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.

$^1$H NMR spectra were recorded on Bruker AvanceIII models HD 400NMR spectrometers, where chemical shifts ($\delta$ in ppm) were determined with a residual proton of the solvent as standard. Fourier transform Infrared (FT-IR) spectra were recorded on a Perkinelmer model FT-IR-frontier infrared spectrometer. The solution UV-visible analyzer was used for shmadzu UV-3600. Solid-state $^{13}$C CP/MAS NMR measurements was 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 shmadzu 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$^\circ$ with 0.02$^\circ$ 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

Tetra(4-bromophenyl)methane (2.04 g, 3.16 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.135 g, 0.18 mmol), CuI (0.024 g, 0.125 mmol), and PPh$_3$ (0.1 g, 0.38 mmol) were put into a 250 mL round-bottom flask; then the flask exchanged 3 cycles under vacuum/N$_2$, anhydrous iPr$_2$NH (30 mL) and trimethylsilylacetylene (2.2 mL, 30.37 mmol) was added via a syringe under the N$_2$. 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 CHCl$_3$ was added to dissolve the residue.
and filtered through a pad of Celite. The filtrate was washed with dilute Na$_2$EDTA solution and then dried over anhydrous Na$_2$SO$_4$; the solution was concentrated, and ethanol was added to obtain tetra(4-trimethylsilylacetylenephenyl)methane as a white solid product (80% yield).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 7.26 (d, 8H), 6.85 (d, 8H), 0.26 (s, 36H).

**Synthesis of tetrakis(4-ethynylphenyl)methane**

NaOH (0.98 g, 24.6 mmol) was dissolved in 10 mL of CH$_3$OH, then added to a solution of tetrakis(4-((trimethylsilyl)ethynyl)phenyl)methane (1.8g, 1.2 mmol) in 20 mL of CH$_2$Cl$_2$, and then stirred for 6 h at room temperature. The reaction mixture was washed with water, and the aqueous phase was extracted with CH$_2$Cl$_2$, and the combined organic phases were washed with brine, and then dried over anhydrous Na$_2$SO$_4$. The solution was concentrated, and ethanol was added to the solution. Tetrakis(4-ethynylphenyl)methane was obtained as light yellow solid (83% yield). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 7.39 (d, 8H), 7.12 (d, 8H), 3.06 (s, 4H).

**Synthesis of $p$-Tetrabromotetraphenylethene (TBTPE)**

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 SiO$_2$ (hexanes/CH$_2$Cl$_2$, 20:1 in vol.) gives TBTPE as a colorless solid (5.94 g) in 61% yield. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 7.26 (d, 8H), 6.85 (d, 8H).
Synthesis of 1,1,2,2-tetrakis[4-(trimethylsilyl)ethynyl]phenyl]ethene\textsuperscript{S3}

TBTPE (1 g, 1.54 mmol) and PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} (25.2 mg, 0.036 mmol) and CuI (3.6 mg, 0.0185 mmol) were put into a 100 mL round-bottom flask, then the flask exchanged 3 cycles under vacuum/N\textsubscript{2}, then added to 50 mL diethylamine. The flask was degassed by freeze-pump-thaw for 3 times, then warmed to R.T., refilled with N\textsubscript{2}, 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). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta\) (ppm): 7.23 (d, 8H), 6.92 (d, 8H), 0.26 (s, 36H).

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

1,1,2,2-Tetrakis(4-(trimethylsilyl)ethynyl)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 MgSO\textsubscript{4}. 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). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) 7.28 (d, 8H), 6.93 (d, 8H), 3.06 (s, 4H).
**Synthesis of SCMP-COOH@1**

2.5-Dibromo thiophene-3-carboxylic acid (174 mg, 0.6 mmol) and 1,3,5-triethynyl benzene (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-Dibromo thiophene-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, H 3.67, O 12.94, S 12.97. Found: C 68.54, H 3.78, O 13.04, S 11.88.

**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, H 3.45, O 11.88, S 11.26.
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

(A)

(B)

(C)
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.

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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 CO$_2$ uptake of SCMPs under wet conditions

Fig. S6 The CO$_2$ 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 CO$_2$/CH$_4$ initial slope selectivity studies for SCMP-COOH@1 (A), SCMP-COOH@2 (B), and SCMP-COOH@3 (C) at 273 K.
Fig. S9 \( \text{CO}_2/\text{N}_2 \) initial slope selectivity studies for SCMP-COOH@1 (A), SCMP-COOH@2 (B), and SCMP-COOH@3 (C) at 273 K.

Fig. S10 (A) \( \text{CO}_2/\text{CH}_4 \) selectivity of SCMP-COOH@1-3 for a molar ratio of 50/50 at 273 K, (B) \( \text{CO}_2/\text{N}_2 \) 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

<table>
<thead>
<tr>
<th>Polymers</th>
<th>( S_{\text{BET}}^a ) /m² g⁻¹</th>
<th>( S_{\text{micro}}^b ) /m² g⁻¹</th>
<th>( V_{\text{total}}^c ) /cm³ g⁻¹</th>
<th>( V_{\text{micro}}^c ) /cm³ g⁻¹</th>
<th>( \text{CO}_2/\text{N}_2^d ) selectivity at 273 K</th>
<th>( \text{CO}_2/\text{CH}_4^d ) selectivity at 273 K</th>
<th>( \text{CO}_2/\text{N}_2^e ) selectivity at 273 K</th>
<th>( \text{CO}_2/\text{CH}_4^e ) selectivity at 273 K</th>
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<tbody>
<tr>
<td>SCMP-COOH@1</td>
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<td>474</td>
<td>1.50</td>
<td>0.78</td>
<td>24.9</td>
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<td>5.1</td>
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<td>313</td>
<td>0.97</td>
<td>0.49</td>
<td>30.5</td>
<td>5.2</td>
<td>29.4</td>
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<tr>
<td>SCMP-COOH@3</td>
<td>820</td>
<td>473</td>
<td>1.32</td>
<td>0.76</td>
<td>36.2</td>
<td>4.5</td>
<td>35.7</td>
<td>5.8</td>
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</table>

\(^a\)Brunauer-Emmett-Teller surface area. \(^b\)Total pore volume determined from the \( \text{N}_2 \) isotherm at \( P/P_0 =0.995 \). \(^c\)Micro-pore volume determined from the \( \text{N}_2 \) isotherm at \( P/P_0 = 0.050 \). \(^d\)Selectivity was calculated by IAST method for \( \text{CO}_2/\text{N}_2 \) (at mole ratio of 15/85) and \( \text{CO}_2/\text{CH}_4 \) (at mole ratio of 50/50) at 273 K. \(^e\)Selectivity was calculated by Henry law for \( \text{CO}_2/\text{N}_2 \) (at mole ratio of 15/85) and \( \text{CO}_2/\text{CH}_4 \) (at mole ratio of 50/50) at 273 K.

Table S2 . The \( \text{CO}_2 \) uptakes at 1.0 bar of SCMPs

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Dried at 298 K (mg / g)</th>
<th>Humidified at 298 K (mg / g)</th>
<th>Dried at 273 K (mg / g)</th>
<th>Humidified at 273 K (mg / g)</th>
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</thead>
<tbody>
<tr>
<td>SCMP-COOH@1</td>
<td>61</td>
<td>48</td>
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<td>69</td>
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<tr>
<td>SCMP-COOH@2</td>
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<td>SCMP-COOH@3</td>
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Section J. Supporting references
