

## Electronic supplementary information

# **Imine-linked 2D covalent organic frameworks based on benzotrithiophene for visible-light-driven selective aerobic sulfoxidation**

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## 1. Materials

Benzo[1,2-b:3,4-b':5,6-b'']trithiophene-2,5,8-tricarbaldehyde (BTT), 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (TAPT), 1,3,5-tris(4-aminophenyl)benzene (TAPB) and *o*-dichlorobenzene were purchased by Adamas. Tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF) and acetic acid were sourced from Sinopharm Chemical Reagent Co. Ltd. Other reagents were obtained from J&K Scientific, TCI, Merck, Fischer Scientific, Sigma-Aldrich, Aladdin, Alfa Aesar, and Sinopharm Chemical Reagent Co. Ltd., etc. All the commercially available reagents were directly used without further purifications. Light-emitting diodes (LEDs) were supplied by Shenzhen Ouying Lighting Science and Technology Co., Ltd.

## 2. Characterizations

The morphologies of the BTT-TAPT-COF and BTT-TAPB-COF were determined by the transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images on a JEM-F200. Scanning electron microscopy (SEM) images of BTT-TAPT-COF and BTT-TAPB-COF were measured on a Zeiss Merlin Compact field emission scanning electron microscope. Powder X-ray diffraction (PXRD) measurement was accomplished using a Rigaku/Miniflex 600 diffractometer with filtered Cu K $\alpha$  radiation, and the data were collected from 2° to 30°. Fourier transform infrared (FTIR) spectroscopy was performed by Nicolet 5700 FTIR spectrometer. The UV–visible absorbance of BTT-TAPT-COF and BTT-TAPB-COF

were measured with a UV-3600 UV-vis spectrophotometer (Shimadzu) equipped with a diffuse reflectance measurement accessory, and BaSO<sub>4</sub> was used as a reflectance standard. The specific surface areas and pore-size distribution were determined by N<sub>2</sub> physisorption using an ASAP automated system and the Brunauer-Emmet-Teller (BET) method. Each sample was degassed under vacuum ( $<1 \times 10^{-5}$  bar) in the Micromeritics system at 200 °C for 3 h prior to N<sub>2</sub> physisorption. <sup>13</sup>C NMR spectra was recorded on a Bruker AVANCE NEO 400 MHz NMR spectrometer. B3LYP/6-31G(d,p) basis set was used to study the building units of BTT-TAPT-COF and BTT-TAPB-COF. Molecular orbitals and energy were obtained. All DFT calculations were performed using the Gaussian 16, Revision C.01. Structural modeling of BTT-TAPT-COF and BTT-TAPB-COF was generated using the Accelrys Materials Studio 7.0 software package. The space groups were obtained from the Reticular Chemistry Structure Resource. The EPR tests were executed on an electron paramagnetic resonance (EPR) spectrometer (JEOL, JES-FA300). Elemental analysis of BTT-TAPT-COF and BTT-TAPB-COF was performed by Element Analyzer (Elementar, UNICUBE). The targeted products sulfoxides and remaining products sulfones were confirmed by the retention time comparison with that of standard samples through a gas chromatograph equipped with a flame ionization detector (GC-FID, Agilent 8890), using N<sub>2</sub> 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.

### 3. Synthesis of the two imine-linked COFs based on benzotrithiophene

In a typical procedure, BTT (0.05 mmol, 16.5 mg) was placed in a Pyrex tube with TAPT (0.05 mmol, 17.7 mg) or TAPB (0.05 mmol, 17.5 mg) to afford BTT-TAPT-COF or BTT-TAPB-COF in 1 mL mixture of mesitylene/1,4-dioxane (v/v = 7/3) and treated with sonication for 5 min. Then, 0.1 mL of 6M aqueous acetic acid was added and treated by three vacuum-degassing cycles. Finally, the Pyrex tube was sealed by flame and placed in a 120 °C oven for 3 days. After the hydrothermal reaction, the precipitate was filtered and washed with DMF and acetone, then extracted with tetrahydrofuran, and finally dried in a vacuum oven at 100 °C to obtain the required two COFs. Anal. Calcd. for BTT-TAPT-COF (C<sub>12</sub>H<sub>6</sub>N<sub>2</sub>S)<sub>n</sub>: C, 68.5; H, 2.9; N, 13.3; S, 15.3. Found: C, 58.0; H, 4.3; N, 10.0; S, 12.9. Anal. Calcd. for BTT-TAPB-COF (C<sub>13</sub>H<sub>7</sub>NS)<sub>n</sub>: C, 74.6; H, 3.4; N, 6.7; S, 15.3. Found: C, 64.6; H, 4.6; N, 5.5; S, 12.1.

### 4. Photocatalytic reaction procedures

For photocatalytic sulfoxidation, methanol (CH<sub>3</sub>OH) and blue light emitting diodes (LEDs) were utilized as the solvent and light sources. 5 mg of imine-linked COFs and 0.3 mmol of methyl phenyl sulfide were dissolved in 1 mL of CH<sub>3</sub>OH in a 10 mL Pyrex tube, and sealed with a rubber stopper. Then the reaction was stirred for 30 min in the dark and carried out under 460 nm blue LEDs. After the reaction, products quantitative analysis of methyl phenyl sulfoxide was carried out by gas chromatograph equipped with a flame ionization detector (GC-FID), which was further confirmed by

gas chromatography–mass spectrometry (GC–MS).

**5. Conversion of sulfide and selectivity of the targeted sulfoxide were defined as follows:**

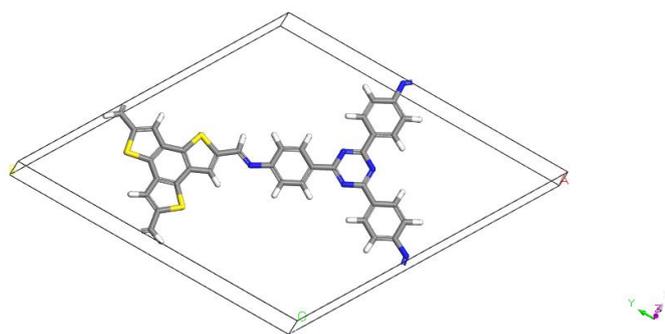
$$\text{Conv. (\%)} = [(C_0 - C_S)/C_0] \times 100$$

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

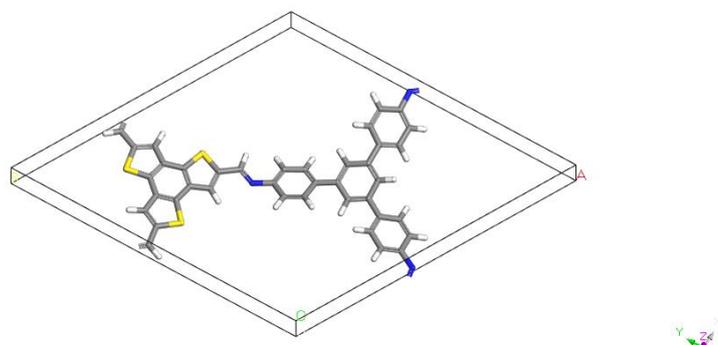
where  $C_0$  is the initial concentration of sulfide, and  $C_S$  and  $C_p$  are the concentrations of sulfide and sulfoxide at a certain time during the photocatalytic reaction.

## **6. Electrochemical measurements**

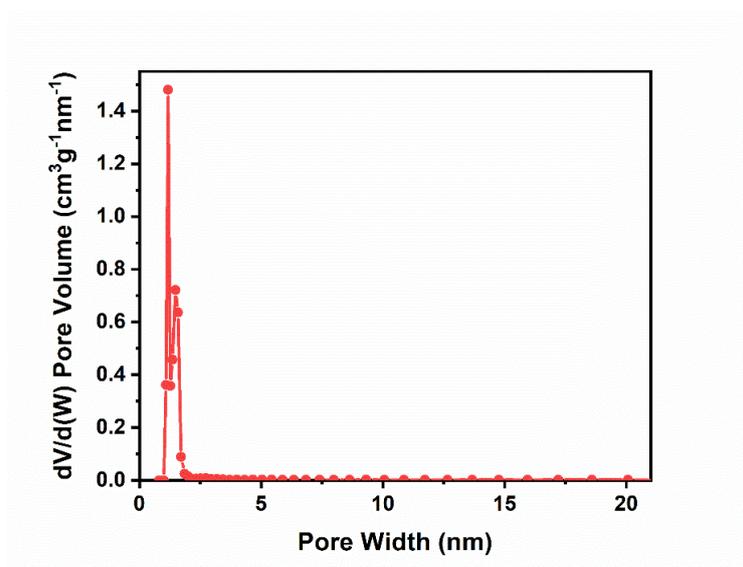
Electrochemical measurements were executed on a Metrohm Autolab PGSTAT302N in a three-electrode electrochemical cell equipped with an electrochemical station. Firstly, 3 mg photocatalysts were dispersed in 1 mL 0.2 wt% Nafion by the ultrasonic instrument. And then the samples were dripped on ITO coated glasses which were placed on top of a glassy carbon served as the working electrode, and the samples were dried under infrared irradiation. With 0.1 M  $\text{Na}_2\text{SO}_4$  aqueous solution or 0.1 M  $\text{NH}_4\text{PF}_6$  acetonitrile solution supplied as the electrolyte, the Ag/AgCl electrode and platinum wire were the reference electrode and counter electrode, respectively. Meanwhile, the  $460 \pm 10$  nm blue LEDs placed at 2 cm away from the photoelectrochemical cell were employed as the light source.



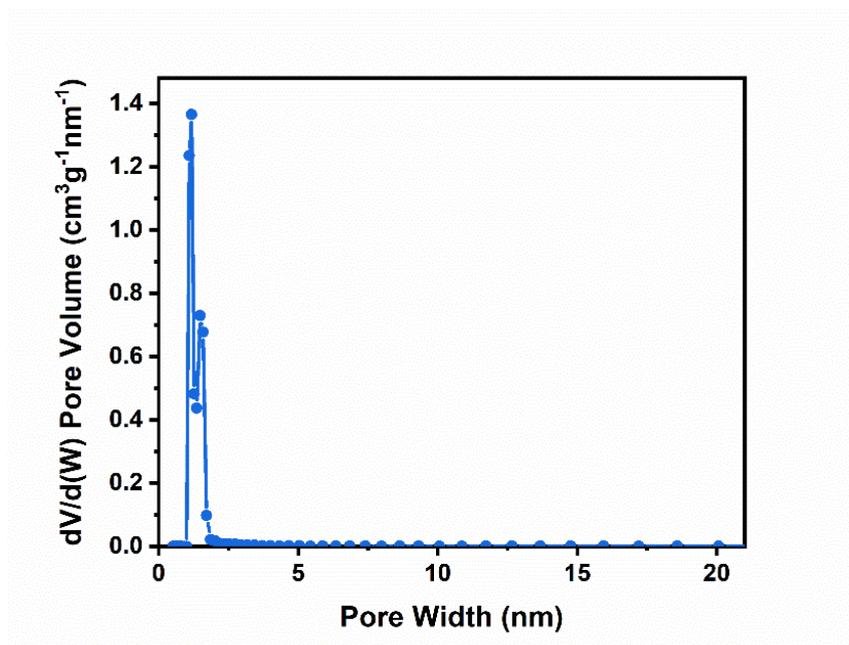
**Fig. S1.** The optimized structures of the BTT-TAPT-COF.



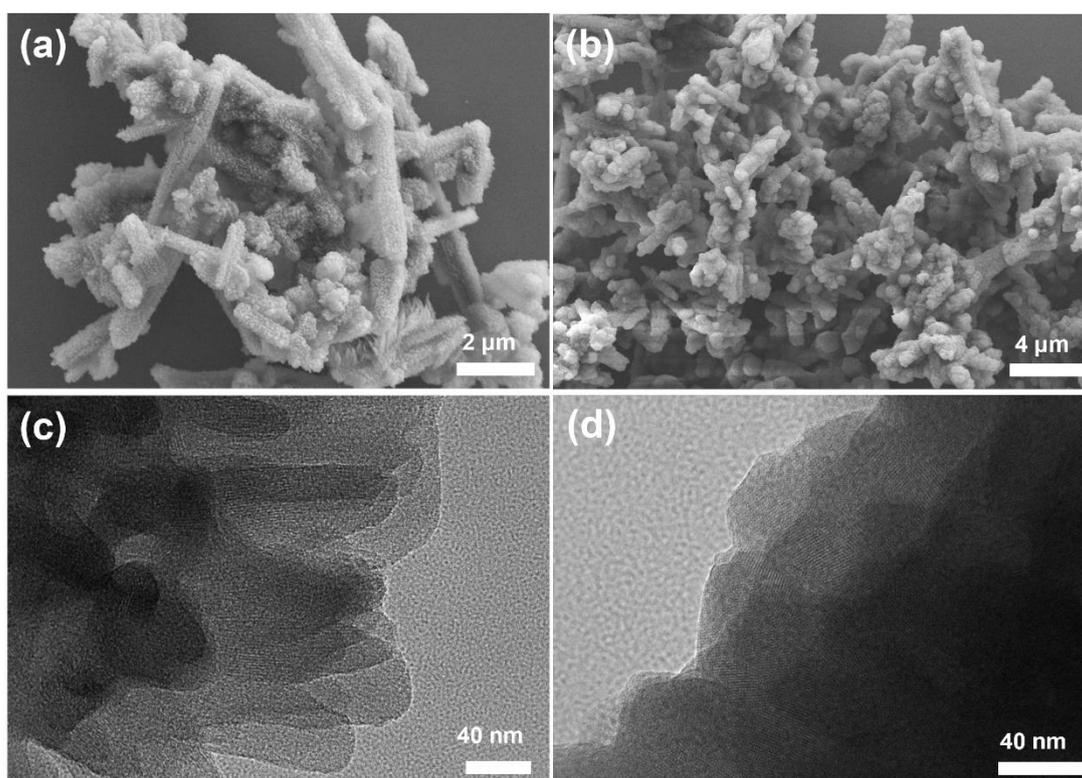
**Fig. S2.** The optimized structures of BTT-TAPB-COF.



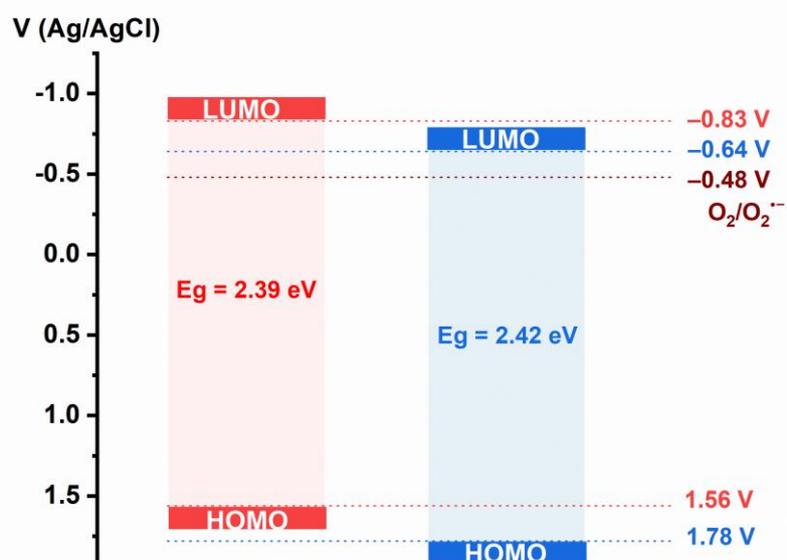
**Fig. S3.** Pore diameter distribution of BTT-TAPT-COF.



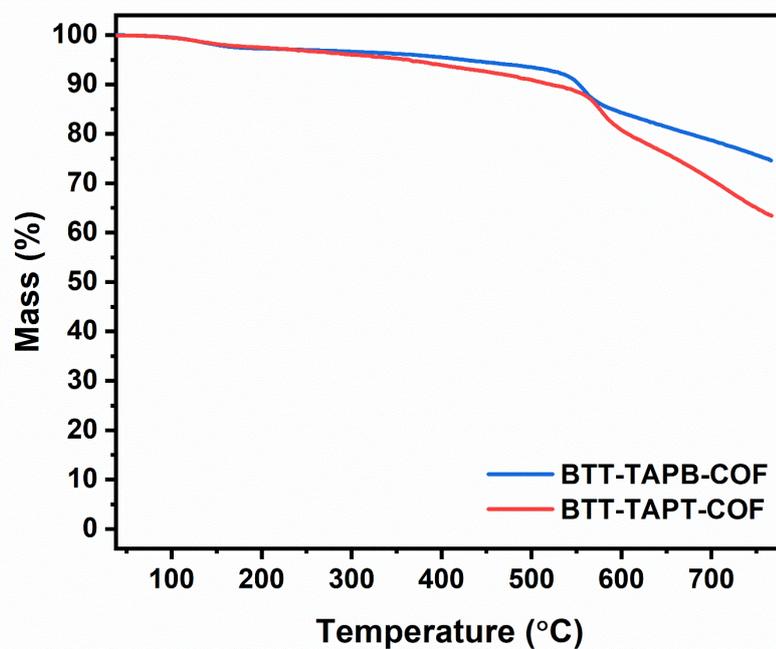
**Fig. S4.** Pore diameter distribution of BTT-TAPB-COF.



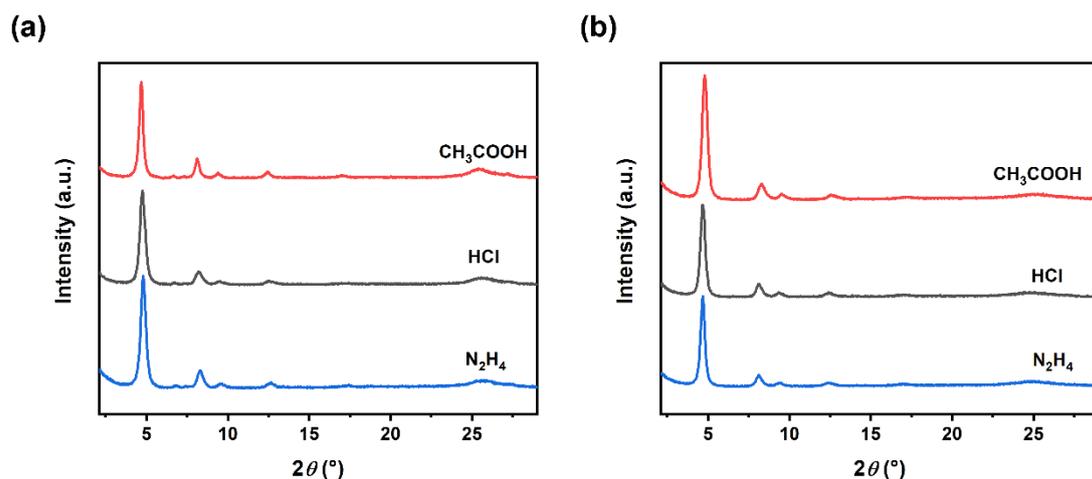
**Fig. S5.** SEM images of BTT-TAPT-COF (a) and BTT-TAPB-COF (b). TEM images of BTT-TAPT-COF (c) and BTT-TAPB-COF (d).



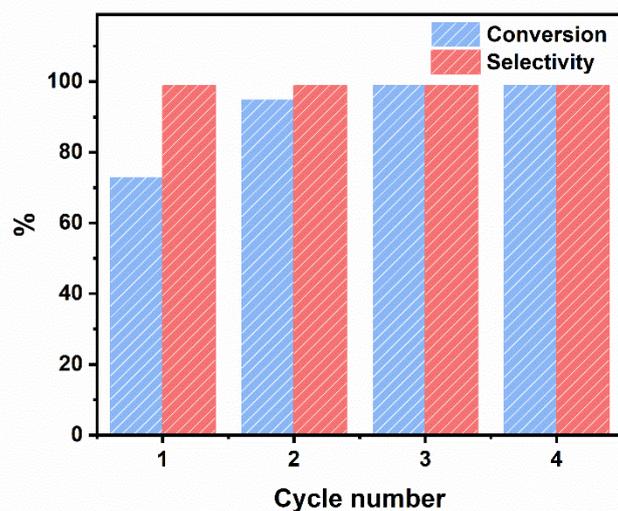
**Fig. S6.** The energy band positions of BTT-TAPT-COF and BTT-TAPB-COF.



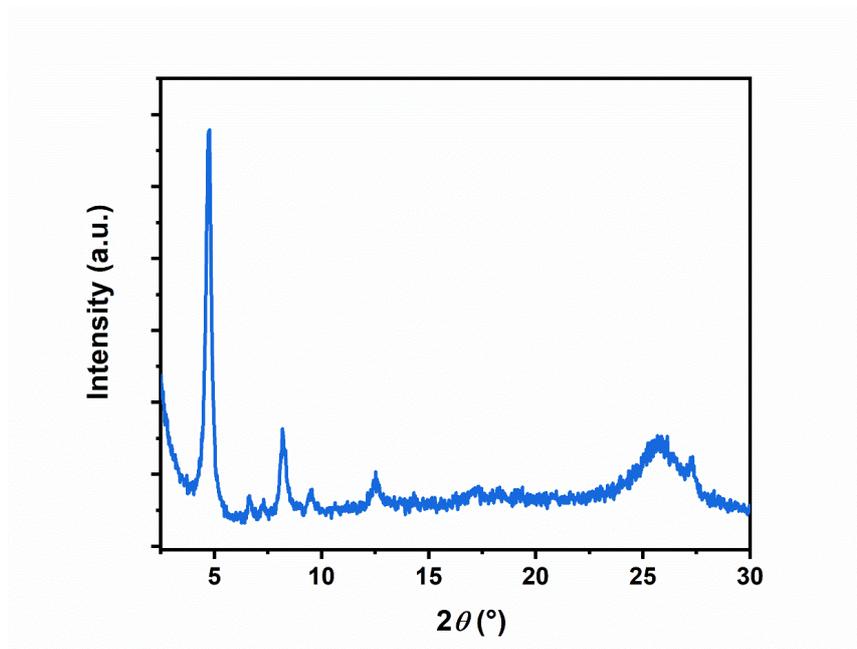
**Fig. S7.** Thermogravimetry analysis curves for BTT-TAPT-COF and BTT-TAPB-COF.



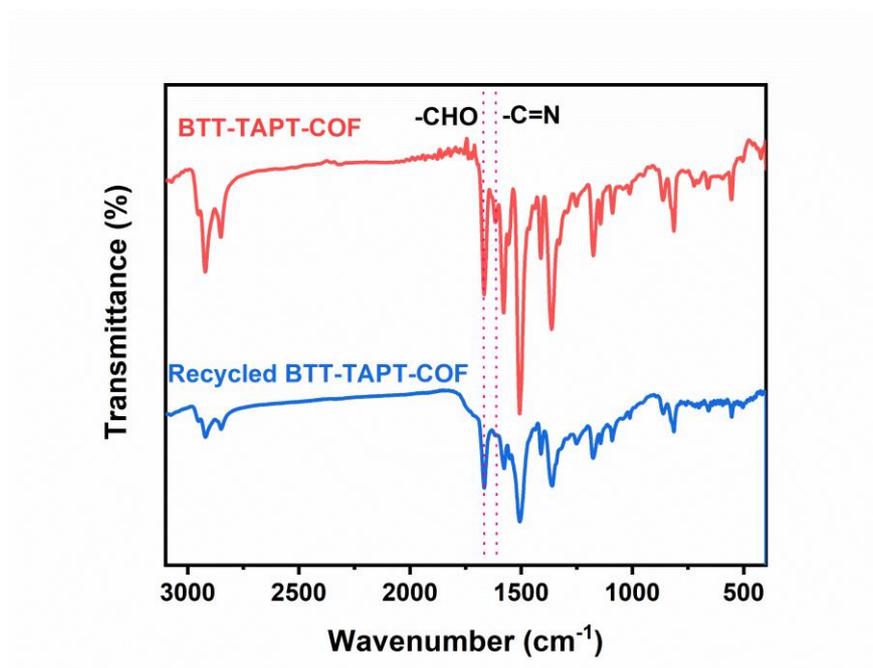
**Fig. S8.** PXRD patterns of BTT-TAPT-COF (a) and BTT-TAPB-COF (b) in different solvents.



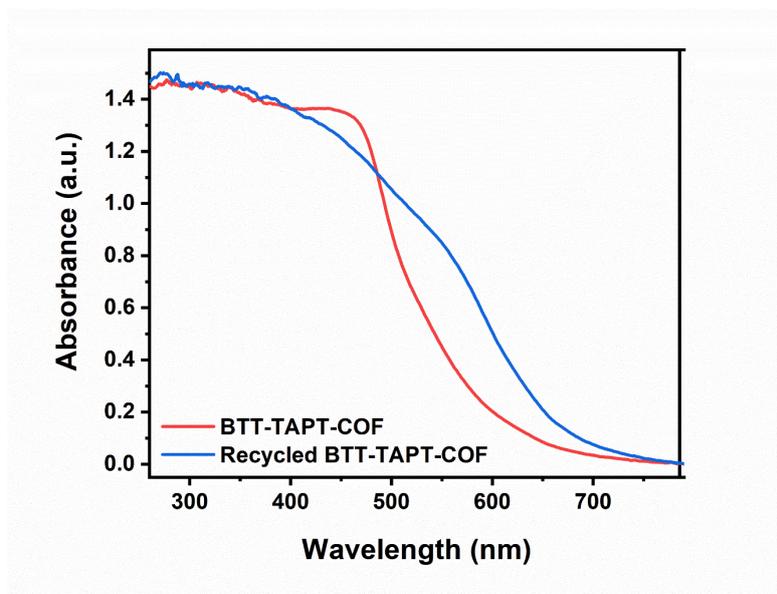
**Fig. S9.** Recycling experiments for selective aerobic sulfoxidation of methyl phenyl sulfide. CH<sub>3</sub>OH (1 mL), BTT-TAPT-COF (5 mg), methyl phenyl sulfide (0.3 mmol), blue LEDs (3 W × 4), O<sub>2</sub> (0.1 MPa), 0.9 h. Traced by GC-FID, conversion of sulfide, selectivity of sulfoxide



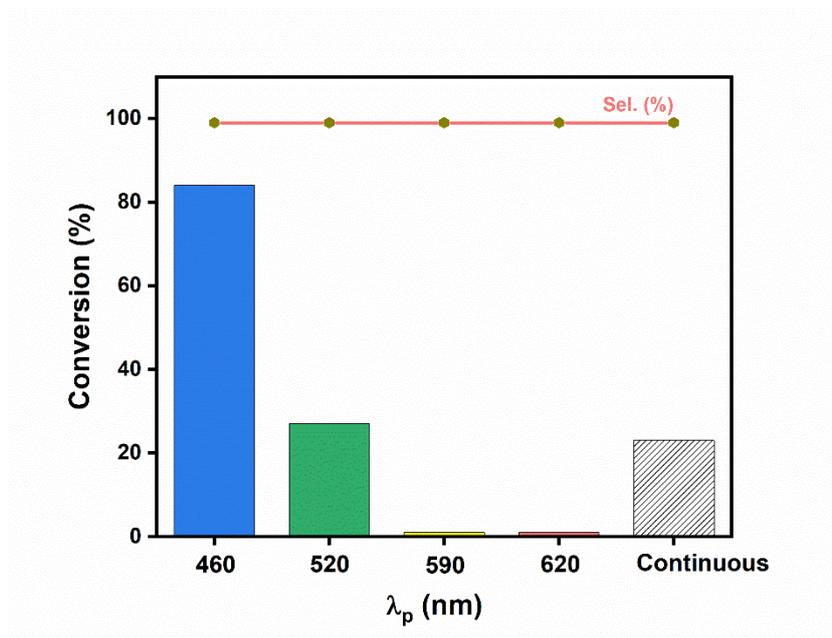
**Fig. S10.** The PXRD pattern of the recycled BTT-TAPT-COF.



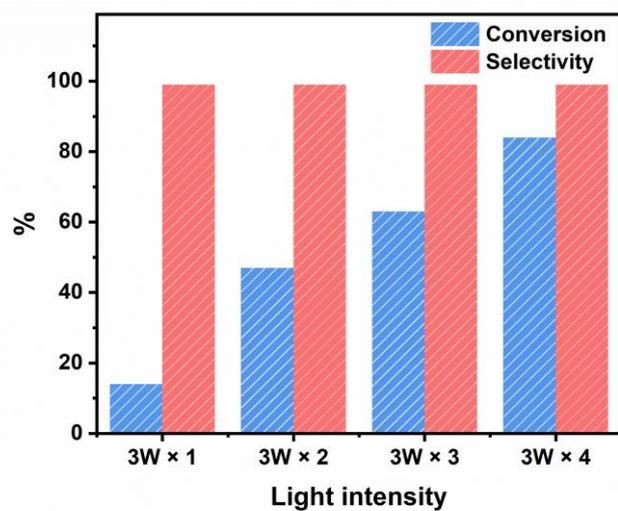
**Fig. S11.** FTIR spectra of BTT-TAPT-COF before and after recycling.



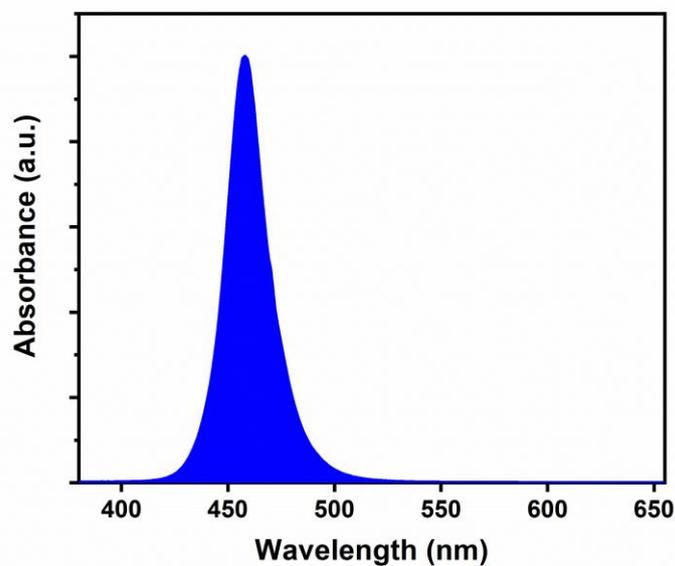
**Fig. S12.** The solid-state UV–visible spectra of BTT-TAPT-COF before and after recycling.



**Fig. S13.** Selective aerobic sulfoxidation of methyl phenyl sulfide under the irradiation of different LEDs. Reaction conditions: CH<sub>3</sub>OH (1 mL), BTT-TAPT-COF (5 mg), methyl phenyl sulfide (0.3 mmol), LEDs (3 W × 4), O<sub>2</sub> (0.1 MPa), 0.9 h. Traced by GC–FID, conversion of sulfide, selectivity of sulfoxide.



**Fig. S14.** The influence of light intensity on selective aerobic sulfoxidation of methyl phenyl sulfide. Reaction conditions: CH<sub>3</sub>OH (1 mL), BTT-TAPT-COF (5 mg), methyl phenyl sulfide (0.3 mmol), blue LEDs, O<sub>2</sub> (0.1 MPa), 0.9 h.



**Fig. S15.** The spectrum of the blue LED.