIX and DANG commands during the least-squares refinement because of the poor geometries. Refinement of the structure converged at a final $R1 = 0.1971$ and $wR2 = 0.4890$ for 20 845 reflections with $I > 2\sigma(I)$, $R1 = 0.2581$ and $wR2 = 0.5277$ for all reflections. The structure refinement was further performed after modification of the data for the non-coordinated lattice solvent molecules (22562 \AA^3 , 71.1% of the crystal volume) using the *SQUEEZE* routine of the PLATON software package (Ver. 310310),^{S5} which led to better refinement and data convergence. Refinement of the structure converged at a final $R1 = 0.0846$ and $wR2 = 0.2347$ for 20 269 reflections with $I > 2\sigma(I)$, $R1 = 0.1247$ and $wR2 = 0.2602$ for all reflections. The largest difference peak and hole were 0.900 and $-0.640 e^{-\text{\AA}^{-3}}$ respectively. Even though

the data were collected using a synchrotron source at 100K, a combination of the large asymmetric unit and the high solvent content led to severe disorder and bad geometry of the ligated solvent molecules, poor thermal behavior of the overall structure, and consequent many serious alerts such as Hirshfeld alerts in the cif check.

A summary of the crystal structure refinement data is given in Table S1. CCDC-772289 contains the supplementary crystallographic data for **1**. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK.

References

- S1. SMART and SAINT, Area Detector Software Package and SAX Area Detector Integration Program; Bruker Analytical X-ray: Madison, WI, 1997.
- S2. A. J. Arvai and C. Nielsen, ADSC Quantum-210 ADX Program, Area Detector System Corporation; Poway, CA, USA, 1983.
- S3. Z. Otwinowski and W. Minor, in *Methods in Enzymology*, Ed. Carter, Jr., C. W.; Sweet, R. M. Academic Press: New York, 1997, **276**, part A, 307.
- S4. G. M. Sheldrick, SHELXTL-Plus, Crystal Structure Analysis Package; Bruker Analytical X-Ray: Madison, WI, USA, 1997.
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Table S1 Crystal data and structure refinement for complex **1**.

Empirical formula	$C_{126}H_{92}N_{14}O_{43}Zn_8$	
Formula weight	3013.10	
Temperature	100(2) K	
Wavelength	0.75000 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 36.130(7)$ Å	$\alpha = 90^\circ$.
	$b = 27.033(5)$ Å	$\beta = 108.81(3)^\circ$.
	$c = 34.291(7)$ Å	$\gamma = 90^\circ$.
Volume	$31704(11)$ Å ³	
Z	4	
Density (calculated)	0.631 Mg/m ³	
Absorption coefficient	0.632 mm ⁻¹	
F(000)	6120	
Crystal size	0.63 x 0.40 x 0.36 mm ³	
Theta range for data collection	1.01 to 23.76°.	
Index ranges	$-38 \leq h \leq 37$, $-29 \leq k \leq 28$, $-36 \leq l \leq 36$	
Reflections collected	149700	
Independent reflections	40052 [R(int) = 0.0811]	
Completeness to theta = 23.76°	97.3 %	
Absorption correction	Empirical	
Max. and min. transmission	0.8045 and 0.6917	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	40052 / 23 / 1626	
Goodness-of-fit on F ²	0.917	
Final R indices [I > 2sigma(I)]	R1 = 0.0846, wR2 = 0.2347	
R indices (all data)	R1 = 0.1247, wR2 = 0.2602	
Largest diff. peak and hole	0.900 and -0.640 e·Å ⁻³	

Table S2 The trigonal angles^a for the four ligands in **1**.

ligands	1	2	3	4
small	96.961(7)	87.306(7)	86.771(7)	97.334(7)
medium	114.008(5)	116.965(5)	115.126 (5)	114.748(5)
large	147.831(6)	151.118(6)	157.477(6)	146.030(6)

^a The trigonal angle was measured from the C atom of the carboxylic group to the dummy atom, the center of the central phenyl ring of the ligand, to another C atom of a neighboring carboxylic group in the ligand, as shown in Fig. 1a.

Table S3 The twisting angles^a for the four ligands in **1**.

ligands	1	2	3	4
	40.5(3)	29.0(3)	25.4(5)	51.8(2)
	74.3 (2)	39.9(3)	38.6(3)	56.7(2)
	52.7(3)	47.7(3)	28.4(4)	131.8(4)

^a The twisting angle was measured from the dihedral angle of the benzoate groups versus the central benzene ring of the ligand.

Table S4 The angles^a around the two Zn₄O(COO)₆ clusters in **1**.

Zn cluster_1					
C1...O1M...C31	90.15(2)	C1...O1M...C52	87.00(2)	C1...O1M...C91	86.63(1)
C1...O1M...C120	83.55(1)	C31...O1M...C52	87.67(1)	C31...O1M...C61	96.21(1)
C31...O1M...C120	90.75(1)	C52...O1M...C61	85.39(1)	C52...O1M...C91	91.43(1)
C61...O1M...C91	86.89(2)	C61...O1M...C120	104.19(2)	C91...O1M...C120	89.61(2)
C1...O1M...C61	169.87(2)	C31...O1M...C91	176.69(2)	C52...O1M...C120	170.41(1)

Zn cluster_2					
C22...O2M...C30	85.46(1)	C22...O2M...C60	99.76(2)	C22...O2M...C82	92.30(1)
C22...O2M...C112	88.24(1)	C30...O2M...C60	79.18(2)	C30...O2M...C90	88.85(1)
C30...O2M...C112	84.69(1)	C60...O2M...C82	113.56(1)	C60...O2M...C90	80.15(1)
C82...O2M...C90	93.03(2)	C82...O2M...C112	82.71(2)	C90...O2M...C112	90.20(2)
C22...O2M...C90	174.21(1)	C30...O2M...C82	167.26(2)	C60...O2M...C112	161.30(2)

^a The angles were measured from the C atom of the carboxylic group in a ligand to the central oxo-anion, to another C atom of a neighboring carboxylic group in the other ligand.

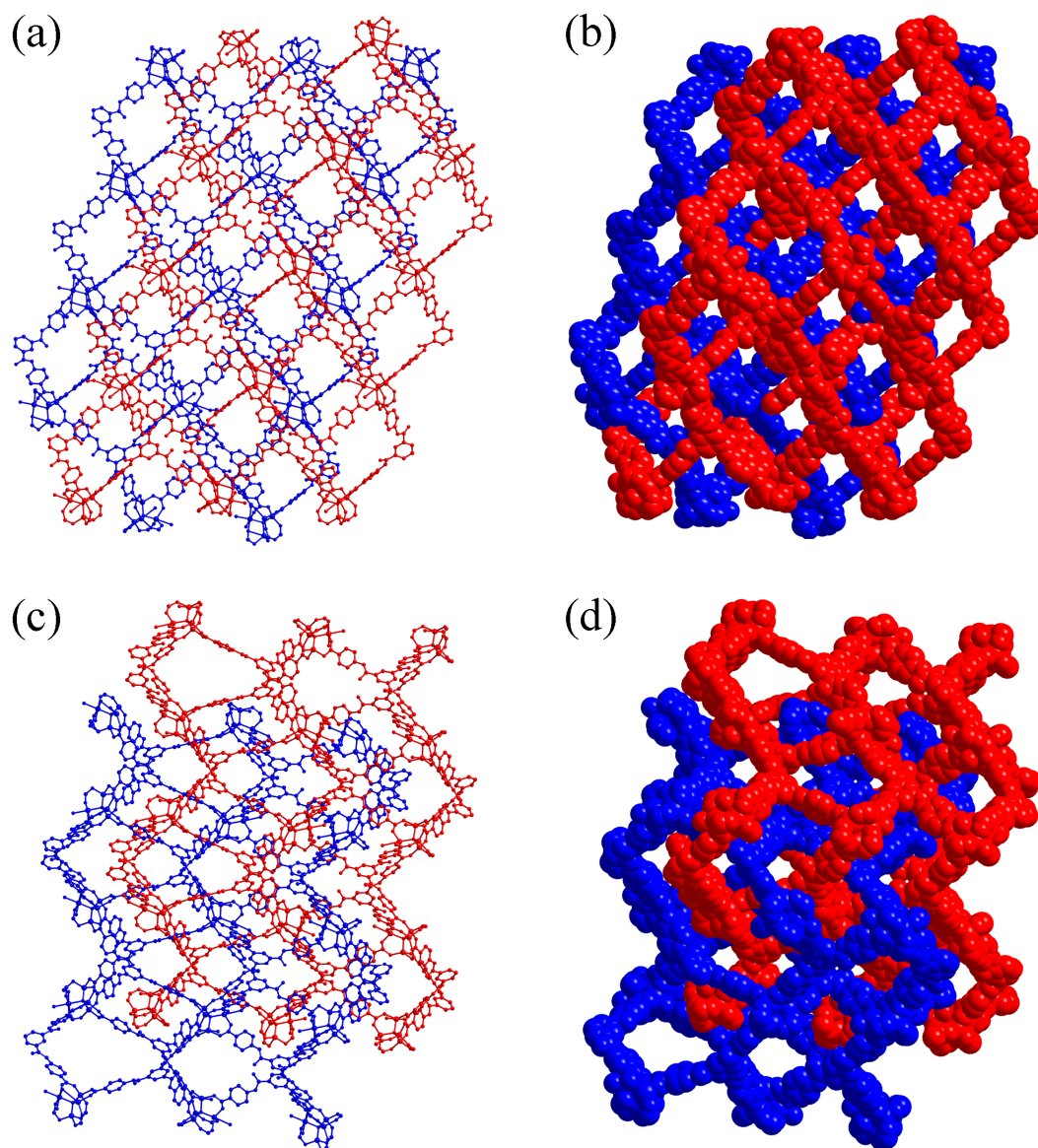


Fig. S1 (a) and (c) A twofold interpenetration in the 3-D porous network of **1** in a ball-and-stick model viewed along the crystallographic *b*-axis and *c*-axis, respectively, where solvent molecules are omitted for clarity. Two individual nets are indicated by different colors (blue and red). (b) and (d) Space-filling views of (a) and (c) showing the 3-D solvent cavity, respectively.

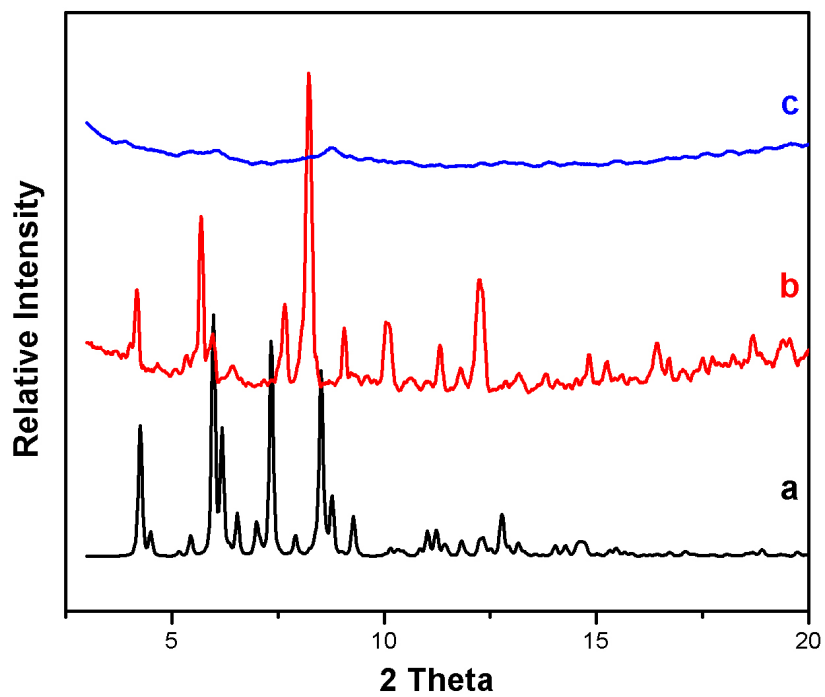


Fig. S2 (a) A simulated PXRD pattern from the single-crystal structure of **1** (black), (b) the as-synthesized sample, **1** (red), and (c) the activated sample, **1a** (cyan).