Tuning the pore structures and photocatalytic properties of a 2D covalent organic framework with multi-branched photoactive moieties

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Fig. S1 UV-Vis diffuse reflectance spectra of CPF-3 (red) and COF-LZU1 (black).



Fig. S2 TGA curves of CPF-3 (red) and COF-LZU1 (black).



Fig. S3 PXRD patterns of CPF-3 (red) and COF-LZU1 (black).



Fig. S4 TEM images of CPF-3 (left) and COF-LZU1 (right).



Fig. S5 BET surface area plot for COF-LZU1 calculated from the adsorption isotherm.



Fig. S6 BET surface area plot for CPF-3 calculated from the adsorption isotherm.



Fig. S7 Sn^{IV} 3d XPS spectra of Sn-CPF-3 (red) and recovered Sn-CPF-3 after photocatalysis (blue).



Fig. S8 PXRD patterns of CPF-3 (black) and Sn-CPF-3 (red).



Fig. S9 SEM image of Sn-CPF-3.



Fig. S10 TEM image of Sn-CPF-3.



Fig. S11 N₂ adsorption-desorption isotherms of Sn-CPF-3.



Fig. S12 BET surface area plot for Sn-CPF-3 calculated from the adsorption isotherm.



Fig. S13 Pore size distribution of Sn-CPF-3.



Fig. S14 UV-Vis diffuse reflectance spectra of Sn-CPF-3 (red) and CPF-3 (black).



Fig. S15 FT-IR spectra of Sn-CPF-3 (red) and CPF-3 (black).



Fig. S16 HAADF-STEM and element mapping images for Sn-CPF-3.



Fig. S17 EPR spectra of different samples in the presence of TEMP under blue light irradiation.



Fig. S18 EPR spectra of Sn-CPF-3 in the presence of DMPO under blue light irradiation.



Fig. S19 Fluorescence spectra of SOSG in D₂O for COF-LZU1, CPF-3 and Sn-CPF-3.

SOSG has been demonstrated special selectivity for detection of singlet oxygen, and does not responsive towards •OH or O_2^{-} . After reacting with singlet ${}^{1}O_2$ to form endoperoxide, SOSG emits green fluorescence with the maximum emission band at ~525 nm. As shown in Fig. S19, photoirradiation of CPF-3 or Sn-CPF-3 in D₂O in the presence of SOSG for 10 min results in stronger fluorescence intensity than that of COF-LZU1, indicating that both CPF-3 and Sn-CPF-3 could lead to the formation of singlet oxygen under photoirradiation and Sn-CPF-3 is more active.



Fig. S20 I-t curves for Sn-CPF-3, CPF-3 and COF-LZU1 under blue light irradiation.



Fig. S21 *I*-*t* curves for Sn-CPF-3 under blue light irradiation.



Fig. S22 The relationship between the UV-Vis absorbance (monitored the absorption peaks at 573 and 666 nm) and TAPP concentration in DMF.



Fig. S23 The UV-Vis absorption spectra of digested CPF-3 in DMF.

After CPF-3 (2.1 mg) was digested by 6 M HCl aqueous solution, the residue was removed by centrifugation, and the supernate was diluted to 4.0 mL by DMF. As shown in Fig. S23, the absorbance at 573 nm is of 1.226 and the absorbance at 666 nm is of 0.626. According to the relationship between the UV-Vis absorbance and TAPP concentration in DMF in Fig. S22, the absorbance at 573 nm corresponds to the TAPP concentration of 0.0500 g/L, and the absorbance at 666 nm corresponds to the TAPP concentration of 0.0494 g/L. Therefore, the mass fraction of TAPP in CPF-3 is of $(0.0497 \text{ g/L} \times 4.0 \text{ mL})/(2.1 \text{ mg}) \times 100 \% = 9.47\%$.



Fig. S24 X-ray photoelectron spectrum for COF-LZU1.



Fig. S25 X-ray photoelectron spectrum for CPF-3.



Fig. S26 X-ray photoelectron spectrum for Sn-CPF-3.



Fig. S27 PXRD patterns of COF-LZU1 (black) and Sn-COF-LZU1 (red).



Fig. S28 PXRD pattern of Sn-CPF-3 after catalysis.



Fig. S29 SEM image for Sn-CPF-3 after catalysis.



Fig. S30 TEM image for Sn-CPF-3 after catalysis.



Fig. S31 Mott-Schottky plots for Sn-CPF-3.



Fig. S32 Mott-Schottky plots for Sn-COF-LZU1.



Fig. S33 Band gap energies for Sn-CPF-3 and Sn-COF-LZU1.



Fig. S34 Electronic band structures for Sn-CPF-3 and Sn-COF-LZU1.

Mott–Schottky Measurement. The working electrode was prepared according to the following procedure: 1.0 mg of Sn-CPF-3 was dispersed in a mixture of EtOH (200 μ L) and aqueous nafion (5%; 20 μ L) to produce the sample suspension; the asobtained suspension was dripped onto the fluorine-doped tin oxide (FTO) substrate (1.0 cm × 1.0 cm), and subsequently dried. The Ag/AgCl electrode (saturated KCl aqueous solution) was used as a reference electrode, the Pt wire as the counter electrode, and 0.2 M Na₂SO₄ aqueous solution as the electrolyte. The Mott–Schottky plots were measured at the frequencies of 2000, 3000 and 4000 Hz.



Fig. S35 PXRD patterns for Sn-CPF-3A and Sn-CPF-3B.

CPF-3A was prepared according to the synthesis method of CPF-3, except the feedstocks for 1,4-diaminobenzene and TAPP are of 44.6 mg (0.413 mmol) and 12.7 mg (0.019 mmol), respectively. UV-Vis absorption spectroscopy analysis results showed that the TAPP content in CPF-3A is of 4.88 wt%.

CPF-3B was prepared according to the synthesis method of CPF-3, except the feedstocks for 1,4-diaminobenzene and TAPP are of 32.4 mg (0.3 mmol) and 50.6 mg (0.075 mmol), respectively. UV-Vis absorption spectroscopy analysis results showed that the TAPP content in CPF-3B is of 18.3 wt%.



Fig. S36 UV-Vis diffuse reflectance spectra of Sn-CPF-3A and Sn-CPF-3B.



Fig. S37 SEM image for Sn-CPF-3A.



Fig. S38 SEM image for Sn-CPF-3B.



Fig. S39 TEM image for Sn-CPF-3A.



Fig. S40 TEM image for Sn-CPF-3B.



Fig. S41 UV-Vis absorption spectra of digested CPF-3A and CPF-3B in DMF.



Fig. S42 FT-IR spectra of Sn-CPF-3A and Sn-CPF-3B.



Scheme S1. Schematic representation of the formation of sulfoxides by reaction of sulfides with ${}^{1}O_{2}$. S1,S2

Entry	Photocatalyst	Light Source	Oxidant Source	TON	Ref.
1	Ru ^{II} phot-Cu ^{II} cat	Blue LED	O ₂	250	S3
2	Mn ^{III} (TBP ₈ Cz)	>400 nm	O ₂	902	S4
3	Ru ^{II} _{chro} -Cu ^{II} _{cat}	Blue LED	Air	18000	S5
4	PdF ₂₀ TPP	Xe Lamp	O ₂	1820	S6
5	SnPor@PAF	White LED	O ₂	7920	S7
6	UNLPF-10	Blue LED	Air	992	S8
7	CMPBDP	Halogen Lamp	Air	984	S9
8	Rose Bengal	Fluorescent Lamp	Air	48	S10
9	[Ru(pybpm)Ru(OH ₂)(bpy)](BF ₄) ₄	>420 nm	N ₂	384	S11
10	Ru _{phot} -Ru _{cat} -H ₂ O	>380 nm	N ₂	1000	S12
11	Sn-CPF-3	Blue LED	O ₂	23334	This work

Table S1 The photocatalytic properties of different catalysts for photocatalyticoxygenation of sulfides.

Table S2 Photocatalytic properties of Sn-TAPP, Sn-CPF-3A and Sn-CPF-3B in photo-oxygenation of sulfides.^a

$R_1 \xrightarrow{S} R_2 + O_2 \xrightarrow{Cat. 3W \text{ Blue LED}} R_1 \xrightarrow{O} R_2 + O_2 \xrightarrow{O} R_2$								
Entry	R ₁	R ₂	Catalyst	Conv. (%) ^b	Sel. (%) ^b			
1		-CH ₃	Sn-TAPP	15	>99			
2		-CH ₃	Sn-CPF-3A	24	>99			
3		-CH ₃	Sn-CPF-3B	17	>99			

^a Reaction conditions: sulfide (0.1 mmol) and catalyst (0.3 mol% based on Sn-TAPP) in MeOH (1 mL) were stirred under the irradiation of a 3 W blue LED for 12 h under O_2 atmosphere (balloon). ^b Conversion% and selectivity% were determined by GC–MS.

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