

Electronic Supporting Information (ESI)

A pillar-layered porous Co^{II}-MOF with dual active sites for selective gas adsorption

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S1. Experimental Section

Materials and methods.

All chemicals were commercially purchased and used as received.

The solid state diffusion reflection spectrum was measured on UV-Vis spectrophotometer (Evolution 220, ISA-220 accessory, Thermo Scientific). IR spectrum was recorded on a PerkinElmer Spectrum Two in the frequency range of 4000-400 cm^{-1} . The elemental analyses (C, H, N contents) were determined on a Vario EL III analyzer. Thermogravimetric analysis (TGA) was done in a TA SDT Q600 thermal analyzer from room temperature to 800 $^{\circ}\text{C}$ under nitrogen atmosphere at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. Gas sorption isotherms were performed on Micromeritics 3Flex apparatus. The samples were firstly exchanged with dehydrated acetonitrile and then activated at 120 $^{\circ}\text{C}$ overnight under vacuum. Powder X-ray diffraction (PXRD) data were measured on a Philips X' Pert Pro MPD X-ray diffractometer ($\text{Cu K}\alpha = 1.5418 \text{ \AA}$) with an X' Celerator detector. 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>.

Syntheses of $[\text{Co}_3(\text{diimpym})(\text{bda})_3(\text{DMF})_2] \cdot 6\text{DMF}$ (SD/Co3)

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol, 0.0291g), 4,6-di(1H-imidazol-1-yl) pyrimidine (0.05mmol, 0.0106g) and *p*-phthalic acid (0.1mmol, 0.0166g) were dissolved in 6mL N,N-Dimethyl formamide. The mixed solution was stirred at room temperature until it became clear. Then the resulted solution was sealed in a 25 mL Teflon-lined stainless steel autoclave and heated at 130 $^{\circ}\text{C}$ for 2000 minutes. After cooling to room temperature, the plate-like pinkish crystals were collected at the bottom of the bottle with a yield of 40%. Anal. Calcd for $\text{C}_{58}\text{H}_{73}\text{Co}_3\text{N}_{14}\text{O}_{20}$, calcd (found): C, 47.61 (46.55); H, 5.03 (5.12) %. IR: 2934 (w), 1649 (m), 1580 (m), 1491 (m), 1374 (s), 1099 (m), 1063 (m), 748 (s), 654 (m), 527 (s) cm^{-1} .

X-ray Crystallography

The crystallographic data of **SD/Co3** was collected on a Rigaku Oxford Diffraction XtaLAB Synergy diffractometer equipped with a HyPix-6000HE area detector and an Oxford Cryosystems CryostreamPlus open-flow N₂ cooling device for data collection at 173 K. Full data collections were carried out using Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$.) with exposure times ranging from 0.5 to 2 seconds, frame widths of 1 degrees, and a detector distance of approximately 3.2 cm. The intensity data were scaled and corrected for absorption, and final cell constants were calculated from the xyz centroids of strong reflections from the actual data collections after integration. Semi-empirical absorption correction based on symmetry equivalent reflections was applied. The structures were solved by direct methods and refined by the full-matrix least-squares method based on F^2 . Structure solution, refinement, and generation of publication materials were performed with the use of the SHELXTL crystallographic software package.^{S1, S2} The metal atoms in **SD/Co3** were found from E-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. The hydrogen atoms of organic ligands were added theoretically, riding on the concerned atoms and refined with fixed thermal factors. Some thermal parameter restraints such as SIMU and SADI were used to make atoms with unusual U_{eq} to be chemically reasonable in the structure. Further details of crystal data and structure refinement for **SD/Co3** were collected in Table S1. Selected bond lengths and angles of **SD/Co3** were given in Table S2. Full crystallographic data for **SD/Co3** have been deposited with the CCDC (No.: 1840660). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.^{S3}

Table S1 Crystal data and structure refinement for **SD/Co3**.

Compound	SD/Co3
Empirical formula	C ₅₈ H ₇₃ Co ₃ N ₁₄ O ₂₀
Formula weight	1463.09
Temperature/K	173.00(10)
Crystal system	orthorhombic
Space group	<i>Pnma</i>
a/Å	18.1925(5)
b/Å	40.2091(13)
c/Å	9.5480(3)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	6984.4(4)
Z	4
ρ _{calc} /cm ³	1.391
μ/mm ⁻¹	6.183
F(000)	3040.0
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	8.796 to 134.142
Index ranges	-21 ≤ h ≤ 14, -48 ≤ k ≤ 47, -10 ≤ l ≤ 11
Reflections collected	40236
Independent reflections	6332 [R _{int} = 0.0895, R _{sigma} = 0.0527]
Data/restraints/parameters	6332/98/459
Goodness-of-fit on F ²	1.046
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0684, wR ₂ = 0.1865
Final R indexes [all data]	R ₁ = 0.0847, wR ₂ = 0.2033
Largest diff. peak/hole / e Å ⁻³	1.39/-1.00

Table S2 The selected bond lengths [\AA] and angles [$^\circ$] of **SD/Co3**.

Co1—O1	2.023 (3)	Co1—N1	2.075 (3)
Co1—O4 ⁱ	2.042 (3)	Co2—O2 ⁱⁱⁱ	2.071 (3)
Co1—O5 ⁱⁱ	2.117 (3)	Co2—O3 ^v	2.049 (3)
Co1—O6 ⁱⁱ	2.257 (3)	Co2—O5 ^v	2.121 (3)
Co1—O7	2.208 (3)		
O1—Co1—O4 ⁱ	99.55 (12)	O2 ⁱⁱⁱ —Co2—O2 ^{iv}	180.00 (12)
O1—Co1—O5 ⁱⁱ	93.70 (11)	O2 ^{iv} —Co2—O5	87.60 (10)
O1—Co1—O6 ⁱⁱ	151.91 (11)	O2 ^{iv} —Co2—O5 ^v	92.40 (10)
O1—Co1—O7	84.29 (12)	O2 ⁱⁱⁱ —Co2—O5	92.40 (10)
O1—Co1—N1	104.35 (13)	O2 ⁱⁱⁱ —Co2—O5 ^v	87.60 (10)
O4 ⁱ —Co1—O5 ⁱⁱ	100.57 (11)	O3 ^v —Co2—O2 ⁱⁱⁱ	86.10 (11)
O4 ⁱ —Co1—O6 ⁱⁱ	95.24 (11)	O3 ^v —Co2—O2 ^{iv}	93.90 (11)
O4 ⁱ —Co1—O7	173.47 (11)	O3—Co2—O2 ^{iv}	86.10 (11)
O4 ⁱ —Co1—N1	88.62 (12)	O3—Co2—O2 ⁱⁱⁱ	93.90 (11)
O5 ⁱⁱ —Co1—O6 ⁱⁱ	60.00 (10)	O3 ^v —Co2—O3	180.0
O5 ⁱⁱ —Co1—O7	84.35 (11)	O3—Co2—O5	88.29 (11)
O7—Co1—O6 ⁱⁱ	83.47 (11)	O3 ^v —Co2—O5 ^v	88.29 (11)
N1—Co1—O5 ⁱⁱ	158.16 (12)	O3 ^v —Co2—O5	91.71 (11)
N1—Co1—O6 ⁱⁱ	99.73 (12)	O3—Co2—O5 ^v	91.71 (11)
N1—Co1—O7	85.30 (12)	O5 ^v —Co2—O5	180.0
Symmetry codes: (i) $x-1/2, y, -z+1/2$; (ii) $-x+3/2, -y+1, z+1/2$; (iii) $x+1/2, y, -z+1/2$; (iv) $-x+3/2, -y+1, z-1/2$; (v) $-x+2, -y+1, -z$.			

Sorption measurements.

Gas adsorption/desorption measurements were carried out using a Micromeritics 3Flex apparatus gas adsorption instrument. UHP-grade gases were used in measurements. Before the measurement, the samples of **SD/Co3** were soaked in anhydrous acetonitrile (CH₃CN) for 7 days to remove DMF solvent molecules in the channels, and then filtrated, and activation of the exchanged **SD/Co3** at 120 °C under high vacuum (less than 10⁻⁵ Torr) overnight led to the formation of activated sample **SD/Co3a**. About 50 mg of the desolvated samples were used for the entire adsorption/desorption measurements. The C₂H₂, C₂H₄, C₂H₆, CO₂ and N₂ adsorption/desorption isotherm measurements were carried out at 273 K in an ice-water bath, and at 298 K in a water bath, respectively.

S2. Figures in Supporting Information

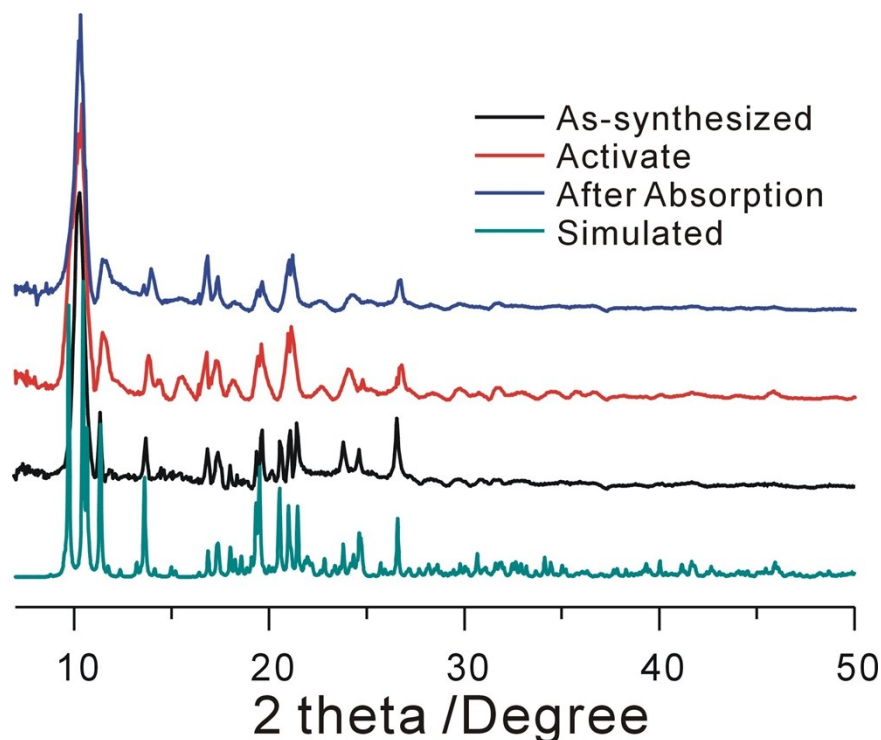


Fig. S1 The PXRD patterns of SD/Co₃.

As shown in **Fig. S1**, the peak positions of simulated and experimental PXRD patterns are in agreement with each other, indicating the phase purity of the compound. The small differences in intensity and positions may be due to the preferred orientation of the crystalline samples and the framework contracted by losing some of solvent molecules.^{13c-i}

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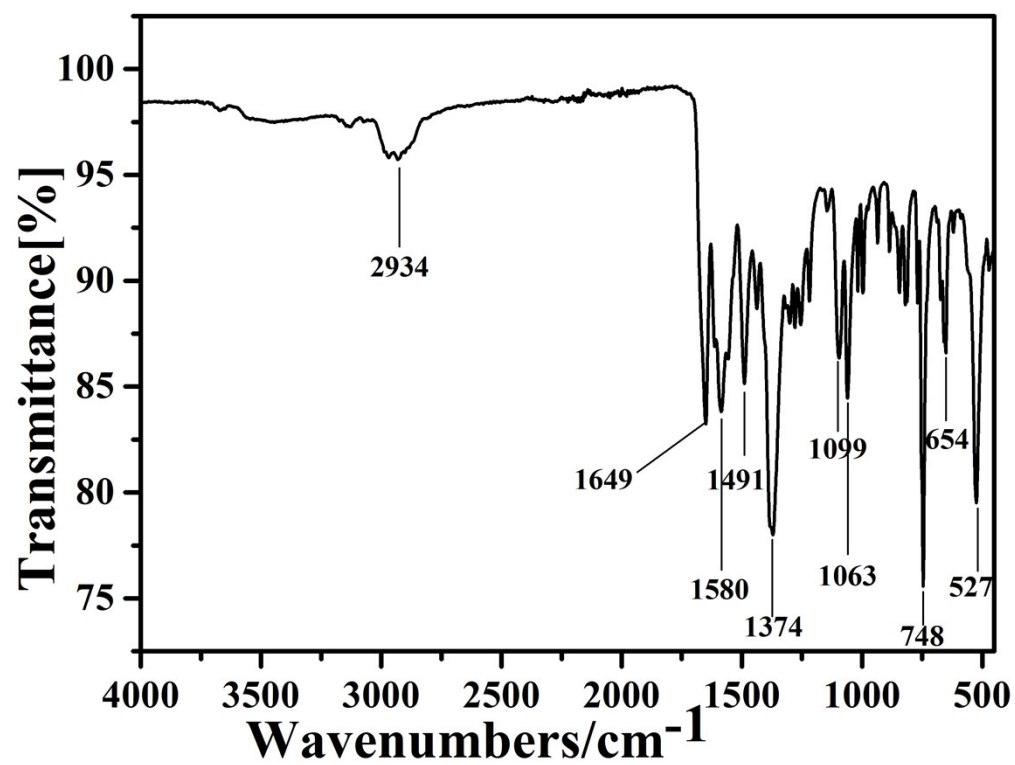


Fig. S2 The IR spectrum of SD/Co3.

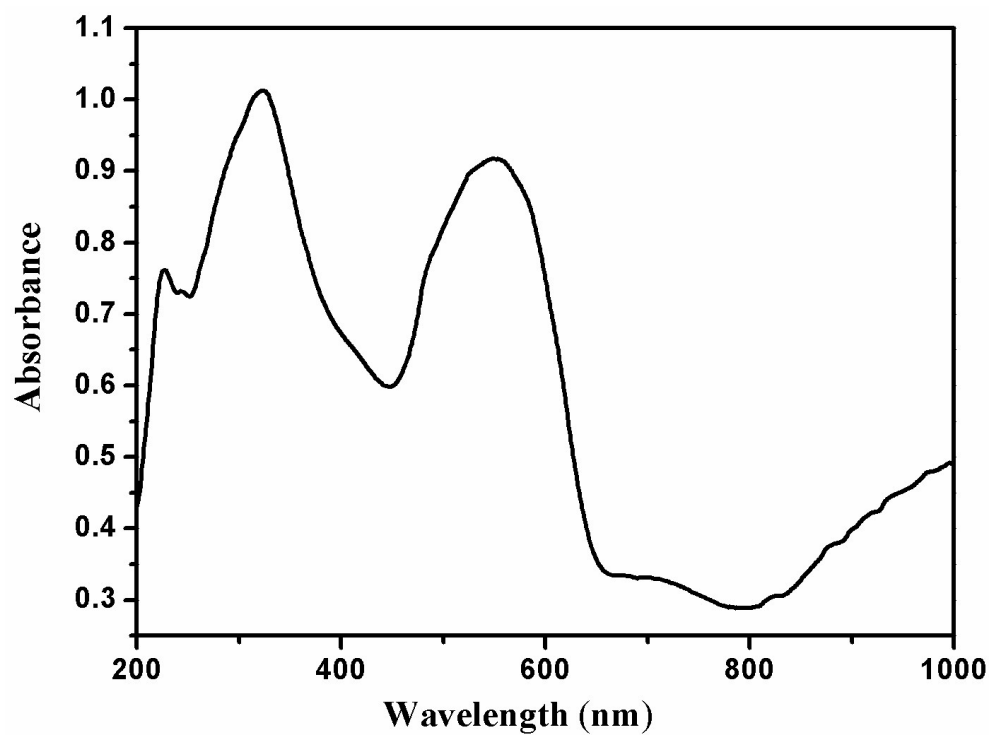


Fig. S3 The UV-vis spectrum of SD/Co₃ in the solid state.

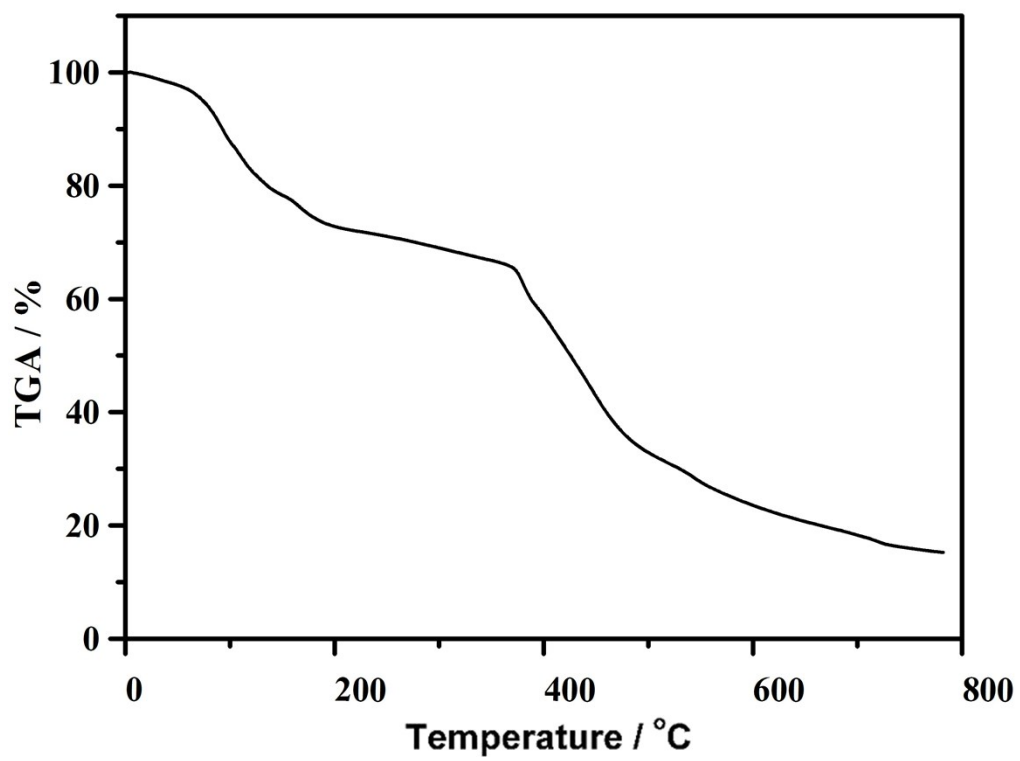


Fig. S4 The TGA of SD/Co3.

S3. IAST adsorption selectivity calculation:^{S4-S5}

The experimental isotherm data for pure C₂H₂, C₂H₄, C₂H₆, CO₂ and N₂ (measured at 273 K) were fitted using a Langmuir-Freundlich (L-F) model:

$$q = \frac{a * b * p^c}{1 + b * P^c}$$

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

Using the pure component isotherm fits, the adsorption selectivity is defined by

$$S_{ads} = \frac{q_1 / q_2}{P_1 / P_2}$$

Where q_i is the amount of i adsorbed and p_i is the partial pressure of i in the mixture.

We used the following written codes to simulate the adsorption selectivity of C₂H₂/C₂H₄, C₂H₂/C₂H₆ and CO₂/N₂ in Fig. 2:

```
28          # No. of Pressure Point
y1, y2      # Molar fraction of binary mixture (y1 and y2, y1 + y2 = 1)
1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 101, 102, 103, 104, 105, 106, 107,
108, 109    #The unit is same parameter b, kPa
a1, a2      # fitting parameter Nsat (A1) for both component (Unit: mmol/g)
b1, b2      # fitting parameter b1 for both components (Unit: kPa-1)
c1, c2      # fitting parameter c1 for both components
0, 0        # fitting parameter Nsat2(A2) for both component(Unit: mmol/g)
0, 0        # fitting parameter b2 for both components (Unit: kPa-1)
1, 1        # fitting parameter c2 for both components
```

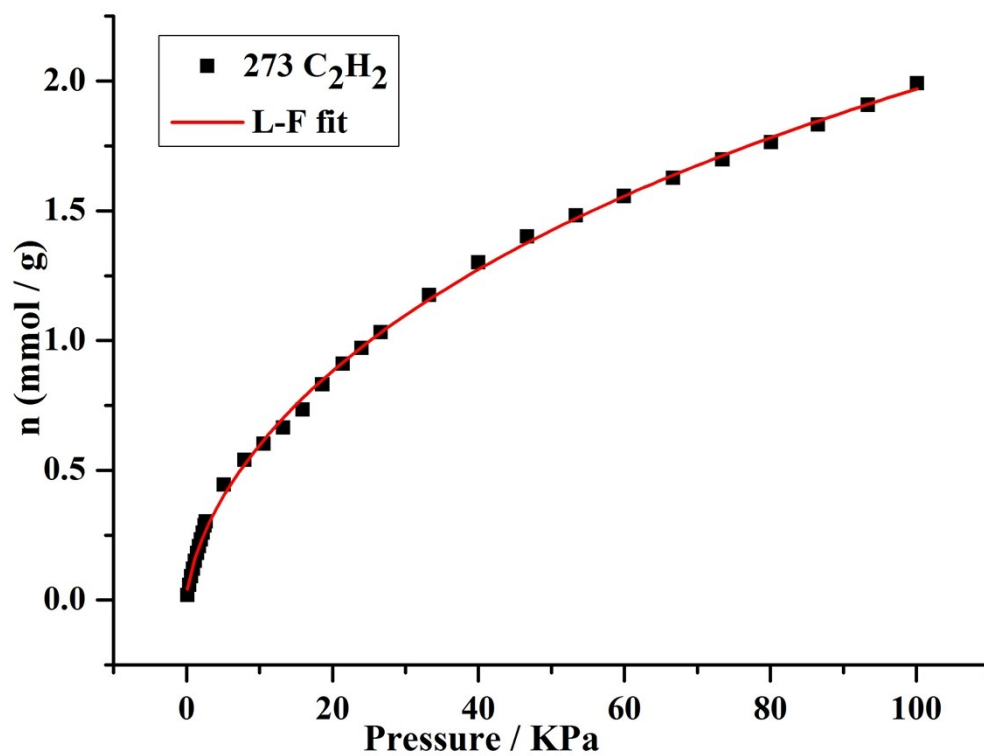


Fig. S5 C_2H_2 adsorption isotherm of SD/Co₃ with fitting by L-F model.

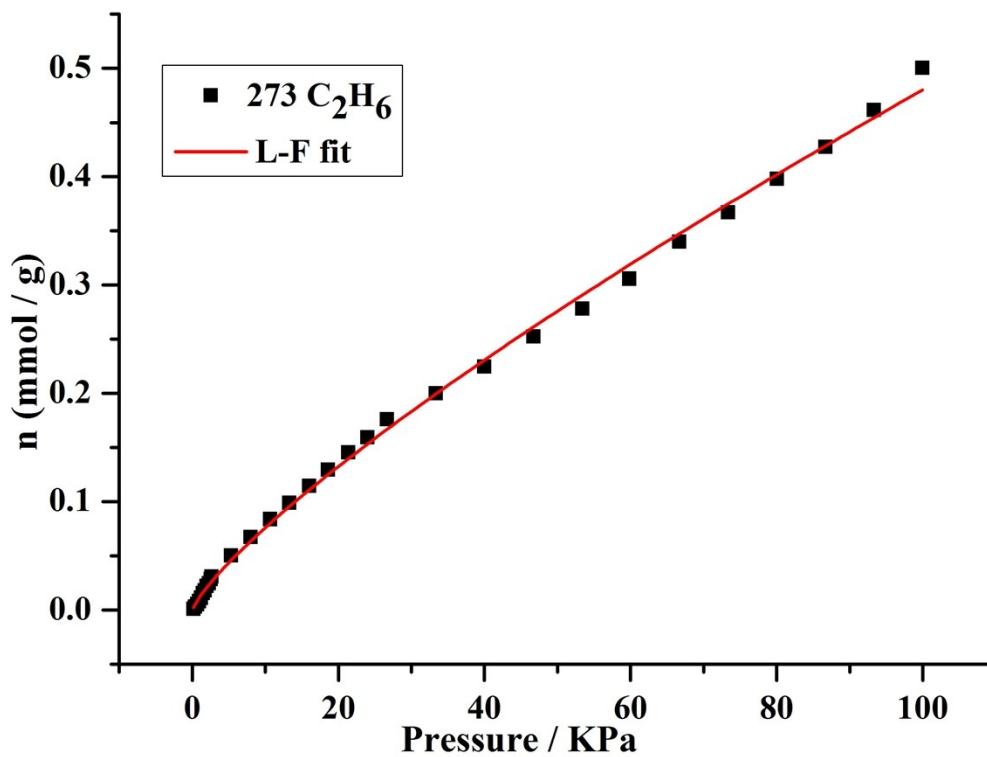


Fig. S6 C_2H_6 adsorption isotherm of SD/Co₃ with fitting by L-F model.

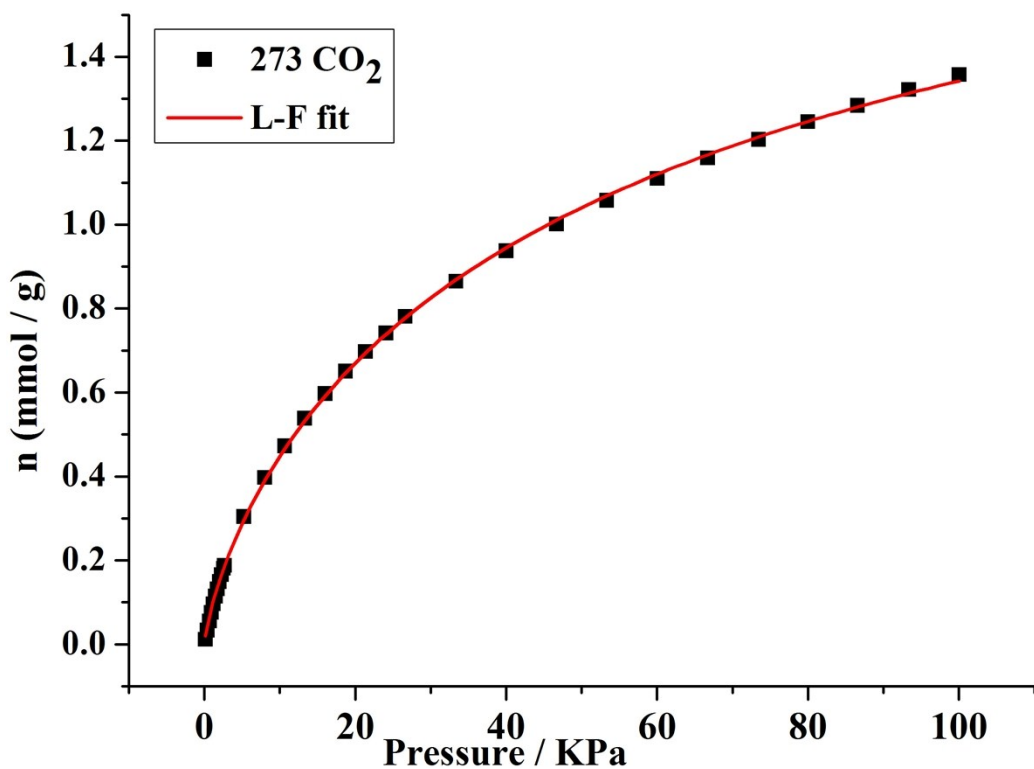


Fig. S7 CO₂ adsorption isotherm of SD/Co₃ with fitting by L-F model.

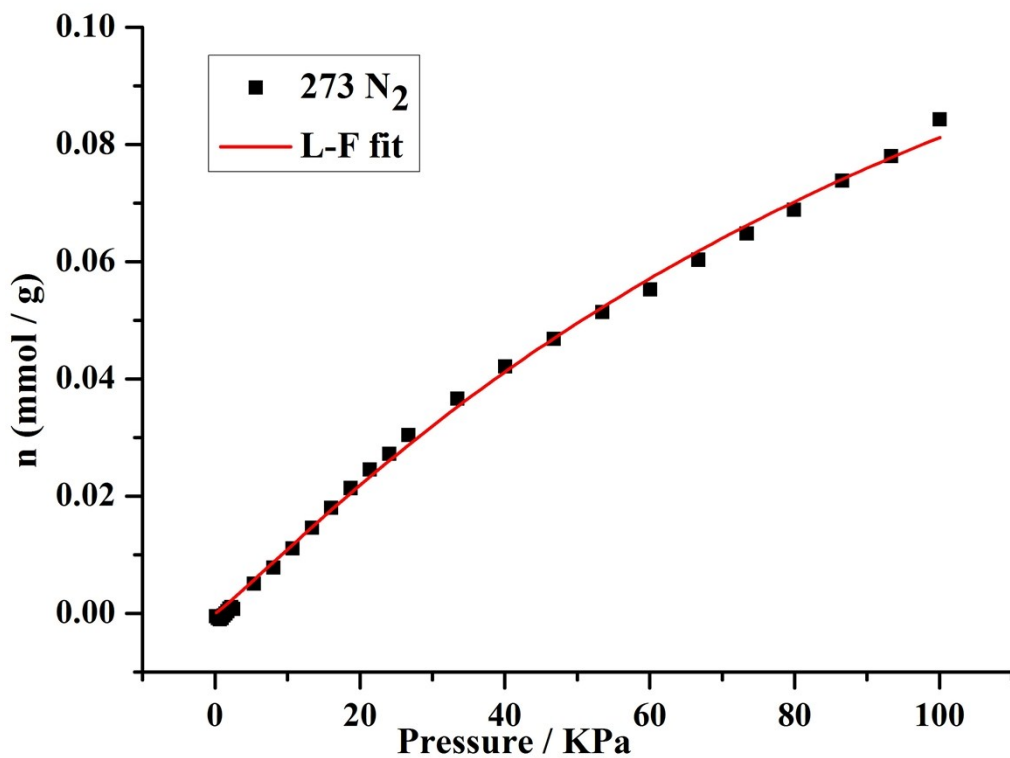


Fig. S8 N₂ adsorption isotherm of SD/Co₃ with fitting by L-F model.

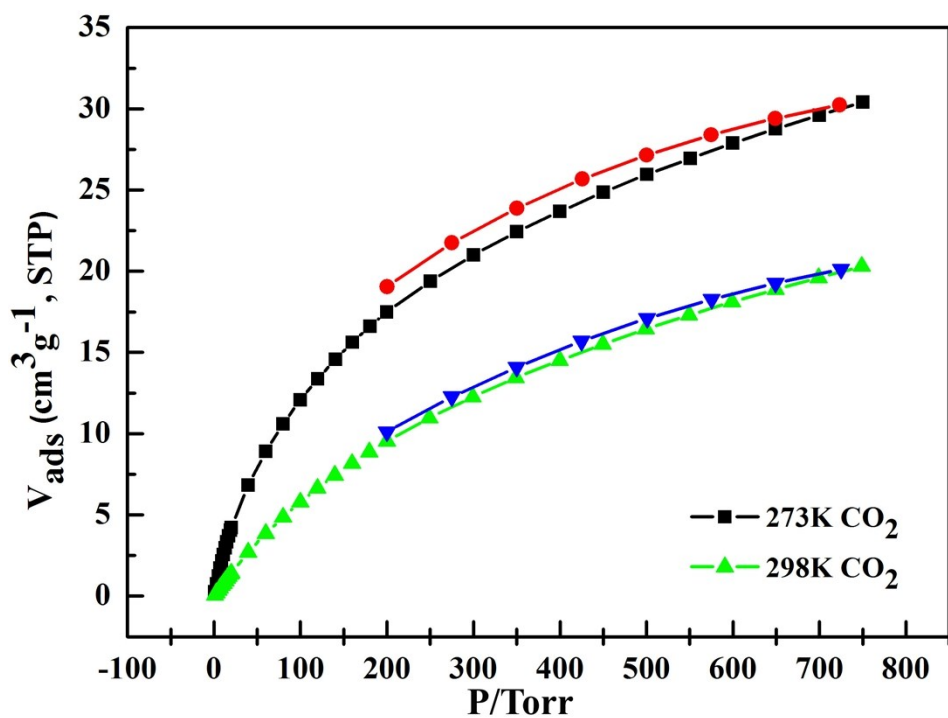


Fig. S9 The CO₂ isotherms of SD/Co3 at 273 K and 298 K.

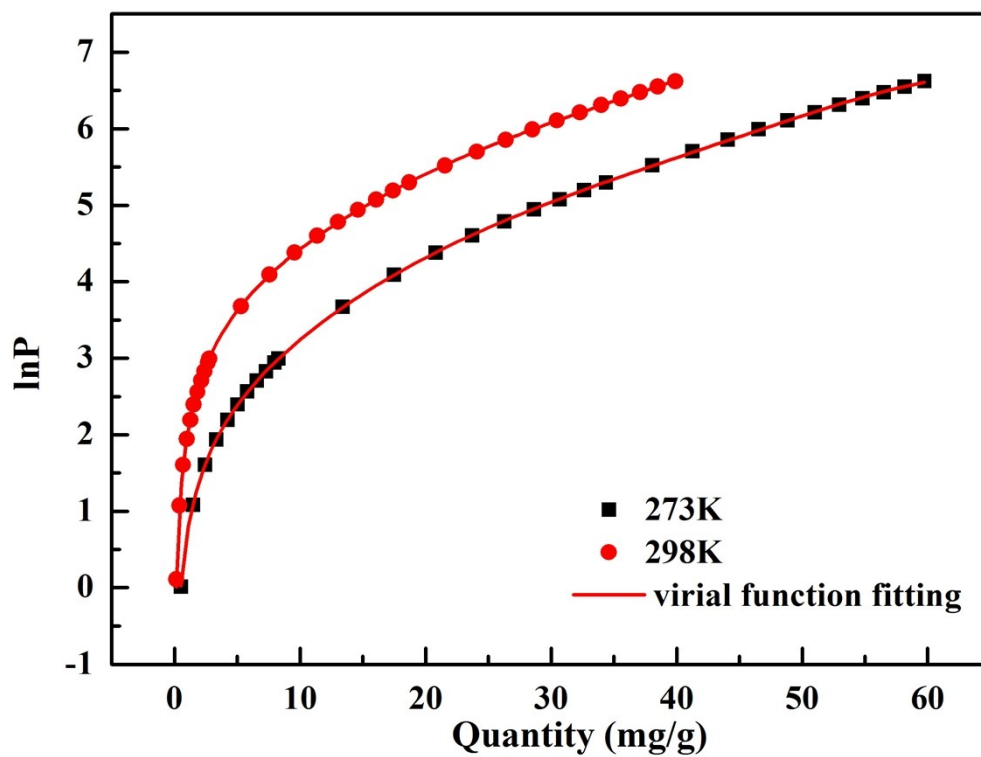


Fig. S10 The CO₂ fit isotherms of SD/Co3 at 273 K and 298 K by virial equation.

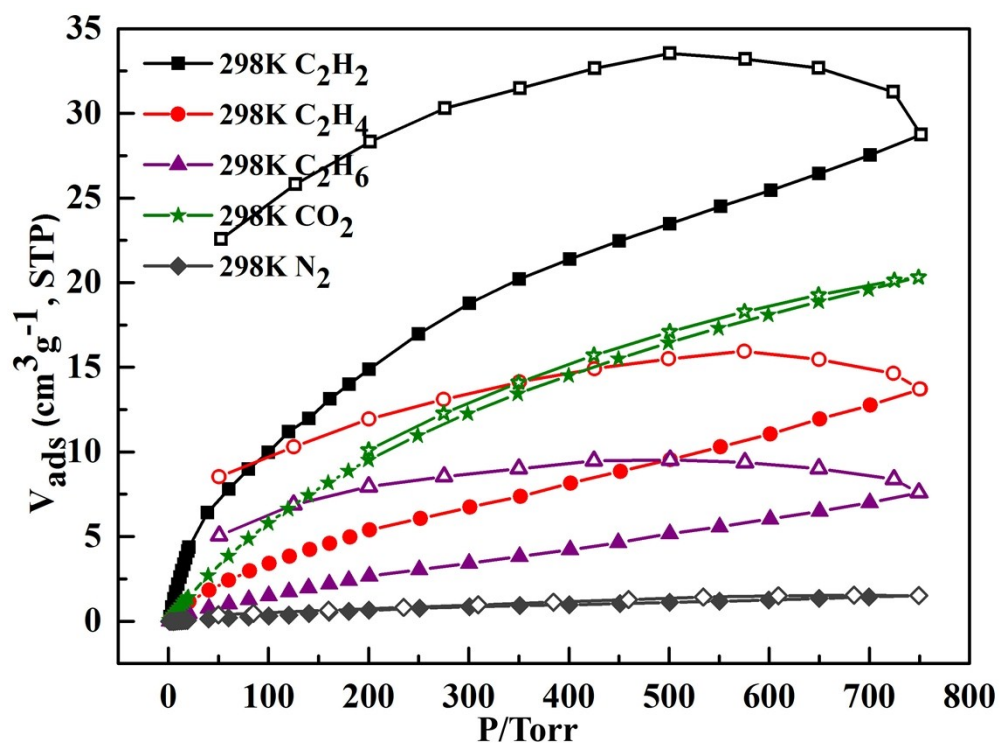


Fig. S11 (a) C₂H₂, C₂H₄, C₂H₆, CO₂ and N₂ sorption isotherms for SD/Co₃a at 298 K.

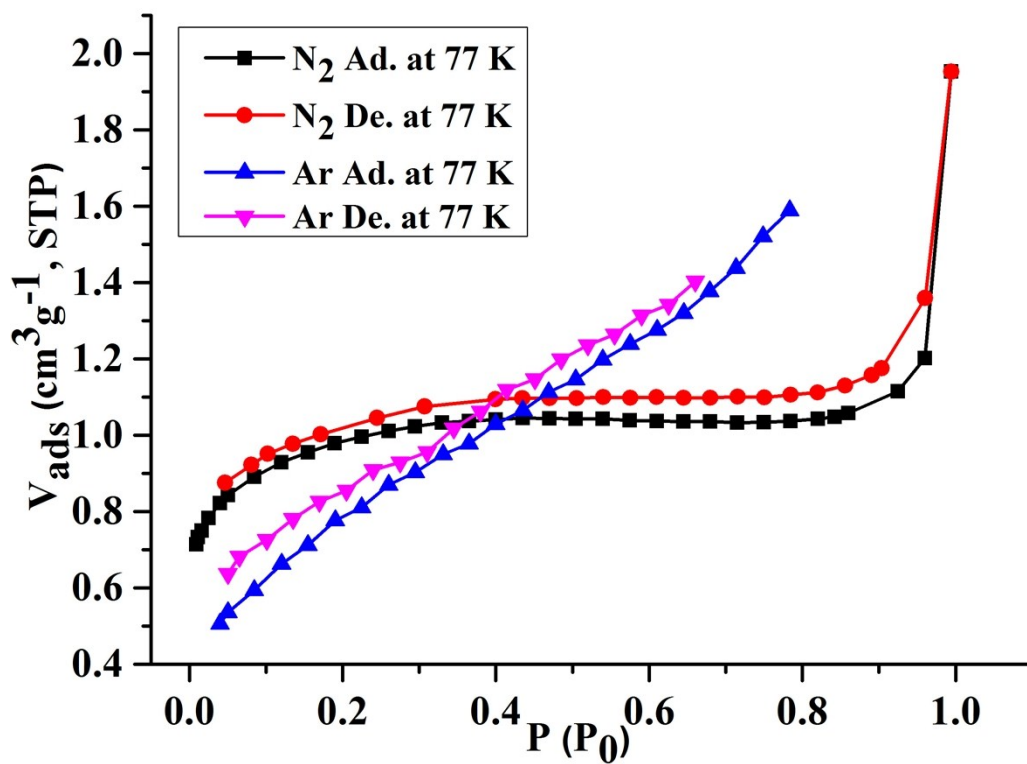
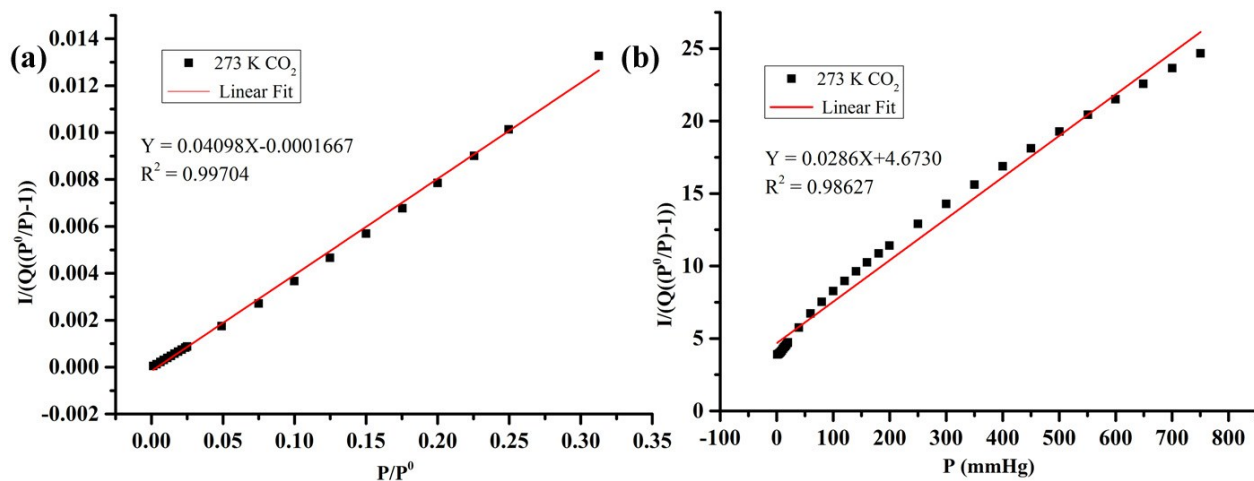


Fig. S12 (a) N₂ and Ar sorption isotherms for SD/Co₃a at 77 K.



$$S_{\text{BET}} = (1/(0.04098-0.0001667))/22414 \times 6.023 \times 10^{23} \times 0.170 \times 10^{-18} = 111.9 \text{ m}^2\text{g}^{-1}$$

$$S_{\text{Langmuir}} = ((1/0.0286)/22414) \times 6.023 \times 10^{23} \times 0.170 \times 10^{-18} = 159.7 \text{ m}^2\text{g}^{-1}$$

Fig. S13 The BET (a) and Langmuir (b) surface areas of **SD/Co3a** obtained from the CO₂ adsorption isotherm at 273 K.

References:

- (S1) Sheldrick, G. M. SHELXL97, Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1997.
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S4 The computational simulation studies of gases adsorption

To further investigate the stronger interactions of C₂H₂ and CO₂ molecules with abundant multiple active sites in **SD/Co3**, grand canonical Monte Carlo (GCMC) simulations were carried out using the Sorption module of Materials Studio 5.0 package.^{S6} The Locate and Metropolis methods^{S7} were used to predict the possible binding sites of C₂H₂ and CO₂ molecules onto the frameworks. The unit cell frameworks of **SD/Co3** were constructed from experimental crystal X-ray diffraction data. The loading number of C₂H₂ and CO₂ adsorbed onto unit cell of the **SD/Co3** framework was choose as 20 based on our experimental data. During the simulation, the C₂H₂ and CO₂ molecules including the frameworks were considered as rigid, and periodic boundary conditions were applied in all three directions. The interaction energy between C₂H₂, CO₂ and framework were calculated by the Coulomb and Lennard-Jones 6-12 (LJ) potentials. A cutoff radius of 12.5 Å for the LJ potentials was used throughout the simulation. All parameters including the partial charges were assigned by the COMPASS force field^{S8} embedded in the Sorption module.

S6 *Accelrys, Materials Studio Getting Started, release 5.0; Accelrys Software, Inc.: San Diego, CA, 2009.*

S7 N. Metropolis and S. Ulam, *J. Am. Stat.l Assoc.*, 1949, **60**, 115–129.

S8 H. Sun, *J. Phys. Chem. B*, 1998, **102**, 7338–7364.