Electronic Supplementary Information for

Synthesis of 9,9'-Spirobifluorene-Based Conjugated Microporous Polymers
by FeCl₃-mediated Polymerization

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Table of Contents

1. FT-IR spectra of COPs and carbonized COPs S2
2. XRD patterns of COPs and carbonized COPs S3
3. TG analysis of COPs and carbonized COPs S4
4. TG profiles of COPs under carbonization condition S5
5. SEM observation of COPs and carbonized COPs S6
6. Synthesis of COP-3F S7
7. Raman spectra of carbonized COPs S8
8. The t-plot analysis of nitrogen adsorption isotherms of COPs and carbonized COPs
   S8
9. The Dubinin-Radushkevich analysis of nitrogen adsorption isotherms of COPs and carbonized COPs S9
10. Pore distributions of COPs and carbonized COPs S10
11. Gas uptake ability of COPs and carbonized COPs S11-12
12. Reusability experiment of COPs and carbonized COPs for CO₂ uptake S12
1. FT-IR spectra of COPs and carbonized COPs.

The FT-IR spectra of COP-3, COP-3-rt and COP-3C were shown in Figure S1. These spectra were closely related with that of 9,9'-spirobifluorene. Several bands appeared around at 1400 cm$^{-1}$, 3000 cm$^{-1}$ are characteristics for aromatic C=C stretching, aromatic C-H stretching respectively, which accounts for the presence of spirobifluorene molecule in COP polymers.

The FT-IR spectra of carbonized COPs showed disappearance of absorption peaks from 800 to 2000 cm$^{-1}$ and around at 3000 cm$^{-1}$. This indicates the complete decomposition of organic groups and H$_2$ elimination from the framework in COPs by carbonization.

Figure S1. FT-IR absorption spectra of COPs and carbonized COPs. COP-3 (blue), COP-3-rt (red), COP-3C (black), 9,9'-spirobifluorene (gray), COP-3-600 (purple), COP-3-rt-600 (orange) and COP-3C-600 (green).
2. **XRD patterns of COPs and carbonized COPs.**

Powder X-ray diffraction (XRD) patterns of COPs show only broad peaks without any sharp diffraction peaks, indicating the amorphous-like pore wall structures (Figure S2a). The XRD patterns of carbonized COPs showed broad peak around at $2\theta = 23^\circ$, which probably depends on an interlayer structure of graphitic carbon (Figure S2b). However, the peaks are very broad, suggesting the amorphous structure of carbonized COPs.

![XRD patterns of COPs and carbonized COPs](image)

**Figure S2.** Powder X-ray diffraction patterns of (a) COPs and (b) carbonized COPs. COP-3 (blue), COP-3-rt (red), COP-3C (black), COP-3-600 (purple), COP-3-rt-600 (orange) and COP-3C-600 (green).
3. TG analysis of COPs and carbonized COPs.

Under nitrogen atmosphere, COP-3C showed almost no weight loss up to 500 °C, possibility due to the strong aromatic carbon-carbon covalent bonding network (Figure S3c). By comparison, COP-3 and COP-3-rt, which also contain aliphatic carbon-aromatic carbon and/or –oxygen bonding, displayed about 6 wt% weight losses from 300 °C to 500 °C (Figures S3b and c). On the other hand, the all of COPs showed significant weight losses over 350 °C under air atmosphere (Figures S3a-c). The carbonized COPs were stable up to 450 °C in air (~5 wt% mass loss) (Figure S3d).

Figure S3. TG profiles under nitrogen (red lines) air atmosphere (black lines) of (a) COP-3, (b) COP-3-rt and (c) COP-3C. (d) TG profiles under air atmosphere of carbonized COPs. COP-3-600 (purple), COP-3-rt-600 (orange) and COP-3C-600 (green).
4. TG profiles of COPs under carbonization condition.

TG analysis under carbonization condition showed that the char yields of COP-3C, COP-3-rt, and COP-3 were 90%, 72%, and 65%, respectively. This means 10-35% weight losses after the carbonization (Figure S4).

**Figure S4.** TG profiles of COPs under carbonization condition. COP-3 (blue line), COP-3-rt (red line) and COP-3C (black line).
5. SEM observation of COPs and carbonized COPs.

Figure S5. SEM images of (a) COP-3, (b) COP-3-rt, (c) COP-3C, (d) COP-3-600, (e) COP-3-rt-600 and (f) COP-3C-600.
6. Synthesis of COP-3F.

A mixture of 9,9'-dimethylfluorene (400 mg, 2.0 mmol) and FeCl₃ (817 mg, 5.0 mmol) were stirred in a 30 mL two-neck round bottom flask. The flask was thoroughly evacuated and filled with argon. Then, dry 1,2-dichloroethane (5-6 mL) was added and the mixture was stirred for 5 min. Later, the mixture was kept for reflux at 80 ºC for 24 h. After the reaction, the sample was filtered and washed with the same procedure for COP-3. The obtained powder was dried over under reduced pressure at 60 ºC to give COP-3F as bright yellow powder (240 mg, 60% yield).

![Figure S6](image.png)

**Figure S6** (a) The nitrogen adsorption/desorption isotherms of COP-3F and (b) t-plot for COP-3F.
7. Raman spectra of carbonized COPs.

![Raman Spectra](image)

**Figure S7.** Raman spectra of COP-3-600 (black), COP-3-rt-600 (red) and COP-3C-600 (blue).

8. The t-plot analysis of nitrogen adsorption isotherms of COPs and carbonized COPs

![t-plot Analysis](image)

**Figure S8.** The t-plot analysis of nitrogen adsorption isotherms of (a) COP-3 (blue), COP-3-rt (red) and COP-3C (black), and (b) COP-3-600 (purple), COP-3-rt-600 (orange) and COP-3C-600 (green).
9. The Dubinin-Radushkevich analysis of nitrogen adsorption isotherms of COPs and carbonized COPs

Figure S9. The Dubinin-Radushkevich (DR) plots analysis of nitrogen adsorption isotherms of (a) COP-3 (blue), COP-3-rt (red) and COP-3C (black), and (b) COP-3-600 (purple), COP-3-rt-600 (orange) and COP-3C-600 (green).
10. Pore distributions of COPs and carbonized COPs.

The pore distributions of COPs and carbonized COPs were obtained by QSDFT analysis of the isotherms, which showed that COPs and carbonized COPS contain micropores around 1 nm (Figures S10a-c).

![Figure S10](image)

**Figure S10.** The pore distributions of (a) COP-3 (blue) and COP-3-600 (purple), (b) COP-3-rt (red) and COP-3-rt-600 (orange), and (c) COP-3C (black) and COP-3C-600 (green).

11. Gas uptake ability of COPs and carbonized COPs
**Figure S11.** CO₂ uptake (at 273 K, 1 atm) changes during cycle adsorption measurement for (a) COP-3 (blue) and COP-3-600 (purple), (b) COP-3-rt (red) and COP-3-rt-600 (orange), and (c) COP-3C (black) and COP-3C-600 (green).

**Figure S12.** CH₄ adsorption (closed circles) and desorption (open circles) isotherms of (a) COP-3 (blue) and COP-3-600 (purple), (b) COP-3-rt (red) and COP-3-rt-600 (orange), and (c) COP-3C (black) and COP-3C-600 (green).
Figure S13. H$_2$ adsorption (closed circles) and desorption (open circles) isotherms at 77 K of (a) COP-3 (blue) and COP-3-600 (purple), (b) COP-3-rt (red) and COP-3-rt-600 (orange), and (c) COP-3C (black) and COP-3C-600 (green).

12. Reusability experiment of COPs and carbonized COPs for CO$_2$ uptake

Figure S14. CO$_2$ uptake (at 273 K, 1 atm) changes during cycle adsorption measurement for COP-3, COP-3-600, COP-3-rt-600