

Microporous covalent organic frameworks via flexible units and rich heteroatoms for gas uptake and radioactive iodine uptake

Materials

Dioxane, mesitylene, n-BuOH, o-DCB, N, N-dimethylformamide (DMF), hexane, tetrahydrofuran, and other chemicals were purchased from TCI, Energy Chemical, and J&K Scientific company.

Methods

The infrared spectra were recorded from 600 to 3500 cm^{-1} on an Avatar FT-IR 360 spectrometer. Elemental analyses were measured by an Elementar model vario EL cube analyser. Powder X-ray diffraction data were performed on a XRD (Ultima IV) diffractometer by depositing powder on glass substrate, from $2\theta = 3.0^\circ$ to 30° with 0.02° . Field emission scanning electron microscopy and energy dispersive spectroscopy for elemental mapping were recorded on a SU8020 model HITACHI microscope. Thermogravimetric analysis (TGA) was performed on a TA Q500 thermogravimeter with the heating at a rate of $10^\circ\text{C min}^{-1}$ from room temperature to 800°C under nitrogen atmosphere. Nitrogen sorption isotherms were measured at 77 K with a JW-BK 132F analyser.

Synthesis of 4,4',4''-((1,3,5-triazine-2,4,6-triyl)tris(oxy))trianiline

The 2,4,6-tris(4-nitrophenoxy)triazine (2.0 g, 4.0 mmol) was added into ethyl acetate (50 mL). Under inert atmosphere, the Pd/C 10% (0.72 g, 6.8 mmol) was slowly added. Pd/C 10% had been added again into the mixture under a H_2 atmosphere. And the mixture was stirred at room temperature at 12 h. The mixture was filtered to remove the Pd/C. The solvent was removed to afford a residue which was washed with diethyl ether (3×15 mL) to give 4,4',4''-((1,3,5-triazine-2,4,6-triyl)tris(oxy))trianiline (0.96 g, 59%). $^1\text{H NMR}$ (400 MHz, DMSO-d_6): δ 6.84 (6H, d), 6.54 (6H, d), 5.07 (6H, S) ppm.

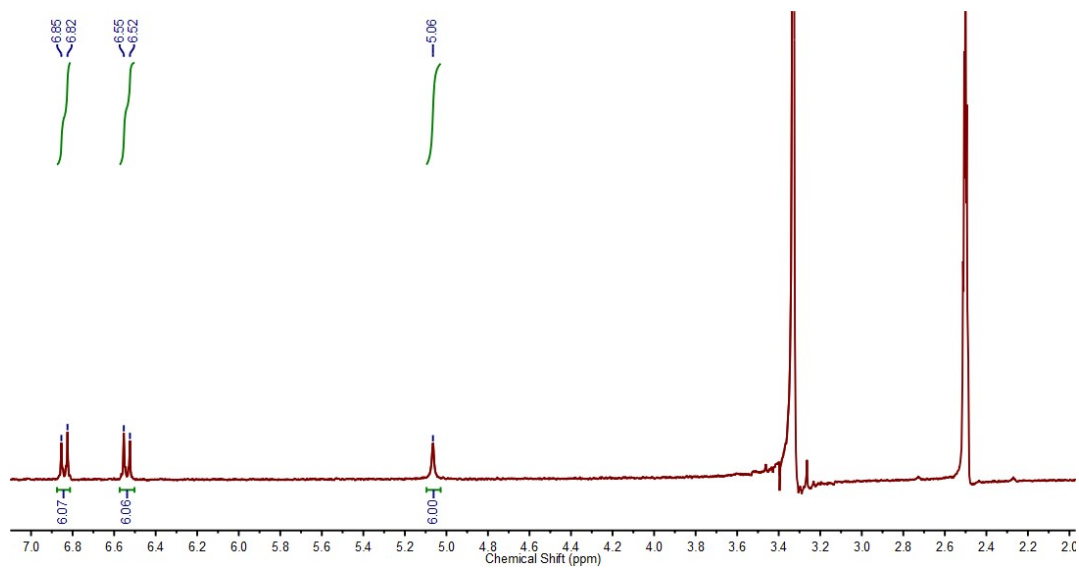


Figure S1. ^1H NMR spectrum of 4,4',4''-((1,3,5-triazine-2,4,6-triyl)tris(oxy))trianiline.

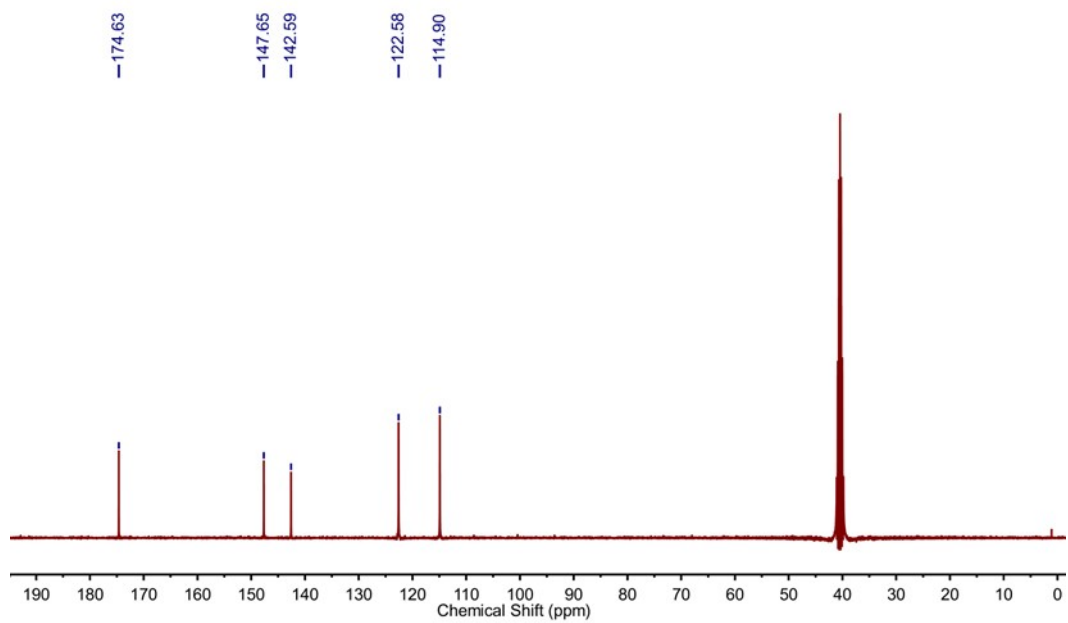
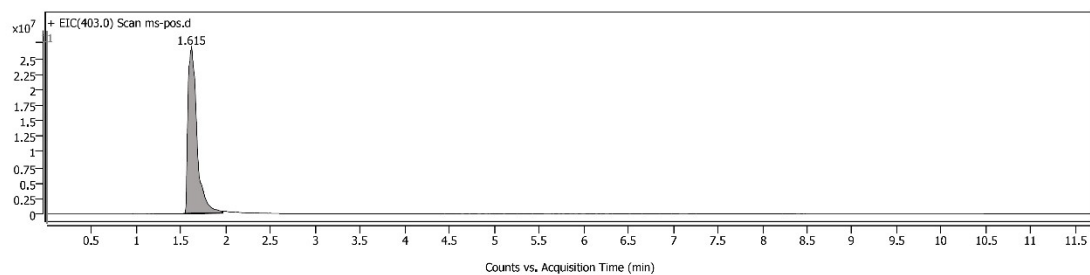


Figure S2. ^{13}C NMR spectrum of 4,4',4''-((1,3,5-triazine-2,4,6-triyl)tris(oxy))trianiline.



Chromatogram Peaks

Peak	RT	Height	Area	Area %
1	1.615	26791664	187431196	100.00

Sample Spectra

+ Scan (rt: 1.628 min)

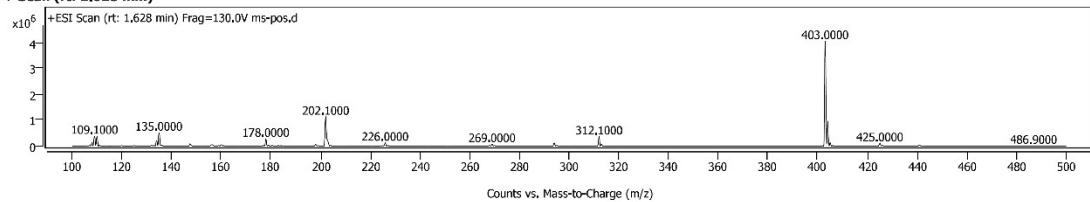


Figure S3. Mass spectroscopy spectrum of 4,4',4''-((1,3,5-triazine-2,4,6-triyl)tris(oxy))trianiline.

Synthesis of 2,4,6-trimethoxy-1,3,5-benzenetricarbaldehyde

The (2,4,6-trimethoxybenzene-1,3,5-triyl)trimethanol (3.0 g, 11.6 mmol), 4 Å molecular sieves (1g), and pyridinium chlorochromate (15 g) were added into dry dichloromethane (60 mL). The mixture was charged with argon and stirred under argon for overnight. The diatomite (5g) and dichloromethane (50 mL) were added and the mixture was stirred at 30 mins. The solid material was removed via suction filtration. The filtrate was removed under vacuum to give the crude product, which was purified via column chromatography (1.67 g, 57%). ^1H NMR (400 MHz, DMSO- d_6): δ 10.24 (6H, s), 3.95 (9H, s) ppm.

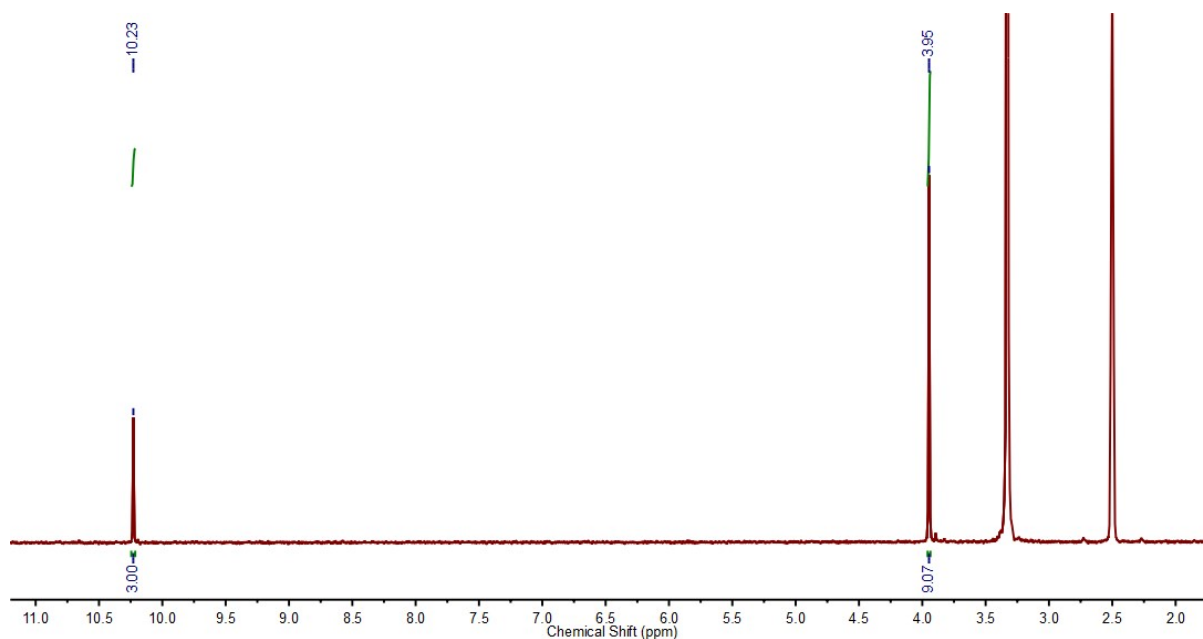


Figure S4. ^1H NMR spectrum of 2,4,6-trimethoxy-1,3,5-benzenetricarbaldehyde.

Synthesis of 1,3,5-triformylbenzene.

The 1,3,5-Tri(hydroxymethyl)benzene (1.5 g, 8.95 mmol), 4 Å molecular sieves (1.0 g), and pyridinium chlorochromate (15 g) were added into dry dichloromethane (80 mL). The mixture was charged with argon and stirred under argon for overnight. The diatomite (3.0 g) and dichloromethane (50 mL) were added and the mixture was stirred at 30 mins. The solid material was removed via suction filtration. The filtrate was removed under vacuum to give the crude product, which was purified via column chromatography (0.88 g, 62%). $^1\text{H NMR}$ (400 MHz, DMSO- d_6): δ 10.22 (3H, s), 8.07 (3H, s) ppm.

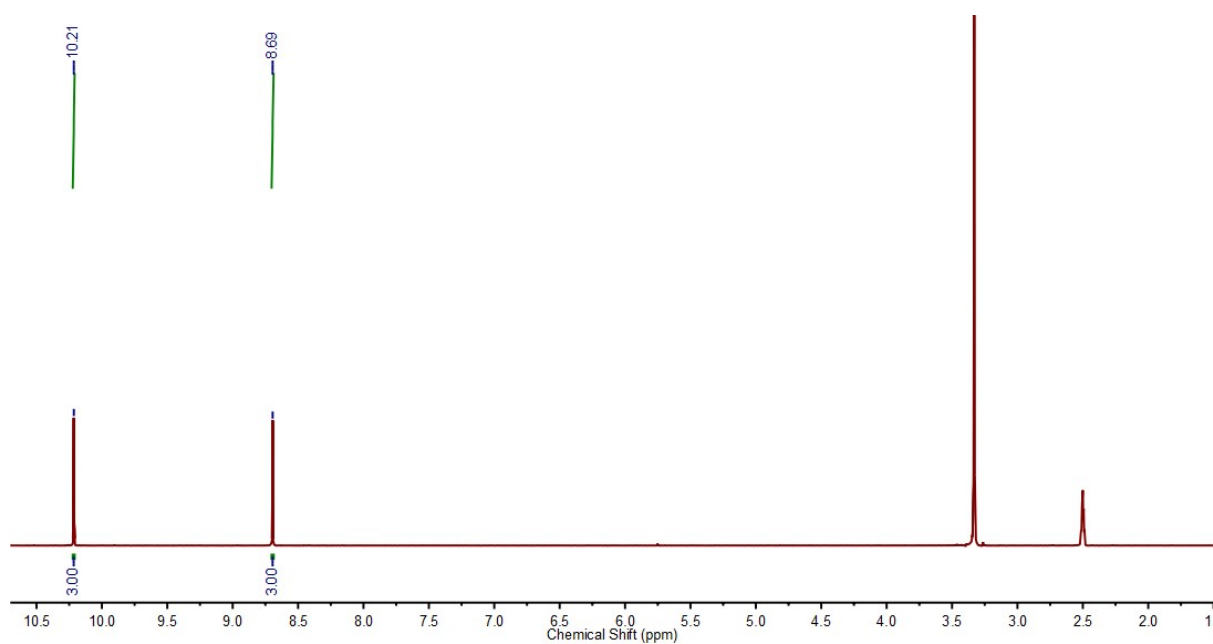


Figure S5. $^1\text{H NMR}$ spectrum of 1,3,5-triformylbenzene.

Synthesis of FM-COF-1

The 4,4',4''-((1,3,5-triazine-2,4,6-triyl)tris(oxy))trianiline (40.2, 0.10 mmol), 1,3,5-triformylbenzene (16.2 mg, 0.1 mmol), dioxane (0.8 mL), mesitylene (0.8 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 white-yellow powder (Yield: 88%).

Synthesis of FM-COF-2

The 4,4',4''-((1,3,5-triazine-2,4,6-triyl)tris(oxy))trianiline (40.2, 0.10 mmol), 2,4,6-trimethoxy-1,3,5-benzenetricarbaldehyde (25.2 mg, 0.1 mmol), o-DCB (0.7 mL), n-BuOH (0.9 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 white-yellow powder (Yield: 89%).

Iodine vapor uptake procedures

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 last vial was used as a reference. The vial containing three vials was sealed and kept at 350 K. After a certain time, the system was cooled down to room temperature. The small vial containing the COF sample was weighted and the result was recorded. One vial was used only once, and each experiment was repeated for three times, and the average result was collected.

Table S1. Fractional atomic coordinates of the AA stacking structure model for FM-COF1

FM-COF1			
Symmetry: P6			
a=b=18.9423 Å, c=3.5121			
$\alpha=\beta=90^\circ$, $\gamma=120^\circ$, Rwp = 4.31%, Rp = 3.18%			
Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	0.25677	0.60403	0.5
C	0.31939	0.59057	0.5
C	0.46255	0.63956	0.5
C	0.67143	0.40397	0.5
C	0.61983	0.49636	0.5
C	0.64363	0.57545	0.5
C	0.59007	0.60117	0.5
C	0.51021	0.54745	0.5
C	0.48583	0.46844	0.5
C	0.53938	0.44261	0.5
H	0.30826	0.53153	0.5
H	0.52011	0.68951	0.5
H	0.70486	0.61781	0.5
H	0.61221	0.66283	0.5
H	0.4245	0.42635	0.5
H	0.51498	0.38102	0.5
N	0.60157	0.33807	0.5
N	0.45178	0.56965	0.5
O	0.68022	0.47856	0.5

Table S2. Fractional atomic coordinates of the AA stacking structure model for FM-COF2

FM-COF2			
Symmetry: P3			
a=b=18.8694 Å, c=3.6619			
$\alpha=\beta=90^\circ$, $\gamma=120^\circ$, Rwp = 6.70%, Rp = 5.03%			
Atom	x	y	z
C	0.25331	0.60731	0.40467
C	0.31273	0.58654	0.39598
C	0.45609	0.62666	0.45311
C	0.67517	0.40664	0.65036
C	0.62453	0.49852	0.59992
C	0.64125	0.5763	0.63799
C	0.58278	0.59602	0.58425
C	0.50609	0.53776	0.49003
C	0.48904	0.46011	0.4486
C	0.54775	0.4407	0.50121
C	0.21672	0.76139	0.16548
H	0.51897	0.67551	0.50764
H	0.70321	0.62445	0.71372
H	0.59725	0.65962	0.61687
H	0.42702	0.4123	0.37158
H	0.53373	0.37733	0.46422
H	0.21311	0.73782	-0.12462
H	0.27439	0.81915	0.19942
H	0.16528	0.77183	0.21331
N	0.73925	0.39762	0.65291
N	0.4446	0.55577	0.43723
O	0.68699	0.48357	0.65369
O	0.21346	0.70576	0.42519

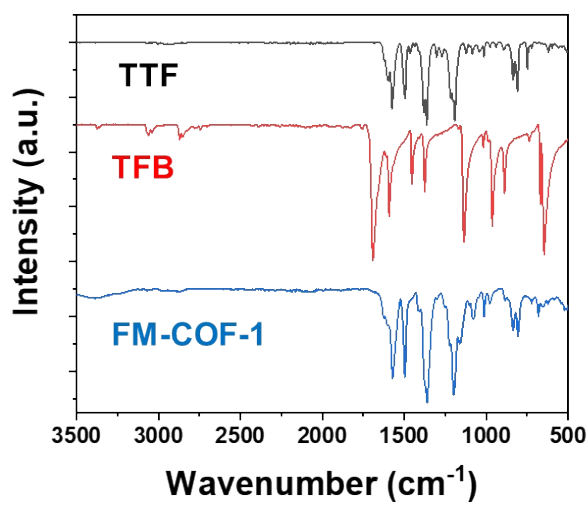


Figure S6. FT IR spectra of FM-COF-1 and building units.

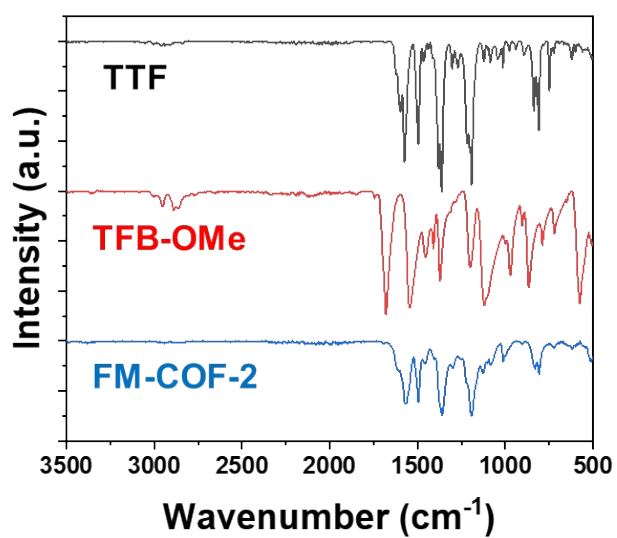


Figure S7. FT IR spectra of FM-COF-2 and building units.

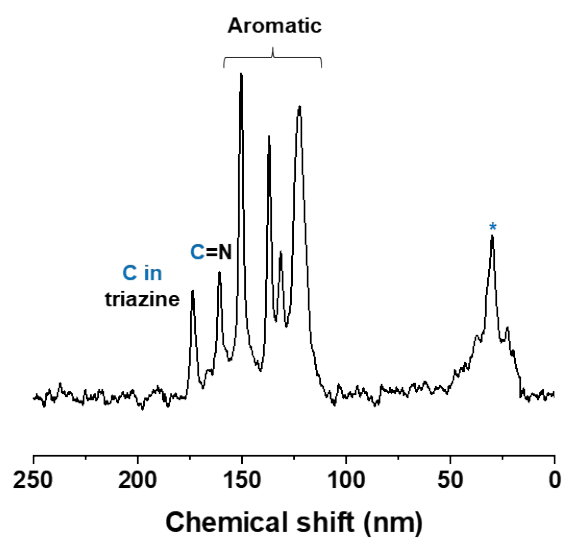


Figure S8. ^{13}C NMR spectrum of FM-COF-1.

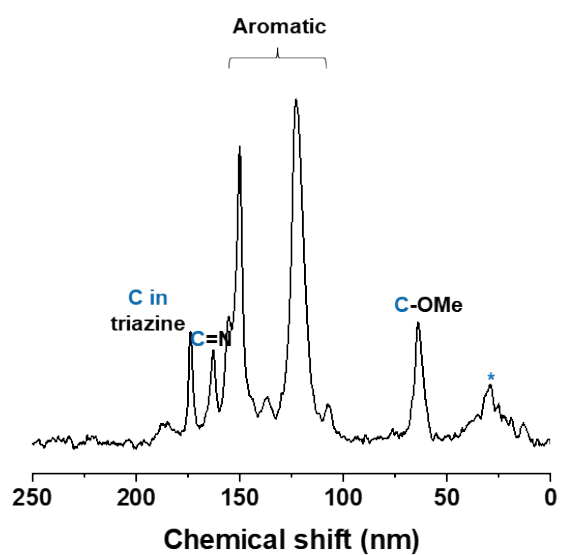


Figure S9. ^{13}C NMR spectrum of FM-COF-2.

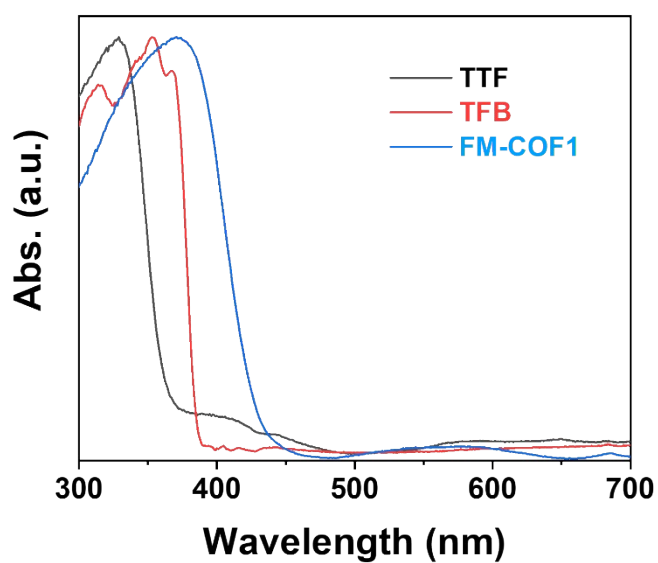


Figure S10. Solid UV spectra of FM-COF-1 and building units.

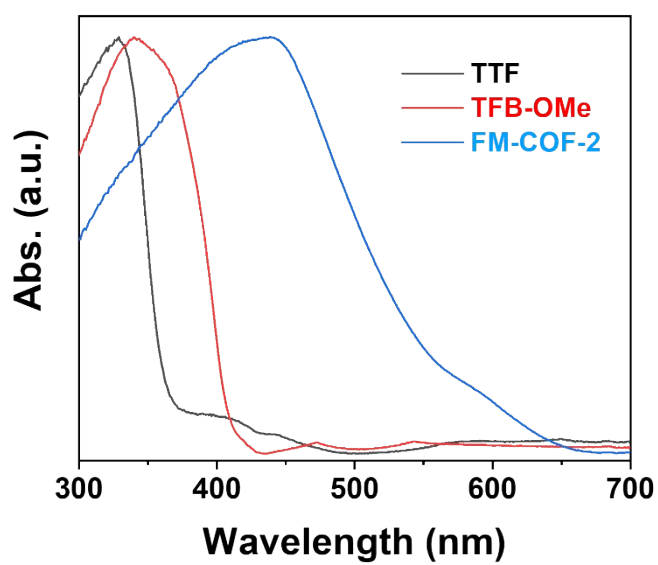


Figure S11. Solid UV spectra of FM-COF-2 and building units.

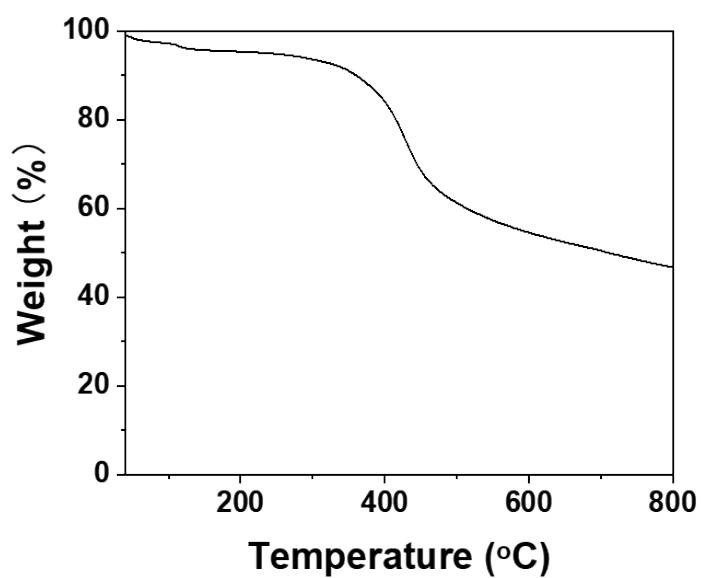


Figure S12. TGA curve of FM-COF-1 nitrogen atmosphere.

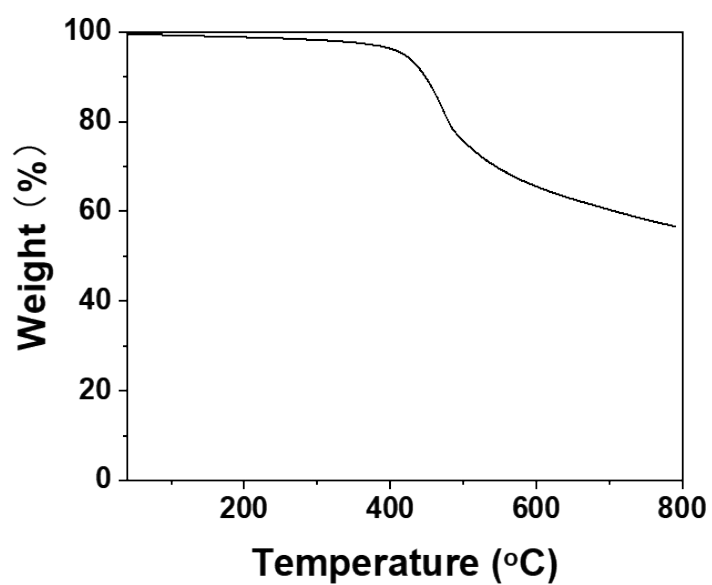


Figure S13. TGA curve of FM-COF-2 nitrogen atmosphere.

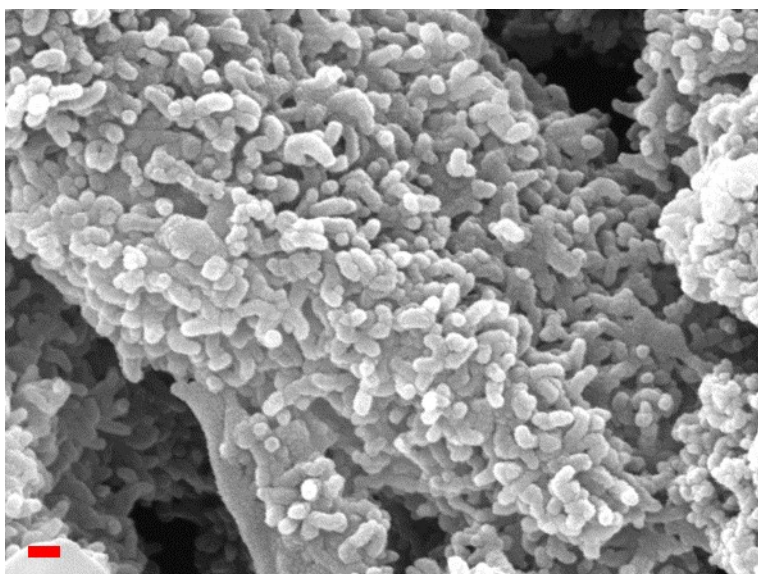


Figure S14. FE SEM image of FM-COF-1 (100 nm).

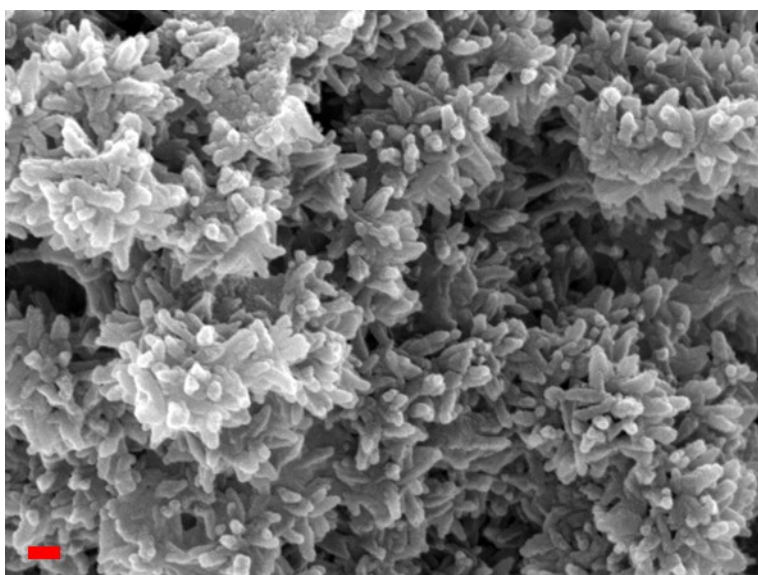


Figure S15. FE SEM image of FM-COF-2 (100 nm)

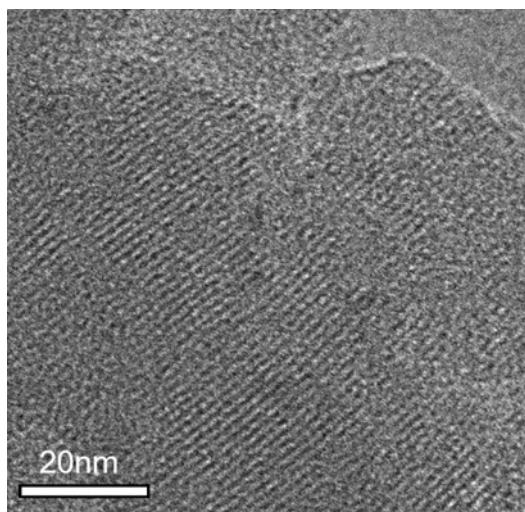


Figure S16. TEM image of FM-COF-1.

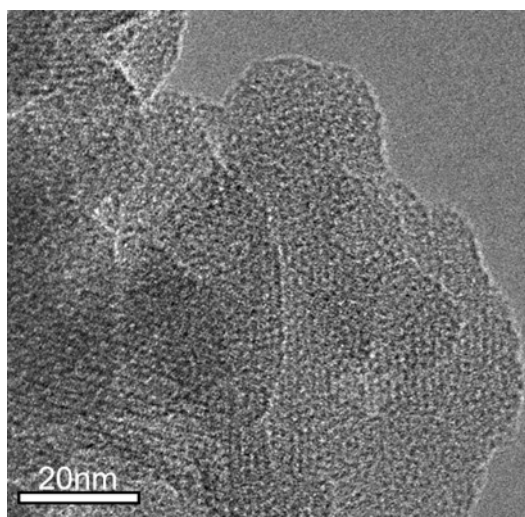


Figure S17. TEM image of FM-COF-2.

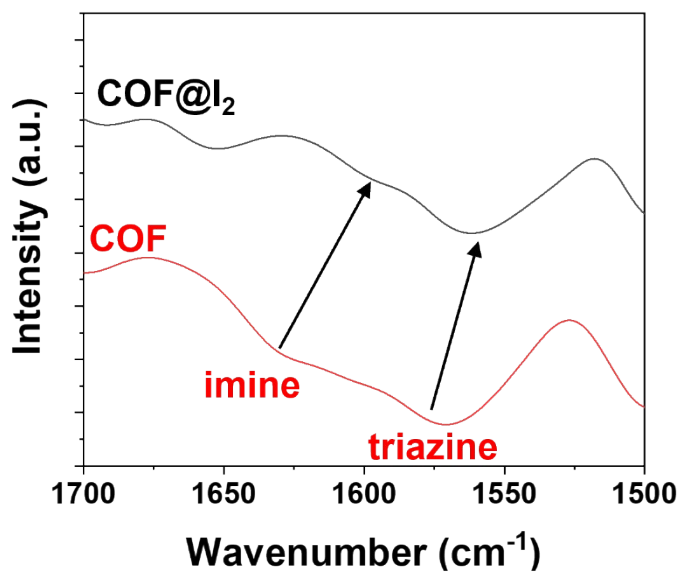


Figure S18. FT IR spectra of FM-COF-1 and FM-COF-1@iodine

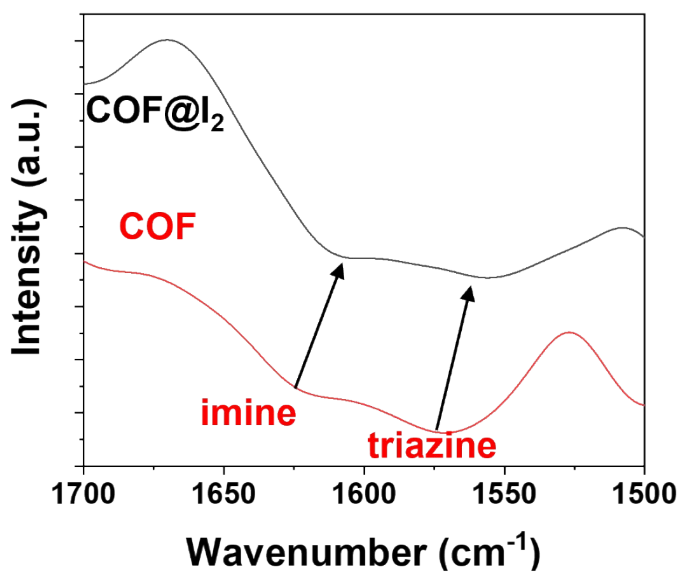


Figure S19. FT IR spectra of FM-COF-2 and FM-COF-2@iodine

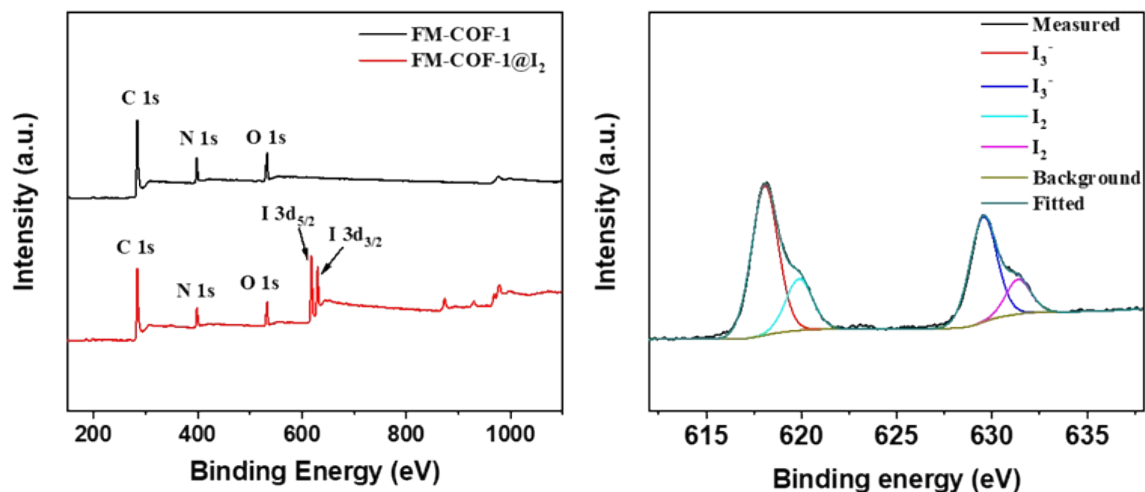


Figure S20. XPS spectra of FM-COF-1 and FM-COF-1@iodine

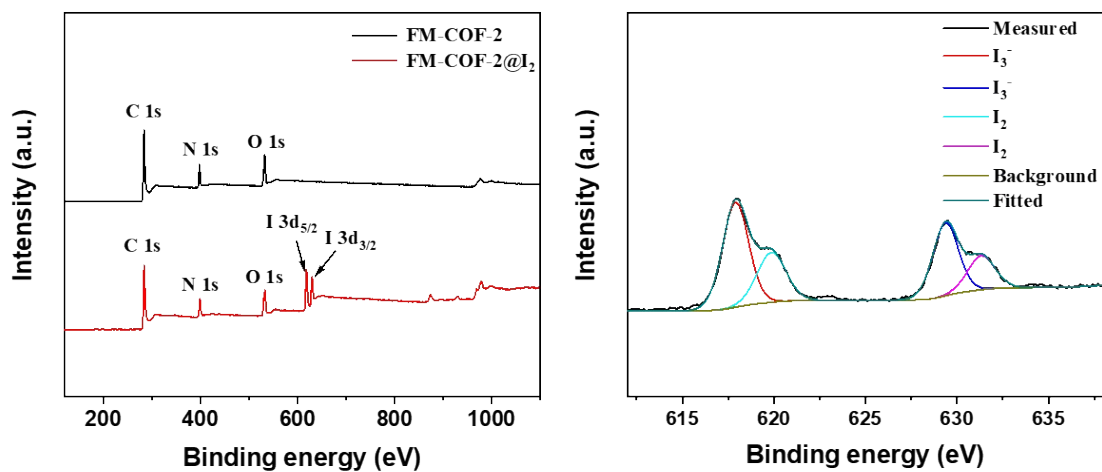


Figure S21. XPS spectra of FM-COF-2 and FM-COF-2@iodine.

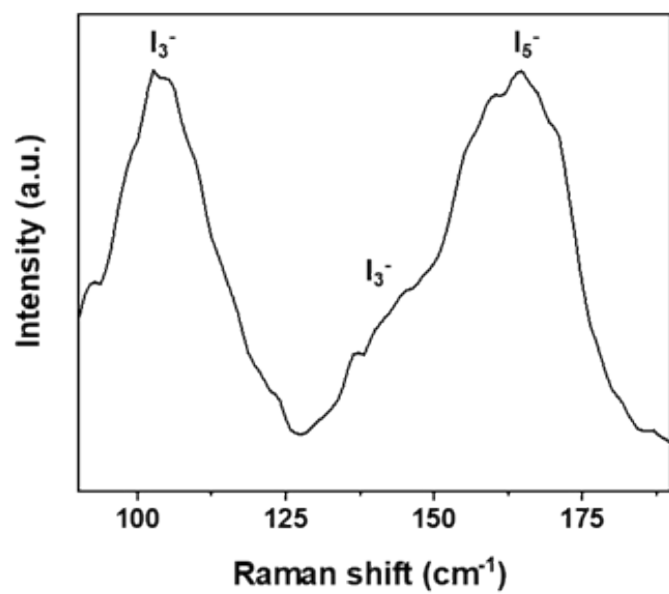


Figure S22. Raman spectrum of FM-COF-2@iodine.

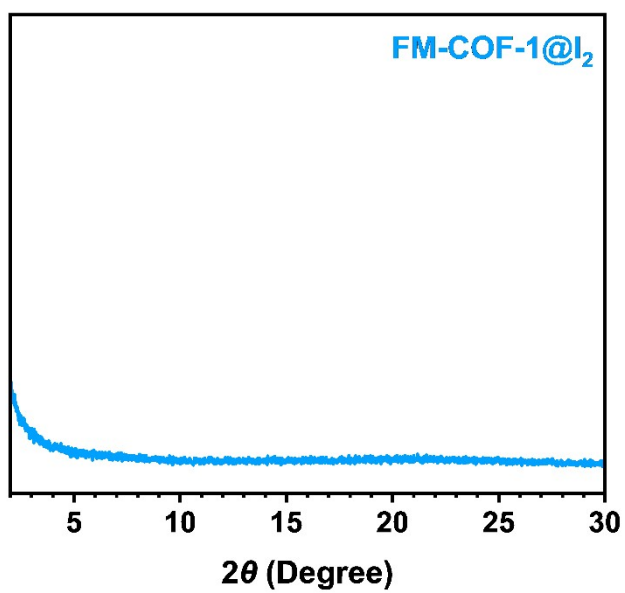


Figure S23. PXRD pattern of FM-COF-1@iodine.

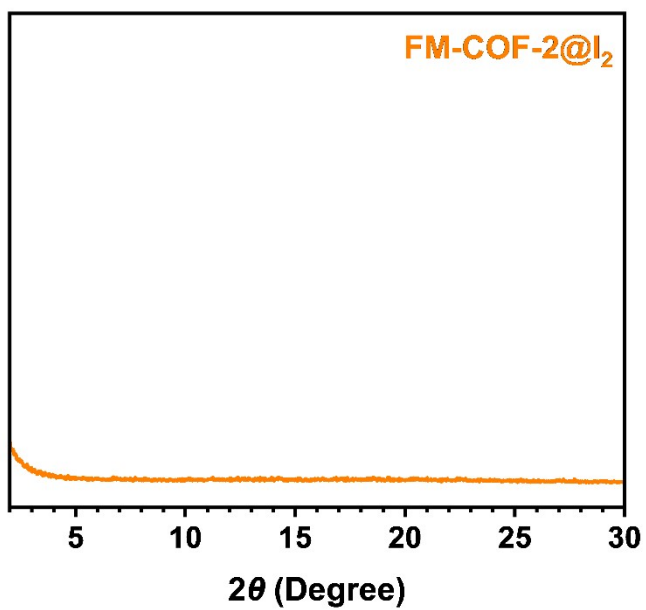


Figure S24. PXRD pattern of FM-COF-2@iodine.

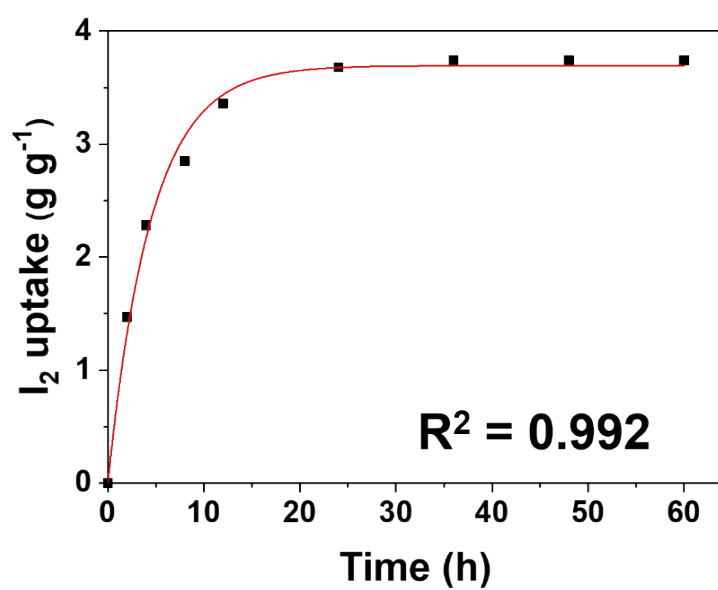


Figure S25. The pseudo-first-order kinetic model of FM-COF-1 for iodine capture process

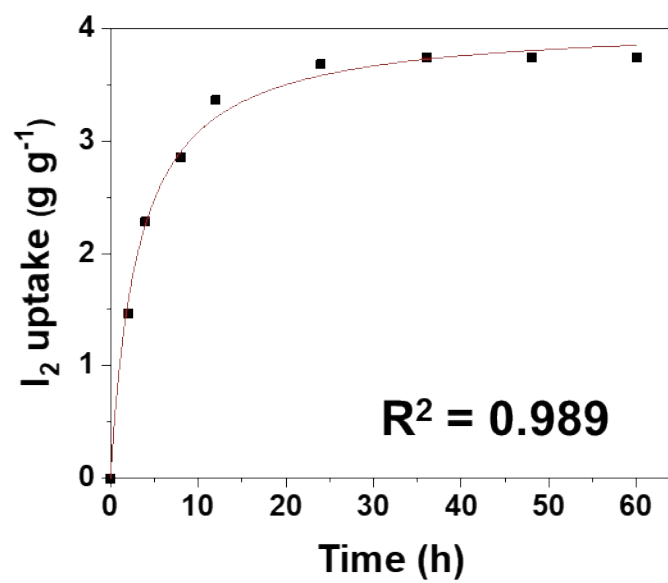


Figure S26. The pseudo-first-order kinetic model of FM-COF-2 for iodine capture process

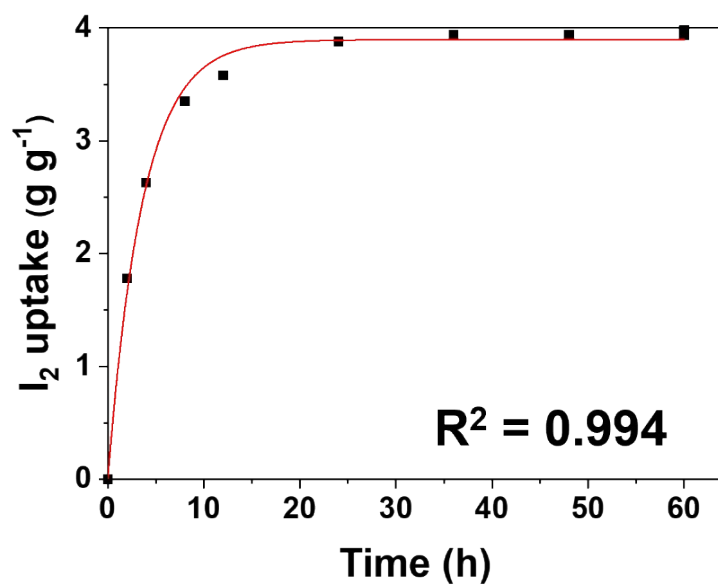


Figure S27. The pseudo-second-order kinetic model of FM-COF-1 for iodine capture process

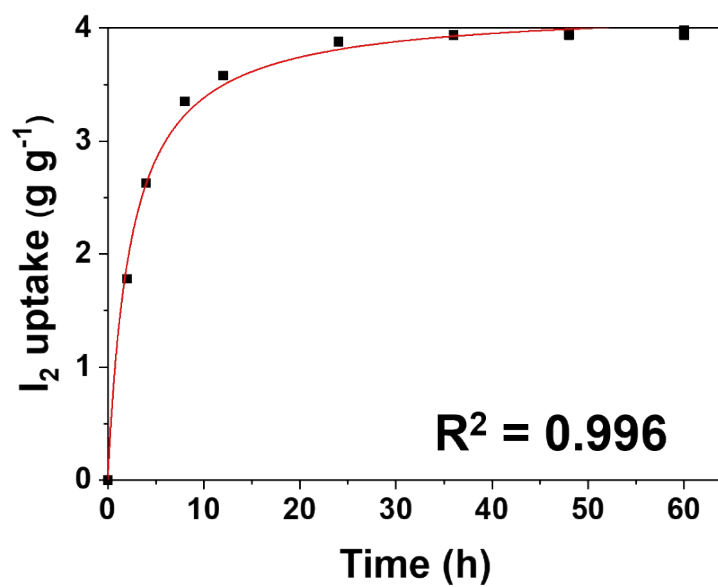


Figure S28. The pseudo-second-order kinetic model of FM-COF-2 for iodine capture process

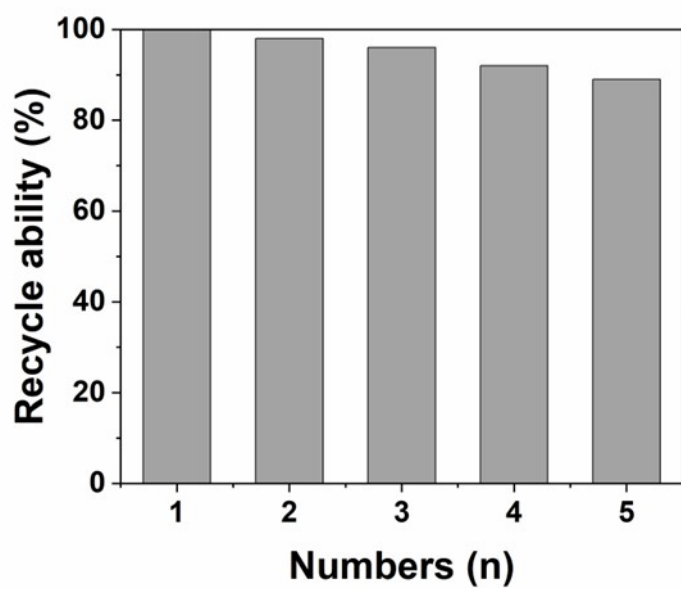


Figure S29. Recycle ability of FM-COF-1

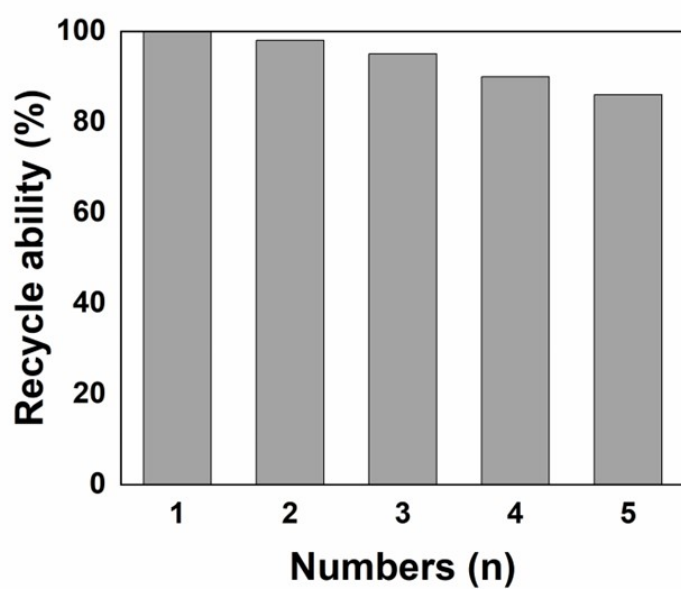


Figure S30. Recycle ability of FM-COF-2.

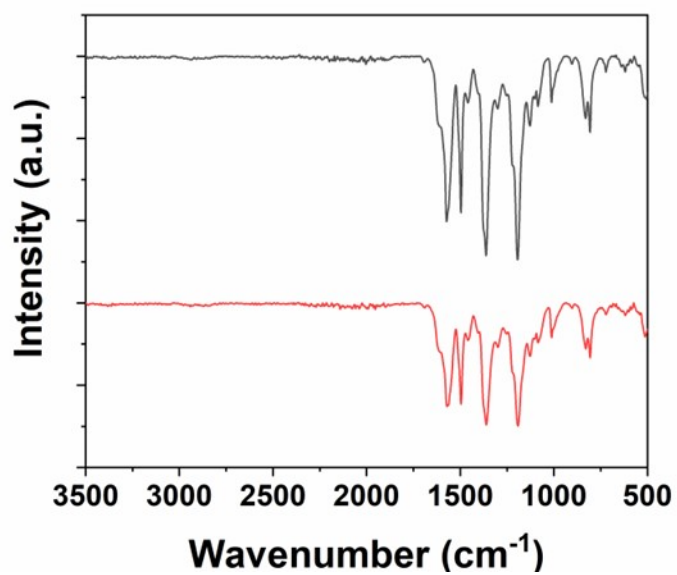


Figure S31. FT IR spectra of FM-COF-1 (as-synthesized: red; regenerated: black).

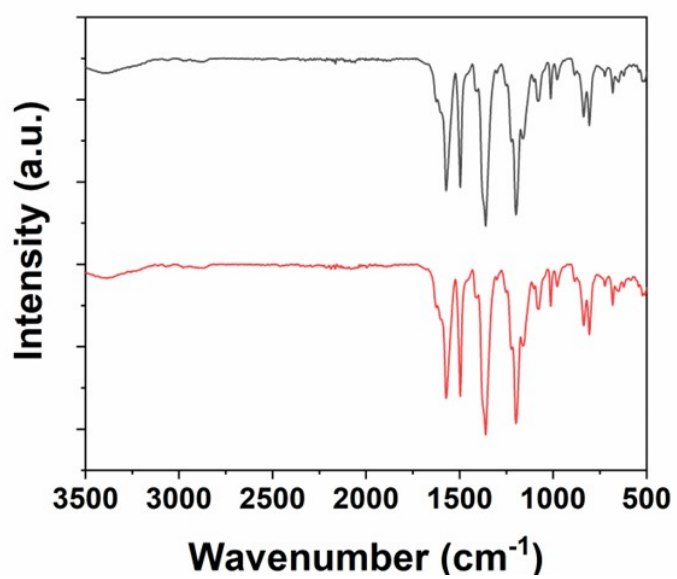


Figure S32. FT IR spectra of FM-COF-2 (as-synthesized: red; regenerated: black).

Table S3. Iodine capture of the reported microporous materials.

Sample	Temperature (K)	Pressure	S_{BET} (cm² g⁻¹)	Iodine uptake (g g⁻¹)	Reference
FM-COF-2	350 K	1 bar	452	3.98	<i>This work</i>
PAF-24	348 K	1 bar	136	2.76	<i>Angew. Chem. Int. Ed.</i> 2015, 54 , 12733–12737.
NiP-CMP	350 K	1 bar	2630	2.02	<i>Chem. Commun.</i> 2014, 50 , 8495–8498.
M-COF	350 K	1 bar	761	4.56	<i>Mater. Lett.</i> 2021, 304 , 130657.
ESM-COF-1	350 K	1 bar	722	4.01	<i>Microporous Mesoporous Mater.</i> 2023, 349 , 112419.
TTA-TMTA-COF	350 K	1 bar	801	3.21	<i>Macromol. Rapid Commun.</i> 2021, 42 , 2100032.
TJNU-203	350 K	1 bar	1833	5.88	<i>Chem. Commun.</i> 2021, 57 , 5558-5561
C-TP-PDA-COF	350 K	1 bar	133	3.05	<i>Mater. Chem. Front.</i> 2021, 5 , 5463-5470.
F-COF-2	350 K	1 bar	1552	5.51	<i>CrystEngComm.</i> 2023, 25 , 525-529
COF-OH	350 K	1 bar	1589	5.71	<i>CrystEngComm</i> 2023, 25 , 1910-1914.
NI-COF-2	350 K	1 bar	1061	4.92	<i>New J. Chem.</i> 2023, 47 , 3668-3671.
ECUT-COF-13	348 K	1 bar	425	10.81	<i>Science China Materials</i> 2023, 66 , 2339-2345.
TFB-DB COF	348 K	1 bar	734	6.40	<i>ACS Appl Mater Interfaces</i> 2021, 13 , 10513-10523.
CPOF-3	348 K	1 bar	640	5.87	<i>Dalton Trans</i> 2023, 52 , 731-736.

TFPPz- MPA- COF	400 K	1 bar	896	5.41	<i>ACS Appl. Polym. Mater.</i> 2023, 5 , 9497–9504.
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