Electronic Supplementary Material (ESI) for Chemical Communications

<Supporting Information>

Unprecedented and highly symmetric (6,8)-connected topology in porous metal-organic framework through Zn-Ti heterometallic approach

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General

All the reagents and solvents were commercially available and used as received. TGA data were obtained on a SCINCO S-1000 instrument with a heating rate of 5 ºC/min in air. Powder X-ray diffraction patterns were recorded at the 2D SMC beamline of the Pohang Accelerator Laboratory, Korea. A crystalline sample of ZTOF-2 was thoroughly ground in an agate mortar and packed in a capillary tube (0.3 mm diameter). Debye-Scherrer diffraction data were collected on an ADSC Quantum-210 detector with a fixed wavelength (λ = 1.40000 Å) and an exposure of 60 sec. The ADX program[S1] was used for data collection, and Fit2D program[S2] was used to convert the 2D to 1D patterns.

Synthesis

To a solution containing $Zn(NO_3)_2 \cdot 6H_2O$ (45.0 mg, 0.15 mmol) and $Ti(O^iPr)_4$ (12.8 μL, 0.04 mmol) in DMF (1.30 mL) added were H_3ondc (46.4 mg, 0.20 mmol) and dabco (4.8 mg, 0.04 mmol). The solution mixture was stirred in open air for 2 h and then charged into a glass tube. After flame-seal, the tube was heated to 80 °C for 1 d and to 100 °C for 3 – 4 days to produce orange-colored hexagonal prism crystals along with some gel-like residue. The product was thoroughly washed with DMF and then soaked in dichloromethane before drying under vacuum overnight (15 mg, 30 %). Calcd for $[Zn_6Ti_2(ondc)_6(dabco)(CO_3)(OH_2)_3](DMF)_3$: C, 45.54; H, 3.52; N, 3.02; Ti, 4.13; Zn, 16.91. Found: C, 45.78; H, 3.10; N, 2.96; Ti, 4.45; Zn, 17.15%.

X-ray crystallography

Single-crystals of as-synthesized ZTOF-2 were directly picked up from the mother liquor with a cryoloop attached to a goniohead, and transferred to a cold stream of liquid nitrogen (-173 ºC). The data collection was carried out using synchrotron X-ray on a ADSC Quantum 210 CCD detector with a silicon (111) double-crystal monochromator at 2D SMC beamline of the Pohang Accelerator Laboratory, Korea. The ADSC Quantum-210 ADX program[S1] was used for data collection, and HKL3000sm (Ver. 703r)[S3] was used for cell refinement, data integration, and absorption correction. After space group determination, the structures were solved by direct methods and subsequent difference Fourier techniques (SHEXLTL).[S4] All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added to their geometrically ideal positions except for the coordinated water molecule which was left without hydrogen atoms. The diffused electron densities in the void space could not be modeled properly, and were removed from the reflection data using the SQUEEZE routine of PLATON.[S5] The results of SQUEEZE process were attached to the CIF file. After final refinements, somewhat high residual electron densities (2.0 e/Å^3) were found at the center of dabco ligand and were ignored. The crystal data and results of structure refinements are summarized in Table S1. The ORTEP diagram of the asymmetric unit is shown in Figure S2.

Gas sorption studies

BET gas sorption isotherms were measured with a Belsorp Mini-II at the following temperatures: liquid nitrogen (77 K), slush baths of dry ice-isopropylalcohol (195 K) and ice-water (273 K). The gases used were of the highest quality available (N60 for H_2, N50 for CO_2 and N_2 and N35 for CH_4). Typically, 150 mg of solvent-exchanged ZTOF-2 was evacuated under a dynamic vacuum at room temperature for 12 h. The equilibrium criteria were set consistent throughout all the measurements (change in adsorption amounts less than 0.1 cm^3/g within 180 sec).

References

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

S2 A. Hammersley, *Fit2D program*, ESRF; 6 Rue Jules Horowitz, BP 220 38043, Grenoble CEDEX 9, France.

S3 Z. Otwinowski, and W. Minor, *Methods in Enzymology*, ed. C. W. Carter, Jr. and R. M. Sweet, Academic Press, New York, 1997, vol. 276, part A, pp. 307.

S4 G. M. Sheldrick, *SHELXTL-PLUS, Crystal Structure Analysis Package*; Bruker Analytical X-Ray, Madison, WI, USA, 1997.

S5 A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7.

Table S1. Crystal data and summary of structure refinements.

Formula	$C_{79}H_{48}N_2O_{36}Ti_2Zn_6$
FW	2089.21
Temp (K)	100(2)
λ (Å)	0.69999
Crystal system	Hexagonal
Space group	$P6_3/m$
a (Å)	20.171(3)
c (Å)	26.197(5)
V (Å^3)	9231(3)
Z	2
ρ_{calc} (g cm^{-3})	0.752
μ (mm^{-1})	0.820
F(000)	2096
Crystal size (mm^3)	0.42 × 0.20 × 0.20
θ range	1.91 – 31.00
h, k, l ranges	-29/29, -29/29, -38/38
Reflections collected	106147
Independent (R_{int})	10470 (0.0531)
Completeness (%)	99.8
Absorption correction	Semi-empirical
T_{max} / T_{min}	0.8531 / 0.7245
Refinement method	Full-matrix least-squares on F^2
Data / restraints / param	10470 / 0 / 195
GOF on F^2	0.997
R_1, wR_2 [I>2σ(I)]	0.0850, 0.2453
R_1, wR_2 (all data)	0.1081, 0.2647
Extinction coefficient	0.050(3)
Largest diff. peak / hole (e/Å^3)	2.022 / -0.678

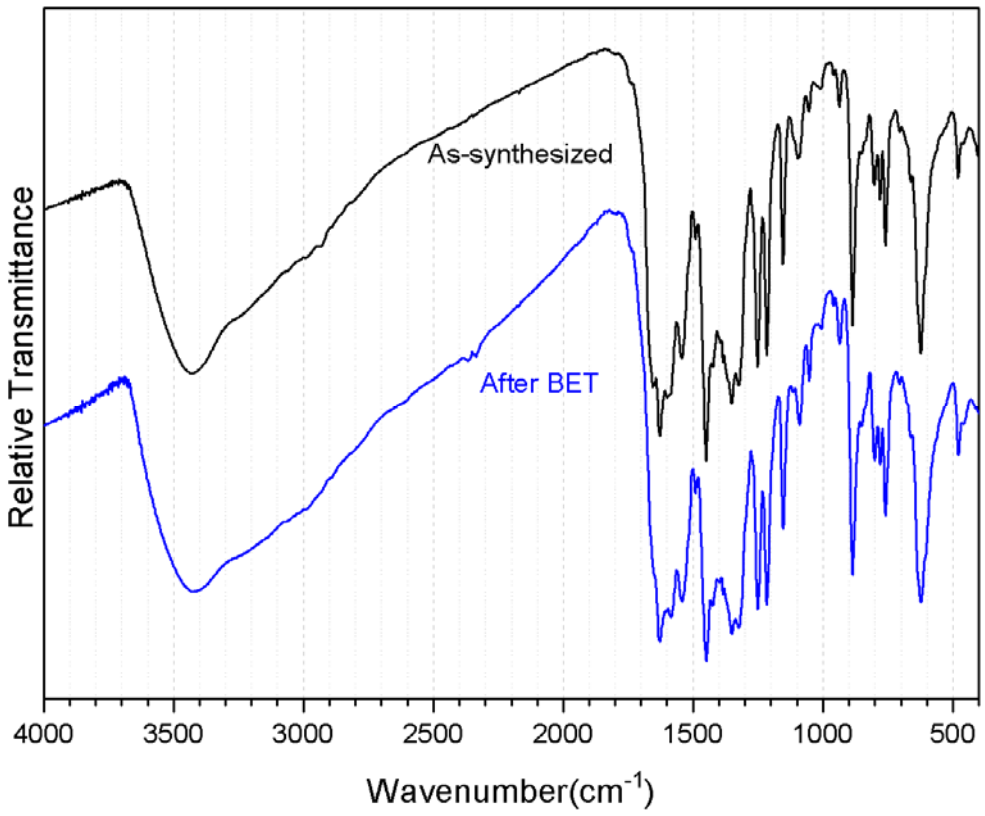

Figure S1. FT-IR spectra for as-synthesized and evacuated ZTOF-2.

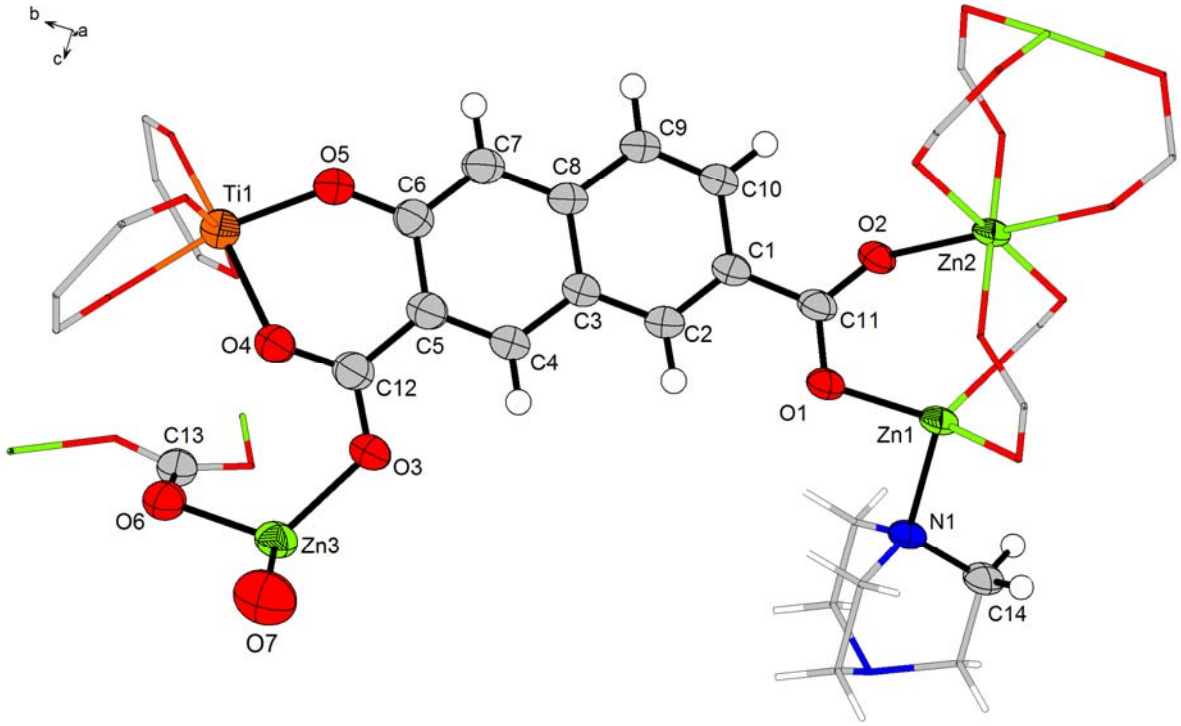

Figure S2. A partially expanded view showing the thermal ellipsoids (30%) of atoms in the crystallographic asymmetric unit for ZTOF-2. Local symmetry of atoms on special positions: Zn1 (3), Zn2 (-3), Zn3 (m), Ti1 (3), O6 (m), O7 (m), N1 (3), C13 (-6).