Electronic Supplementary Information for

Synthesis of 9,9'-Spirobifluorene-Based Conjugated Microporous Polymers by $FeCl_3$-mediated Polymerization

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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.

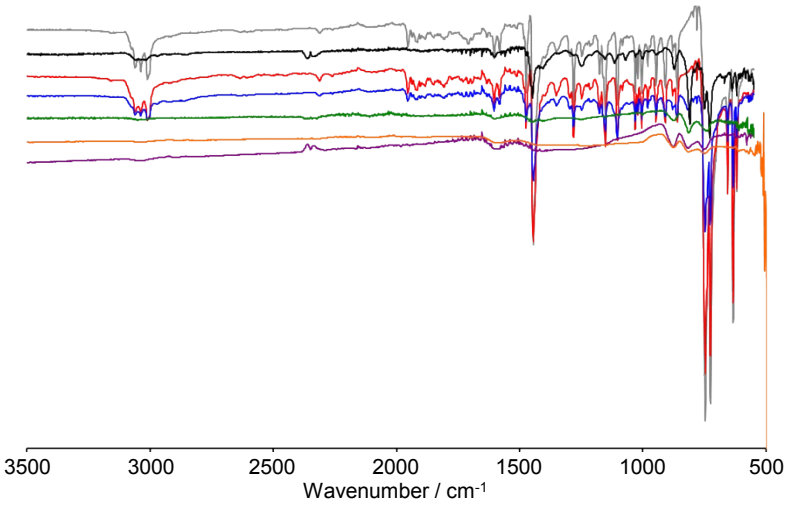

Figure S1. FT-IR absorption spectra of COPs and carbonized COPs. **COP-3** (blue), **COP-3-rt** (red), **COP-3C** (black), 9,9'-spirobifluorene (gray), **COP-3-600** (purple), **COP-3-rt-600** (orange) and **COP-3C-600** (green).

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 $2\theta = 23^{o}$, 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.

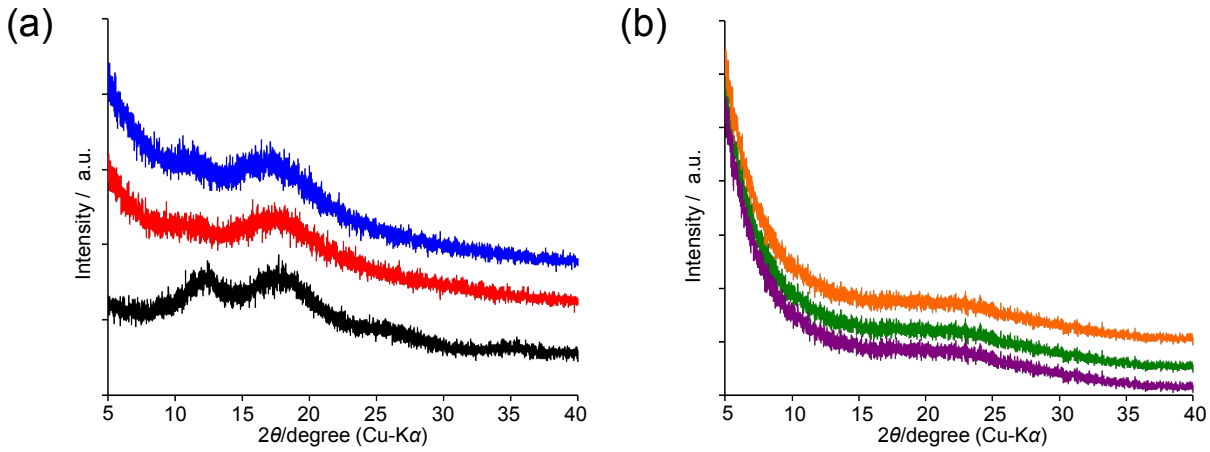

Figure S2. Powder X-ray diffraction patterns of (a) COPs and (b) carbonized COPs. **COP-3** (blue), **COP-3-rt** (red), **COP-3C** (black), **COP-3-600** (purple), **COP-3-rt-600** (orange) and **COP-3C-600** (green).

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 band, 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).

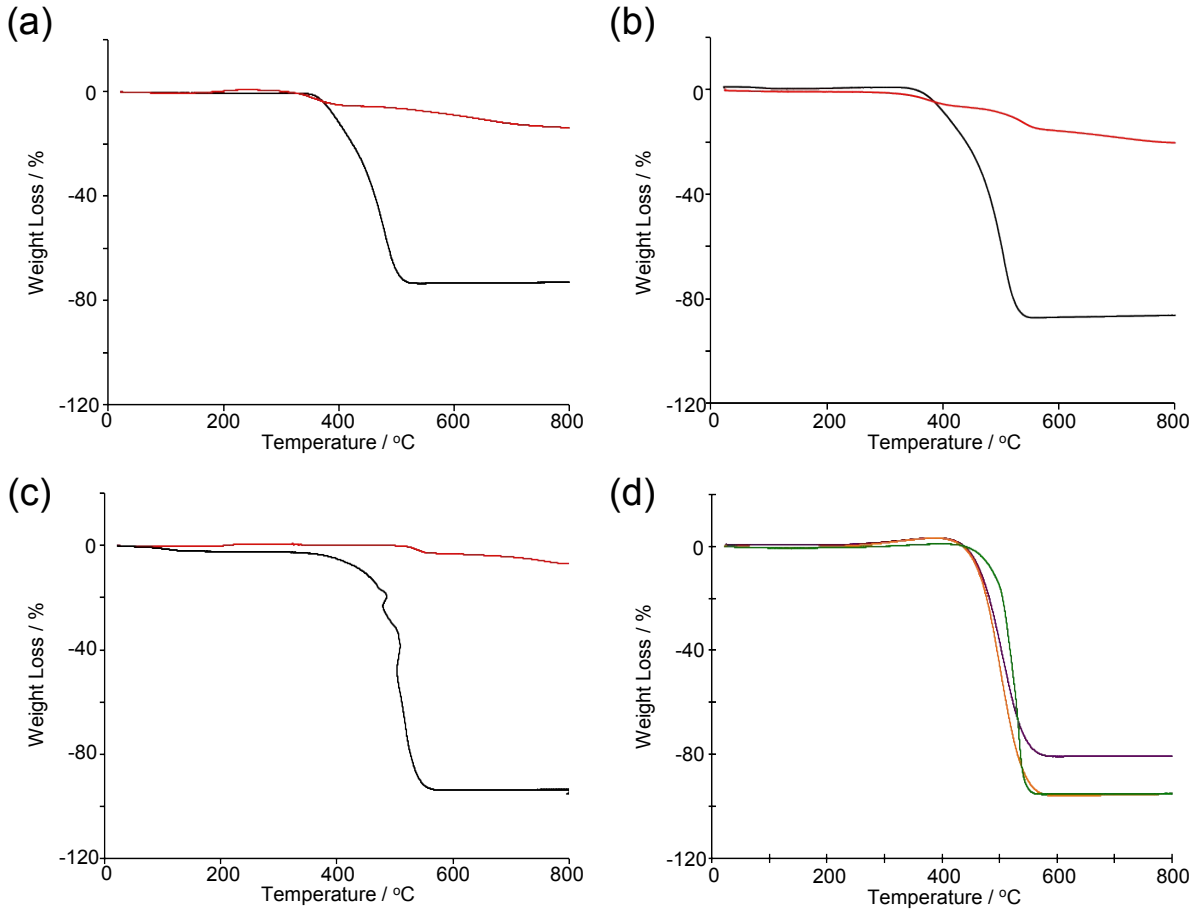

Figure S3. TG profiles under nitrogen (red lines) air atmosphere (black lines) of (a) **COP-3**, (b) **COP-3-rt** and (c) **COP-3C**. (d) TG profiles under air atmosphere of carbonized COPs. **COP-3-600** (purple), **COP-3-rt-600** (orange) and **COP-3C-600** (green).

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).

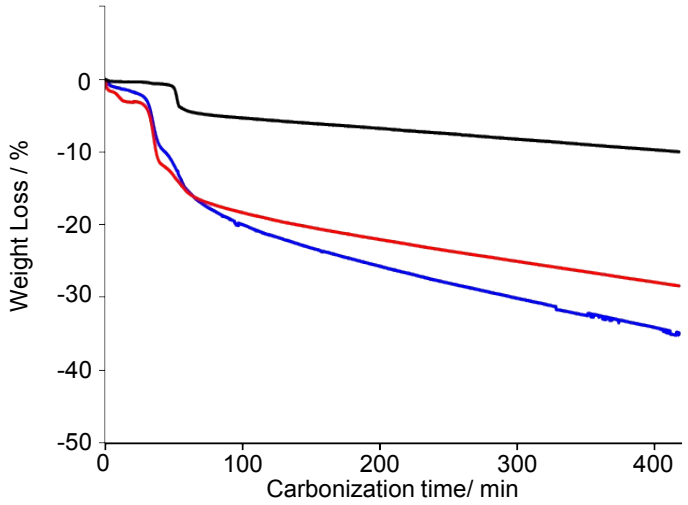

Figure S4. TG profiles of COPs under carbonization condition. **COP-3** (blue line), **COP-3-rt** (red line) and **COP-3C** (black line).

5. SEM observation of COPs and carbonized COPs.

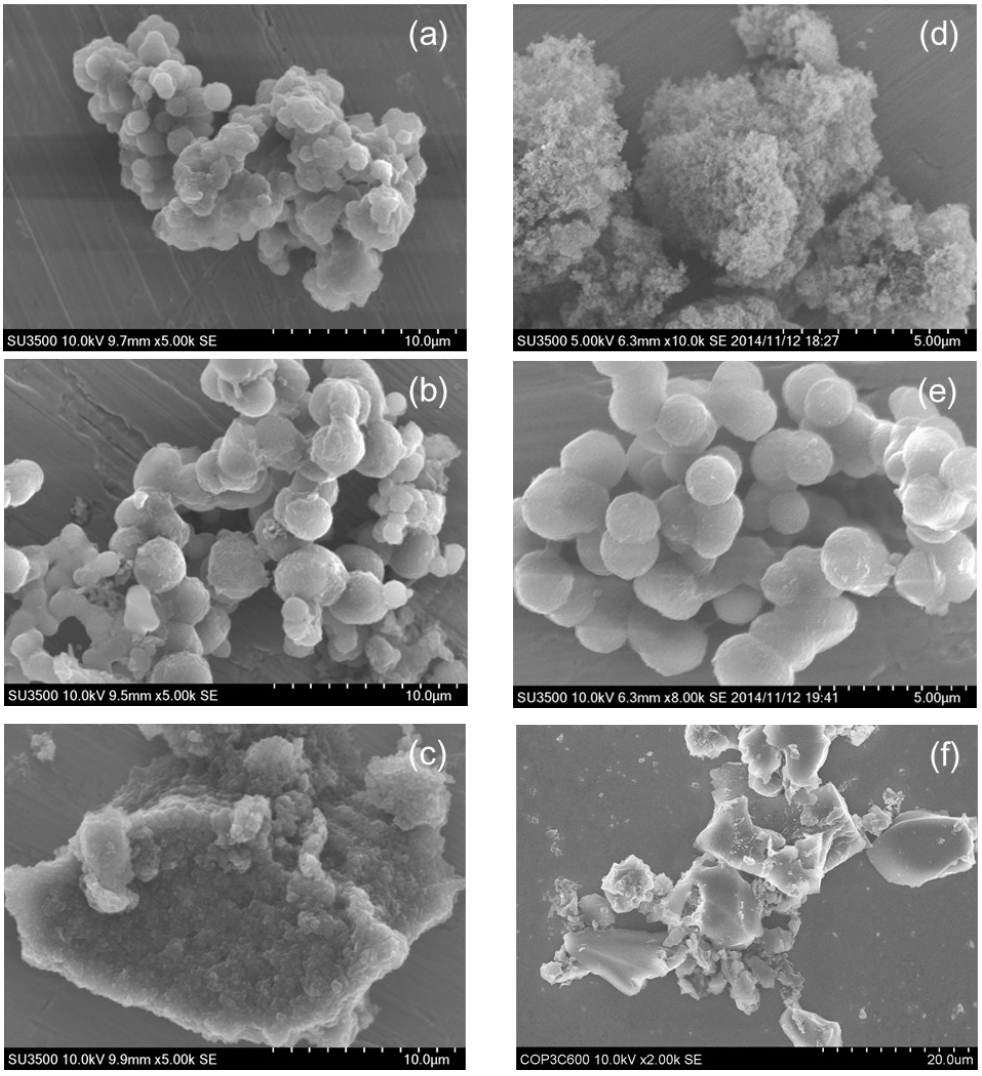

Figure S5. SEM images of (a) **COP-3**, (b) **COP-3-rt**, (c) **COP-3C**, (d) **COP-3-600**, (e) **COP-3-rt-600** and (f) **COP-3C-600**.

6. Synthesis of COP-3F.

A mixture of 9,9'-dimethylfluorene (400 mg, 2.0 mmol) and $FeCl_3$ (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).

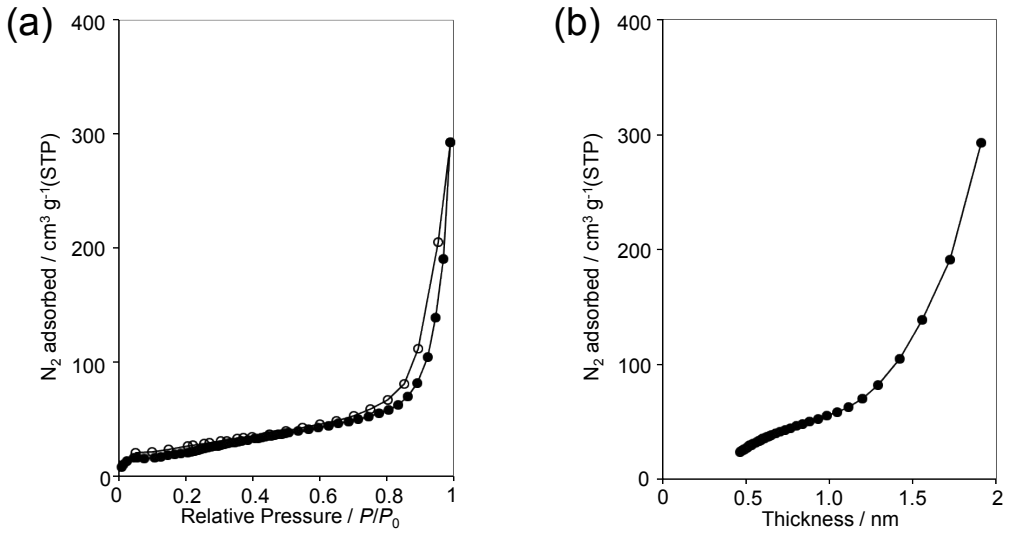

Figure S6 (a) The nitrogen adsorption/desorption isotherms of **COP-3F** and (b) *t*-plot for **COP-3F**.

7. Raman spectra of carbonized COPs.

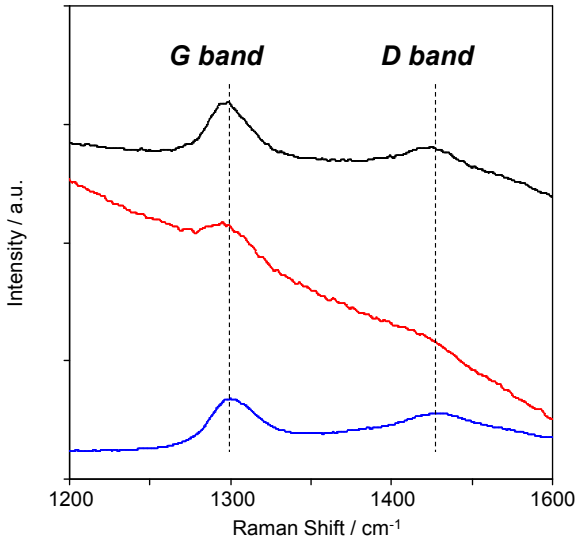

Figure S7. Raman spectra of **COP-3-600** (black), **COP-3-rt-600** (red) and **COP-3C-600** (blue).

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

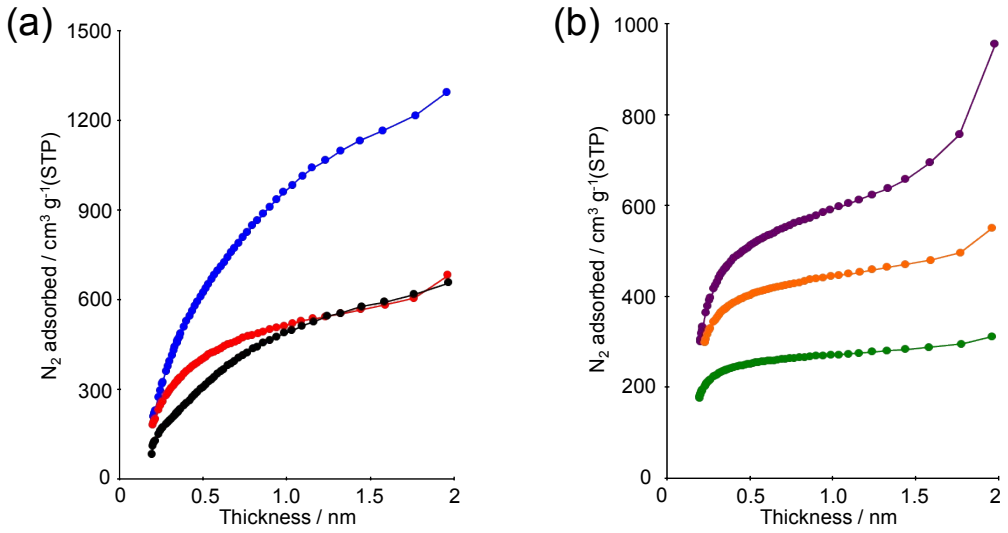

Figure S8. The *t*-plot analysis of nitrogen adsorption isotherms of (a) **COP-3** (blue), **COP-3-rt** (red) and **COP-3C** (black), and (b) **COP-3-600** (purple), **COP-3-rt-600** (orange) and **COP-3C-600** (green).

9. The Dubinin-Radushkevich analysis of nitrogen adsorption isotherms of COPs and carbonized COPs

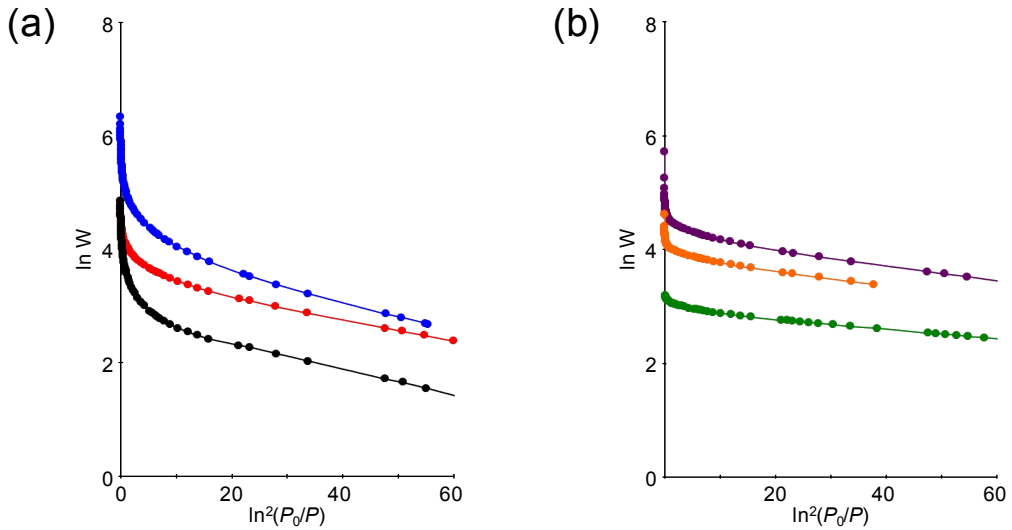

Figure S9. The Dubinin-Radushkevich (DR) plots analysis of nitrogen adsorption isotherms of (a) **COP-3** (blue), **COP-3-rt** (red) and **COP-3C** (black), and (b) **COP-3-600** (purple), **COP-3-rt-600** (orange) and **COP-3C-600** (green).

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).

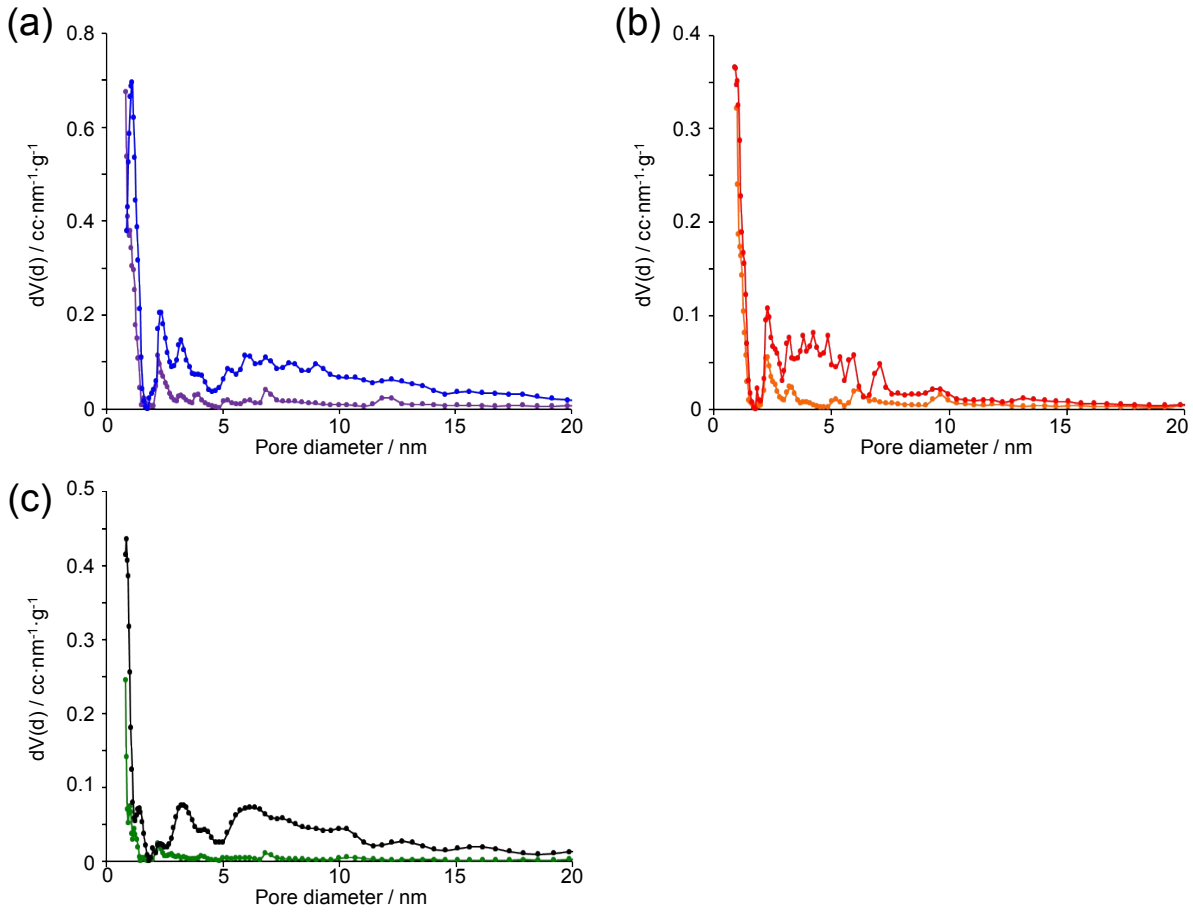

Figure S10. The pore distributions of (a) **COP-3** (blue) and **COP-3-600** (purple), (b) **COP-3-rt** (red) and **COP-3-rt-600** (orange), and (c) **COP-3C** (black) and **COP-3C-600** (green).

11. Gas uptake ability of COPs and carbonized COPs

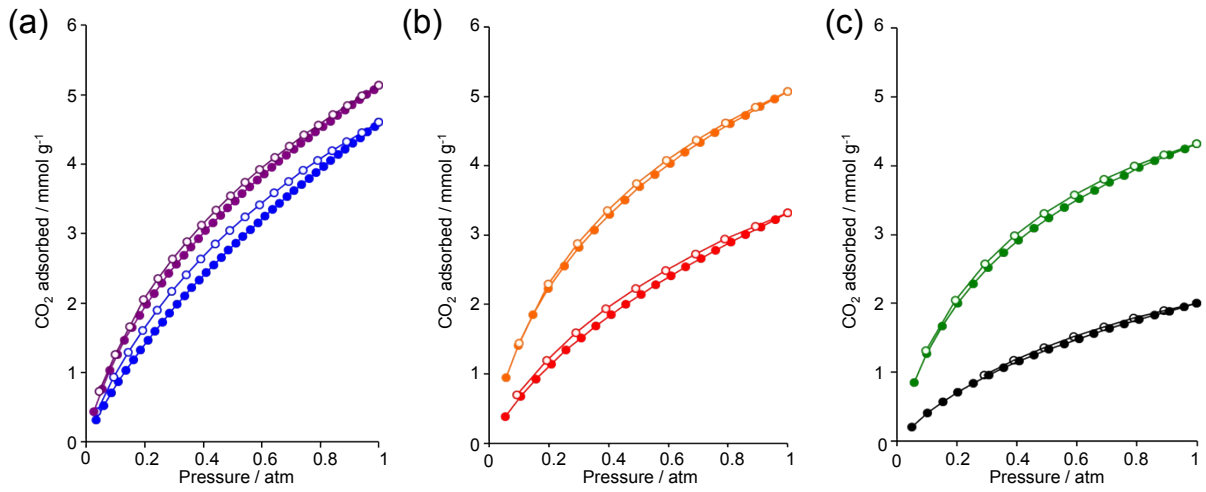

Figure S11. CO_2 uptake (at 273 K, 1 atm) changes during cycle adsorption measurement for (a) **COP-3** (blue) and **COP-3-600** (purple), (b) **COP-3-rt** (red) and **COP-3-rt-600** (orange), and (c) **COP-3C** (black) and **COP-3C-600** (green).

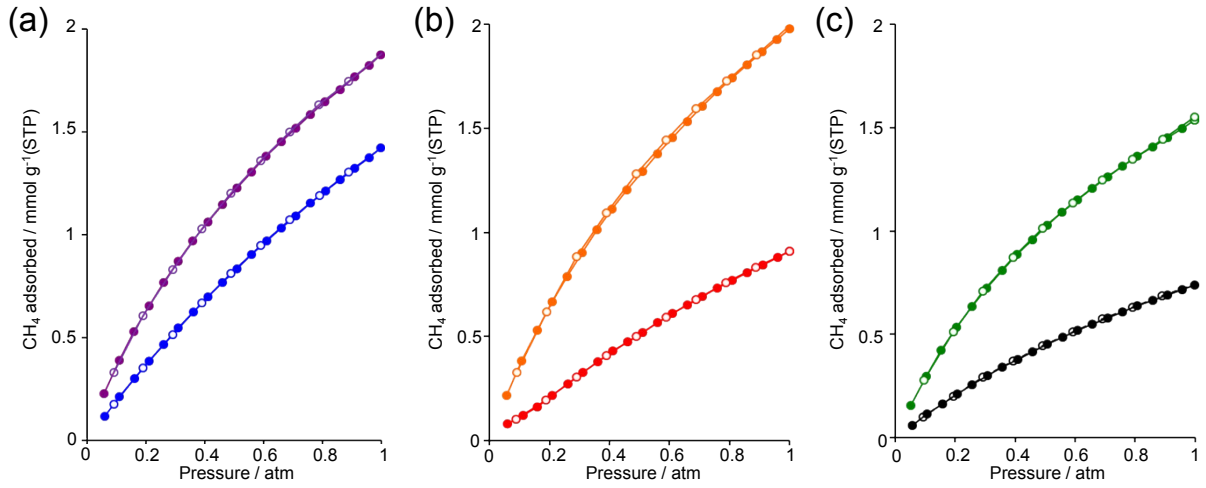

Figure S12. CH_4 adsorption (closed circles) and desorption (open circles) isotherms of (a) **COP-3** (blue) and **COP-3-600** (purple), (b) **COP-3-rt** (red) and **COP-3-rt-600** (orange), and (c) **COP-3C** (black) and **COP-3C-600** (green).

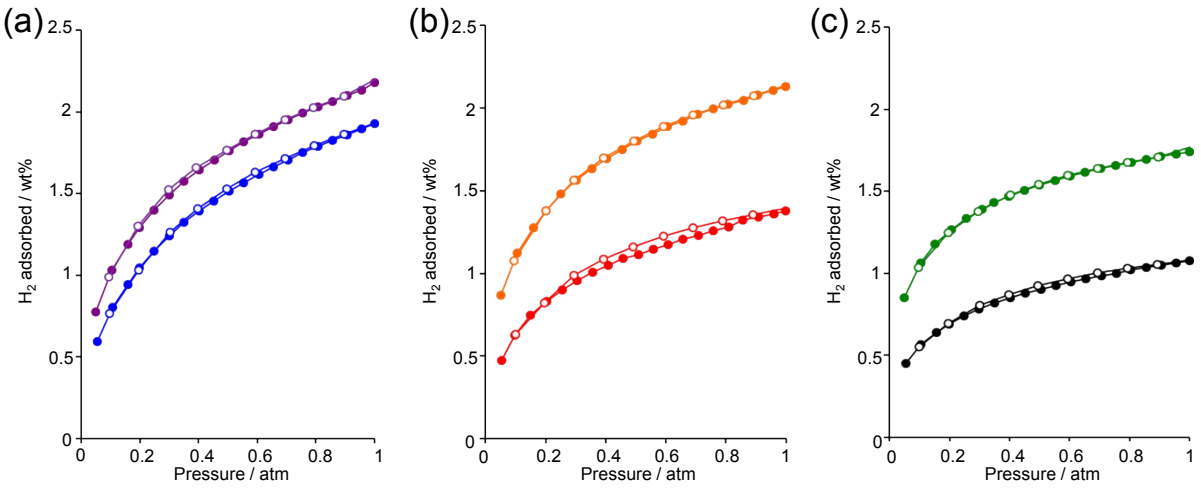

Figure S13. H_2 adsorption (closed circles) and desorption (open circles) isotherms at 77 K of (a) **COP-3** (blue) and **COP-3-600** (purple), (b) **COP-3-rt** (red) and **COP-3-rt-600** (orange), and (c) **COP-3C** (black) and **COP-3C-600** (green).

12. Reusability experiment of COPs and carbonized COPs for CO_2 uptake

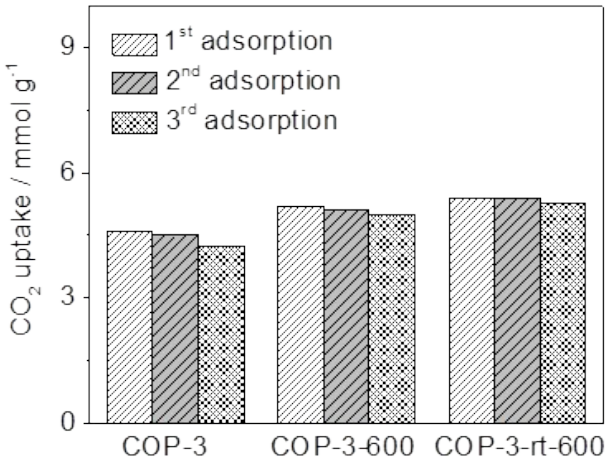

Figure S14. CO_2 uptake (at 273 K, 1 atm) changes during cycle adsorption measurement for **COP-3**, **COP-3-600**, **COP-3-rt-600**