Electronic supplementary information

Carbon-to-nitrogen atom transmutations in a covalent organic framework transform visible light-triggered selective oxidation of sulfides

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1 Materials and Methods

1.1 Materials

Reagents like 2,4,6-triformylphloroglucinol (Tp), and [1,1′-biphenyl]-4,4′-diamine (BD) were purchased from Adamas and used as received. [5,5′-Bipyrimidine]-2,2′-diamine (Bmd) was synthesized through the Suzuki cross-coupling reaction inspired by a previously reported protocol.[1] Other reagents, including the organic sulfides and solvents, were purchased from Sigma-Aldrich, TCI, Innochem, Adamas, Alfa Aesar, Sinopharm Chemical Reagent, and J&K Scientific Co., Ltd., etc.

1.2 Characterization

Powder X-ray diffraction (PXRD) measurement was carried out using a Rigaku/Miniflex 600 diffractometer with filtered Cu Kα radiation, and the data were collected from 2 to 30° (scan speed: 4° min^{-1}) at room temperature. The N_2 isotherms and specific surface areas were determined by using an Automated Surface Area and Pore Size Analyzer (Micromeritics ASAP 2460) with the Brunauer–Emmet–Teller (BET) method. The pore size distribution was derived from the sorption curve using the DFT model. The morphologies of TpBD-COF and TpBmd-COF were analyzed through scanning electron microscopy (SEM) and transmission electron microscopy (TEM), which were captured on a Zeiss Merlin Compac and a JEM-F200, respectively. Solid-state ^{13}C NMR spectra of both COFs were recorded on a Bruker AVANCE NEO 400 MHz NMR spectrometer. Fourier transform infrared (FTIR) spectra were recorded from 400 to 4000 cm^{-1} on Nicolet 5700 FTIR Spectrometer using KBr pellets. UV–

visible diffuse reflectance spectra of COFs and building blocks were measured from 300–800 nm using a UV-3600 UV-vis spectrophotometer (Shimadzu, Japan) configured with a diffuse reflectance measurement accessory. Thermogravimetric analysis (TGA) spectra were recorded on an SDT Q600 thermogravimeter from 30 °C to 800 °C at a rate of 15 ºC min^{-1} under N_2 atmosphere. Structural modelling and subsequent Pawley refinement of TpBD-COF and TpBmd-COF were achieved by using the Material Studio 2020 software package. The electron paramagnetic resonance (EPR) tests were executed on an EPR spectrometer (JEOL, JES-FA300). The targeted organic sulfoxide products and remaining organic sulfides were analyzed by the retention time compared with that of standard samples through 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 Helium as the carrier gas. DFT calculations were performed based on Gaussian 09W program package. Molecular geometries were optimized using B3LYP/6-31G (d) basis set. Subsequently, the ESP maps, LUMO and HOMO were visualized on Gauss View and Visual Molecular Dynamics (VMD).[2]

1.3 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 photocatalyst was added into 1.5 mL 0.2 wt%

Nafion. The mixture was then sonicated to obtain a homogenous solution. Then the samples were dripped on indium tin oxide (ITO) coated glasses which were placed on top of a glassy carbon serving as the working electrode. Upon the samples were dried under infrared irradiation, the glasses were fixed in the working electrode. With 0.1 M Na_2SO_4 solution acting 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 ± 15 nm were placed 2 cm away from the photoelectrochemical cell and employed as the light source for the generation of photocurrent.

1.4 The typical operation for the selective oxidation of sulfides

COF (5 mg), methanol (1 mL), and sulfide (0.3 mmol) were subsequently added into a Pyrex reactor (10 mL), which was stirred under darkness for 10 min to achieve adsorption–desorption equilibrium. After that, the reactor was irradiated directly by 460 nm blue LEDs (3 W × 4) and kept stirring at 1500 r min^{-1} under air atmosphere. The conversion and selectivity of the reaction were monitored by analyzing the supernatant by GC–FID using bromobenzene as the internal standard. The products were also verified by GC–MS.

Conversion of organic sulfide and selectivity of organic sulfoxide were calculated as follows:

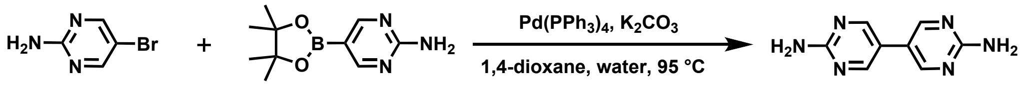
$$\text{Conversion (\%)} = [(C_0 - C_S)/C_0] \times 100$$

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

where C_0 is the initial concentration of sulfide substrate; C_S and C_p are the concentrations of organic sulfide and sulfoxide product at a certain time during the photocatalytic reaction.

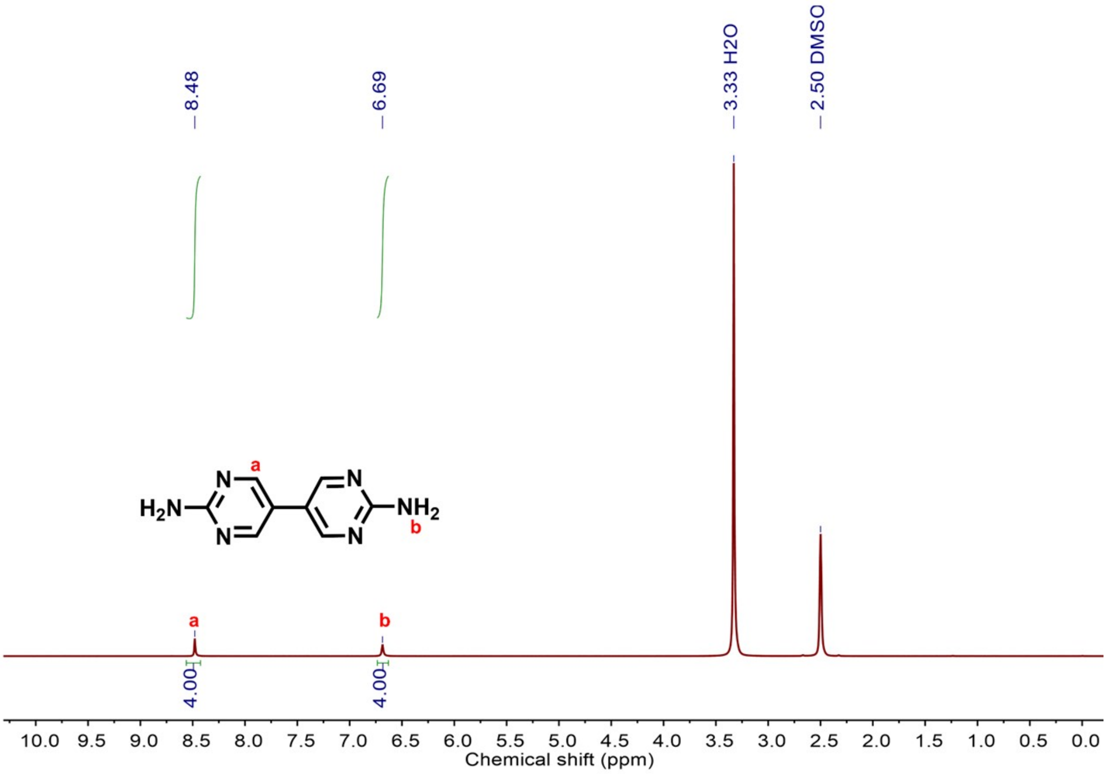
2 Synthetic Procedures

2.1 Synthesis of [5,5′-bipyrimidine]-2,2′-diamine (Bmd):



Scheme 1. Synthesis route of [5,5′-bipyrimidine]-2,2′-diamine (Bmd).

A two-necked Schlenk tube filled with 2-amino-5-bromopyrimidine (200 mg, 1.15 mmol), 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrimidin-2-amine (317 mg, 1.44 mmol), K_2CO_3 (476.8 mg, 3.45mmol) and $Pd(PPh_3)_4$ (40 mg, 3 mol%) was degassed and refilled with N_2. Then, a mixed solution (15 mL 1,4-dioxane and 5 mL water) was injected into the tube after degassing through N_2 bubbling for 15 min. The mixture reacted at 95 °C with stirring for 48 h. After cooling down to room temperature, the mixture was poured into water (50 mL). The precipitate was collected by filtration and rinsed with water, methanol, and chloroform sequentially. Then, it was dried under a vacuum to give the product as a white powder (150 mg, 69%). ^{1}H NMR (400 MHz, DMSO-d6) δ 6.69 (s, 4H), 8.48 (s, 4H). ^{1}H NMR spectrum of Bmd is shown as follows:



2.2 Synthesis of TpBD-COF:

TpBD-COF was synthesized according to our prior report[3] with some slight modifications. First, BD (0.12 mmol, 22.1 mg) and Tp (0.08 mmol, 16.8 mg) were put into a 10 mL ampule. 1,4-dioxane (1 mL) was subsequently added as the solvent. After ultrasonication for 10 min, 6 M acetic acid (100 μL) was added dropwise as the catalyst. The ampule was flash-frozen by liquid nitrogen and flame-sealed under reduced pressure after three freeze–pump–thaw cycles. Upon warming to room temperature, it was transferred into a 120 °C oven for 120 h, yielding an orange precipitate. The product was then collected through filtering and washed several times using methanol and tetrahydrofuran, respectively. After further purification through Soxhlet extraction in tetrahydrofuran for 24 h, the sample was dried at 80 °C for 12 h under vacuum to afford TpBD-COF as orange powder.

2.3 Synthesis of TpBmd-COF:

Firstly, Bmd (0.12 mmol, 22.1 mg) and Tp (0.08 mmol, 16.8 mg) were put into a 10 mL ampule. To the mixture, 1,4-dioxane (1 mL) was added. The ampule was then bathed in water with ultrasonication for 10 min. After that, 6 M acetic acid (100 μL) was added dropwise. Subsequently, the ampule was flash-frozen by liquid nitrogen and flame-sealed under reduced pressure after three freeze–pump–thaw cycles. Upon warming to room temperature, it was transferred into a 120 °C oven for 120 h, yielding a brown precipitate. The product was then collected through filtering and rinsed several times using *N,N*-dimethylformamide, water, and methanol, respectively. After further purification through Soxhlet extraction in tetrahydrofuran for 24 h, the sample was dried at 80 °C for 12 h under vacuum to afford TpBmd-COF as brown-red powder.

3. Supplementary Figures and Tables

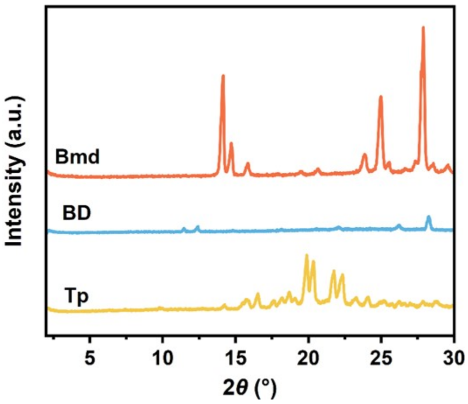


Fig. S1 PXRD patterns of Bmd, BD, and Tp.

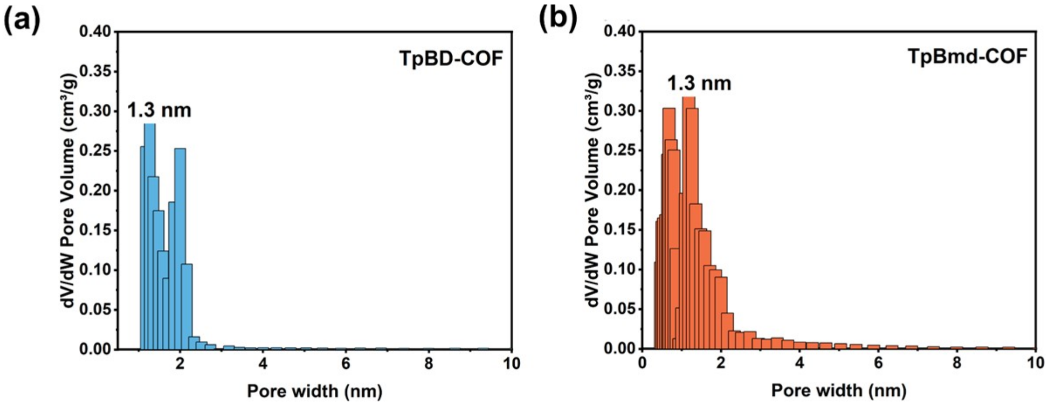


Fig. S2 Pore size distribution of TpBD-COF (a) and TpBmd-COF (b) calculated based on non-local DFT model.

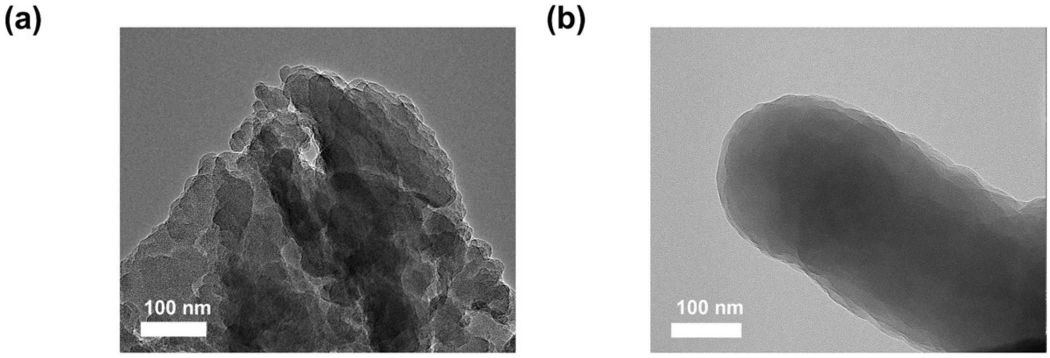


Fig. S3 TEM images of TpBD-COF (a) and TpBmd-COF (b).

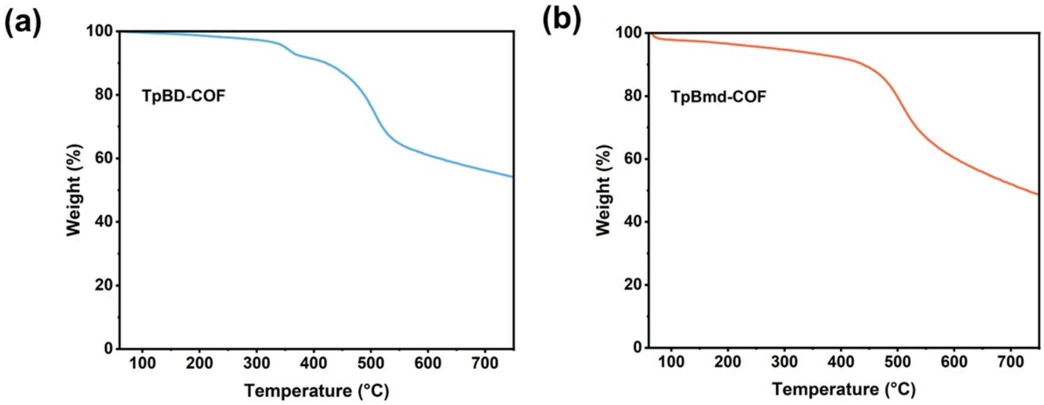


Fig. S4 TGA curves of TpBD-COF (a) and TpBmd-COF (b).

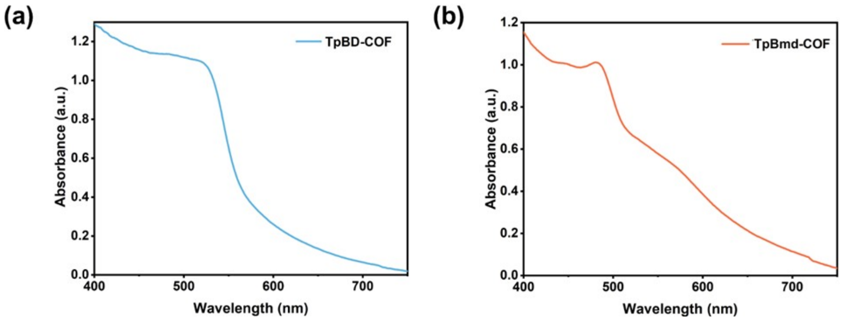


Fig. S5 UV–vis DRS spectra of TpBD-COF (a) and TpBmd-COF (b).

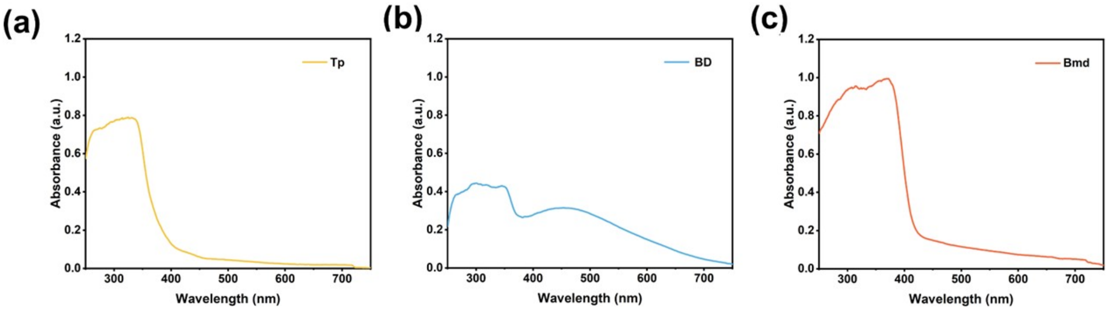


Fig. S6 UV–vis DRS spectra of building blocks, Tp, BD and Bmd.

Table S1. Comparison of photocatalytic activity of the building blocks for the selective oxidation of thioanisole.[a]

Entry	Photocatalyst	Conv. (%) [b]	Sel. (%) [b]
1	Tp	0	--
2	BD	0	--
3	Bmd	0	--

[a]Reaction conditions: thioanisole (0.3 mmol), methanol (1 mL), building block (Tp: 0.011 mmol, BD: 0.017 mmol, Bmd: 0.017 mmol), blue LEDs (3 W × 4), air (1 atm), 60 min. [b] The conversion and selectivity were determined by GC–FID.

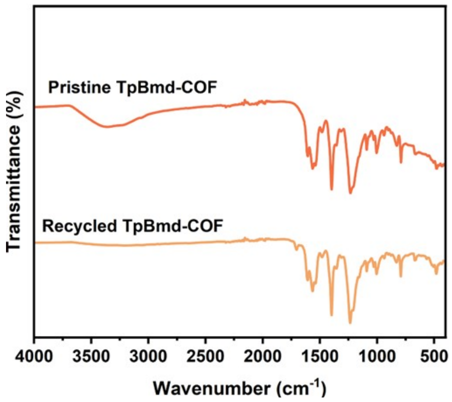


Fig. S7 FTIR spectra of the pristine TpBmd-COF and recycled TpBmd-COF.

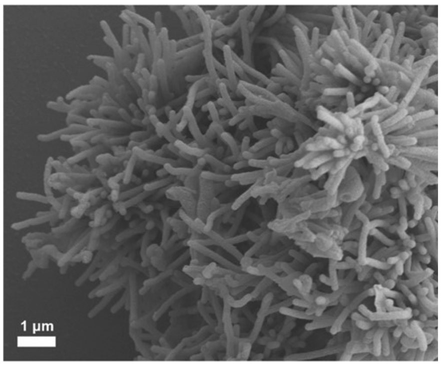


Fig. S8 SEM image of the recycled TpBmd-COF.

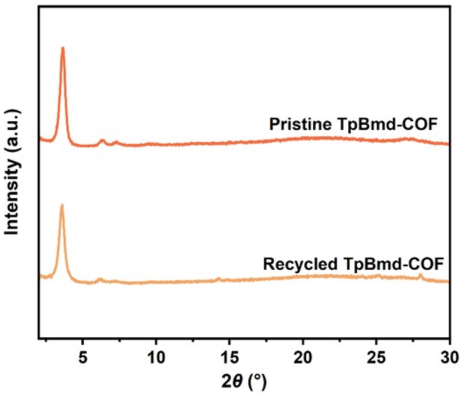


Fig. S9 PXRD patterns of the pristine and recycled TpBmd-COF.

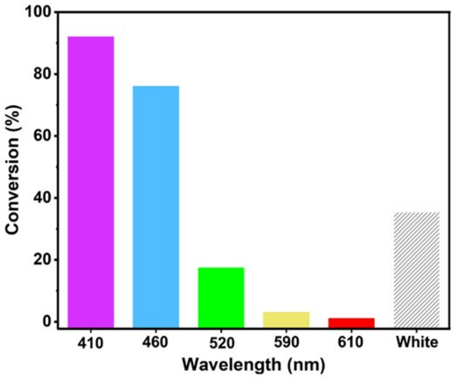


Fig. S10 The impact of different wavelength LED irradiation on the selective conversion of thioanisole over TpBmd-COF. Reaction conditions: thioanisole (0.3 mmol), methanol (1 mL), TpBmd-COF (5 mg), LEDs (3 W × 4), air (1 atm), 50 min.

References

1. J. L. Li, J. Jia, J. Q. Suo, C. Y. Li, Z. W. Wang, H. Li, V. Valtchev, S. L. Qiu, X. M. Liu and Q. R. Fang, *J. Mater. Chem. A*, 2023, **11**, 18349–18355.
2. W. Humphrey, A. Dalke and K. Schulten, *J. Mol. Graph. Model.*, 1996, **14**, 33–38.
3. K. H. Xiong, Y. X. Wang, F. L. Zhang, X. Li and X. J. Lang, *Appl. Catal. B*, 2023, **322**, 122135.