

Electronic Supplementary Information

Zirconium metal–organic framework photocatalysis with TEMPO for blue light-powered aerobic sulfoxidation

Bing Zeng, Yuexin Wang, Kanghui Xiong, Keke Zhang, Siyu Zhang and Xianjun Lang*

*Hubei Key Lab on Organic and Polymeric Optoelectronic Materials, College of
Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China.*

*To whom correspondence should be addressed (Prof. X. J. Lang). E-mail address:

xianjunlang@whu.edu.cn.

Contents

1.1 Materials and solvents.....	S4
1.2 The synthesis of NU-1003	S4
1.3. General procedure for selective aerobic oxidation of sulfides.....	S5
1.4 The recycling experiment	S5
2.1 Characterizations.....	S5
2.2 Conversion of sulfides and selectivity of the targeted sulfoxides.....	S7
2.3 Electrochemical measurements.....	S7
3. Results.....	S8
Fig. S1. PXRD pattern of the PTNA ligand.....	S8
Fig. S2. TGA curve of NU-1003.	S8
Fig. S3. The Mott–Schottky plots (a) and band structure (b) of NU-1003.....	S9
Table S1. The effect of different solvents on oxidation of methyl phenyl sulfide to sulfoxide by NU-1003 and TEMPO. ^a	S9
Fig. S4. The aerobic oxidation of methyl phenyl sulfide by NU-1003 with TEMPO under different wavelength LED irradiation. Standard reaction condition: NU-1003 photocatalyst (5 mg), methyl phenyl sulfide (0.3 mmol), TEMPO (12 μmol, 4 mol%), LEDs, solvent (CF ₃ CH ₂ OH, 1 mL), air (1 atm), 1 h.....	S10
Fig. S5. The light-emitting spectrum of the blue LED.	S10
Fig. S6. The recycling of NU-1003 for the blue light-powered aerobic oxidation of methyl phenyl sulfide. Reaction condition: NU-1003 photocatalyst (5 mg), methyl phenyl sulfide (0.3 mmol), TEMPO (12 μmol, 4 mol%), blue LEDs, solvent	

(CF ₃ CH ₂ OH, 1 mL), air (1 atm), 1 h.....	S11
Fig. S7. The SEM image of NU-1003 after four cycles.	S11
Fig. S8. The FTIR spectra of NU-1003 after four cycles.	S12
Table S2. Blue light-powered aerobic sulfoxidation by NU-1003 photocatalyst with TEMPO. ^a	S13
References.....	S14

1.1 Materials and solvents

All chemicals were utilized as received without further purification. $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (98%) was purchased from Adamas. Furthermore, the PTNA ligand (97%) was supplied by Bidepharm. Benzoic acid (97%) was provided by TCI. Anhydrous DMF (>99.9%) and TEMPO (98%) were procured from INNOCHEM. Trifluoroacetic acid (TFA, 99.5%) was provided by ACROS. Additional reagents were supplied by a number of commercial vendors, such as Sigma-Aldrich, Adamas, J&K Scientific, Alfa Aesar.

1.2 The synthesis of NU-1003

NU-1003 was synthesized by slightly modifying the procedure reported.¹ A 35 mL Pyrex tube was charged with $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (40 mg, 0.12 mmol), benzoic acid (0.50 g, 4.10 mmol), and 10 mL of anhydrous DMF. The solution was kept in an oven at 80 °C for 1 h. After that, the tube was allowed to cool naturally for 10 min, and flowing water was subsequently used to arrive at room temperature. Next, the PTNA ligand (16 mg, 0.02 mmol) and 10 mL of DMF were added to the Pyrex tube to form a clear solution. After adding 200 μL of TFA (5.89 mmol), the mixture was subjected to a 10 min sonication. The reaction mixture was then heated at 120 °C for 3 h, during which time a light yellow suspension emerged. The suspension was centrifuged for 5 min at 10000 rpm when cooling to room temperature. Following a rinse with fresh DMF (3 \times 30 mL), the precipitate was left to soak overnight at room temperature in 40 mL of fresh DMF mixed with 40 μL of TFA. The solid was rinsed with DMF (3 \times

30 mL) and ethanol (3×30 mL). Finally, the light-yellow powders were dried at 70 °C in a dynamic vacuum to attain NU-1003.

1.3. General procedure for selective aerobic oxidation of sulfides

Generally, 5 mg of NU-1003 photocatalyst and 0.3 mmol of sulfide substrate were uniformly dispersed in 1 mL of $\text{CF}_3\text{CH}_2\text{OH}$ in a 10 mL Pyrex reaction vessel equipped with a pierced rubber stopper linked to the system with the outer atmosphere. The reaction vessel was stirred at 1500 rpm and powered with $3 \text{ W} \times 4$ blue light-emitting diodes (LEDs). Before and after irradiation, the suspension was taken out and centrifuged at 10000 rpm to remove the photocatalyst. The supernatant was quantitatively analyzed using a gas chromatograph (GC) with a flame ionization detector (FID) to calculate the conversion and selectivity.

1.4 The recycling experiment

After irradiation, the fresh NU-1003 underwent centrifugation from the reaction mixture, twice rinsing with CH_3OH and subsequent centrifugation to remove residue over NU-1003. The reused photocatalyst was directly added to the subsequent runs without additional treatment. The reaction was carried out under blue LED irradiation at room temperature with magnetic stirring.

2.1 Characterizations

Powder X-ray diffraction (PXRD) measurement was implemented by adopting a Rigaku/Miniflex 600 diffractometer with a filtered Cu K_α radiation, and the result was

recorded from 2 to 20° at room temperature. The Fourier transform infrared (FTIR) spectra were carried out by NICOLET 5700 FTIR Spectrometer with Continuum IR Microscope ranging from 400–4000 cm^{-1} . The thermogravimetric analysis (TGA) spectrum was recorded on an SDT Q600 thermogravimeter from 30 to 800 °C at a rate of 10 °C min^{-1} under an N_2 atmosphere. The N_2 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 non-local density functional theory (NLDFT) model, the material was degassed in vacuum ($< 1 \times 10^{-5}$ bar) at 120 °C for 3 h. Scanning electron microscopy (SEM) was measured on a Zeiss Merlin Compact running at the acceleration voltage between 0.1 and 20 kV. High-resolution transmission electron microscopy (HRTEM) images of NU-1003 were recorded on a JEM-200 operating at 200 kV. The UV–visible spectra were recorded on a Shimadzu UV-3600 UV-vis spectrophotometer with a diffuse reflectance measurement accessory. The electron paramagnetic resonance (EPR) spectra were collected on an EPR spectrometer (JES-FA300, JEOL, Japan).

The targeted product sulfoxides and remaining products sulfone were confirmed by the retention time comparison 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 He as the carrier gas.

2.2 Conversion of sulfides and selectivity of the targeted sulfoxides

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

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

where C_0 is the initial concentration of sulfides, and C_S and C_p are the concentrations of sulfides and sulfoxides at a certain time during the reaction.

2.3 Electrochemical measurements

Electrochemical measurements were executed on a Metrohm Autolab PGSTAT302N in a three-electrode electrochemical cell equipped with an electrochemical station. The working electrodes were prepared as follows: 6 mg of catalyst was dispersed in 3.0 mL absolute ethanol, and 50 μL Nafion mixture solution, which was ultrasonically dispersed for 30 min, and then 60 μL of mixture solution was dropped onto the ITO with $\pi \times (0.2)^2 \text{ cm}^2$ illuminated area and dried at room temperature, and the samples were dried under infrared irradiation. With 0.1 M Na_2SO_4 aqueous solution or 0.1 M NH_4PF_6 acetonitrile solution supplied as the electrolyte, the Ag/AgCl electrode and platinum wire were the reference and counter electrodes, respectively. Meanwhile, the blue LEDs (Shenzhen Ouying Lighting Science and Technology Co., Ltd.) placed 2 cm away from the photoelectrochemical cell as the light source.

3. Results

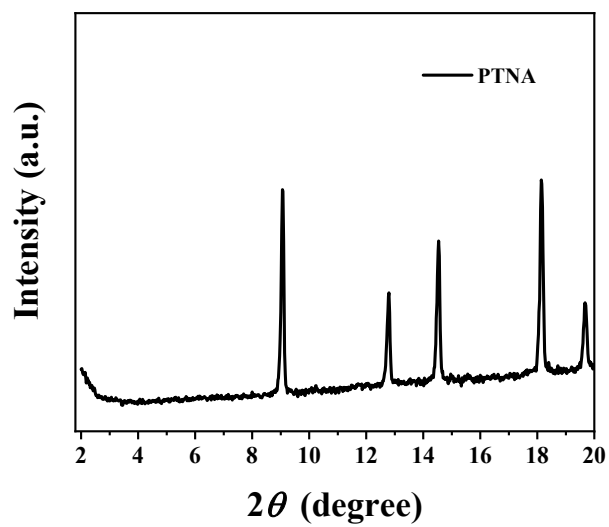


Fig. S1. PXRD pattern of the PTNA ligand.

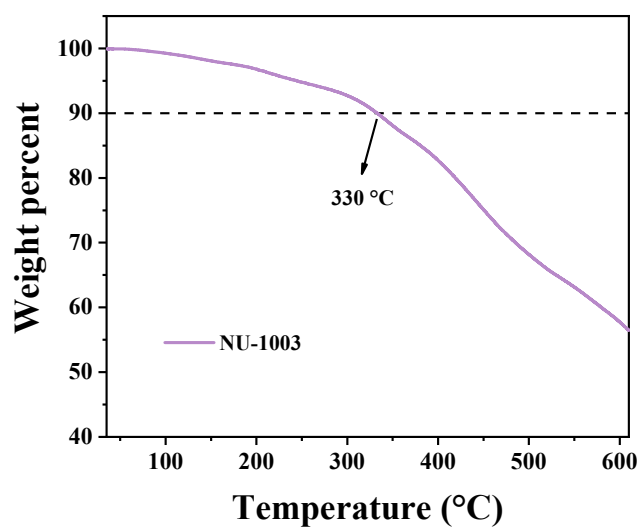


Fig. S2. TGA curve of NU-1003.

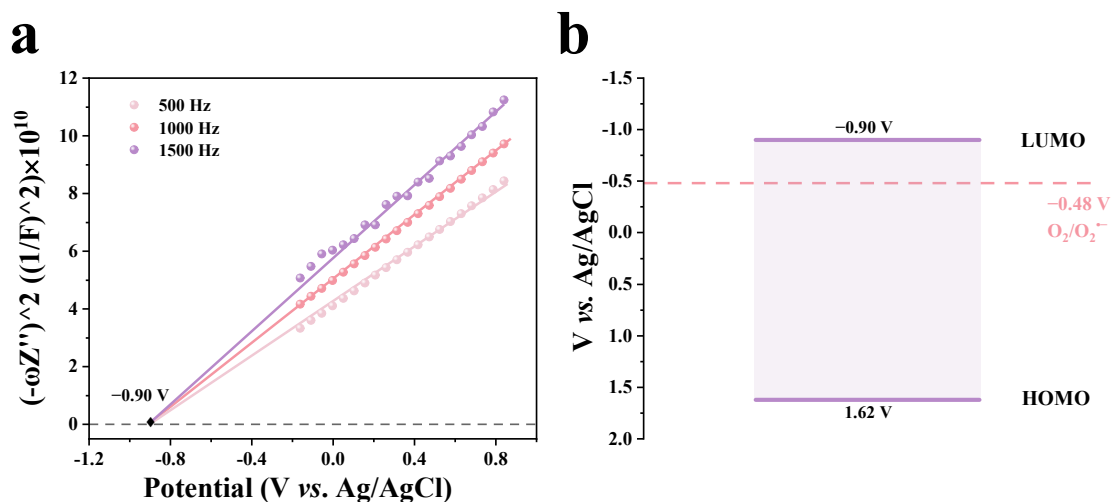
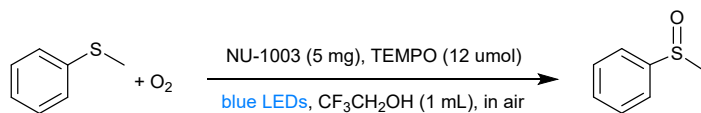


Fig. S3. The Mott–Schottky plots (a) and band structure (b) of NU-1003.

Table S1. The effect of different solvents on oxidation of methyl phenyl sulfide to sulfoxide by NU-1003 and TEMPO.^a



Entry	Solvents	Conv. (%)	Sel. (%)
1	CF ₃ CH ₂ OH	91	97
2	CH ₃ OH	86	86
3	CH ₃ CH ₂ OH	67	89
4	CH ₃ CN	3	81

^a Reaction conditions: NU-1003 (5 mg), methyl phenyl sulfide (0.3 mmol), TEMPO (12 μmol, 4 mol%), solvent (1 mL), blue LEDs, air (1 atm), 1 h.

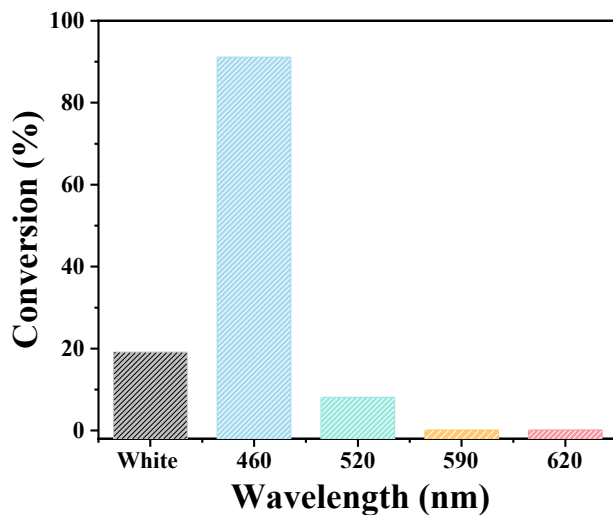


Fig. S4. The aerobic oxidation of methyl phenyl sulfide by NU-1003 with TEMPO under different wavelength LED irradiation. Standard reaction condition: NU-1003 photocatalyst (5 mg), methyl phenyl sulfide (0.3 mmol), TEMPO (12 μ mol, 4 mol%), LEDs, solvent ($\text{CF}_3\text{CH}_2\text{OH}$, 1 mL), air (1 atm), 1 h.

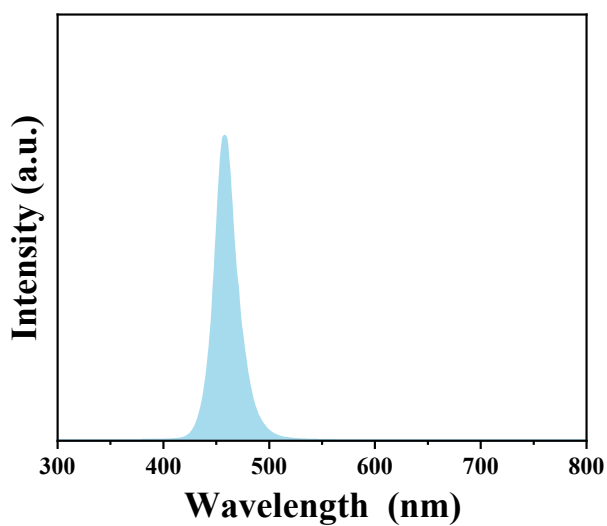


Fig. S5. The light-emitting spectrum of the blue LED.

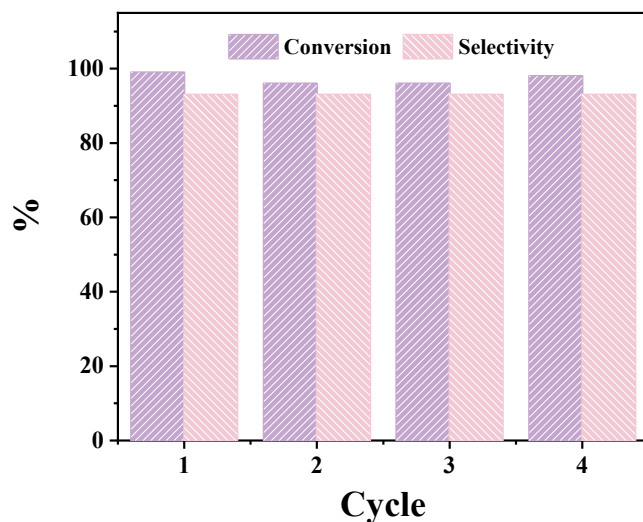


Fig. S6. The recycling of NU-1003 for the blue light-powered aerobic oxidation of methyl phenyl sulfide. Reaction condition: NU-1003 photocatalyst (5 mg), methyl phenyl sulfide (0.3 mmol), TEMPO (12 μmol , 4 mol%), blue LEDs, solvent ($\text{CF}_3\text{CH}_2\text{OH}$, 1 mL), air (1 atm), 1 h.



Fig. S7. The SEM image of NU-1003 after four cycles.

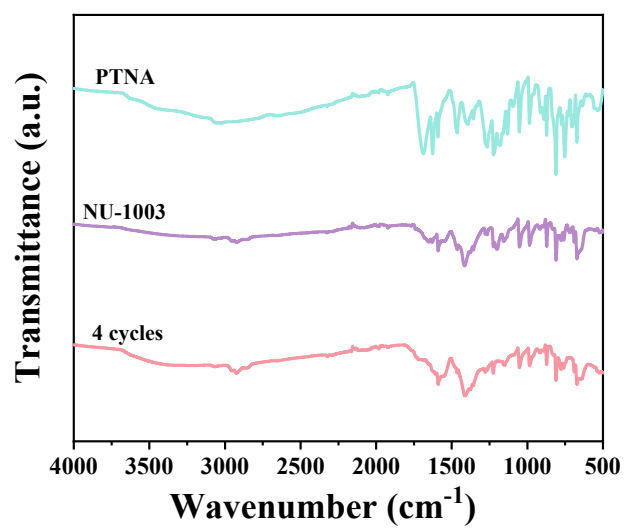
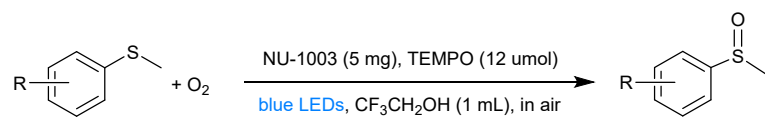
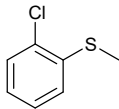
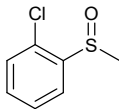
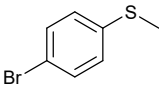
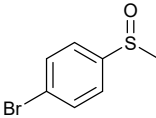
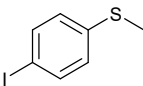
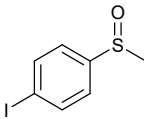
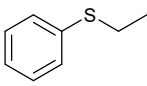
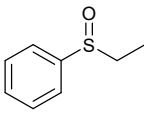
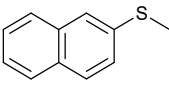
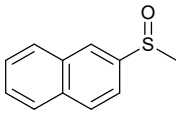

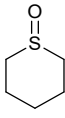


Fig. S8. The FTIR spectra of NU-1003 after four cycles.

Table S2. Blue light-powered aerobic sulfoxidation by NU-1003 photocatalyst with TEMPO.^a



Entry	Substrate	Product	<i>t</i> (h)	Conv. (%) ^b	Sel. (%) ^b
1			1.0	91	97
2			0.8	90	97
3			0.8	97	97
4			1.5	75	97
5			1.5	66	100
6			1.3	92	95
7			1.3	81	96
8			1.8	86	91

9			1.9	55	100
10			1.3	92	93
11			1.3	97	88
12			1.2	83	95
13			2.3	30	100
14			0.8	84	100

^a Reaction conditions: NU-1003 photocatalyst (5 mg), sulfide (0.3 mmol), TEMPO (12 μ mol, 4 mol%), blue LEDs, solvent ($\text{CF}_3\text{CH}_2\text{OH}$, 1 mL), air (1 atm).

^b Determined by GC-FID using bromobenzene as the internal standard, conversion of the substrate, and selectivity of sulfoxide.

References

1. P. Li, S. Y. Moon, M. A. Guelta, L. Lin, D. A. Gómez-Gualdrón, R. Q. Snurr, S. P. Harvey, J. T. Hupp and O. K. Farha, *ACS Nano*, 2016, **10**, 9174–9182.