Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Electronic supplementary information

A 2D Porphyrin-based Covalent Organic Framework with TEMPO for Cooperative Photocatalysis in Selective Aerobic Oxidation of Sulfides

Keyu Feng†, Huimin Hao†, Fengwei Huang, Xianjun Lang* and Cheng Wang*

Sauvage Center for Molecular Sciences and Key Laboratory of Biomedical Polymers (Ministry of Education), College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, China.

† These authors contributed equally to this work.

* Email: xianjunlang@whu.edu.cn (X. J. Lang); chengwang@whu.edu.cn (C. Wang).

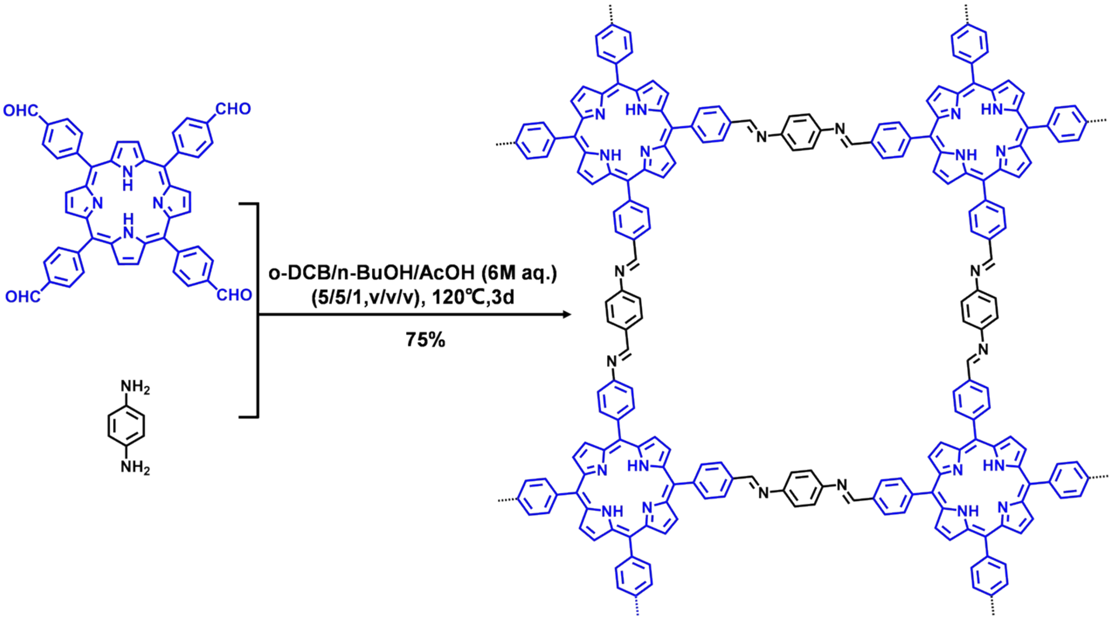
Section S1. Reagents and Solvents

All the reagents were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF), *o*-dichlorobenzene, *n*-butanol, dichloromethane (DCM), *N, N*-dimethylformamide (DMF) were purchased from Acros chemicals. 1,4-phenylenediamine, was purchased from TCI chemicals. 5,10,15,20-Tetrakis(4-benzaldehyde)porphyrin (*p*-Por-CHO) was synthesized according to the reported literatures[S1].

Powder X-ray diffraction (PXRD) patterns were obtained on a Rigaku Smartlab with Cu K_α line. Thermogravimetric analysis (TGA) from 30-800 °C was carried out on a TA Q500 in nitrogen atmosphere using a 10 °C/min ramp without equilibration delay. The UV-visible absorbance of Por-COF sample was collected on a UV visible spectrophotometer (Shimadzu UV 3600) equipped with a diffuse reflectance measurement accessory. $BaSO_4$ was used as a reflectance standard.

The nitrogen isotherm was measured at 77 K. Before measurement, the sample was degassed in vacuum at 110 °C for 12 h. Oil-free vacuum pumps and oil-free pressure regulators were used for measurements to prevent contamination of the sample during the degassing process and isotherm measurement. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area. The electron paramagnetic resonance (EPR) spectrum was detected by a JEOL, JES-FA200 EPR spectrometer. Gas chromatographic (GC) analysis was carried out on an Agilent 7890B instrument equipped with a flame ionization detector (FID) using high pure N_2 as the carrier gas.

Section S2. Synthesis and Characterization of Por-COF



Scheme S1 Synthesis of Por-COF.

Synthesis of Por-COF: The Por-COF was synthesized according to our reported literature[S2]. A pyrex tube was charged with p-Por-CHO (72.6 mg, 0.10 mmol), p-phenylenediamine (21.6 mg, 0.20 mmol), 2.5 mL of butanol, 2.5 mL of *o*-dichlorobenzene, and 0.5 mL of 6 mol/L aqueous acetic acid. After being degassed by freeze-pump-thaw technique for three times and then sealed under vacuum, the tube was placed in an oven at 120 °C for 3 d. The mixture was cooled to room temperature and the precipitate was collected by centrifugation, washed with dichloromethane for several times, Soxhlet extracted in tetrahydrofuran and dichloromethane for 3 days and dried under vacuum at 80 °C for 12 h to afford the final product. The Por-COF was isolated as a purple solid in 75% yield.

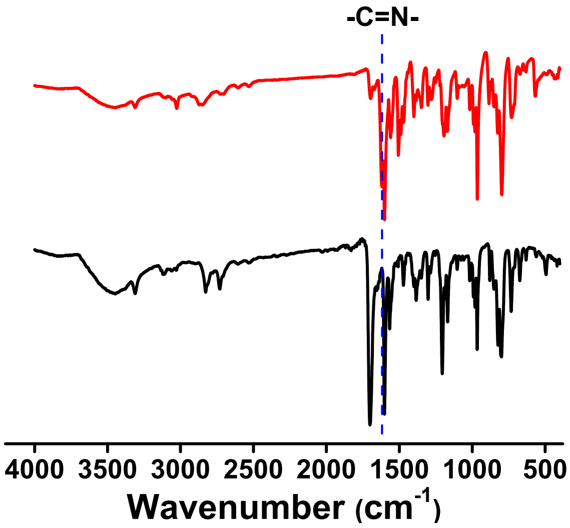


Figure S1 The FTIR spectra of *p*-Por-CHO (black curve) and Por-COF (red curve).

The newly appeared peak at 1619 cm^{-1} is belonging to the imine bond.

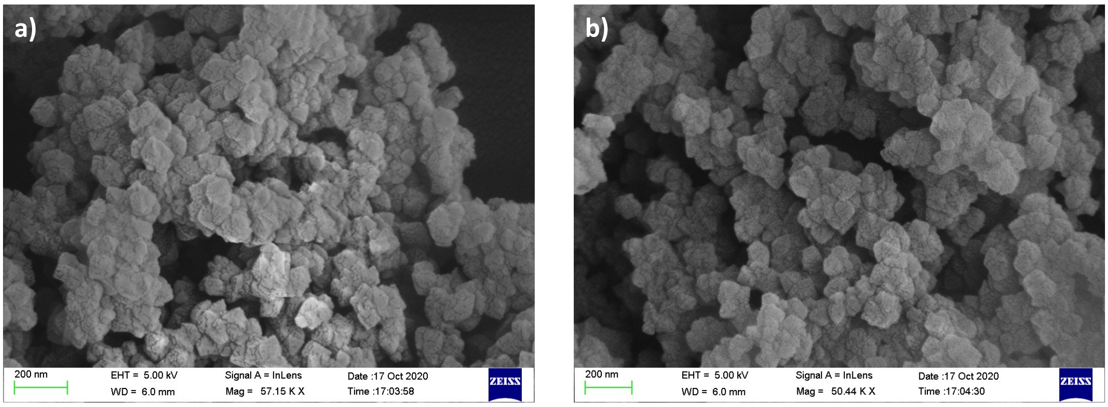


Figure S2 SEM images of Por-COF.

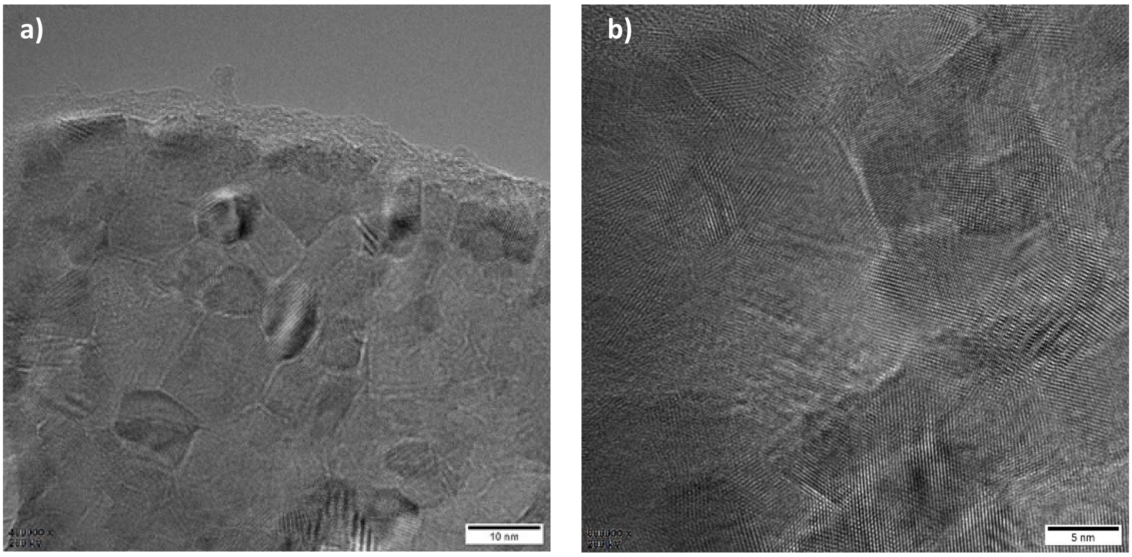


Figure S3 TEM images of Por-COF.

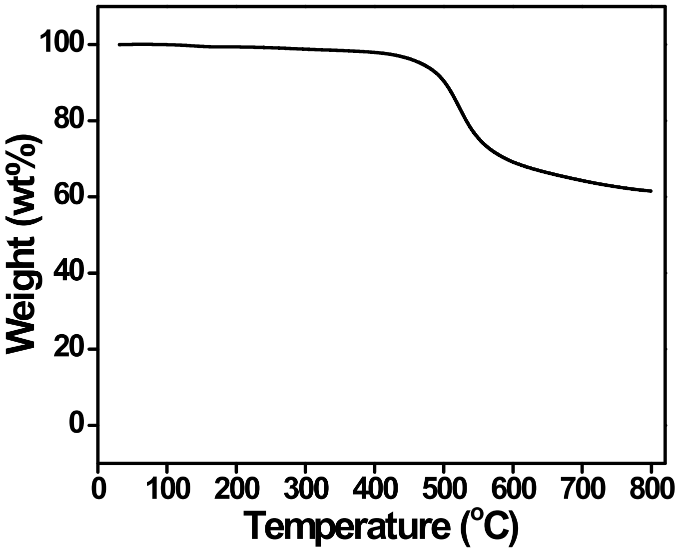


Figure S4 The TGA profile of Por-COF in N_2 atmosphere.

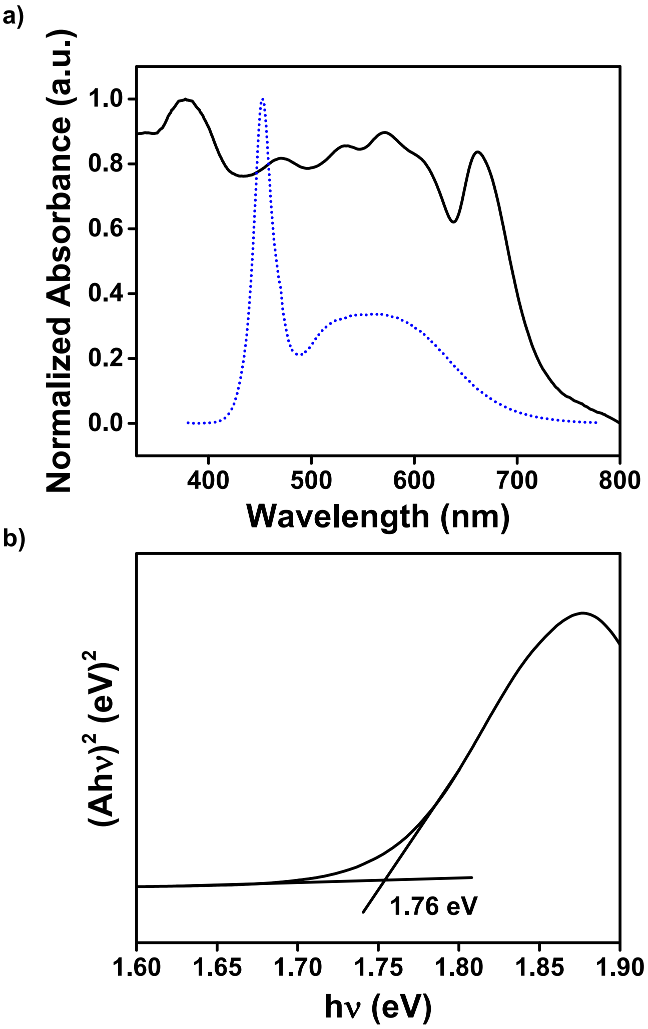
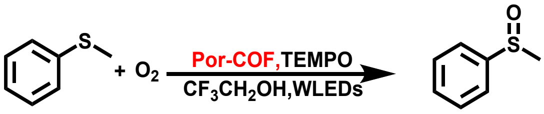


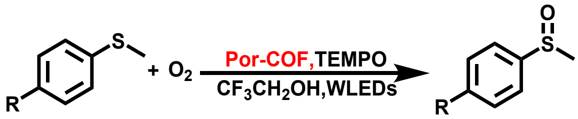
Figure S5 a) UV-Vis absorption spectra of Por-COF (black line) and relative light emitting spectrum distribution of WLEDs (blue dash line). b) Tauc plot for absorption spectra obtained with Kubelka-Munk function of Por-COF.

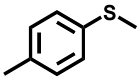
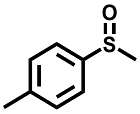
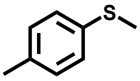
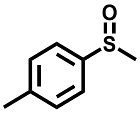
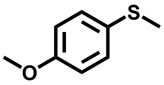
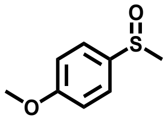
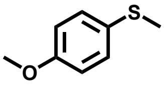
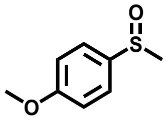
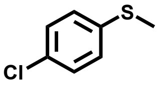
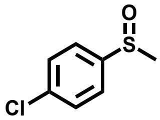
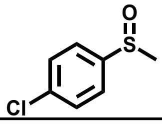
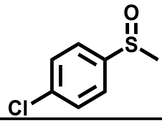
Section S3. Photocatalytic Experiments



Substrate (0.3 mmol), photocatalyst (0.005 mmol), and CF_3CH_2OH (1 mL) were added to a 10 mL Pyrex vessel, which was capped with butyl rubber septum. The mixture was stirred for 30 min in dark to reach an adsorption equilibrium. The reaction mixture was magnetically stirred at 1500 rpm and illuminated with WLEDs in 0.1 MPa O_2 at room temperature. At the end of reaction, the COF particles were separated from the reaction mixture by centrifugation and the products were quantitatively analyzed by gas chromatography (GC) equipped with a flame ionization detector (FID) using bromobenzene as the internal standard. The structures of products were confirmed by comparison with the retention time with authentic samples and further confirmed by gas chromatography-mass spectrometry (GC-MS).

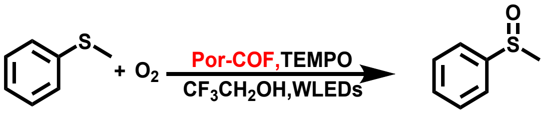
Table S1 The difference between with and without TEMPO in selective aerobic oxidation of sulfides by Por-COF photocatalysis[a].



Entry	Substrate	Product	TEMPO[b]	Conv. [%][c]	Sel. [%][c]
1			-	41	99
2			+	83	99
3			-	54	99
4			+	87	99
5			-	61	99
6			+	90	99

[a] Reaction conditions: substrate (0.3 mmol), Por-COF (0.005 mmol), O_2 (0.1 MPa), WLEDs (3 W × 4), CF_3CH_2OH (1 mL), 0.5 h. [b] +, TEMPO (0.006 mmol); -, no TEMPO. [c] Determined by GC-FID using bromobenzene as the internal standard, conversion of sulfides, selectivity of sulfoxides.

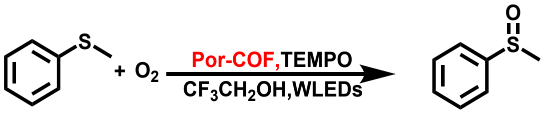
Table S2 The influence of amount of TEMPO on the TEMPO-mediated selective aerobic oxidation of sulfides by Por-COF photocatalysis[a].



Entry	Amount of TEMPO (mmol)	Conv. [%][b]	Sel. [%][b]
1	0	40	99
2	0.0015	86	99
3	0.003	85	99
4	0.006	83	99
5	0.009	90	99
6	0.012	88	99

[a] Reaction conditions: thioanisole (0.3 mmol), Por-COF (0.005 mmol), O_2 (0.1 MPa), W LEDs (3 W × 4), CF_3CH_2OH (1 mL), 0.5 h. [b] Determined by GC-FID using bromobenzene as the internal standard, conversion of thioanisole, selectivity of methyl phenyl sulfoxide.

Table S3 The influence of light intensity on the TEMPO-mediated selective aerobic oxidation of sulfides by Por-COF photocatalysis[a].



Entry	Light intensity	Conv. [%][b]	Sel. [%][b]
1	25%	33	99
2	50%	54	99
3	75%	67	99
4	100%	83	99

[a] Reaction conditions: thioanisole (0.3 mmol), Por-COF (0.005 mmol), TEMPO (0.006 mmol), O_2 (0.1 MPa), WLEDs irradiation, CF_3CH_2OH (1 mL), 0.5 h. [b] Determined by GC-FID using bromobenzene as the internal standard, conversion of methyl phenyl sulfide, selectivity of methyl phenyl sulfoxide.

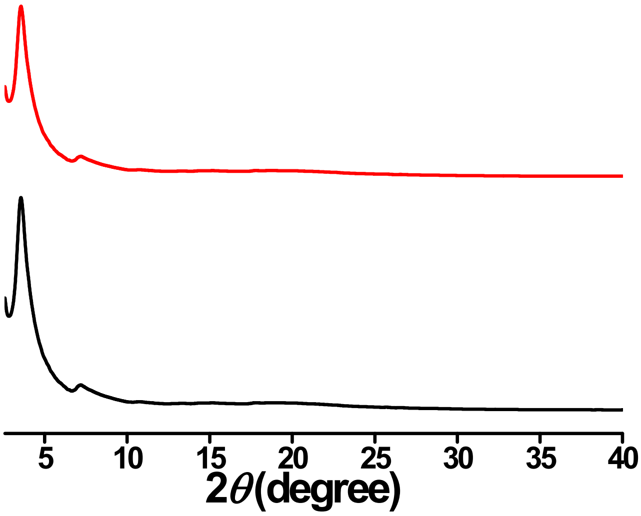


Figure S6 PXRD patterns of Por-COF (black line), recycled after third run of photocatalysis (red line) for the selective oxidation of thioanisole to methyl phenyl sulfoxide.

Section S4. References

S1 A. Osuka, B. L. Liu, K. Maruyama, *Chem. Lett.* 1993, **22**, 949.

S2 H. P. Liao, H. M. Wang, H. M. Ding, X. S. Meng, H. Xu, B. S. Wang, X. P. Ai and C. Wang, *J. Mater. Chem. A.*, 2016, **4**, 7416-7421.