

Supporting Information

Dynamic Zn-based metal–organic framework: Stepwise adsorption, Hysteretic desorption and Selective carbon dioxide uptake

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Materials and Measurements. All solvents and starting materials for synthesis were purchased commercially and were used as received. Infrared spectra were obtained from KBr pellets on a Bruker TENSOR 27 Fourier Transform Infrared spectrometer in the 400–4000 cm^{-1} region. Photoluminescence analyses were performed on a Perkin-Elmer LS55 luminescence spectrometer. Thermalgravimetric analyses (TGA) were carried out in nitrogen stream using a Seiko Extar 6000 TG/DTA equipment at a heating rate of 5 $^{\circ}\text{C}/\text{min}$. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer ($\text{Cu K}\alpha$, 1.5418 Å), and the variable-temperature PXRD patterns were recorded with a Rigaku D/MAX-3C diffractometer.

Synthesis of $[\text{Zn}(\text{dcpa})]\cdot x\text{S}$ ($1\cdot x\text{S}$). A mixture of 5-(3-carboxylphenyl)nicotic acid (0.1 mmol, 0.024 g) and $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.2 mmol, 0.065 g) in DMF (8 mL) was placed in a Teflon-lined stainless steel vessel (15 mL) and heated at 120 $^{\circ}\text{C}$ for 48 h, and then cooled to room temperature at a rate of 0.1 $^{\circ}\text{C}/\text{min}$. The colorless polyhedral crystals thus obtained (yield: 89.3%, based on H_2dcpa). Elem anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{N}_3\text{O}_6\text{Zn}$ ($[\text{Zn}(\text{dcpa})]\cdot 2\text{C}_3\text{H}_7\text{NO}$): C, 50.38; H, 4.64; N, 9.28%. Found: C, 50.33; H, 4.97; N, 9.16%.

Sorption Measurements. All the gas sorption isotherms were measured by using a ASAP 2020M adsorption equipment. The as-synthesized samples were treated by heating at 180 $^{\circ}\text{C}$ for 8 h in a quartz tube under vacuum to remove the solvent molecules prior to measurements.

Crystallography. The diffraction data were collected at 296(2) K with a Bruker-AXS SMART CCD area detector diffractometer at 296(2) K using ω rotation scans with a scan width of 0.3 $^{\circ}$ and $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073$ Å). Absorption corrections were carried out utilizing SADABS routine. The structure was solved by the direct methods and refined by full-matrix least-squares refinements based on F^2 . All non-hydrogen atoms were refined anisotropically with the hydrogen atoms added to their geometrically ideal positions and refined isotropically except that the hydrogen atoms on the coordinated water molecules were located from the electron density and then refined using a riding model. The void volume of each framework was estimated by the PLATON program. The final formula was determined by combining single-crystal structures, elemental microanalyses and TGA. Crystal data of **1**: $\text{C}_{13}\text{H}_7\text{NO}_4\text{Zn}$, $M = 306.57$, 296 K, tetragonal

$P4_32_12$, $a = 13.4641(2) \text{ \AA}$, $b = 13.4641(2) \text{ \AA}$, $c = 23.3751(4) \text{ \AA}$, $V = 4237.48(11) \text{ \AA}^3$, $Z = 8$, $D_c = 0.961 \text{ g cm}^{-3}$, $\mu = 1.671 \text{ mm}^{-1}$, $R_{\text{int}} = 0.0435$, final $R_1 = 0.0736$, $wR_2 = 0.2395$. CCDC-903982 contains the crystallographic data for this paper.

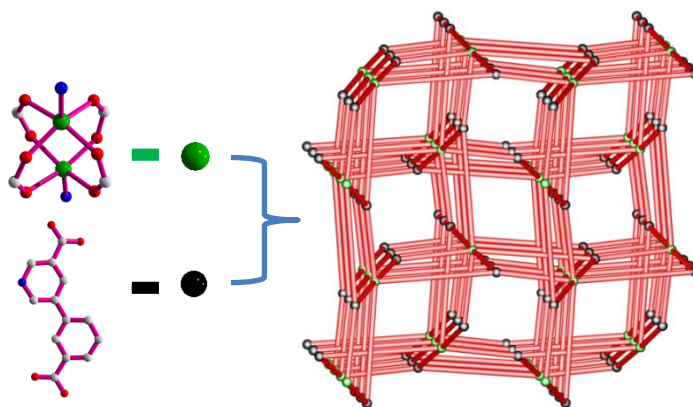


Figure S1. Schematic representation of the (3,6)-connected 3D framework of **1**.

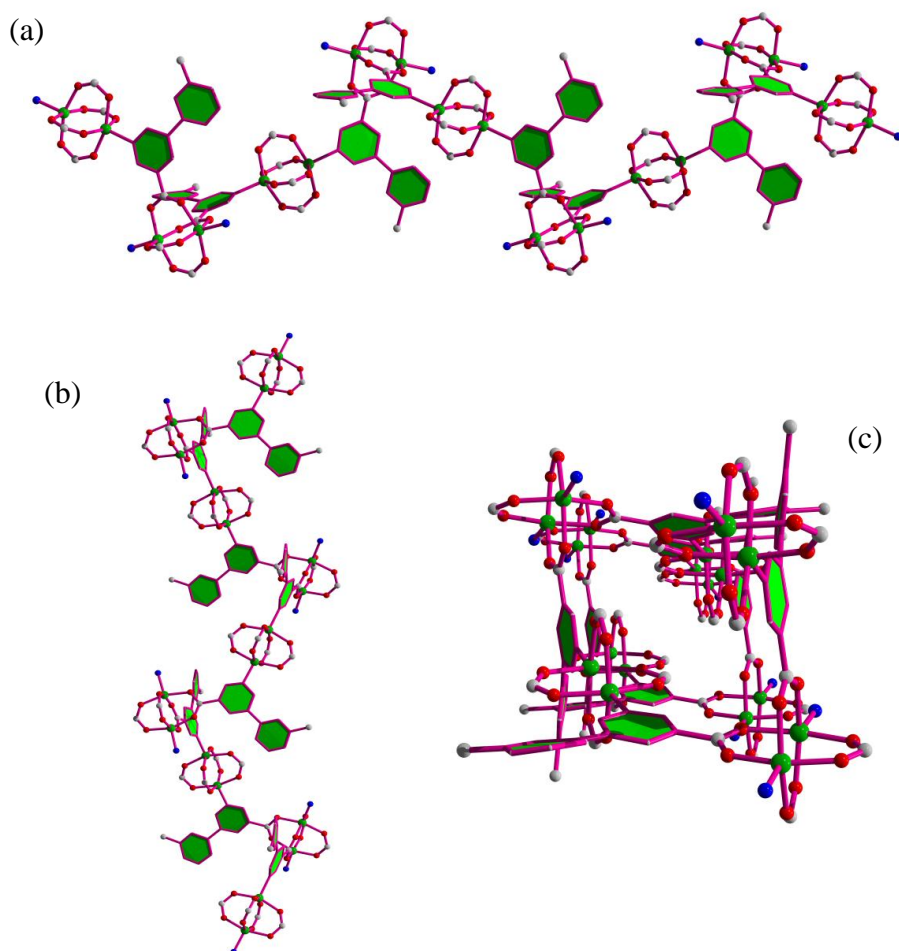


Figure S2. View of the helical arrays related by the chiral 4_1 screw axis along (a) c -axis, (b) a -axis and (c) b -axis.

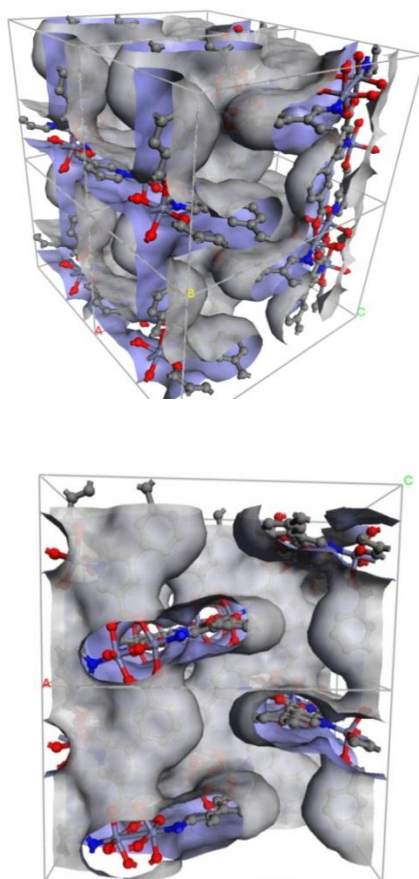


Figure S3. View of the continuous percolated pore network of **1**.

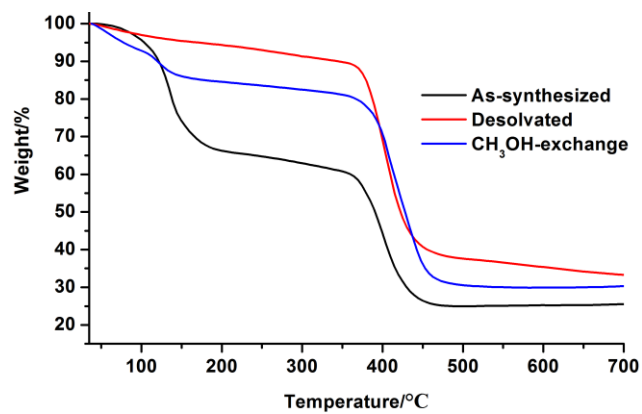


Figure S4. TGA plots of the as-synthesized, desolvated and CH₃OH-exchange samples of **1**.

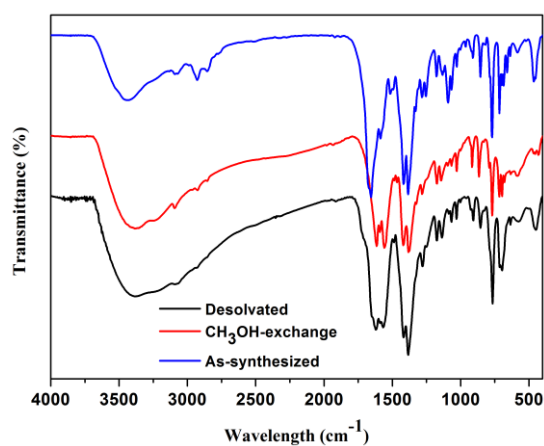


Figure S5. IR spectra for the as-synthesized, desolvated and CH₃OH-exchange samples of **1**.

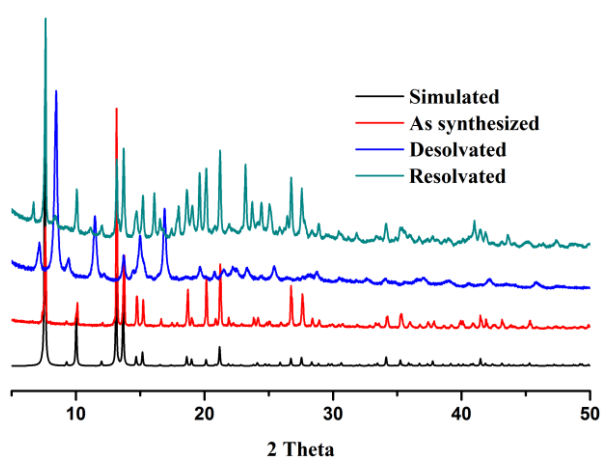


Figure S6. PXRD patterns of **1** simulated from the X-ray single-crystal structure, as-synthesized, desolvated and resolved samples.

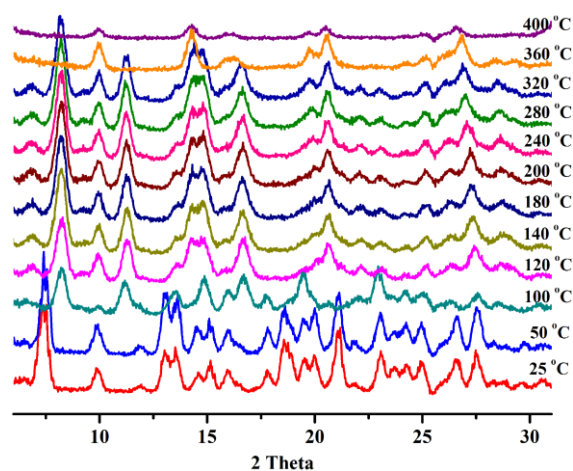


Figure S7. The variable-temperature PXRD patterns of **1·xS**.

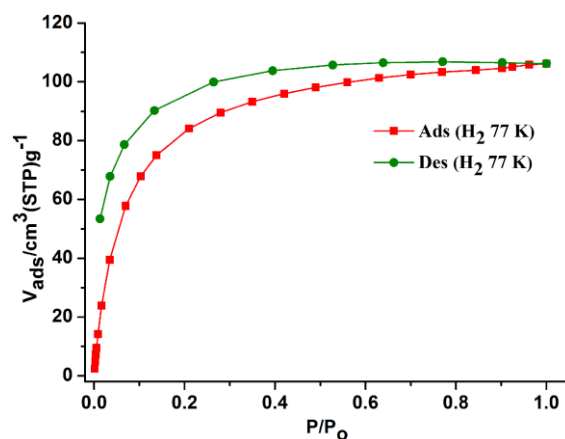


Figure S8. Gas sorption isotherms of **1** for H₂ at 77 K.

Calculation of sorption heat for CO₂ uptake using Virial 2 model

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

The above equation was applied to fit the combined CO₂ isotherm data for **1** at 273 and 293 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.

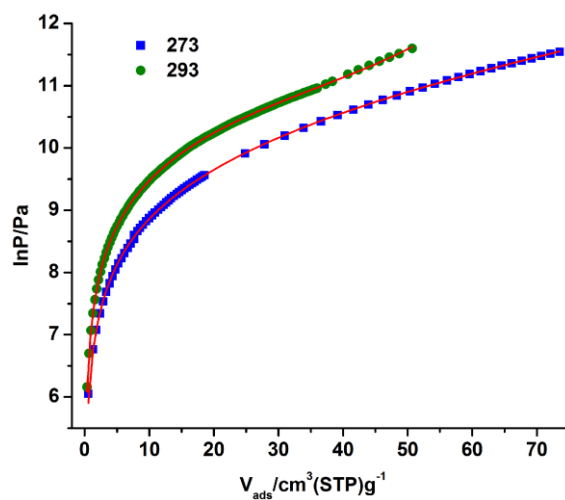


Figure S9. CO₂ adsorption isotherms for **1** with fitting by Virial 2 model. Fitting results: $a_0 = -3401.36241$, $a_1 = 49.04816$, $a_2 = 7.97705$, $a_3 = 11.48594$, $a_4 = 4.33726 \times 10^{-6}$, $b_0 = 18.94617$, $b_1 = -0.17426$, $b_2 = -0.02902$, $b_3 = -0.04208$. $\chi^2 = 0.000236$, $R^2 = 0.99981$.

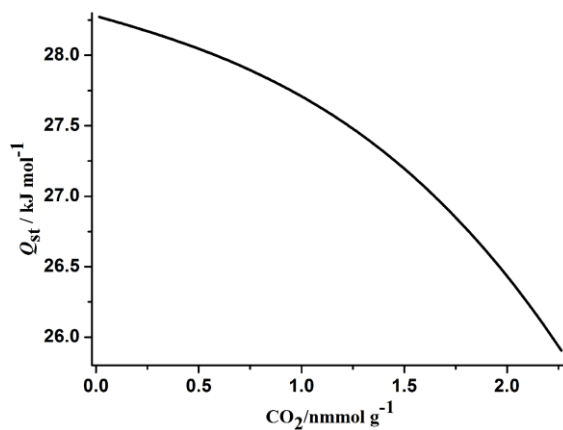
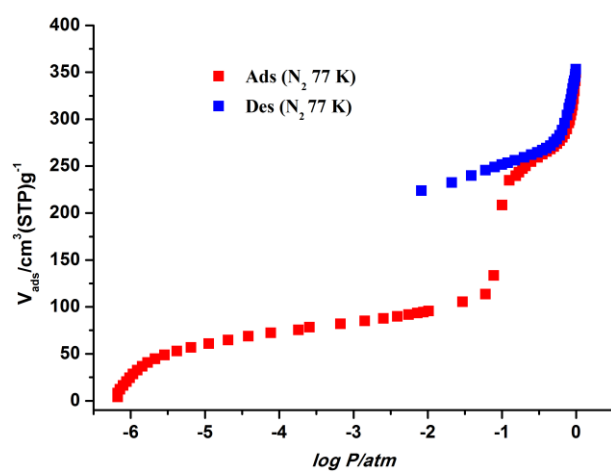
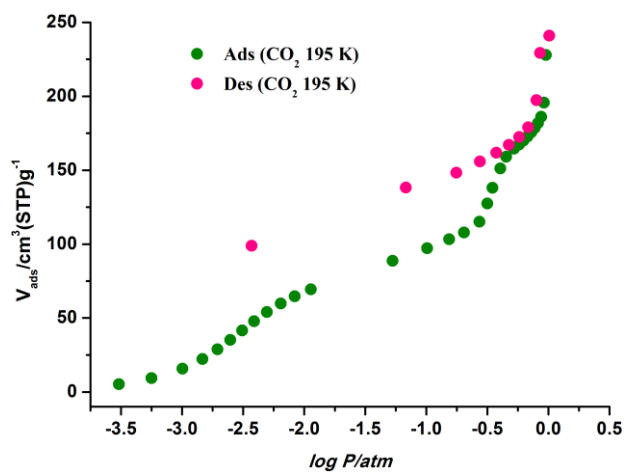


Figure S10. Isosteric heat of adsorption for CO₂ at different CO₂ loadings in **1**.



(a)



(b)

Figure S11. Gas sorption isotherms: (a) N₂ 77 K and (b) CO₂ 195 K.