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Supporting information

Construction of rigid amine-linked three-dimensional covalent

organic frameworks for selectively capturing carbon dioxide

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1. Supporting Methods

1.1 General materials and methods

The reagents and solvents employed were commercially available and used without further purification. ¹H and ¹³C NMR spectra were performed on 400 MHz spectrometers (Bruker AVANCE NEO 400 Ascend) in the indicated solvents at room temperature. Chemical shifts were reported in δ (ppm) relative to TMS (δ = 0). Unless stated otherwise, column chromatography was carried out on silica gel (200-300 mesh). Thin-layer chromatography (TLC) analysis was performed on precoated silica gel plates (0.2 mm thick). Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometery (MALDI-TOF MS) analysis was performed on a Bruker Microflex-LRF mass spectrometer in positive ion, reflection mode.

Scanning Electron Microscope (SEM, JEOL, JSM-7500F, Japan) was used to investigate the structure of the as-prepared **SP-CA-COF-IM** and **SP-CA-COF-AM** at an accelerating voltage of 5.0 kV.

Transmission electron microscope (TEM) was performed on a JEM-2100 electron microscope with an accelerating voltage of 200 kV.

TGA was carried out on an American TA-Q20 in a nitrogen atmosphere using a 10 °C/min ramp without equilibration delay.

Powder X-ray diffraction (PXRD) patterns were obtained on a PANalytical Empyrean X-Ray diffractometer with Cu K α line focused radiation at 40 kV and 40 mA from $2\theta = 2^{\circ}$ up to 40° with 0.02° increment by Bragg-Brentano. The powdered sample was added to the glass and compacted for measurement.

N₂ adsorption isotherms were measured up to 1 bar at 77 K using a Micrometrics ASAP 2460 surface area analyzer. CO₂ adsorption isotherms were measured at 273 and 298 K up to 1000 mbar. Prior to measurements, samples (ca. 40 mg) were degassed for over 12 h at 120 °C. High-purity gas (99.999%) was used for adsorption experiments. Oil-free vacuum pumps and oil-free pressure regulators were used for measurements to

prevent contamination of the samples during the degassing process and isotherm measurement.

1.2 Synthesis procedure



Compounds A and B were synthesized based on the previously published literature (Fig. 1).^{1,2}



Model compound C

3,3',6,6'-tetraamine-9,9'-spirobifluorene (10 mg, 0.026mmol) and benzaldehyde (11.02 mg, 0.10 mmol) were added to ethanol (3 mL) and chloroform (3 mL). The mixture was refluxed overnight and then dropped into petroleum ether. The precipitate was centrifuged and washed with ethanol and acetone before being dried to obtain a light yellow solid (17.8 mg, 92% yield). The ¹H NMR, ¹³C NMR, and MS results can be found in our previous work.³



Model compound D

Model compound **C** (10 mg, 0.014 mmol) was stirred in 3 mL chloroform at 25 °C, conducted by directly adding NaBH(OAc)₃ (90 mg, 0.42 mmol, 30 equiv.) into the reaction system. After 24 h, the solids were filtered off, and the filtrate was neutralized with a saturated NaHCO₃ solution. The organic phase was dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was dissolved in the minimum amount of CH₂Cl₂ and filtered through a plug of silica gel using CH₂Cl₂ as eluent, causing the precipitation of pure model compound **D** as a light yellow solid (5.2 mg, 51% yield). ¹H NMR (400 MHz, CDCl₃) 7.34 (d, J = 8.1 Hz, 2H), 7.28 (t, J = 7.4 Hz, 2H), 7.22 (d, J = 7.1 Hz, 1H), 6.93 (s, 1H), 6.48 (d, J = 8.2 Hz, 1H), 6.33 (d, J = 10.4 Hz, 1H), 5.32 – 5.23 (m, 1H), 4.30 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) 150.20, 142.65, 139.71, 138.85, 128.11, 127.34, 126.83, 123.87, 112.66, 104.29, 63.15, 48.59 ppm. MALDI-TOF MS: calcd for C₅₃H₄₄N₄ [M + H]⁺: 736.4; found: 736.6 (Fig. S13).

Synthesis of SP-CA-COF-IM

A (20 mg, 0.053 mmol) and B (40 mg, 0.053 mmol) were administered into a mixture of mesitylene (1 mL), benzyl alcohol (1 mL), and 6 M acetic acid (200 μ L) and then heated up to 120 °C for 7 days. The obtained precipitates were then collected, washed with THF, and dried at 120 °C under vacuum for 12 h to give a light-yellow powder with a yield of 79%.

Synthesis of SP-CA-COF-AM

SP-CA-COF-IM (40 mg) and NaBH(OAc)₃ (400 mg, 1.89 mmol) were dispersed into 60 mL chloroform. The reaction system was stirred at 25 °C for 2 days. The resulting mixture was filtered, and the resulting filtered material was washed with water and then dried; in this way light-yellow powders of SP-CA-COF-AM were obtained with a yield of 82%.

L. Z. and D. W. carried out the synthesis and characterization analysis; M. C. performed the simulation; X. J. and Z. L helped with the synthesis; L. H. and C. L.

supervised the carrying out of the COF synthesis; and Y. Z. contributed to the conception of the project, guided the project, and wrote the paper.

1.3 References

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2. Supporting Figures and Legends



Fig. S1. FT-IR spectra of reference compounds C and D.



Fig. S2. SEM images of **SP-CA-COF-IM** (a, b), and **SP-CA-COF-AM** (e, f). TEM images of **SP-CA-COF-IM** (c, d), and **SP-CA-COF-AM** (g, h).



Fig. S3. TGA curves of SP-CA-COF-IM and SP-CA-COF-AM.



Fig. S4. The experimental PXRD profiles of **SP-CA-COF-IM** (purple) compared with PXRD profiles calculated from **SP-CA-COF-IM** models with different degrees of interpenetration.



Fig. S5. The experimental PXRD profiles of **SP-CA-COF-AM** (purple) compared with PXRD profiles calculated from **SP-CA-COF-AM** models with different degrees of interpenetration.



Fig. S6. The simulated crystal model of SP-CA-COF-IM.



Fig. S7. The N₂ and CO₂ adsorption isotherms of SP-CA-COF-AM at 298 K.



Fig. S8. CO₂ adsorption isotherms of SP-CA-COF-AM in three cycles at 298 K



Fig. S9. Density field map of CO_2 at 10 bar for SP-CA-COF-IM (a, 298.15 K; b,

273.15 K) and $\ensuremath{\textbf{SP-CA-COF-AM}}$ (c, 298.15 K; d, 273.15 K), respectively.



Fig. S10. Digital photograph of SP-CA-COF-IM (a) and SP-CA-COF-AM (b).



Fig. S11. ¹H NMR spectrum of the reference compound D in CDCl₃.



Fig. S12. ¹³C NMR spectrum of the reference compound **D** in CDCl₃.



Fig. S13. MALDI mass spectrum of reference compound D.