Electronic supplementary information

The synergy between a benzoselenadiazole covalent organic framework and TEMPO for selective photocatalytic aerobic oxidation of organic sulfides

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1. Characterizations

^1H NMR spectra were made on a Bruker AVANCE III HD 400 MHz NMR spectrometer. The Fourier transform infrared spectroscopy (FTIR) was recorded from 400 to 4000 cm^{-1} on Nicolet 5700 FTIR Spectrometer by using KBr pellets. All spectra were collected neatly in an ambient atmosphere. The signals are given in transmittance (%) against wavenumbers (cm^{-1}). Solid-state ^{13}C cross-polarization/magic angle spinning nuclear magnetic resonance (CP-MAS NMR) experiments were performed on a Bruker AVANCE III 400 WB spectrometer operating at 100.62 MHz for ^{13}C using a double resonance 4 mm MAS NMR probe and a sample spinning rate of 10 kHz. The cross-polarization time was 1 ms. The chemical shifts were referenced with trimethylsilane. The high-resolution transmission electron microscopy (HRTEM) images of COF photocatalysts were estimated on a JEOL JEM-2100 operating at an accelerating voltage of 200 kV. Powder X-ray diffraction (PXRD) measurement was marched adopting a Rigaku/Miniflex 600 diffractometer with a filtered Cu Kα line, and the spectra were gathered from 2° to 30° at room temperature. Field emission scanning electron microscopy (FE-SEM) was measured on a Zeiss Merlin Compact running at the acceleration voltage between 2 and 10 kV. The N_2 isotherms and specific surface areas were determined at 77 K employing a Micromeritics ASAP 2460 automated system with the Brunauer–Emmet–Teller (BET) model, the samples were degassed in a vacuum (< 1×10^{-5} bar) at 120 °C for 8 h in the Micromertics system before N_2 physisorption. Meantime, porosity distributions were determined from the Nonlocal

Density Functional Theory (NLDFT) method. With $BaSO_4$ as a reflectance standard, the UV-vis DRS of two covalent organic frameworks was estimated from 300−800 nm by a UV-3600 UV-vis spectrophotometer (Shimadzu, Japan) configured with a diffuse reflectance measurement accessory. The thermogravimetric analysis (TGA) curves were recorded on an SDT Q600 thermogravimeter from 30 to 800 °C at a rate of 10 °C/min under an N_2 atmosphere. After completion, the reaction mixture was detected by a gas chromatograph equipped with a flame ionization detector (GC-FID, Agilent 8890), using N_2 as the carrier gas and bromobenzene as the internal standard. The products were further verified by gas chromatography-mass spectrometry (GC-MS, Agilent 8890-5977B), using He as the carrier gas.

2. Electrochemical measurements

Electrochemical measurements were executed on a Metrohm Autolab PGSTAT302N in a three-electrode electrochemical cell equipped with an electrochemical station. The working electrodes were prepared as follows: 2 mg of photocatalyst was dispersed in 1.0 mL absolute ethanol and 50 μL Nafion mixture solution, which was ultrasonically dispersed for 30 min, and then 50 μL of mixture solution was dropped onto the ITO with $\pi \times (0.2)^2$ cm^2 illuminated area and dried at room temperature, and the samples were dried under infrared irradiation. With 0.1 M Na_2SO_4 aqueous solution supplied as the electrolyte, the Ag/AgCl electrode and platinum wire were the reference electrode and counter electrode, respectively.

Meanwhile, the 3 W×4 blue LEDs (Shenzhen Ouying Lighting Science and Technology Co., Ltd.) with a wavelength of 460 ± 10 nm placed at 2 cm away from the photoelectrochemical cell were employed as the light source. The photocurrents were tested under blue LEDs irradiation with light on-off cycles at a time interval of 30 s and the scan rate was 100 mV/s. The electrochemical impedance spectroscopy (EIS) was carried out at a bias potential of + 0.5 V in the dark. In cyclic voltammetry measurements, the reference electrode was replaced with Ag/AgCl electrode (corrected with Ferrocenium/ferrocene (Fc/Fc^+) as internal reference), with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in CH_3CN as the supporting electrolyte with a sweep rate of 5 mV/s.

3. Structure Modeling and PXRD Refinement of TpBSe-COF and TpDT-COF

Structural modeling of COFs was generated using the Accelrys Materials Studio 7.0 software package. The space groups were obtained from the Reticular Chemistry Structure Resource. The model was constructed in the initial lattice with the space group of P1. The proposed model was geometry optimized using the MS Forcite molecular dynamics module (Universal force fields, Ewald summations) to obtain the optimized lattice parameters. AB stacking of TpBSe-COF and TpDT-COF was built by offsetting the stacked units from the AA model. Pawley refinement was applied to define the lattice parameters by Reflex module, producing the refined PXRD profile.

4. The procedure of selective photocatalytic oxidation of sulfides.

COF (5 mg), TEMPO (10 μmol), and sulfides (0.5 mmol) were put into a Pyrex reactor (10 mL) and dispersed by CH_3OH (1 mL). Stirring for 15 min to achieve the adsorption and desorption equilibrium. Subsequently, the Pyrex reactor was filled with oxygen and irradiated by 460 nm blue LED for photocatalytic reaction. After reaction, analysis, and detection of target products were used gas chromatography with a flame ionization detector (GC-FID). Furthermore, the products were validated through gas chromatography-mass spectrometry (GC-MS).

Conversion and selectivity for the oxidation of sulfides to sulfoxides were defined as follows:

$$\text{Conv. (\%)} = [(C_0 - C_S)/C_0] \times 100$$

$$\text{Sel. (\%)} = [C_p/(C_0 - C_S)] \times 100$$

where C_0 is the initial concentration of sulfide, and C_S and C_p are the concentrations of sulfides and corresponding sulfoxide at a certain time during the photocatalytic reaction.

5. Synthetic procedures

5.1 Synthesis of 4,4'-(benzoselenadiazole-4,7-diyl)dianiline
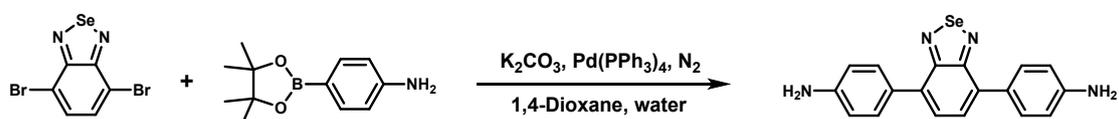
4,7-Dibromo-2,1,3-benzoselenadiazole (300 mg, 0.88 mmol), 4-aminophenylboronic acid pinacol ester (424 mg, 1.94 mmol), K_2CO_3 (268 g, 1.94 mmol) and $Pd(PPh_3)_4$ (51 mg, 0.044 mmol) were added into the mixture solution of 1,4-dioxane (16 mL) and water (4 mL). The mixture was degassed for 15 min and then refluxed under an N_2 atmosphere for 3 days. After cooling down to room temperature, the formed precipitate was poured into water and extracted by dichloromethane for three times. After the solvent was evaporated, the crude product was chromatographed on silica gel using DCM/PE=4/1 as an eluent to afford a red solid. Yield: 241.9 mg (75%). ^1H NMR (400MHz, DMSO-d6): δ 7.68 (d, 4H), δ 7.52 (s, 2H), δ 6.68 (d, 4H), δ 5.32 (s, 4H). ^1H NMR spectrum of BSe was shown in Figure S15.

5.2 Synthesis of TpBSe-COF and TpDT-COF

TpBSe-COF was synthesized with an organobase catalyzed approach.[1] Specifically, Tp (8.4 mg, 0.04 mol), BSe (21.9 mg, 0.06 mol) was put into a 10 mL Pyrex tube. Upon addition of o-dichlorobenzene (o-DCB, 950 μL), and n-Butanol (n-BuOH, 50 μL), the mixture was sonicated for 5 min. Then, pyrrolidine (20 μL) as a catalyst was added to the Pyrex tube and ultrasound again for 1 min. Subsequently, under 77 K nitrogen, the tube was frozen, degassed, and sealed with a flame. After heating for 96 h under 120 °C, the product was collected and washed with tetrahydrofuran (4 × 5 mL) and methanol (CH_3OH, 4 × 5 mL), followed by Soxhlet

extraction with tetrahydrofuran for 48 h. The reddish powder was obtained with a yield of 60% after drying for 24 h under 100 °C.

TpDT-COF was synthesized by a prior report with some modifications.[2] On the whole, the synthesis procedure of TpDT-COF is similar to TpBSe COF. The only difference was that the monomer is DT instead of BSe. The obtained TpDT-COF was yellowish powder with a yield of 83%.

6. Supplementary Figures and Tables
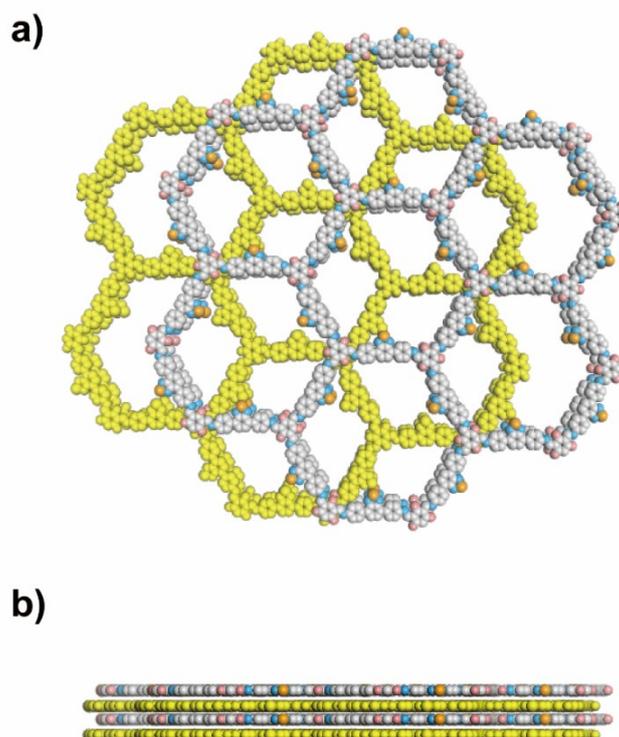
Fig. S1 a) Top view and b) side view of TpBSe-COF with AB stacking mode, hydrogen atoms are omitted for clarity.
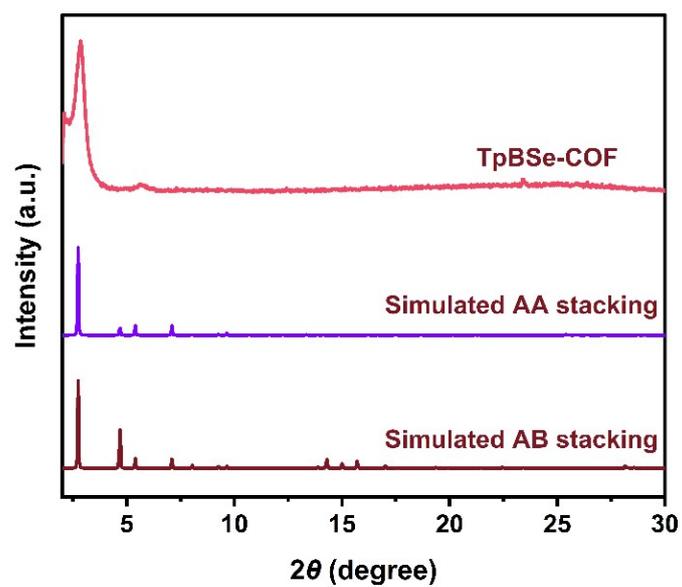
Fig. S2 Experimental PXRD pattern of TpBSe-COF and the simulated PXRD patterns for AA and AB stacking models.
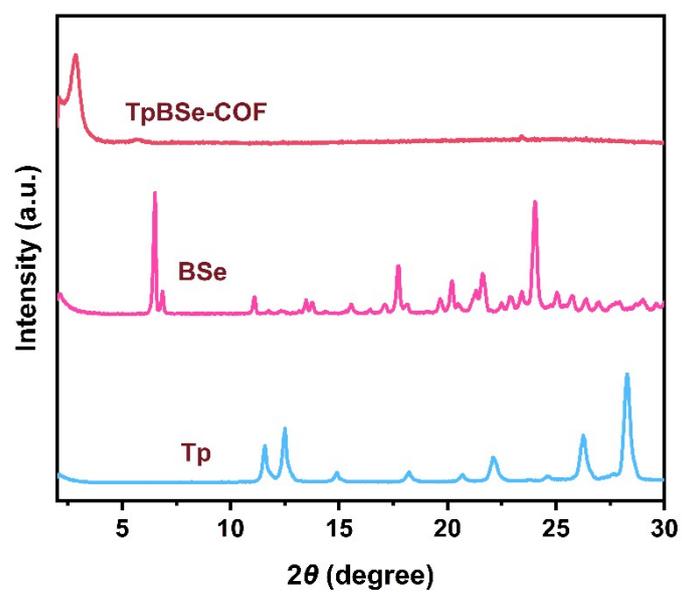
Fig. S3 PXRD patterns of TpBSe-COF and its monomers.
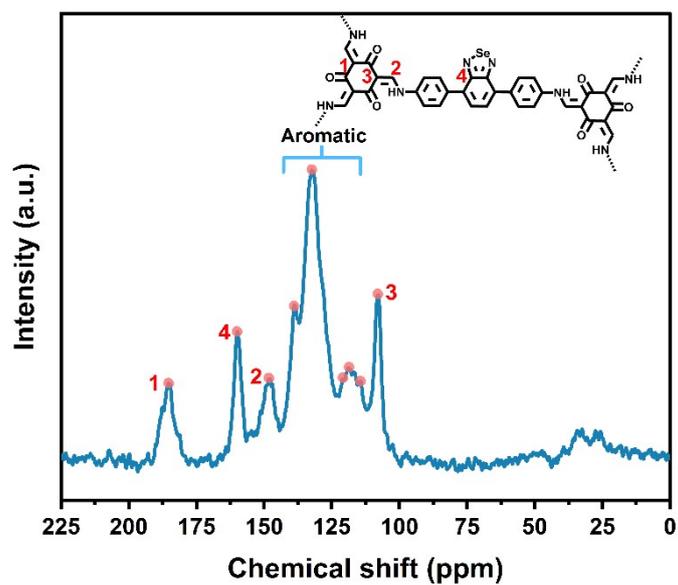
Fig. S4 Solid-state ^{13}C CP-MAS NMR of TpBSe-COF.
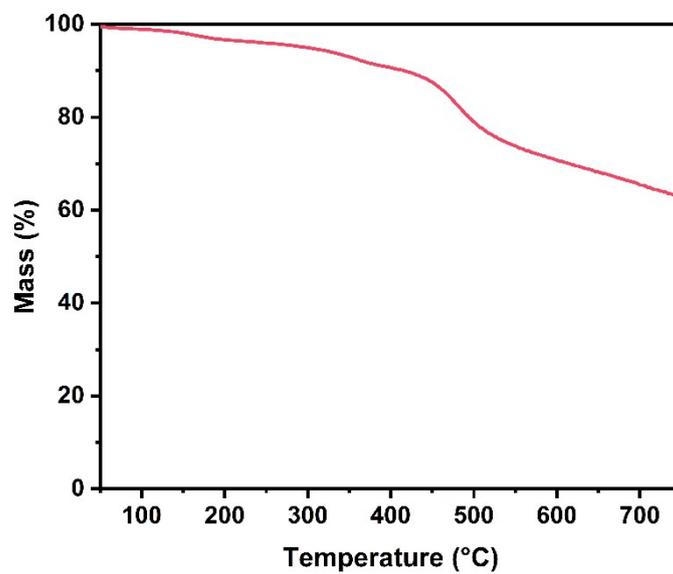
Fig. S5 TGA curve of TpBSe-COF.
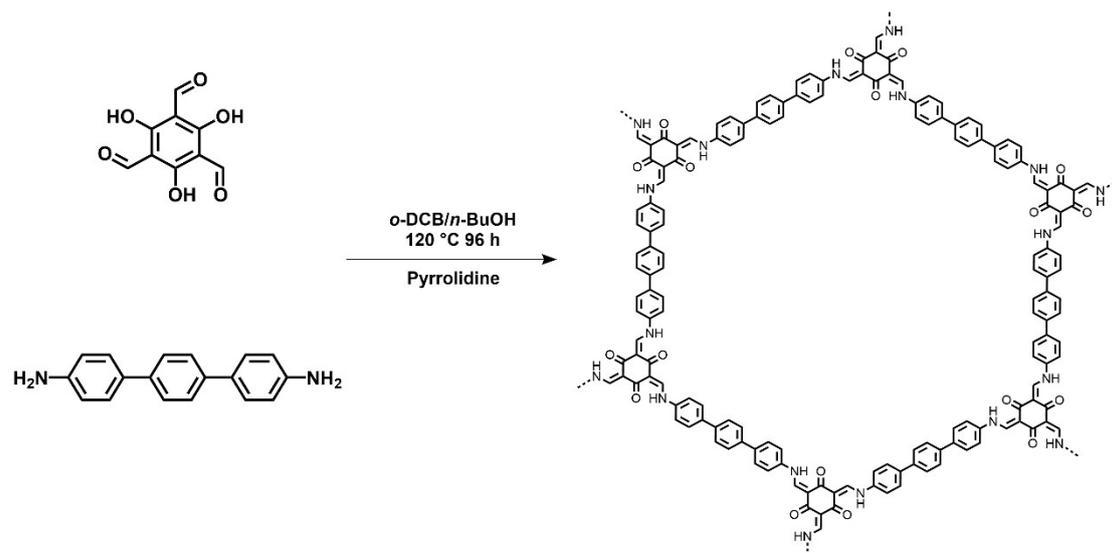
Fig. S6 Synthesis scheme of TpDT-COF.
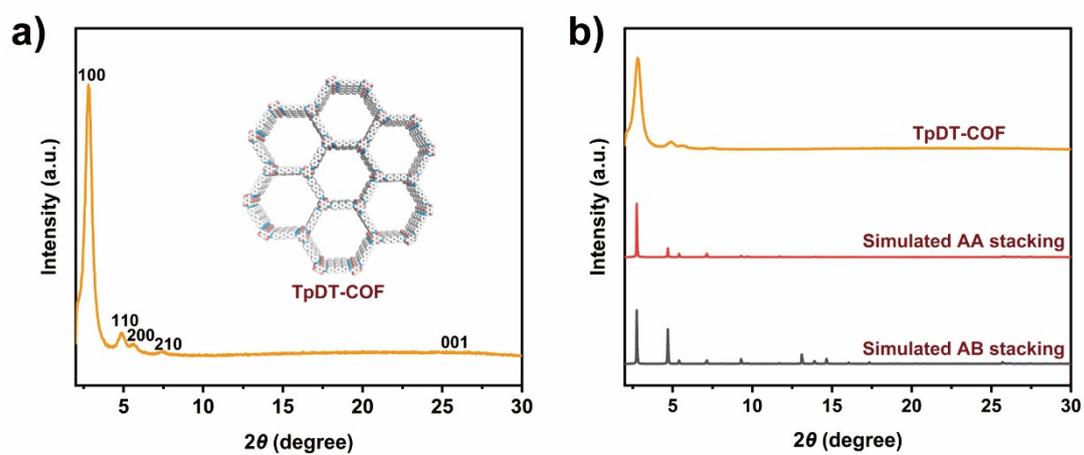
Fig. S7 a) Experimental PXRD pattern of TpDT-COF. b) The simulated PXRD patterns

for AA and AB stacking models.
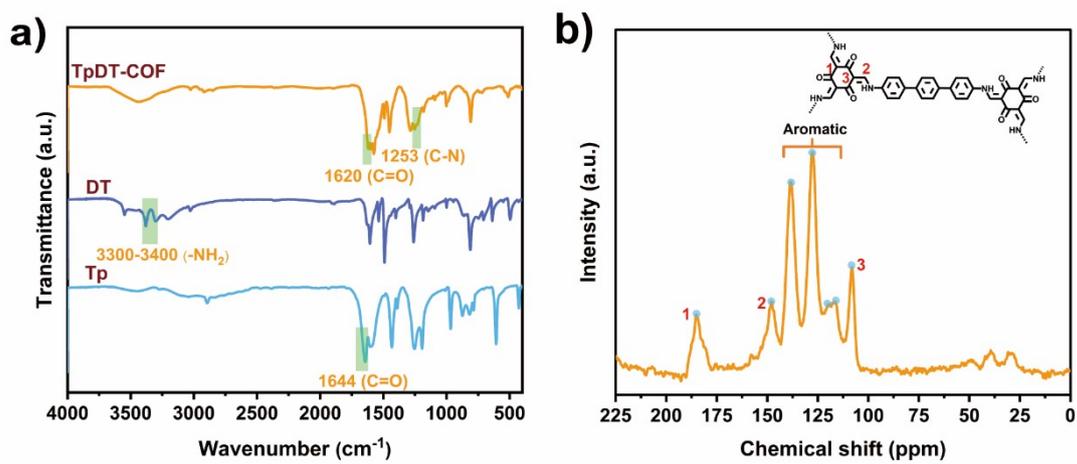
Fig. S8 a) FTIR spectra of the monomers and TpDT-COF. b) Solid-state ^{13}C CP-MAS NMR spectrum of TpDT-COF.
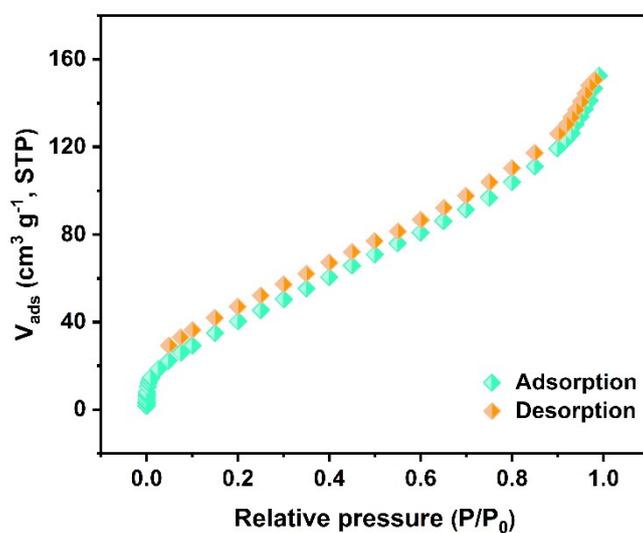
Fig. S9 N_2 sorption isotherms of TpDT-COF at 77 K.
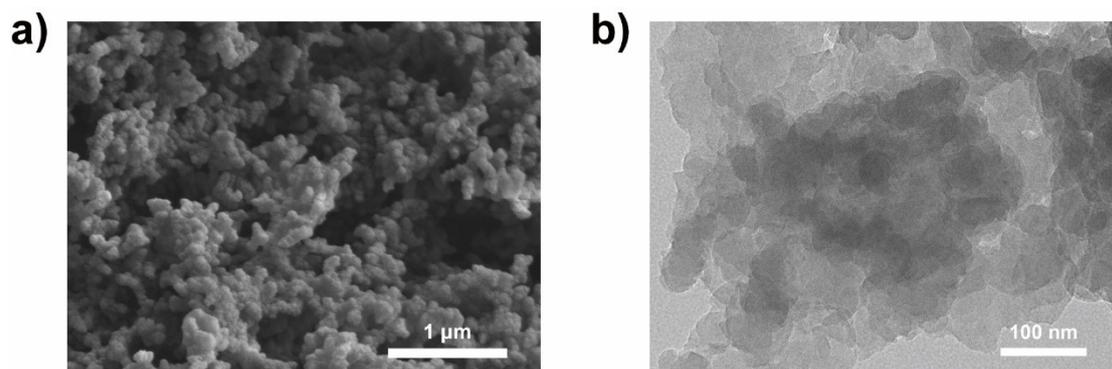
Fig. S10 a) SEM image of TpDT-COF. b) TEM image of TpDT-COF.
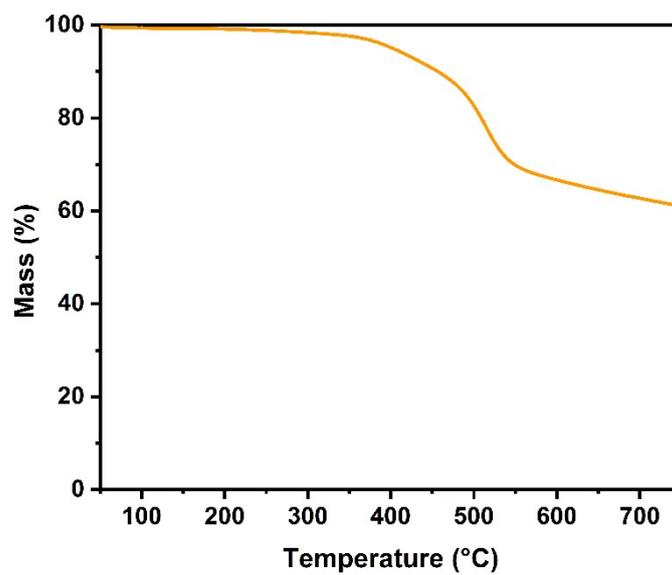
Fig. S11 TGA curve of TpDT-COF.
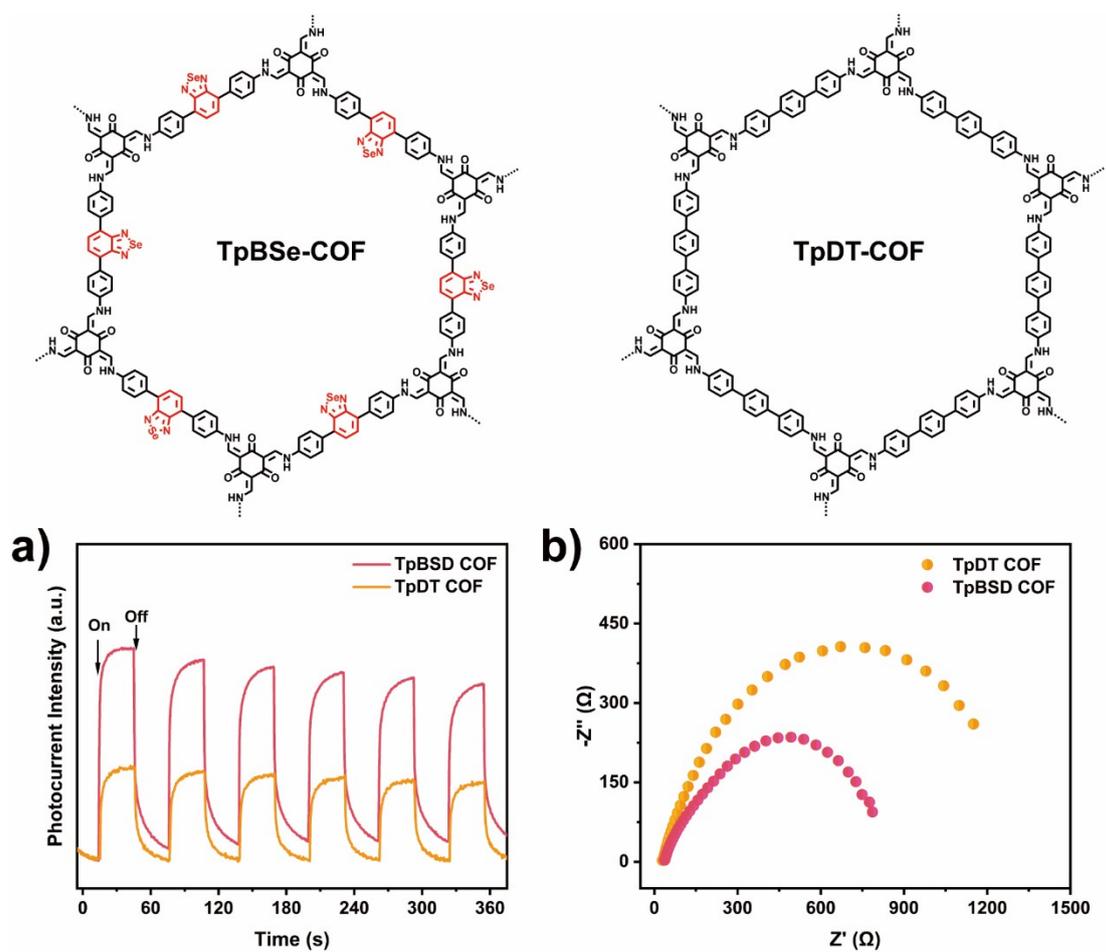
Fig. S12 TpBSe-COF and TpDT-COF: a) photocurrent responses, b) EIS Nyquist plots.
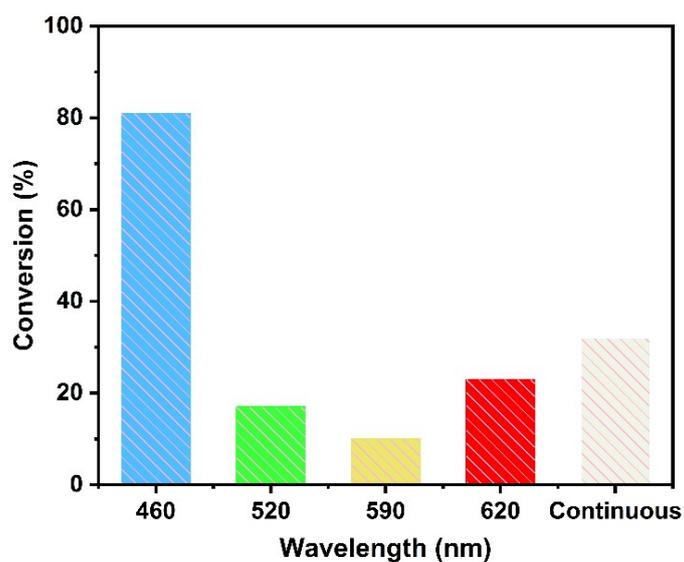
Fig. S13 The influence of different peak wavelengths of LEDs on the photocatalytic aerobic oxidation of methyl phenyl sulfide over TpBSe-COF.
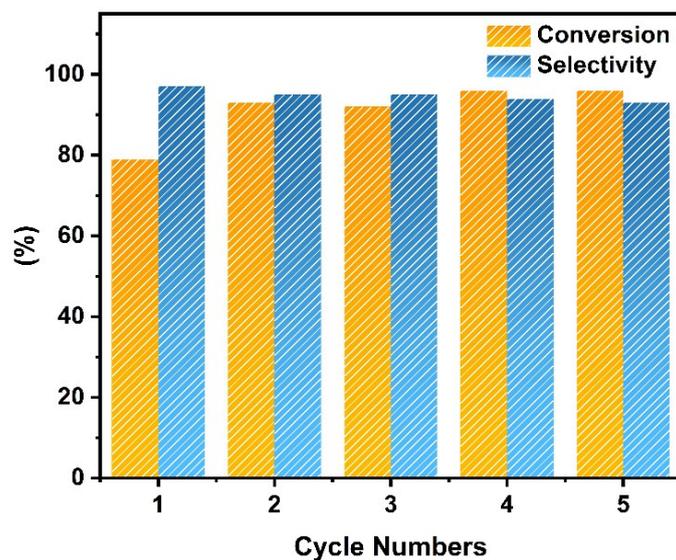
Fig. S14 The recycling tests of TpBSe-COF photocatalyst for aerobic oxidation of methyl phenyl sulfide.
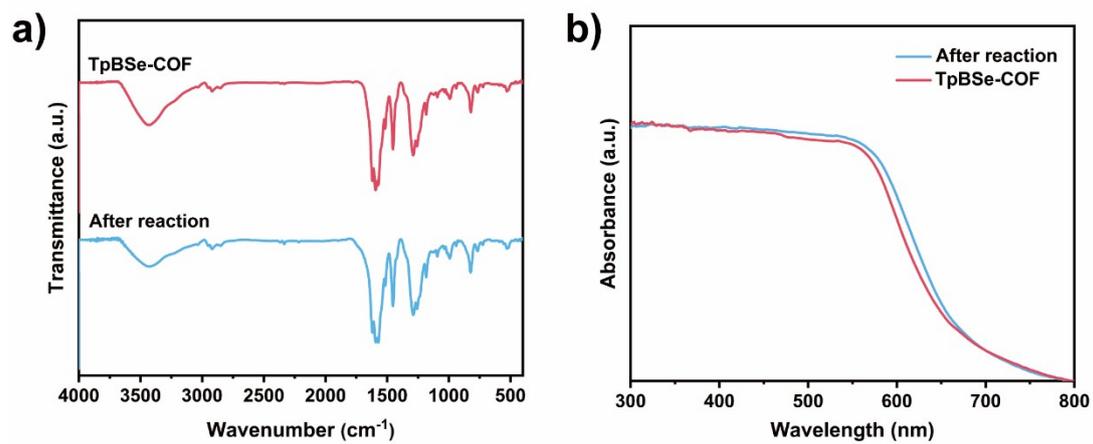
Fig. S15 Comparison of TpBSe-COF before and after reaction. a) FTIR spectra; b) UV vis-DRS.
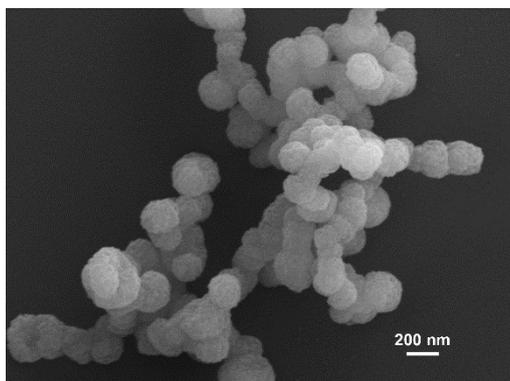
Fig. S16 SEM image of TpBSe-COF (after reaction).
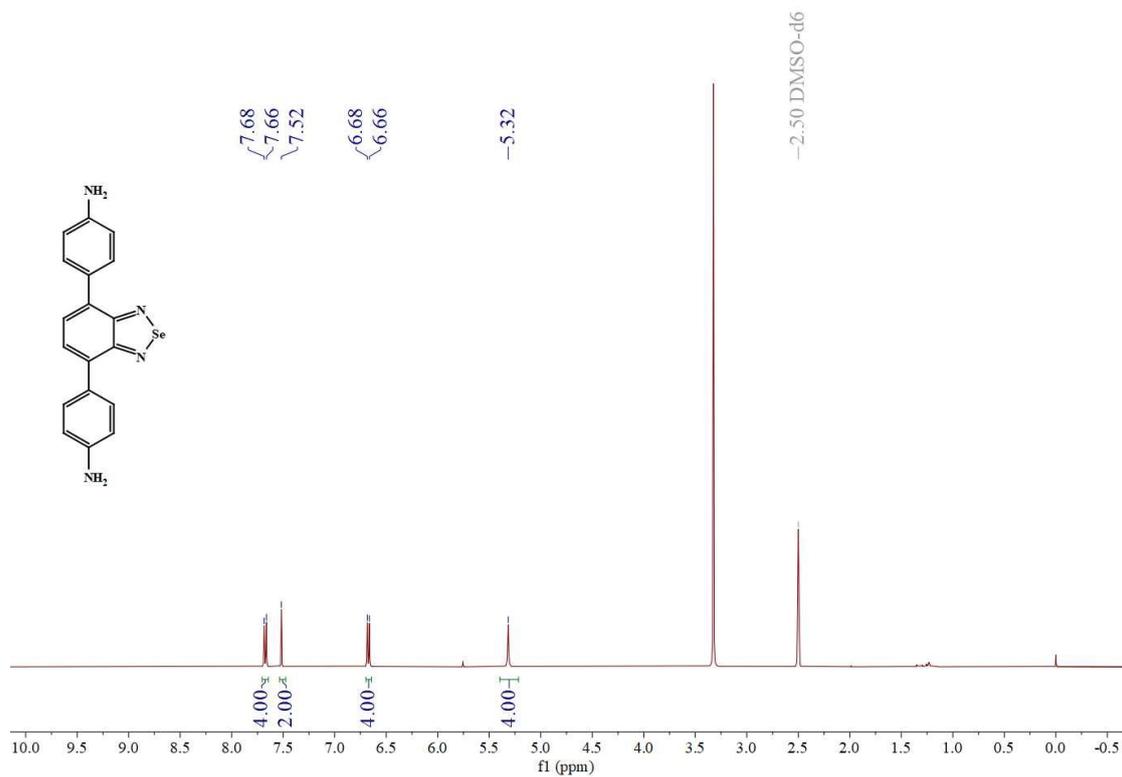
Fig. S17 ^{1}H NMR spectrum of BSe.

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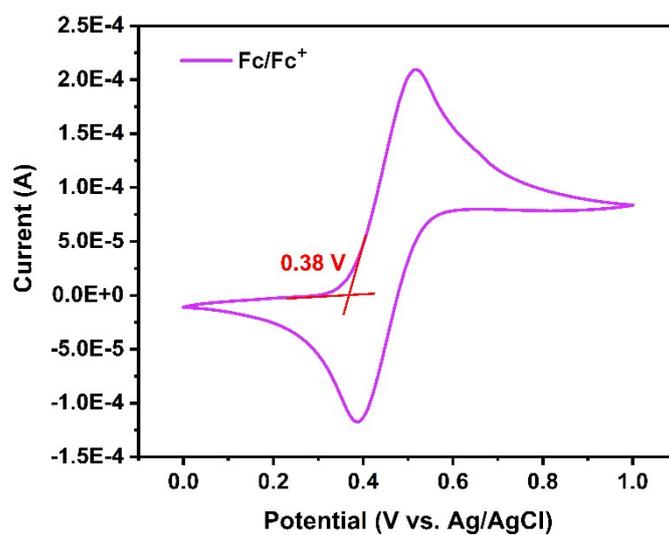
Fig. S18 Cyclic voltammetry measurements of ferrocene/ferrocenium couple to calibrate the Ag/AgCl pseudo-reference electrode.

Table S1 The photocatalytic activity of the two building blocks of TpBSe-COF[a]

Entry	Photocatalyst	TEMPO [%]	Conv. (%)[b]	Sel. (%)[b]
1	Tp	0	0	--
2	Tp	2	0	--
3	BSe	0	6	99
4	BSe	2	7	99

[a] Reaction conditions: Tp (0.0071 mmol), BSe (0.0106 mmol), the amounts of Tp and BSe were calculated based on their respective amounts in 5mg TpBSe-COF, phenyl methyl sulfide (0.5 mmol), CH_3OH (1 mL), blue LEDs (460 ± 10 nm, 3 W × 4), O_2 (0.1 MPa), 0.5 h. [b] Conversion of sulfide and selectivity of sulfoxide were determined by GC-FID.

Table S2 Selective photocatalytic oxidation of phenyl methyl sulfide over TpDT-COF under violet light irradiation[a]

Entry	Photocatalyst	TEMPO [%]	Conv. (%)[b]	Sel. (%)[b]
1	TpDT-COF	0	16	99
2	TpDT-COF	2	35	99

[a] Reaction conditions: TpDT-COF (5 mg), phenyl methyl sulfide (0.5 mmol), CH_3OH (1 mL), violet LEDs (415 ± 5 nm, 3 W × 4), O_2 (0.1 MPa), 2.0 h. [b] Conversion of sulfide and selectivity of sulfoxide were determined by GC-FID.

Table S3 Fractional atomic coordinates for the unit cell of TpBSe-COF

TpBSe-COF			
AA Stacking Space group: *P6*			
$a = b = 38.4861$ Å, $c = 3.5579$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$			
Atom	x/a	y/b	z/c
C1	0.77387	-0.3247	0
C2	0.762	-0.31827	0
C3	0.75006	-0.32719	0
C4	0.76131	-0.30301	0
C5	0.77305	-0.29508	0
C6	0.77256	-0.28114	0
C7	0.76032	-0.27439	0
C8	0.74865	-0.282	0
C9	0.74908	-0.29594	0
C10	0.77034	-0.25085	0
C11	0.76958	-0.23722	0
C12	0.78238	-0.22968	0
C13	0.53018	-0.13547	0
C14	0.51705	-0.13085	0
C15	0.50627	-0.13968	0
C16	0.50812	-0.15372	0
C17	0.52154	-0.15818	0
C18	0.53229	-0.14929	0
C19	0.49625	-0.16333	0
C20	0.49749	-0.17818	0
C21	0.66539	-0.16847	0
C22	0.60401	-0.12145	0
C23	0.5653	-0.12015	0
C24	0.57908	-0.12569	0
N1	0.73789	-0.32303	0
N2	0.75921	-0.26004	0
N3	0.5409	-0.12585	0
N4	0.50867	-0.18453	0
Se1	0.72541	-0.33703	0

O1	0.74623	-0.23517	0
O2	0.58032	-0.13776	0
H1	0.7495	-0.25646	0
H2	0.53781	-0.11597	0
H3	0.78323	-0.31951	0
H4	0.78292	-0.29923	0
H5	0.78193	-0.27592	0
H6	0.73905	-0.27707	0
H7	0.73953	-0.30068	0
H8	0.78021	-0.25511	0
H9	0.5151	-0.12024	0
H10	0.49663	-0.13503	0
H11	0.5243	-0.16849	0
H12	0.54215	-0.15352	0
H13	0.6575	-0.1757	0
H14	0.61171	-0.11395	0

References

1. R. Wang, W. F. Kong, T. Zhou, C. C. Wang and J. Guo, *Chem. Commun.*, 2021, **57**, 331–334.

2. K. H. Xiong, Y. X. Wang, F. L. Zhang, X. Li and X. J. Lang, *Appl. Catal., B*, 2023, **322**, 122135.