

Electronic supplementary information

Converting the covalent organic framework linkage from hydrazone to thiadiazole toward blue light-powered selective conversion of organic sulfides

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1 Experimental section

1.1 Reagents and solvents

The organic sulfides, 1,3,5-tris(4-formylphenyl)triazine (TFPT), and 2,5-diethoxyterephthalohydrazide (DETH) were purchased from Adamas. Unless otherwise specified, the other reagents were purchased from Sigma-Aldrich, TCI, Innochem, Adamas, Alfa Aesar, Sinopharm Chemical Reagent, and J&K Scientific Co., Ltd., etc.

2.2 Syntheses of TFPT-COF and TDA-COF

TFPT-COF was synthesized referring to a reported procedure.¹ Firstly, 0.044 mmol TFPT and 0.066 mmol DETH were put into a 10 mL Pyrex tube with 1 mL mixed solvent of 1,4-dioxane and mesitylene (1:2). After 5 min of ultrasonic treatment to ensure uniform dispersion, 0.1 mL 6 M acetic acid was rapidly added as a catalyst. Consequently, degassed through three freeze–pump–thaw cycles under vacuum, the Pyrex tube was flame-sealed. Finally, the resulting faint yellow precipitate was heated for 3 d at 120 °C. The precipitate was washed sequentially with acetone and tetrahydrofuran and then extracted with tetrahydrofuran (THF) for 24 h in a Soxhlet extractor. After evaporating and adequately grinding the faint yellow solid, the TFPT-COF powder was obtained.

TDA-COF was synthesized through post-synthetic modifications according to a literature method.² First, 89 mg TFPT-COF powder, 100 mg 4-

(dimethylamino)pyridine, and 227 mg Lawesson's reagent were dispersed in 40 mL toluene. After refluxing for 24 h, the mixture was rinsed with *N,N*-dimethylformamide (DMF) and THF and dried in a vacuum at 70 °C for 12 h. After repeating the preceding steps for the obtained powder, TDA-COF was obtained.

1.2 Process for the photocatalytic selective conversion with O₂

A 10 mL Pyrex glass tube was charged with 0.3 mmol sulfide, 4 mg TDA-COF, and 1 mL CH₃OH. The Pyrex tube was first stirred for 30 min without irradiation to achieve equilibrium of desorption–adsorption. Subsequently, it was exposed to blue LED irradiation (light-emitting diodes) and an O₂ atmosphere at room temperature. After releasing the excess O₂, the internal supernatant from the centrifugated mixture was detected through gas chromatography–mass spectrometry (GC–MS) and further precisely quantified by flame ionization detection (GC–FID).

1.3 DFT calculations

The density functional theory (DFT) calculations were performed using the Gaussian 16, Revision C.01. Besides, the optimization and the point energy were implemented by B3LYP/6-31G(d,p) with correction terms in D3(BJ). The DOS were carried out through Multiwfn³ based on fchk of Gaussian 16.

1.4 Electrochemical measurements

Electrochemical measurements were executed on a Metrohm Autolab PGSTAT302N in a three-electrode electrochemical cell equipped with an

electrochemical station. Firstly, 2 mg photocatalyst were dispersed in 1 mL 0.2 wt% Nafion by the ultrasonic instrument. 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 Na₂SO₄ aqueous solution supplied as the electrolyte, the Ag/AgCl electrode and platinum wire were the reference electrode and counter electrode, respectively. Meanwhile, the 460 ± 10 nm blue LEDs (Shenzhen Ouying Lighting Science and Technology Co., Ltd.) placed 2 cm away from the photoelectrochemical cell were employed as the light source.

1.5 Characterizations instrumentations

The Fourier transform infrared (FTIR) spectra were carried out by NICOLET 5700 FTIR Spectrometer with Continuum IR Microscope ranging from 400–4000 cm⁻¹. Solid-state ¹³C NMR spectra were performed on 400 MHz spectrometers (AVANCE NEO 400). The crystal phase composition of solid samples was identified by powder X-ray diffraction (PXRD) using a Rigaku Miniflex 600 diffractometer. Elemental analysis was performed by Thermo FLASH2000. Field-emission scanning electron microscopy (FE-SEM) images of organic materials were measured on Zeiss Merlin Compact field emission scanning electron microscope. The high-resolution transmission electron microscopy (HRTEM) images of organic materials were estimated on a JEM-F200. The N₂ isotherms and specific surface areas were determined at 77 K employing a Micromeritics ASAP 2460 automated system with the Brunauer–Emmet–Teller (BET) model, and the pore size and volume were derived

from the sorption curve by using the DFT model, the materials were degassed in vacuum ($< 1 \times 10^{-5}$ bar) at 120 °C for 12 h. The UV–visible absorption spectra were detailed on a Shimadzu UV-3600 UV-VIS spectrophotometer with a diffuse reflectance measurement accessory. The electron paramagnetic resonance (EPR) spectra were collected on a JEOL, JES-FA300 EPR spectrometer.

2 Results

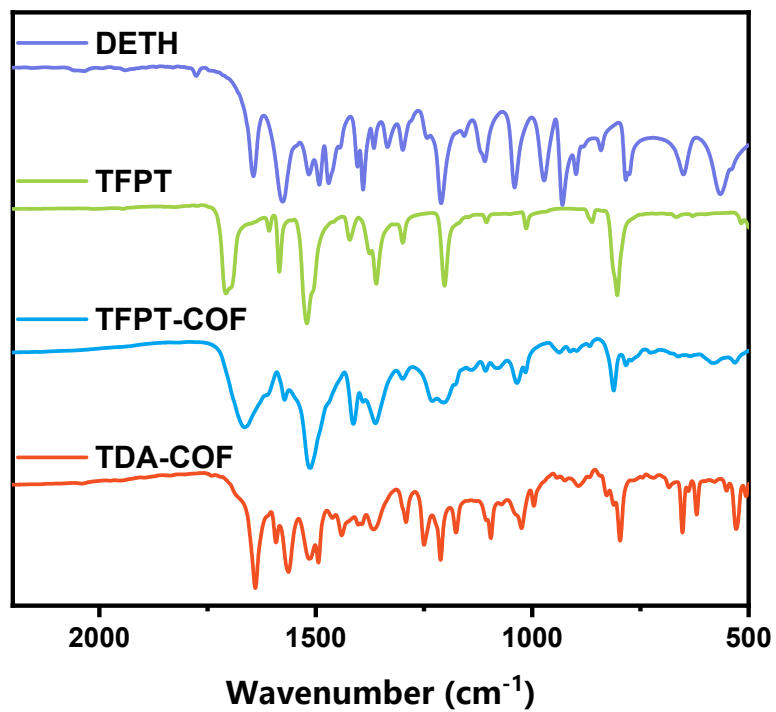


Figure S1 FTIR spectra of DETH, TFPT, TFPT-COF, and TDA-COF.

Table S1 Elemental analysis of the TFPT-COF and TDA-COF.

		N (%)	C (%)	H (%)	S (%)
TFPT-COF	Measured	15.2	62.7	4.9	0.0
	Expected	16.5	66.1	4.7	0.0
TDA-COF	Measured	12.0	56.5	4.7	12.8
	Expected	15.7	62.7	3.7	11.9

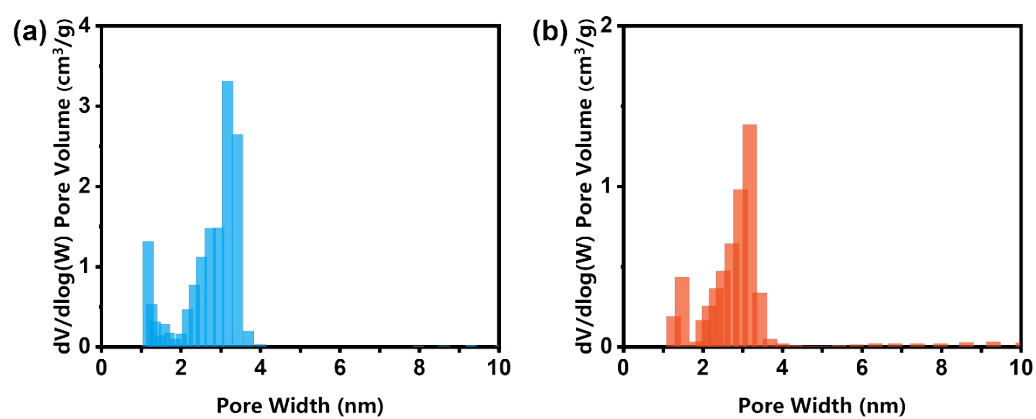


Figure S2 The pore size distributions derived from DFT models of TFPT-COF (a) and TDA-COF (b).

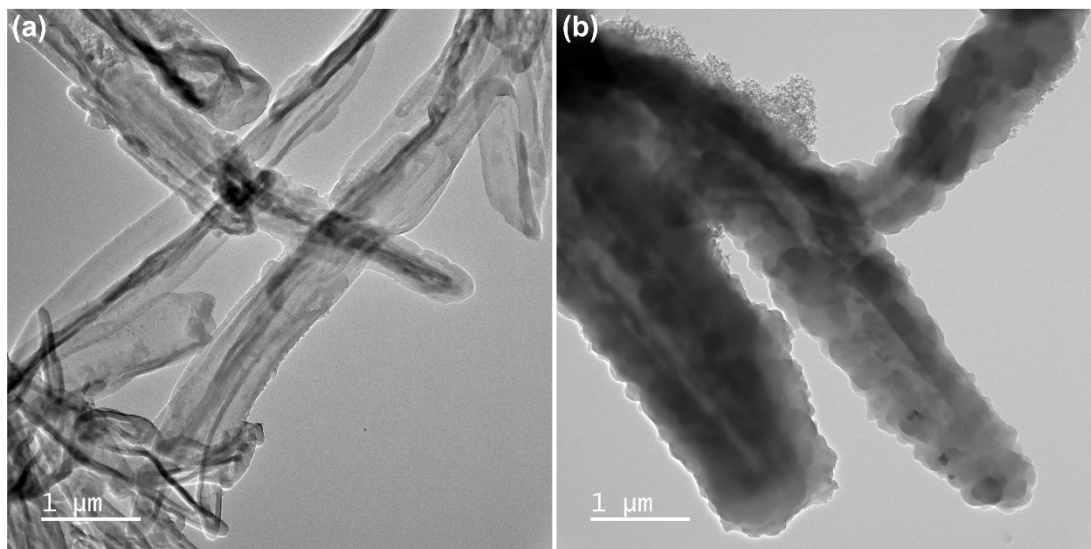


Figure S3 TEM images of TFPT-COF (a) and TDA-COF (b).

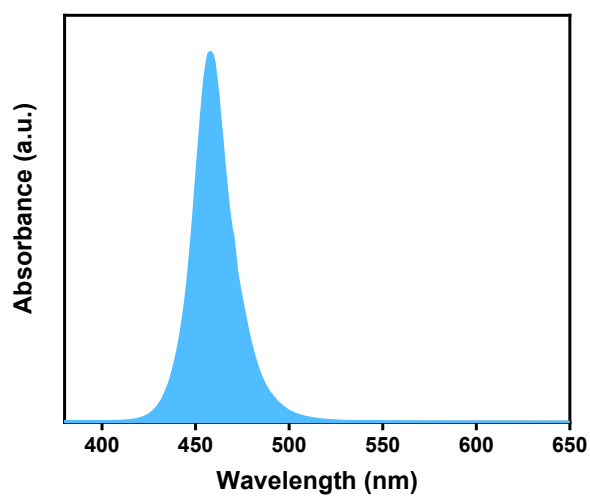


Figure S4 The emission spectrum of the blue LED.

Table S2 Comparison of TFPT, DETH, TFPT-COF, and TDA-COF blue light-powered selective conversion of thioanisole.^[a]

Entry	Photocatalyst	Conv. (%) ^[b]	Sel. (%) ^[b]
1	TFPT	0	--
2	DETH	0	--
3	TFPT-COF	0	--
4	TDA-COF	89	99

[a] Reaction conditions: thioanisole (0.3 mmol), CH₃OH (1 mL), photocatalyst (4 mg), O₂ (1 atm), blue LED irradiation (460 ± 10 nm), 20 min.

[b] Determined by GC–FID using bromobenzene as the internal standard, conversion of thioanisole, selectivity of methyl phenyl sulfoxide.

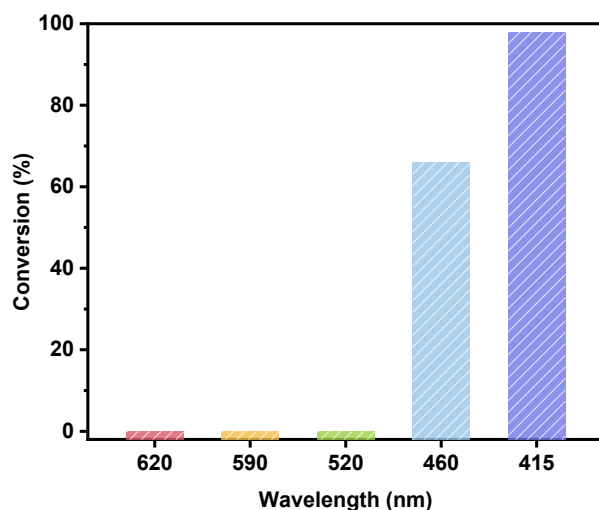


Figure S5 The influence of various λ_p LED irradiation over TDA-COF for selective conversion of thioanisole with O_2 . Reaction conditions: thioanisole (0.3 mmol), CH_3OH (1 mL), TDA-COF (4 mg), O_2 (1 atm), blue LED irradiation (460 ± 10 nm), 15 min.

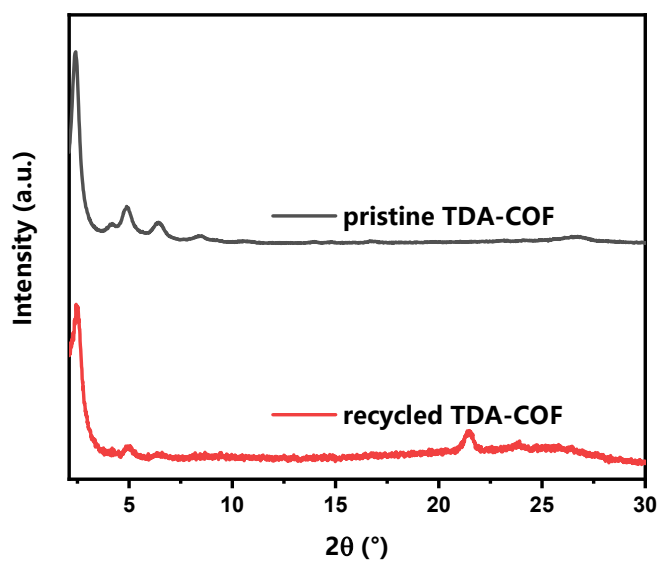


Figure S6 The PXRD patterns of the pristine and recycled TDA-COF.

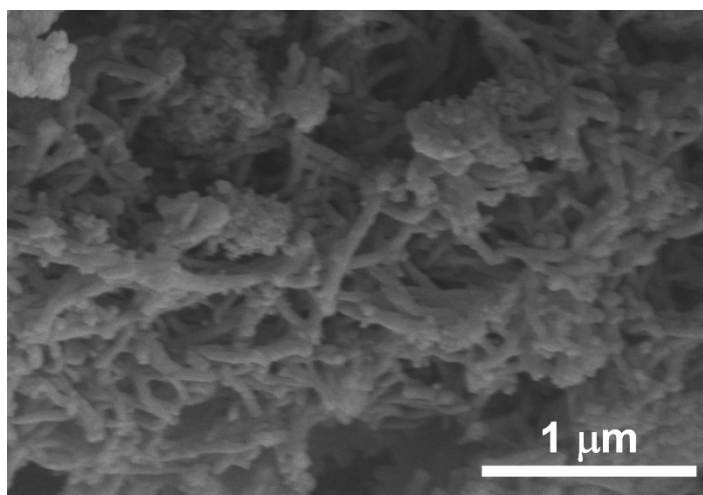


Figure S7 The SEM image of the recycled TDA-COF.

References

1. L. Stegbauer, K. Schwinghammer and B. V. Lotsch, *Chem. Sci.*, 2014, **5**, 2789–2793.
2. S. L. Yang, Z. Chen, L. Zou and R. Cao, *Adv. Sci.*, 2023, **10**, 2304697.
3. T. Lu and F. W. Chen, *J. Comput. Chem.*, 2012, **33**, 580–592.