

Supporting Information

Thiophene-based conjugated microporous polymers: preparation, porosity, exceptional carbon dioxide absorption and selectivity

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Section A. Materials and methods

1,3,5-Triethynylbenzene was purchased from TCI. 2,5-Dibromothiophene-3-carboxylic acid was purchased from Alfa. Tetrakis(triphenylphosphine)palladium(0), copper(I) iodide and tetra(4-bromophenyl)methane were purchased from Aladdin. All the solvents used were purchased from Aladdin.

^1H NMR spectra were recorded on Bruker Avance III models HD 400 NMR spectrometers, where chemical shifts (δ in ppm) were determined with a residual proton of the solvent as standard. Fourier transform Infrared (FT-IR) spectra were recorded on a Perkin-Elmer model FT-IR-frontier infrared spectrometer. The solution UV-visible analyzer was used for Shimadzu UV-3600. Solid-state ^{13}C CP/MAS NMR measurements were recorded using a Bruker AVANCE III 400 WB spectrometer at a MAS rate of 5 kHz and a CP contact time of 2 ms. Photoluminescence spectra were recorded on a Shimadzu F-4600 spectrometer (JAPAN) spectrofluorometer. Field-emission scanning electron microscopy (FE-SEM) images were performed on a JEOL model JSM-6700 operating at an accelerating voltage of 5.0 kV. The samples were prepared by drop-casting a THF suspension onto mica substrate and then coated with gold. High-resolution transmission electron microscopy (HR-TEM) images were obtained on a JEOL model JEM-3200 microscopy. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from $2\theta = 1.5^\circ$ up to 60° with 0.02° increment. The elemental analysis was carried out on a EuroEA-3000. TGA analysis was carried out using a Q5000IR analyser (TA Instruments) with an automated vertical overhead thermobalance. Before measurement, the samples were heated at a rate of 5°C min^{-1} under a nitrogen atmosphere.

Nitrogen sorption isotherms were measured at 77 K with ASIQ (iQ-2) volumetric adsorption analyzer. Before measurement, the samples were degassed in vacuum at 150°C

for more than 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume. The nonlocal density functional theory (NLDFT) method was applied for the estimation of pore size and pore size distribution.

Carbon dioxide sorption isotherms were measured at 298 K and 273 K with a Bel Japan Inc. model BELSORP-max analyzer, respectively. Before measurement, the samples were also degassed in vacuum at 120 °C for more than 10 h.

Carbon dioxide sorption isotherms were measured at 318 K and 60 bar with a iSorbHP2 analyzer, respectively. Before measurement, the samples were also degassed in vacuum at 120 °C for more than 10 h.

Methane and nitrogen sorption isotherms were measured at 273 K with a Bel Japan Inc. model BELSORP-max analyzer, respectively. Before measurement, the samples were also degassed in vacuum at 120 °C for more than 10 h.

Section B. Synthetic procedures

Synthesis of tetrakis(4-((trimethylsilyl)ethynyl)phenyl)methane^{S1}

Tetra(4-bromophenyl)methane (2.04 g, 3.16 mmol), PdCl₂(PPh₃)₂ (0.135 g, 0.18 mmol), CuI (0.024 g, 0.125 mmol), and PPh₃ (0.1 g, 0.38 mmol) were put into a 250 mL round-bottom flask; then the flask exchanged 3 cycles under vacuum/N₂, anhydrous iPr₂NH (30 mL) and trimethylsilylacetylene (2.2 mL, 30.37 mmol) was added via a syringe under the N₂. The reaction mixture was brought to reflux at 90 °C for 24 h, and then cooled down to room temperature. Solvent was removed in vacuum, and CHCl₃ was added to dissolve the residue

and filtered through a pad of Celite. The filtrate was washed with dilute Na₂EDTA solution and then dried over anhydrous Na₂SO₄; the solution was concentrated, and ethanol was added to obtain tetra(4-trimethylsilylacetylenophenyl)methane as a white solid product (80% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.26 (d, 8H), 6.85 (d, 8H), 0.26 (s, 36H).

Synthesis of tetrakis(4-ethynylphenyl)methane^{S1}

NaOH (0.98 g, 24.6 mmol) was dissolved in 10 mL of CH₃OH, then added to a solution of tetrakis(4-((trimethylsilyl)ethynyl)phenyl)methane (1.8g, 1.2 mmol) in 20 mL of CH₂Cl₂, and then stirred for 6 h at room temperature. The reaction mixture was washed with water, and the aqueous phase was extracted with CH₂Cl₂, and the combined organic phases were washed with brine, and then dried over anhydrous Na₂SO₄. The solution was concentrated, and ethanol was added to the solution. Tetrakis(4-ethynylphenyl)methane was obtained as light yellow solid (83% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.39 (d, 8H), 7.12 (d, 8H), δ 3.06 (s, 4H).

Synthesis of *p*-Tetrabromotetraphenylethene (TBTPE)^{S2}

Powdered 1,1,2,2-tetraphenylethene (5.00 g, 15.0 mmol) was treated with bromine (7.50 mL, 0.15 mol) and the mixture was kept for 16 h at room temperature. The resulting solid was dissolved in hot toluene (120 mL), concentrated to about 20 mL, and the precipitate was isolated. Purification using flash chromatography on SiO₂ (hexanes/CH₂Cl₂, 20:1 in vol.) gives TBTPE as a colorless solid (5.94 g) in 61% yield. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.26 (d, 8H), 6.85 (d, 8H).

Synthesis of 1,1,2,2-tetrakis[4-(trimethylsilylethynyl)phenyl]ethene^{S3}

TBTPE (1 g, 1.54 mmol) and PdCl₂(PPh₃)₂ (25.2 mg, 0.036 mmol) and CuI (3.6 mg, 0.0185 mmol) were put in to a 100 mL round-bottom flask, then the flask exchanged 3 cycles under vacuum/N₂, then added to 50 mL diethylamine. The flask was degassed by freeze-pump-thaw for 3 times, then warmed to R.T., refilled with N₂, trimethylsilylacetylene(1 mL, 7.392 mmol) was slowly added via a syringe. The mixture was heated at 50 °C for 15 h. After this the reaction mixture was cooled to room temperature, concentrated to about 10 mL. The crude product was purified by silica gel column chromatography using hexane as eluent. A white solid was obtained (72% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm): 7.23 (d, 8H), 6.92 (d, 8H), 0.26 (s, 36H).

Synthesis of 1,1,2,2-tetrakis(4-ethynylphenyl)ethene^{S3}

1,1,2,2-Tetrakis(4-(trimethylsilylethynyl)phenyl)ethene (1.5 g, 2.1 mmol) and THF (40 mL) were placed were put into a 250 mL round-bottom flask. Then, KOH (1.8 g, 32 mmol) dissolved in 40 mL of methanol was added. The mixture was stirred at room temperature overnight. After most of the solvent was evaporated, 100 mL of 1 M aqueous HCl solution was added and the mixture extracted with dichlormethane three times. The organic phases were combined and washed with water and brine and then dried over MgSO₄. After filtration and solvent evaporation, the crude product was purified by a silica gel column chromatography using hexane/dichlormethane (100:1 by volume) mixture as eluent. A yellow solid was obtained (81% yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.28 (d, 8H), 6.93 (d, 8H), 3.06 (s, 4H).

Synthesis of SCMP-COOH@1

2,5-Dibromothiophene-3-carboxylic acid (174 mg, 0.6 mmol) and 1,3,5-triethynylbenzene (60 mg, 0.4 mmol) were put into a 50 mL two-necked round-bottom flask, then the flask exchanged 3 cycles under vacuum/N₂. Then added to 2 mL DMF and 2 mL triethylamine, the flask was further degassed by three freeze-pump-thaw cycles, purged with N₂. When the solution had reached reaction temperature, a slurry of tetrakis(triphenylphosphine)palladium(0) (27.7 mg, 0.024 mmol) in the 1 mL DMF and copper(I) iodide (5.7 mg, 0.032 mmol) in the 1 mL Et₃N was added, and the reaction was stirred at 120 °C under nitrogen for 48 h. The solid product was collected by filtration and washed well hot reaction solvent for 4 times with THF, methanol, acetone, and water, respectively. Further purification of the polymer was carried out by Soxhlet extraction with methanol, and THF for 24 h, respectively, to give SCMP-COOH@1 as yellow solid (93.6% yield). Elemental Analysis (%) Calcd. (Actual value for an infinite 2D polymer) C 63.14, H 3.18, O 16.82, S 16.86. Found: C 66.02, H 3.06, O 14.86, S 15.07.

Synthesis of SCMP-COOH@2

2,5-Dibromothiophene-3-carboxylic acid (150 mg, 0.50 mmol) and 1,1,2,2-tetrakis(4-ethynylphenyl)ethane (98.3 mg, 0.26 mmol) were put into a 50 mL two-necked round-bottom flask, then the flask exchanged 3 cycles under vacuum/N₂. Then added to 2 mL DMF and 2 mL triethylamine, the flask was further degassed by freeze-pump-thaw for 3 times. When the solution had reached reaction temperature, a slurry of tetrakis(triphenylphosphine)palladium(0) (17.9 mg, 0.015 mmol) in the 1 mL DMF and copper(I) iodide (3.7 mg, 0.02 mmol) in the 1 mL Et₃N was added, and the reaction was stirred at 120 °C under nitrogen for 48 h. The solid product was collected by filtration and washed well hot reaction solvent for 4 times with THF, methanol, acetone, and water,

respectively. Further purification of the polymer was carried out by Soxhlet extraction with methanol, and THF for 24 h, respectively, to give SCMP-COOH@2 as yellowish-brown powder (94.3% yield). Elemental Analysis (%) C 70.43, H3.67, O12.94, S12.97. Found: C 68.54, H3.78, O13.04, S11.88.

Synthesis of SCMP-COOH@3

2,5-Dibromothiophene-3-carboxylic acid (125 mg, 0.43 mmol) and tetrakis(4-ethynylphenyl)methane (100 mg, 0.22 mmol) were put into a 50 mL two-necked round-bottom flask, then the flask exchanged 3 cycles under vacuum/N₂. Then added to 2 mL DMF and 2 mL triethylamine, the flask was further degassed by freeze-pump-thaw for 3 times. When the solution had reached reaction temperature, a slurry of tetrakis(triphenylphosphine)palladium(0) (19.9 mg, 0.017 mmol) in the 1 mL DMF and copper(I) iodide (3.1 mg, 0.017 mmol) in the 1 mL Et₃N was added, and the reaction was stirred at 120 °C under nitrogen for 48 h. The solid product was collected by filtration and washed well hot reaction solvent for 4 times with THF, methanol, acetone, and water, respectively. Further purification of the polymer was carried out by Soxhlet extraction with methanol, and THF for 24 h, respectively, to give SCMP-COOH@3 as yellow powder (88.7% yield). Elemental Analysis (%) C 69.11, H 3.06, O 13.90, S 13.93. Found: C 70.20, H3.45, O11.88, S11.26.

Section C. FT-IR spectral profiles

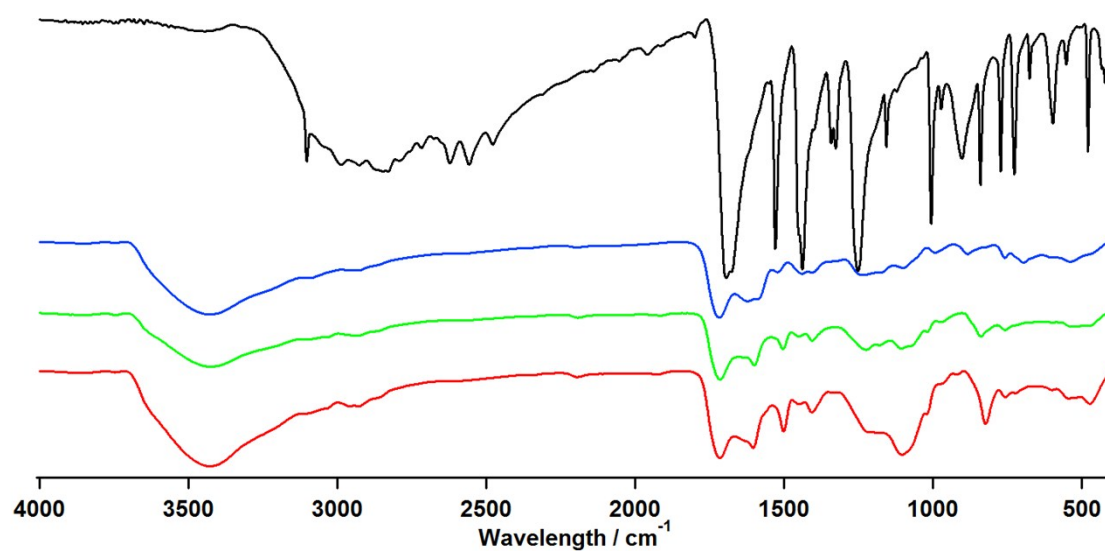


Fig. S1 FT-IR spectra of 2,5-dibromothiophene-3-carboxylic acid (DTCA) (black), SCMP-COOH@1 (blue), SCMP-COOH@2 (green) and SCMP-COOH@3 (red).

Section D. The solid-state ^{13}C CP-MAS NMR

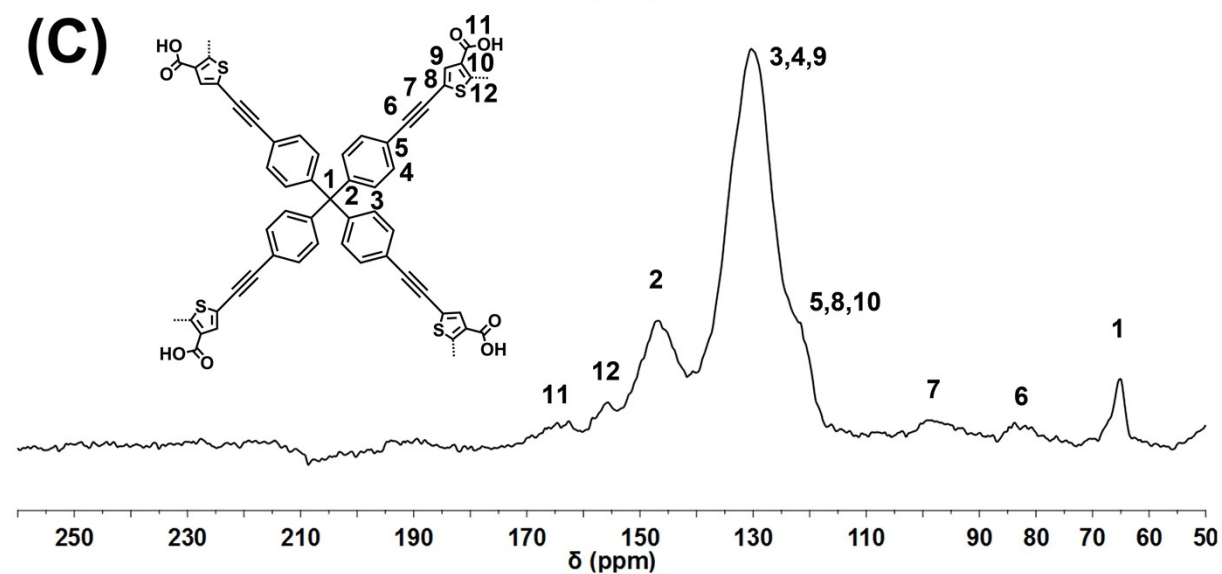
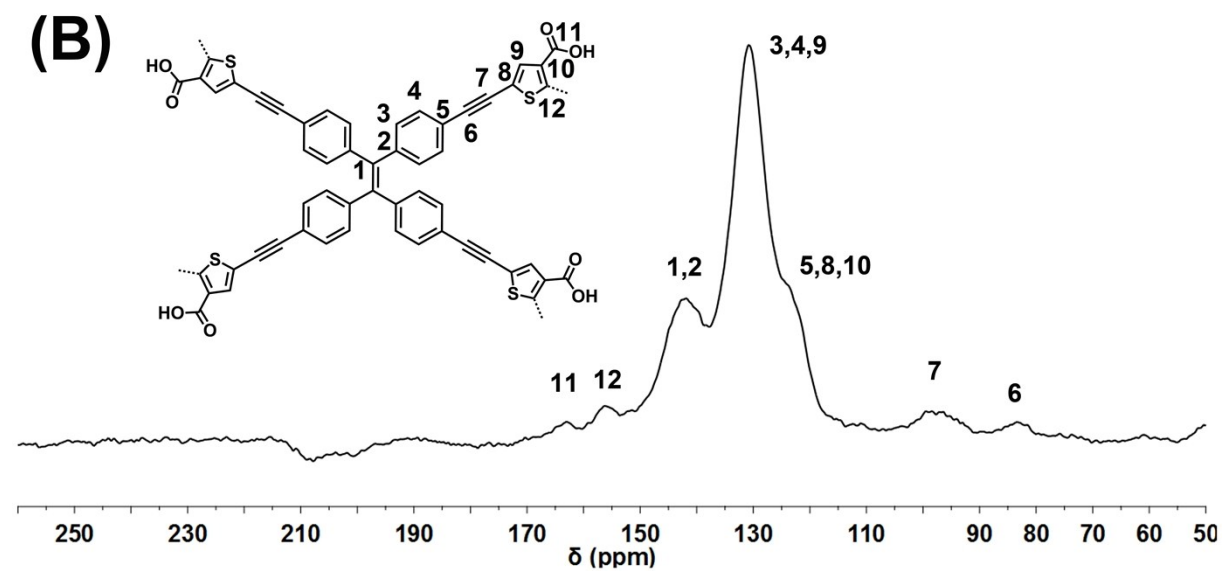
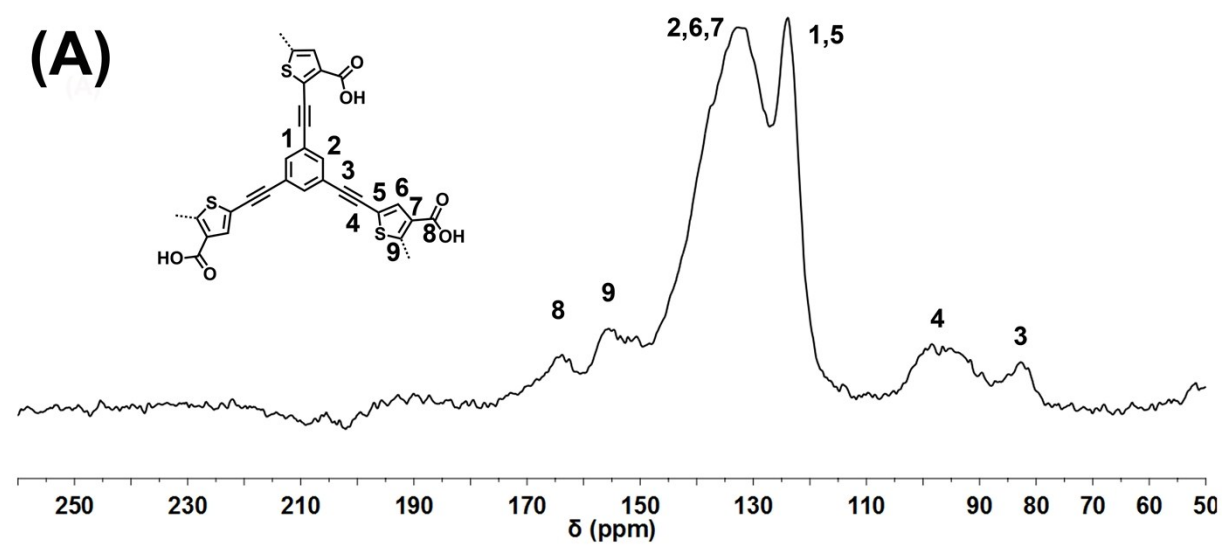


Fig. S2 The solid-state ^{13}C CP-MAS NMR of (A) SCMP-COOH@1, (B) SCMP-COOH@2, and (C) SCMP-COOH@3.

Section E. TGA curves

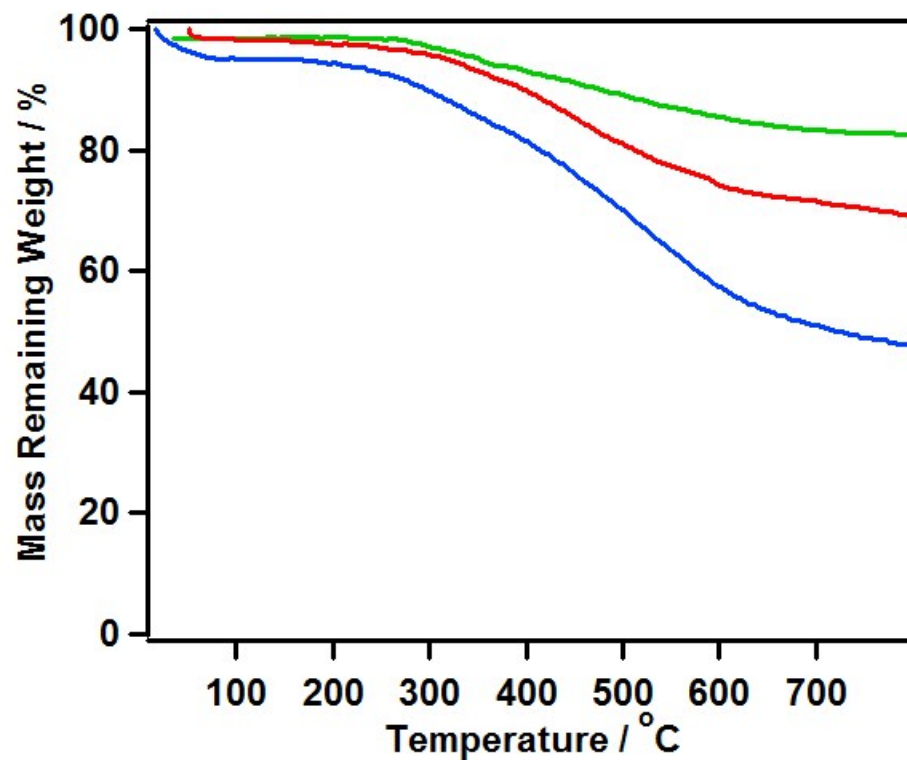


Fig. S3 TGA curves of SCMP-COOH@1 (blue), SCMP-COOH@2 (green), and SCMP-COOH@3 (red).

Section F. HR-TEM images

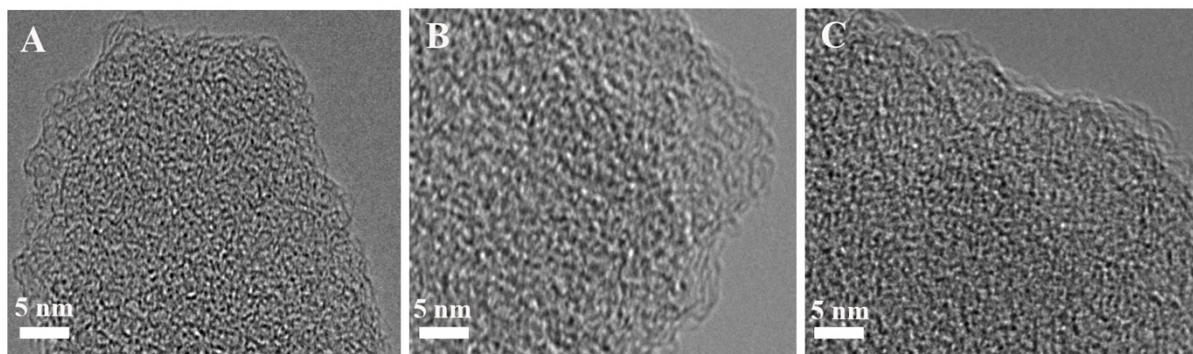


Fig. S4 HR-TEM images of (A) SCMP-COOH@1, (B) SCMP-COOH@2, and (C) SCMP-COOH@3.

Section G. Powder X-ray diffraction patterns

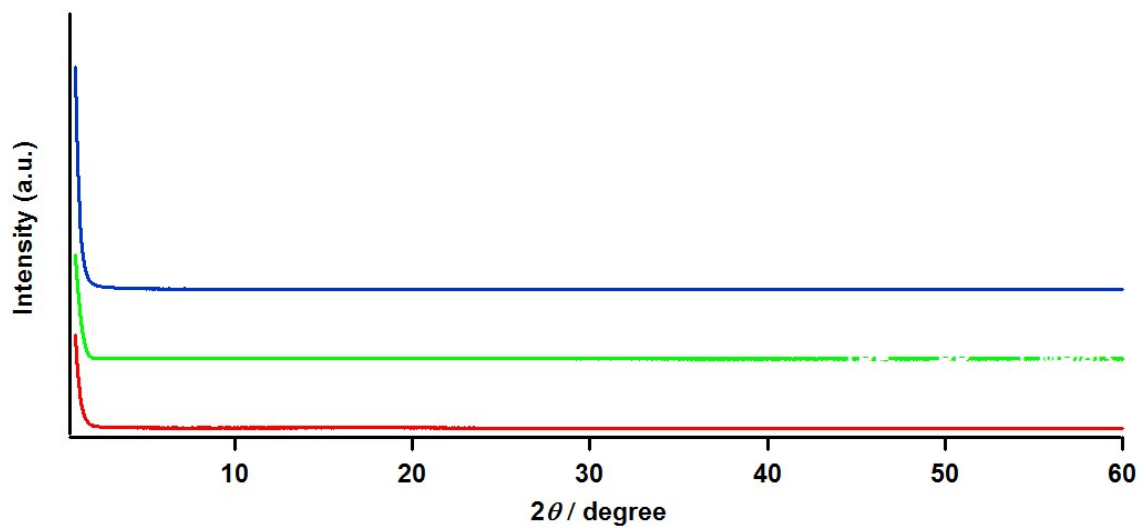


Fig. S5 Powder X-ray diffraction profiles of SCMP-COOH@1 (blue), SCMP-COOH@2 (green), and SCMP-COOH@3 (red).

Section H. The CO₂ uptake of SCMPs under wet conditions

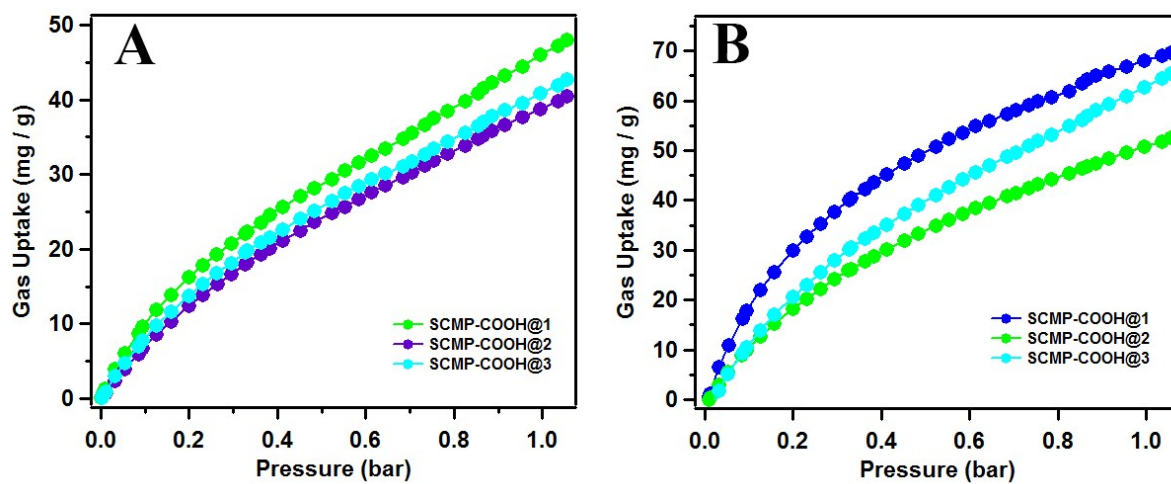


Fig. S6 The CO₂ uptake of SCMPs under wet conditions (A) at 298 K and 1.0 bar, and (B) at 273 K and 1.0 bar.

Section I. Gas adsorption isotherms

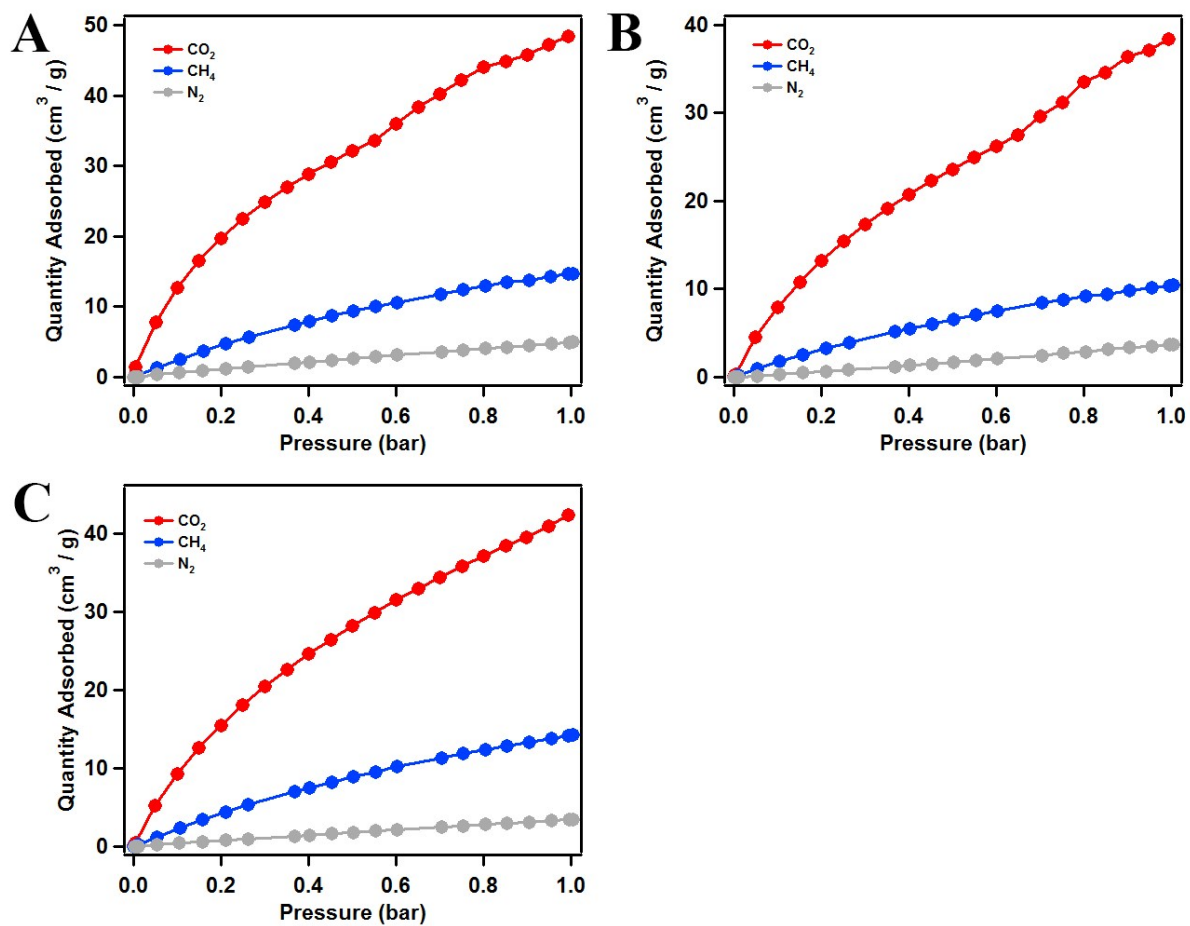


Fig. S7 Gas adsorption isotherms of polymers SCMP-COOH@1 (A), SCMP-COOH@2 (B), and SCMP-COOH@3(C)

at 273 K and 1.0 bar.

Section J. Corresponding data of gas selectivity analyses

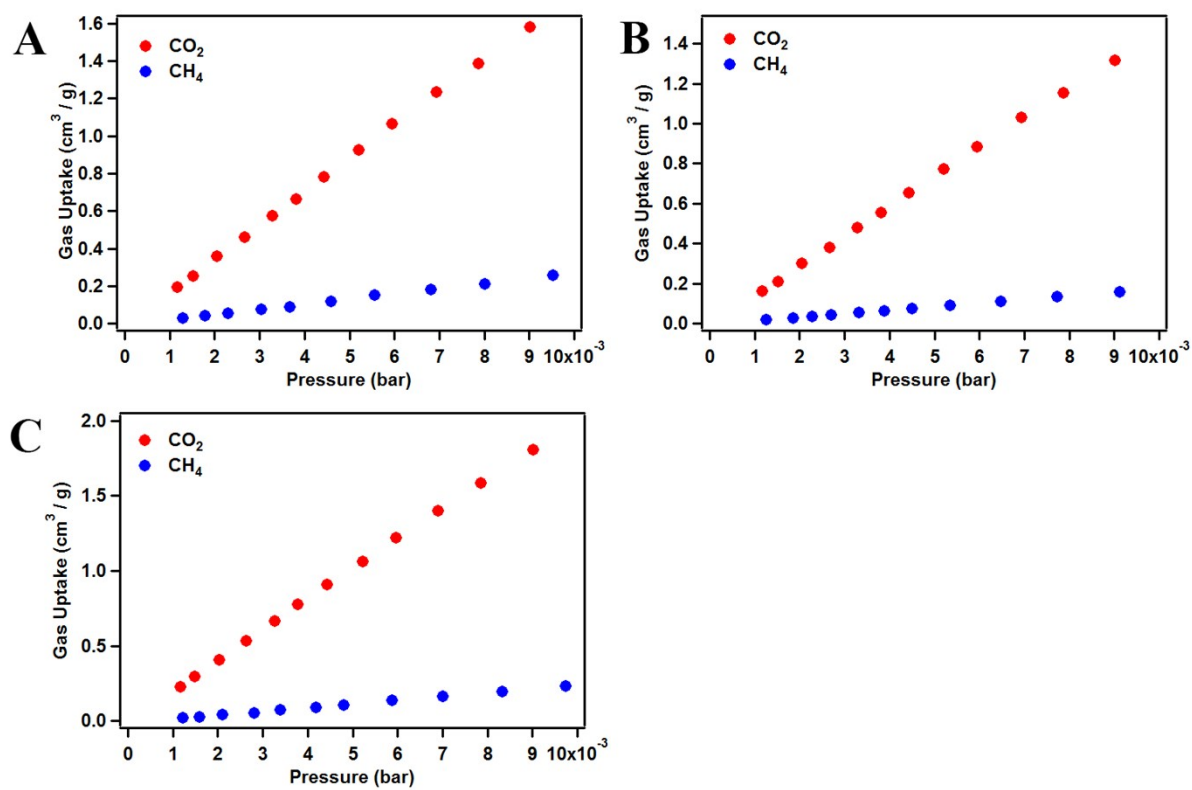


Fig. S8 CO₂/CH₄ initial slope selectivity studies for SCMP-COOH@1 (A), SCMP-COOH@2 (B), and SCMP-COOH@3 (C) at 273 K.

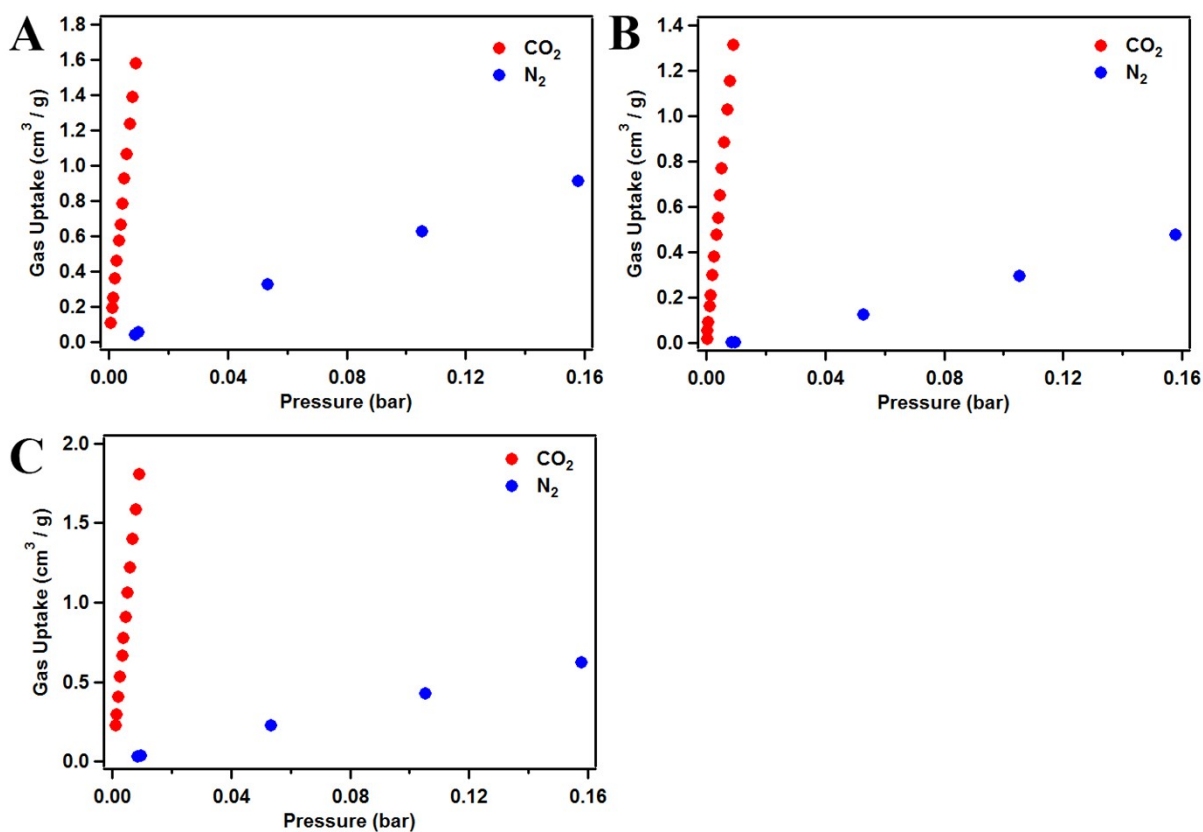


Fig. S9 CO₂/N₂ initial slope selectivity studies for SCMP-COOH@1 (A), SCMP-COOH@2 (B), and SCMP-COOH@3 (C) at 273 K.

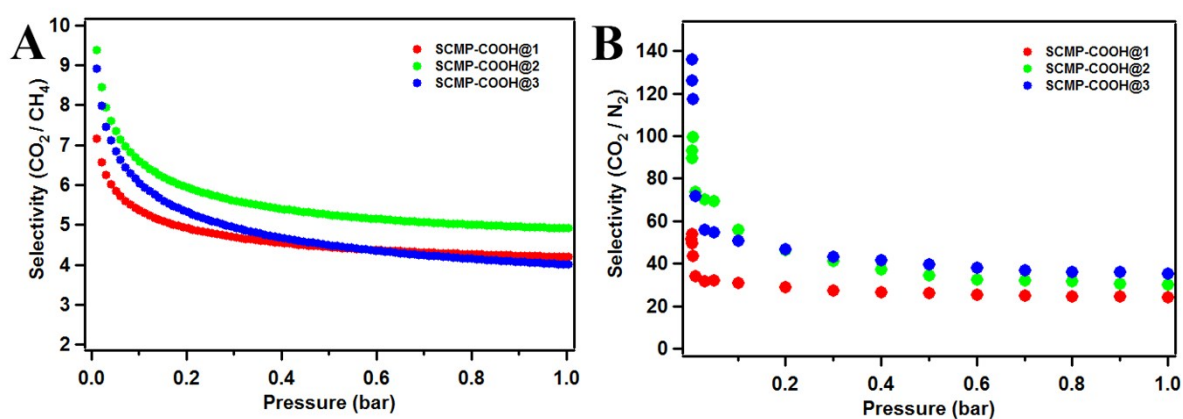


Fig. S10 (A) CO₂/CH₄ selectivity of SCMP-COOH@1-3 for a molar ratio of 50/50 at 273 K, (B) CO₂/N₂ selectivity of SCMP-COOH@1-3 for a molar ratio of 15/85 at 273 K

Table S1 Porosity properties and gas uptake for the polymers

Polymers	$S_{\text{BET}}^{\text{a}}$ /m ² g ⁻¹	$S_{\text{micro}}^{\text{b}}$ /m ² g ⁻¹	$V_{\text{total}}^{\text{c}}$ /cm ³ g ⁻¹	V_{micro} /cm ³ g ⁻¹	CO ₂ /N ₂ ^d selectivity at 273 K	CO ₂ /CH ₄ ^d selectivity at 273 K	CO ₂ /N ₂ ^e selectivity at 273 K	CO ₂ /CH ₄ ^e selectivity at 273 K
SCMP-COOH@1	911	474	1.50	0.78	24.9	4.4	24.8	5.1
SCMP-COOH@2	622	313	0.97	0.49	30.5	5.2	29.4	6.8
SCMP-COOH@3	820	473	1.32	0.76	36.2	4.5	35.7	5.8

^aBrunauer-Emmett-Teller surface area. ^bTotal pore volume determined from the N₂ isotherm at P/P₀ = 0.995. ^cMicro-pore volume determined from the N₂ isotherm at P/P₀ = 0.050. ^dSelectivity was calculated by IAST method for CO₂/N₂ (at mole ratio of 15/85) and CO₂/CH₄ (at mole ratio of 50/50) at 273 K. ^eSelectivity was calculated by Henry law for CO₂/N₂ (at mole ratio of 15/85) and CO₂/CH₄ (at mole ratio of 50/50) at 273 K.

Table S2 . The CO₂ uptakes at 1.0 bar of SCMPs

Polymers	Dried at 298 K (mg / g)	Humidified at 298 K (mg / g)	Dried at 273 K (mg / g)	Humidified at 273 K (mg / g)
SCMP-COOH@1	61	48	96	69
SCMP-COOH@2	47	36	76	52
SCMP-COOH@1	55	43	84	61

Section J. Supporting references

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S2. Schultz, A.; Laschat, S.; Diele, S.; Nimtz, M. *Eur. J. Org. Chem.* **2003**, 2829-2839.

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