Supporting Information

An ionic porous coordination framework exhibiting high CO₂ affinity and CO₂/CH₄ selectivity

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Experiment Section

Materials and Methods. Commercially available reagents were used as received without further purification. H₂ppt (3-(2-phenol)-5-(4-pyridyl)-1,2,4-triazole) was prepared according to a reported method.¹ Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 elemental analyzer. The FT-IR (KBr pellet) spectra were recorded from KBr pellets in the range of 400-4000 cm⁻¹ on a Bruker TENSOR 27 FT-IR spectrometer. Thermal gravimetric analysis was performed under N₂ using a TA TGA Q50 system. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance diffractometer (Cu K α). Gas sorption isotherms were measured on a volumetric adsorption apparatus (Bel-max).

Synthesis of (Me₂NH₂)(Hdmf)[Co₃Cl₄(ppt)₂]·2H₂O·dmf (1·2H₂O·dmf). A mixture of Hppt (0.060 g, 0.25 mmol), CoCl₂·6H₂O (0.090 g, 0.375 mmol), EtOH (6 mL) and dmf (0.5 mL) was sealed in a 15-mL Teflon-lined reactor and heated at 160 °C for 3 days, and then cooled by 5 °C/hr to room temperature to give blue crystals of 1·2H₂O·dmf (yield: 90 mg, 71%). Anal. calcd (%) for C_{34}H_{43}Cl_4Co_3N_{11}O_6: C, 40.02; H, 4.25; N, 15.10. Found: C, 39.98; H, 4.22; N, 15.09. IR: 3410m, 3062m, 1672m, 1616s, 1568m, 1502m, 1471s, 1423s, 1290m, 1265m, 1236s, 1167w, 1120m, 1053w, 1033w, 1012m, 962w, 846m, 756m, 723m, 667w, 625w, 588w, 550w, 478w, 455w cm⁻¹.

Crystal Structure Determination. Intensity data were collected on a Bruker Apex CCD area-detector diffractometer (Mo K α). Absorption corrections were applied by using the multi-scan program SADABS.² The structures were solved with direct method and refined with a full-matrix least squares technique with the SHELXTL program package.³ Anisotropic thermal parameters were applied to all non-hydrogen atoms except the guest molecules. The organic hydrogen atoms were generated geometrically. The empirical formula of 1·g was estimated by elemental and thermal gravimetric analyses. TGA of 1·g exhibits a weight loss of 10.8% from 302 to 573 K corresponding to one dmf and two H₂O molecules per (Me₂NH₂)(Hdmf)[Co₃Cl₄(ppt)₂] unit (calculated 10.7%). The dmf guest molecules in the channel were refined as water molecules due to the severe disorder. The guest-free single crystal was prepared by heating a single-crystal of 1·g at 453 K for 4 hrs. Single-crystal X-ray diffraction intensity data of the desolvated structure were then collected in situ at 293 and 120 K under a dry dinitrogen atmosphere. On the other hand, the CO₂-loaded single crystal was prepared by sealing CO₂ (about 1 atm) inside the glass capillary at 273 K, in which the single crystal of activated 1 was fixed.

Enthalpies of Adsorption

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

A virial-type expression of the above form was used to fit the combined isotherm data for 1 at 273 and 298 K, where P is the pressure described in Pa, N is the adsorbed amount in mmol/g, T is the temperature in K, 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.

Complex	1 3H ₂ O	1	1	1 CO ₂
Formula	C ₃₁ H ₃₈ Cl ₄ Co ₃ N ₁₀ O ₆	C ₃₁ H ₃₂ Cl ₄ Co ₃ N ₁₀ O ₃	C ₃₁ H ₃₂ Cl ₄ Co ₃ N ₁₀ O ₃	$C_{32}H_{32}Cl_4Co_3N_{10}O_5$
Formula weight	965.30	911.26	911.26	955.27
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	<i>C</i> 2/ <i>c</i>	C2/c	<i>C</i> 2/ <i>c</i>
a/Å	20.4490(17)	20.545(5)	20.787(2)	20.471(2)
b/Å	15.5529(13)	15.456(4)	15.4366(18)	15.3812(17)
c/Å	13.6581(11)	13.721(4)	13.7906(15)	13.8175(16)
β/Å	90.197(2)	90.865(4)	90.899(2)	90.271(2)
V/Å ³	4343.8(6)	4356.5(19)	4424.6(9)	4350.6(9)
Ζ	4	4	4	4
$D_{\rm c}/{\rm g~cm^{-3}}$	1.476	1.389	1.368	1.458
μ /mm ⁻¹	1.429	1.415	1.393	1.424
temperature / K	120(2)	120(2)	293(2)	120(2)
reflns coll.	7790	15296	10532	9080
unique reflns	3721	3852	3737	3838
$R_{\rm int}$	0.0360	0.0610	0.0652	0.0535
$R_1 \left[I > 2 \ \sigma(I) \right]^{[a]}$	0.0621	0.0614	0.0715	0.0667
$wR_2 [I > 2 \sigma(I)]^{[b]}$	0.1786	0.1641	0.1834	0.1827
R_1 (all data)	0.0830	0.0905	0.1241	0.0996,
wR_2 (all data)	0.2039	0.1911	0.2219	0.2100
GOF	1.007	1.004	1.004	1.008

Table S1. Crystallographic data.

 $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|. \ wR_2 = \left[\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2\right]^{1/2}.$



Fig. S1 Coordination environments of cobalt, chloride ions and ppt²⁻ ligands. Hydrogen atoms are omitted for clarity.



Fig. S2 Thermogravimetric analysis (TGA) of $1.2H_2O.dmf$ and 1 after being activated at 200 $^{\circ}C$ under N_2 .

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Fig. S3 Variable temperature PXRD patterns under N_2 for 1.



Fig. S4 $N_2(77 \text{ K})$ and CO_2 (195 K) sorption isotherms for 1.



Fig. S5 CO_2 (left) and CH_4 (right) adsorption isotherms for 1 with fitting by virial method.

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Fig. S6 CO_2 (left) and CH_4 (right) adsorption isotherms for **1** with fitting by Langmuir-Freundlich method.



Fig. S7 Mixture isotherms and selectivity of CO_2 over CH_4 in **1** predicted by IAST for $y_{CH_4} = 0.95$ at 298 K.

- 1 E. J. Browne, Aust. J. Chem., 1975, 28, 2543.
- 2 G. M. Sheldrick. *SADABS 2.05*. University Göttingen: Göttingen, Germany, 2002.
- 3 SHELXTL 6.12. Bruker Analytical Instrumentation: Madison, WI, 2000.