

**Stable and micro-porous covalent organic frameworks via weak interaction for gas uptake**

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## Materials

N-butanol (n-BuOH), ortho dichlorobenzene (o-DCB), N, N-dimethylformamide (DMF), acetone, tetrahydrofuran, tris(4-aminophenyl)amine, and other chemicals were purchased from TCI and Sigma-Aldrich, tris(4-aminophenyl)amine, 1,3,5-tris(4-formyl-3-hydroxyphenyl)-benzene and 1,3,5-tris(4-formyl-3-fluorophenyl)-benzene, has been synthesized by the reported method.<sup>S1</sup>

## Synthesis of COF-OH

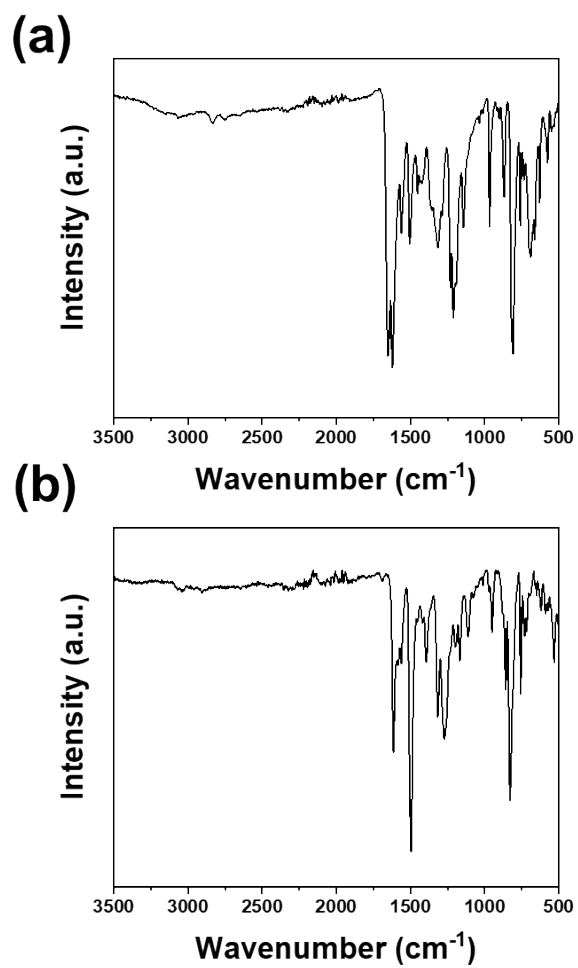
The tris(4-aminophenyl)amine (43.5, 0.15 mmol), 1,3,5-tris(4-formyl-3-hydroxyphenyl)-benzene (65.7 mg, 0.15 mmol), o-DCB (1.2 mL), n-butanol (0.4 mL), and acetic acid (6 M, 0.2 mL) were added into a Pyrex tube (10 mL). The tube was then flash frozen at 77 K and degassed by three freeze-pump-thaw cycles. The tube was sealed off and then heated at 120 °C for 3 d. After cooling down to room temperature, the sample was filtered and washed by DMF, and acetone. The sample was Soxhleted by THF for 12 h and dried in vacuum at 60 °C for 12 h to a dark yellow powder (Yield: 88%).

## Synthesis of COF-F

The tris(4-aminophenyl)amine (43.5, 0.10 mmol), 1,3,5-tris(4-formyl-3-fluorophenyl)-benzene (66.6, 0.15 mmol), o-DCB (1.2 mL), n-butanol (0.4 mL), and acetic acid (6 M, 0.2 mL) were added into a Pyrex tube (10 mL). The tube was then flash frozen at 77 K and degassed by three freeze-pump-thaw cycles. The tube was sealed off and then heated at 120 °C for 3 d. After cooling down to room temperature, the sample was filtered and washed by DMF, and acetone. The sample was Soxhleted by THF for 12 h and dried in vacuum at 60 °C for 12 h to give a dark yellow powder (Yield: 89%).

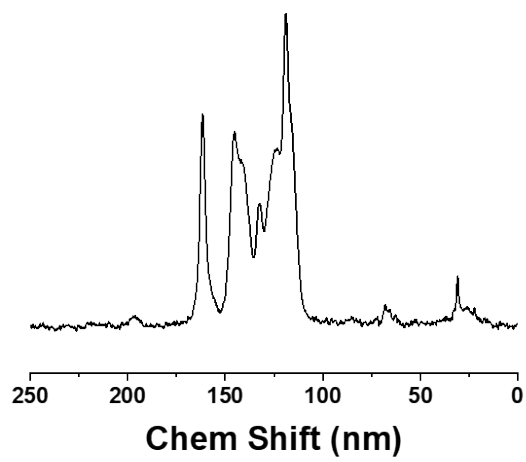
## Iodine vapor uptake experiment

Three open vials (5 mL) with COFs samples were placed in a large vial (70 mL) containing iodine, which was sealed and kept at 350 K. The first vial kept COFs samples (10 mg) and the second tube was selected to accommodate excess iodine. The vials were cooled down to room temperature by the selected time. The small vial containing the COFs samples and blank vial were recorded. One vial was used only once. Each experiment was repeated for three times and the final results was collected via the average value. The COFs@iodine samples were added into EtOH (30 mL) and stirred for 3 h under room temperature. The COFs samples were collected by filtration and washed with EtOH for several times. The operation was repeated for five times until there was colourless solution. The regenerated COFs samples were collected and dried under vacuum for the next experiment.

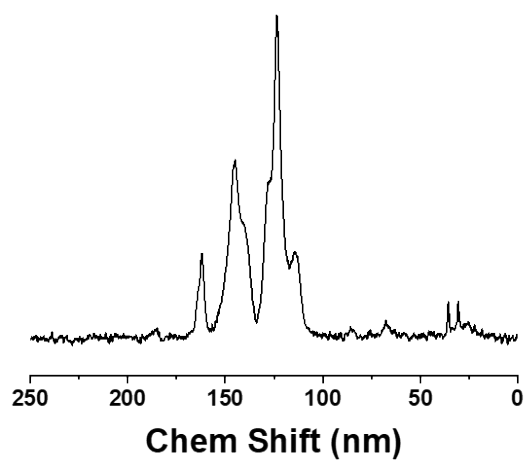


**Fig. S1.** FT IR spectra of (a) COF-OH and (b) COF-F.

**(a)**



**(b)**



**Fig. S2.**  $^{13}\text{C}$  NMR spectra of (a) COF-OH and (b) COF-F.

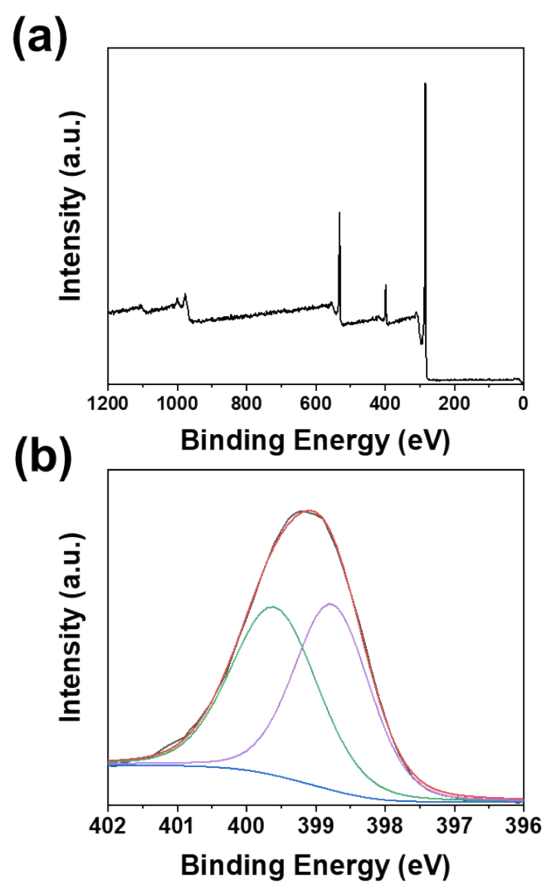
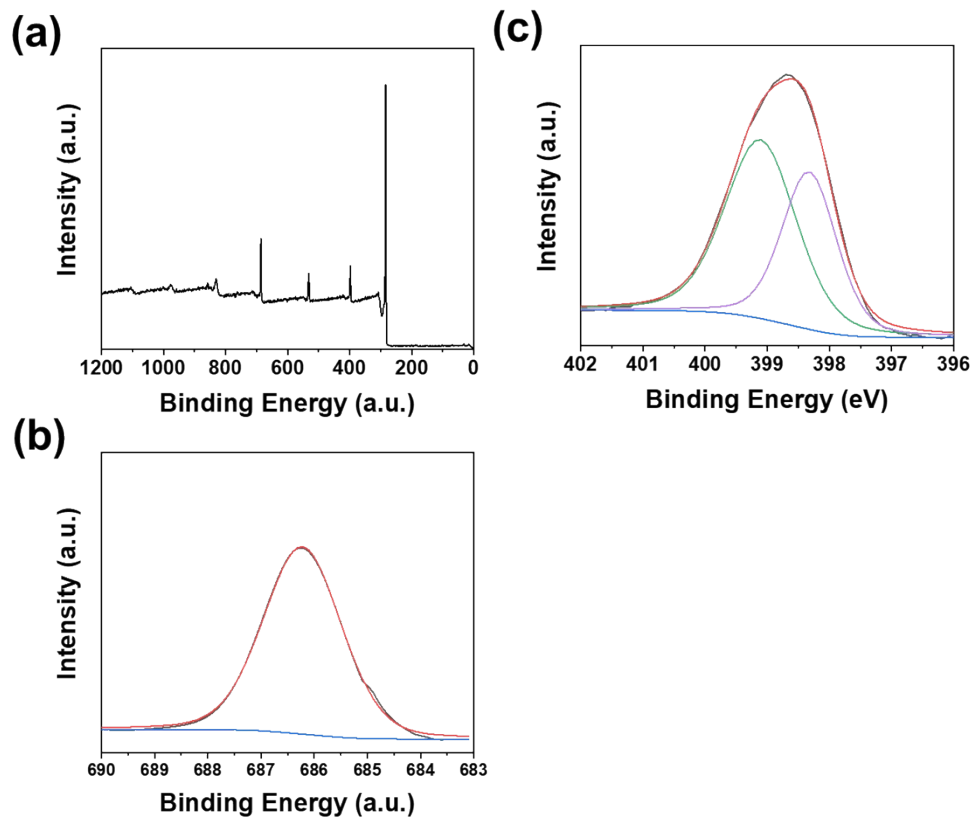
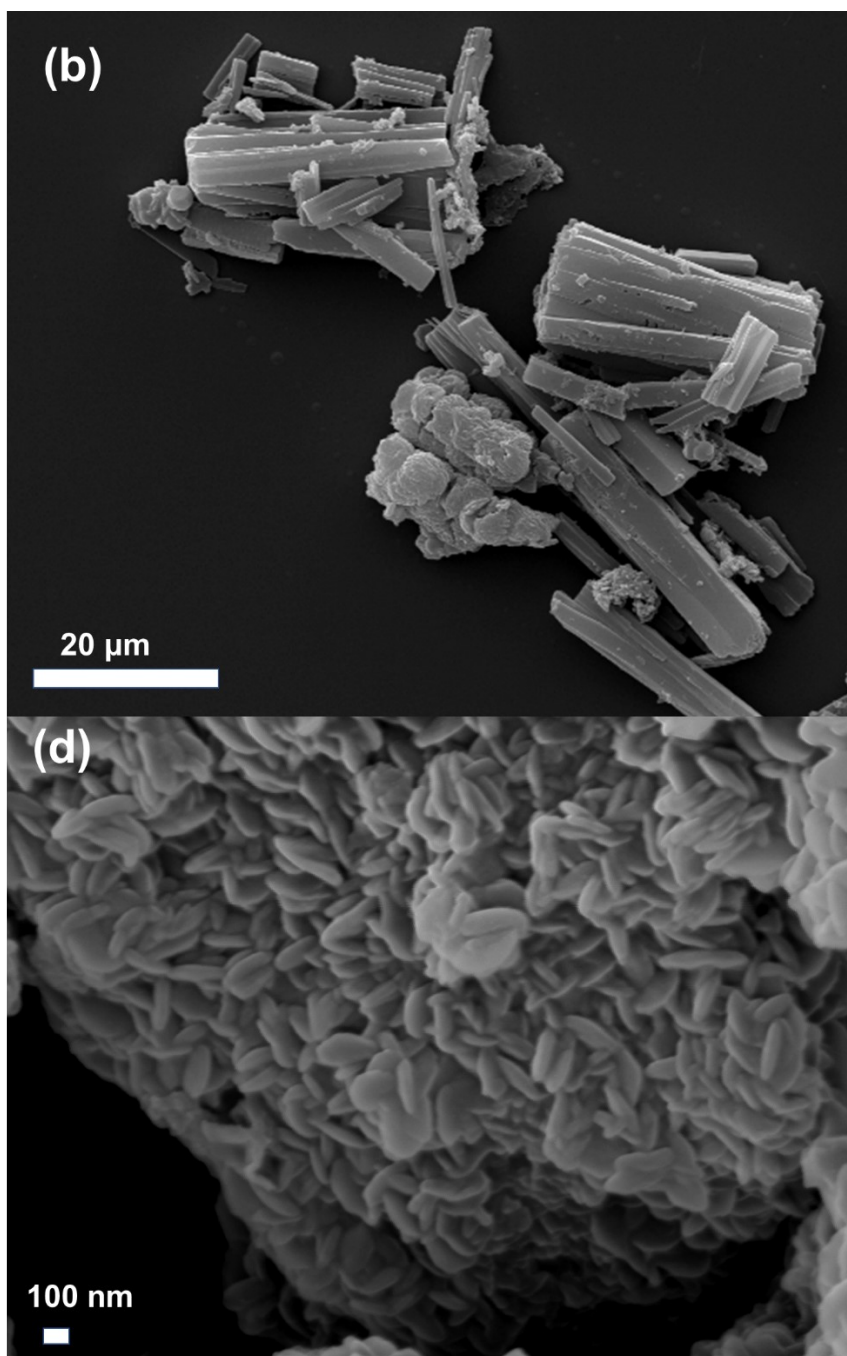


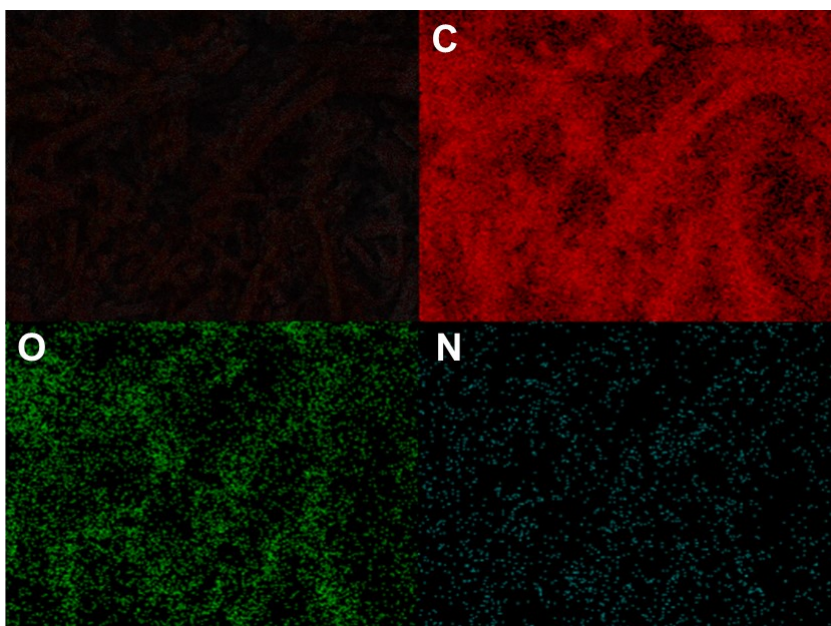
Fig. S3. (a) XPS spectrum of COF-OH. (b) N 1s spectrum of COF-OH.



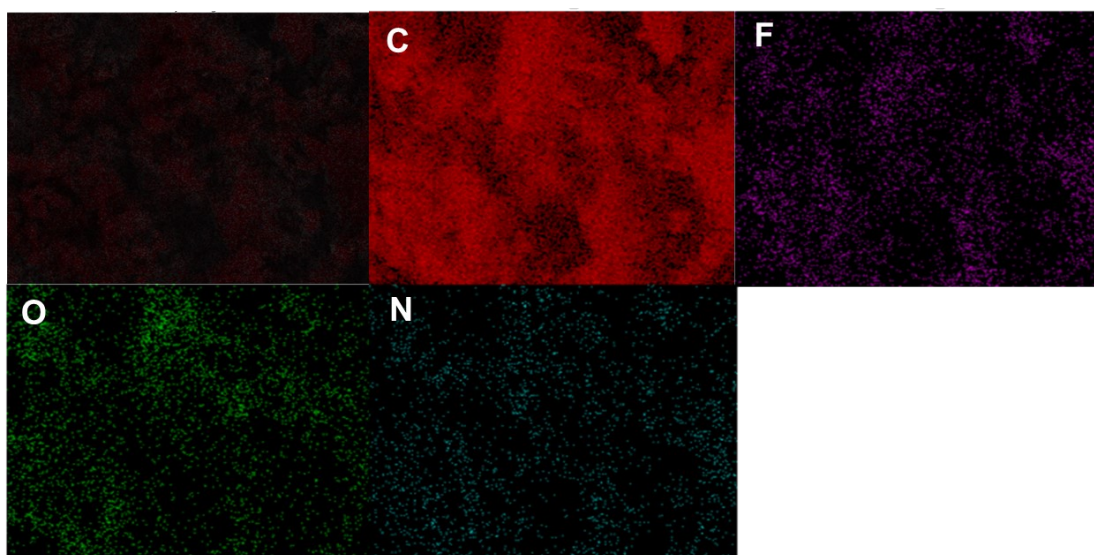
**Fig. S4.** (a) XPS spectrum of COF-F. (b) N 1s spectrum of COF-F. (c) F 1s spectrum of COF-F.



**Fig. S5.** FE SEM images of (a) COF-OH and (b) COF-F.

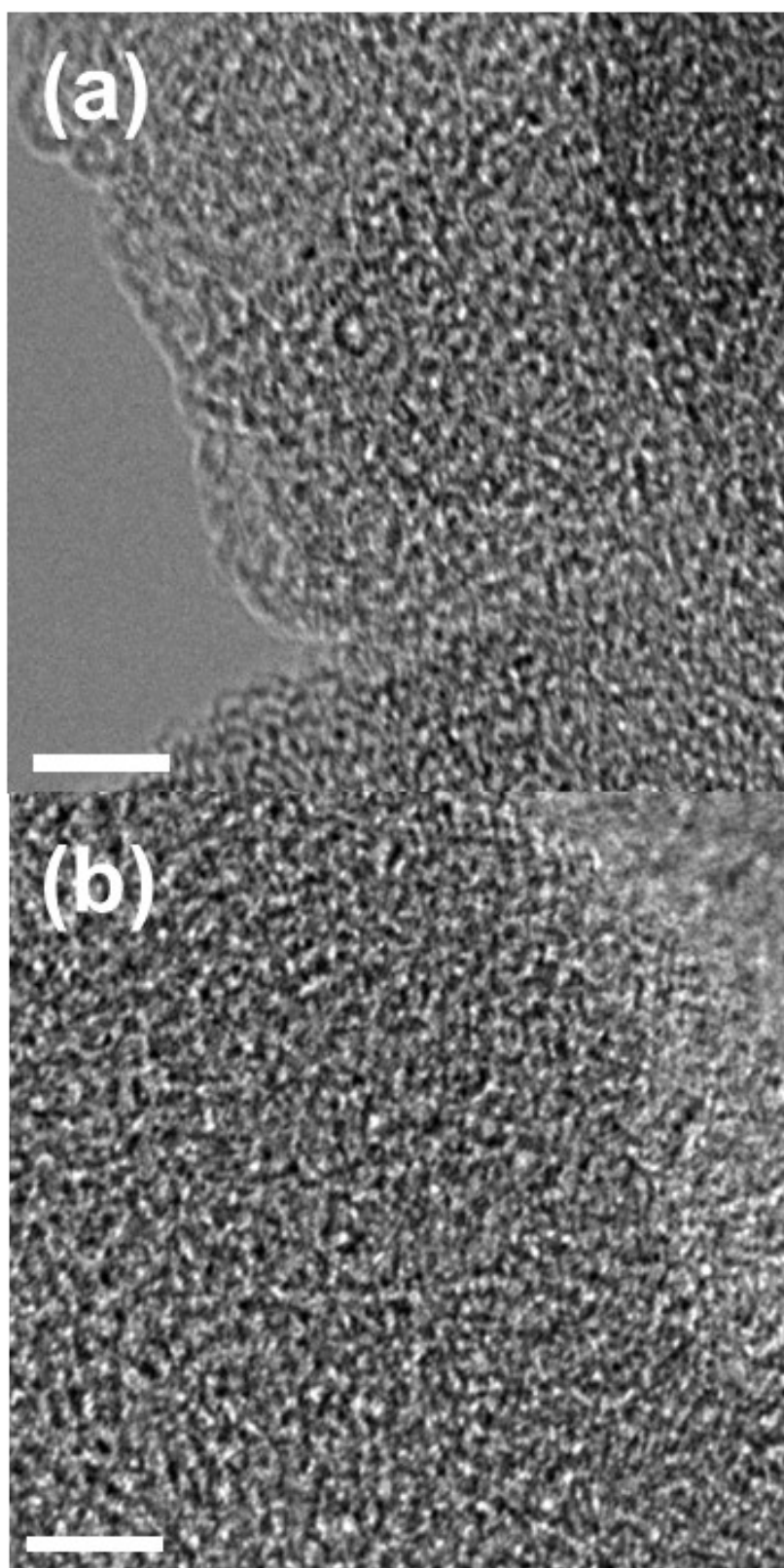


**Fig. S6.** EDS Mapping images of COF-F.

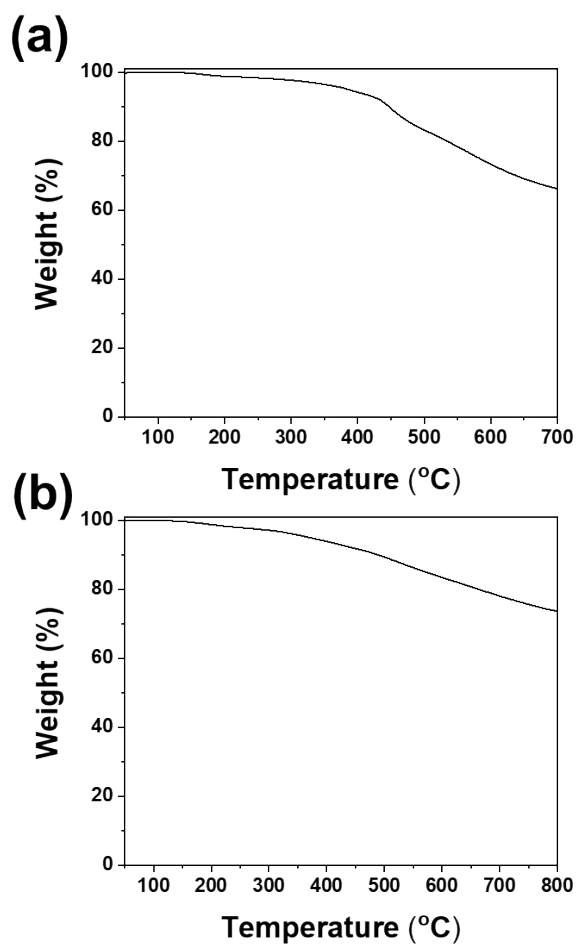


**Fig. S7.** EDS Mapping images of COF-F.

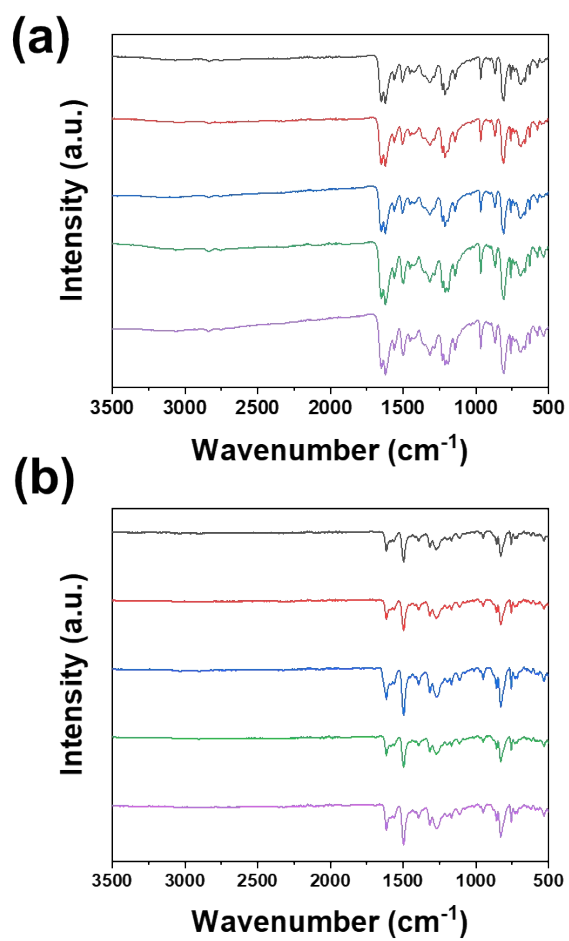




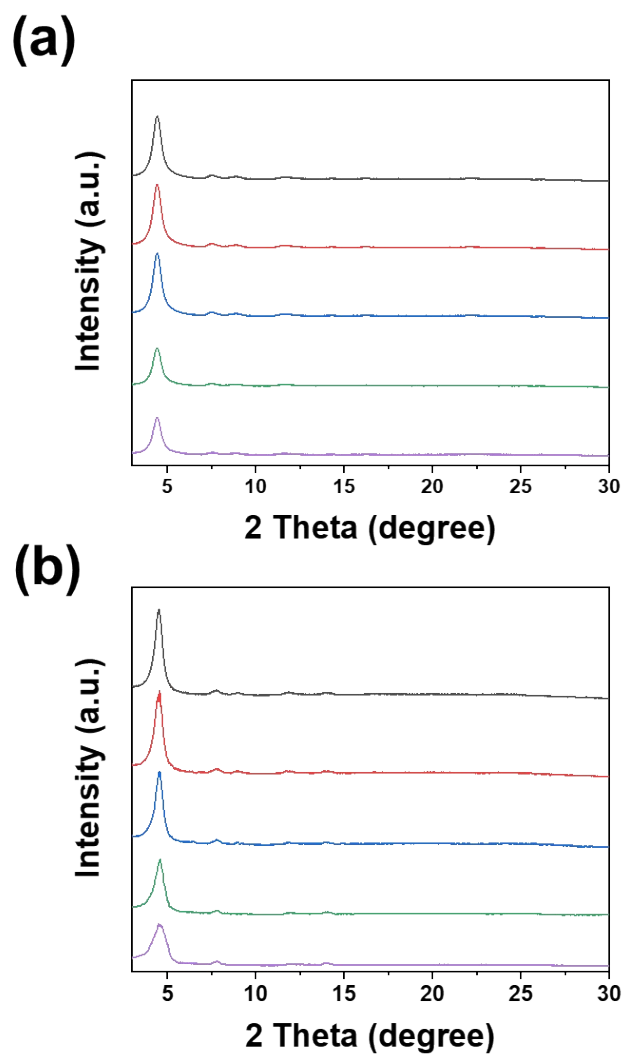
**Fig. S8.** TEM images of (a) COF-OH and (b) COF-F.



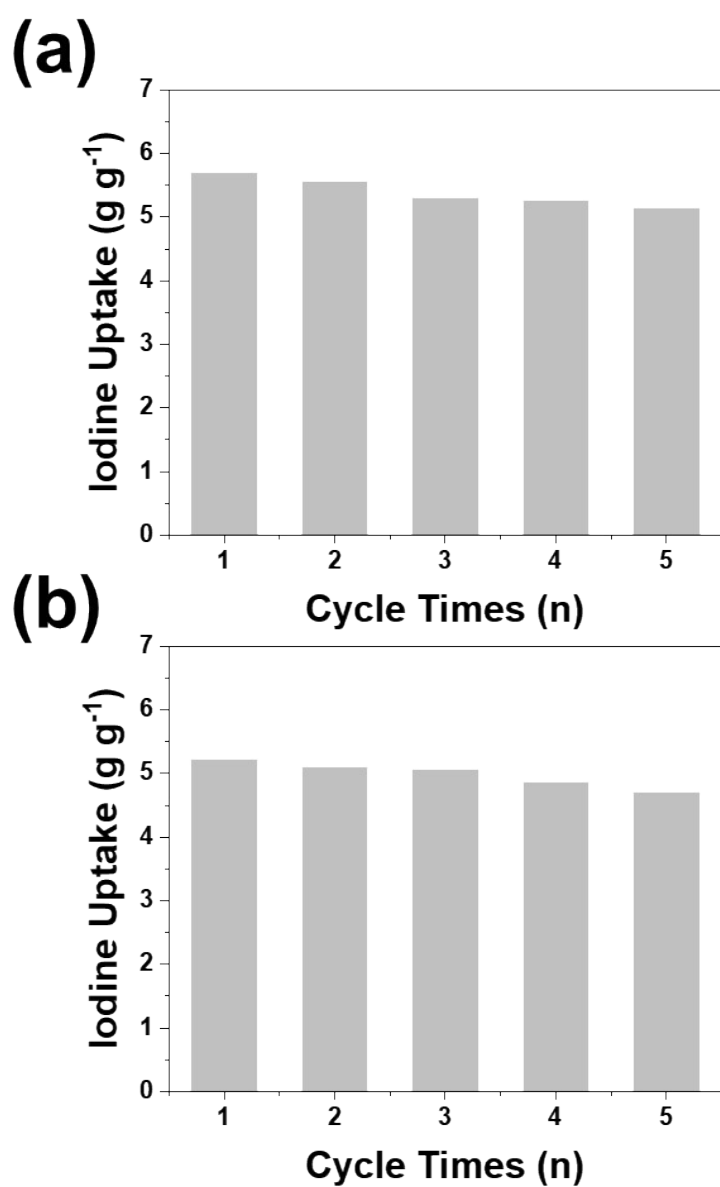
**Fig. S9.** TGA curves of (a) COF-OH and (b) COF-F.



**Fig. S10.** FT IR spectra of (a) COF-OH and (b) COF-F. (As-synthesized: black; Water: red; Hexane: blue; 1 M HCl: green; 1 M NaOH: purple).



**Fig. S11.** PXRD pattern of (a) COF-OH and (b) COF-F. (As-synthesized: black; Water: red; Hexane: blue; 1 M HCl: green; 1 M NaOH: purple).



**Fig. S12.** Iodine recycled performance of (a) COF-OH and (b) COF-F.

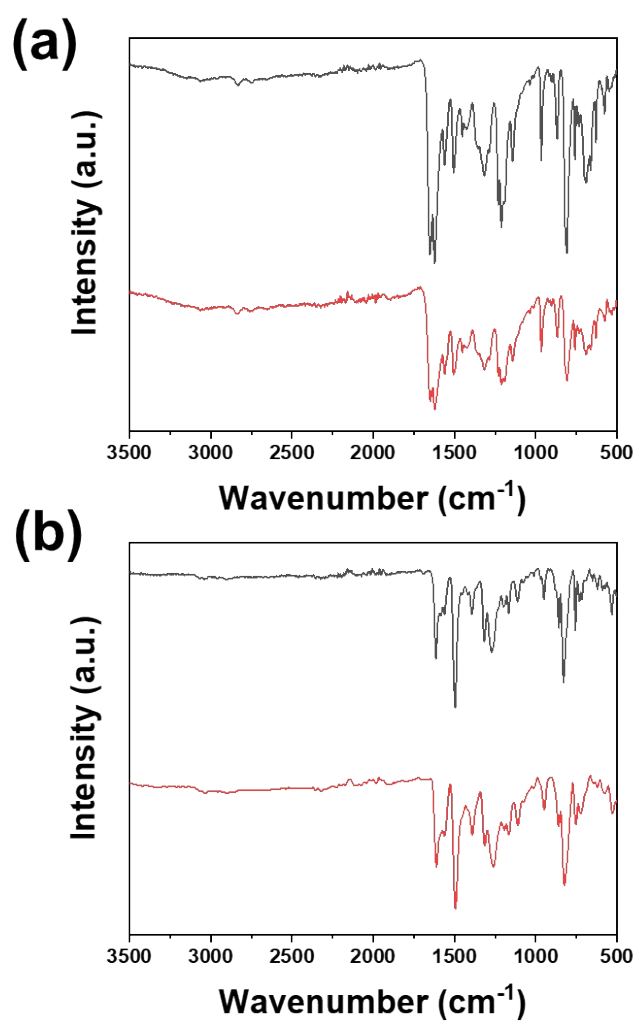


Fig. S13. FT IR spectra of (a) COF-OH and (b) COF-F (as-synthesized: black; re-used: red).

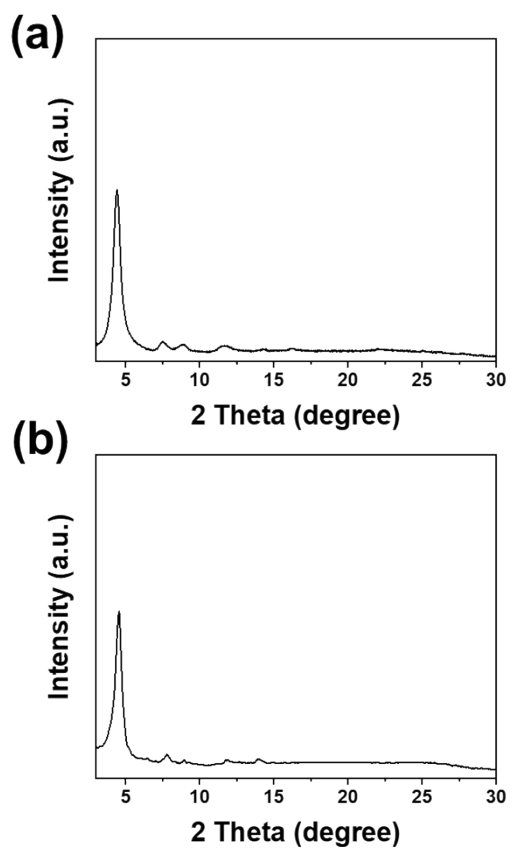
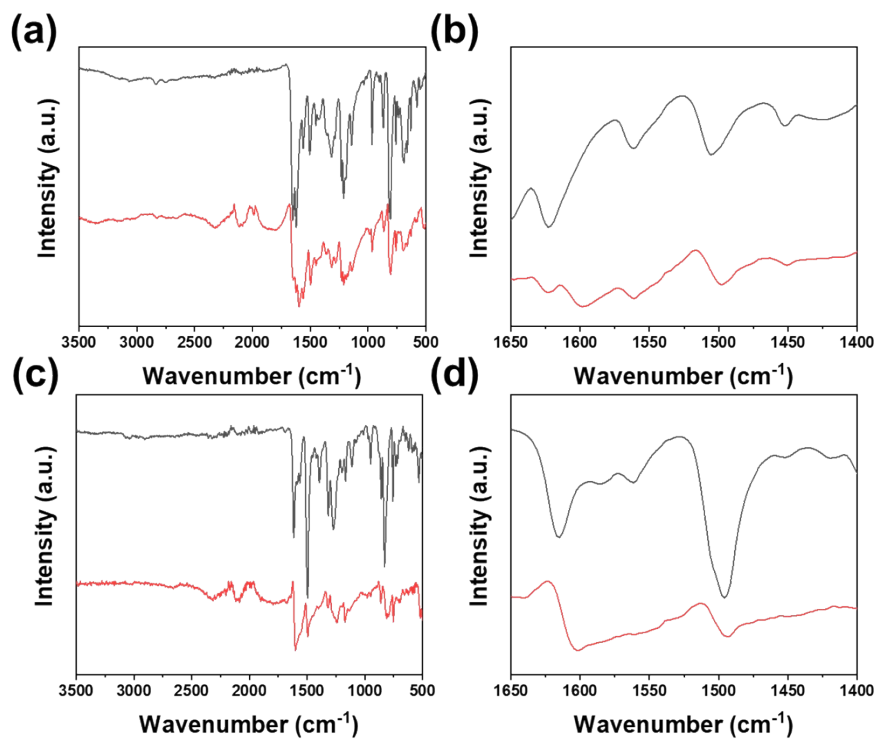


Fig. S14. XRD patterns of (a) COF-OH and (b) COF-F.



**Fig. S15.** FT IR spectra of (a) (b) COF-OH and (c) (d) COF-F (COFs: black; COFs@iodine: red).



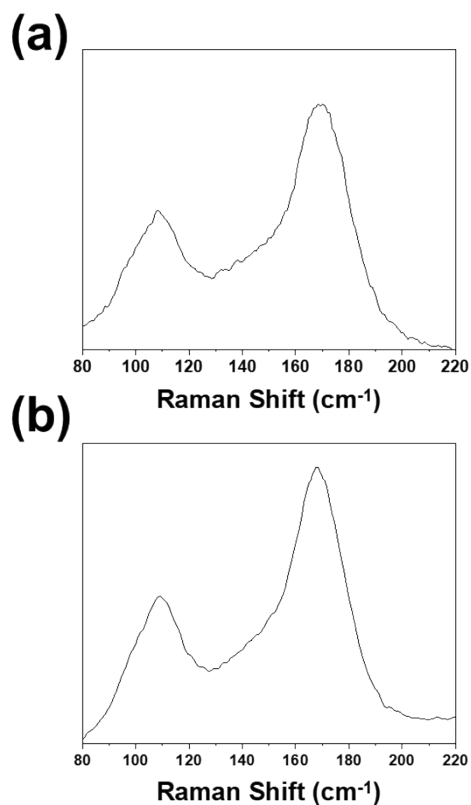


Fig. S16. Raman spectra of (a) COF-OH@iodine and (b) COF-F@iodine.

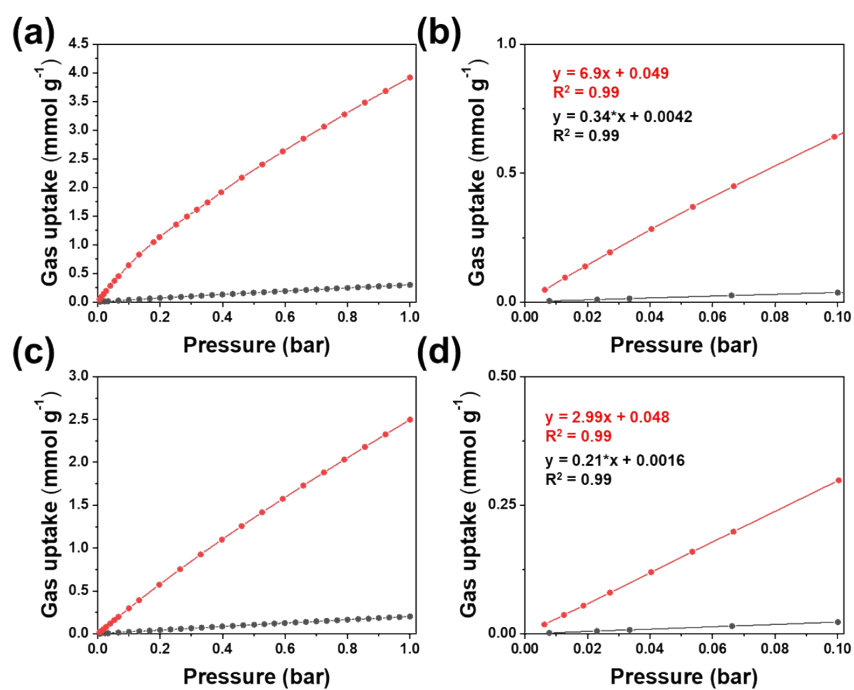


Fig. S17. Gas uptake of (a) (b) COF-OH and (c) (d) COF-F (Carbon dioxide: red; nitrogen: black).

#### Reference

- S1. H. Liu, C. Li, H. Li, Y. Ren, J. Chen, J. Tang, Q. Yang, *ACS Appl. Mater. Interfaces*, 2020, **12**, 20354–20365.