

## Electronic Supplementary Information

### **2D $\beta$ -ketoenamine-linked triazine covalent organic framework photocatalysis for selective oxidation of sulfides**

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## **1. Instrumentations**

### **PXRD**

The crystal phase composition of solid samples was identified by X-ray powder diffraction (PXRD) using a Rigaku Miniflex 600 diffractometer.

### **BET**

The nitrogen isotherms were measured at 77 K using an Autosorb-iQ (Quantachrome) surface area size analyzer. The specific surface areas of the TpTAPT-COF and TpTAPB-COF were calculated by using the Brunauer–Emmett–Teller (BET) method and the pore size and volume were derived from the sorption curve by using the quenched solid density functional theory (QSDFT) model.

### **FTIR spectra**

The FTIR spectra of solid samples were carried out by NICOLET 5700 FTIR Spectrometer with Continuum IR Microscope ranging from 400–4000  $\text{cm}^{-1}$ .

### **UV-visible spectra**

The UV-visible absorption spectra of the TpTAPT-COF and TpTAPB-COF were detailed on a Shimadzu UV-3600 UV-VIS spectrophotometer with a diffuse reflectance measurement accessory.

## **NMR measurement**

Solid-state  $^{13}\text{C}$  CP/MAS NMR measurements of TpTAPT-COF and TpTAPB-COF were conducted by using a Bruker AVANCE III 400M spectrometer.

## **SEM**

Scanning electron microscopy (SEM) images of TpTAPT-COF and TpTAPB-COF were measured on a Zeiss Merlin Compact field emission scanning electron microscope.

## **HRTEM**

High-resolution transmission electron microscopy (HRTEM) images of TpTAPT-COF and TpTAPB-COF were measured on JEM-2100 transmission electron microscopy.

## **TGA**

Thermogravimetric analysis (TGA) of TpTAPT-COF and TpTAPB-COF were conducted on an SDT Q600 thermogravimeter under an  $\text{N}_2$  atmosphere with a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  from room temperature to  $750\text{ }^\circ\text{C}$ .

## GC and GC–MS

Gas chromatography (GC) quantitative measurements of the conversions of substrates and the selectivities of products were carried out on a gas chromatograph equipped with a flame ionization detector (GC–FID, Agilent 7890B) using high-purity N<sub>2</sub> as the carrier gas and an Agilent J & W DB-5 capillary column (30 m × 0.32 mm × 0.25 μm, 19091 J-413) or an Agilent J&W DB-17 capillary column (30 m × 0.32 mm × 0.25 μm, 123–1732). GC–FID standard analysis conditions: injector temperature 250 °C detector temperature 280 °C, and column temperature program: 50 °C (hold 1 min) raised to 280 °C (hold 2 min) at a rate of 20 °C min<sup>-1</sup>. The results were all obtained using a split mode with a split ratio of 30: 1. Gas chromatography-mass spectrometry (GC–MS) analysis was performed on an Agilent GC 8890 gas chromatograph equipped with an Agilent 5977B GC/MSD mass spectrometer using an Agilent (HP-5 MS) capillary column (30 m × 0.25 mm × 0.25 μm) with high-purity He as the carrier gas. Conversion and selectivity for selective oxidation of the substrate to the target product were defined as follows:

$$\text{Conversion (\%)} = [(C_0 - C_r)/C_0] \times 100$$

$$\text{Selectivity (\%)} = [C_p/(C_0 - C_r)] \times 100$$

Where C<sub>0</sub> is the initial concentration of reactant, C<sub>r</sub> and C<sub>p</sub> are the concentrations of substrate and target product, respectively, at a certain time after the photocatalytic reaction.

## **EPR**

The EPR experiments were carried out on an electron paramagnetic resonance (EPR) spectrometer (JEOL, JES-FA300). The sample under standard conditions was irradiated in the light chamber of the EPR spectrometer irradiated by a high-pressure Hg lamp with a filter to select the band of  $460 \pm 10$  nm visible light.

## **2. Experimental section**

### **2.1 Reagents and solvents**

The *n*-butanol (*n*-BuOH) and 1,2-dichlorobenzene (*o*-DCB) were purchased from J&K. All the solvents were purchased from Adamas Reagent and used as received without further purification.

### **2.2 The preparations for TpTAPT-COF and TpTAPB-COF**

Referring to previous works with some alterations, the preparation of TpTAPT-COF<sup>1</sup> and TpTAPB-COF was executed. First, 0.08 mmol Tp, 0.08 mmol TAPT or TAPB were charged into a Pyrex tube and mixed with 0.5 mL *o*-dichlorobenzene (*o*-DCB), 0.5 mL *n*-butanol (*n*-BuOH) and 20  $\mu$ L pyrrolidine. After 10 min of ultrasonication, the reaction mixture underwent three freeze–pump–thaw cycles before being sealed in the Pyrex tube. The reaction proceeded at 120 °C for 3 d. Afterward, the product was filtered and rinsed with acetone, methanol, dichloromethane, and tetrahydrofuran, respectively, succeeded by the Soxhlet

extraction with tetrahydrofuran for 3 d. The obtained solids, i.e., TpTAPT-COF and TpTAPB-COF, were dried at 60 °C in vacuum for 48 h.

### **2.3 Photocatalytic oxidation of sulfides**

To begin, 0.3mmol phenyl methyl sulfide, 5 mg photocatalyst, together with 1 mL CH<sub>3</sub>OH were charged into a 10 mL Pyrex photoreactor. Then, the mixture was stirred under dark conditions for 30 min. An equilibrium of adsorption–desorption was achieved. Next, filled with O<sub>2</sub> to 0.1 MPa, the photoreactor was irradiated with blue light LEDs under magnetic agitation of 1500 rpm. Gas chromatography–flame ionization detector (GC–FID) was used to quantify the reaction products, and GC–mass spectrometry (GC–MS) was utilized to confirm the products.

### **2.4 Typical procedure for photoelectrochemical tests**

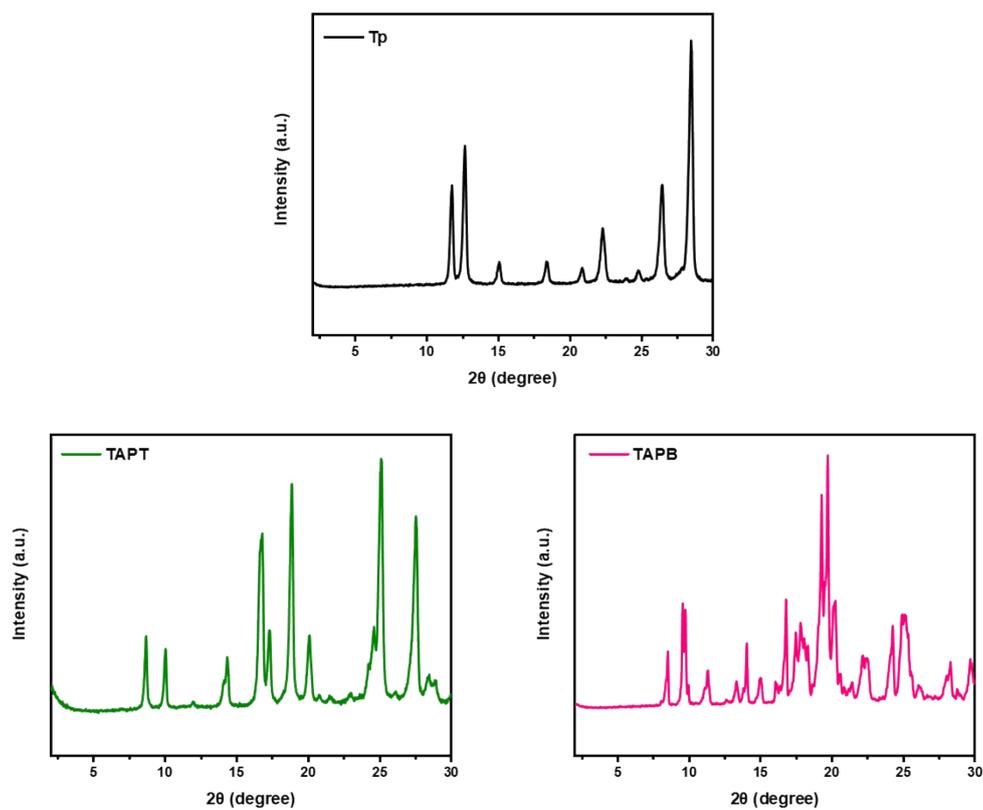
The Electrochemical impedance spectroscopy (EIS) measurements and Mott–Schottky plots were determined by a Metrohm PGSTAT302N electrochemical workstation in a conventional three-electrode configuration with Ag/AgCl (saturated KCl) as the reference electrode and Pt wire as the counter electrode. 0.2 mol/L Na<sub>2</sub>SO<sub>4</sub> aqueous solution was used as the electrolyte. The working electrodes were prepared as follows: 6 mg of the as-prepared photocatalyst was suspended in 3 mL dilute Nafion dispersion to produce a slurry, which was then dropped 5 μL onto an indium tin oxide (ITO) glass electrode and the film was dried by an infrared lamp,

then the working electrode was obtained after ten cycles.

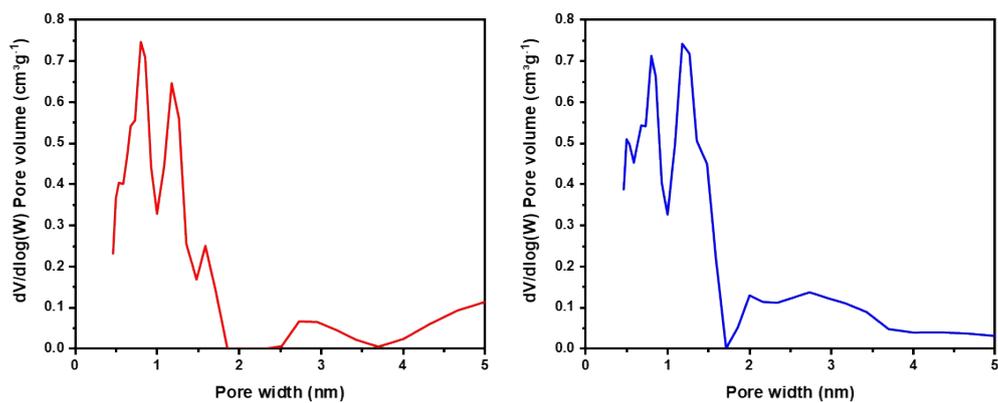
## **2.5 Testing the recycled photocatalyst**

A recycled photoactivity test on the used photocatalyst was done as the following. Typically, after the reaction of 1.5 h under blue light irradiation, the liquid and photocatalyst were separated by centrifugation. The liquid was decanted, while the used photocatalyst was washed 3 times with 1 mL of methanol. Then the used photocatalyst was subjected to the 2nd run of photoactivity testing under standard conditions. In analogy, the recycled 3rd run and 4th run photoactivity tests were performed.

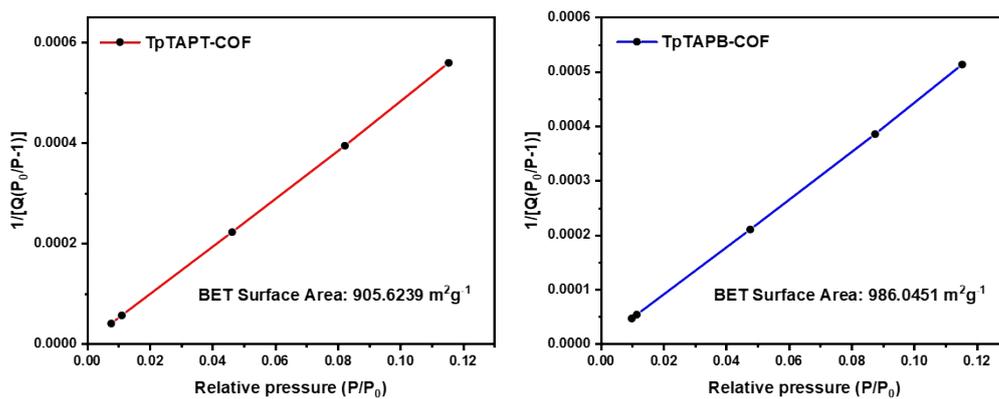
### 3. Results



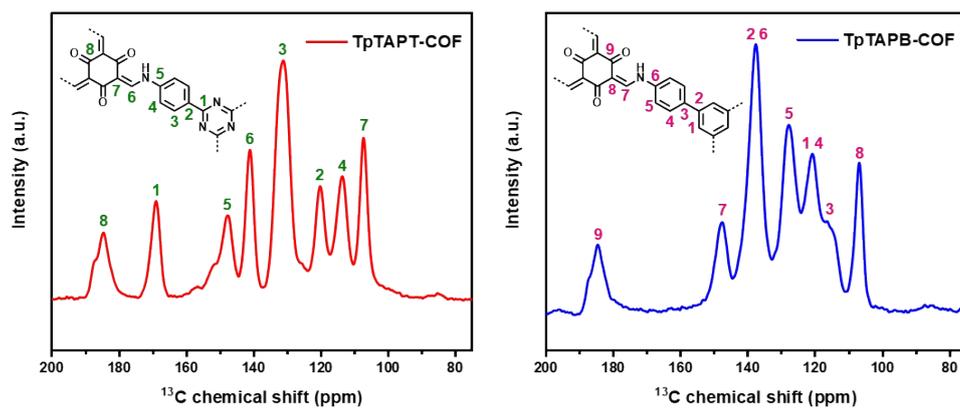
**Fig. S1.** PXRD patterns of Tp, TAPT, and TAPB.



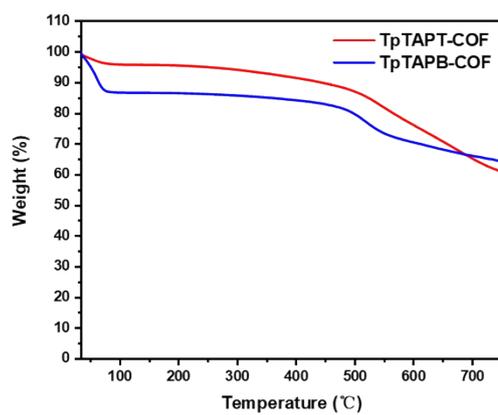
**Fig. S2.** Pore size distributions of TpTAPT-COF and TpTAPB-COF calculated from NLDFT.



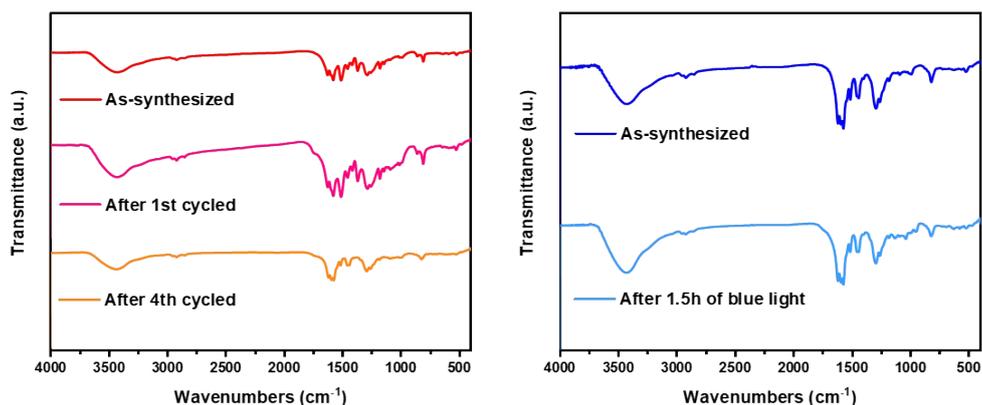
**Fig. S3.** Plots of the linear region for the BET equation calculated from the isotherm of TpTAPT-COF and TpTAPB-COF.



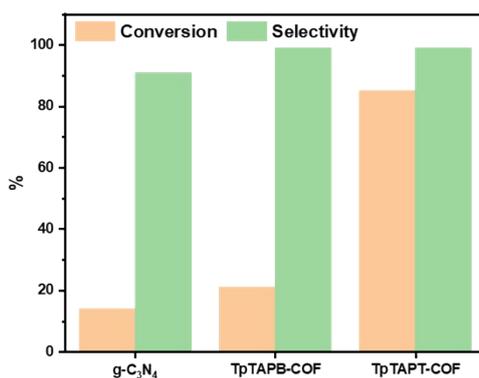
**Fig. S4.** The  $^{13}\text{C}$  CP/MS solid-state NMR spectra of TpTAPT-COF and TpTAPB-COF.



**Fig. S5.** TGA curves of TpTAPT-COF and TpTAPB-COF.



**Fig. S6.** (a) FTIR spectra of TpTAPT-COF after first cycled and fourth cycled. (b) FTIR spectra of TpTAPB-COF after 1.5 h irradiation of blue light.



**Fig. S7.** The comparison of photocatalytic activity of TpTAPT-COF, TpTAPB-COF, and g-C<sub>3</sub>N<sub>4</sub>. Reaction conditions: CH<sub>3</sub>OH (1 mL), g-C<sub>3</sub>N<sub>4</sub>/ TpTAPT-COF (5 mg), sulfides (0.3 mmol), blue LEDs (460 ± 10 nm, 3 W × 4), O<sub>2</sub> (0.1 MPa), 1.5 h.

**Table S1.** The photocatalytic activity of the building blocks on the selective aerobic oxidation of phenyl methyl sulfide.<sup>a</sup>

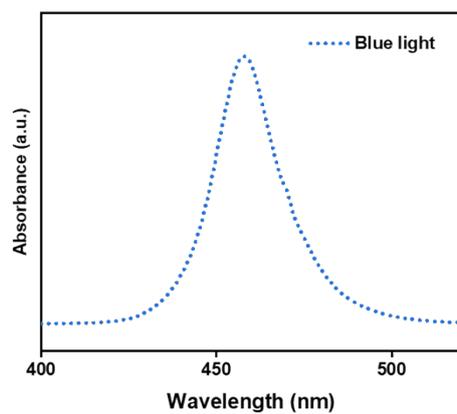
Entry	Building block	Conv. (%)	Sel. (%)
1	Tp	0	-
2	TAPT	0	-
3	TAPB	0	-

<sup>a</sup> Reaction conditions: CH<sub>3</sub>OH (1 mL), building block (5 mg), sulfides (0.3 mmol), blue LEDs (460 ± 10 nm, 3 W × 4), O<sub>2</sub> (0.1 MPa), 1.5 h.

**Table S2.** The impact of different solvents on the selective photocatalytic aerobic oxidation of phenyl methyl sulfide.<sup>a</sup>

Entry	Solvent	Conv. (%)	Sel. (%)
1	CH <sub>3</sub> OH	85	99
2	CH <sub>3</sub> CN	34	90

<sup>a</sup> Reaction conditions: TpTAPT-COF (5 mg), sulfides (0.3 mmol), blue LEDs (460 ± 10 nm, 3 W × 4), O<sub>2</sub> (0.1 MPa), 1.5 h.



**Fig. S8.** The light-emitting spectrum of the blue LEDs.

## Reference

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