

## Supporting Information

### 2D Bi-based porphyrin metal organic frameworks photocatalysis for white light-driven selective oxidation of sulfides

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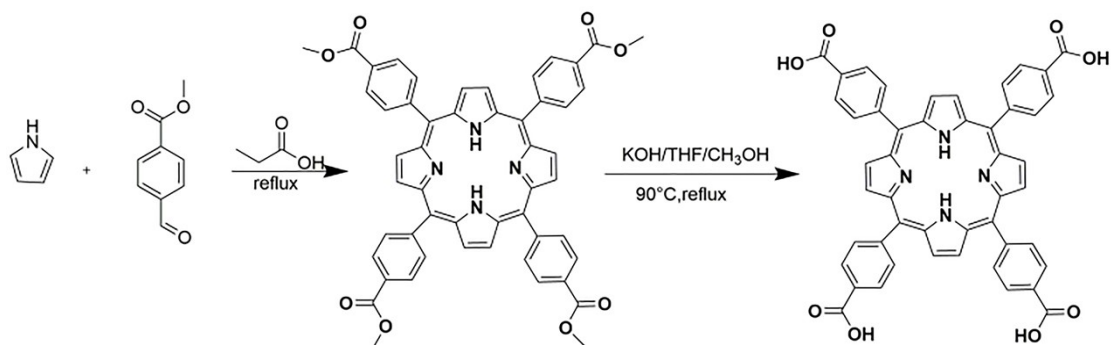
#### 1. Materials and Methods.

<sup>1</sup>H NMR (600 Hz), <sup>13</sup>C NMR (150 Hz) and were recorded in CDCl<sub>3</sub>/DMSO using 0.03% TMS as internal standard. Data for <sup>1</sup>H NMR are reported as follows: chemical shift (ppm, scale), multiplicity, coupling constant (Hz) and integration. Data for <sup>13</sup>C NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). All the reactions were conducted in oven-dried schlenk tubes. All solvents were obtained from commercial suppliers. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh). Thermogravimetric analysis (TGA) data were obtained on a TGA-8000. Thermogravimetric analyzer with a heating rate of 10°C min<sup>-1</sup> under air atmosphere. The UV-vis absorption spectra were recorded on Agilent UV-2450

spectrophotometer. The IR absorption spectra were recorded on Thermo Fisher IR spectrophotometer. The MOFs sample were observed by using a SU8020 Scanning Electron Microscope (SEM, Hitachi, Japan) and X-ray Photoelectron Spectroscopy (XPS, Thermo, America). The rotating target X-ray diffractometer were recorded on a rigaku D diffractometer. The fluorescence emission spectrum were recorded on HITACHI F7000. The conversions of the reactants and the yields of products were measured by Shimadzu QP2100 plus gas chromatograph spectrometry (GC). The Catalyst loading were measured by NEPTUNE PlusMC-ICP-MS. Single-crystal X-Ray data were obtained by X - ray single crystal diffractometer (Bruker D8 Venture). Reactive oxygen species by Paramagnetic resonance spectrometer (Bruker EMXplus). Electrochemical Workstation data were obtained on KM1-CS1006 with glassy carbon electrode as working electrode and calomel electrode as reference electrode.

## **2. Synthesis of Ligand H<sub>2</sub>TCPP.**

The commercial chemicals are purchased unless mentioned otherwise. Pyrrole, 4-carboxybenzaldehyde, were purchased from Energy Chemical Corporation. Propionic acid was purchased from Ark Pharm, Inc. The syntheses of these ligands have been previously described<sup>1</sup>. Typically, we obtained these ligands by four steps as follows:



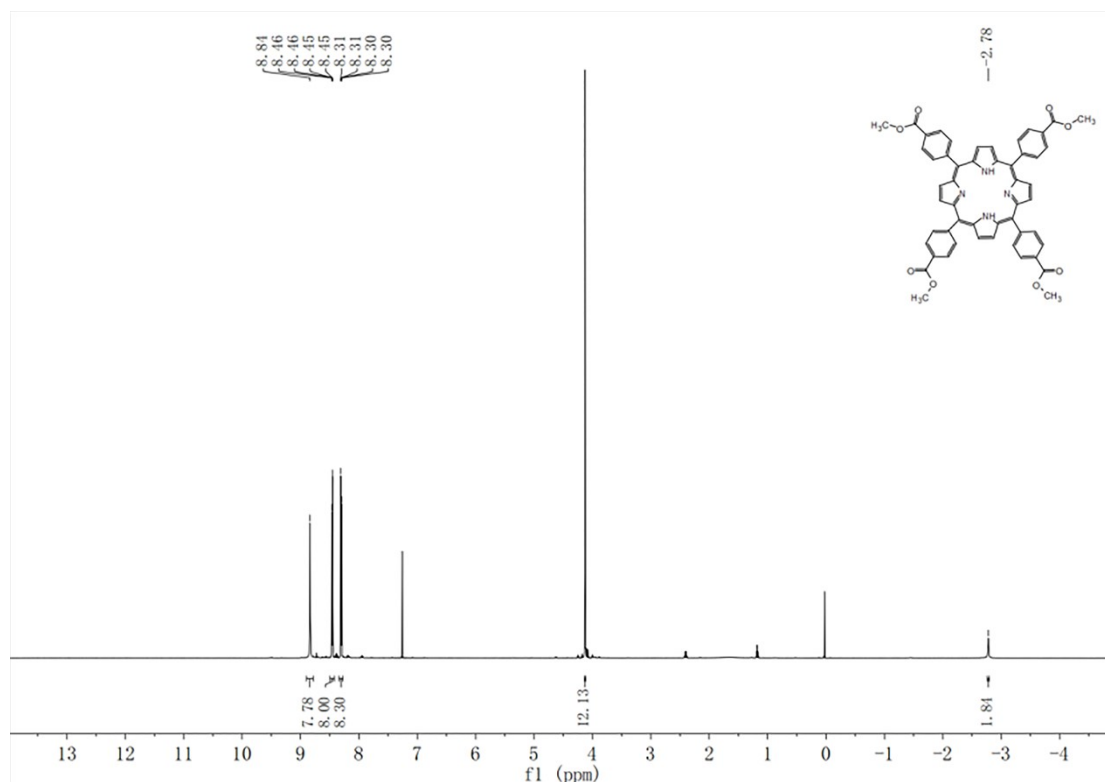
**(1) 5,10,15,20-Tetrakis (4-methoxycarbonylphenyl) porphyrin (TPPCOOMe).**

In a 500-mL three necked flask, methyl *p*-formylbenzoate (7.3 g, 0.044 mol) was dissolved in propionic acid (100 mL). Pyrrole was then added dropwise (3 g, 0.045 mol) and the solution was refluxed for 12 h. After the reaction mixture was cooled down to room temperature, precipitates were collected by suction-filtration and washed with methanol, ethyl acetate and THF. After dried in the oven, purple solid was obtained as pure product. (2.3 g, 2.71 mmol, 22% yield). MALDI-TOF HRMS for C<sub>52</sub>H<sub>38</sub>N<sub>4</sub>O<sub>8</sub> [M]<sup>+</sup> calcd 846.2723, found 846.2767. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 8.84 (s, 8H), 8.46 (d, *J* = 8.2 Hz, 8H), 8.31 (d, *J* = 8.1 Hz, 8H), 4.13 (s, 12H), -2.78 (s, 2H). FTIR: ν = 1719 (s), 1606 (s), 1435 (m), 1399 (w), 1309 (w), 1272 (s), 1215 (w), 1191 (w), 1089 (s), 1018 (m), 959 (m), 801 (s), 735 (s), 704 (s) cm<sup>-1</sup>.

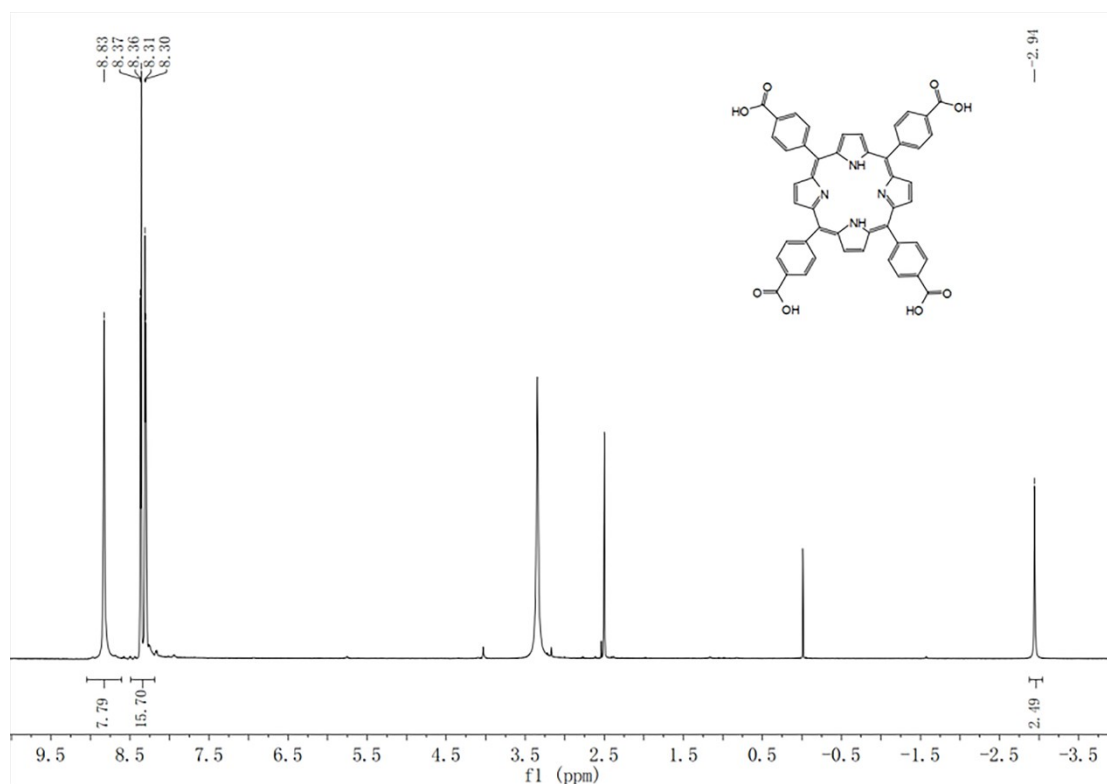
**(2) Tetrakis(4-carboxyphenyl)porphyrin (H<sub>2</sub>TCPP)**

The obtained TPPCOOMe (4.2g,5mmol)was stirred in THF (80 mL) and MeOH (80 mL) mixed solvent, and was added to an 80 mL aqueous

solution of KOH (0.24 mol, 13.5 g). Then the mixture was refluxed for 24 h. After reaction, the mixture was cooled to room temperature. Before evaporating THF and MeOH, the mixture was filtered by a filter paper (Grade 2, 8  $\mu\text{m}$ ). Additional water was added into the resulting water phase. The water phase solution was filtered by the filter paper again. Then the solution was acidified with 1 M HCl until pH 2. The precipitate was washed with water, collected by centrifugation, and dried under vacuum by using a Schlenk line (4.7 mmol, 3.7 g, yield 96%).  $^1\text{H}$  NMR (600MHz, DMSO- $d_6$ ): 8.81(s, 8H), 8.3 (ddd, 16H, J=20 Hz), -2.94 (s, 2H).



**Figure S1.**  $^1\text{H}$ -NMR spectrum for TPPCOOMe.



**Figure S2.**  $^1\text{H}$ -NMR spectrum for TCPP.

### (3) Synthesis of the PCN-224.

$\text{ZrCl}_4$  (160 mg), TCPP(30 mg), and 1200 mg of benzoic acid in 6 mL of DMF were ultrasonically dissolved in a 10 ml autoclave. The mixture was heated in  $120^\circ\text{C}$  oven for 24 h. After cooling down to room temperature, cubic dark purple crystals were harvested by filtration (18 mg, 45% yield)

### 3. SINGLE CRYSTAL X RAY DIFFRACTION

Single-crystal X-Ray data were obtained in a Bruker four-circle kappa diffractometer equipped with a Mo INCOATED microsource (Mo  $K\alpha$  radiation,  $\lambda = 0.71073$ ). The main experimental data of single crystal are in **Table S1**.

**Table S1** Crystal data and structure refinement for Bi-PMOFs.

Identification code	Bi-PMOFs
Empirical formula	C <sub>48</sub> H <sub>28</sub> BiN <sub>4</sub> O <sub>9</sub>
Formula weight	1013.72
Color/Shape	Purple Block
Temperature/K	296.15
Crystal system	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a/Å	17.300(3)
b/Å	17.400
c/Å	18.975(3)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	5712.0(14)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.179
μ/mm <sup>-1</sup>	3.133
F(000)	1996.0
Crystal size/mm <sup>3</sup>	0.5 × 0.4 × 0.3
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.176 to 54.476
Index ranges	-17 ≤ h ≤ 22, -22 ≤ k ≤ 22, -23 ≤ l ≤
Reflections collected	31822
Independent reflections	11196 [R <sub>int</sub> = 0.0842, R <sub>sigma</sub> =
Data/restraints/parameters	11196/341/561
Goodness-of-fit on F <sup>2</sup>	0.719
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0474, wR <sub>2</sub> = 0.0899
Final R indexes [all data]	R <sub>1</sub> = 0.0786, wR <sub>2</sub> = 0.0964
Largest diff. peak/hole / e Å <sup>-3</sup>	1.21/-0.70
Flack parameter	0.196(11)

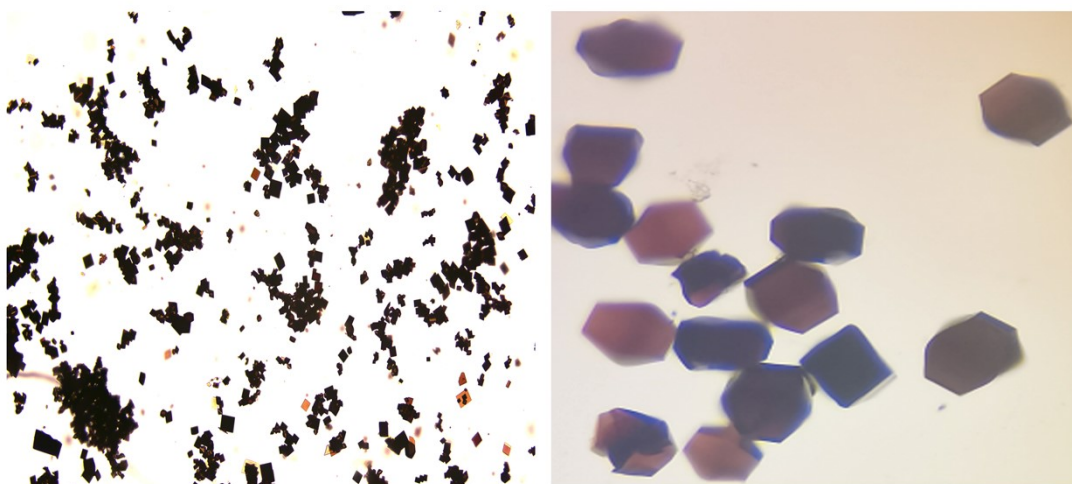


Figure. S3 Optical microscope Image of single crystalline Bi-PMOFs.

#### 4. Additional Characterizations.

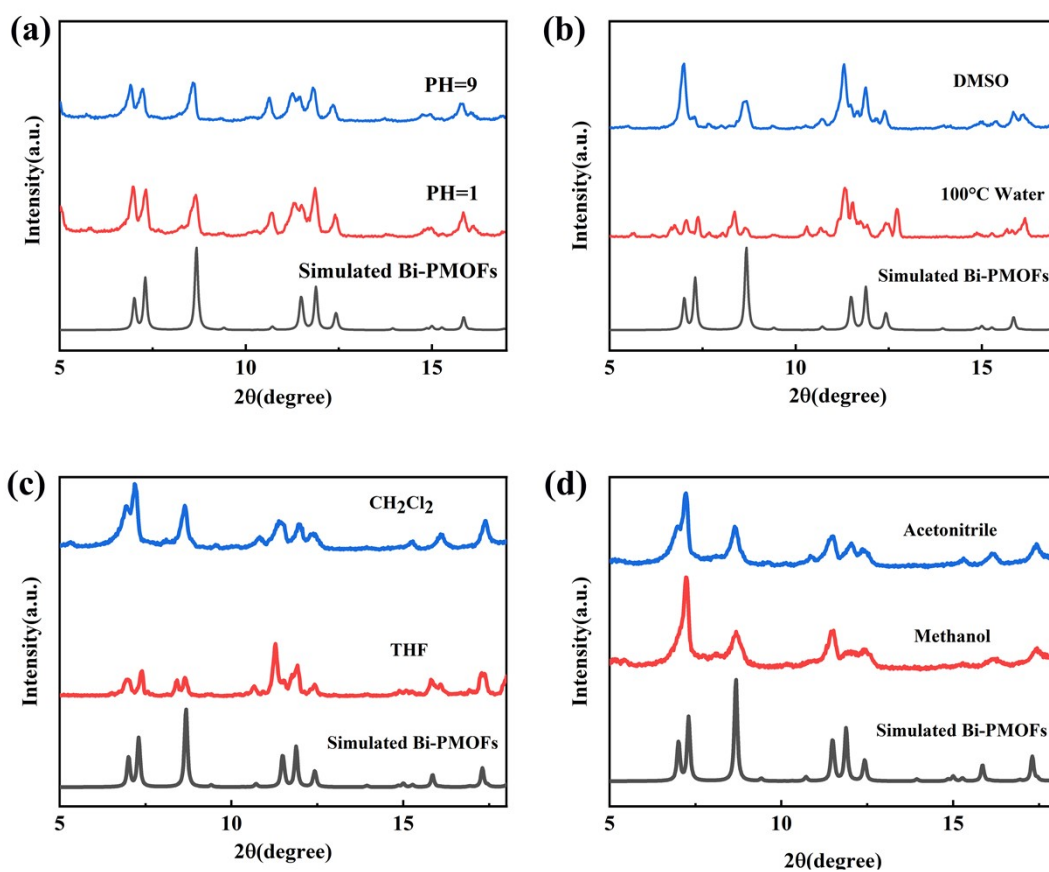
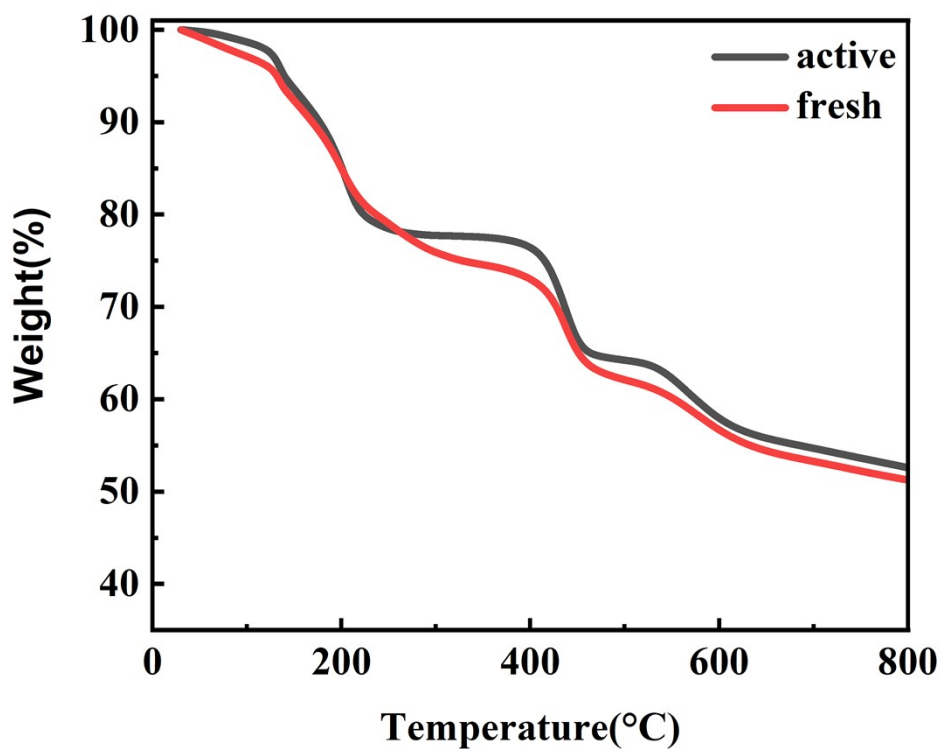
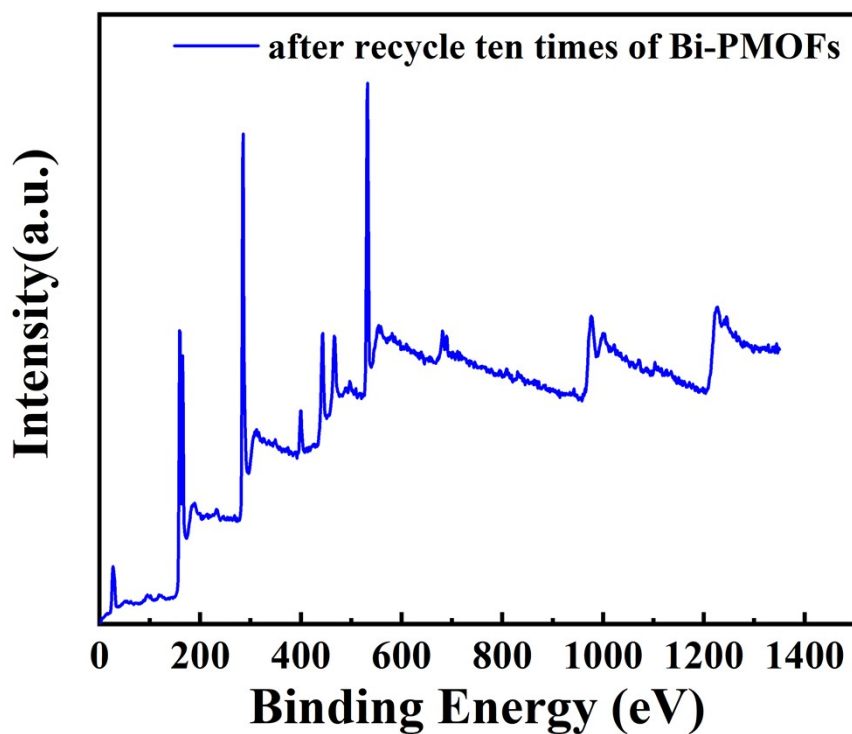


Figure S4. PXRD patterns of Bi-PMOFs upon the addition of solvents.



**Figure S5.** Thermogravimetric analysis trace of Bi-PMOFs fresh sample confirms solvent content (red). 26% weight loss is expected for DMF within the pores (30-170°C) for the fresh sample. The decomposition temperature is around 400 °C for both fresh (red) and activated samples (black).



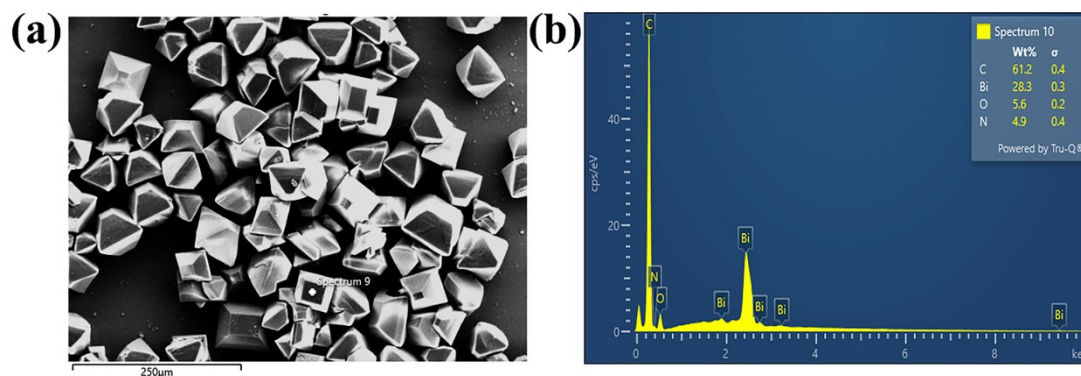


**Figure S6.** XPS scans including a) Bi4f (red) and b) C1s signals (blue) c) N1s signals (green).

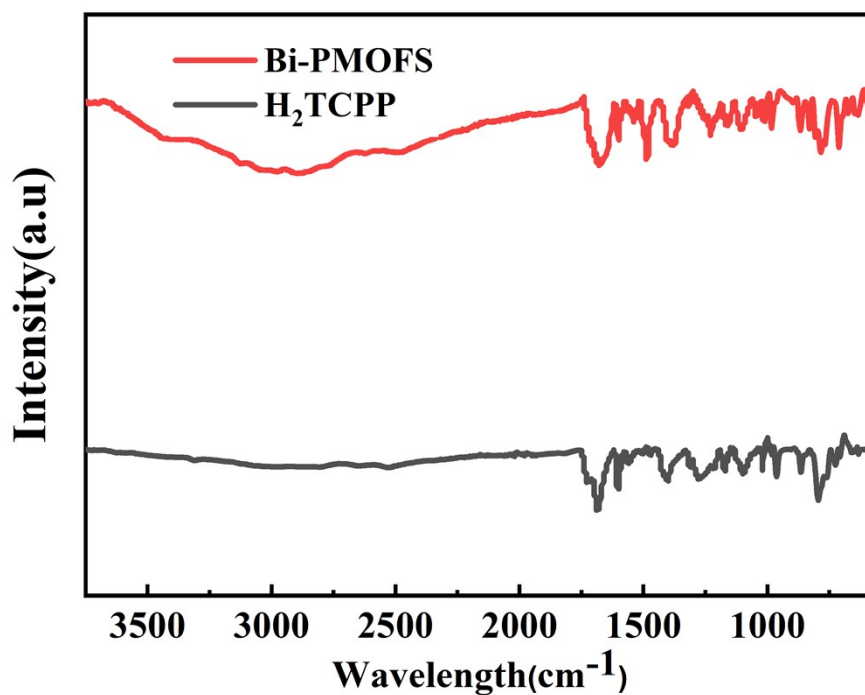
**Table S2.** XPS analysis of Bi-PMOFs.

Signals	Binding Energy (eV)	FWHM (eV)	Atomic %
O1s(RC=O/O-C=O)	531.73	1.76	19.02
O 1s (*O-C=O)	533.5	1.32	
Bi4f <sub>7/2</sub>	159.81	1.39	2.09
Bi4f <sub>5/2</sub>	165		

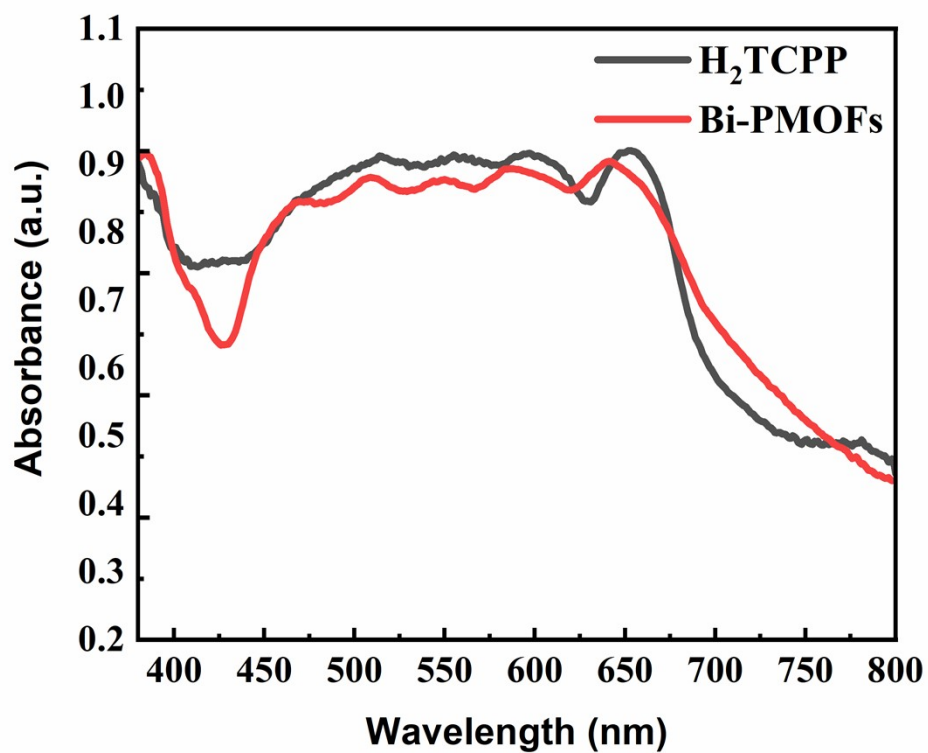
C1s (C-C)	284.82		71.13
C1s (COO)	288.5	1.4	



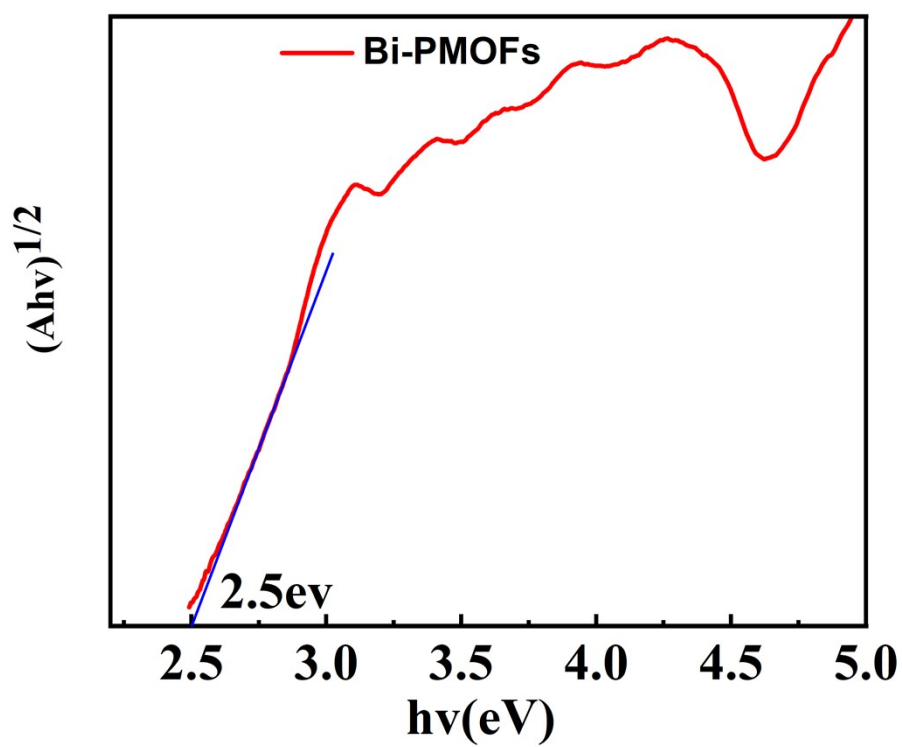
**Figure S7** EDX of Bi-PMOFs.



**Figure S8.** FTIR spectra for H<sub>2</sub>TCPP (black) and Bi-PMOFs (red).



**Figure S9.** UV-vis DRS spectrum of H<sub>2</sub>TCPP powder and Bi-PMOFs.



**Figure S10.** Tauc plot for calculation of the band gap of Bi-PMOFs.<sup>2</sup>

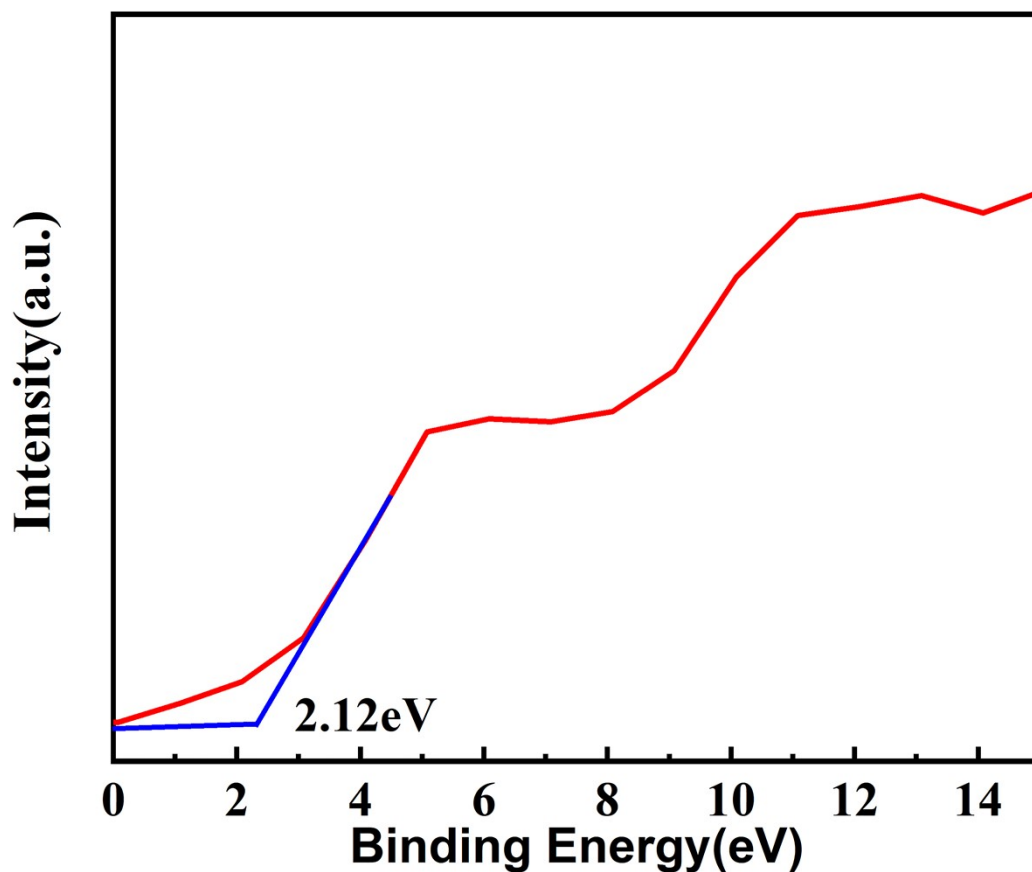
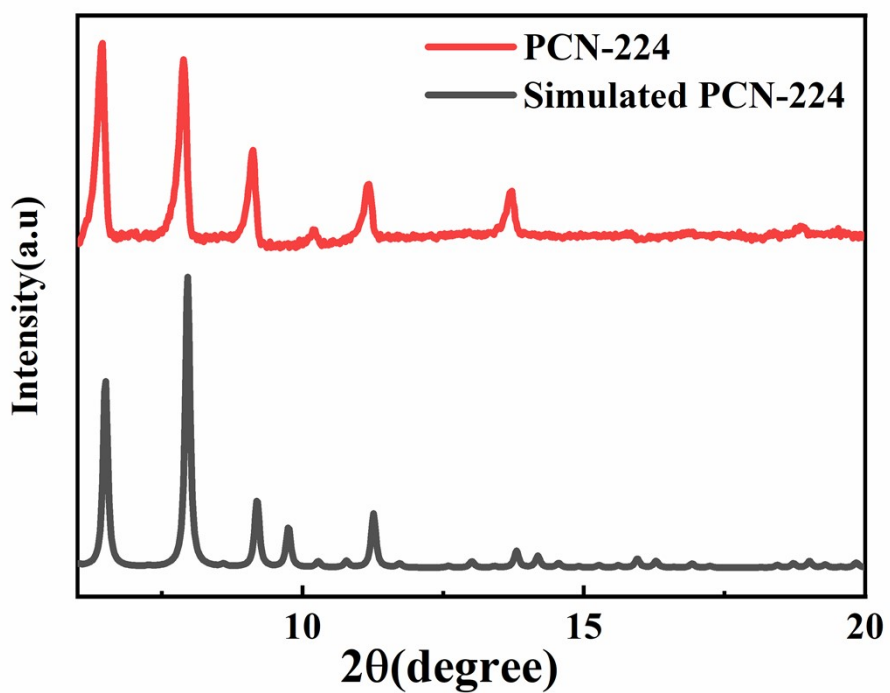


Figure S11. Valence band (VB) XPS spectra of Bi-PMOFs

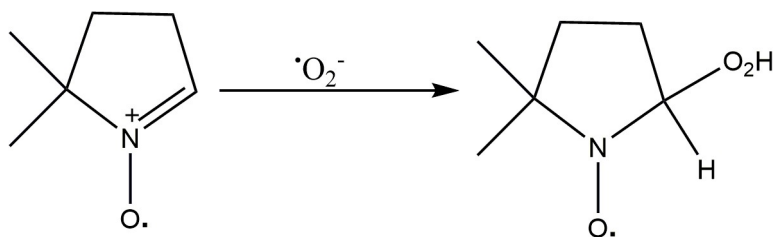


**Figure S12** XRD of synthesized PCN-224.

### Study of Reactive Oxygen Species (ROSs) Generations

#### (1) 5,5-dimethyl-1-pyrroline-N-oxide (DMPO)

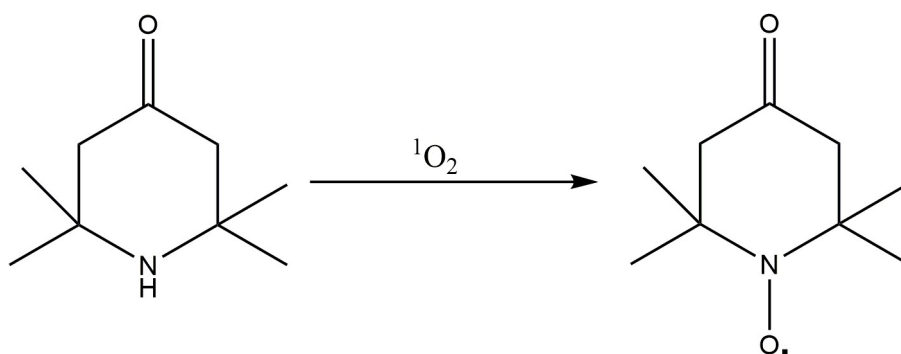
To identify the formation of superoxide ( $\cdot\text{O}_2^-$ ) by Bi-PMOFs upon light irradiation, DMPO was used as a spin trap agent. 5 mg of Bi-PMOFs dispersed in methanol solution of DMPO (20 mM).



Reaction of DMPO and superoxide.

#### (2) 2,2,6,6-tetramethyl-4-piperidone (4-oxo-TMP)

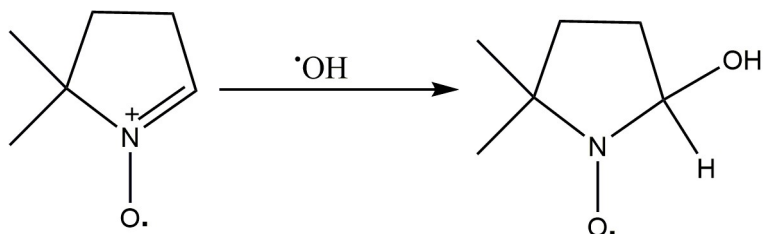
The well-known probe agent for  $^1\text{O}_2$ , 4-oxo-TMP has been used to verify generation of  $^1\text{O}_2$ . 5 mg of Bi-PMOFs was dispersed in water solution of 4-oxo-TMP (10 mM).



Reaction of 4-oxo-TMP and singlet oxygen

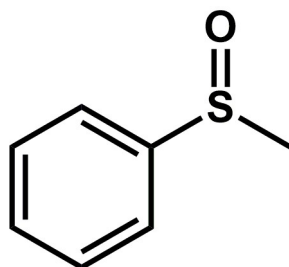
#### (1) 5,5-dimethyl-1-pyrroline-N-oxide (DMPO)

To identify the formation of superoxide( $\cdot\text{OH}$ ) by Bi-PMOFs upon light irradiation, DMPO was used as a spin trap agent. 5 mg of Bi-PMOFs dispersed in methanol solution of DMPO (20 mM).

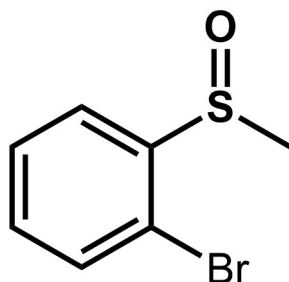


Reaction of DMPO and Hydroxyl radical.

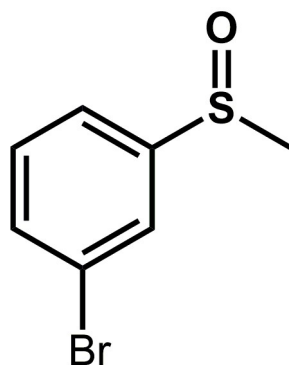
### 3. Spectral Data for Products



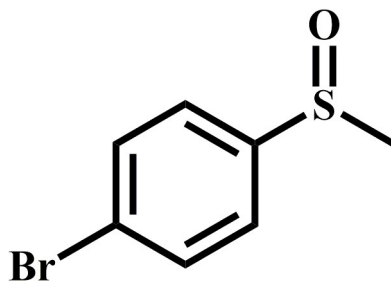
$^1\text{H}$  NMR (600 MHz, Methanol- $d_4$ )  $\delta$  7.63 (d,  $J = 8.0$  Hz, 1H), 7.51 (q,  $J = 6.8$  Hz, 2H), 2.72 (s, 2H).  $^{13}\text{C}$  NMR (151 MHz, Methanol- $d_4$ )  $\delta$  144.56 , 131.18 , 129.25 , 123.42 , 42.15 . MS 140.12



$^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.94 (dd,  $J = 7.8, 1.6$  Hz, 1H), 7.65 – 7.53 (m, 2H), 7.37 (td,  $J = 7.8, 1.6$  Hz, 1H), 2.81 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  145.35 , 132.90 , 132.24 , 128.72 , 125.68 , 118.40 , 41.89 .

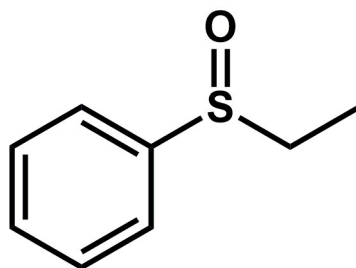


<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.80 (s, 1H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 2.73 (s, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 148.00 , 134.09 , 130.81 , 126.46 , 123.58 , 122.04 , 44.03 .

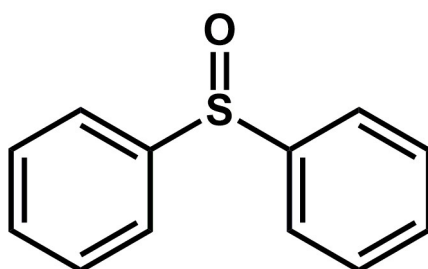


<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 2.71 (s, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 144.87 , 132.55 , 125.44 , 125.12 , 43.98 .



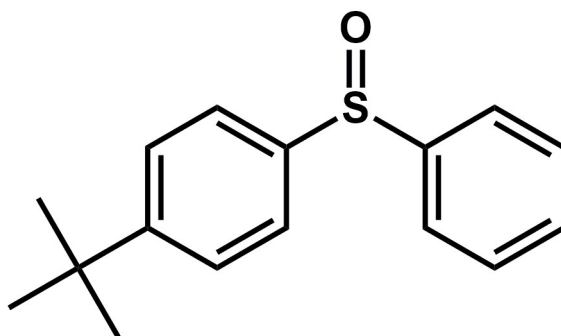


$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.74 – 7.40 (m, 5H), 2.83 (ddd, 2H), 1.19 (t, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  143.32 , 130.91 , 129.11 , 124.16 , 50.34 , 29.66 .

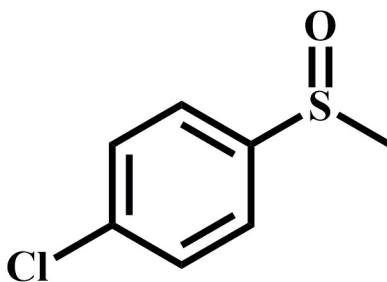


$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.64 (d,  $J = 7.4$  Hz, 4H), 7.45 (q,  $J = 6.3$  Hz, 6H).

$^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  145.55 , 131.04 , 129.30 , 124.78 .



$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.65 (d,  $J = 7.8$  Hz, 2H), 7.56 (d,  $J = 8.3$  Hz, 2H), 7.45 (dd,  $J = 12.7, 6.3$  Hz, 5H), 1.29 (s, 9H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  154.70 , 145.57 , 142.24 , 130.86 , 129.23 , 126.39 , 124.77 (d,  $J = 13.2$  Hz), 34.95 , 31.14 .



<sup>1</sup>H NMR (600 MHz, Chloroform-*d*)  $\delta$  7.59 (d,  $J$  = 8.5 Hz, 2H), 7.51 (d,  $J$  = 8.4 Hz, 2H), 2.71 (s, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*)  $\delta$  137.24 , 129.64 , 126.88 , 124.95 , 44.09 .

### Reference

1. Y. Keum, S. Park, Y. P. Chen and J. Park, *Angew Chem Int Ed Engl*, 2018, **57**, 14852-14856.
2. J. Tauc, R. Grigorovici and A. Vancu, *physica status solidi (b)*, 1966, **15**, 627-637.