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Supporting Information

A Chiral Tetragonal Magnesium-Carboxylate Framework with Nanotubular Channel System

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Contents

Materials and Measurements:

All starting materials, except for biphenyl-3,3',5,5'-tetracarboxylic acid (H_4bptc), were purchased commercially and used without further purification. ^{1}H and ^{13}C spectra were recorded on a Varian Inova 400 spectrometer. Proton (^{1}H) chemical shifts are reported in parts per million (δ) with respect to tetramethylsilane (TMS, δ=0), and referenced internally with respect to the protic solvent impurity. All mass spectra were acquired on a Voyager-DE STR BioSpectrometry Workstation mass spectrometer. Powder XRD patterns were obtained using a Bruker D8 Advance X-ray powder diffractometer with Cu *K*α radiation (λ = 1.54056 Å). Thermal stability studies were carried out on a TA-Q500 thermoanalyzer with a heating rate of 5 °C/min under nitrogen atmosphere. Gas adsorption experiments were performed on Micromeritics ASAP 2020 surface area and pore size analyzer.

Synthesis of Biphenyl-3,3',5,5'-tetracarboxylic acid **(H_4bptc):**

Biphenyl-3,3',5,5'-tetracarboxylic acid (H_4bptc) was synthesized oxidizing 3,3',5,5'-tetramethylbiphenyl with $KMnO_4$ in tert-butanol/water (250/250 mL) containing NaOH (4.0 g, 0.1 mol). Yield: 10.9 g, 50.6%. Anal. Calcd (Found) for $C_{16}O_8H_{10}$: C, 58.19 (58.12); H, 3.05 (3.11)%. ^{1}H NMR (DMSO, 300 MHz): δ = 8.85 (1H); 8.49 (2H); 4.39 (4H), 1.43 (6H). MS (ESI) $[M-H]^-$ calcd for $C_{16}O_8H_{10}$: 329.04; Found: 329.03.

Synthesis of Metal-Carboxylate Frameworks:

Synthesis of $[Mg_2(H_2O)_2(bptc)]\cdot x(solv)$ (**1**, CPF-1): A solid mixture of biphenyl-3,3',5,5'-tetracarboxylic acid (H_4bptc, 0.033 g, 0.10 mmol), and $Mg(NO_3)_2\cdot(H_2O)_6$ (0.052 g, 0.20 mmol), dissolved in a mixture of N-ethylformamide (NEF)/H_2O (4.0/0.8 g) in an 10-mL glass vial, was heated

at 120° for 3 days, and then cooled to room temperature. Pure colorless needle crystals were obtained (yield: 31 % based on H_4bpt).

Synthesis of $Zn_2(bptc)_2 \cdot (H_3NEt)_4 \cdot (H_2O)_7$ (**2**, CPF-2): A mixture of H_4bptc (0.033 g, 0.10 mmol), $Zn(NO_3)_2 \cdot (H_2O)_6$ (0.058 g, 0.20 mmol), together with mixed solution NEF/H_2O (4.0/0.8 g), placed in a 10-mL glass vial, was heated at 120° for 3 days, and then cooled to room temperature. Grains of colorless crystals of Znbptc were obtained. The highest yield was obtained by using a mixed solvent N,N-dimethylacetamide (DMA)/H_2O (4.0/0.8 g), containing 3 drops of HBF_4(50 wt%) (yield: 35 % based on H_4bptc).

X-ray Crystallography:

Each crystal was glued to a glass fiber with epoxy resin and mounted on a Bruker APEX II diffractometer equipped with a fine focus, 2.4 kW sealed tube X-ray source (MoKα radiation, λ = 0.71073 Å) operating at 50 kV and 30 mA. The empirical absorption correction was based on equivalent reflections. Each structure was solved by direct methods using SHELXTL and refined by full-matrix least-squares on F^2 using SHELX-97. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All hydrogen atoms of the organic molecule were placed by geometrical considerations and were added to the structure factor calculation. Solvent molecules in the crystals of **1** are highly disordered, and attempts to locate and refine solvent molecules were unsuccessful. Contributions to scattering from all solvent molecules were removed using the SQUEEZE routine of PLATON; the structures were then refined again using the data.

Sorption Measurements:

As-synthesized sample of **1** was immersed in methanol for 3 days; during the exchange the methanol was refreshed three times. The resulting methanol-exchanged sample of **1** was transferred as a suspension to a busher funnel and the solvent was decanted. The wet sample was then evacuated (10^{-3} torr) at room temperature for 10 h. Obtained samples were immersed in dichloromethane for 12 h, during which the activation solvent was replenished three times. The wet sample was then evacuated (10^{-3} torr) at room temperature for 12 h then at 80℃ for 12h. Low-pressure gas adsorption experiments were carried out on a Micromeritics ASAP 2020 surface area and pore size analyzer.

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Table S1. Crystal Data and Structure Refinements for CPF-1, CPF-2.

Compound reference	CPF-1 (**1**)	CPF-2 (**2**)
Chemical formula	$C_8H_5MgO_5$	$C_{40}H_{50}N_4O_{23}Zn_2$
Formula Mass	205.426	1092.68
Crystal system	Tetragonal	Tetragonal
a/Å	15.2927(11)	22.467(2)
b/Å	15.2927(11)	22.467(2)
c/Å	12.3010(18)	29.858(3)
α/°	90.00	90.00
β/°	90.00	90.00
γ/°	90.00	90.00
Unit cell volume/Å^3	2876.8(5)	15071(3)
Temperature/K	150(2)	150(2)
Space group	$I4_122$	$I\bar{4}\ 2d$
Z (No. of formula units per unit cell)	8	8
No. of reflections measured	3113	19195
No. of independent reflections	1256	5815
R_{int}	0.0198	0.1055
Final R_1 values ($I > 2\sigma(I)$)	0.0875	0.0986
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2672	0.2534
Final R_1 values (all data)	0.0896	0.1384
Final $wR(F^2)$ values (all data)	0.2790	0.2843
Goodness of fit on F^2	1.383	1.063
Flack parameter	0.2(8)	0.48(4)

$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR = \{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$.

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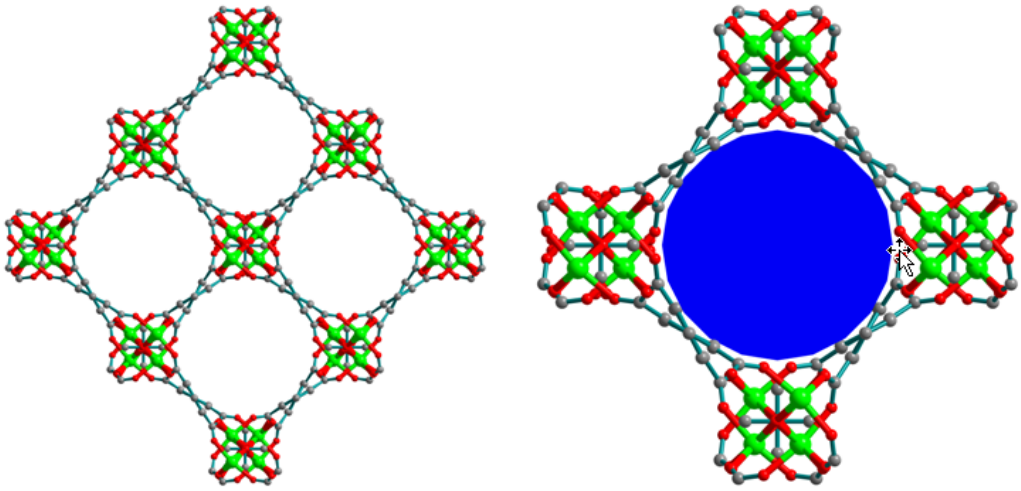

Figure S1. View of the 3D network with 1D nano-sized channels (left), underlying nanotube (right) in **1**.

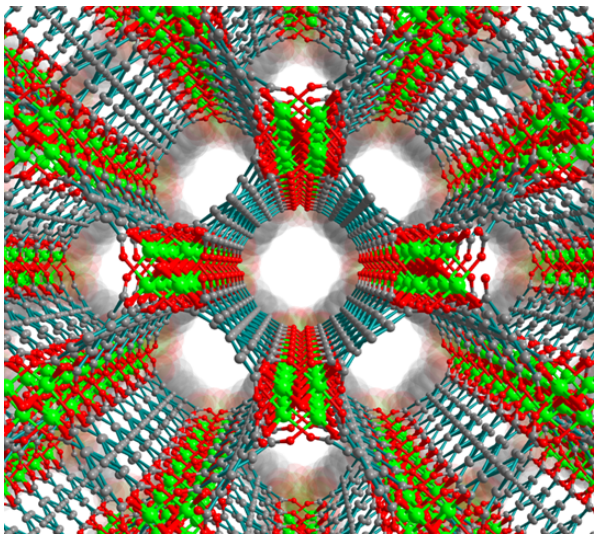

Figure S2. Central projectional view of the channel packing in **1**.

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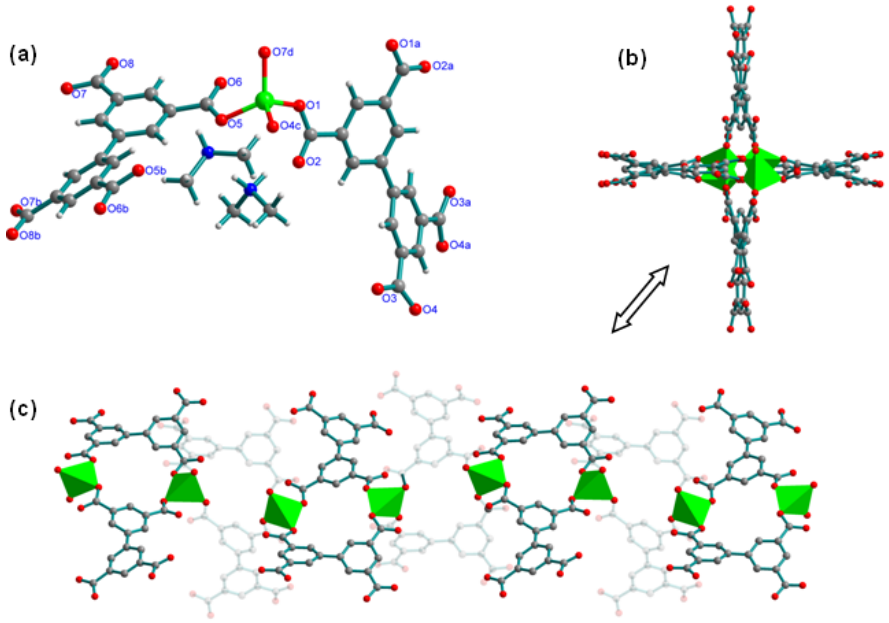

Figure S3. The molecular structure (zinc site possesses 4-connected tetrahedral geometry) of **2** (a); and desymmetrical helical chain viewed along [001] (b) and [110] in **2**.

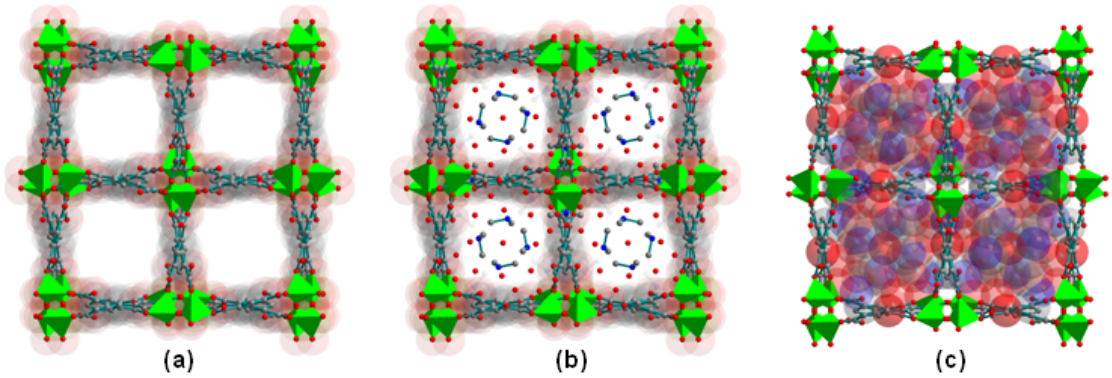

Figure S4. A portion of the crystal structure of **2** as viewed down the [001] direction (a). Green tetrahedra represent ZnO_4, guest $NH_2(CH_3)_2^+$ and H_2O molecules (ball-stick (b) and space-filling (c) mode) reside in the channesl.

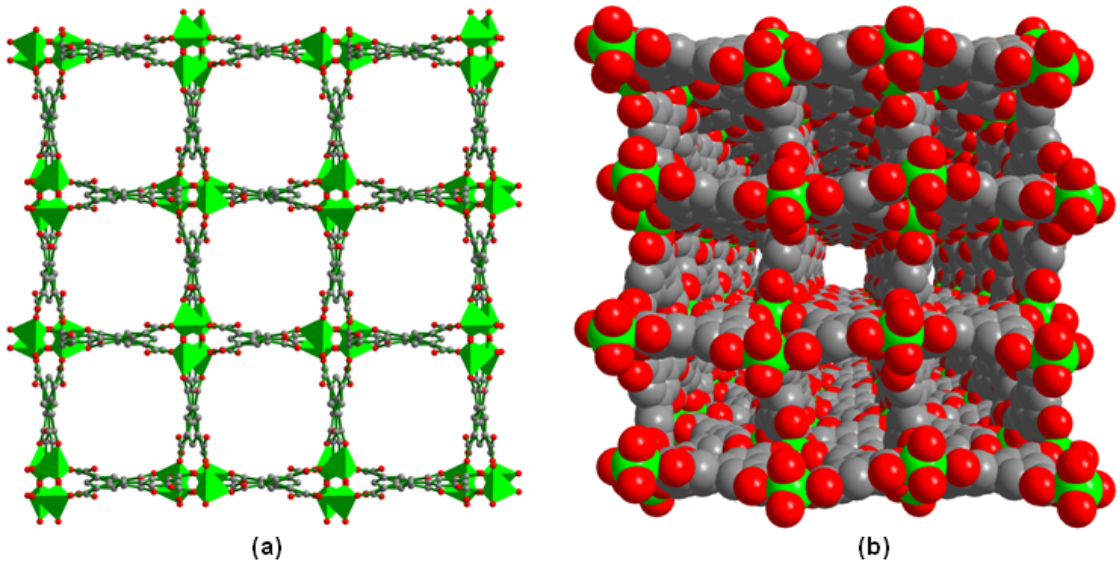

Figure S5. Ball-stick (a) and space-filling (c) mode of a portion of the crystal structure of **2** as viewed down the [001] direction. Green tetrahedra represent ZnO_4.

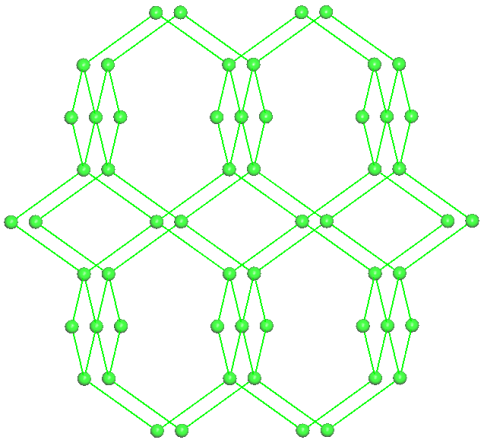

Figure S6. PtS topology of **2**. Tetrahedral and square nodes represent Zn^{2+} and $bptc^{4-}$, respectively.

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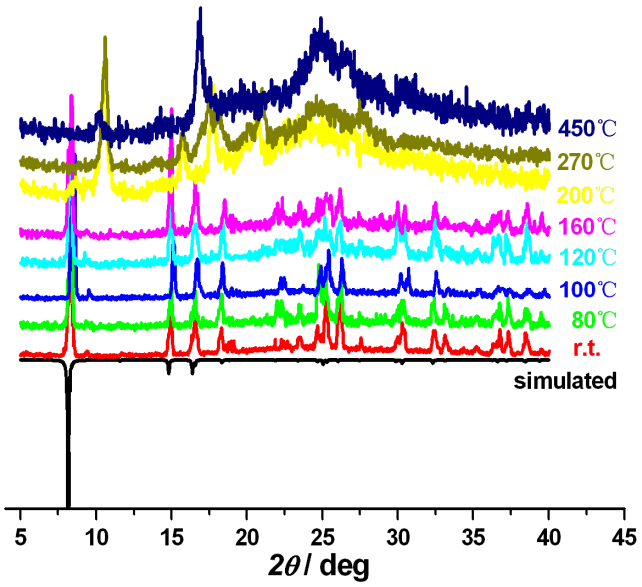

Figure S7. PXRD pattern for as-synthesized and desolvated **1**.

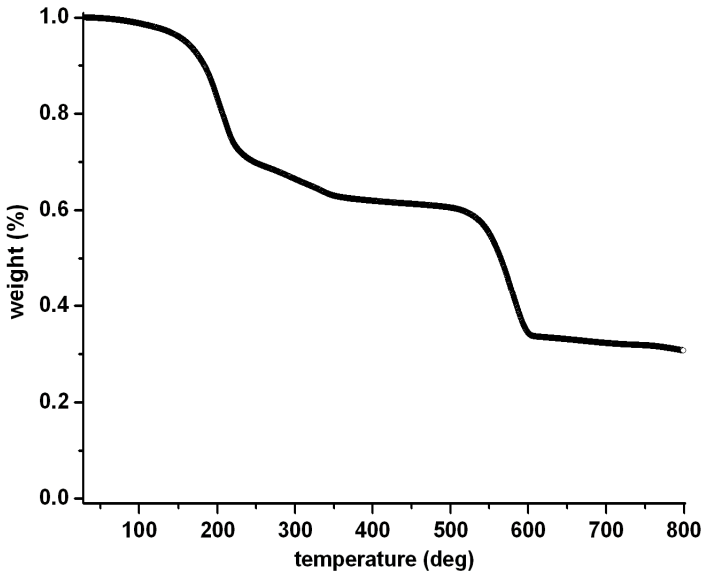

Figure S8. TGA curves of **1**.

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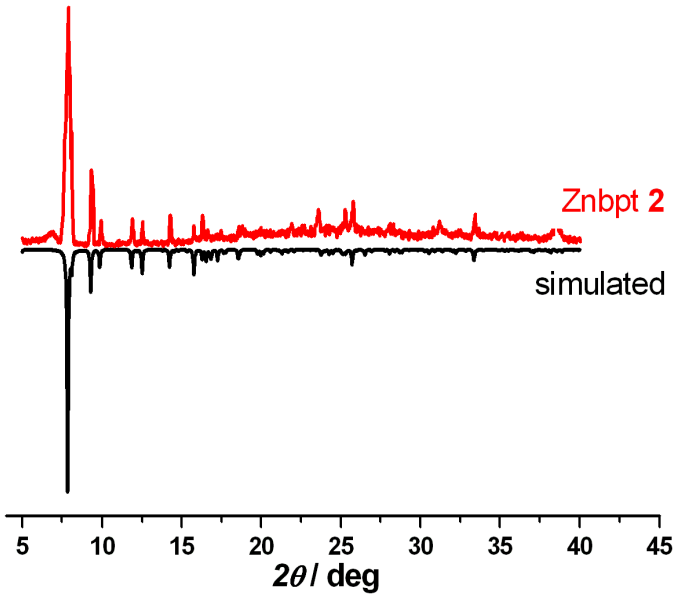

Figure S9. PXRD pattern for as-synthesized and simulated **2**.

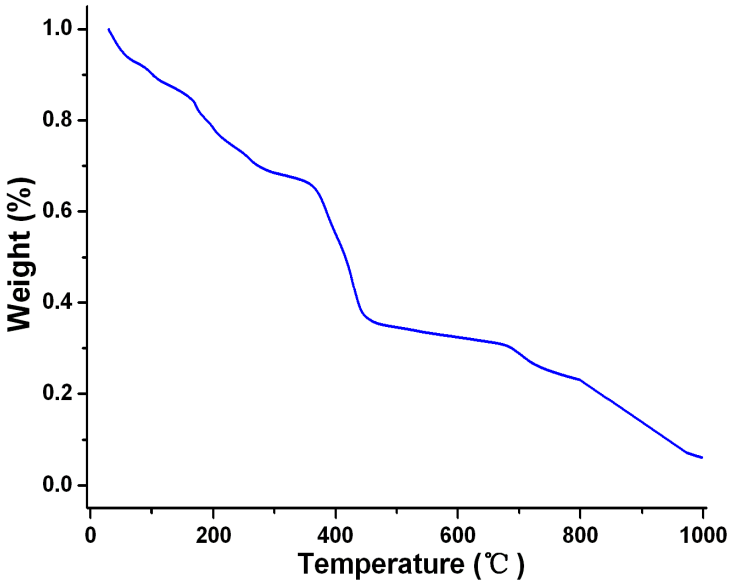

Figure S10. TGA curve of **2**.

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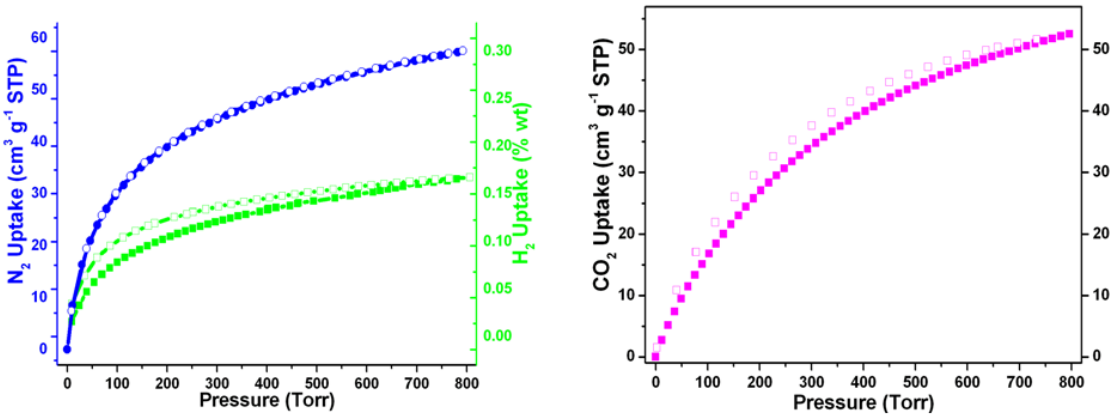

Figure S11. (Left) N_2 (blue) and H_2 (green) isotherms of **2** at 77 K (solid symbols, adsorption; open symbols, desorption). (Right) CO_2 isotherm of **2** at 273 K (solid symbols, adsorption; open symbols, desorption).