

## *Supporting Information*

### **Blue-Light-Driven Aerobic Oxidation via Superoxide Radical-Generating Zinc(II)-Organic Framework Photocatalyst**

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## Experimental Section

### Materials and Measurements.

All reagents and solvents are commercially available (Beijing innoChem Science & Technology Co. Ltd.), and they were further dried by the vacuum rotary evaporator to remove all traces of water and then stored in the air-filled glovebox. The 20 mL Schlenk tube charged with a magnetic stirrer, which was used as the reactor in the thioether oxidation reaction. The light was provided by a 30 W blue LED light.

The chemical structures of the products were confirmed by comparison with standard chemicals and GC-MS (Agilent Technologies, GC 7890B, MS 5977A) data. GC equipped with a FID detector (Agilent Technologies, GC 7890 B) and a HP-5 5% phenyl methyl siloxane column (30m × 0.32mm × 0.5 μm), which was used for the quantifiable measure of (methylsulfinyl)benzene. The transmission electron microscopy (TEM) images were measured on a Thermo Scientific Talos F200S G2 microscope with an acceleration voltage of 200 kV. A Varian Cary 500 UV-Vis spectrophotometer was used to record the UV-Vis diffuse reflectance spectra (DRS) of various solid samples. The photoelectrochemical characterization was performed on a Metrohm-Autolab AUT302N Electrochemical workstation. Photocurrent measurements were carried out in a typical three-electrode configuration with an Ag/AgCl electrode, a coiled Pt wire as the reference and counter electrode, respectively. X-ray diffraction (XRD) studies of catalyst were carried out with a Bruker D8 Advance instrument. The electron paramagnetic resonance (EPR) experiments were carried out on Bruker A300 instrument operating in the X-band at room temperature.

**Recycling method for Zn-1D:** Upon completion of the reaction, centrifuge the reaction mixture to sediment the Zn-1D catalyst. Separate and collect the supernatant for product analysis and characterization. Wash the remaining solid catalyst in the centrifuge tube by adding 2 mL of anhydrous methanol, agitating to rinse, centrifuging again, and discarding the supernatant. Repeat this washing procedure 4–5 times to ensure thorough removal of surface-adsorbed impurities. After washing, place the centrifuge tube in an oven at 60 °C for 6 hours to dry. Finally, add the recovered and dried Zn-1D solid directly to a fresh reaction mixture to initiate the next catalytic cycle experiment.

### Single-crystal X-ray crystallography.

Diffraction data for all complexes were measured on a Bruker SMART CCD diffractometer (Mo K $\alpha$  radiation and  $\lambda = 0.71073 \text{ \AA}$ ) in  $\Phi$  and  $\omega$  scan modes. All structures were solved by direct methods, followed by difference Fourier syntheses, and then refined by full-matrix least-squares techniques on  $F^2$  using SHELXL.<sup>[1]</sup> All other non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in the calculated position and refined in the isotropic direction using a

riding model. Table S1 summarizes X-ray crystallographic data and refinement details for the complexes. The CCDC reference numbers are 2496891 for **Zn-1D**.

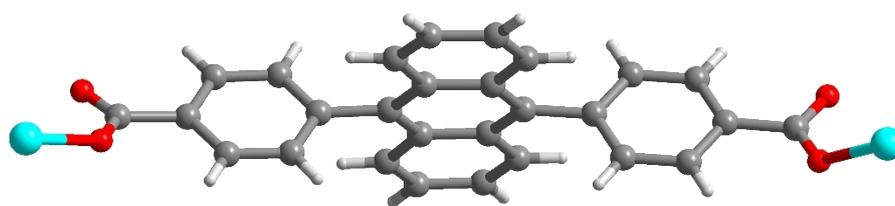
**Table S1.** Crystallographic data of the complex **Zn-1D**.

Complex	Zn-1D
Formula	C <sub>62</sub> H <sub>48</sub> ZnN <sub>2</sub> O <sub>10</sub>
Formula weight	1046.39
<i>T</i> (K)	293 (2)
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	9.0458 (3)
<i>b</i> (Å)	11.4454 (3)
<i>c</i> (Å)	12.9865 (4)
<i>α</i> (°)	72.811 (2)
<i>β</i> (°)	77.128 (2)
<i>γ</i> (°)	86.718 (2)
<i>V</i> (Å <sup>3</sup> )	1252.14 (7)
<i>Z</i>	1
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.388
<i>μ</i> (mm <sup>-1</sup> )	1.220
Reflns coll.	13810
Unique reflns	4823
<i>R</i> <sub>int</sub>	0.0620
<sup>a</sup> <i>R</i> <sub>1</sub> [ <i>I</i> ≥ 2σ( <i>I</i> )]	0.0752
<sup>b</sup> <i>wR</i> <sub>2</sub> (all data)	0.2253
GOF	1.063

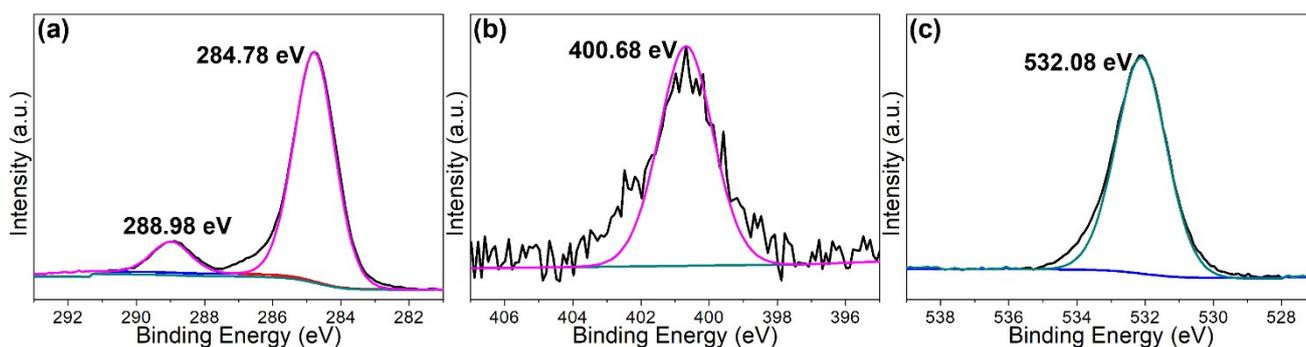
$$^aR_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$$

**Table S2.** Selected bond lengths (Å) and angles (°) of complex **Zn-1D**.

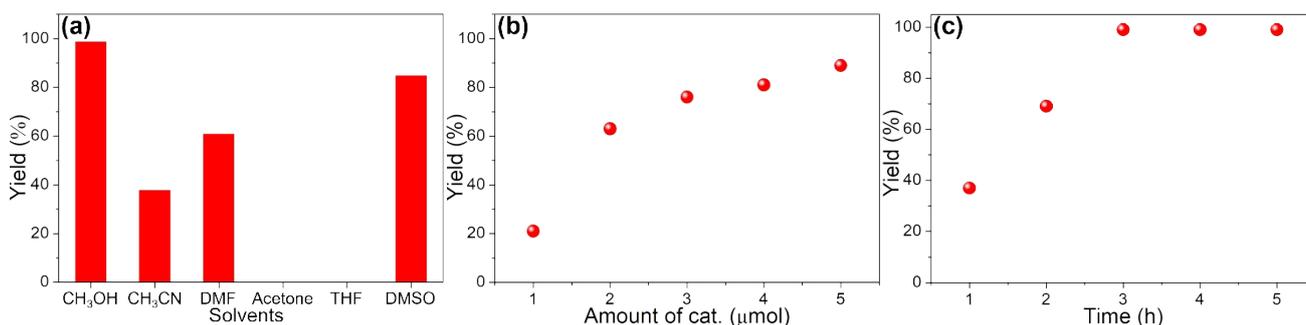
Bond lengths (Å)					
Zn1—O1	2.143 (2)	Zn1—O4 <sup>ii</sup>	2.182 (3)	Zn1—O5	2.172 (3)
Bond angles (°)					
O1 <sup>i</sup> —Zn1—O1	180.0	O1—Zn1—O5 <sup>i</sup>	86.98 (11)	O5—Zn1—O4 <sup>ii</sup>	93.79 (11)
O1—Zn1—O4 <sup>ii</sup>	89.83 (10)	O1—Zn1—O5	93.02 (11)	O5—Zn1—O4 <sup>iii</sup>	86.21 (11)
O1 <sup>i</sup> —Zn1—O4 <sup>ii</sup>	90.17 (10)				
Symmetry codes: (i) - <i>x</i> , - <i>y</i> +1, - <i>z</i> ; (ii) - <i>x</i> +1, - <i>y</i> , - <i>z</i> +1; (iii) <i>x</i> -1, <i>y</i> +1, <i>z</i> -1; (iv) <i>x</i> +1, <i>y</i> -1, <i>z</i> +1.					



**Figure S1.** The coordinated mode of HL1<sup>-</sup> ligand for Zn-1D.



**Figure S2.** XPS spectra of C 1s (a), N 1s (b), O 1s (c).



**Figure S3.** (a) Yields of (methylsulfinyl)benzene in different solvents for Zn-1D; (b) the influence of photocatalyst amounts and (c) irradiation times of Zn-1D on the yield of (methylsulfinyl)benzene.

**Table S3.** The conversion of sulfide oxidation in recent references.

Entry	Photocatalyst	time (h)	Conversion (%)	Ref.
1	Zr-MOF	2.5	98	2
2	UiO-67- Ru(bpy) <sub>3</sub> /TiO <sub>2</sub> film	/	99	3
3	In-MOF	4	99	4
4	MP8@MIL-101(Cr)-NH <sub>2</sub>	2	99	5
5	Zr <sub>12</sub> -NBC	10	99	6
6	NPF-500-H <sub>2</sub> TCPP	1	99	7

7	Mo-MFU-4l	0.17	99	8
8	UiO-66(Ce)	14	99	9
9	Co <sup>II</sup> TPP- Br <sub>4</sub> @UiO-66	0.17	99	10
10	Zn-MOF	1.5	99	11
11	Zr-BTDB	4	95	12
12	Ir-Zr-MOF	7	99	13
13	Mn-MOF	2	99	14
14	Zn-MOF	6	99	15
15	Zn-1D	3	99	This work

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GC-MS data of products:

