Electronic Supporting Information

Rational construction of a stable Zn_4O-based MOF for highly efficient CO_2 capture and conversion

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EXPERIMENTAL SECTION

Materials and Measurements.

All reagents and solvents were commercially available and were used without further purification. Infrared spectra were obtained in KBr discs on a Nicolet Avatar 360 FTIR spectrometer in the 400-4000 cm^{-1} region. Elemental analyses (C, H and N) were performed with a PerkinElmer 2400C Elemental Analyzer. 1 H NMR spectra were recorded on Varian instrument (400 MHz) and (100 MHz). Thermal gravimetric analyses (TGA) were carried out in nitrogen stream using a Netzsch TG209F3 equipment at a heating rate of 5 °C/min. Powder X-ray diffraction (PXRD) data were recorded on a Japan Rigaku SmartLab rotation anode X-ray diffractometer or Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα, 1.5418 Å).

Synthesis of $[Zn_4(\mu_4\text{-}O)(PDBDC)_{1.5}]\cdot 1.5DMF\cdot 2H_2O$ (1).

A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (29.8 mg, 0.1 mmol) and H_4PDBDC (20.4 mg, 0.05 mmol) was dissolved in DMF (3 mL), anhydrous alcohol (3 mL) and HNO_3 (1mL, aq) (1mL HNO_3 in 10 mL H_2O) at room temperature in a 8 mL screw-capped glass vial. Then the glass vial was placed in an oven at 105 ºC for 72 h. After cooling down to room temperature at a rate of 0.5 °C min^{-1}. The resulting colorless rodlike crystals of **1** were isolated. Anal. Calcd for $Zn_8C_{63}H_{27}N_3O_{26}$ (activated **1**): C, 42.87; H, 1.54; N, 2.38%. Found: C, 42.80; H, 1.47; N, 2.42%.

Sorption Measurements.

All the gas sorption isotherms were measured by using a ASAP 2020M adsorption equipment. The activated samples were prepared by soaking the as-synthesized samples in acetone for 3 days and subsequently drying the material overnight at 140 °C under vacuum to remove the solvent molecules prior to measurements.

X-ray Crystallography

Diffraction data were collected at 296(2) K with a Mo Kα radiation (λ = 0.71073 Å) on a Bruker-AXS SMART CCD area detector diffractometer. Absorption corrections were carried out utilizing SADABS routine. The structure was solved by the direct methods and refined using the SHELXTL program package.[1] All non-hydrogen atoms were refined anisotropically with the hydrogen atoms added to their geometrically ideal positions and refined isotropically. The contribution of the disordered solvent molecules in the structure was subtracted from the reflection data by the SQUEEZE method as implemented in PLATON program.[2] The final formulas of **1** was determined by combining the single-crystal structures, elemental microanalyses and TGA data. Data collection and structure refinement parameters and crystallographic data for **1** is given in Table S2.

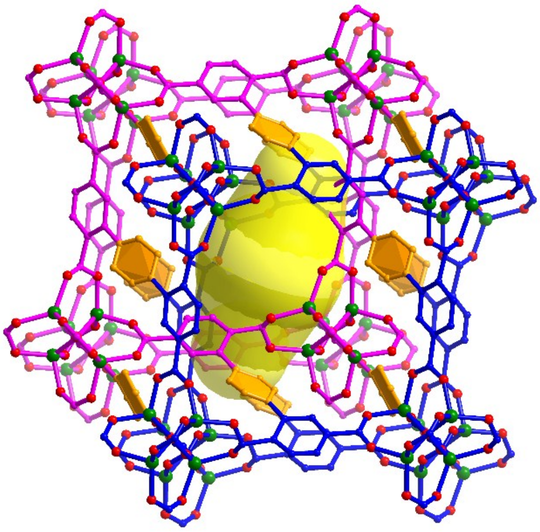
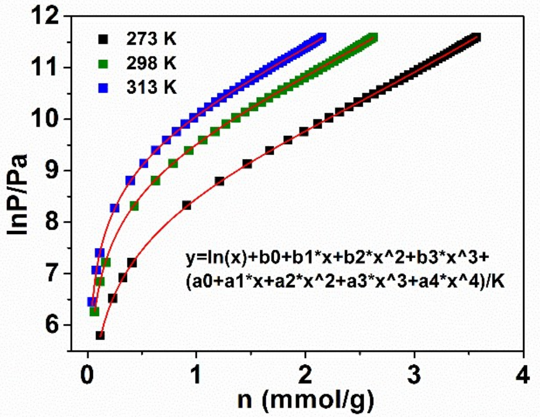


Fig. S1 Spheres denote the pores in the framework.

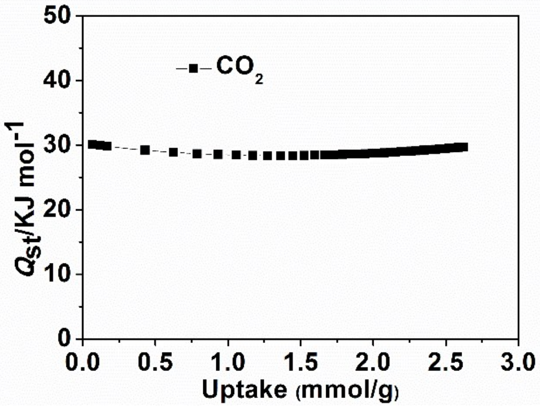
Calculation of sorption heat for CO_2 uptake using Virial 2 model

$$\ln P = \ln N + 1/T\sum_{i=0}^{m} aiN^{i} + \sum_{i=0}^{n} biN^{i} \qquad Q_{st} = -R\sum_{i=0}^{m} aiN^{i}$$

The above equation was applied to fit the combined CO_2 isotherm data for **1** at 273 K, 298 K and 313 K, where P is the pressure, N is the adsorbed amount, T is the temperature, ai and bi are virial coefficients, and m and n are the number of coefficients used to describe the isotherms. Q_{st} is the coverage-dependent enthalpy of adsorption and R is the universal gas constant.



(a)



(b)

Fig. S2 (a) CO_2 adsorption isotherms for **1** with fitting by Virial 2 model. Fitting results: a0 = -3637.11783 ± 29.48309, a1 = 359.94234 ± 97.32903, a2 = -159.59377 ± 79.82605, a3 = 13.89150 ± 19.68074, a4 = -0.74475 ± 0.65312, b0 = 21.13714 ± 0.09767, b1 = -0.60155 ± 0.31530, b2 = 0.46901 ± 0.25086, b3 = -0.01093 ± 0.05653, Chi^2 = 1.30966×10^{-4}, R^2 = 0.99992. (b) CO_2 adsorption heat calculated according to the virial equation.

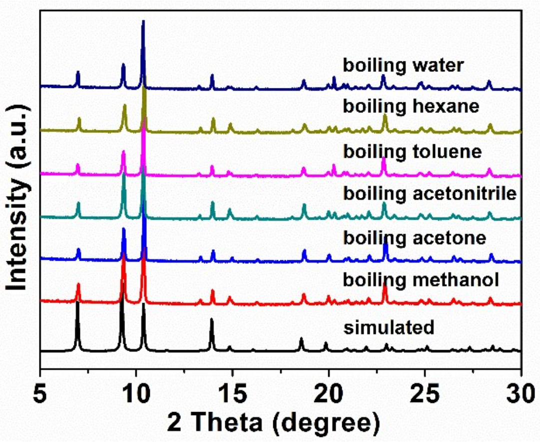


Fig. S3 Powder XRD patterns of **1** after being soaked in various boiling solvents and water for 12h.

Thermogravimetric analysis

Thermogravimetric (TG) analysis of **1**·solvent shows a significant weight loss of ~15.5% in the range of 50-215 ˚C, which could be attributed to the loss of free DMF and H_2O molecules in the pores of the MOF. Following that, a plateau is observed until the collapse of the framework at 350 °C (Fig. S4).

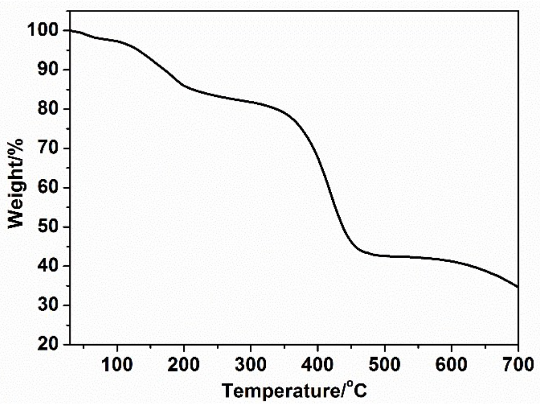


Fig. S4 TG Plot of **1** in N_2 atmosphere.

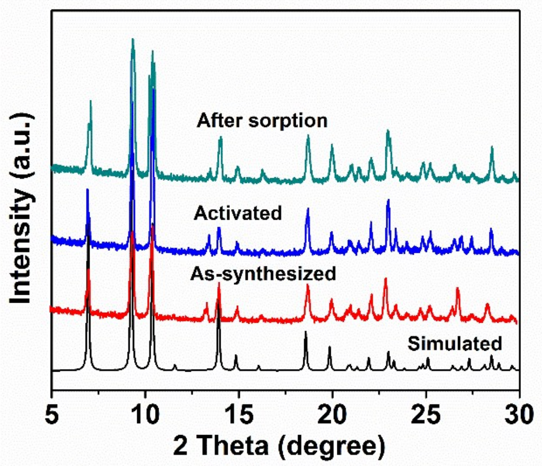


Fig. S5 Powder XRD patterns of **1** (Simulated: black; As-synthesized: red; Activated: blue; after sorption: brown).

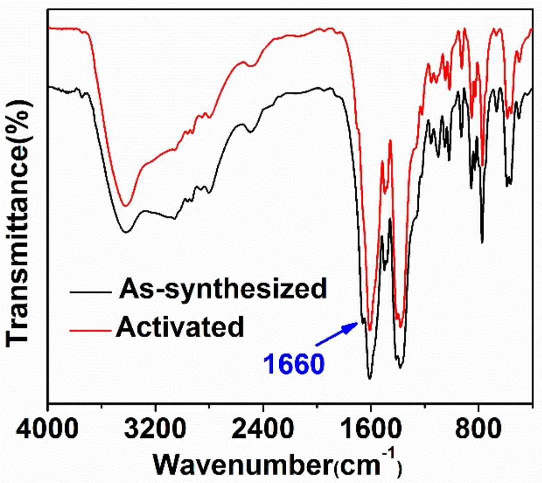
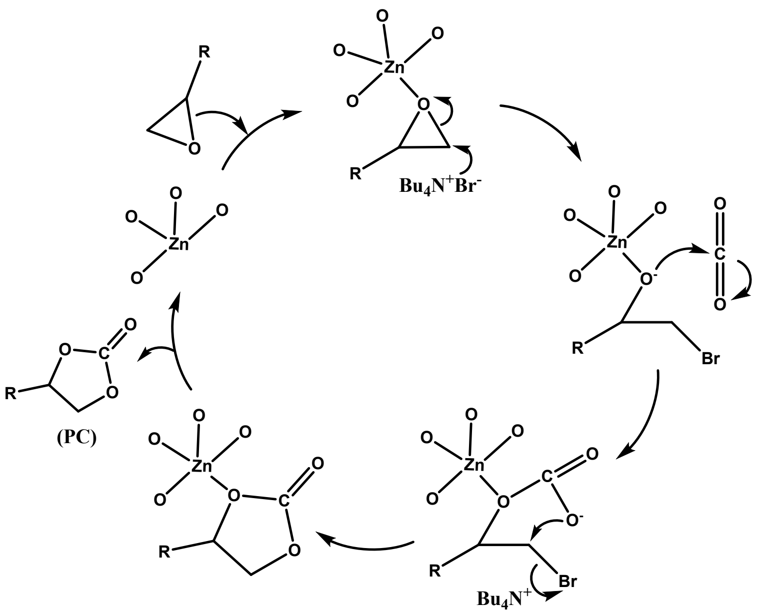


Fig. S6 IR spectra of the as-synthesized and activated sample of **1**.



Scheme S1 The plausible reaction mechanism for the cycloaddition of CO_2 with epoxides catalyzed by **1** and n-Bu_4NBr.

Table S1 The comparison of CO_2 adsorption amounts in **1** and reported MOFs.

MOF	CO_2 loading (mmol g^{-1})	Temperature (K), Pressure (atm)
Mg_2(dobdc), MOF-74(Mg)	8.01	313 K, 1.0 atm [3]
$Cr_3(BTC)_2$	2.78	314 K, 1.0 atm [4]
$Co_2(ad)_2(C_2H_5CO_2)_2$, bio-MOF-12	2.46	313 K, 1.0 atm [5]
SIFSIX-3-Zn	2.40	308 K, 1.0 atm [6]
$[(Zn_4O)(PDBDC)_{1.5}]$ (**1**), **This work**	2.16	313 K, 1.0 atm
$H_3[(Cu_4Cl)_3(BTTri)_8]$	2.15	313 K, 1.1 atm [3]
$Zn_8(ade)_4(bpdc)_6O\cdot 2TEA$, TEA@bio-MOF-1	1.66	313 K, 1.0 atm [7]
$Cu_3(BTC)_2$	1.52	313 K, 1.0 atm [8]
$Zn_4O(BDC\text{-}NH_2)_3$, IRMOF-3	1.20	313 K, 1.0 atm [8]
$Zn_4O(BDC)_3$, MOF-5	1.13	313.7 K, 1.0 atm [9]
UiO(bpdc)	1.1	313 K, 1.0 atm [10]
$Cr_3O(H_2O)F(BDC)_3$, MIL-101(Cr)	1.0	319 K, 1.0 atm [11]
$H_3[(Cu_4Cl)_3(BTTri)_8]$-en	0.92	313 K, 1.0 atm [12]
$Be_{12}(OH)_{12}(BTB)_4$	0.83	313 K, 1.0 atm [3]
$Zn_4O(BTB)_2$, MOF-177	0.80	313 K, 1.3 atm [3]
$[Fe(btzx)_3](ClO_4)_2$	0.64	313 K, 1.0 atm [13]
Co(BDP)	0.24	313 K, 1.3 atm [3]

Table S2 Crystal Data and Refinement Results for **1**.

Compound	**1**
Empirical formula	$Zn_8C_{63}H_{27}N_3O_{26}$
Formula weight	1765.00
Crystal system	Trigonal
Space group	*R*-3
T (K)	296(2)
a (Å)	19.093(4)
b (Å)	19.093(4)
c (Å)	19.869(9)
α (deg)	90
β (deg)	90
γ (deg)	120
V (Å^3)	6273(3)
Z	6
D_c/g·cm^{-3}	1.402
μ/mm^{-1}	2.321
Reflns collected	10196
Reflns unique	2429
R(int)	0.0481
GOF	1.268
$R_1{}^a$, $wR_2{}^b$ [I > 2σ(I)]	0.1103, 0.3168
R_1, wR_2 (all data)	0.1412, 0.3408

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $^bwR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

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