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Electronic Supplementary Information (ESI) for

# Molecular engineering of covalent triazine frameworks for highly enhanced photocatalytic aerobic oxidation of sulfides

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# **General method and materials**

Unless specifically mentioned, all chemicals are commercially available and were used as received. 3,7-dibromo-10-(4-bromophenyl)-10H-phenothiazine (PTZ-3Br) was prepared according to the reported literature method.<sup>S1</sup><sup>1</sup>H and <sup>13</sup>C NMR spectra were taken on a Bruker AV400 at room temperature. High-resolution mass spectrometry (HR-MS) was performed on a Thermo ultimate Q-Exactive in positive mode. Solid-state <sup>13</sup>C cross-polarization- magic angle spinning nuclear magnetic resonance (<sup>13</sup>C CP-MAS NMR) experiments were performed on a Bruker AVANCE III 400 WB spectrometer operating at 100.62 MHz for <sup>13</sup>C using a double resonance 4 mm MAS NMR probe and a sample spinning rate of 6 kHz. The powder X-ray diffraction measurements were taken on a Bruker D8 diffractometer using  $Cu-K_a$ radiation ( $\lambda = 1.5418$  Å) at room temperature. Low-pressure gas sorption measurements were performed by using Quantachrome Instruments Autosorb-iQ with the extra-high pure gases. Brunauer-Emmett-Teller (BET) surface area and pore size distribution were calculated from the N<sub>2</sub> sorption isotherms at 77 K based on Non-Local Density Functional Theory (NL-DFT) model in the Quantachrome ASiQwin 2.01 software package. UV-vis diffuse reflectance spectra (UV-vis DRS) were recorded at room temperature on an Agilent Cary 7000 Spectrophotometer. Photoluminescence (PL) spectra were obtained with an Edinburgh FLS920 spectrophotometer. The infrared spectra were recorded on a Thermo Scientific Nicolet iS10 FT-IR spectrometer as KBr pellets. Thermal gravimetric analyses (TGA) were performed on a TA-Q50 thermoanalyzer thermogravimetric analyzer in nitrogen atmosphere from at the rate of 10  $\,^{\circ}$ C min<sup>-1</sup>. Ultraviolet photoelectron spectroscopy (UPS) was performed on Thermo Scientific Escalab 250Xi. Field-emission scanning electron microscopy (FE-SEM) images were obtained on a HITACHI S-8010 instrument operating at 10 kV. Transmission electron microscopy (TEM) images were obtained on a JEM 2100F operating at 200 kV. All quantum chemical calculations were performed by the Gaussian 16 package<sup>S2</sup> using density functional theory (DFT) functional B3LYP.<sup>S3-S5</sup> Geometry optimization and time-dependent density functional

theory (TD-DFT) calculations were carried out with the 6-31 G (d, p) basis set.<sup>S6-S7</sup> Solvation effects were considered throughout the calculations with the conductor-like polarizable continuum model (CPCM) method.<sup>S8</sup> The natural transition orbitals (NTOs) generation and electron excitation analyses were performed using the Multiwfn program.<sup>S9</sup> The figures of charge distribution were prepared by Multiwfn and VMD.<sup>S9-S11</sup>

# **Photoelectrochemical measurements**

The working electrode was prepared on fluorine-doped tin oxide (FTO) glass that was thoroughly cleaned by ultrasonication in an order of ethanol, acetone and de-ionized water for 10 min, respectively. The clean FTO glass substrate was dried at 60 °C for 24 h. To prepare the photoelectrode, 5 mg of fully ground CTF sample was ultrasonicated in 0.5 mL of ethanol to disperse it evenly to get a slurry. The slurry was spread onto FTO glass, whose side part was previously protected using Scotch tape with an exposed area of  $1.0 \times 1.0 \text{ cm}^2$ . After naturally drying in air, the Scotch tape was unstuck. The photocurrents were recorded by an electrochemical workstation (CHI760E) equipped with a conventional three-electrode cell. A Pt plate was used as the counter electrode, and Hg/HgCl<sub>2</sub> electrode was used as the reference electrode. Electrolyte: NaH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> (0.025 M) buffer solution with pH 6.8. The working electrode was illuminated by a 300 W Xe lamp with a 420 nm cut-off filter from the backside to minimize the impact of thickness of the semiconductor layer. The transient photocurrent responses with time (I–t curve) was measured at a bias potential of 0.2 V during repeated on-off illumination cycles.

# Photocatalytic aerobic oxidation of sulfides

The photocatalytic oxidation of organic sulfides was performed in a Schlenk tube by using blue light emitting diodes (LEDs,  $\lambda_{max} = 450$  nm, 3 W×4) as light source and air as the green oxidant. In a typical experiment, 2.0 mg CTF photocatalyst and 0.1 mmol thioanisole were added to 1 mL CD<sub>3</sub>CN solvent. The mixture was stirred and irradiated by blue LEDs for 2 h under air atmosphere at room temperature. At the end of reaction, the CTF particles were separated from the reaction mixture by centrifugation. Subsequently, the solution was subjected to <sup>1</sup>H NMR analysis in order to identify the product and calculate the yield. To carry out recycling experiments, the CTF photocatalyst was recycled by centrifugation and washed by acetonitrile for three times, and then dried under vacuum at 60  $\,^{\circ}$ C overnight.

# **Synthesis and Characterizations**

#### Synthesis of CN-precursors



Scheme S1 Synthetic routes for precursors PTZ-CN, TPA-CN and TPB-CN.

#### Synthesis of PTZ-CN:

3,7-dibromo-10-(4-bromophenyl)-10*H*-phenothiazine (PTZ-3Br, 1.02 g, 2.0 mmol), Zn(CN)<sub>2</sub> (0.70 g, 6.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.23 g, 0.2 mmol) were added into 50 mL anhydrous DMF under the protection of nitrogen. The reaction mixture was heated to 110  $^{\circ}$ C and stirred for 12 hours. After that, the solution was poured into water and extracted with dichloromethane, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated to obtain a yellow solid. The crude product was purified by column chromatography over a silica gel column using petroleum ether-dichloromethane (v/v, 1/3) as the eluent to afford PTZ-CN as a yellow solid (0.53 g, 1.5 mmol, yield: 75%). <sup>1</sup>H NMR (400

MHz,  $d_6$ -DMSO)  $\delta$  8.22 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 1.8 Hz, 2H), 7.37 (dd, J = 8.6, 1.9 Hz, 2H), 6.10 (d, J = 8.6 Hz, 2H). <sup>13</sup>C NMR (101 MHz,  $d_6$ -DMSO)  $\delta$  145.2, 142.6, 135.9, 132.3, 131.6, 130.0, 119.7, 118.1, 116.5, 112.5, 106.0. EI-HRMS: m/z calcd for C<sub>21</sub>H<sub>10</sub>N<sub>4</sub>S: 350.0626, found: 350.0620 [M]<sup>+</sup>.



**Fig. S1** <sup>1</sup>H NMR of PTZ-CN (400 MHz, *d*<sub>6</sub>-DMSO).



**Fig. S2** <sup>13</sup>C NMR of PTZ-CN (101 MHz, *d*<sub>6</sub>-DMSO)



Fig. S3 EI-HRMS of PTZ-CN.

For TPA-CN: it was synthesized by the same procedure as PTZ-CN. <sup>1</sup>H NMR (400 MHz,  $d_6$ -DMSO)  $\delta$  7.81 (d, J = 8.3 Hz, 6H), 7.23 (d, J = 8.3 Hz, 6H). This <sup>1</sup>H NMR data is in agreement with the previous report, <sup>S12</sup> confirming its correct chemical structure.



**Fig. S4** <sup>1</sup>H NMR of TPA-CN (400 MHz, *d*<sub>6</sub>-DMSO).

For TPB-CN: it was synthesized by the same procedure as PTZ-CN. <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  8.21-8.13 (m, 9H), 7.99 (d, J = 8.3 Hz, 6H). This <sup>1</sup>H NMR data is in agreement with the previous report,<sup>\$13</sup> confirming its correct chemical structure.



**Fig. S5** <sup>1</sup>H NMR of TPB-CN (400 MHz, *d*<sub>6</sub>-DMSO).

#### Synthetic procedures for CTFs



Scheme S2 Synthetic routes for CTFs (CTF-PTZ, CTF-TPA and CTF-TPB).

**Synthesis of CTF-PTZ:** The PTZ-CN precursor (350 mg, 1 mmol) was added into 5 mL TfOH at 0 °C and stirred until it was dissolved for ~5 min, the solution was further gradually heated to at 110 °C and then stirred for another 1 h. After cooled down to room temperature, the solution was poured into water. Resultant solid precipitate was filtered and sequentially washed with diluted ammonia, acetone and dichloromethane. The solid was Soxhlet extracted with THF for 24 h and was dried under vacuum for 12 h at 80 °C to give orange powder in 89% yield.

The other two CTFs CTF-TPA and CTF-TPB were prepared by the similar procedure, with a yield of 96% and 86% in yellow and white grey powders, respectively.

Entry	Names of CTFs	Synthetic Conditions	BET (m <sup>2</sup> /g)	Applications	References	
1	CTP-1 CTP-2 CTP-3	TfOH, 0 °C 1.5 h, 100 °C 20 min	5 8 9	photocatalysis for oxygen evolution	Angew. Chem. Int. Ed. <b>2018</b> , 57, 470.	
2	asy-CTF CTF-Th-Ph CTF-Th	TfOH, 100 °C 24 h	52 62 78	photocatalysis for synthesis of benzophosphole oxides	Angew. Chem. Int. Ed. <b>2018</b> , 57, 8316.	
3	CTF-BT/Th-x	TfOH, 50 °C 0.5 h, 100 °C 2 h	32~92	photocatalysis for hydrogen evolution	Angew. Chem. Int. Ed. <b>2019</b> , 58, 8676.	
4	CTF-2BT	TfOH, 100 °C 24 h	non-porous materials <sup>a</sup>	organic photoredox catalysis	Angew. Chem. Int. Ed. <b>2020</b> , 59, 18368.	
5	CTP-Th	TfOH, 100 °C 1 h	72	photocatalysis for hydrogenation of maleic acid and furfural	Angew. Chem. Int. Ed. <b>2020</b> , 59, 14378.	
6	CTF-1@TFMS	TfOH, CHCl <sub>3</sub> , 0 °C 2 h, 24 h at room temperature	62	iodine capture	<i>Chem. Eng. J.</i> <b>2019</b> , <i>371</i> , 314.	
7	CTF-T1	TfOH, 0 °C 5 min, 72 h at room temperature	19	photocatalysis for hydrogen and oxygen evolution	Macromol. Rapid Commun. <b>2015</b> , 36, 1799.	
8	A-CTF-2	TfOH, CHCl <sub>3</sub> , 0 °C 1.5 h, 24 h at room temperature	24	photocatalysis for amine oxidative couplings	ACS Catal. <b>2021</b> , 11, 7429.	
9	CTF-1-100W	TfOH, microwave, 100 W, 30 s	~1	photocatalysis for hydrogen and oxygen evolution	Energy Environ. Sci. <b>2018</b> , 11, 1617.	
10	BC-CTF Ph-BC-CTF	TfOH, CHCl <sub>3</sub> , 0 °C 1 h, 15 h at room temperature	934 967	photocatalysis for oxidation of thioanisoles and RhB degradation	<i>Macromolecules</i> <b>2019</b> , <i>52</i> , 9786.	
11	P1~P6	TfOH, CHCl <sub>3</sub> , 0 °C 2.5 h, overnight at room temperature	2~1152	CO <sub>2</sub> uptake	Adv. Mater. <b>2012</b> , 24, 2357.	
12	CTF-PTZ CTF-TPA CTF-TPB	TfOH, 0 °C 5 min, 110 °C 1 h	78 37 116	photocatalysis for aerobic oxidation of sulfides	this work	

Table S1 Comparison for BET surface areas of CTFs prepared by TfOH-catalysis and their

# applications in reported literatures.

<sup>*a*</sup>There is only nitrogen sorption isotherm available in this work. Authors claimed their CTFs are non-porous materials. No corresponding BET data is reported.

Entry Solvents		Temp. (°C)	Time (h)	$S_{\text{BET}} (\text{m}^2 \text{ g}^{-1})^b$	Yield (%)
CTF-PTZ-1	CF <sub>3</sub> SO <sub>3</sub> H	R.T.	24 h	0.8	86
CTF-PTZ-2	CF <sub>3</sub> SO <sub>3</sub> H	90	2 h	69	87
CTF-PTZ-3 <sup>c</sup>	CF <sub>3</sub> SO <sub>3</sub> H	110	1 h	78	89
CTF-PTZ-4	CF <sub>3</sub> SO <sub>3</sub> H	130	1 h	34	89
CTF-PTZ-5	CHCl <sub>3</sub> /CF <sub>3</sub> SO <sub>3</sub> H (V/V: 10/1)	30	24 h	18	84
CTF-PTZ-6	CHCl <sub>3</sub> /CF <sub>3</sub> SO <sub>3</sub> H (V/V: 10/1)	60	24 h	5	88

Table S2 Optimizing synthetic conditions of CTF-PTZ for seeking higher BET surface area.<sup>a</sup>

<sup>*a*</sup>General reaction conditions: PTZ-CN (1 mmol), CF<sub>3</sub>SO<sub>3</sub>H (5 mL). Yields were determined after isolation, purification and dryness. <sup>*b*</sup>The corresponding nitrogen sorption isotherms were shown in Fig. S6. <sup>*c*</sup>This CTF-PTZ-3 sample is the one that was investigated in this work. Also, the reaction conditions were used to synthesize the other two CTFs.



Fig. S6 Nitrogen sorption isotherms for different CTF-PTZ samples under various synthetic conditions.









**Fig. S8** <sup>13</sup>C NMR of PTZ monomer in  $d_6$ -DMSO.



Fig. S9 The comparison for <sup>13</sup>C ssNMR of CTF-PTZ with <sup>13</sup>C NMR of PTZ-CN and PTZ.

The characteristic peaks at 105.96 and 112.53 ppm from PTZ-CN ( $C_k$  and  $C_j$ , they are directly connected with CN groups in PTZ-CN) is completely disappeared in <sup>13</sup>C ssNMR of CTF-PTZ, indicating that almost all of CN groups in PTZ-CN have been polymerized into triazine units in CTF-PTZ. Because there are two peaks at around 116 and 119 ppm in both of PTZ-CN and PTZ ( $C_h$  and  $C_g$ ), therefore, the peak at around 115 ppm in CTF-PTZ should be attributed to the convergent combination of  $C_h$  and  $C_g$  in CTF-TPZ. Since the peak of CN in PTZ-CN is ~118 ppm that is coincidently located at between these two peaks of  $C_h$  and  $C_g$ , thus, it is very likely to ascribe it to CN groups by accident. However, actually, this peak at ~115 ppm in CTF-PTZ is not from CN groups.



**Fig. S11** <sup>13</sup>C NMR of TPA monomer in  $d_6$ -DMSO.



Fig. S12 The comparison for <sup>13</sup>C ssNMR of CTF-TPA with <sup>13</sup>C NMR of TPA-CN and TPA. The characteristic peak at ~106 ppm from TPA-CN (C<sub>j</sub>, they are directly connected with CN groups in TPA-CN) is completely disappeared in <sup>13</sup>C ssNMR of CTF-TPA. And the terminal CN signal at ~118 ppm also vanishes in <sup>13</sup>C ssNMR of CTF-TPA. These results indicated that almost all of CN groups in TPA-CN have been polymerized into triazine units in CTF-TPA.



Fig. S14  $^{13}$ C NMR of TPB monomer in  $d_6$ -DMSO.



Fig. S15 The comparison for <sup>13</sup>C ssNMR of CTF-TPB with <sup>13</sup>C NMR of TPB-CN and TPB. The characteristic peak at ~110 ppm from TPB-CN (*C<sub>j</sub>*, they are directly connected with CN groups in TPB-CN) is completely disappeared in <sup>13</sup>C ssNMR of CTF-TPB. And the terminal CN signal at ~118 ppm also vanishes in <sup>13</sup>C ssNMR of CTF-TPB. These results indicated that almost all of CN groups in TPB-CN have been polymerized into triazine units in CTF-TPB.



**Fig. S16** The comparison for FT-IR spectra of CTFs with their corresponding precursor nitriles. The FT-IR signal intensity of CN in CTFs is quite significantly decreased in comparison to their corresponding precursor nitrile compounds, indicating the high polymerization of CN groups into triazine networks.



Fig. S17 SEM images of CTF-PTZ (a), CTF-TPA (b) and CTF-TPB (c) as well as CTF-PTZ after photocatalysis (d).



Fig. S18 TEM images of CTF-PTZ (a), CTF-TPA (b) and CTF-TPB (c) as well as CTF-PTZ after

photocatalysis (d).



**Fig. S19** PXRD patterns of CTF-PTZ (a), CTF-TPA (b) and CTF-TPB (c). All of them showed two broad peaks at around 16 ° and 23 ° upon amplification, suggesting the existence of partially crystalline structures in the three CTFs.



Fig. S20 TGA curves for CTF-PTZ, CTF-TPA and CTF-TPB under  $N_2$  atmosphere with a heating

rate of 10 °C/min.



Fig. S21 Orbital energy levels (HOMO/LUMO) of basic building units in the three CTFs

calculated at the B3LYP/6-31G(d,p) level.

Fragment	State	Energy	Composition	Contribution
		4.371 eV	HOMO→LUMO	31.9 %
			HOMO-1→LUMO+1	15.7 %
	$\mathbf{S}_1$		HOMO-2→LUMO	9.3 %
			HOMO→LUMO+2	6.4 %
			HOMO-8→LUMO	5.5 %
		4.375 eV	HOMO-2→LUMO+1	16.5 %
			HOMO-4→LUMO+1	12.8 %
			HOMO-1→LUMO	10.6 %
CTF-TPB	c		HOMO-2→LUMO	6.5 %
	$\mathbf{S}_2$		HOMO→LUMO+1	6.2 %
			HOMO-8→LUMO+1	5.6 %
			HOMO-1→LUMO+2	5.4 %
			HOMO-4→LUMO	5.1 %
		4.526 eV	HOMO-18→LUMO+1	24.6 %
	c		HOMO-19→LUMO	23.7 %
	$\mathbf{S}_3$		HOMO-18→LUMO	19.2 %
			HOMO-19→LUMO+1	18.8 %
	$S_1$	3.744 eV	HOMO→LUMO	39.1 %
			HOMO-1→LUMO+1	18.3 %
			HOMO-2→LUMO	18.2 %
			HOMO-1→LUMO+2	10.2 %
	$S_2$	3.744 eV	HOMO→LUMO+1	38.8 %
CTF-TPA			HOMO-2→LUMO+1	18.4 %
			HOMO-1→LUMO	18.3 %
			HOMO-2→LUMO+2	10.1 %
	$S_3$	4.090 eV	HOMO-2→LUMO+1	39.4 %
			HOMO-1→LUMO	39.4 %
			HOMO→LUMO+2	10.8 %
	$\mathbf{S}_1$	3.601 eV	HOMO→LUMO+1	74.0 %
			HOMO→LUMO+2	9.2 %
			HOMO→LUMO	5.8 %
CTF-PT7	$S_2$	3.608 eV	HOMO-1→LUMO	41.3 %
			HOMO-1→LUMO+1	37.8 %
			HOMO-1→LUMO+2	9.9 %
	$\mathbf{S}_3$	3.615 eV	HOMO-2→LUMO	74.2 %
			HOMO-2→LUMO+2	10.5 %

**Table S3** The contribution of MOs for the transition of electronic state calculated by TDDFT/B3LYP/6-31G (d, p) based on the optimized molecular geometries.



Fig. S22 NTOs for the electronic excitation from the ground state to the first excited state ( $S_0 \rightarrow S_1$  transition) of oligomer model in CTF-TPB, with the corresponding contribution from NTO pairs labeled on the arrow.



Fig. S23 NTOs for the electronic excitation from the ground state to the first excited state ( $S_0 \rightarrow S_1$  transition) of oligomer model in CTF-TPA, with the corresponding contribution from NTO pairs labeled on the arrow.



Fig. S24 NTOs for the electronic excitation from the ground state to the first excited state ( $S_0 \rightarrow S_1$  transition) of oligomer model in CTF-PTZ, with the corresponding contribution from NTO pairs labeled on the arrow.



Fig. S25 High-resolution valence band ultraviolet photoelectron spectra (UPS) of CTF-PTZ (a), CTF-TPA (b) and CTF-TPB (c).



**Fig. S26** Chemical structure of control polymer without D-A structure (top) and the PL lifetime decay trace for the control polymer (bottom, inset: its PL spectra measured in the solid state). The control polymer was synthesized by Suzuki-Miyaura polycondensation reaction, according to the previous literation reported procedure.<sup>S14</sup>



Fig. S27 <sup>1</sup>H NMR spectra of PTZ monomer, PTZ + PhSMe after photocatalysis (2 mg PTZ and 0.1 mmol PhSMe in 1 mL CD<sub>3</sub>CN, blue LEDs, 2 h at room temperature in air), sulfide PhSMe and sulfoxide PhSOMe in CD<sub>3</sub>CN. No sulfoxide PhSOMe can be observed in the reaction mixture of PTZ and PhSMe after photocatalysis. This result revealed that the donor-acceptor structure in CTF-PTZ played a crucial role in the photocatalytic aerobic oxidation of sulfides.



**Fig. S28** EPR spectra of a mixture of CTF-PTZ in CH<sub>3</sub>CN with TEMP upon light irradiation and in the dark (left) as well as DMPO upon light irradiation and in the dark (right).



Fig. S29 Investigation on reusability of CTF-PTZ for photocatalytic aerobic oxidation reaction of methyl phenyl sulfide.

Entry	Photocatalyst	Reaction conditions	Atm. <sup>a</sup>	Time & Yield	TOF [mmol·g·h <sup>-1</sup> ] <sup>b</sup>	Ref.
1	CTF-PTZ (2 mg)	sulfide (0.1 mmol), CH <sub>3</sub> CN (1 mL), blue LEDs	air	2 h, 93%	23	This study
2	Degussa P25 TiO <sub>2</sub> (40 mg)	sulfide (0.3 mmol) + TEA (0.3 mmol), CH <sub>3</sub> OH (5 mL), 300 W Xe lamp	1 atm O2	10 h, 84%	0.63	S15
3	ARS-TiO <sub>2</sub> (9.6 mg)	sulfide (0.3 mmol) + TEMPO (0.006 mmol), CH <sub>3</sub> OH (5 mL), 300 W Xe lamp	1 atm O2	3 h, 84%	8.8	S16
4	A2B2-Por-COF (5 mg)	sulfide (0.2 mmol), CH <sub>3</sub> CN (2 mL) + CH <sub>3</sub> OH (0.8 mL), 300 W Xe lamp	1 atm O <sub>2</sub>	1.16 h, 96%	33	S17
5	CF-HCP (5 mg)	sulfide (0.2 mmol), CH <sub>3</sub> CN (2 mL) + CH <sub>3</sub> OH (0.8 mL), green LEDs	1 atm O <sub>2</sub>	6 h, 99%	11	S18
6	MOF Zn-CP (5 mg)	sulfide (0.16 mmol), CHCl <sub>3</sub> /CH <sub>3</sub> OH (4:1, 1.25 mL), 300 W Xe lamp	1 atm O2	3.5 h, 99%	9	S19
7	MOF Zr <sub>12</sub> -BNC (6 mg)	sulfide (0.3 mmol), CH <sub>3</sub> OH (4 mL), blue LEDs	air	10 h, 100%	5	S20
8	MOF NNU-45 (4 mg)	sulfide (0.4 mmol) + H <sub>2</sub> O <sub>2</sub> (1 mmol), CH <sub>3</sub> OH + CHCl <sub>3</sub> (0.4 + 1.6 mL), 300 W Xe lamp	air	4 h, 99%	25	S21
9	C60@PCN-222 (20 mg)	sulfide (0.2 mmol), CH <sub>3</sub> OH (5 mL), LED lamp	air	3 h, 99%	3.3	S22
10	CdS/C <sub>3</sub> N <sub>4</sub> (5 mg)	sulfide (0.3 mmol), CH <sub>3</sub> OH (3 mL), white LEDs	1 atm O <sub>2</sub>	6 h, 62%	6.2	S23
11	BN@TTCOP-1 (10 mg)	sulfide (0.2 mmol), CH <sub>3</sub> CN (3 mL), white LEDs	1 atm O <sub>2</sub>	8 h, 64%	1.6	S24

Table S4 The comparison of different representative heterogeneous photocatalysts for selective

# oxidation of sulfides.

<sup>*a*</sup>Atmosphere, <sup>*b*</sup>The turnover frequency (TOF) values were calculated as the moles of products divided by the mass of photocatalyst and the reaction time.



Fig. S30 Solid-state <sup>13</sup>C CP/MAS NMR of CTF-PTZ and recycled CTF-PTZ after photocatalysis.



Fig. S31 FT-IR spectra for as-synthesized and after-photocatalytic CTF-PTZ.



Fig. S32 Nitrogen sorption isotherms for as-synthesized and after-photocatalytic CTF-PTZ.



Scheme S3 Selective photooxidation of HD simulant CEES into less toxic CEESO catalyzed by CTF-PTZ under blue-LEDs irradiation in an open air atmosphere; and <sup>1</sup>H NMR spectra after photocatalysis with 15 min irradiation.

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