

Electronic Supplementary Information

A Porous Cobalt-based MOF with High CO₂ Selectivity and Uptake Capacity

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EXPERIMENTAL SECTION

1. Materials and General methods.

All chemical reagents were obtained from commercial sources and, unless otherwise noted, were used as received without further purification. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 II CHNS/O analyzer. The IR spectra were recorded in the 400-4000 cm^{-1} on a Bruker VERTEX 80V spectrometer using KBr pellets. ^1H NMR spectra were recorded on a Bruker AVANCE III 600 MHz spectrometer with tetramethylsilane as an internal reference. Thermal gravimetric analyses (TGA) were performed under N_2 atmosphere (100 ml/min) with a heating rate of 5 $^\circ\text{C}/\text{min}$ using a 2960 SDT thermogravimetric analyzer. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 ADVANCE X-ray diffractometer with $\text{Cu K}\alpha$ radiation. The gas sorption measurements were performed on Micromeritics ASAP2020 HD88 surface area analyzer. The detail of the method for activitate as-synthesized sample with supercritical carbon dioxide (SCD) was prepared according to the literature (J. T. Hupp and et al., Nature Chemistry, 2010, 2, p. 944; DOI: 10.1038/nchem.834). The as-synthesized samples were placed inside the supercritical CO_2 dryer and the mother liquor (DAM: CH_3OH = 5:1) was exchanged with CO_2 (liq.) over a period of 3 h. The rate of venting of CO_2 (liq.) was always kept below the rate of filling so as to maintain a full drying chamber. Following venting, the chamber was sealed and the temperature was raised to 40 $^\circ\text{C}$ (i.e., above the critical temperature for carbon dioxide), at which time the chamber was slowly vented over the course of 3 h. The color of the MOF changed from purple to gray.

2. Preparation of 5-(pyrimidin-5-yl) isophthalic acid(L).

Into a flask flushed with N_2 , pyrimidin-5-ylboronic acid (1.62 g, 13.06 mmol), diethyl 5-iodoisophthalate (3.50 g, 10.05 mmol), and K_3PO_4 (4.66 g, 17.05 mmol) was placed and 60 mL of 1,4-dioxane was added. Tetrakis (triphenylphosphine) palladium(0) (0.466g, 0.404 mmol) was added to the reaction mixture with stirring, and heated to 80 $^\circ\text{C}$ for 3 days. The resultant mixture was evaporated to dryness and taken up in CHCl_3 which had been dried over MgSO_4 . The volatiles were removed by evaporation under reduced pressure, and the solid residue was purified by column chromatography with ethyl acetate / petroleum ether solution. Yield = 1.94 g(64.2%).

A sample of potassium hydroxide (7.26g, 129.3mmol) was dissolved in 100mL methanol. To this was added 5-(pyrimidin-5-yl) isophthalic acid diethyl ester (1.94g, 6.5mmol), after which the solution was stirred for 24h at 80 $^\circ\text{C}$. The volatiles were removed by evaporation under reduced pressure. The residue dissolved in 100mL of water was acidified to pH~2-3 using 1.0M HCl and stirred for 24h. The white precipitate was separated by filtration, washed with water, and freeze-dried. Yield=1.48g (94.3%). ^1H NMR (600 MHz, DMSO-d_6 , δ ppm): 13.31 (br, 2H, COOH), 9.26 (s, 1H, ArH), 9.23 (s, 2H, ArH), 8.55 (t, $J=1.5\text{Hz}$, 1H, ArH), 8.49 (d, $J=1.5\text{Hz}$, 2H, ArH).

3. Synthesis of NJFU-2 and NJFU-2a.

A solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (8.73 mg, 0.03 mmol) in 0.35 mL of methanol was mixed with the L (7.32 mg, 0.03 mmol) in 1.65 mL of N,N-Dimethylacetamide (DMA). The mixture was sealed in a Pyrex tube and heated to 90 $^\circ\text{C}$ for 72 h. The violet block crystals obtained were filtered and washed with DMA. Yield: 37%. Anal. Calcd (Found) for $[\text{C}_{12}\text{H}_6\text{CoN}_2\text{O}_4] \cdot x\text{S}$ (Solvent Guest Molecule): Found: C, 48.60; H, 4.05; N, 10.74. Selected IR (KBr, cm^{-1}): 3035, 2927, 1628, 1591, 1563, 1503, 1452, 1407, 1378, 1305, 1265, 1189, 1172, 1121, 1055, 1035, 1011, 933, 908, 881, 781, 724.

The activated sample, NJFU-2a, was prepared by supercritical carbon dioxide (SCD) and then degassed under high vacuum at room temperature for 12 h to obtain the fully desolvated sample. Anal. Calcd (Found) for $[\text{C}_{12}\text{H}_6\text{CoN}_2\text{O}_4]$: C, 47.82; H, 1.99; N, 9.30; Found: C, 47.60; H, 2.05; N, 9.07. Selected IR (KBr, cm^{-1}): 3078, 2929, 1620, 1563, 1452, 1404, 1373, 1177, 1116, 1054, 930, 903, 778, 720.

4. X-ray Structure Determination

Single crystal suitable for X-ray structure determination were selected and sealed in a capillary under a microscope. The X-ray diffraction intensity data were measured on a Bruker Smart Apex CCD diffractometer at room temperature using graphite monochromated $\text{Mo/K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data reduction was made with the Bruker SAINT program. The structures were solved by direct methods and refined with full-matrix least squares technique using the SHELXTL package. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to $1.2 \times U_{\text{eq}}$ of the attached atom. The unit cell includes a large region of disordered solvent molecules, which could not be modeled as discrete atomic sites. Crystal data and refinement conditions are shown in Table S1. The crystal data for

NJFU-2 have been deposited in CSD database, and labeled as 1020952. Copies of the data can be obtained, free of charge, on application to the CCDC (e-mail: deposit@ccdc.cam.ac.uk).

Table S1. Crystal data and structure refinement for NJFU-2.

Identification code	NJFU-2
CCDC number	1020952
Empirical formula	C ₁₂ H ₆ CoN ₂ O ₄
Formula weight	301.12
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/c
a	10.8161(13) Å
b	12.6809(15) Å
c	13.4170(16) Å
α	90°
β	111.147(2)°
γ	90°
Volume	1716.3(4) Å ³
Z	4
Density (calculated)	1.165 g cm ⁻³
Absorption coefficient	1.007 mm ⁻¹
F(000)	604
Crystal size	0.2 × 0.16 × 0.12 mm
Theta range for data collection	2.02 to 25.01 °
Limiting indices	-12 ≤ h ≤ 12, -14 ≤ k ≤ 15, -10 ≤ l ≤ 15
Reflections collected unique	9234 / 3018 [R(int) = 0.1117]
Completeness	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.946 and 0.830
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3012 / 0 / 172
Goodness-of-fit on F²	1.033
Final R indices [I > 2σ(I)]	R1 = 0.0381, wR2 ^a = 0.1075
R indices (all data)	R1 = 0.0423, wR2 ^a = 0.1096
Largest diff. peak and hole	0.504 and -0.458 e. Å ⁻³

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

Figure S1. IR spectra of the as-synthesized complex NJFU-2 (violet), and activated sample NJFU-2a (dark gray).

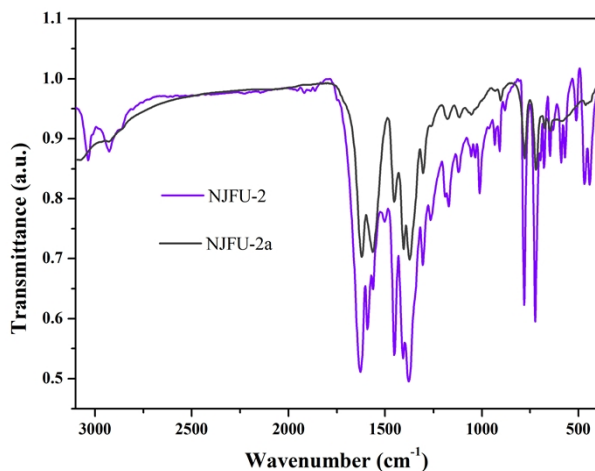


Figure S2. PXRD patterns of as-synthesized complex NJFU-2, the simulated, activated and soaked with the solvent.

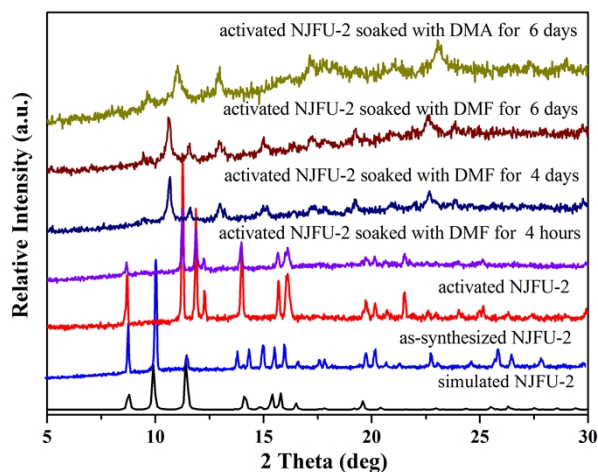


Figure S3. TGA data of as-synthesized sample of NJFU-2.

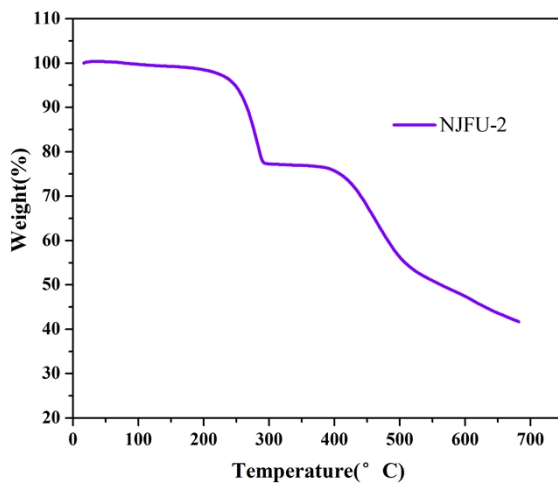


Figure S4. Nitrogen sorption isotherm at 77 K. The N₂-adsorption/desorption isotherms show a typical type I curve demonstrating the existence of microporous structure and physical adsorption mechanism. Adsorption curve (filled circles), desorption curve (open circles).

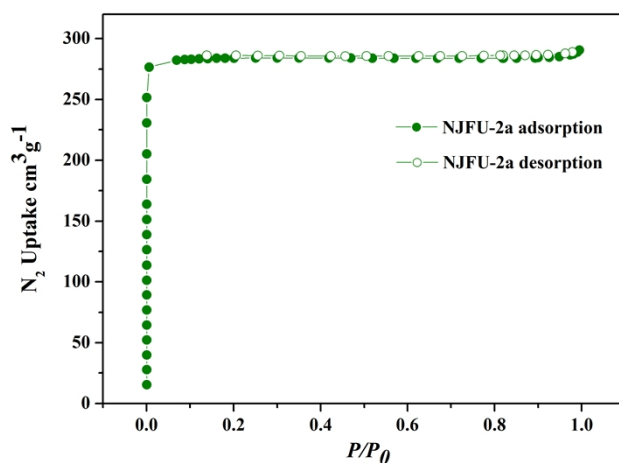


Figure S5. Plot of the linear region for the BET equation, which satisfies the second consistency criteria for application of the BET theory: (1) The pressure range selected should have values of $Q(P_0-P)$ increasing with P/P_0 . (2) The y intercept of the linear region must be positive to yield a meaningful value of the c parameter, which should be greater than zero.

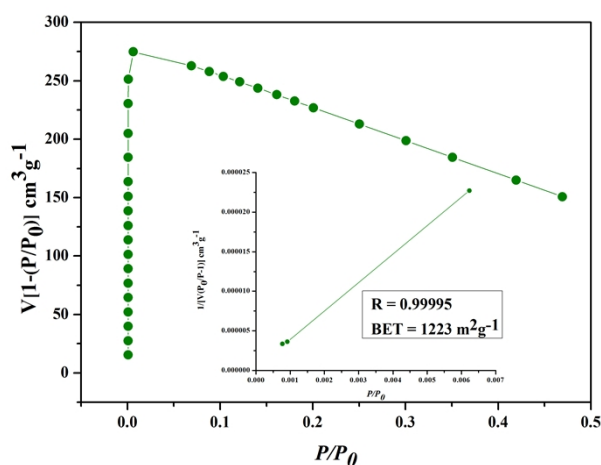


Figure S6. The CO_2 isosteric adsorption enthalpy for NJFU-2a calculated from the adsorption at 313K, 298 K and 273 K through the virial method.

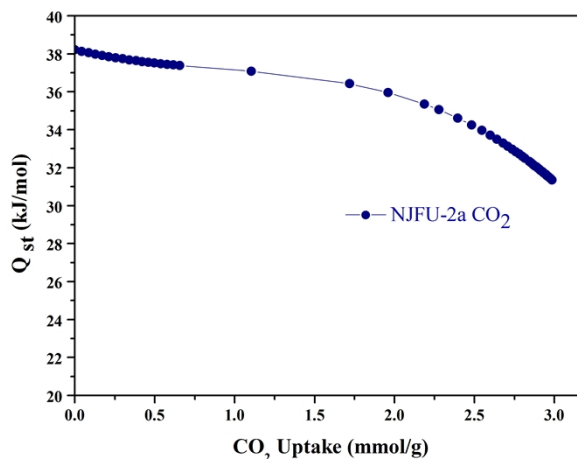
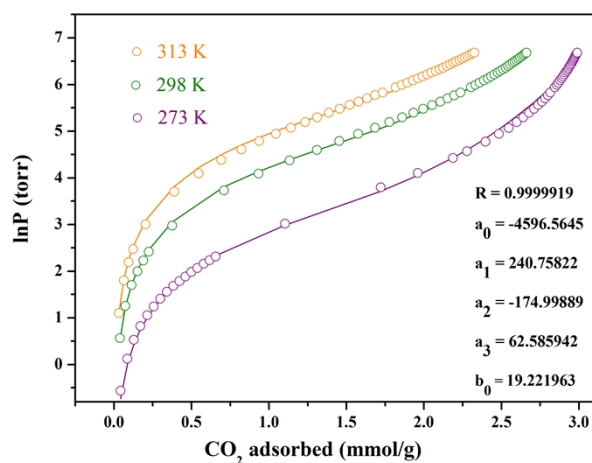


Figure S7. The CO_2 isotherms at 273 K, 298 K and 313K (purple, olive and orange symbols, respectively) and the corresponding virial equation fits (purple, olive and orange, respectively) for NJFU-2a.



Dual Site Langmuir-Freundlich Model for CO₂/CH₄ and CO₂/N₂ Adsorption Isotherms

$$N = \frac{N_{m,1}b_1p^{1/n_1}}{1+b_1p^{1/n_1}} + \frac{N_{m,2}b_2p^{1/n_2}}{1+b_2p^{1/n_2}}$$

Where p (unit: KPa) is the pressure of the bulk gas at equilibrium with the adsorbed phase, N is the adsorption quantity, $N_{m,1}$ and $N_{m,2}$ are the saturation capacities of sites 1 and 2, b_1 and b_2 (unit: 1/KPa) are the affinity coefficients of sites 1 and 2, and n_1 and n_2 represent the deviations from an ideal homogeneous surface. Here, the single-component CO₂, CH₄, and N₂ adsorption isotherms have been fit to enable the application of IAST in simulating the performance of NJFU-2a under a mixed component gas. The fitting parameters of DSLF equation are listed in Table S2.

Table S2 Dual site Langmuir-Freundlich fitting parameters for gas Adsorption for NJFU-2a.

Adsorbates	$N_{m,1}$	b_1	$1/n_1$	$N_{m,2}$	b_2	$1/n_2$
CO ₂ (273 K)	0.03546	1.7393×10^{-8}	3.9592	3.0838	0.1996	1.0361
CH ₄ (273 K)	0.6752	0.00855	1.2382	1.5789	0.000705	1.2671
N ₂ (273 K)	1.2439	0.00245	1.0773	0.0727	3.6338×10^{-8}	3.5662
CO ₂ (298 K)	2.9189	0.05491	1.0013	0.1724	0.01072	1.6523
CH ₄ (298 K)	2.2285	0.002934	1.0594	0.01316	2.3006×10^{-13}	6.6359
N ₂ (298 K)	0.5021	0.000136	1.5945	0.1955	0.00991	0.9659
CO ₂ (313 K)	0.03985	0.40337	1.0305	2.9996	0.02298	1.0573
N ₂ (313 K)	0.4768	0.000242	1.4372	0.06376	0.01692	0.9808

Figure S8. DSLF models fitting for the CO₂ adsorption isotherms of NJFU-2a. Dots are experimental data; lines are fitting curves.

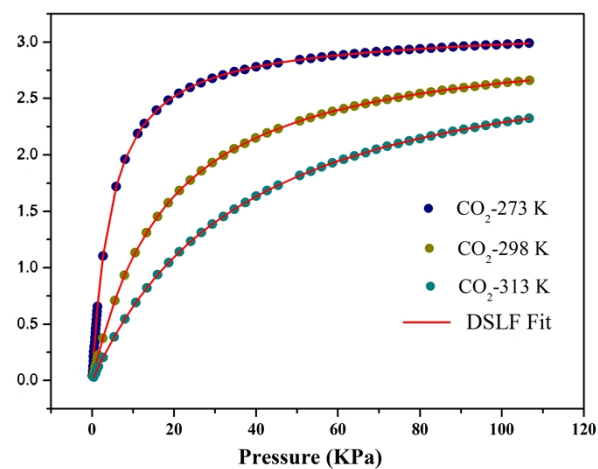


Figure S9. DSLF models fitting for the CH₄ adsorption isotherms of NJFU-2a. Dots are experimental data; lines are fitting curves.

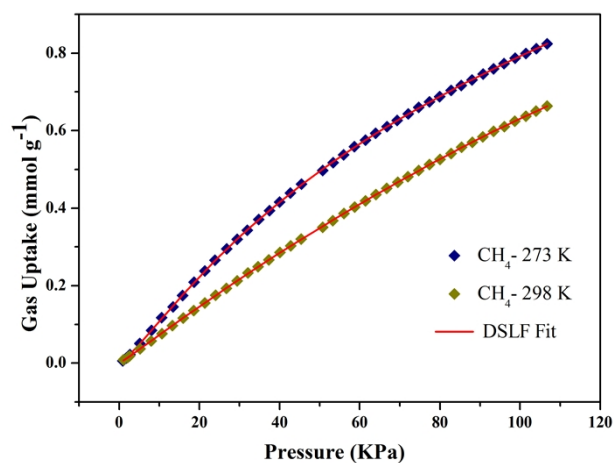


Figure S10. DSLF models fitting for the N₂ adsorption isotherms of NJFU-2a. Dots are experimental data; lines are fitting curves.

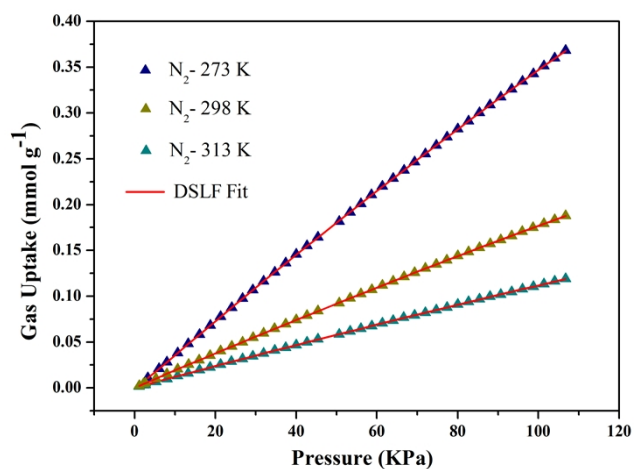


Figure S11. Mixture adsorption isotherms and adsorption selectivity predicted by IAST of NJFU-2a for CO₂ (15%) and N₂ (85%) at 298 K.

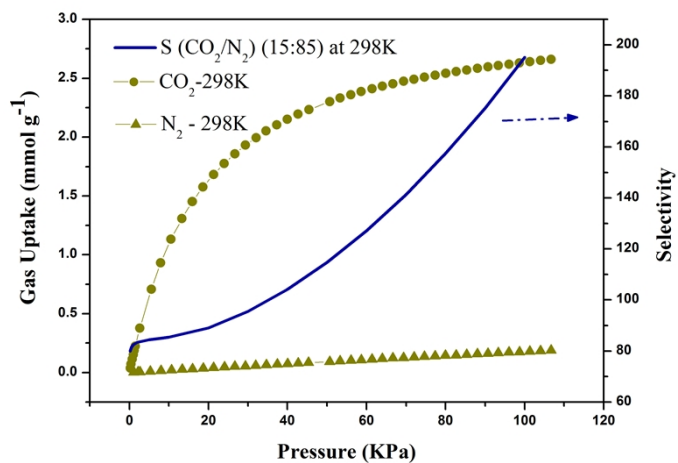


Figure S12. Mixture adsorption isotherms and adsorption selectivity predicted by IAST of NJFU-2a for CO₂ (50%) and CH₄ (50%) at 298 K.

