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Flexible covalent organic frameworks: high porosity, crystallinity, and iodine uptake

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Experimental

Materials

Acetic acid, tetrahydrofuran, n-butanol, o-DCB, DMF, and other chemicals were obtained from J&K Scientific company, TCI, Wako, and Sigma-Aldrich.

Material Characterization

Recording Fourier Transform Infrared (FT-IR) Spectrum with FT-IR Frontier Infrared Spectrometer with Perkin-Elmer Model. For all FT-IR tests, a small amount of sample can be directly mixed with potassium bromide and ground into a powder, compressed, Photoluminescence spectra were recorded on JASCO model FP-8600 spectrofluorometer. Elemental analysis (C, H, and N) was performed on a Euro Vector EA3000 elemental analyzer. 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. 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 for SEM by drop-casting a tetrahydrofuran suspension onto mica substrate and then coated with gold. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from $2\theta = 1.5°$ up to 30° with 0.02° increment. 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 60 °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.

Synthesis of F-COF-1

4,4',4''-(1,3,5-Triazine-2,4,6-triyl)tribenzaldehyde (39.3 mg, 0.1 mmol) and 4,4',4''-(benzene-1,3,5-triyltris(oxy))trianiline (39.9 mg, 0.1 mmol), o-DCB (0.4 mL), n-butanol (1.6 mL), acetic acid (3 M, 0.2 mL) were added into the system and the mixture was heated about 120 °C for 72 h. After cooling down to room temperature, the sample was filtered, washed by DMF, acetone, and ethanol, Soxhleted by THF for 6 h, and dried in vacuum at 80 °C for 6 h to afford a yellow powder (F-COF-1, Yield: 81%).

Synthesis of F-COF-2

4,4',4''-(1,3,5-Triazine-2,4,6-triyl)tribenzaldehyde (39.3 mg, 0.1 mmol) and 4,4',4''-((1,3,5-Triazine-2,4,6-triyl)tris(oxy))trianiline (40.2 mg, 0.1 mmol), o-DCB (0.8 mL), n-butanol (1.2 mL), acetic acid (3 M, 0.2 mL) were added into the system and the mixture was heated about 120 °C for three days. After cooling down to room temperature, the sample was filtered, washed by DMF, acetone, and ethanol, Soxhleted by THF for 6 h, and dried in vacuum at 80 °C for 6 h to afford a yellow powder (F-COF-2, Yield: 83%).

Iodine sorption

Three open vials (5 mL) with COFs samples were kept in a large bottle (70 mL) containing iodine (3.0 g). The large bottle was sealed and stored at 350 K. Three open vials were cooled down to room temperature and weighted to observe iodine capture value by the selected time. The large vial was restored at 350 K to observe iodine capture.

Stability measurements

COF samples were dispersed in water, tetrahydrofuran, aqueous HCl (1 M) and NaOH (1 M) solutions at room temperature for 24 h. The samples were collected by filtration, and washed with THF, water, and acetone. For acid condition, the ammonia water was used to wash for three times. For basic condition, a little acetic acid and large water were used to wash for three times. Finally, the samples were dried under vacuum at 80 °C overnight.

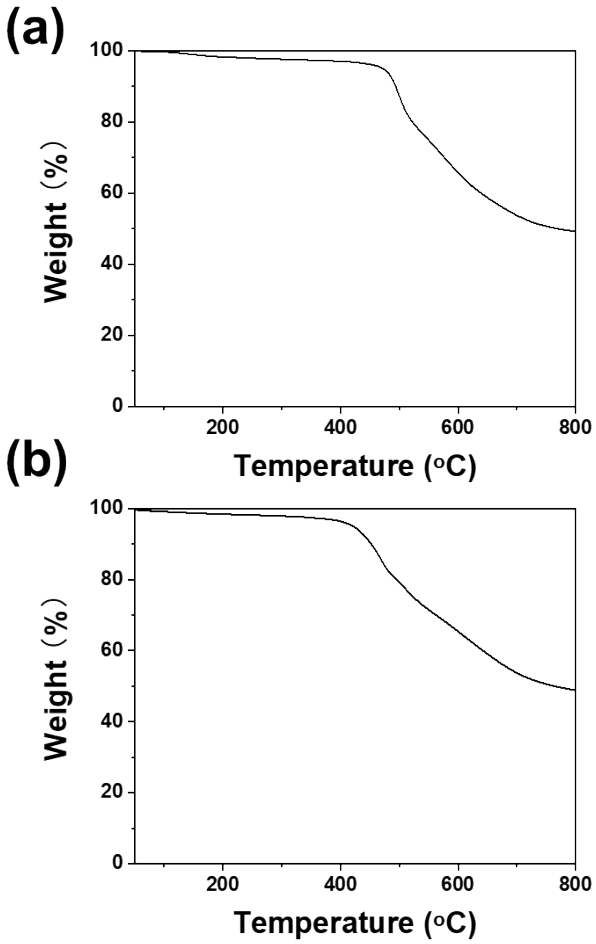

Fig. S1. TGA curves of (a) F-COF-1 and (b) F-COF-2.

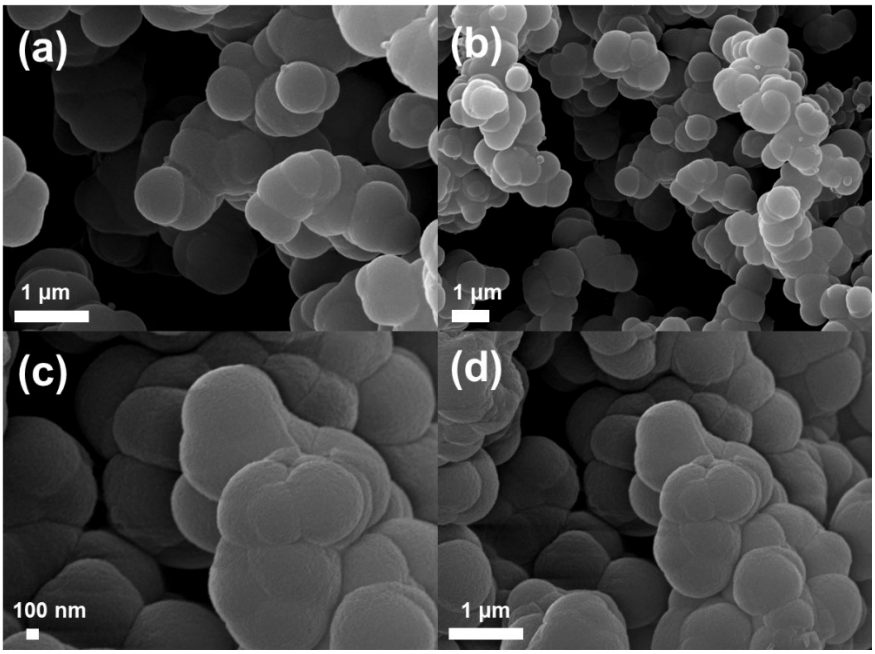

Fig. S2. SEM images of (a) (b) F-COF-1 and (c) (d) F-COF-2.

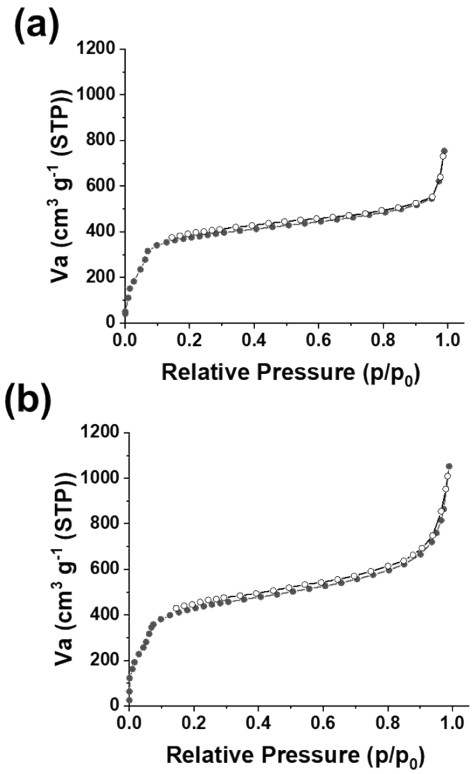

Fig. S3. Nitrogen adsorption-desorption isotherms of (a) F-COF-1 and (b) F-COF-2 measured at 77K (●: adsorption, ○: desorption).

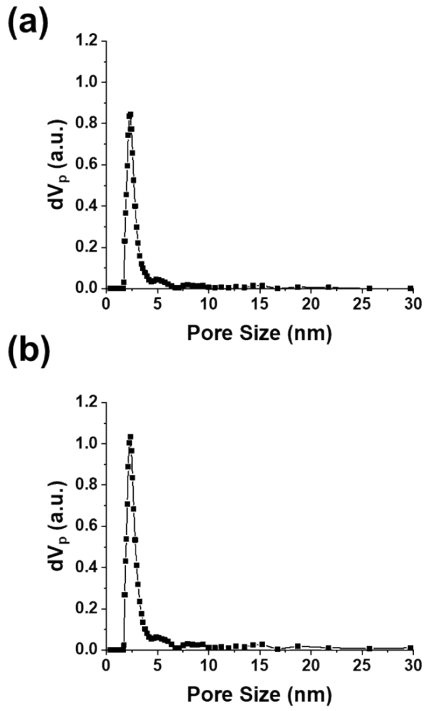

Fig. S4. Pore size distribution profile of (a) F-COF-1 and (b) F-COF-2.

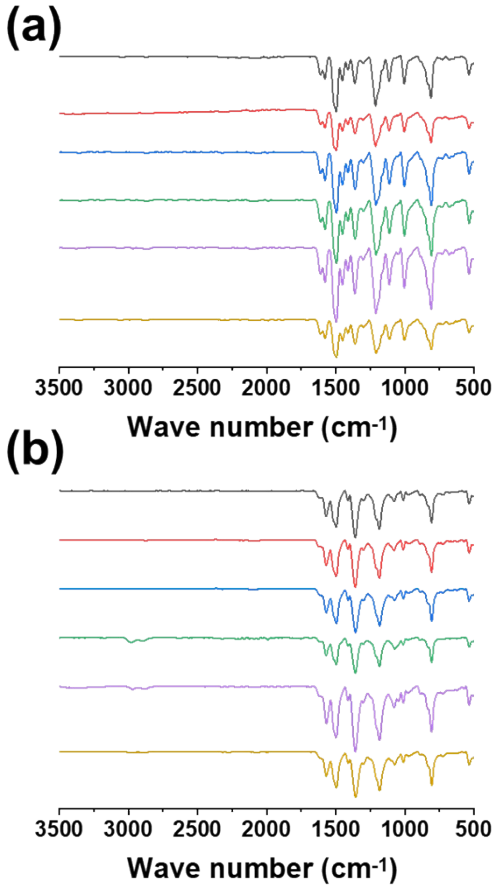

Fig. S5. FT IR spectra of (a) F-COF-1 and (b) F-COF-2 under different conditions. (Black: as-synthesized; red: hexane; blue: N, N-dimethylformamide; water: green; HCl: purple; NaOH: yellow).

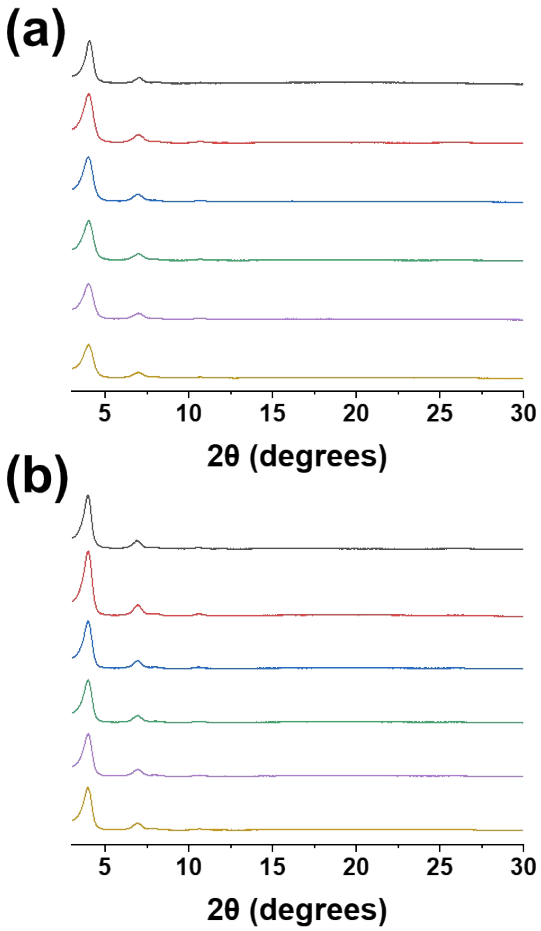

Fig. S6. PXRD patterns of (a) F-COF-1 and (b) F-COF-2 under different conditions. (Black: as-synthesized; red: hexane; blue: N, N-dimethylformamide; water: green; HCl: purple; NaOH: yellow).

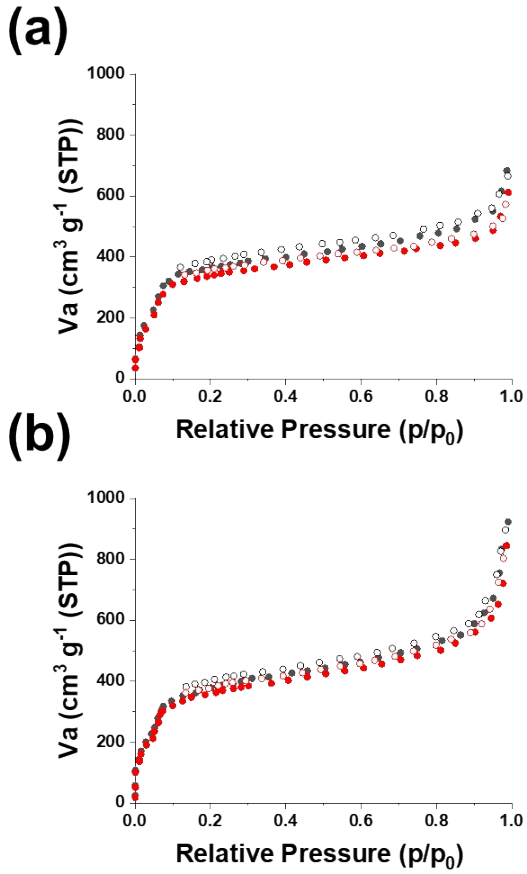

Fig. S7. Nitrogen adsorption-desorption isotherms of (a) F-COF-1 and (b) F-COF-2 measured at 77K (●: adsorption, ○: desorption). (Black: HCl; red; NaOH).

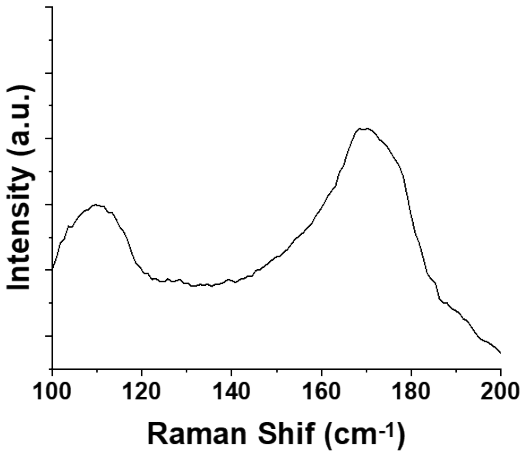

Fig. S8. Raman spectra of F-COF-2@iodine.

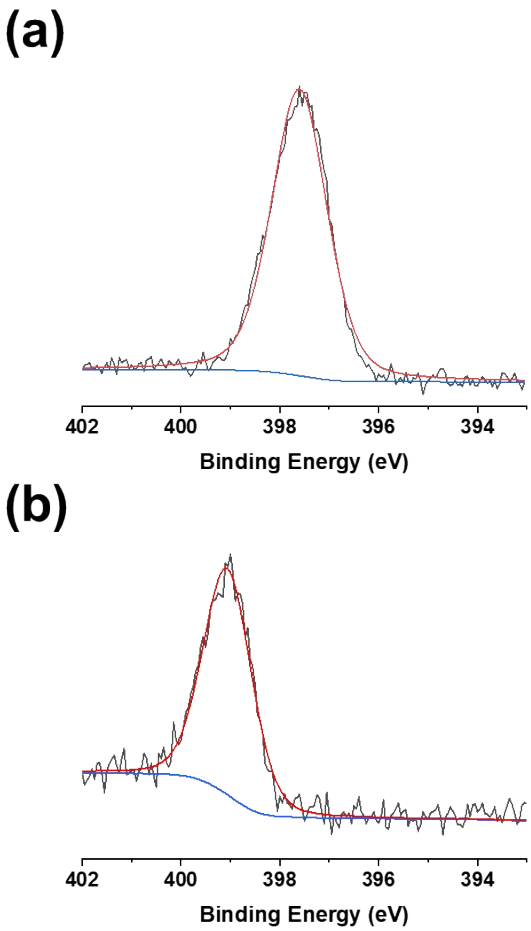

Fig. S9. N 1s XPS spectra of (a) F-COF-2 and (b) F-COF-2@I_2.

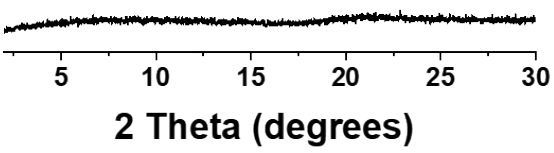

Fig. S10. PXRD patterns of F-COF-2@Iodine

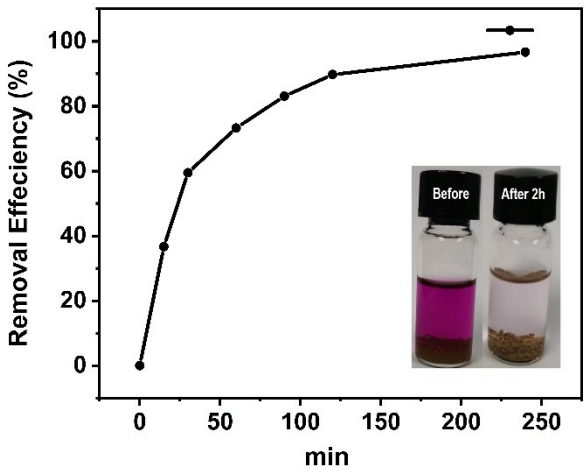

Fig. S11. Iodine uptake of F-COF-2 (15 mg) in hexane (iodine: 1.5 mmol L^{-1}, 4 mL).

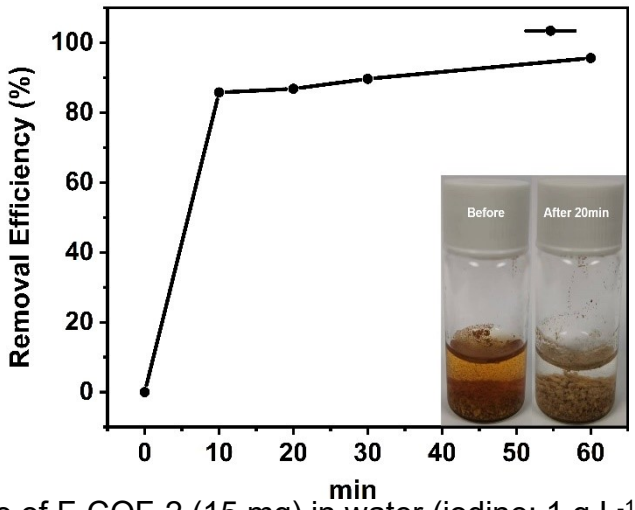

Fig. S12. Iodine uptake of F-COF-2 (15 mg) in water (iodine: 1 g L^{-1}, 4 mL).

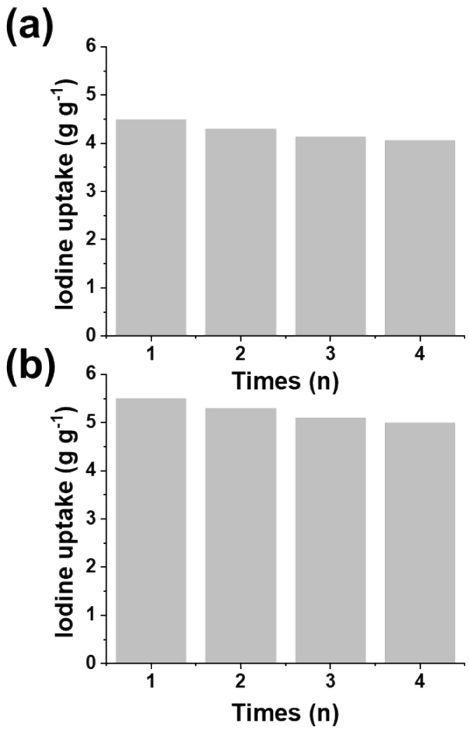

Fig. S13. Recycle performances of (a) F-COF-1 and (b) F-COF-2.

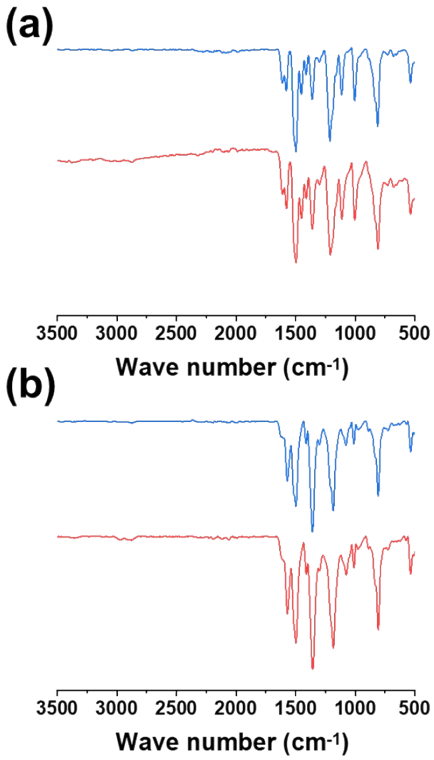

Fig. S14. FT-IR spectra of (a) F-COF-1 and (b) F-COF-2 (regenerated COFs: red).

Table S1. Elemental analysis of COFs.

		C (%)	N (%)	H (%)
F-COF-1	Observed	77.65	10.21	4.45
	Experiment	78.03	11.38	4.09
F-COF-2	Observed	72.61	16.74	3.88
	Experiment	72.87	16.99	3.67

Table S2. Atomic coordinates of F-COF-1.

P3, a = b = 25.5440 Å, c = 3.7356 Å, α = β = 90°, and γ = 120°			
C	0.31829	0.60983	-0.6878
O	0.24984	0.69947	-0.67605
C	0.19031	0.65914	-0.62155
C	0.15058	0.67546	-0.74548
C	0.09041	0.63854	-0.70139
C	0.06869	0.58425	-0.53311
C	0.10834	0.56849	-0.39226
C	0.1686	0.60616	-0.42939
N	0.00655	0.54795	-0.49966
N	0.60773	0.30272	-0.34825
C	0.63815	0.27399	-0.34801
C	0.60224	0.39297	-0.35524
C	0.62999	0.45329	-0.28646
C	0.59854	0.48282	-0.29981
C	0.53884	0.45275	-0.38414
C	0.5109	0.39246	-0.45123
C	0.54223	0.36282	-0.43585

C	0.5067	0.48498	-0.40449
H	0.16702	0.71685	-0.88333
H	0.06025	0.65137	-0.80592
H	0.09348	0.52876	-0.23897
H	0.19751	0.5947	-0.29241
H	0.67605	0.4775	-0.22072
H	0.62088	0.52926	-0.2453
H	0.4649	0.36849	-0.51824
H	0.51982	0.31645	-0.49262
H	0.53029	0.53127	-0.3483
N	0.34825	0.72326	0.30656

Table S3. Atomic coordinates of F-COF-2.

P3, a = b = 26.5574 Å, c = 3.8114 Å, α = β = 90°, and γ = 120°			
C	0.2764	0.62037	-0.81267
C	0.32228	0.60881	-0.80003
O	0.24265	0.69298	-0.8091
C	0.18407	0.65506	-0.71646
C	0.14323	0.67005	-0.83224
C	0.08414	0.63463	-0.75808
C	0.06444	0.58306	-0.56855
C	0.10549	0.56934	-0.43398
C	0.16478	0.60597	-0.49861
N	0.00302	0.54749	-0.50814
N	0.60786	0.30211	-0.27294
C	0.63889	0.27411	-0.27243
C	0.60115	0.3913	-0.28761

C	0.62788	0.45133	-0.2222
C	0.59624	0.48024	-0.25127
C	0.53746	0.44987	-0.34855
C	0.5104	0.38971	-0.40917
C	0.5419	0.3607	-0.37783
C	0.50563	0.4818	-0.39186
H	0.22917	0.58259	0.16615
H	0.15824	0.71204	0.00935
H	0.05113	0.64775	0.14697
H	0.09024	0.52784	0.7298
H	0.19845	0.59624	0.6264
H	0.67621	0.47705	0.85604
H	0.61842	0.52938	0.80482
H	0.46197	0.36401	0.51478
H	0.51934	0.31131	0.57399
H	0.52781	0.53048	0.67758