

Supplementary Information

Constructing cationic covalent organic frameworks by post-function for exceptional iodine capture via electrostatic interaction

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Characterization. Fourier transform infrared (FT IR) spectra were recorded on a JASCO model FT IR-6100 infrared spectrometer. X-ray diffraction (XRD) data were recorded on a Bruker D8 Focus Powder X-ray Diffractometer by using powder on glass substrate, from $2\theta = 1.5^\circ$ up to 30° with 0.01° increment. Elemental analysis was performed on an Elemental vario MICRO cube elemental analyzer. Nitrogen sorption isotherms were measured at 77 K with a TriStar II instrument (Micromeritics). The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using the non-local density functional theory (NLDFT) model, the pore volume was derived from the sorption curve. Morphology images were characterized with a Zeiss Merlin Compact field emission scanning electron microscope (FE-SEM) at an electric voltage of 5 KV.

The crystalline structures of COFs were determined using the density-functional tight-binding (DFTB⁺) method including Lennard-Jones (LJ) dispersion. The calculations were carried out with the DFTB⁺ program package version 1.2. DFTB is an approximate density functional theory method based on the tight binding approach and utilizes an optimized minimal LCAO Slater-type all-valence basis set in combination with a two-center approximation for Hamiltonian matrix elements. The Coulombic interaction between partial atomic charges was determined using the self-consistent charge (SCC) formalism. Lennard-Jones type dispersion was employed in all calculations to describe van der Waals (vdW) and π -stacking interactions with starting structures created by AuToGraFSS1 and pre-optimized using a topology-preserving force field were used to optimize the monolayer and were further extended to layered frameworks with different stacking modes. The lattice dimensions were optimized simultaneously with the geometry. Standard DFTB parameters for X-Y element pair (X, Y = C, H, O, and N) interactions were employed from the mio-0-1 set10. The accessible surface areas were calculated from the Monte Carlo integration technique using a nitrogen-size probe molecule (diameter = 3.68 Å) roll over the framework surface with a grid interval of 0.25 Å. The XRD pattern simulation was performed in a software package for crystal determination from PXRD pattern, implemented in MS modeling version 4.4 (Accelrys Inc.). We performed Pawley refinement to optimize the lattice parameters iteratively until the R_p and R_{wp} values converge. The pseudo-Voigt

profile function was used for whole profile fitting and Berrar-Baldinozzi function was used for asymmetry correction during the refinement processes.

Synthesis of TP-PDA-COF

A pyrex tube (10 ml) is charged with 2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde (50 mg, 0.24 mmol), pyridine-2,5-diamine (39 mg, 0.36 mmol), and 2 mL dioxane/mesitylene (v/v, 1:2), and 0.2 mL of 6 M aqueous acetic acid. 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 days. The powder collected was washed with N, N'-dimethylacetamide, tetrahydrofuran, and methanol several times, and then dried at 100 °C under vacuum for 12 hours to get the target COF sample in 86% isolated yield (64 mg).

Synthesis of TP-BPDA-COF

A pyrex tube (10 ml) is charged with 2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde (50 mg, 0.24 mmol), [2,2'-bipyridine]-5,5'-diamine (67 mg, 0.36 mmol), and 2 mL N, N'-dimethylacetamide (DMAc) and o-dichlorobenzene (o-DCB) (v/v, 1:3), and 0.2 mL of 6 M aqueous acetic acid. 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 days. The powder collected was washed with N, N'-dimethylacetamide, tetrahydrofuran, and methanol several times, and then dried at 100 °C under vacuum for 12 hours to get the target COF sample in 84% isolated yield (85 mg).

Synthesis of C-TP-PDA-COF and C-TP-BPDA-COF^{S1}

TP-PDA-COF (50 mg) was dispersed in bromoethane (2.0 mL) in a flask. The mixture was degassed by three freeze-pump-thaw cycles. The mixture was refluxed at 12 h under nitrogen protection. The product was filtered, washed with THF, ethanol, and acetone, and dried under vacuum for 12 hours to afford the C-TP-PDA-COF (82 mg). C-TP-BPDA-COF was prepared under the same condition.

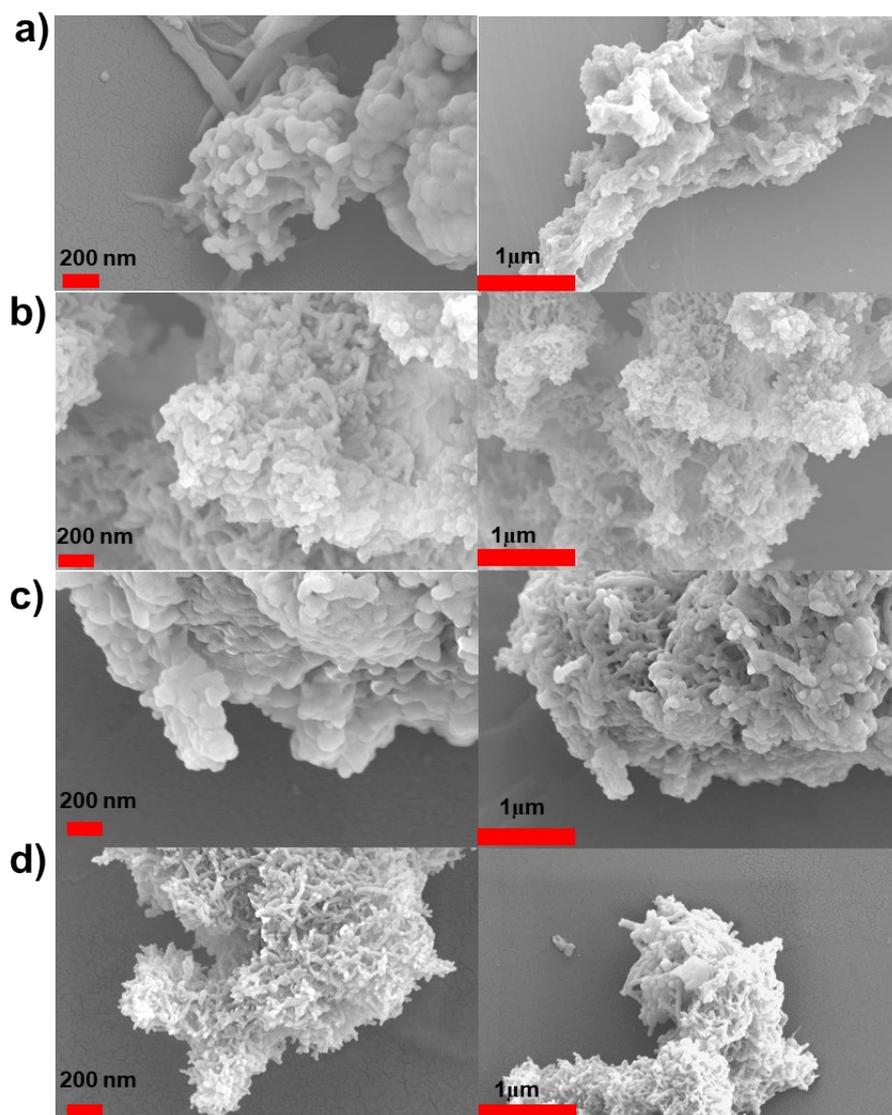


Fig. S1. FE SEM images of (a) TP-PDA-COF, (b) TP-BPDA-COF, (c) C-TP-PDA-COF, and (d) C-TP-BPDA-COF.

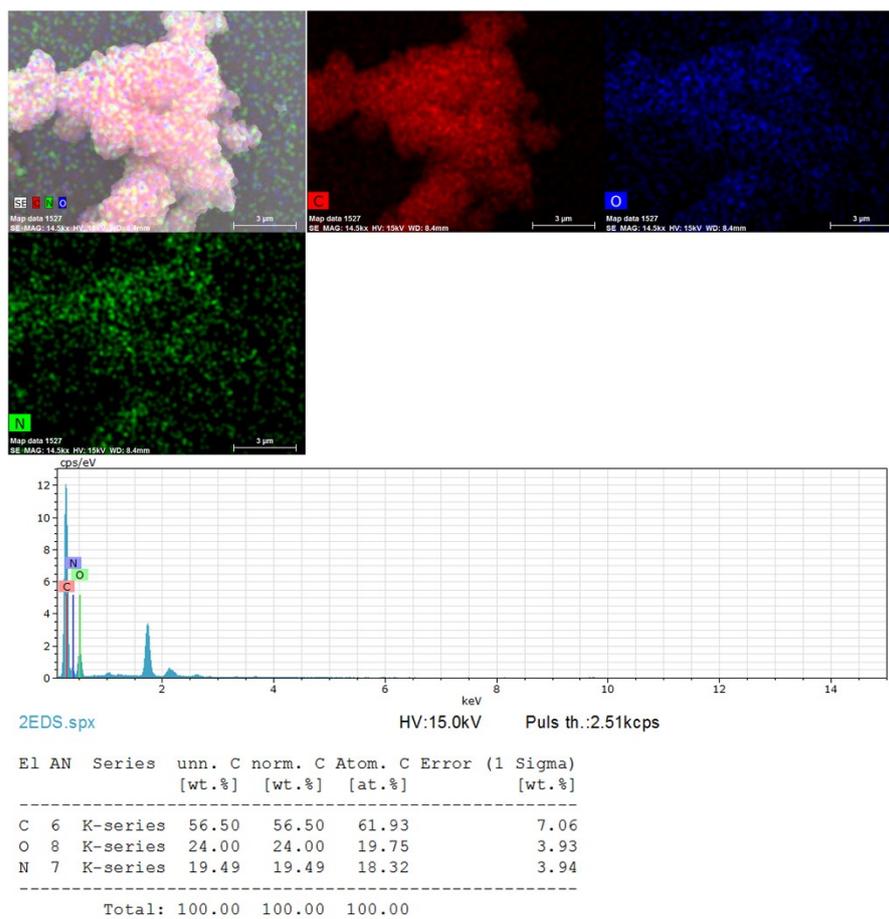


Fig. S2. EDS mapping images of TP-PDA-COF.

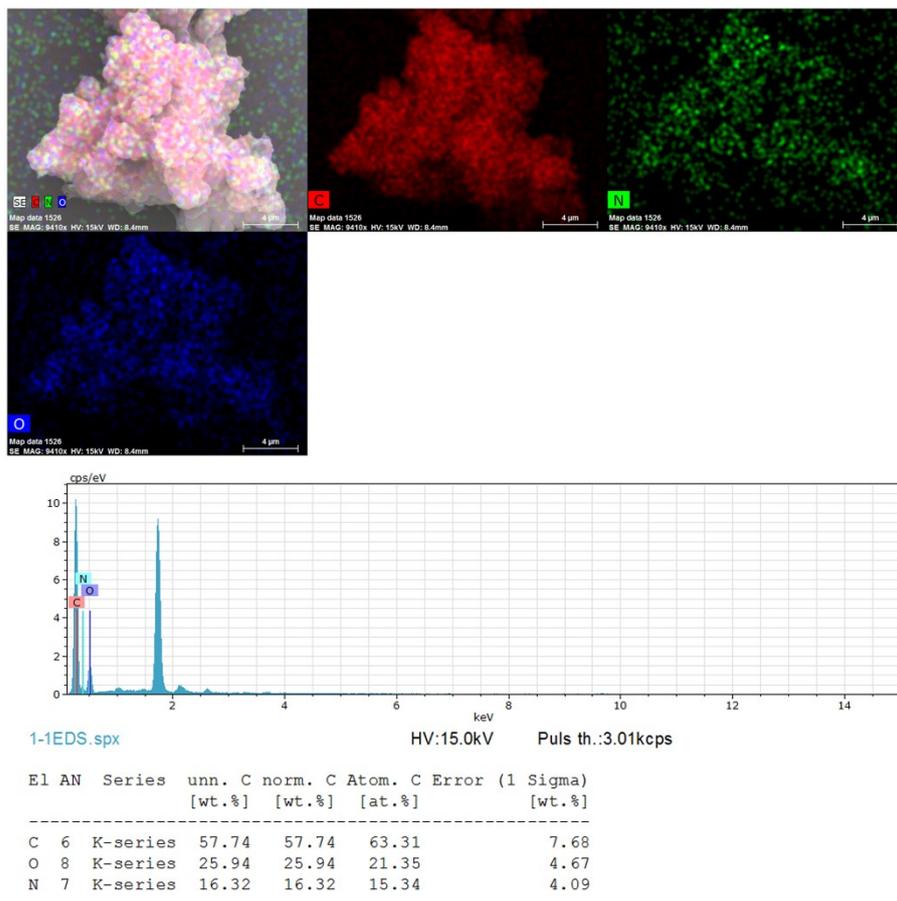
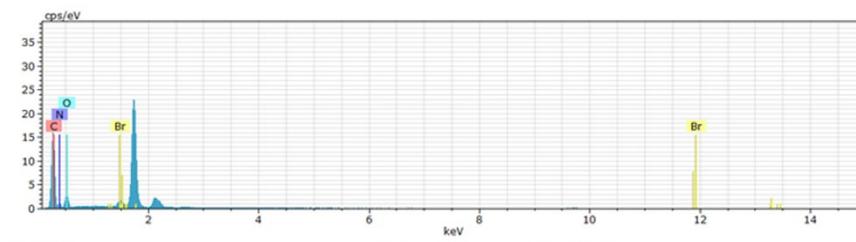
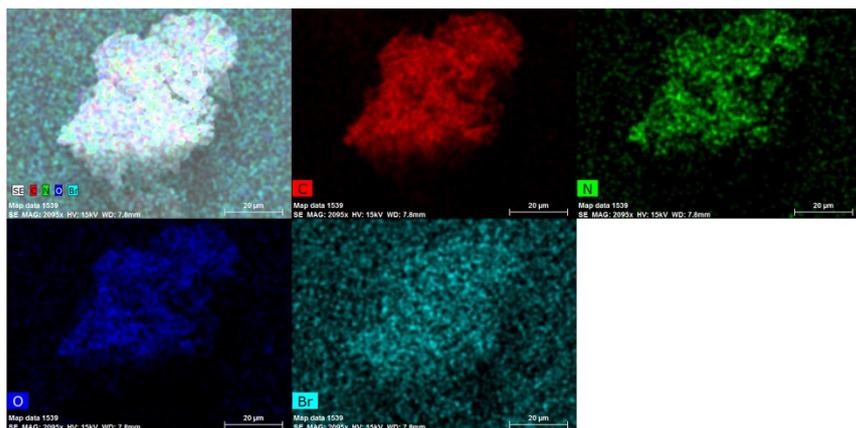


Fig. S3. EDS mapping images of TP-BPDA-COF.



1-1EDS.spx

HV:15.0kV Puls th.:7.35kcps

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
C	6	K-series	52.76	52.76	60.24	6.94
O	8	K-series	22.23	22.23	19.05	3.81
N	7	K-series	20.33	20.33	19.90	4.19
Br	35	L-series	4.68	4.68	0.80	0.28
Total:			100.00	100.00	100.00	

Fig. S4. EDS mapping images of C-TP-PDA-COF.

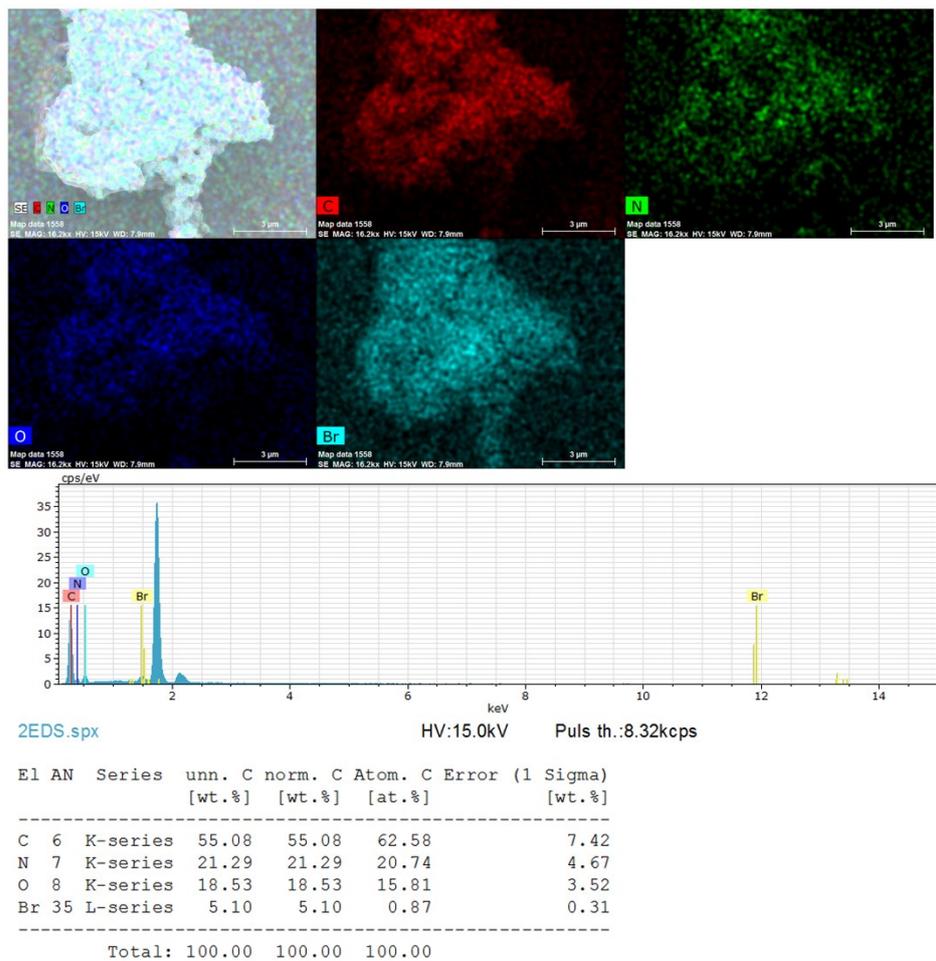


Fig. S5. EDS mapping images of C-TP-BPDA-COF.

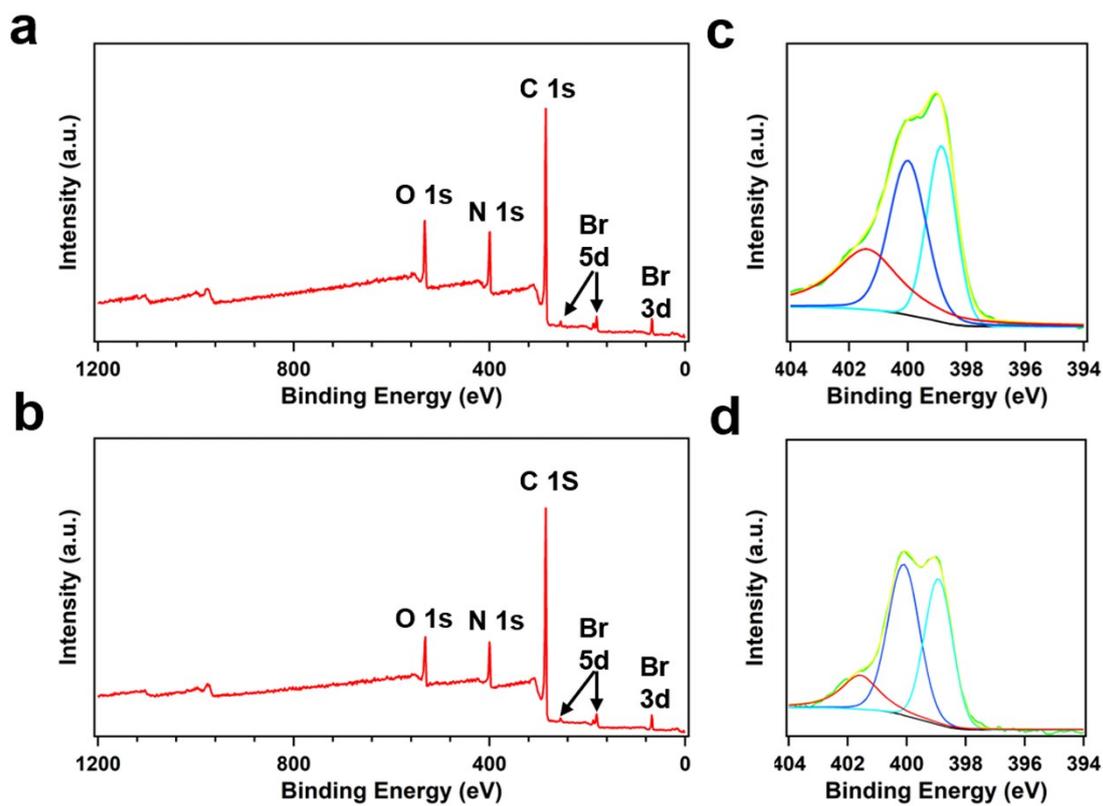
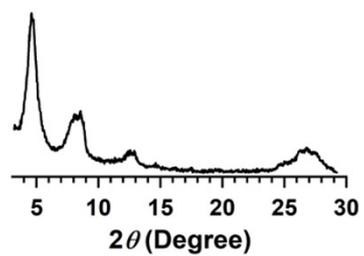


Fig. S6. X-ray photoelectron spectroscopy (XPS) spectra of (a) C-TP-PDA-COF and (b) C-TP-BPDA-COF; N 1s spectra of (c) C-TP-PDA-COF@N and (d) C-TP-BPDA-COF@N.

a



b

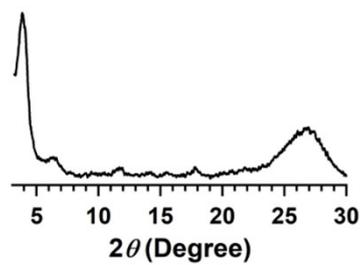


Fig. S7. PXRD patterns of (a) C-TP-PDA-COF and (b) C-TP-BPDA-COF.

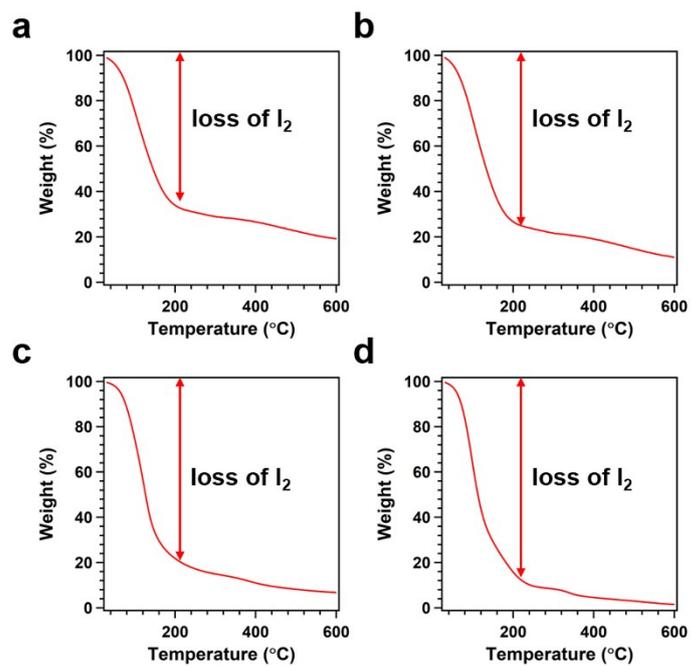


Fig. S8. TGA curves of (a) TP-PDA-COF@I₂, (b) P-BPDA-COF@I₂, (c) C-TP-PDA-COF@I₂ and (d) C-TP-BPDA-COF@I₂.

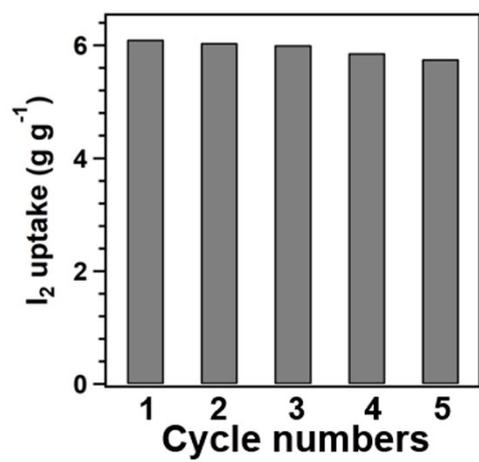


Fig. S9. Recycle performance of iodine capture for C-TP-BPDA-COF.

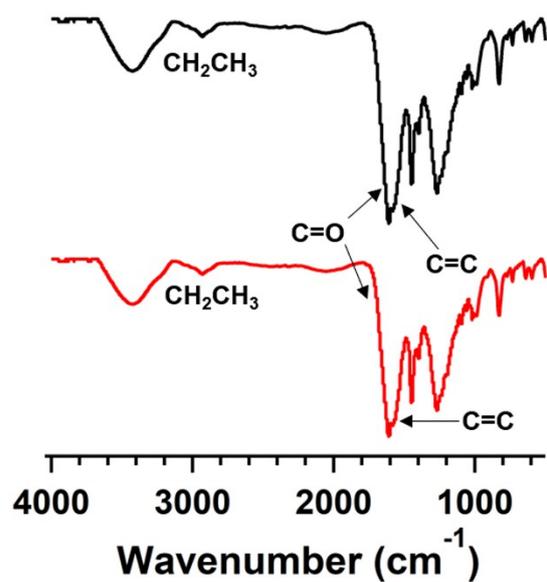


Fig. S10. FT IR spectra of for C-TP-BPDA-COF (red curve) and recycle-C-TP-BPDA-COF (black curve).

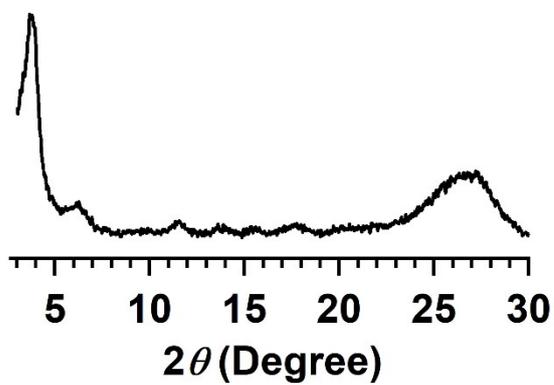


Fig. S11. PXRD pattern of recycle-C-TP-BPDA-COF.

Reference

- S1. Z. Mi, T. Zhou, W. Weng, J. Unruangsri, K. Hu, W. Yang, C. Wang, K. A. I. Zhang, J. Guo, Covalent organic frameworks enabling site isolation of viologen-derived electron-transfer mediators for stable photocatalytic hydrogen evolution, *Angew. Chem. Int. Ed.*, 2021, **60**, 9642-9649.