
Electronic Supplementary Information for

A Co^{II}-based metal–organic framework based on $[Co_6(\mu_3\text{-}OH)_4]$ units exhibiting selective sorption of C_2H_2 over CO_2 and CH_4

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Experimental Section

Materials and Methods. All the chemicals purchased were of reagent grade and used without further purification. Analyses for C, H, and N were carried out on a Perkin-Elmer 240 CHN elemental analyzer. IR spectra were recorded in 4000–400 cm^{-1} on a Tensor 27 OPUS (Bruker) FT-IR spectrometer with KBr pellets. Thermogravimetric (TG) analysis experiments were carried out on a Perkin-Elmer Diamond SII thermal analyzer from room temperature to 800 °C under N_2 atmosphere at a heating rate of 10 °C/min. The powder X-ray diffraction patterns (PXRD) of **1** and **1a** was recorded on a Rigaku D/Max-2500 diffractometer, operated at 40 kV and 100 mA, using a Cu-target tube and a graphite monochromator. Simulation of the PXRD spectra was carried out by the single-crystal data and diffraction-crystal module of the *Mercury* (Hg) program available free of charge *via* the Internet at *http://www.iucr.org*. The gas sorption isotherms were collected on a Micromeritics 3Flex surface area and pore size analyzer under ultrahigh vacuum in a clean system, with a diaphragm and turbo pumping system. Ultrahigh-purity-grade (> 99.999%) N_2, C_2H_2, CO_2, H_2, and CH_4 gases were applied in all measurements. The experimental temperatures were maintained by liquid nitrogen (77 K) and temperature-programmed water bath (273 and 293 K).

Synthesis of $\{[Co_6(\mu_3\text{-}OH)_4(Ina)_8](H_2O)_{10}(DMA)_2\}_n$ (1). A mixture of HIna (9.5 mg, 0.05 mmol), $CoCl_2\cdot 6H_2O$ (24 mg, 0.1 mmol) was dissolved in DMA (2 mL) in a screw-capped vial. After addition of six drops of HBF_4 (37%, aq), the vial was heated at 120 °C for 48 h under autogenous pressure. Red crystals were obtained after filtration, washed with DMA. Yield: 52% based on the HIna ligand. IR (KBr dicks, selected bands, cm^{-1}): 3397w, 1665s, 1628s, 1553s, 1407s, 1232m, 1059m, 1014m, 776s, 688s. Elemental analysis found (calcd.) for $C_{38}H_{74}Co_3N_{16}O_{23}$: C, 35.19 (35.11); H, 5.99 (5.74); N, 17.95 (17.24).

X-ray Single Crystal Analysis. Single-crystal X-ray diffraction data were collected on an Agilent

Technologies SuperNova Diffractometer equipped with graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å). The structures of **1** were solved by SHELXS (direct methods) and refined by SHELXL (full matrix least-squares techniques) in the Olex2 package.[1]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. For the highly disordered nature of the solvents, they could not be finely made out in the refinement, so the SQUEEZE routine of PLATON was applied to remove the diffraction contributed from the highly disordered guest molecules.[2] The chemical formula of **1** was determined by the combination of the crystal data, TGA, and elemental analysis.

GCMC simulation methodology. Grand canonical Monte Carlo (GCMC) simulations were performed for the adsorption of N_2, C_2H_2 and CO_2 in **1a** by the sorption module of Material Studio. The host framework and gas molecules were considered to be rigid. The partial charges for gas molecules were derived from ESP charges via DMOL3 module. The partial charges for atoms were derived from QEq method and QEq_neutral1.0 parameter. 2*2*2 unit cells were used during the simulations. All the parameters for gas molecules and atoms of **1** were modeled with the universal force field (UFF) embedded in the MS modeling package. The N_2 sorption isotherm at 77 K was simulated employing the Adsorption isotherm task. Equilibration steps were set to 2500000, production steps were set to 100000, fugacity steps were set to 40, and the sorption isotherm was set to logarithmic. The snapshots and the average loading of the C_2H_2 and CO_2 molecules at 298 K and 1 bar were derived from the Fix Pressure task. The equilibration steps and the production steps were all set to 20000000, the electrostatic interactions and the van der Waals interactions were handled using the Ewald and Atom based summation method, respectively.

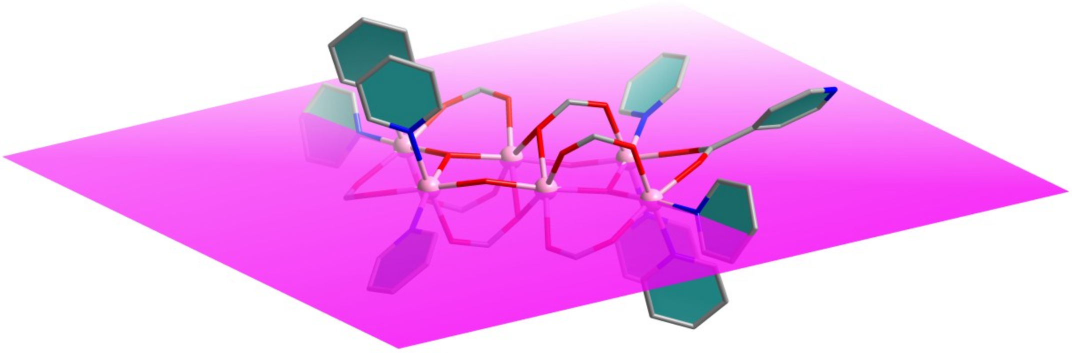


Fig. S1 View of the planar Co_6 cluster in **1**.

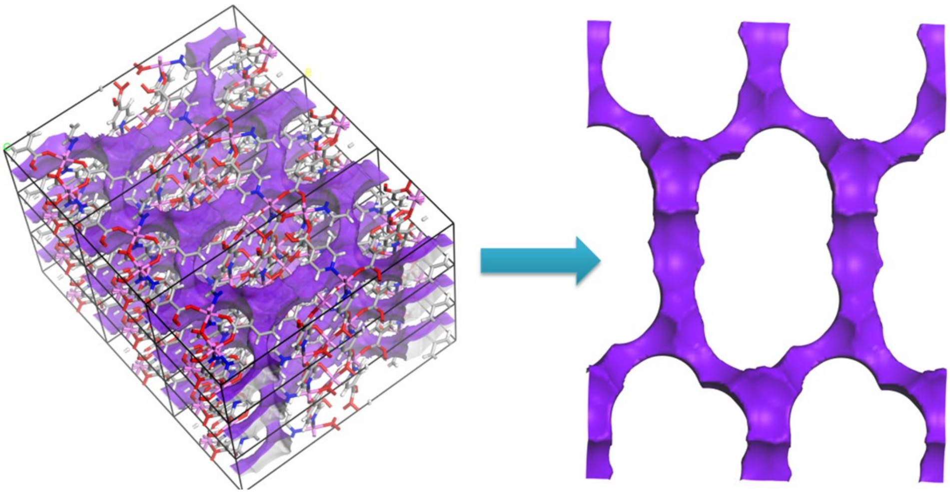


Fig S2 The representation for the 2D honeycomb-like cavities in **1**.

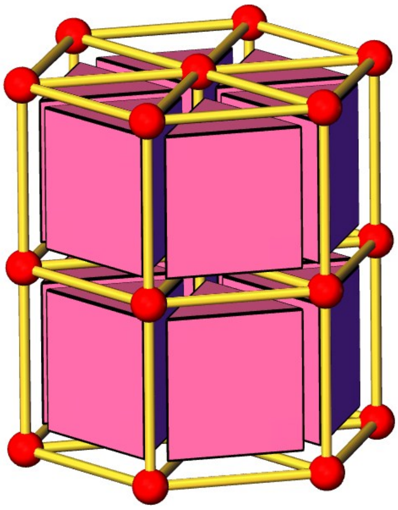


Fig S3 Natural tiling of **1**.

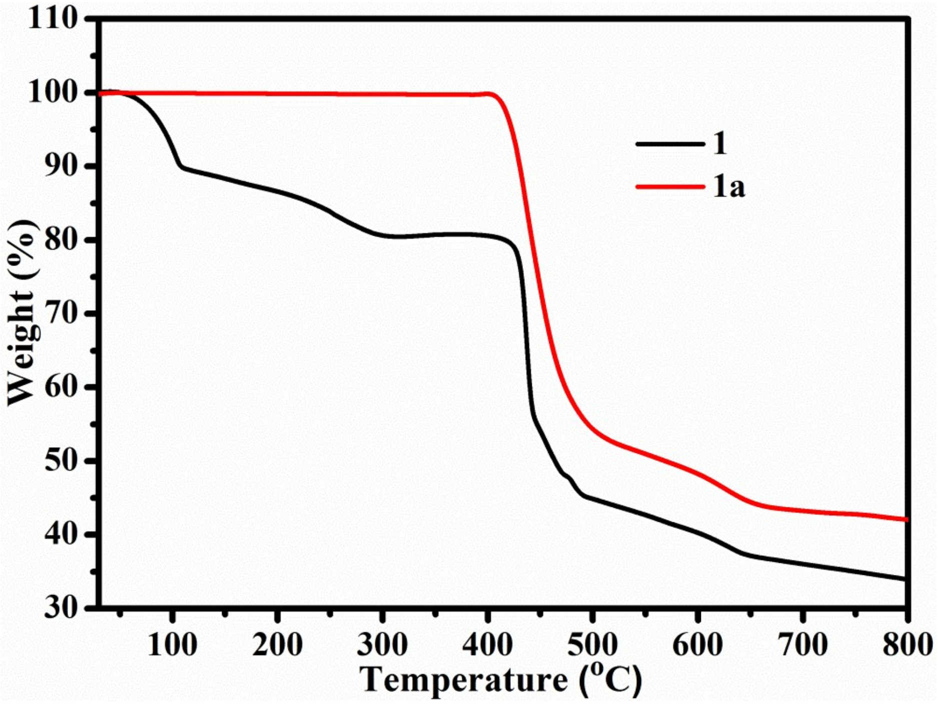


Fig S4 TGA curves for **1** and **1a**.

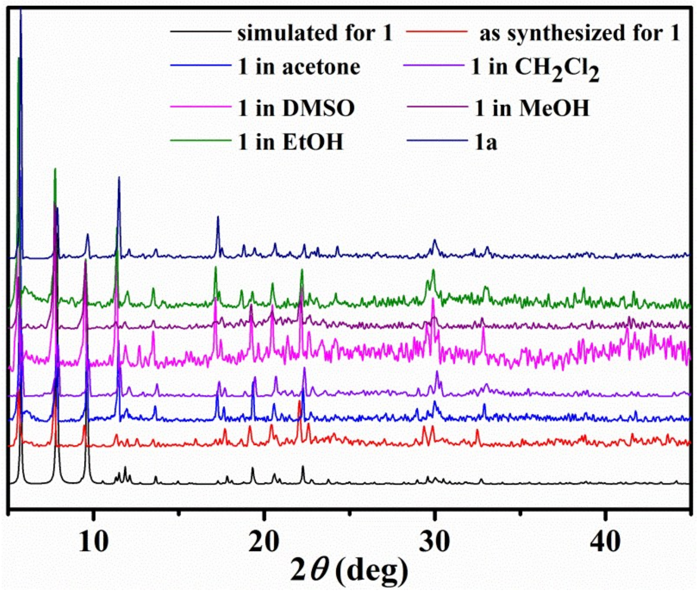


Fig S5 PXRD patterns of **1** in different solvents.

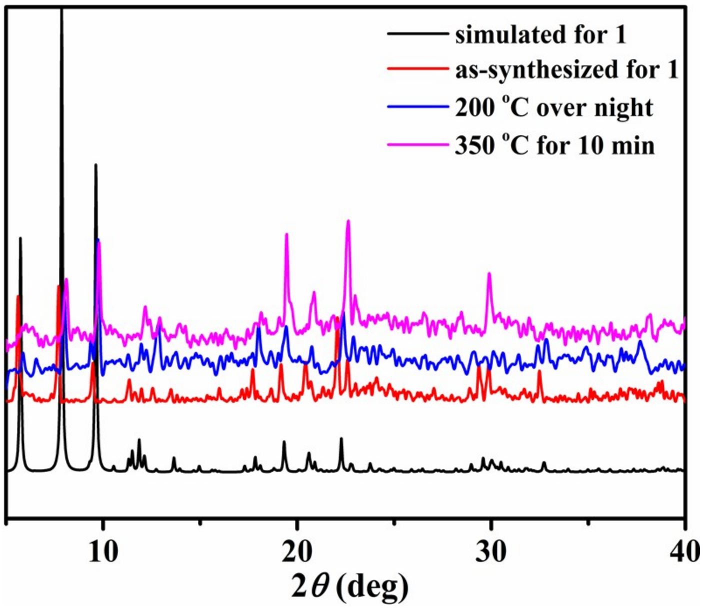


Fig S6 PXRD patterns of **1** upon different heat treatments.

Analysis of H_2 Adsorption Isotherms:

The carbon dioxide adsorption isotherms of **1a** are fitted to the Langmuir-Freundlich according to the literature. An accurate fit was obtained by using this equation which results a precise prediction over the quantity of gas adsorbed at saturation. A variant of the Clausius-Clapeyron equation was used to calculate enthalpy of adsorption.

$$ln\frac{P_1}{P_2} = \Delta H_{ads} \times \frac{T_2 - T_1}{R \times T_2 \times T_1} \qquad \text{(I)}$$

where T_1 and T_2 are the two isotherm temperatures (273 and 298 K), P_1 and P_2 are pressures at T_1 and T_2, respectively, for a given uptake, and R is the universal gas constant (R = 8.3147 J / (K·mol)). Pressure as a function of the amount of gas adsorbed was determined using the Langmuir-Freundlich fit for the isotherms.

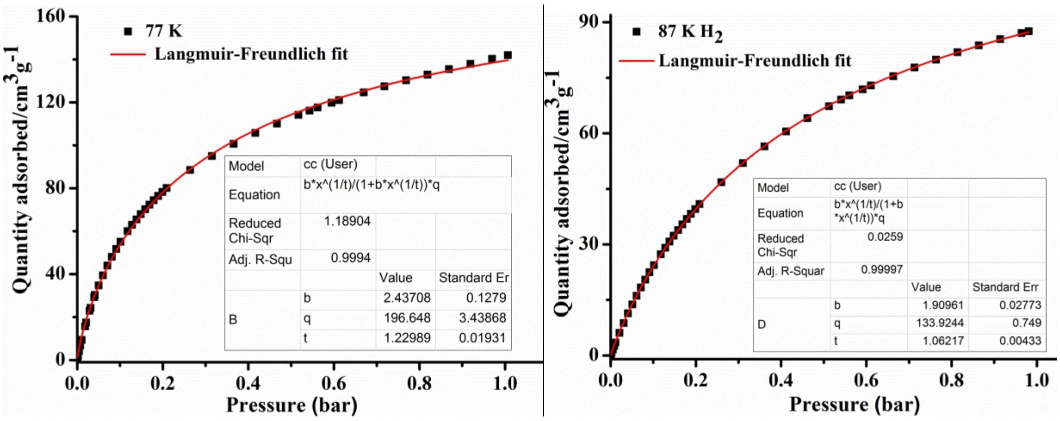
$$\frac{q_i}{q} = \frac{bp^{(1/t)}}{1 + bp^{(1/t)}} \qquad \text{(II)}$$

Where q_i = the amount adsorbed, q = the amount adsorbed at saturation, p = pressure, b and t = constants. The equation (II) rearranges to:

$$p = \left(\frac{\frac{q_i}{q}}{b - b\frac{q_i}{q}}\right)^t \quad (III)$$

$$\Delta H_{ads} = \frac{RT_1T_2}{T_2 - T_1} \times ln(\frac{P_1}{P_2}) \qquad \text{(IV)}$$

(IV)



(a) **(b)**

Fig S7 The Langmuir-Freundlich fits for H_2 sorption isotherms of **1** at 77 K (a) and 87 K (b).

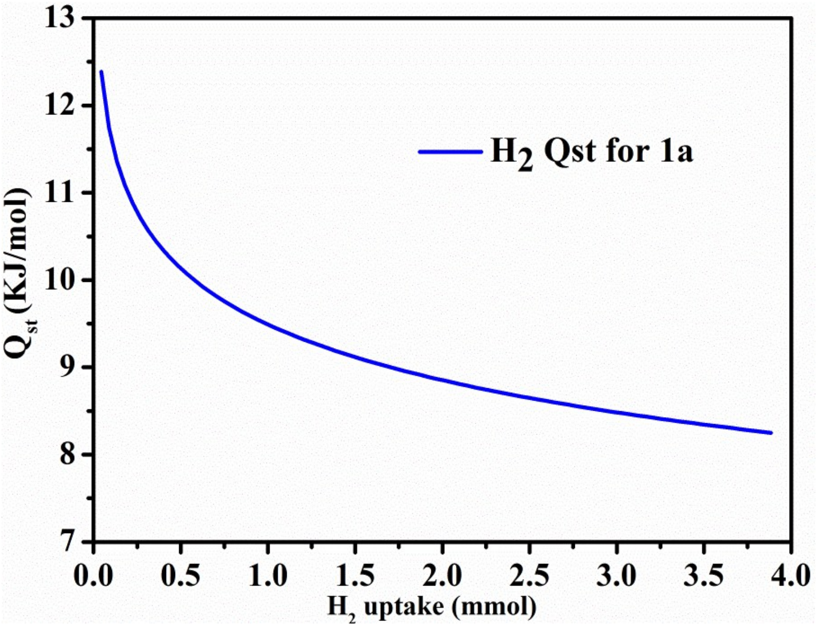
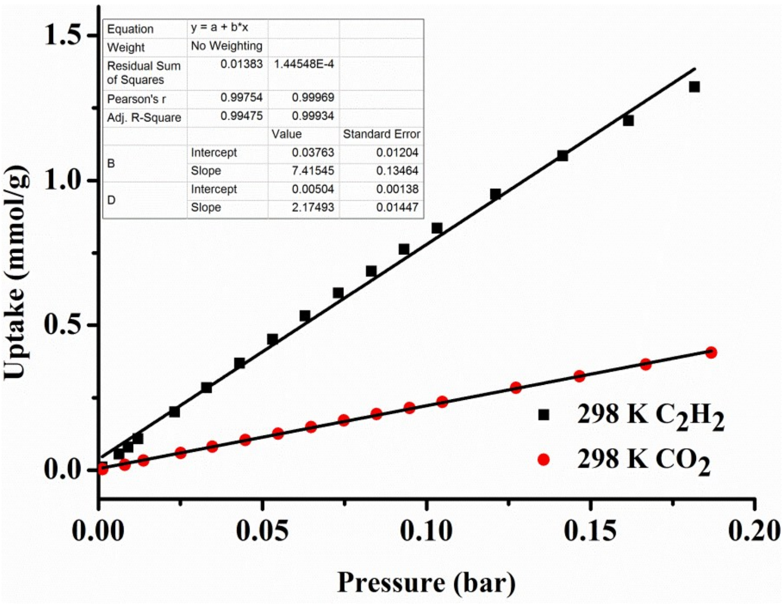
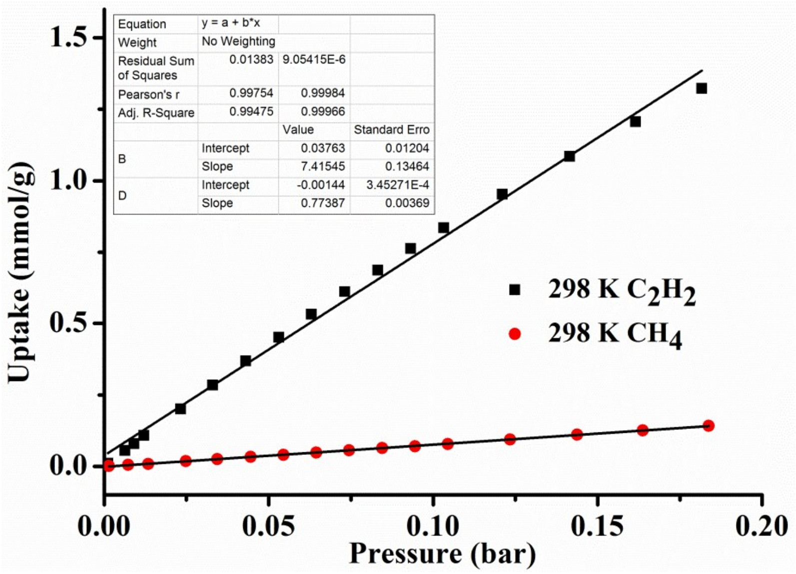


Fig S8 The isosteric heats of adsorption of H_2 for **1a**.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.01383	1.44548E-4	
Pearson's r	0.99754	0.99969	
Adj. R-Square	0.99475	0.99934	
		Value	Standard Error
B	Intercept	0.03763	0.01204
	Slope	7.41545	0.13464
D	Intercept	0.00504	0.00138
	Slope	2.17493	0.01447

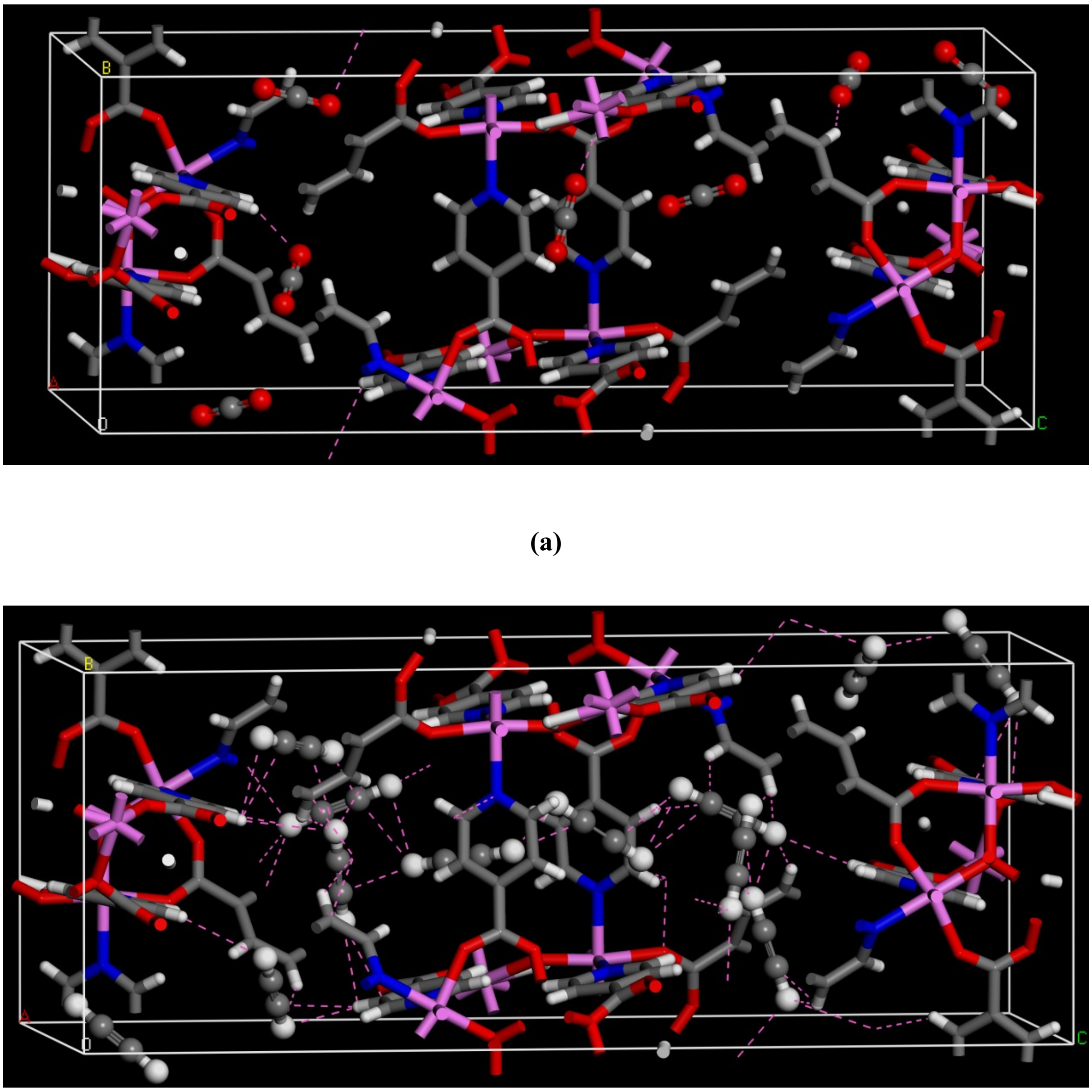
(a)



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.01383	9.05415E-6	
Pearson's r	0.99754	0.99984	
Adj. R-Square	0.99475	0.99966	
		Value	Standard Erro
B	Intercept	0.03763	0.01204
	Slope	7.41545	0.13464
D	Intercept	-0.00144	3.45271E-4
	Slope	0.77387	0.00369

(b)

Fig S9 Comparison of linear fitting of the low-pressure region of sorption isotherms measured at 298 K: (a) for C_2H_2 and CO_2 and (b) for C_2H_2 and CH_4.



(a)

(b)

Fig S10 Views of the close contacts between the framework **1a** and different gas molecules from the GCMC simulations, (a) for CO_2 and (b) for C_2H_2 (contact distance < 3.0 Å).

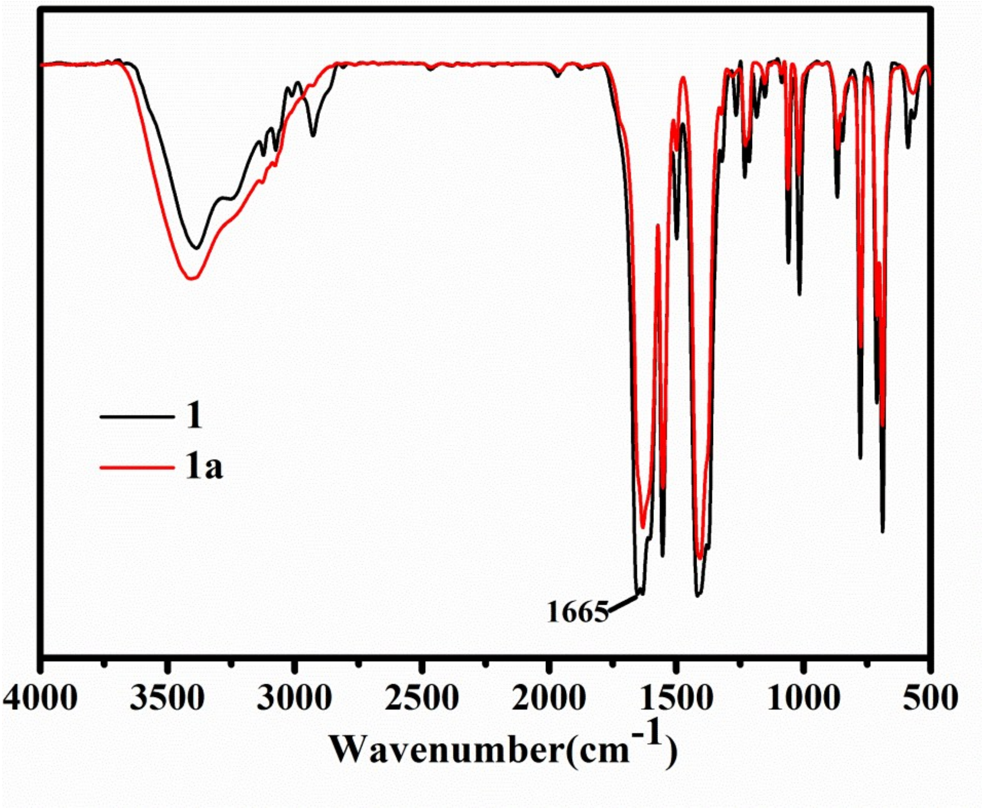


Fig S11 IR spectra for **1** and **1a** (the absence of peak at 1665 cm^{-1} for **1a** indicates the complete removal of DMA molecules).

Table S1 Crystal data and structure refinement for **1**.

Empirical formula	$C_{24}H_{18}Co_3N_4O_{10}$
Formula weight	699.21
Temperature/K	285.9(6)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.2607(2)
b/Å	12.0677(3)
c/Å	31.0183(7)
α/°	90
β/°	97.604(3)
γ/°	90
Volume/Å^3	3435.98(15)
Z	4
ρ_{calc}g/cm^3	1.352
μ/mm^{-1}	1.481
Radiation	MoKα
2Θ range for data collection/	5.57 to 49.998
Reflections collected	29718
Independent reflections	6048 [R_{int} = 0.0680, R_{sigma} = 0.0560]
Data/restraints/parameters	6048/120/407
Goodness-of-fit on F^2	1.094
Final R indexes [I>=2σ (I)]	R_1 = 0.0582, wR_2 = 0.1905
Final R indexes [all data]	R_1 = 0.0836, wR_2 = 0.2157
Largest diff. peak/hole / e Å^{-3}	1.20/–0.78

Table S2 Selected bond lengths for **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co1	O6[1]	1.986(4)	N3	C20	1.344(10)
Co1	O5	2.201(4)	C28	C27	1.379(11)
Co1	O3	2.070(5)	N1	C5	1.329(15)
Co1	O8	2.098(5)	N1	C1	1.358(15)
Co1	N1	2.209(6)	N1	C2	1.31(2)
Co1	N4[2]	2.171(6)	N1	C6	1.32(2)
Co2	O1[3]	2.065(5)	O4	C11	1.234(9)
Co2	O5	2.135(4)	N2	Co2[7]	2.180(6)
Co2	O9	2.081(5)	N2	C14	1.356(9)
Co2	N3[2]	2.168(6)	N2	C15	1.343(10)
Co2	O4	2.030(5)	C22	C21	1.376(11)
Co2	N2[4]	2.180(6)	C22	C18	1.369(10)
Co3	O6	1.975(4)	C19	C18	1.397(10)
Co3	O2[3]	2.091(5)	C19	C20	1.371(11)
Co3	O10	2.048(5)	C13	C14	1.357(10)
Co3	O5	2.070(4)	C13	C12	1.381(10)
Co3	O7[1]	2.136(4)	C25	C26	1.386(10)
Co3	O7	2.206(5)	N4	Co1[6]	2.171(6)
O6	Co1[1]	1.986(4)	N4	C27	1.347(10)
O1	Co2[5]	2.065(5)	N4	C26	1.344(9)
O1	C10	1.249(8)	C16	C12	1.395(10)
O2	Co3[5]	2.091(5)	C16	C15	1.364(10)
O2	C10	1.243(8)	C18	C17	1.512(10)
O10	C17	1.252(9)	C10	C9	1.513(10)
O3	C11	1.243(8)	C12	C11	1.522(9)
O7	Co3[1]	2.137(4)	C9	C8	1.392(16)
O7	C23	1.282(8)	C9	C4	1.362(16)
O8	C23	1.233(8)	C9	C3	1.37(2)
O9	C17	1.255(9)	C9	C7	1.35(2)
C24	C28	1.375(10)	C8	C5	1.392(19)
C24	C25	1.391(10)	C4	C1	1.363(19)
C24	C23	1.498(9)	C2	C3	1.37(3)
N3	Co2[6]	2.168(6)	C6	C7	1.38(3)
N3	C21	1.330(10)			

Table S3 Selected bond angles for **1**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O6^1	Co1	O5	93.91(15)	C21	N3	Co2^6	115.9(5)
O6^1	Co1	O3	170.43(18)	C21	N3	C20	117.0(6)
O6^1	Co1	O8	90.37(17)	C20	N3	Co2^6	127.1(5)
O6^1	Co1	N1	87.61(19)	C24	C28	C27	120.3(7)
O6^1	Co1	N4^2	86.81(18)	C5	N1	Co1	122.6(7)
O5	Co1	N1	170.3(2)	C5	N1	C1	116.5(10)
O3	Co1	O5	94.76(17)	C1	N1	Co1	120.0(7)
O3	Co1	O8	94.82(19)	C2	N1	Co1	125.2(9)
O3	Co1	N1	84.5(2)	C2	N1	C6	115.4(14)
O3	Co1	N4^2	88.2(2)	C6	N1	Co1	119.3(10)
O8	Co1	O5	82.24(17)	C11	O4	Co2	136.6(5)
O8	Co1	N1	88.2(2)	C14	N2	Co2^7	121.5(5)
O8	Co1	N4^2	176.8(2)	C15	N2	Co2^7	121.5(5)
N4^2	Co1	O5	96.47(19)	C15	N2	C14	117.0(6)
N4^2	Co1	N1	93.2(2)	C18	C22	C21	120.5(7)
O1^3	Co2	O5	94.49(17)	C20	C19	C18	118.5(7)
O1^3	Co2	O9	94.0(2)	C14	C13	C12	119.6(7)
O1^3	Co2	N3^2	87.3(2)	C26	C25	C24	120.2(7)
O1^3	Co2	N2^4	84.8(2)	N2	C14	C13	123.1(7)
O5	Co2	N3^2	85.16(19)	N3	C21	C22	122.7(7)
O5	Co2	N2^4	176.77(19)	C27	N4	Co1^6	118.6(5)
O9	Co2	O5	96.33(18)	C26	N4	Co1^6	125.1(5)
O9	Co2	N3^2	177.9(2)	C26	N4	C27	116.3(6)
O9	Co2	N2^4	86.9(2)	N4	C27	C28	123.6(7)
N3^2	Co2	N2^4	91.7(2)	C15	C16	C12	119.2(7)
O4	Co2	O1^3	168.2(2)	C22	C18	C19	117.5(7)
O4	Co2	O5	97.33(18)	C22	C18	C17	119.8(7)
O4	Co2	O9	85.0(2)	C19	C18	C17	122.7(7)
O4	Co2	N3^2	93.4(2)	N3	C20	C19	123.9(7)
O4	Co2	N2^4	83.4(2)	O1	C10	C9	114.6(6)
O6	Co3	O2^3	90.49(18)	O2	C10	O1	127.2(7)
O6	Co3	O10	86.45(18)	O2	C10	C9	118.2(6)
O6	Co3	O5	174.46(16)	C13	C12	C16	118.0(6)
O6	Co3	O7	86.79(16)	C13	C12	C11	122.6(6)
O6	Co3	O7^1	84.84(16)	C16	C12	C11	119.4(6)
O2^3	Co3	O7^1	90.75(19)	O10	C17	O9	127.1(7)

Symmetry codes: ^{1}2–X, –Y, 1–Z; ^{2}1+X, +Y, +Z; ^{3}+X, 1+Y, +Z; ^{4}2–X, 1/2+Y– 1/2–Z; ^{5}+X, –1+Y, +Z; ^{6}–1+X, +Y, +Z; ^{7}2–X, –1/2+Y, 1/2–Z.

References

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2 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.