

Supporting Information

A new layers-stacked porous framework showing sorption selectivity for CO₂ and luminescence

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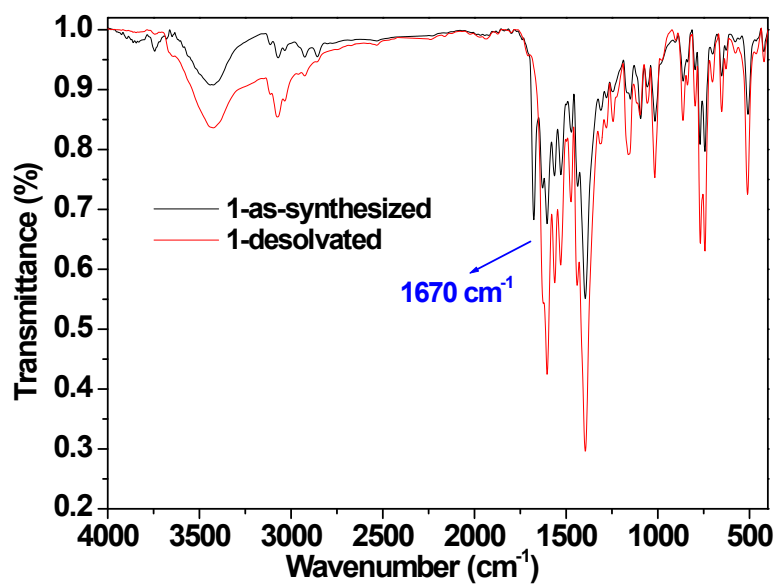


Fig. S1 IR spectra of as synthesized and desolvated samples of complex **1**.

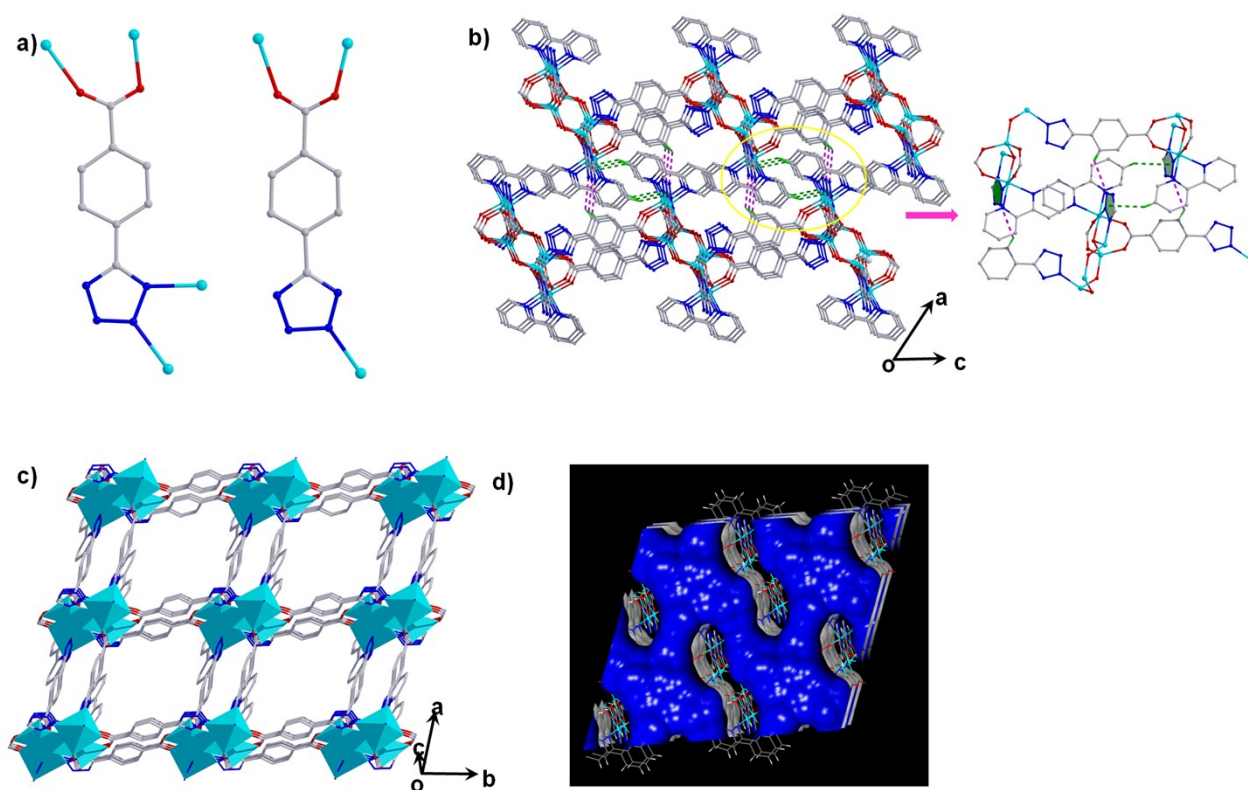


Fig. S2 a) Different coordination fashions of tzba^{2-} ligands in complex **1**. b) 3D supramolecular framework of complex **1**. c) 2D stacked layers of complex **1** viewed along the $(10\bar{1})$ direction. d) Cross-sectioned pores in complex **1**.

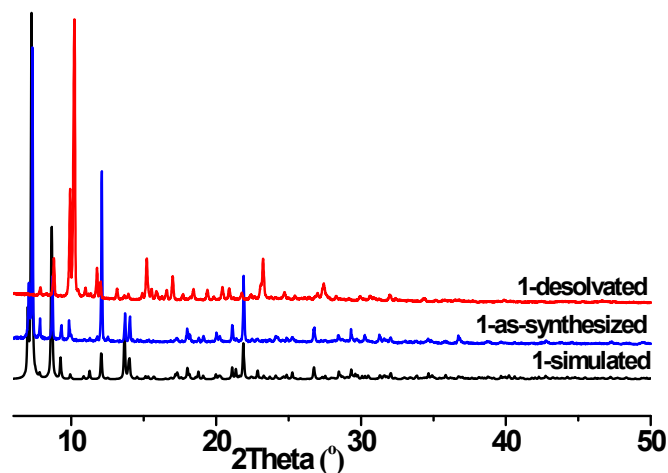


Fig. S3 PXRD patterns of complex **1**. Compared to the PXRD patterns between the as-synthesized sample and desolvated sample, some diffraction peaks strengthens or weakens, this is due to a slight deformation of the framework, for example, slipping occurs between the layers.

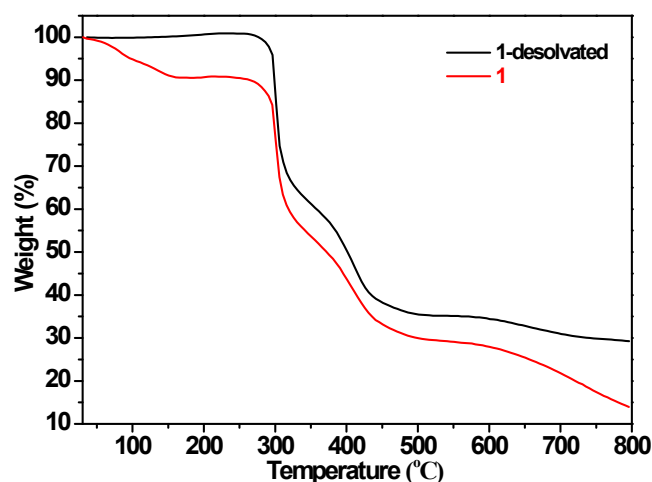


Fig. S4 TGA curves of as-synthesized and desolvated samples of complex **1**.

CO₂/CH₄ selectivity prediction via IAST

The experimental isotherm data for pure CO₂, and CH₄ were fitted using a dual Langmuir-Freundlich (L-F) model:

$$q = \frac{a_1 * b_1 * P^{c_1}}{1 + b_1 * P^{c_1}} + \frac{a_2 * b_2 * P^{c_2}}{1 + b_2 * P^{c_2}}$$

Where q and p are adsorbed amounts and the pressure of component i , respectively.

The adsorption selectivities for binary mixtures of CO₂/CH₄, defined by

$$S_{i/j} = \frac{x_i * y_j}{x_j / y_i}$$

were respectively calculated using the Ideal Adsorption Solution Theory (IAST) of Myers and Prausnitz. Where x_i is the mole fraction of component i in the adsorbed phase and y_i is the mole fraction of component i in the bulk.

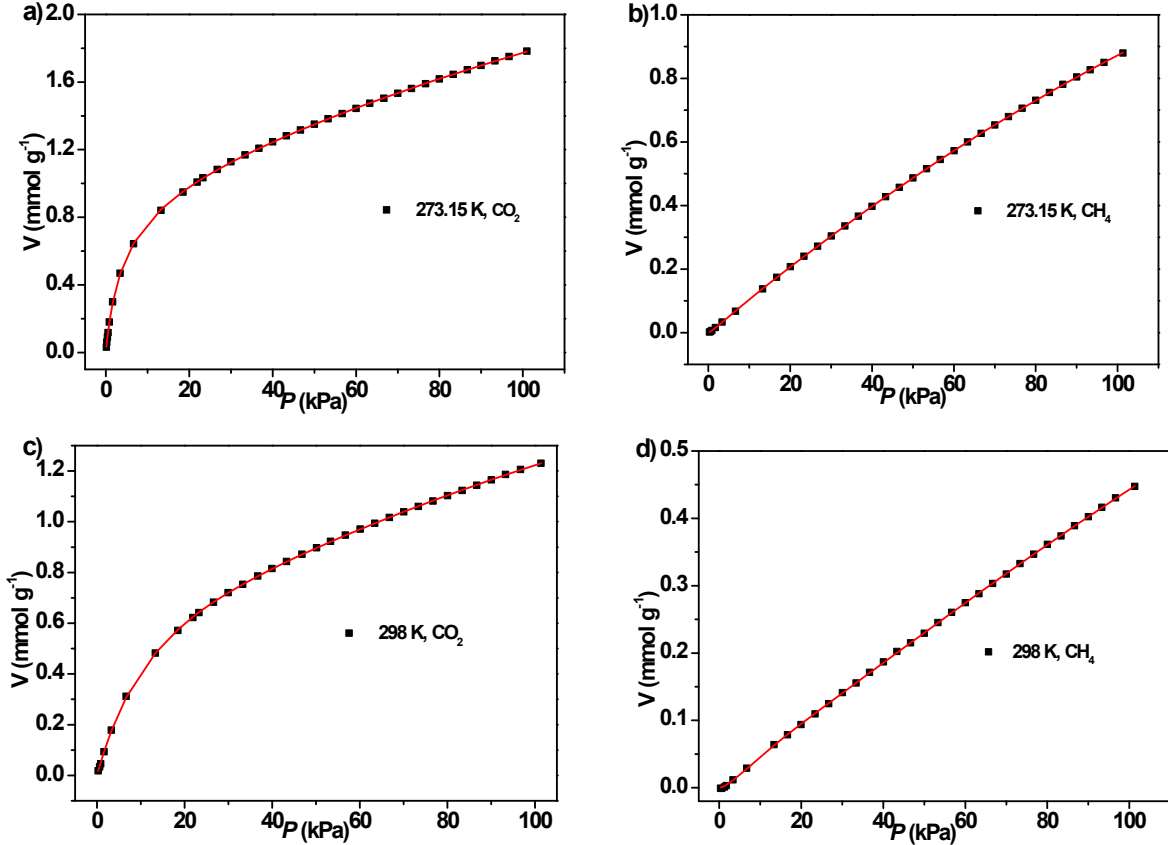


Fig. S5 (a) CO₂ adsorption isotherms of complex **1a** with fitted by dual L-F model: 273.15 K, $a_1 = 0.90366$, $b_1 = 0.26991$, $c_1 = 0.95533$, $a_2 = 4.79653$, $b_2 = 0.003$, $c_2 = 0.94606$, $\text{Chi}^2 = 6.7977\text{E-}6$, $R^2 = 0.99998$; (b) CH₄ adsorption isotherms of complex **1a** with fitting by L-F model: 273.15 K, $a_1 = 2.42095$, $b_1 = 0.0016$, $c_1 = 1.24142$, $a_2 = 0.08661$, $b_2 = 0.04774$, $c_2 = 1.2267$, $\text{Chi}^2 = 4.5509\text{E-}7$, $R^2 = 1$; (c) CO₂ adsorption isotherms of complex **1a** with fitted by dual L-F model: 298 K, $a_1 = 1.00121$, $b_1 = 0.06235$, $c_1 = 1.02864$, $a_2 = 0.97447$, $b_2 = 0.00006$, $c_2 = 1.99542$, $\text{Chi}^2 = 3.2931\text{E-}6$, $R^2 = 0.99998$; (d) CH₄ adsorption isotherms of complex **1a** with fitting by L-F model: 298 K, $a_1 = 0.05098$, $b_1 = 0.01549$, $c_1 = 1.69281$, $a_2 = 1.58611$, $b_2 = 0.00007$, $c_2 = 1.33575$, $\text{Chi}^2 = 9.5587\text{E-}7$, $R^2 = 0.99996$.

Calculation of sorption heat for CO₂ uptake using Virial 2 model

$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^m a_i N^i + \sum_{i=0}^n b_i N^i \quad Q_{\text{st}} = -R \sum_{i=0}^m a_i N^i$$

The above virial expression was used to fit the combined isotherm data for **1a** at 273.15 and 298 K, where P is the pressure, N is the adsorbed amount, T is the temperature, a_i and b_i 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.

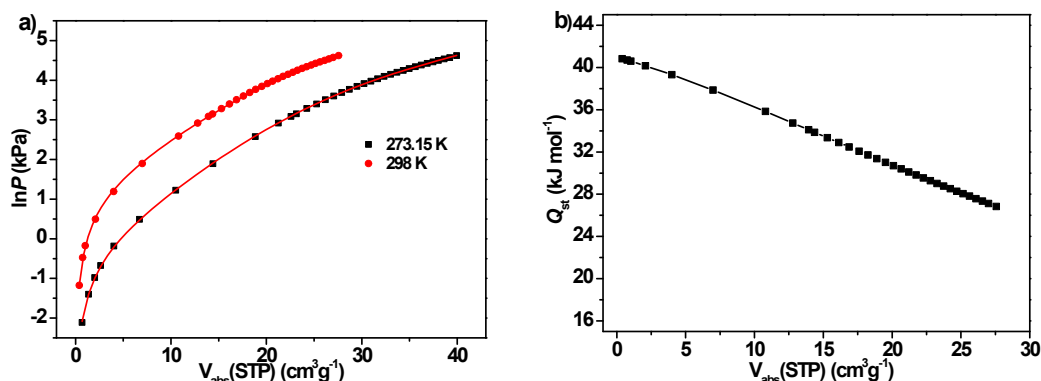


Fig. S6 a) CO₂ adsorption isotherms for complex **1a** fitted by Virial 2 model. Fitting results: $a_0 = -5051.67716$, $a_1 = 154.56192$, $a_2 = -11.91459$, $a_3 = 0.48905$, $a_4 = -0.00615$, $b_0 = 16.74849$, $b_1 = -0.54618$, $b_2 = 0.04899$, $b_3 = -0.00195$, $b_4 = 0.00002$, $\chi^2 = 0.00008$, $R^2 = 0.99998$. (b) Adsorption heat of CO₂ adsorption in complex **1a**.

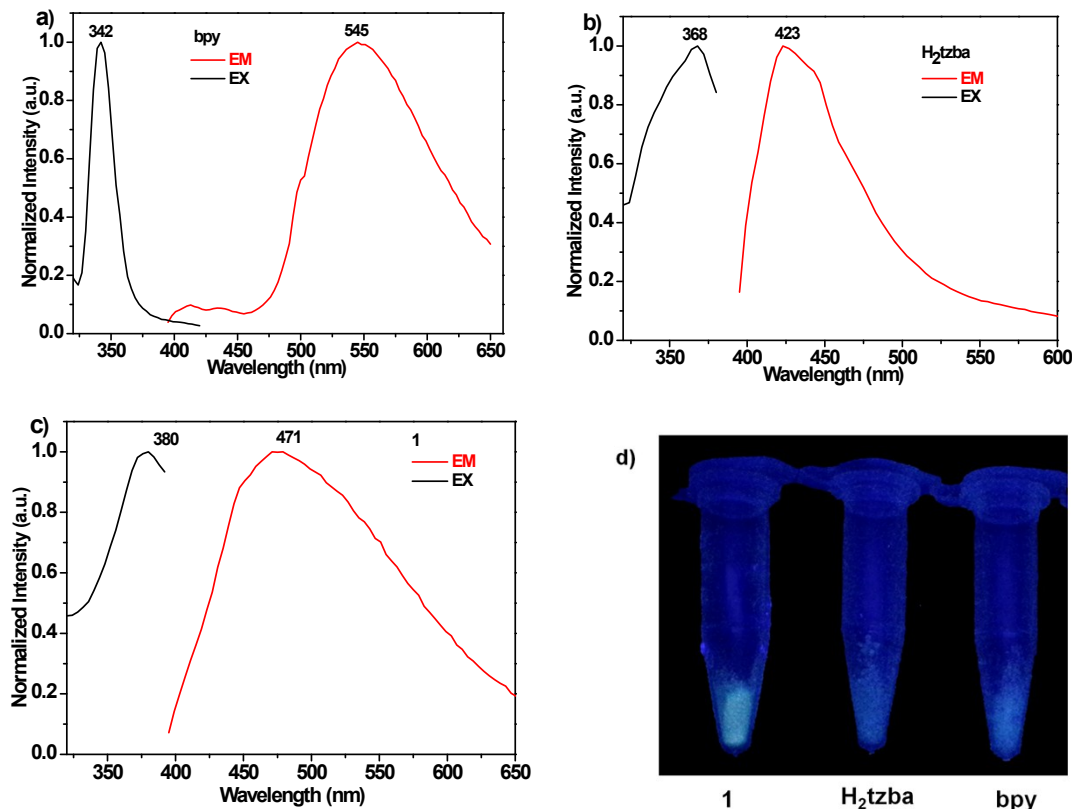


Fig. S7 Emission and excitation spectra of bpy (a), H₂tzba (b), complex **1** (c) and snapshots under UV light (365 nm) (d).

Table S1. Crystallographic data and structural refinements for complex **1**.

Complex	1
Chemical formula	C ₂₆ H ₁₉ N ₁₀ O ₆ Zn ₃
Formula weight	763.62
T (K)	296(2)
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	12.1420(15)
<i>b</i> (Å)	12.5243(16)
<i>c</i> (Å)	13.6323(17)
α (°)	78.056(2)
β (°)	69.652(2)
γ (°)	79.849(2)
<i>V</i> (Å ³)	1889.3(4)
<i>Z</i>	2
<i>D</i> _c (g cm ⁻³)	1.342
μ (mm ⁻¹)	1.935
Reflns collected/unique	10224/7202
GOF	1.071
<i>R</i> _{int}	0.0230
<i>R</i> ₁ ^a [<i>I</i> > 2 σ]	0.0792
<i>wR</i> ₂ ^b [<i>I</i> > 2 σ]	0.2439
^a <i>R</i> ₁ = $\Sigma F_o - F_c / \Sigma F_o $; ^b <i>wR</i> ₂ = $[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.	

Table S2. Selected bond lengths (Å) and bond angles (°) for complex **1**.

O(5)-Zn(1)	1.990(4)	O(3)-Zn(2)-O(5)	93.8(2)
Zn(1)-N(1)	2.014(5)	N(10)-Zn(2)-O(5)	87.9(2)
Zn(1)-N(7)#4	1.979(6)	O(3)-Zn(2)-O(2)#1	178.24(17)
O(1W)-Zn(1)	1.895(4)	N(10)-Zn(2)-O(2)#1	90.1(2)
O(3)-Zn(2)	2.099(5)	O(5)-Zn(2)-O(2)#1	88.7(2)
Zn(2)-N(10)	2.109(6)	O(3)-Zn(2)-N(2)	91.99(17)
Zn(2)-O(2)#1	2.141(4)	N(10)-Zn(2)-N(2)	90.3(2)
Zn(2)-N(2)	2.141(5)	O(5)-Zn(2)-N(2)	90.9(2)
Zn(2)-N(9)	2.143(6)	O(2)#1-Zn(2)-N(2)	88.47(17)
O(5)-Zn(2)	2.134(4)	O(3)-Zn(2)-N(9)	179.4(2)
O(5)-Zn(3)#1	1.991(4)	N(10)-Zn(2)-N(9)	168.4(2)
Zn(3)-O(1W)#3	1.888(4)	O(5)-Zn(2)-N(9)	77.3(2)
Zn(3)-O(4)#2	1.921(5)	O(2)#1-Zn(2)-N(9)	101.16(18)
O(1)-Zn(3)	1.980(5)	N(2)-Zn(2)-N(9)	82.4(2)
O(1W)-Zn(1)-N(7)#4	129.7(6)	O(1W)#3-Zn(3)-O(4)#2	97.1(2)
O(1W)-Zn(1)-O(5)	110.7(2)	O(1W)#3-Zn(3)-O(1)	114.2(3)
N(7)#4-Zn(1)-O(5)	108.77(18)	O(4)#2-Zn(3)-O(1)	108.3(2)
N(7)#4-Zn(1)-N(1)	110.4(2)	O(1W)#3-Zn(3)-O(5)#2	110.9(3)
O(5)-Zn(1)-N(1)	113.0(2)	O(4)#2-Zn(3)-O(5)#2	108.87(18)
O(1W)-Zn(1)-N(1)	113.2(2)	O(1)-Zn(3)-O(5)#2	102.3(2)
O(3)-Zn(2)-N(10)	100.36(18)		

Symmetry transformations used to generate equivalent atoms: #1 *x*, *y*-1, *z*; #2 *x*, *y*+1, *z*; #3 -*x*+1, -*y*+2, -*z*; #4 -*x*+1, -*y*+1, -*z*+1.

Table S3. Comparison of CO₂ adsorption amounts at 1 atm and 298 K of complex **1a** and selected other MOFs.

MOFs	Adsorption amount (wt%)	References
[Zn ₃ (μ ₃ -OH)(tzba) ₂ (bpy)(H ₂ O)]	5.4	This work
SNU-70	3.5	1
MOF-177	3.4	2
IRMOF-3	4.7	3
UMCM-1	3.8	3
IRMOF-9-I	3.1	4
UCY-1	4.3	5
MOF-5	4.5	5
JLU-Liu33	3.9	6
MOF-205-OBn	4.1	7

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Table S4. Comparison of CO₂ separation performances at 1 atm and 298 K of complex **1a** and selected other MOFs.

MOFs	Selectivity	References
UTSA-49	33.7	1
MPM-1-TIFSIX	20.3	2
[Eu(Hpzbc) ₂ (NO ₃)]	10.3 ^a /12.8 ^b	3

NJU-Bai33	8.9 ^b	4
[Zn₃(μ₃-OH)(tzba)₂(bpy)(H₂O)]	10.5^a/7.9^b	This work
SNU-151'	7.2 ^b	5
UiO-66	6.87 ^b	6
JLU-Liu6	6.8 ^a	7
Zr-UiO-67 _{AcOH}	6.8 ^a	8
Co ₉ -INA	6.2 ^b	9
[Zn(TPTA) _{0.5} (BIBP)]	6.0 ^b	10
[Cd(L4)]	5.1 ^a /6.0 ^b	11
ZIF-100	5.9 ^b	12
JLU-Liu38	5.4 ^a /5.6 ^b	13
JLU-Liu18	5.4 ^a / 4.5 ^b	14
Cu-MOF 1	4.9–5.4	15
JLU-5	4.3 ^a /4.6 ^b	16
NOTT-101	4.5 ^b	17
[Cu(INIA)]	4.3 ^b	18
dia-7i-1-Co	4.0 ^a /4.1 ^b	19
JLU-Liu37	3.8 ^a /3.8 ^b	13
Ni ₂ (bdc) ₂ (dabco)	3.3 ^a	20
DMOF	3.2 ^b	21
ZIF-25	2.53 ^b	22
MIL-53(Al)	2.3 ^b	23
Cu ₃ (btc) ₂	2.28 ^b	23
MOF-205	2.2 ^b	24
UMCM-1	1.82 ^b	23
ZIF-8	1.32 ^a	23

^aCO₂/CH₄ = 5:95; ^bCO₂/CH₄ = 50:50.

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GCMC Simulation Methodlody

Grand canonical Monte Carlo (GCMC) simulations were performed for the adsorption of CO₂ in complex by Material Studio.¹ The framework and CO₂ molecule were considered to be rigid. The partial charges for carbon and oxygen atoms of CO₂ molecules were 0.576e and -0.288e, respectively,² which are similar to the values in reports.³ The partial charges for atoms of complex were derived from QEq method and QEq_neutral1.0 parameter (Table S5). One unit cell was used during the simulations. The interaction energies between CO₂ and framework were computed through the Coulomb and Lennard-Jones 6-12 (LJ) potentials. All parameters for CO₂ molecule and atoms of complex were modeled with the universal forcefield (UFF) embedded in the MS modeling package. A cutoff distance of 12.5 Å was used for LJ interactions, and the Coulombic interactions were calculated by using Ewald summation. For each run, the 5×10^6 maximum loading steps, 1×10^7 production steps, automated temperature control in the annealing cycles and 40 temperature cycles were employed.

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Table S5. The atomic partial charges (e) in complex **1a**.

Zn1	0.320281	O3	-0.470761	C14	-0.126622	H3	0.153598
Zn2	0.350049	O4	-0.465163	C15	-0.124026	H4	0.155201
Zn3	0.368399	O5	-0.498917	C16	0.680672	H6	0.160405
N1	-0.196104	C1	0.287428	C17	0.0414661	H7	0.170151
N2	-0.0144975	C2	0.00249194	C18	-0.119171	H11	0.138008
N3	-0.150917	C3	-0.139143	C19	-0.143366	H12	0.148249
N4	-0.262908	C4	-0.135447	C20	-0.158148	H14	0.151071
N5	-0.279908	C5	0.0263794	C21	0.183690	H15	0.160519
N6	-0.140398	C6	-0.137133	C22	0.188322	H17	0.157880

N7	0.00160322	C7	-0.141677	C23	-0.162146	H18	0.163036
N8	-0.246201	C8	0.649530	C24	-0.146161	H19	0.152204
N9	-0.262053	C9	0.336823	C25	-0.137811	H20	0.106017
N10	-0.225937	C10	0.0187771	C26	0.0559297	H23	0.103053
O1	-0.489926	C11	-0.140015	H1W A	0.327581	H24	0.138982
O1W	-0.782179	C12	-0.138521	H1WB	0.311685	H25	0.160600
O2	-0.465831	C13	0.0164634	H5A	0.367678	H26	0.146861