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Supporting Information

An unprecedented acylamide-functionalized 2D→3D microporous metal−organic polycatenation framework exhibiting highly selective CO_2 capture

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Materials and Measurements. All reagents and solvents were commercially available and were used without further purification. The 4,4',4''-[1,3,5-Benzenetriyltris(carbonylimino)]trisbenzoic acid (H_3bcta) was synthesized according to literature procedures.[1] IR 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 Perkin Elmer 2400C Elemental Analyzer. Thermalgravimetric 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 Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα, 1.5418 Å). All the gas sorption isotherms were measured by using a ASAP 2020M adsorption equipment.

Synthesis of [Zn_2(bcta)(dipy)(μ_2-OH)]·2DMF·H_2O (1)

A mixture of $Zn(NO_3)_2·6H_2O$ (0.2 mmol, 0.059 g), H_3bcta (0.1 mmol, 0.062 g) and dipy (0.1 mmol, 0.018 g) in DMF (6 mL) and water (2 mL) was placed in a Teflon-lined stainless steel vessel (25 mL) and heated at 120 °C for 72 h, and then cooled to room temperature at a rate of 5 °C min^{-1}. The resulting colorless block crystals of **1** were isolated by washing with DMF/H_2O and dried in air. The yield was 0.092 g (86.7%, based on H_3bcta). Anal. Calcd for $C_{48}H_{45}N_7O_{13}Zn_2$: C, 54.56; H, 4.28; N, 9.26. Found: C, 54.49; H, 3.88; N, 9.32.

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 ºC for 8 h in a quartz tube under vacuum to remove the solvent molecules prior to measurements.

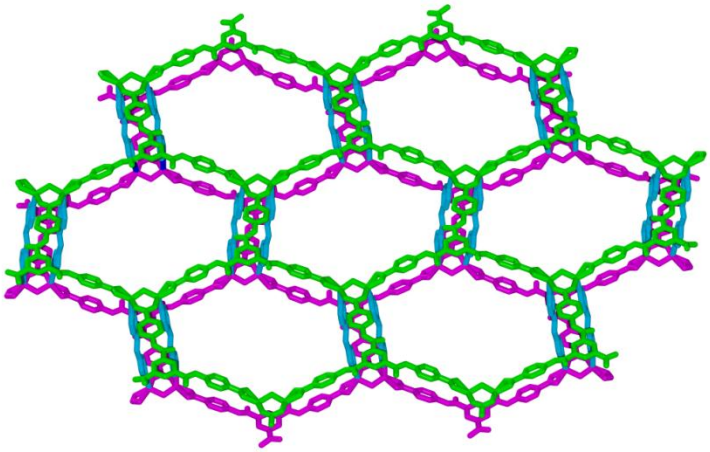
Crystallography.

Diffraction data were collected 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 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. However, the hydrogen atoms of the water solvates and some DMF molecules cannot be located from the difference Fourier maps. Crystal data of **1**: $C_{48}H_{45}N_7O_{13}Zn_2$, M = 1058.68, 296(2) K, monoclinic, space group $P2_1/c$, a = 10.405(3) Å, b = 24.813(7) Å, c = 19.681(5), β = 106.200(13)º, V = 4879(2) $Å^3$, Z = 4, Dc = 1.437 g cm^{-3}, μ = 1.054 mm^{-1}, 31706 reflections collected. Refinement of 8678 reflections (635 parameters) with $I > 2\text{sigma}(I)$ converged at final R_1 = 0.0559, wR_2 = 0.1203, GOF = 1.011. CCDC-931075 contains the crystallographic data for this paper.

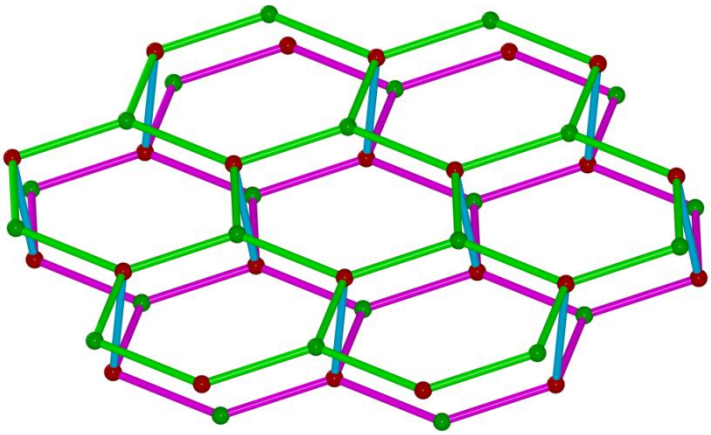
The final formulas for the complexes were determined by combining single-crystal structures, elemental microanalysis and TGA.

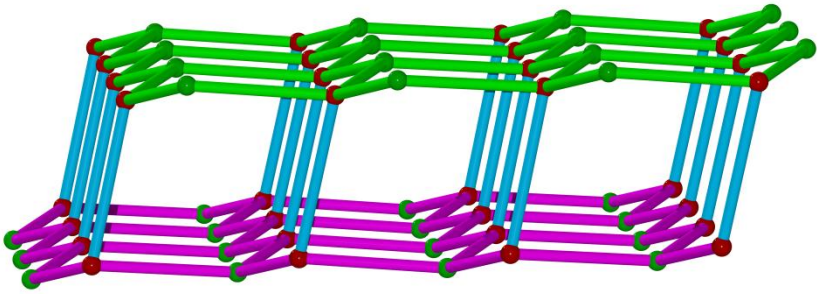
References

1 X. Song, Y. Zou, X. Liu, M. Oh and M. S. Lah, *New J. Chem*., 2010, **34**, 2396–2399.



(a)





(b)

Fig. S1 The two layers are connected by dipy to generate a bilayer (a) and its simplified net (along two different directions) (b). Note that two identical layers are highlighted in green and pink, while the pillars of dipy are colored in blue.

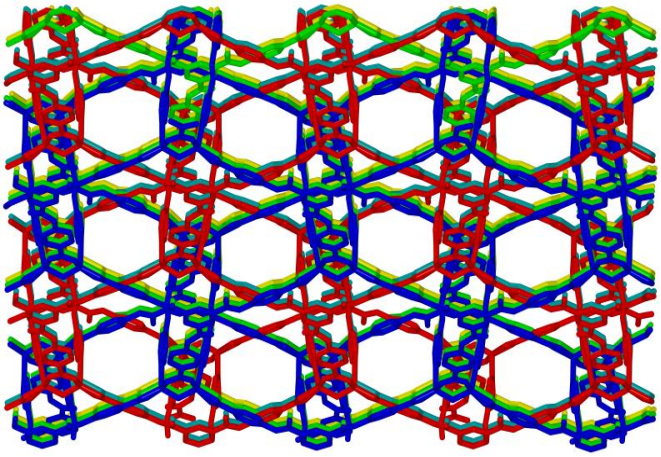


Fig. S2 View of the 2D → 3D microporous framework of **1**: each color presents one bilayer net.

Table S1 Summary of the linking modes of the 6-membered shortest ring within 3D net of **1**

Cycle 1	Cycle 2	Chain	Cross	Mult
6a	6a	inf.	1	4
6a	6b	inf.	1	8
6a	6c	inf.	1	4
6b	6a	inf.	1	8
6b	6c	inf.	1	4
6c	6a	inf.	1	8
6c	6b	inf.	1	8

[a]Chain: the bond amount of the shortest chain that interconnected two rings.
*b*Cross: the times of each ring crossing another ring.
[c]Mult: the ring numbers of each ring crossed by other one.

Thermogravimetric analyses (TGA) and Powder X-ray diffraction (PXRD)

The TGA curve of **1** reveals a total weight loss of 16.6% below 250 °C under N_2 atmosphere (Fig. S3), corresponding to the loss of two DMF and one lattice water molecules per formula unit (calcd. 15.6%). The guest molecules of **1** can also be removed by heating at 180 °C under vacuum for 8 h, which is verified by TGA and IR on the desolvated **1**. PXRD of the desolvated **1** exhibits weakening and high-angle shifting of some peaks which remains highly crystalline, implying slight framework distortion due to the solvent release (Fig. S4). However, the PXRD pattern of **1** can be reversibly restored from solvent-free **1** while the solvents were re-adsorbed.

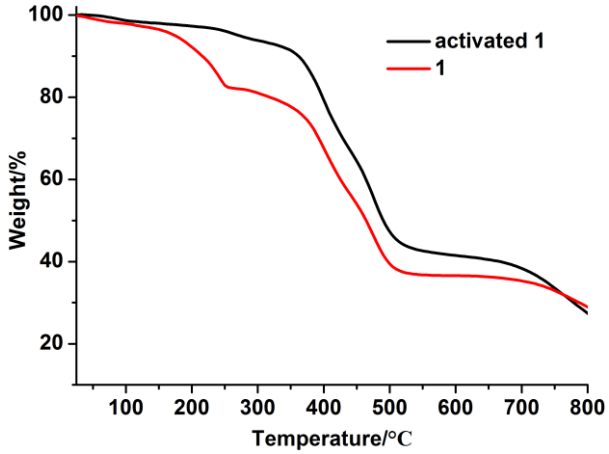


Fig. S3 TGA curves for **1** and activated samples measured under nitrogen.

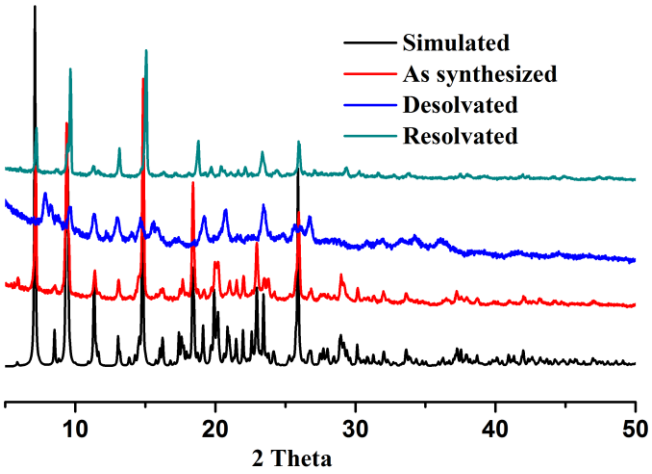


Fig. S4 PXRD patterns of **1** simulated from the X-ray single-crystal structure, as-synthesized, desolvated and resolvated samples.

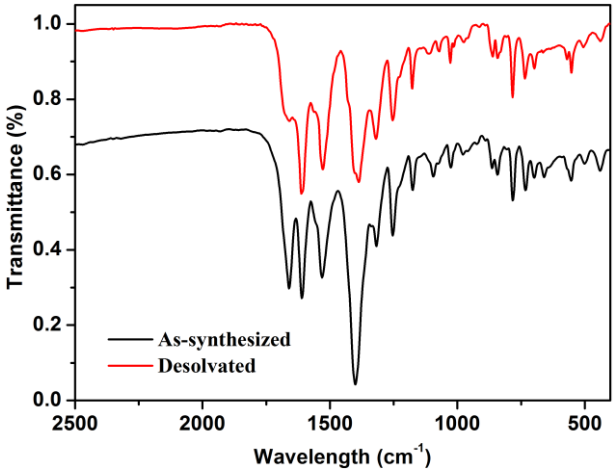


Fig. S5 The FTIR spectra of **1** and desolvated **1** samples.

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 and 295 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.

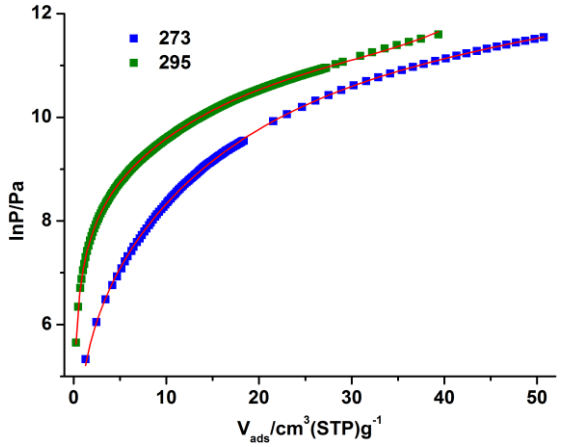


Figure S6. CO_2 adsorption isotherms for **1** with fitting by Virial 2 model. Fitting results: a0 = -3635.98961, a1 = 53.99218, a2 = 7.44731, a3 = 11. 49206, a4 = -4.81578 × 10^{-5}, b0 = 19.21214, b1= -0.16808, b2 = -0.02832, b3 = -0.04212. Chi^2 = 0.000147, R^2 = 0.99988.