

**Vinylene-linked donor-acceptor covalent organic polymers with
low exciton binding energy for enhanced photocatalytic
oxidation of sulfides**

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Contents

1 Materials	3
2 Characterizations	3
3 Synthesis of COPs	4
3.1 Synthesis of Btt-Bdd	4
3.2 Synthesis of Btt-Btd	4
3.3 Synthesis of Btc-Bdd	5
4 Photoelectrochemical measurements	6
5 Photocatalytic experiments	6
6 References	15

Experimental Section

1 Materials.

Benzotrithiophene-2,5,8-tricarbaldehyde (Btt) and 5,5', 5'' - (benzene-1,3,5-triyl) tri (thiophen-2-formaldehyde) (Btc) were purchased from Jilin Chinese Academy of Sciences-Yanshen Technology Co. Ltd. 2,2'-(Benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(4,1-phenylene)diacetonitrile (Bdd), 4,4'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)dianiline (Btd) were purchased from Bidepharm. Tetrabutylammonium hydroxide (TBAH) methanol solution (25%), Thioanisole and CH₃COOH were acquired from Shanghai Macklin Biochemical Technology Co., Ltd. Other chemicals were provided by Sinopharm Chemical Reagent Co, Ltd. All reagents were used without further purification unless otherwise stated.

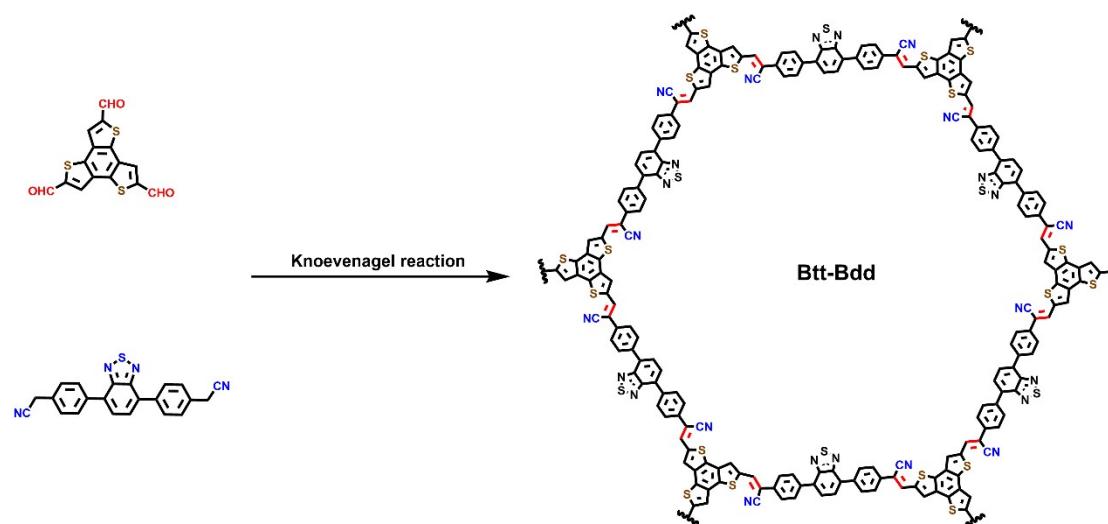
2 Characterizations.

Powder X-ray diffraction (PXRD) data were collected on a D8 Advance diffractometer, and the data were collected from 2° to 30° with 0.02° increment. Fourier transform infrared (FT-IR) spectra were collected in the range of 800~4000 cm⁻¹ on Nicolet 6700 spectrometer. Thermogravimetric analysis (TGA) was recorded on a TGA/1100SF heating from 30-800 °C at the rate of 10 °C/min with N₂ flow rate of 50 mL·min⁻¹. X-ray photoelectron spectroscopy (XPS) were measured with an AXIS Supra by Kratos Analytical Inc. Using monochromatized Al K α radiation ($h\nu = 1486.6$ eV, 225 W) as X-ray source with a base pressure of 10⁻⁹ torr. All binding energies were calibrated by C 1s at 284.8 eV. The morphology and elemental distributions of the samples were characterized by the scanning electron microscopy (SEM, S-4800, with an acceleration voltage of 5 kV) with an EDX detector and transmission electron microscope (TEM, Talos F200X G2, with an acceleration voltage of 200 kV). Photoluminescent (PL) spectra and time-resolved PL spectra were recorded on a Lifespec II fluorescence spectrometer. Sulfoxide is produced by catalytic oxidation of sulfides were detected utilizing a gas chromatograph (Shimadzu, Nexis GC-2030 ATF). The gas chromatography-mass spectrometry (GC-MS) was measured on Shimadzu GCMS-QP2020 NX. X-ray photoelectron spectroscopy (XPS) was carried out with an AXIS Supra by Kratos Analytical Inc using monochromatized Al K α radiation ($h\nu = 1486.6$

eV, 150 W) as X-ray source with a base pressure of 10^{-9} torr. Electron paramagnetic resonance spectroscopy (EPR) was conducted on a Bruker EMX PLUS in the dark or irradiated with a Xe lamp (> 420 nm, 300 W). Ultraviolet-visible (UV-Vis) diffuse reflectance spectra were collected on a Shimadzu Corporation UV-2600 spectrometer. The specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method and the pore size distributions were determined by non-local density functional theory (NLDFT). ^{13}C solid-state nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker Avance Neo 400WB.

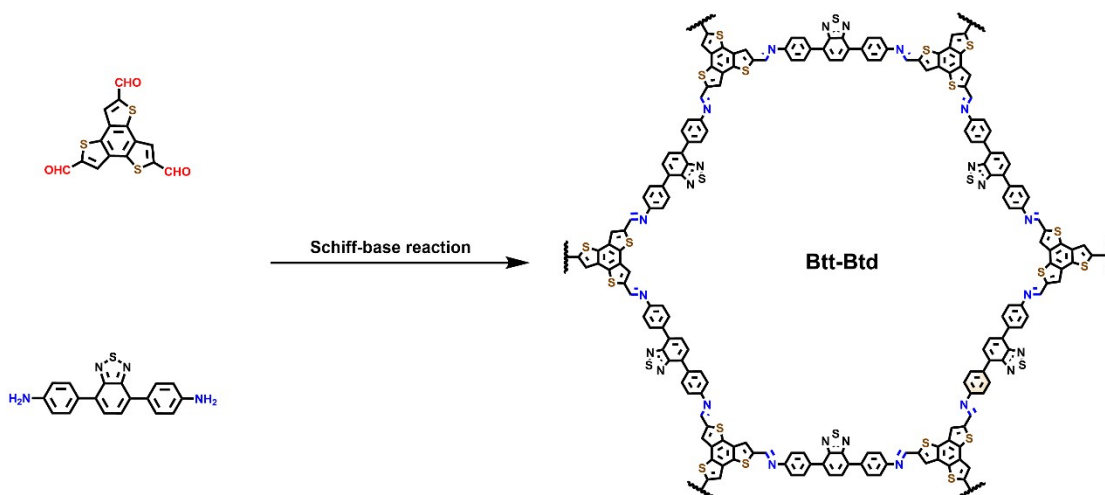
3 Synthesis of COPs.

3.1 Synthesis of Btt-Bdd.



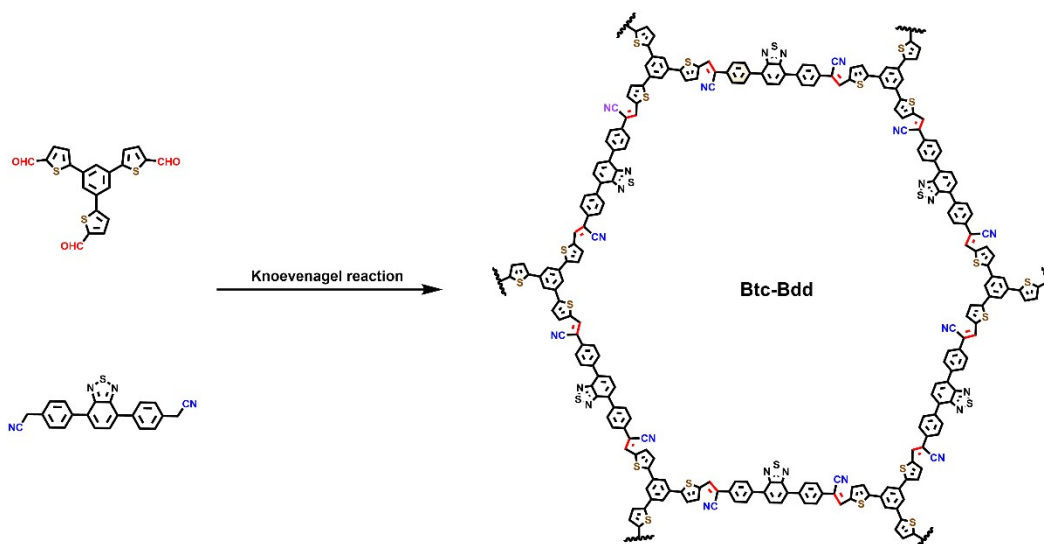
A 10 mL Pyrex tube was charged with Btt (0.04 mmol, 13.2 mg) and Bdd (0.06 mmol, 22.0 mg) in a mixed solution of *o*-dichlorobenzene (*o*-DCB) and *n*-butyl alcohol (*n*-BuOH) ($v/v=2:1$, 2.1 mL). The tube was sonicated for 5 min, and then added 3 M TBAH (0.2 mL) as a catalyst for the reaction. The mixture was degassed by freeze-pump-thaw technique for three times and sealed under vacuum, and then heated under $120\text{ }^{\circ}\text{C}$ for 3 days. After being cooled to room temperature, the precipitate was isolated by filtration and washed with tetrahydrofuran (THF) and acetone several times until the filtrate is colorless. The solid was freeze-dried for 24 h to obtain the final product in 93% isolated yield.

3.2 Synthesis of Btt-Btd.



The synthesis of Btt-Btd was prepared based on literature reports. A 10 mL Pyrex tube was charged with Btt (0.04 mmol, 13.2 mg) and Bdd (0.06 mmol, 22.0 mg) in a mixed solution of mesitylene and 1,4-dioxane (v/v=1:1, 1.0 ml). The tube was sonicated for 5 minutes then added 6 M aqueous acetic acid (0.1 mL) as a catalyst for the reaction. The mixture was degassed by freeze-pump-thaw technique for three times and sealed under vacuum, and then heated under 120 °C for 3 days. After being cooled to room temperature, the precipitate was isolated by filtration and washed with tetrahydrofuran (THF) and acetone several times until the filtrate is colorless. The solid was freeze-dried for 24 h to obtain the final product in 89% isolated yield.

3.3 Synthesis of Btc-Bdd.



A 10 mL Pyrex tube was charged with Btc (0.04 mmol, 13.2 mg) and Bdd (0.06 mmol, 22.0 mg) in a mixed solution of *o*-dichlorobenzene (*o*-DCB) and *n*-butyl alcohol (*n*-

BuOH) (v/v=1:1, 1 mL). The tube was sonicated for 5 min, and then added 3 M DBU (0.2 mL) as a catalyst for the reaction. The mixture was degassed by freeze-pump-thaw technique for three times and sealed under vacuum, and then heated under 120 °C for 3 days. After being cooled to room temperature, the precipitate was isolated by filtration and washed with tetrahydrofuran (THF) and acetone several times until the filtrate is colorless. The solid was freeze-dried for 24 h to obtain the final product in 93% isolated yield.

4 Photoelectrochemical measurements.

The photoelectrochemical measurements were performed on the CHI660E electrochemical workstation using the three-electrode method. The photocatalyst-coated FTO glass, mercuric sulfate electrode and carbon rod were used as the working electrode, reference electrode and counter electrode, respectively. The preparation process of working electrode was as follows: 2 mg of photocatalysts were dissolved in the mixture of 200 μ L ethanol and 10 μ L Nafion, and then dropped on the surface of FTO glass with an area of 1 cm² to form a film. The photocurrent response curves were tested under a 300 W Xenon lamp (PLS SXE300) with a 420 nm cut-off filter in the three-electrode system and 0.2 M Na₂SO₄ aqueous solution was used as the electrolyte solution. The electrochemical impedance spectra (EIS) were tested with the frequency range of 0.01 Hz-10000 Hz, alternating amplitude of 10 mV. The Mott-Schottky (M-S) plots were collected on a standard three-electrode system, containing COPs-coated ITO as the working electrode, a Pt plate as the counter electrode, and the Ag/AgCl electrode as the reference electrode. The M-S plots were tested at the frequencies of 1000, 1200, and 1500 Hz in the dark. Na₂SO₄ solution (0.5 M, pH = 6.8) was used as the electrolyte. The applied potentials vs. Ag/AgCl were converted to NHE potentials using the following equation:

$$E_{\text{NHE}} = E_{(\text{Ag}/\text{AgCl})} + E^{\theta}_{(\text{Ag}/\text{AgCl})} \quad (E^{\theta}_{(\text{Ag}/\text{AgCl})} = 0.199 \text{ V})$$

5 Photocatalytic experiments.

Under white LEDs light irradiation, the sulfide achieves selective conversion on the Btt-Bdd photocatalyst. Generally, the reaction system composed of CH₃OH (5 mL), thioanisole (0.1 mmol), and Btt-Bdd (5 mg) was thoroughly stirred for 30 min in dark.

Then, turning on the white LEDs (10 W) light, the system filled with 0.1 MPa O₂ began to undergo organic conversion with continuous stirring. Next, using bromobenzene as the internal standard, the supernatant was collected by centrifugation after reaction for 8h. The supernatant after solids removal was analyzed by gas chromatography with flame ionization detection (GC-FID). The conversion of organic sulfide and the selectivity of organic sulfoxide were determined by internal standard method. Finally, the products in the supernatant were clearly identified by gas chromatography-mass spectrometry (GC-MS). The error estimates from three repetitions were calculated as $\pm 2\%$.

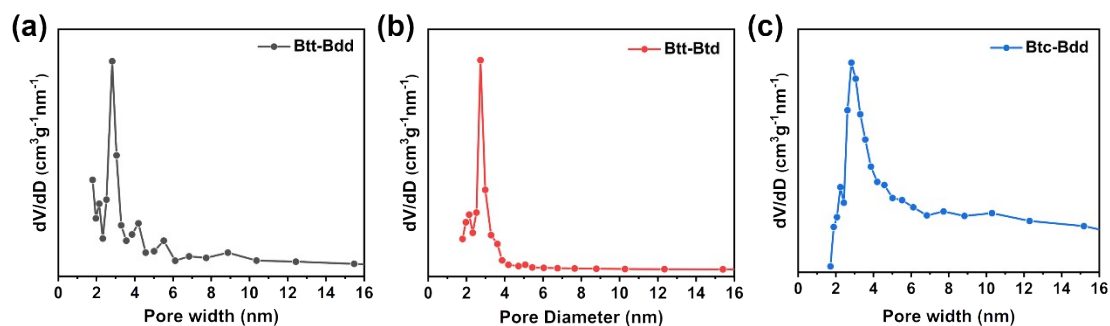


Figure S1. The pore width distributions of the Btt-Bdd (a), Btt-Btd (b), and Btc-Bdd (c).

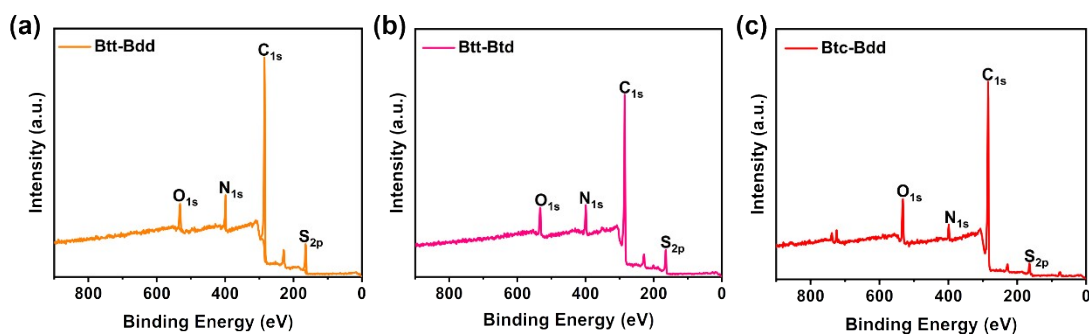


Figure S2. The XPS full spectra of Btt-Bdd (a), Btt-Btd (b) and Btc-Bdd (c).

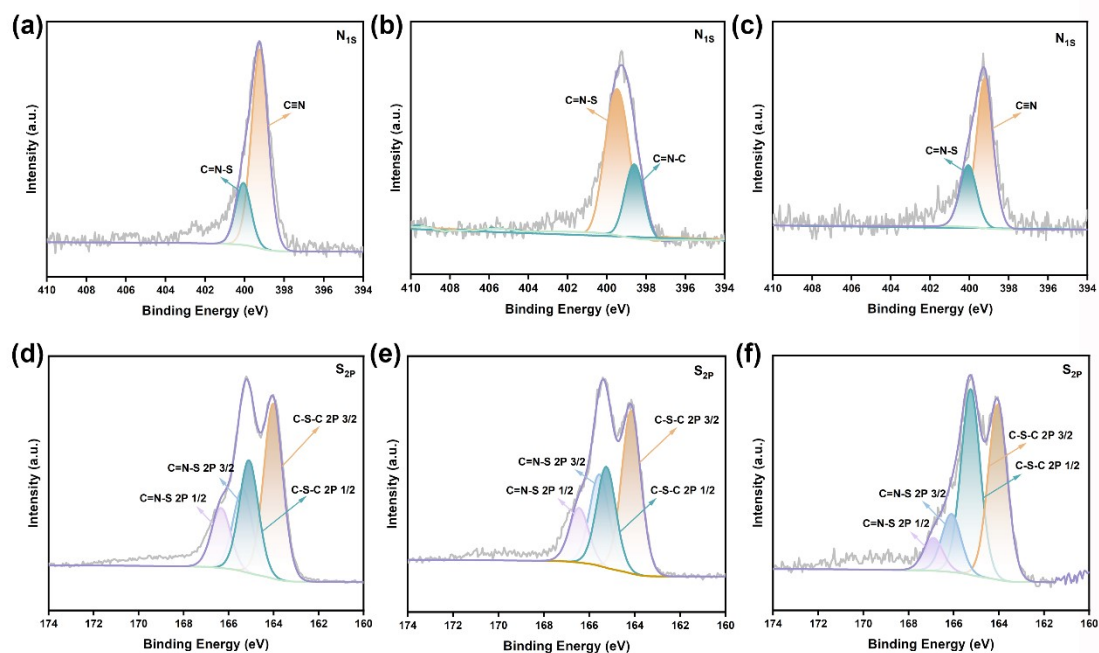


Figure S3. N 1s XPS spectra of Btt-Bdd (a), Btt-Btd (b) and Btc-Bdd (c). S 2p XPS spectra of Btt-Bdd (d), Btt-Btd (e) and Btc-Bdd (f).

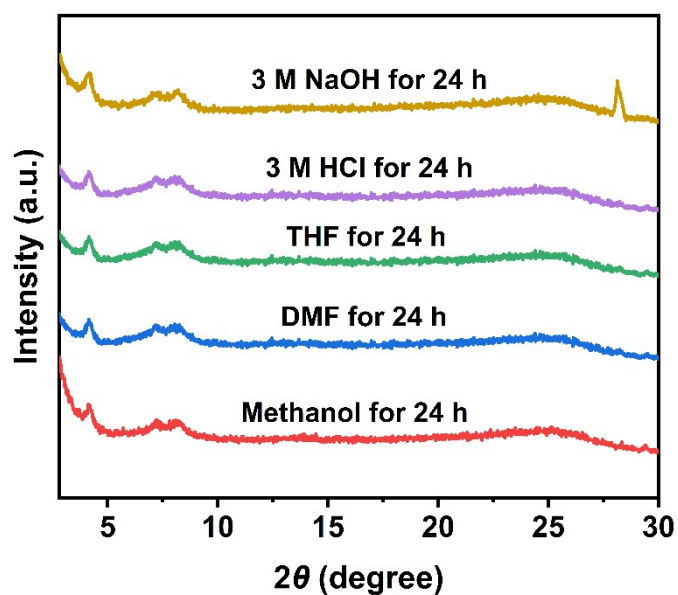


Figure S4. PXRD patterns of Btt-Bdd after immersion in different solvents for 24 h.

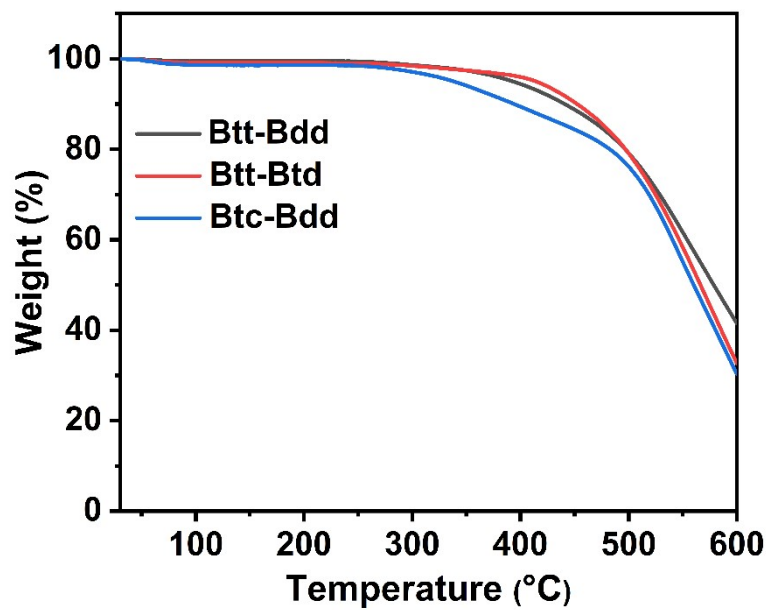


Figure S5. TGA curves of Btt-Bdd, Btt-Btd and Btc-Bdd.

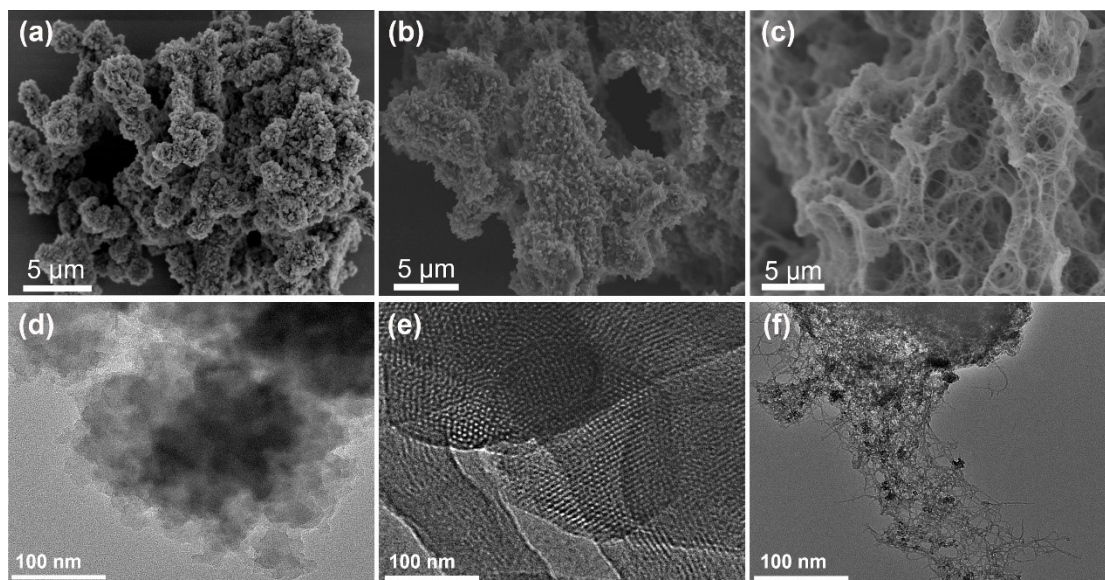


Figure S6. The SEM and TEM images of Btt-Bdd (a) and (d), Btt-Btd (b) and (e), Btc-Bdd (c) and (f).

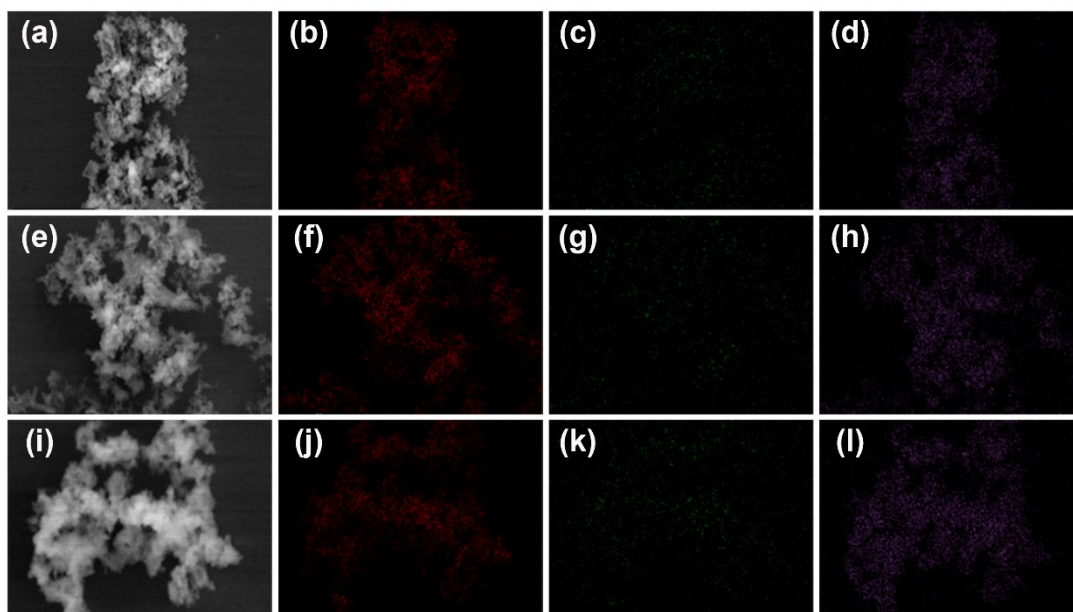


Figure S7. The SEM elemental mappings of Btt-Bdd (a-d), Btt-Btd (e-h) and Btc-Bdd (i-l); C: red; N: green; S: purple.

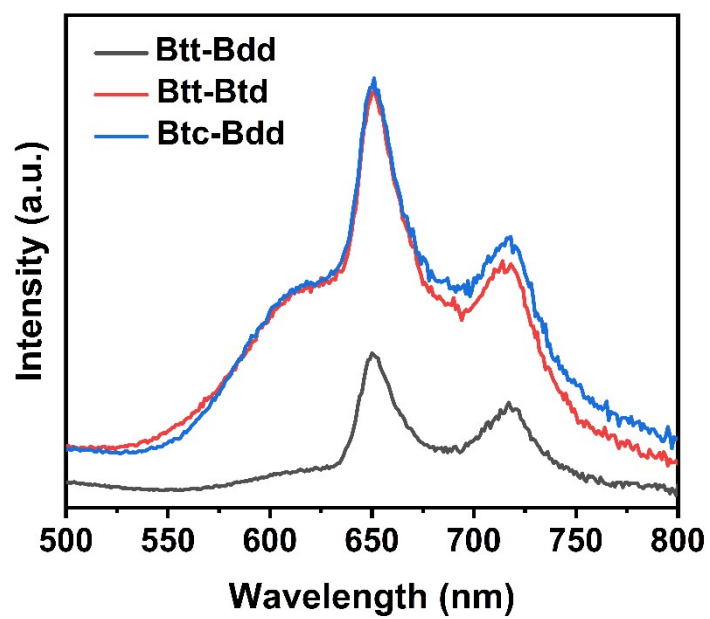


Figure S8. Photoluminescence (PL) spectra of the obtained COPs.

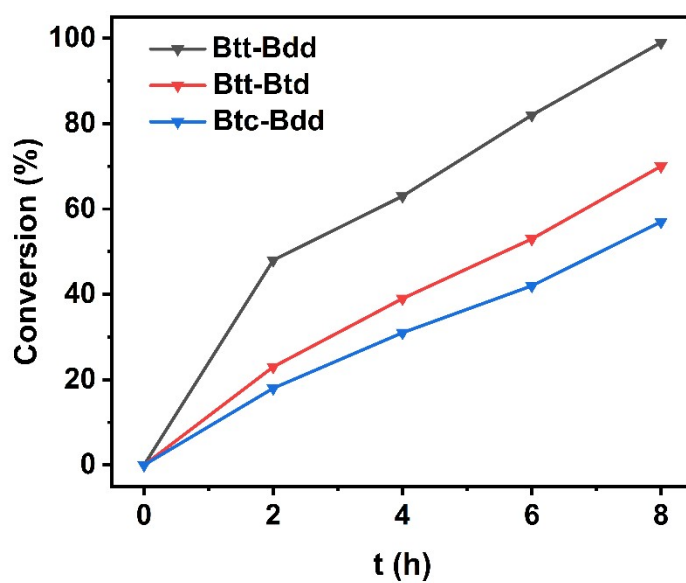


Figure S9. Kinetic curves for the selective oxidation of sulfide.

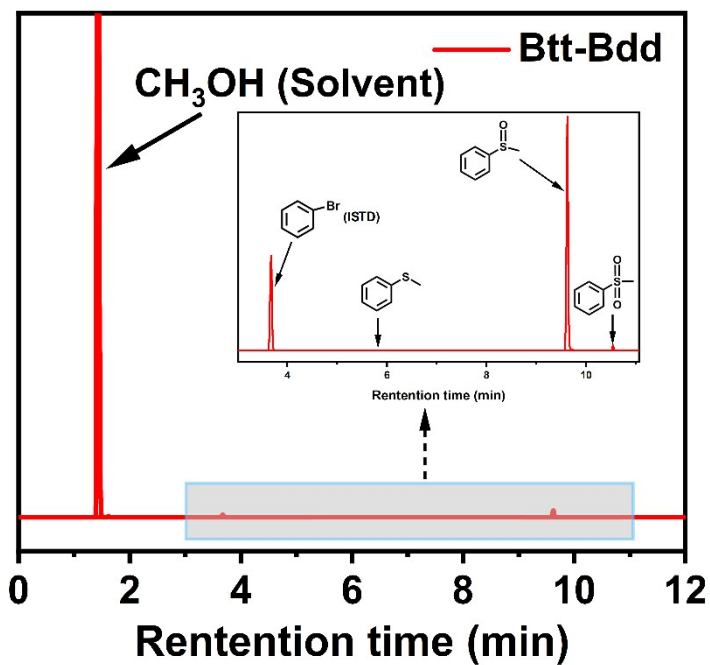


Figure S10. The GC-MS curve of the reaction filtrate for the oxidation of thioanisole to methyl phenyl sulfoxide with Btt-Bdd as catalysis. Reaction condition: thioanisole (0.1 mmol), catalyst (5 mg), CH₃OH (5 mL), white light, room temperature, 8 h.

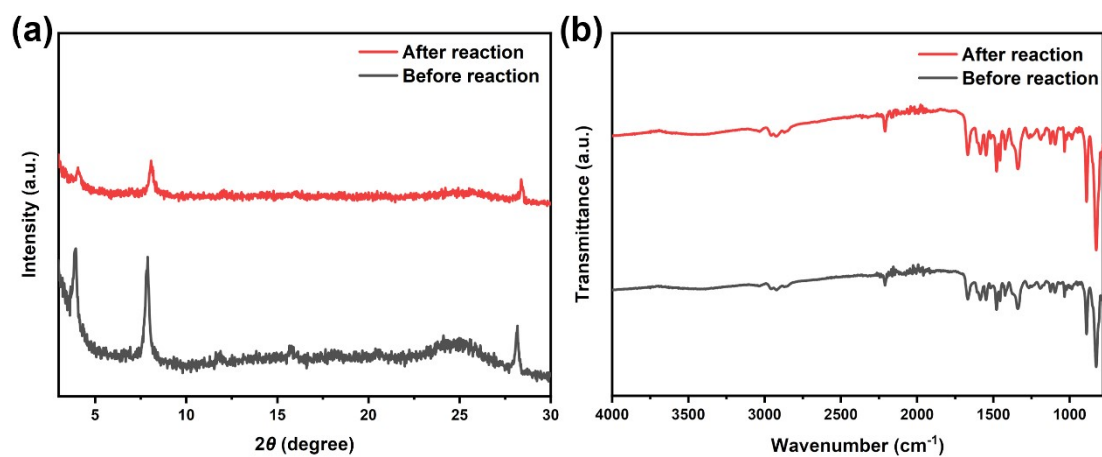


Figure S11. (a) PXRD patterns and (b) FT-IR spectra of the Btt-Bdd before and after photocatalysis.

Table S1. The influence of different solvents on the selective photocatalytic aerobic oxidation of sulfides with O₂.^[a]

Entry	Solvent	Conv. (%) ^[b]	Sel. (%) ^[b]
1	CH ₃ OH	99	96
2	C ₂ H ₅ OH	73	94
3	CH ₃ CN	5	95
4	DMF	7	82

[a] Reaction conditions: sulfide (0.1 mmol), Btt-Bdd (5 mg), white LEDs irradiation, O₂ (1 atm), 8h.

[b] Determined by GC-FID using bromobenzene as the internal standard, conversion of sulfides, and selectivity of sulfoxides.

Table S2. The influence of solvent amounts on the selective photocatalytic aerobic oxidation of sulfides with O₂. ^[a]

Entry	CH ₃ OH (mL)	Conv. (%) ^[b]	Sel. (%) ^[b]
1	1	83	88
2	3	91	91
3	5	99	96
4	7	85	82

[a] Reaction conditions: sulfide (0.1 mmol), Btt-Bdd (5 mg), white LEDs irradiation, O₂ (1 atm), 8h.

[b] Determined by GC-FID using bromobenzene as the internal standard, conversion of sulfides, and selectivity of sulfoxides.

Table S3. Comparisons of different photocatalysts for selective photocatalytic oxidation of sulfide.

Photocatalysts	Additive	Light source	Time (h)	Conv. (%)	Sel. (%)	Ref.
P25 TiO ₂	TEA	Xe lamp (300 W, $\lambda > 420$ nm)	10	84	92	[1]
ARS-sensitized TiO ₂	TEMPO	300 W Xe lamp, $\lambda > 450$ nm	10	81	91	[2]
NNU-45	H ₂ O ₂	Visible-Light	4	94	95	[3]
Py-Azine-COF	TEMPO	blue LEDs ($\lambda_p = 460$ nm, 3 W \times 4)	1.5	93	98	[4]
NQ-COF _{TfppyPh}	NO	LED lamp (18 W, 460-465 nm)	12	99	--	[5]
TCPP-CMP	NO	white LED (100 W)	16	99	97	[6]
Pt@COF	NO	LED ($\lambda = 450$ nm)	12	96	--	[7]
TPP ₄ H ₂ [V ₁₀ O ₂₈]	NO	visible light ($\lambda > 400$ nm, 300 W Xe lamp)	24	92	75	[8]
TiO ₂ @Polydopamine	TEMPO (5 mol%)	460 nm blue LEDs (3 W \times 4)	6	86	84	[9]
pTCT	NO	26 W white CFL	12	99	97	[10]
Btt-Bdd	NO	White LEDs (5 W)	8	99	96	This work

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