

Electronic Supporting Information for

A stable metal azolate framework with rare nonintersecting one-/two-dimensional pore channels

Yi Heng, Mu-Yang Zhou, Le Ye, Xiao-Tong Lu, Dong-Dong Zhou,* and Jie-Peng Zhang

*MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, GBRCE for Functional Molecular Engineering,
School of Chemistry, IGCME, Sun Yat-Sen University, Guangzhou 510275, China*

*Email: zhoudd3@mail.sysu.edu.cn

Materials, Measurement, and Characterization

Commercially available reagents and solvents were used as received without further purification. Dibenzo[*b,e*][1,4]dioxine-2,3,7,8-tetraamine was prepared according to the previously reported synthesis (*J. Am. Chem. Soc.*, 2019, **141**, 13858). Mass spectrum (MS) was obtained on an LTQ Orbitrap Elite LC/MS (ESI) equipment with methanol (MeOH) as the mobile phase. ¹H-nuclear magnetic resonance (¹H NMR) spectrum was obtained on a Bruker advance III (400 MHz) NMR spectrometer. Elemental analyses (EA) were performed with an Elementar Vario EL Cube elemental analyzer. Powder X-ray diffraction (PXRD) patterns were collected on a Smart Lab X-ray powder diffractometer with Cu K α radiation. Thermogravimetry (TG) analyses were performed on a TA Q50 thermogravimetric analyzer under nitrogen at a heating rate of 10 °C min⁻¹. Gas and vapor isotherms were measured with an automatic volumetric adsorption apparatus (ASAP 2020M or BELSORP max). The temperature was controlled by a liquid-nitrogen bath or water bath. The MeOH-exchanged sample was placed in the sample tube and dried for 5 h under vacuum at 130 °C to remove the remaining solvent molecules prior to measurement.

Synthesis of 1,7-bis(trifluoromethyl)-[1,4]dioxino-[2,3-*f*:5,6-*f'*]bisbenzimidazole (H₂fdbb)

A mixture of dibenzo[*b,e*][1,4]dioxine-2,3,7,8-tetraamine (5 g, 0.02 mmol) and trifluoroacetic acid (50 mL) were stirred under N₂ atmosphere for 30 min, then heated to reflux for 6 h. After that, the solvent was evaporated under nitrogen atmosphere and the crude product was precipitated. After recrystallization in MeOH)/trimethylamine (*v:v* 100:1), the resulting white powders were filtered, and then washed three times with MeOH (10 mL). Finally, the samples were dried in air (yield: ~84%). ESI-MS *m/z* calculated for H₂fdbb (C₁₆H₆N₄F₆O₂): 400.24, found: 401.24 [M+H]⁺. EA calculated for H₂fdbb (C₁₆H₆F₆N₄O₂): C, 48.01; H, 1.51; N, 14.00. Found (%): C, 48.19; H, 1.55; N, 14.00.

Synthesis of [Zn₂(OH)(CH₃COO)(fdbb)]·Guest (MAF-50, 1·G)

A mixture of Zn(NO₃)₂·6H₂O (16.5 mg, 0.055 mmol), CH₃COONa (2.5 mg, 0.03 mmol) and H₂fdbb (10 mg, 0.025 mmol) in a solvent mixture of *N*-methylpyrrolidone (NMP, 3 mL), isopropanol (IPA, 3 mL) and CH₃COOH (10 μ L) was sealed in a Teflon-lined reactor and heated at 160 °C for 24 h, then cooled to room temperature at a rate of 5 °C h⁻¹. Colorless leaf-shaped crystals of 1·G were collected by filtration, washed three times with MeOH (10 mL), and dried under vacuum (yield: ~80%). Microcrystals of 1·G could be synthesized by mixing Zn(NO₃)₂·6H₂O (1.49 g, 5 mmol), CH₃COONa (0.21 g, 2.5 mmol) and H₂fdbb (1.00 g, 2.5 mmol) in a solvent mixture of NMP (50 mL) and ethanol (EtOH, 25 mL) under stirring conditions and heating at 160 °C for 12 h, then white microcrystalline sample of 1·G was obtained after filtration, washed with MeOH (1.22 g, yields: ~80%). The sample was dispersed in MeOH and heated at

333 K for guest exchanging, then filtrated and activated at 403 K to give the activated one, finally the sample was stored in the air. EA calculated for $\mathbf{1} \cdot 1.5\text{H}_2\text{O}$ ($\text{C}_{18}\text{H}_{11}\text{N}_4\text{O}_{6.5}\text{F}_6\text{Zn}_2$): C, 34.20; H, 1.75; N, 8.86. Found (%): C, 33.87; H, 1.93; N, 9.16.

Crystal Structure Determination

Single-crystal X-ray diffraction (SCXRD) data of H_2fdbb ligand and $\mathbf{1} \cdot \mathbf{G}$ was collected on an Agilent SuperNova diffractometer by using graphite monochromated $\text{Cu K}\alpha$ radiation, with absorption corrections applied by using the multiscan program *CrysAlisPro*. The structure was solved with the direct method and refined with a full-matrix least-squares technique with the SHELXTL software package. Anisotropic thermal parameters were applied to all non-hydrogen atoms, and the hydrogen atoms were generated geometrically. The PLATON *SQUEEZE* treatment was applied for $\mathbf{1} \cdot \mathbf{G}$ because the guest molecules are extremely disordered and cannot be modeled. CCDC 2343053–2343054 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

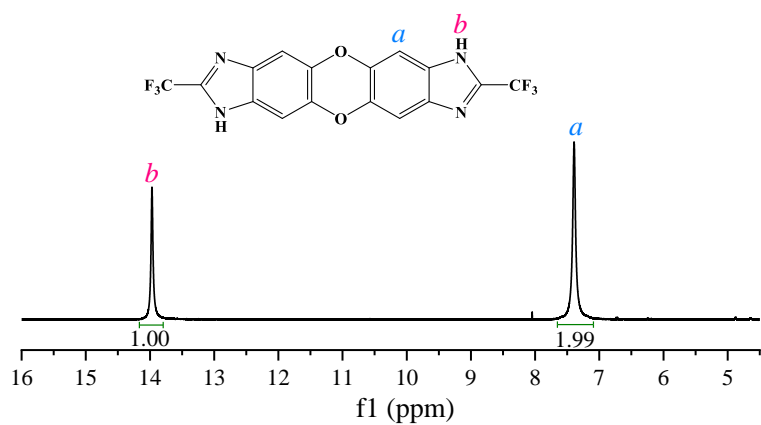


Fig. S1 ¹H-NMR spectrum (400 MHz, DMSO-*d*₆, 298 K) of H₂fdbb.

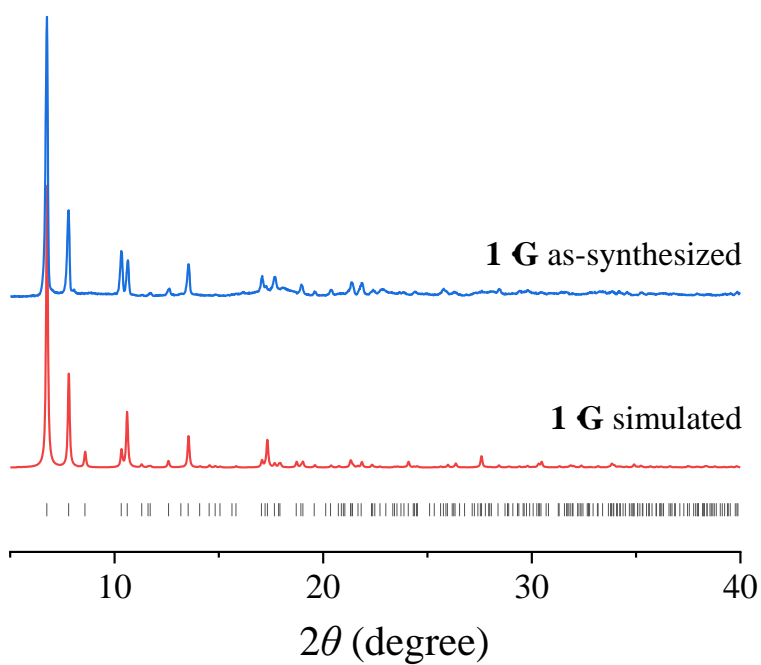


Fig. S2 PXRD patterns of 1 G.

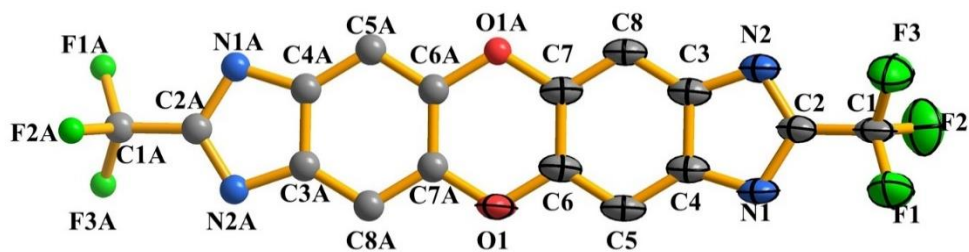


Fig. S3 The molecule unit of H₂fdbb ligand. Symmetry codes: A = $-x, 1-y, 1-z$. Atoms in the asymmetric unit are drawn with thermal ellipsoids.

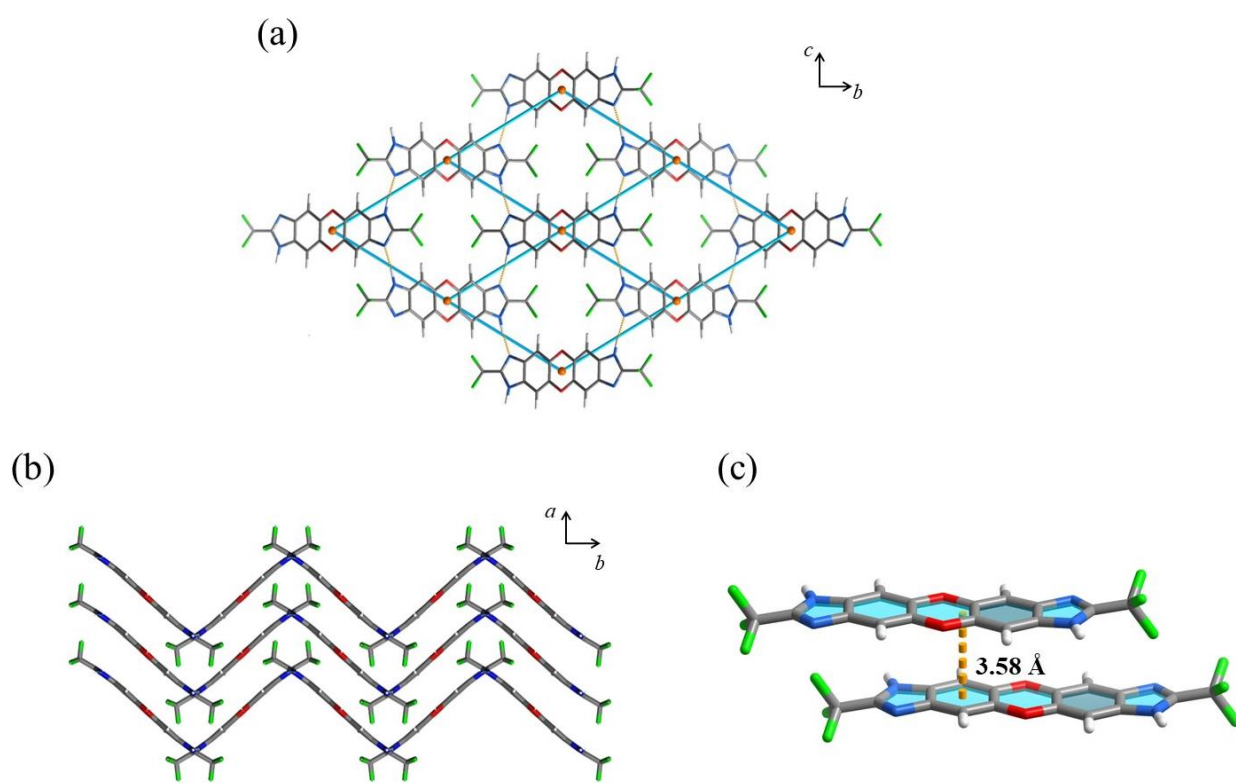


Fig. S4 (a) The topological representation of hydrogen-bonded network, (b) wavy layers, and (c) π - π stacking interaction of H₂fdbb ligands.

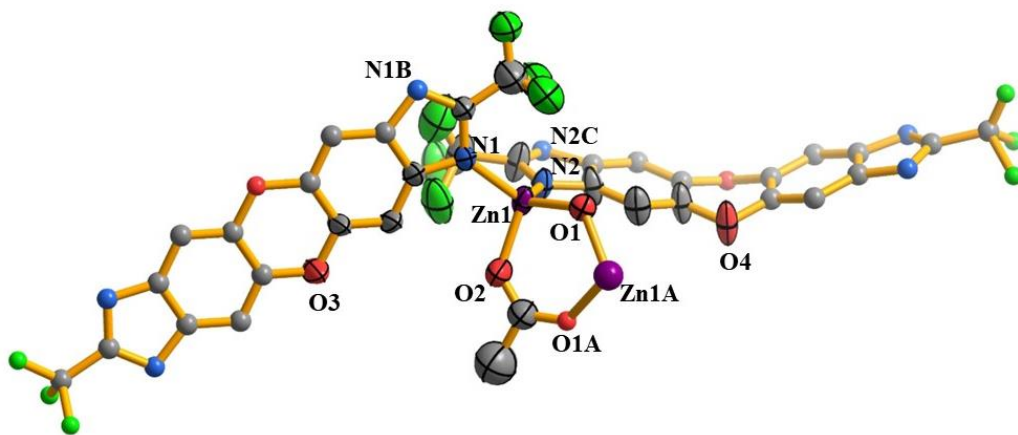


Fig. S5 The coordination environment of **1·G**. Symmetry codes: A = $-x+y, y, 1-z$; B = y, x, z ; C = $x, y, 1/2-z$. Atoms in the asymmetric unit are drawn with thermal ellipsoids (H atoms are omitted for clarify).

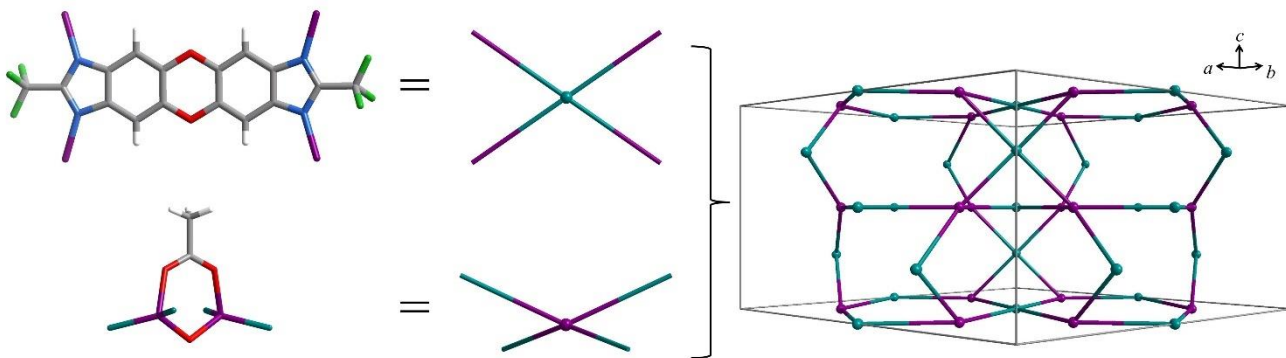


Fig. S6 The topological representation of **1**.

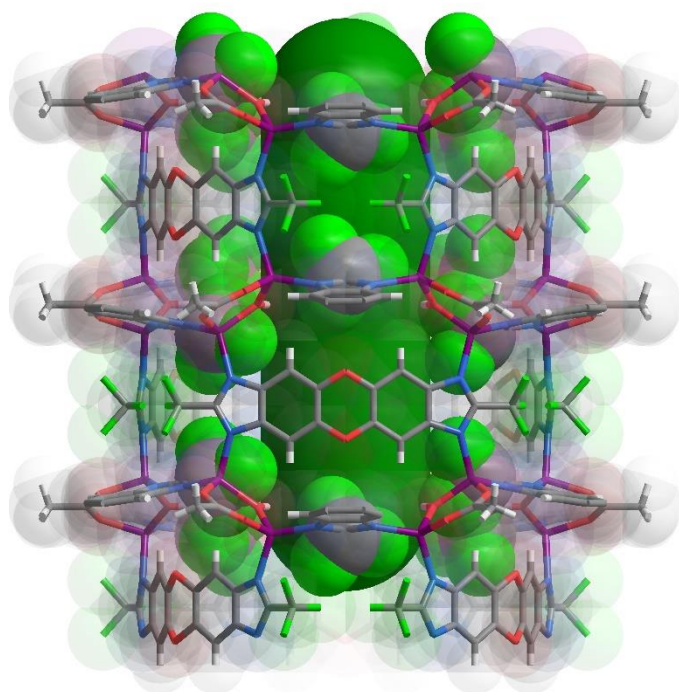
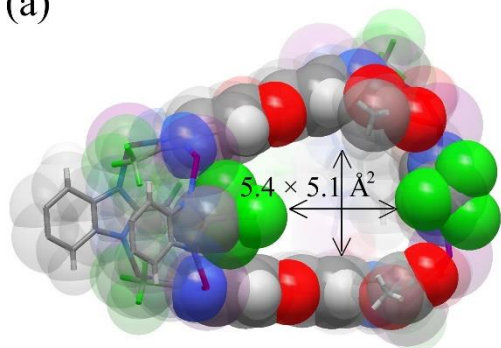


Fig. S7 The pore environment of 1D channel (green) in **1**.

(a)



(b)

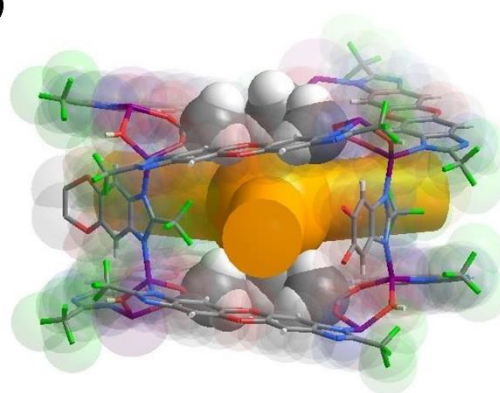


Fig. S8 The pore (a) aperture and (b) cavity environment of 2D channel (yellow) in **1**.

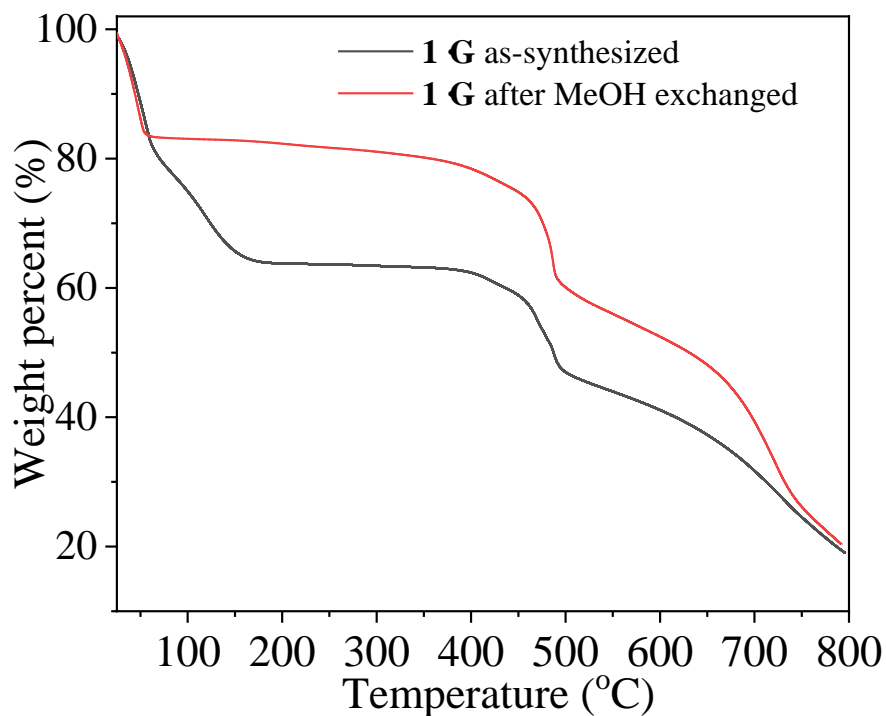


Fig. S9 TG curves of as-synthesized and MeOH-exchanged 1·G.

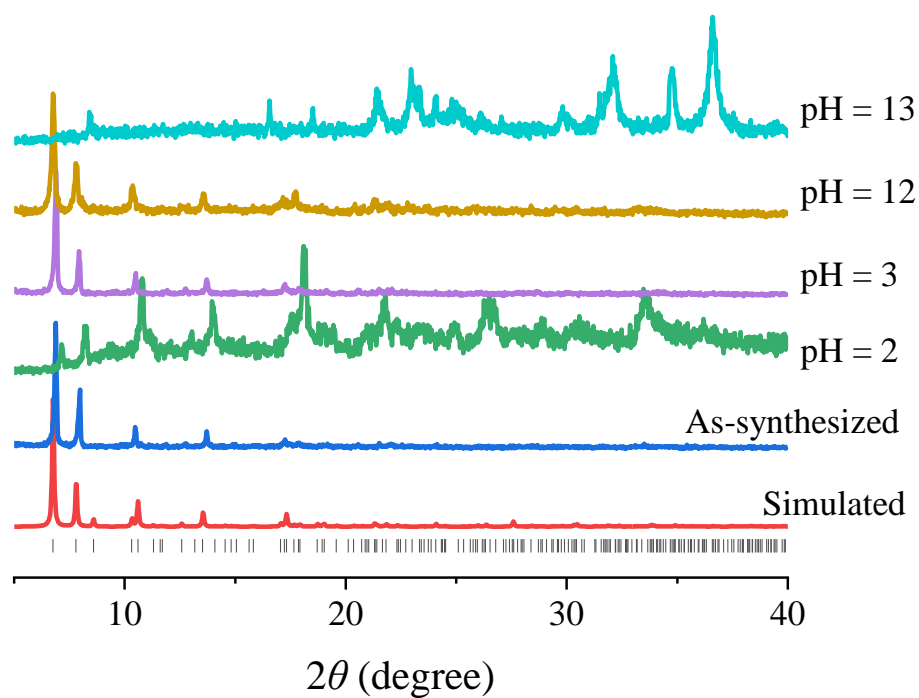


Fig. S10 PXRD patterns of 1 in the aqueous solution with different pH.

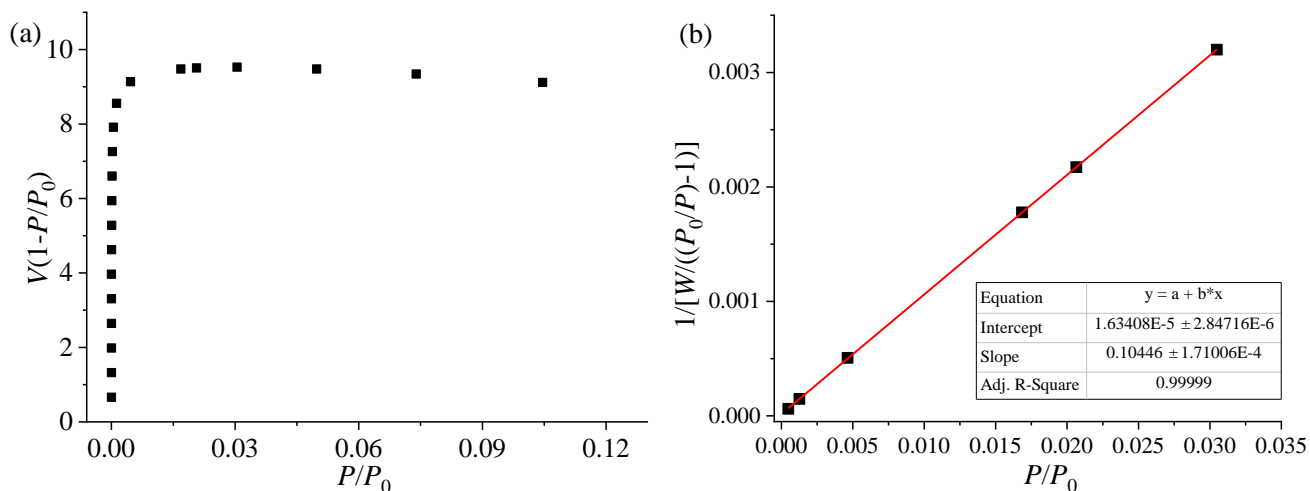


Fig. S11 (a) $V(1-P_0-P)$ vs P/P_0 curve and (b) plot of the linear region on the N_2 isotherm of **1** for the BET equation.

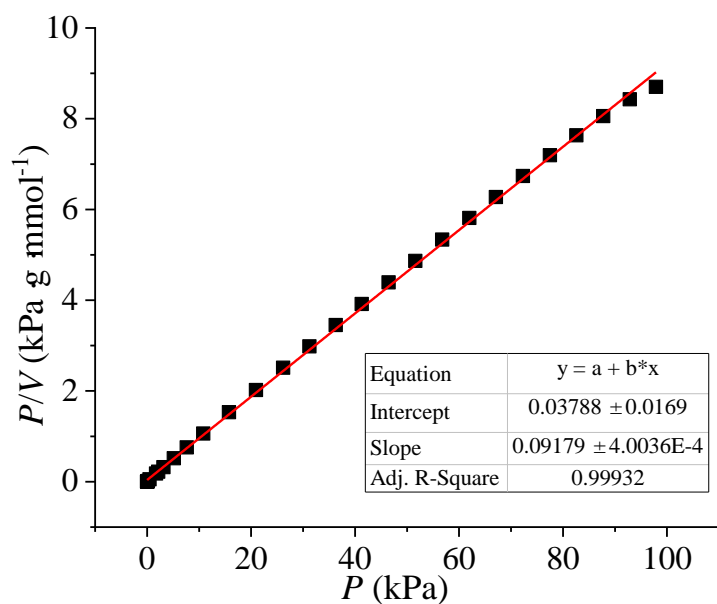


Fig. S12. Langmuir fitting of the adsorption isotherms for N_2 in **1**.

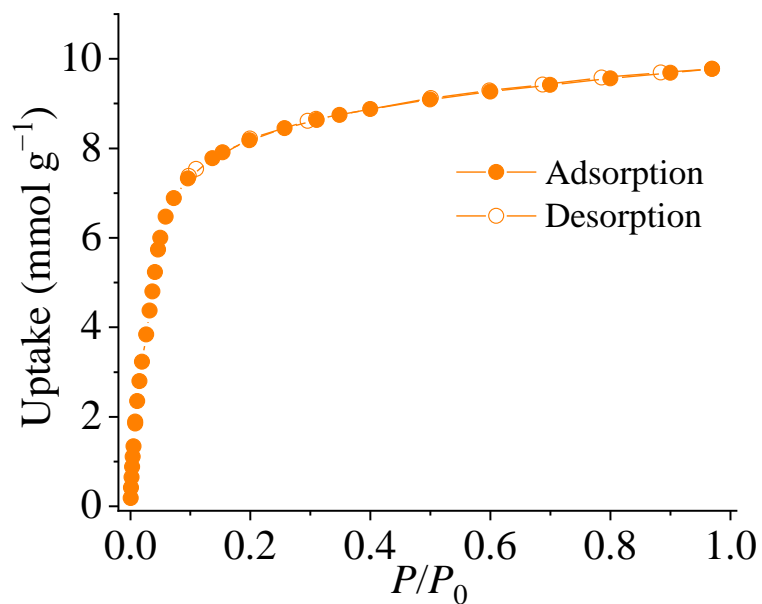


Fig. S13 CO₂ adsorption and desorption isotherms at 195 K.

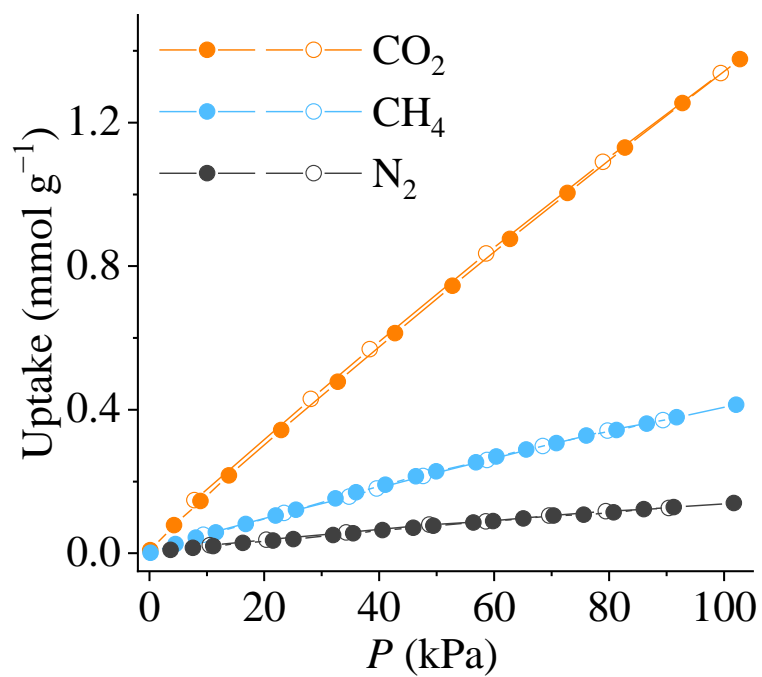


Fig. S14 N₂, CH₄ and CO₂ adsorption (solid) and desorption (open) isotherms at 298 K.

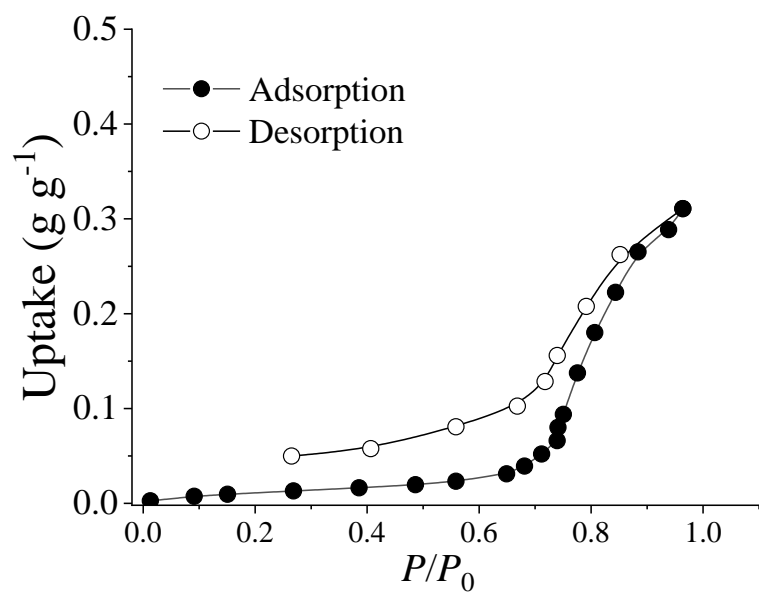


Fig. S15 Water vapor sorption isotherms of **1** at 298 K.

Table S1. Crystallographic data and structural refinement details.

Compound	H ₂ fddb	1·G
Formula	C ₁₆ H ₆ F ₆ N ₄ O ₂	Zn ₂ C ₁₈ N ₄ O ₅ F ₆ H ₈
Mass formula / (g mol ⁻¹)	400.24	605.09
Temperature / K	100(2)	250(2)
Crystal system	monolitic	hexagonal
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 6 ₃ / <i>mcm</i>
<i>a</i> / Å	4.7256(3)	26.1617(4)
<i>b</i> / Å	16.4363(11)	26.1617(4)
<i>c</i> / Å	9.9536(6)	16.6663(3)
<i>V</i> / Å ³	772.76(9)	9878.7(3)
<i>Z</i>	2	12
<i>D_c</i> / (g cm ⁻³)	1.72	1.219
<i>R</i> _{int}	0.0409	0.0351
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0788	0.0891
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^b	0.1939	0.2478
<i>R</i> ₁ (all data)	0.0864	0.1015
<i>wR</i> ₂ (all data)	0.1991	0.2666
GOF	1.045	1.025

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$