

Supporting information

Enabling Homochirality and Hydrothermal Stability in Zn₄O-Based Porous Crystals

Xiang Zhao,^{†,‡} Huajun Yang,[†] Edward T. Nguyen,[†] Joshua Padilla,[†] Xitong Chen,[‡] Pingyun Feng,^{*,‡} and Xianhui Bu^{*,†}

[†] *Department of Chemistry and Biochemistry, California State University, Long Beach, 1250 Bellflower Boulevard, Long Beach, CA 90840*

[‡] *Department of Chemistry, University of California, Riverside, 92521*

Experimental details:

Ligand Synthesis:

Synthesis of (1R, 3R)-(-)-1,2,2-Trimethylcyclopentane-1,3-dicarboxylic acid (RR-cam): To a 23 ml Teflon-line cup, 7.5 g D-camphoric acid, 4.0 g glacial acetic acid and 0.5 g concentrated hydrochloric acid was added and sealed in a stainless steel autoclave without further mixing. Then it was heated at 180 °C for 10 hours. The resulted product was transferred to a flask and washed with small amount of water. The flask was heated for about one hour to evaporate the extra acid upon which a clear brownish solution was resulted. Then the heating was stopped and the solution was cooled down to room temperature naturally and left still overnight to give out off-white crystalline products. After the solid was filtered and dried under vacuum. At this point, the solid is a mixture of unreacted RS-cam and RR-cam. Then the mixture was grounded to fine powder and react with one-third its weight of acetyl chloride and allowed to stand for one hour with occasional stirring to convert RS-cam to its anhydride. A quantity of water was added to quench the reaction followed immediately by filtering to remove extra acid. Then the mixture was treated with sodium carbonate solution and filtered again. RR-cam was precipitated from the filtrate by addition of hydrochloric acid. It can be further purified by recrystallization in alcohol.

Synthesis of homochiral MOFs:

CPM-300, [Zn₄O(RR-cam)₃]. (1R, 3R)-(-)-Camphoric acid (60.0 mg), Zn(NO₃)₂•6H₂O (119.1 mg) were dissolved in a mixed solvent containing 2.5 g of N,N-dibutylformamide (DBF), 0.5 g of ethanol and 0.5 g of DI water in a 15 ml glass vial and stirred for 30 min. The vial was then sealed and heated at 100 °C for 5 days. Colorless hexagonal prism crystals were obtained.

CPM-301, [Zn₄O(RR-cam)₃][Zn₉(btz)₁₂(RR-cam)₃]. 1H-benzotriazole (75.6 mg), (1R, 3R)-(-)-Camphoric acid (40.2 mg), Zn(NO₃)₂•6H₂O (150.4 mg) were dissolved in a mixed solvent containing 2.0 g of N,N-dimethylformamide (DMF) and 0.5 g of DI water in a 15 ml glass. After stirring, the vial was sealed and heated at 120 °C for 4 days. Pure colorless crystals were obtained.

Characterizations

Powder X-ray diffraction: Powder X-ray diffraction experiments were performed on a PANalytical X'Pert Pro MPD diffractometer, equipped with a linear X'Celerator detector, which was operating at 40 kV and 35 mA (Cu K_α radiation, λ = 1.5418Å). The data collection was performed at room temperature in the range from 5° to 40° with a step size of ~0.008°.

Single crystal X-ray diffraction: Single-crystal X-ray analysis was performed on a Bruker Smart

APEX II CCD area diffractometer with nitrogen-flow temperature controller using graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$), operating in the ω and ϕ scan mode. The SADABS program was used for absorption correction. The structure was solved by direct methods followed by successive difference Fourier methods. All non-hydrogen atoms were refined anisotropically. Computations were performed using SHELXTL and final full-matrix refinements were against F^2 .^[1]

Contact angle measurement: Water and hexadecane contact angle measurement was performed on a KSV CAM 200 Contact Angle and Surface Tension Meter. The purified and dried crystalline sample was grounded thoroughly using a mortar. The pressed pellet was prepared by sandwiching the powder sample between two glass slides and apply pressure uniformly until a flat surface was obtained, which can be further examined under the camera. Continuous images were recorded with an interval of 33 millisecond was used from prior to the droplet delivery to the end of wetting or a stationary drop is built.

Thermal gravimetric measurement: The thermal analysis was performed on TA Instruments TGA Q500 under the flowing nitrogen atmosphere. The samples were heated from 30 °C to 900 °C at a rate of 5 °C/min under nitrogen flow. The flow rate of the nitrogen gas was controlled at about 60 milliliters per minute.

Gas sorption measurement: Gas sorption experiments were carried out on a Micromeritics ASAP 2020 PLUS surface area and pore size analyzer. Prior to the measurement, the as-synthesized CPM-300 was refluxed in EtOH for 24 hours or soaked in MeOH for 3 days during which period the MeOH was refreshed twice per day. For the water refluxed sample, it was further refluxed in MeOH for 24 hours before transferring to the sample tube. After filtered and dried in the vacuum oven for overnight, the sample was further dried by using the “degas” function of the surface area analyzer for 10 hours at 80 °C. The N₂ and H₂ sorption measurements were performed in liquid nitrogen bath at 77 K. The CO₂ sorption was carried out at both 195 K and 273 K.

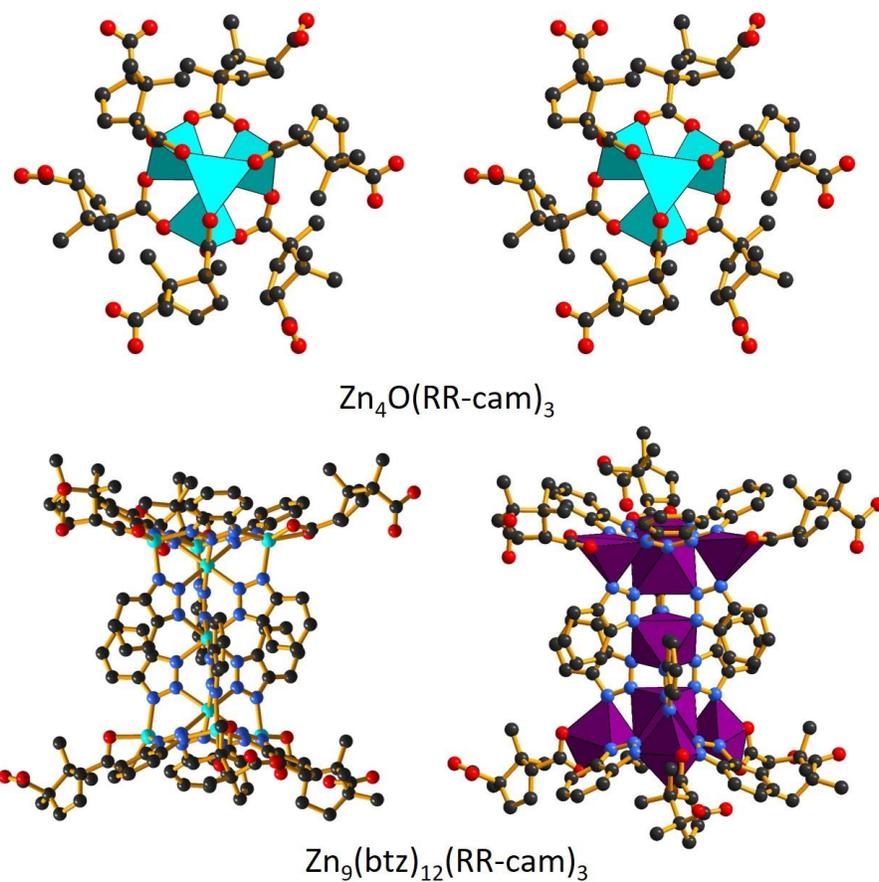


Figure S1. Structure illustration of CPM-301. Two types of SBU in CPM-301, (a) the $Zn_4O(CO_2)_6$ cluster and (b) $Zn_9(btz)_{12}(CO_2)_6$ cluster.

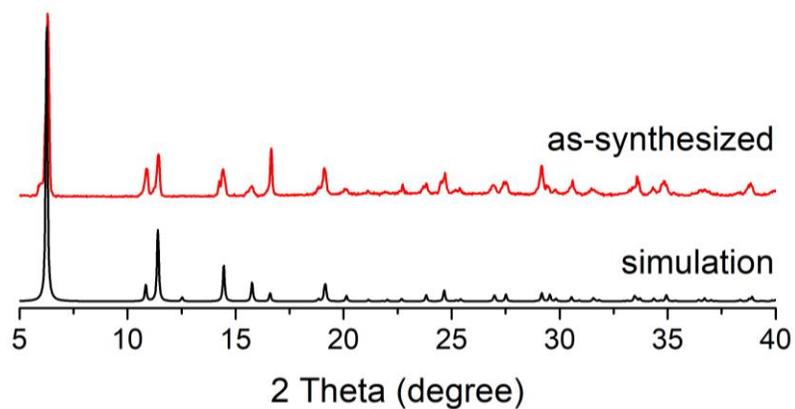


Figure S2. Powder X-ray diffraction of the as-synthesized CPM-300.

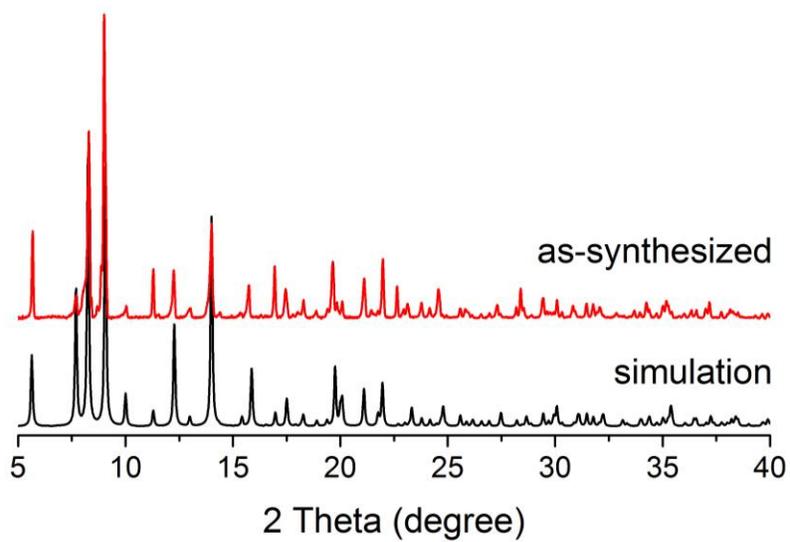


Figure S3. Powder X-ray diffraction of the as-synthesized CPM-301.



Figure S4. Contact angle measurement of hexadecane on compressed pellet of CPM-300. The oil droplet will wet the CPM-300 sample immediately upon contact, giving an initial transient contact angle of $\sim 17.8^\circ$, and complete wetting can be seen in less than 10 seconds.

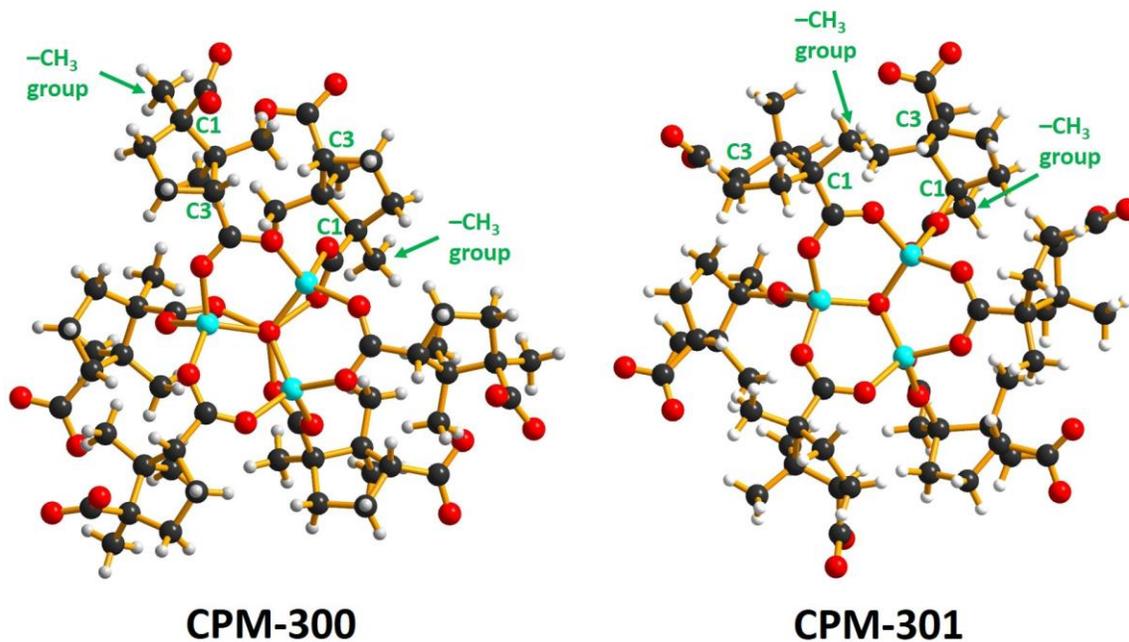


Figure S5. A comparison of the arrangement of RR-cam around Zn₄O core in CPM-300 and CPM-301, respectively. It is seen that in CPM-300, three C1s and three C3s is pointing to the Zn₄O cluster, while in CPM-301, all six C1s are pointing to the Zn₄O cluster, and C3s are pointing to the Zn₉(btz)₁₂ cluster.

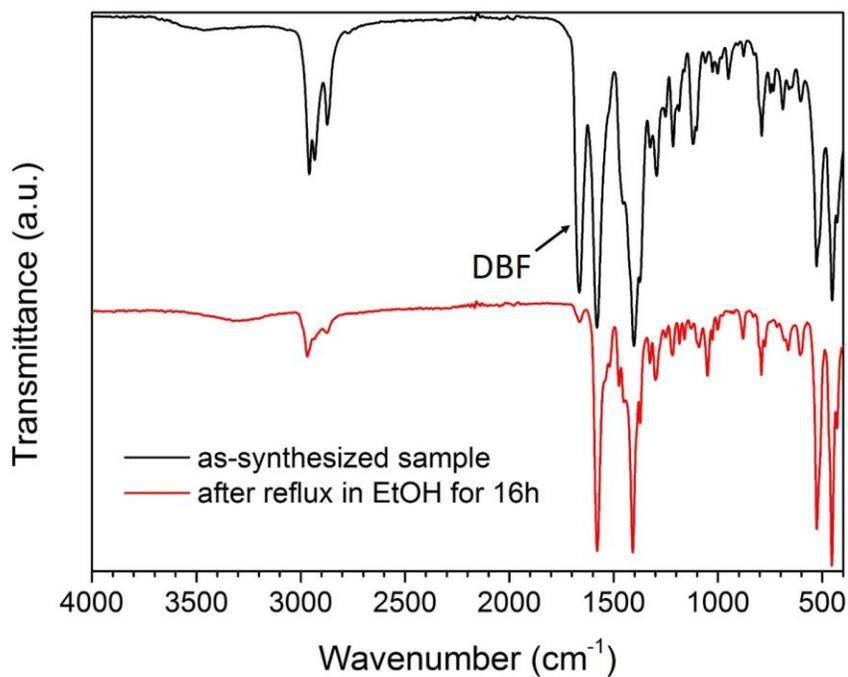


Figure S6. FT-IR spectrum of compound CPM-300 showing the complete removal of DBF guest solvent after the reflux treatment, compared to the as-synthesized sample.

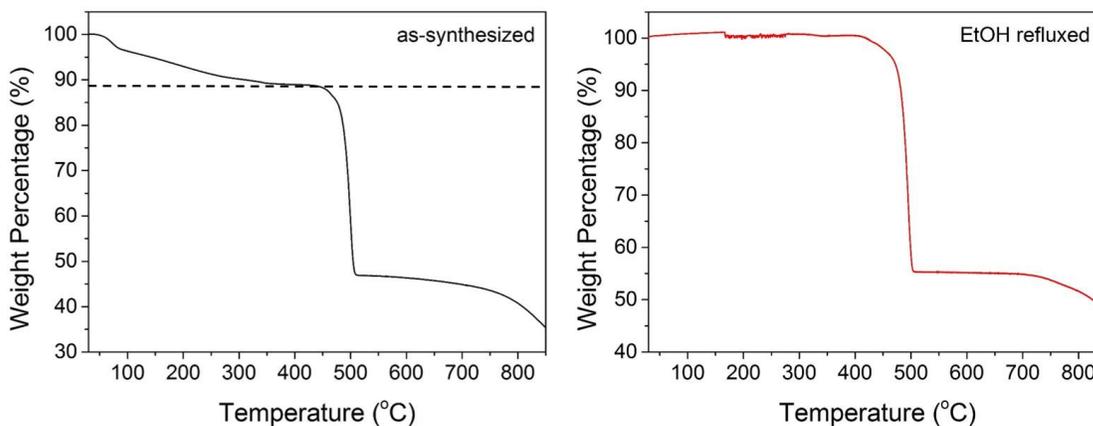


Figure S7. Thermogravimetric measurement of (Left) as-synthesized sample and (Right) EtOH refluxed sample of compound CPM-300. It can be seen that there is no apparent weight loss of the refluxed sample until ~ 420 $^{\circ}\text{C}$, which indicates the reflux treatment has successfully remove all the pre-existing guest from the pores.

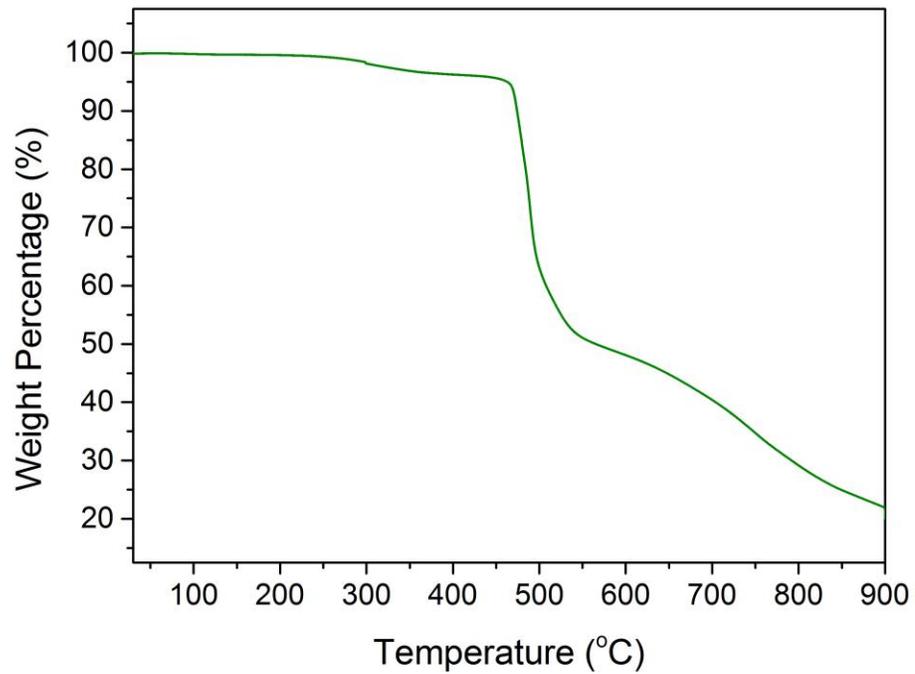


Figure S8. Thermogravimetric plot for as-synthesized CPM-301.

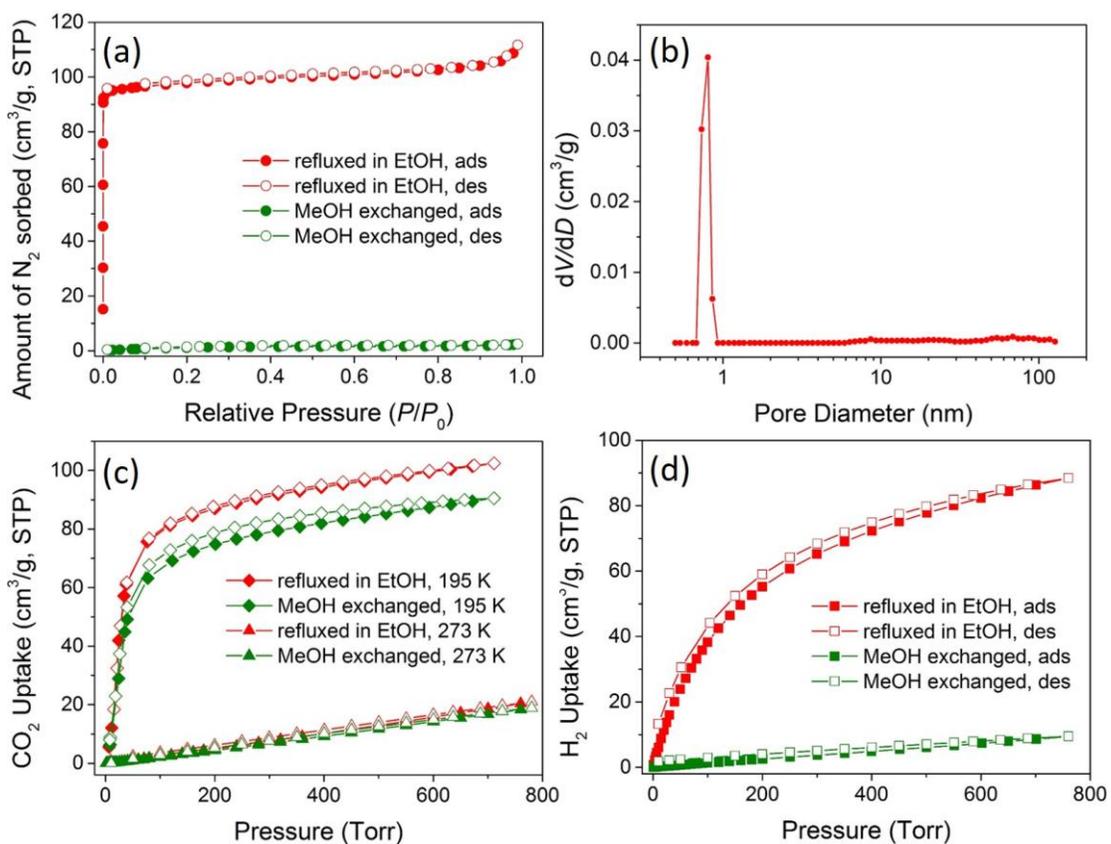


Figure S9. Gas sorption properties of compound CPM-300 under different treatment methods, refluxing in EtOH and solvent exchange by MeOH at room temperature. It can be seen that the treatment method resulted in dramatic difference in N₂ and H₂ sorption while the difference is minor for CO₂ sorption. (a) N₂ sorption at 77 K, (b) Pore size distribution of CPM-300 sample after reflux treatment in EtOH, (c) CO₂ sorption in both 195 K and 273 K and (d) H₂ sorption at 77 K.

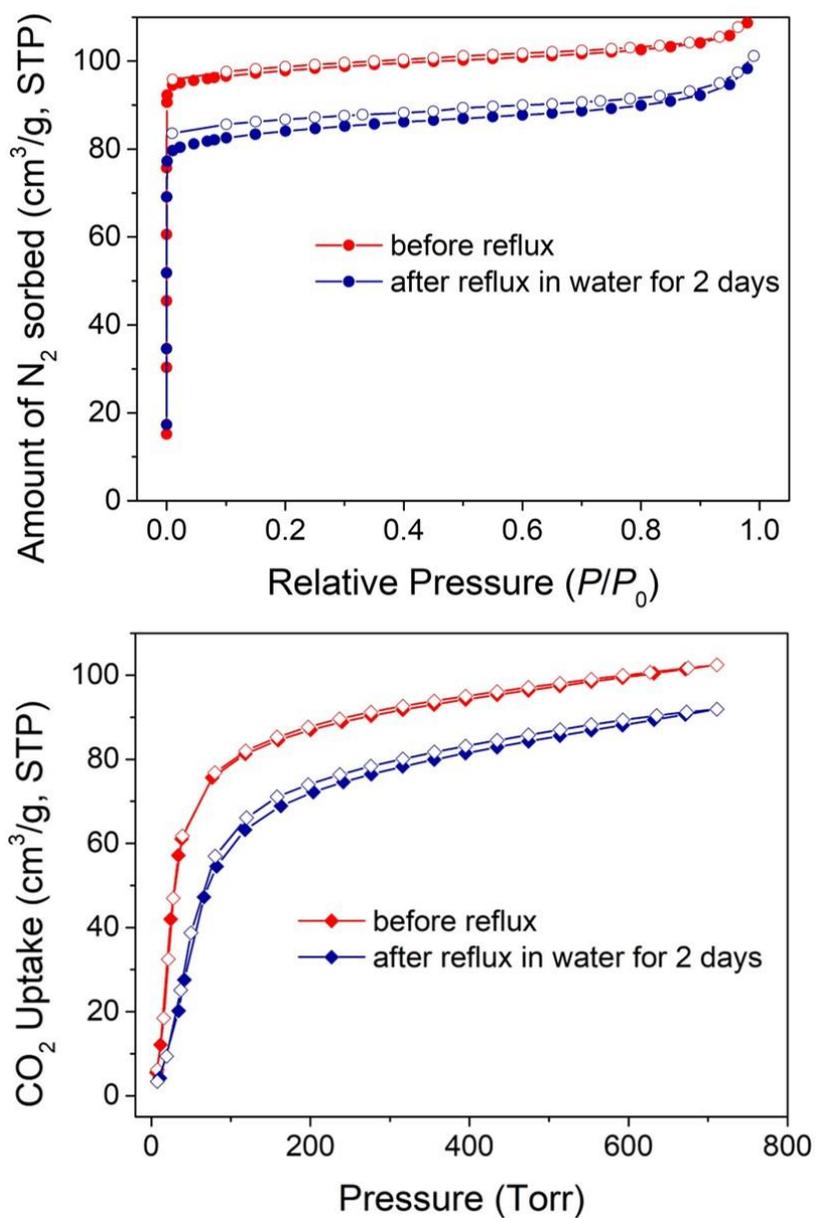


Figure S10. Gas sorption properties of compound CPM-300 before and after reflux in water for two days. (Top) N₂ sorption at 77K, (Bottom) CO₂ sorption at 195K. It can be seen that, after the treatment in the harsh condition, only small drop was observed for the absolute value of adsorbed amount of N₂ or CO₂, the majority of the porosity was retained.

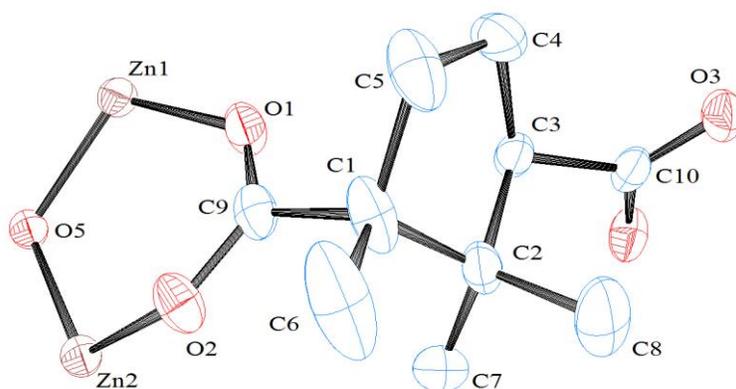


Figure S11. Ortep drawing of the asymmetric unit in CPM-300. Thermal ellipsoids were displayed with 50% probability.

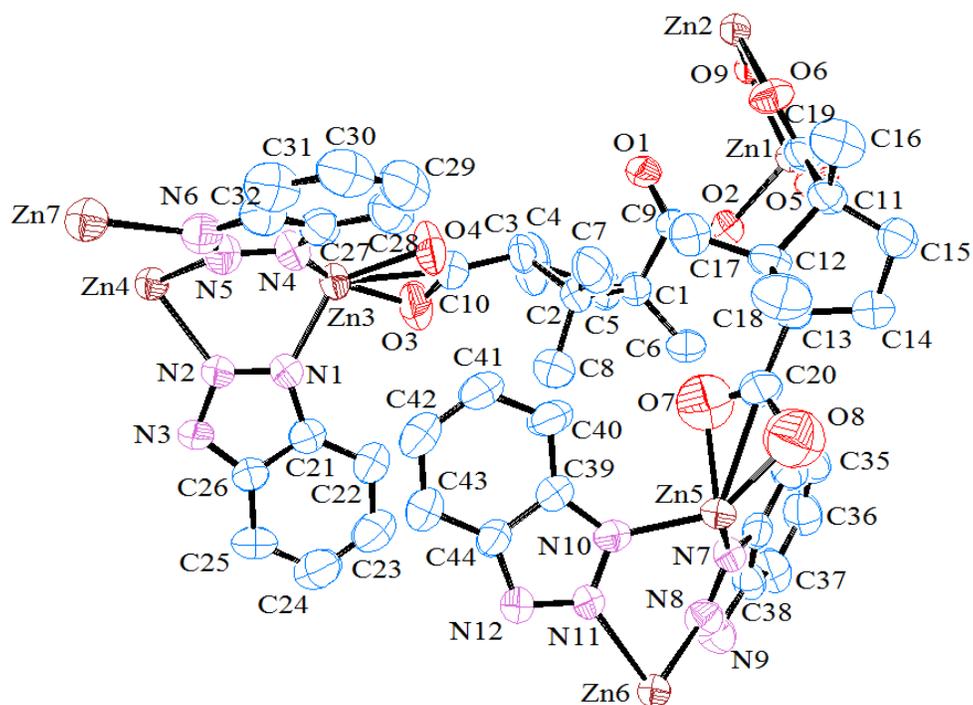


Figure S12. Ortep drawing of the asymmetric unit in CPM-301. Thermal ellipsoids were displayed with 50% probability.

Table S1. The detailed distribution of atoms around the $\text{Zn}_4\text{O}(\text{CO}_2)_6$ core in CPM-300 showing their distance to the core, atomic type, origins and the configuration.

Distance from cluster center	MOF-5		CPM-300	
	Sum	Details	Sum	Details
< 4 Å	$\text{Zn}_4\text{O}(\text{CO}_2)_6$	cluster core	$\text{Zn}_4\text{O}(\text{CO}_2)_6$	cluster core
4-4.5 Å	none	N/A	6H	4.19 Å --- H8C x3 4.46 Å --- H7A x3
4.5-5 Å	none	N/A	none	N/A
5-5.5 Å	6 C	5.07 Å --- C2 x6 (in COO plane)	12 C 18 H	5.03 Å --- C3 x3 (in COO plane) 5.06 Å --- C8 x3 5.09 Å --- H7B x3 5.13 Å --- C1 x3 (in COO plane) 5.20 Å --- H8A x3 5.28 Å --- H3A x3 5.33 Å --- C7 x3 5.44 Å --- H6C x3 5.48 Å --- H3A x3 5.50 Å --- H7C x3
5.5-6 Å	12 C 12 H	5.67 Å --- H1 x6 (in COO plane) 5.89 Å --- C3 x6 (in COO plane)	21 C 21 H	5.54 Å --- H7C x3 (adjacent cluster) 5.55 Å --- H5A x3 5.57 Å --- H4B x3 5.58 Å --- C2 x3 5.60 Å --- H6C x3 5.68 Å --- H6B x3 5.74 Å --- H8B x3 5.77 Å --- C2 x3 5.78 Å --- C6 x3 5.83 Å --- C7 x3 5.90 Å --- C5 x3 5.90 Å --- H8B x3 (adjacent cluster) 5.93 Å --- C4 x3 5.98 Å --- C3 x3
6-6.5 Å	none	N/A	9 C 18 H	6.02 Å --- H7B x3 6.04 Å --- H4A x3 6.28 Å --- H6A x3 6.29 Å --- C4 x3 6.29 Å --- C6 x3 (adjacent cluster) 6.39 Å --- H7A x3 6.43 Å --- H4A x3 6.43 Å --- H7C x3 6.49 Å --- C7 x3 (adjacent cluster)
6.5-7 Å	none	N/A	3 C 15 H 3 O	6.71 Å --- H6A x3 6.73 Å --- H6B x3 (adjacent cluster) 6.75 Å --- H7B x3 (adjacent cluster) 6.76 Å --- H5B x3 6.80 Å --- C8 x3 (adjacent cluster) 6.88 Å --- O2 x3 (adjacent cluster) 6.97 Å --- H7A x3 (adjacent cluster)

Table S2. Crystal data and structure refinement for CPM-300 and CPM-301.

Sample code	Zn ₄ O(RR-cam) ₃	[Zn ₄ O(RR-cam) ₃][Zn ₉ (btz ₁₂)(RR-cam) ₃]
Empirical formula	C ₃₀ H ₄₂ Zn ₄ O ₁₃	C ₁₃₂ H ₁₃₂ N ₃₆ Zn ₁₃ O ₂₅
Formula weight	872.11	3472.54
Temperature	174(2) K	174(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	hexagonal	trigonal
Space group	<i>P</i> 6 ₃	<i>R</i> 3
Unit cell parameters	<i>a</i> = <i>b</i> = 16.3036(7) Å <i>c</i> = 9.2767(4) Å $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	<i>a</i> = <i>b</i> = 21.407(4) Å <i>c</i> = 29.254(6) Å $\alpha = \beta = 90^\circ, \gamma = 120^\circ$
Volume	2135.5(2) Å ³	11610(5) Å ³
Z	2	3
Density (calculated)	1.356 g/cm ³	1.490 g/cm ³
Absorption coefficient	2.270	2.049
F(000)	892	5298
Theta range for data collection	1.442 to 34.818	1.300 to 26.857
Reflections collected	17396	20997
Independent reflections	5481 [<i>R</i> _{int} = 0.0519]	8777 [<i>R</i> _{int} = 0.0254]
Completeness	100.0% (to theta full = 25.242)	100.0% (to theta full = 25.242)
Absorption correction	Multi-scan	Multi-scan
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	5481 / 1 / 142	8777 / 491 / 620
Goodness-of-fit on <i>F</i> ²	0.886	0.899
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0382, <i>wR</i> ₂ = 0.0657	<i>R</i> ₁ = 0.0397, <i>wR</i> ₂ = 0.1109
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0668, <i>wR</i> ₂ = 0.0724	<i>R</i> ₁ = 0.0493, <i>wR</i> ₂ = 0.1171
Flack parameter	0.011(11)	0.019(7)
Largest diff. peak and hole	0.363 and -0.384 e.Å ⁻³	1.216 and -0.617 e.Å ⁻³
CCDC deposition number	1837658	1837657

References:

[1] G. M. Sheldrick, *SHELX97—Programs for Crystal Structure Analysis*, release 97–2; Institut für Anorganische Chemie der Universität Göttingen, Göttingen, Germany, **1998**.