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Supporting Information

Engineering earth-abundant copper(I) sensitizing center in Metal-

Organic Frameworks for efficient photosynthesis

Guang-Chen Guo,^a Lihua Ma,*ab Xiao-Di Li,^a Song Guo,*a Tong-Bu Lu^a and Zhi-

Ming Zhang*a

Institute for New Energy Materials & Low Carbon Technologies, School of Materials

Science & Engineering, Tianjin University of Technology, Tianjin 300384, China

Email: malh987@hotmail.com; guosong@email.tjut.edu.cn; zmzhang@email.tjut.edu.cn

Table of Contents

1. Materials and methods	S2
2. Photophysical properties measurement for MOFs	S2
3. Electron spin resonance (ESR) detection of ${}^{1}O_{2}$ and O_{2}	S3
4. Photocatalytic measurements	S3
5. Electrochemical measurements	S4
6. H ₂ O ₂ detection methods	S4
7. Characterization of materials	S5
8. References	S16

1. Materials and methods

All chemicals were commercially available and used without further purification. Powder X-ray diffraction (PXRD) data were collected by a Smart X-ray diffractometer (SmartLab 9 KW, Rigaku, Japan) with Cu K α radiation ($\lambda = 1.54178$ Å). UV-vis diffuse reflectance spectra were taken using a UV-vis near-infrared spectrophotometer (Lambda 750 UV/VIS/NIR, PerkinElmer, America). The photoluminescence (PL) spectra were conducted on a fluorescence spectrophotomer (F-7000, Hitachi, Japan). Fluorescence lifetime data were acquired using a F-4600 steady and transient state fluorescence spectrometer (Hitachi). Scanning electron microscope (SEM) images were obtained on Verios 460L SEM (FEI). Transmission electron microscope (TEM) images and EDS mapping images were were performed on TALOS using 200 kV acceleration voltages (F200X, FEI, America). X-ray photoelectron spectroscopy (XPS) was detected with Al Ka as the excitation source on an ESCALAB 250 Xi spectrometer (Thermo scientific). ¹H NMR spectra were collected by digital NMR spectrometer (AVANCE III HD 400 MHz). Electron spin resonance (ESR) spectra were acquired at room temperature in air using a Bruker EMXplus-6/1 spectrometer. Electrochemical measurements were performed on a CHI 760E electrochemical workstation at room temperature.

2. Photophysical properties measurement for MOFs

The UV-vis absorption and fluorescence of MOFs were tested with solid state samples, which were fully ground and activated. Typically, the samples (15.0 mg)

were laid flat in the sample pool and then compacted to ensure that they did not fall off during the test.

3. Electron spin resonance (ESR) detection of ¹O₂ and O₂⁻⁻

Cu-5-MOF was dispersed to 5 mL CH₃CN under ultrasonic condition. 100 μ L of the above suspension was mixed with 250 μ L of 4-oxo-TMP solution (300 mM) and then diluted to 600 μ L for ¹O₂ detection. Cu-5-MOF was dispersed to 5 mL DMSO under ultrasonic condition. 100 μ L of the above suspension was mixed with 250 μ L of DMPO solution (300 mM) and then diluted to 600 μ L for O₂⁻⁻ detection. ESR measurements were carried out upon irradiation with a Xenon lamp (300 W, λ > 400 nm) at room temperature under air. In order to track the evolution of ¹O₂ and O₂⁺⁻ in the catalytic process, the ESR signals were detected under the same condition before and after adding benzylamine or 2-chloroethyl ethyl sulfide (CEES).

4. Photocatalytic measurements

Photooxidation of CEES

5.0 mg photocatalyst was added into the mixed solvent of 1.0 mL CH₃CN and 1.0 mL CH₂Cl₂ in a glass vial for ultrasonic dispersion. 0.02 mmol CEES was added into the above mixture, which was stirred in air at room temperature upon irradiation with a 300 W Xe lamp (100 mW/cm², $\lambda > 400$ nm). After the reaction was complete, the solvent was concentrated to dryness under reduced pressure. The conversion rate of crude products was determined by ¹H NMR. For the recycling experiments, the photocatalyst was collected by centrifugation and washed with CH₂Cl₂. After drying

in a vacuum oven at 50 °C for 3 h, the sample powder was used for the next round of photocatalysis.

5. Electrochemical measurements

A fluoride-tin oxide (FTO) glassy electrode (area of 1 cm²) was used as the working electrode. The catalyst (2.0 mg) was dispersed in 10 μ L Nafion and 1 mL ethanol to obtain a suspension followed by ultrasonication for 60 min. Then, 50 μ L of the suspension was scattered on the FTO electrode and then dried at ambient temperature. Electrochemical measurements were performed on an electrochemical analyzer (CHI760E) in a standard three-electrode cell with working electrode (FTO), reference electrode (Ag/AgCl) and counter electrode (platinum plate) in 0.2 M Na₂SO₄ electrolyte (pH = 6.8) at room temperature. The Mott-Schottky measurements of MOFs were measured at frequencies of 500, 1000, 1500 Hz, respectively. Photocurrent measurements were performed with a 300 W Xe lamp as light source.

6. H₂O₂ detection methods

The liquid product of H_2O_2 was determined by the DPD (N,N-diethyl-pphenylenedianine)/POD (horseradish pemxidase) method. The first step was to configure the appropriate solution. 100 mg of DPD was dissolved in 10 mL of 0.05 M H_2SO_4 solution to make DPD solution; 10 mg of POD was dissolved in 10 mL of ultrapure water to make POD solution. Reaction solution (1 mL) was added into tube, following addition of 0.4 mL 0.5 M pH = 6 phosphate buffer. Then, 5 µL DPD and 5 µL POD solutions were quickly added into above system. If there was H_2O_2 in the solution, H_2O_2 can oxidize POD. Then, the oxidation product of POD can oxidize DPD into positive ion radical DPD⁺, which was a pink compound. DPD⁺ had two characteristic absorption peaks at wavelengths of 510 nm and 551 nm.



7. Characterization of materials

Fig. S1. The pore size of UiO-67-bpy and the molecular size of Phen with different functional groups. The pore size of UiO-67-bdy was determined as 1.93 nm, significantly larger than the molecular size of Phen with different functional groups. This indicates that Phen with different functional groups can be trapped into the pore of UiO-67-bpy.



Fig. S2. Optical pictures of UiO-67-bpy and Cu-MOFs.



Fig. S3. PXRD patterns of UiO-67-bpy and Cu-MOFs.



Fig. S4. (a) The survery spectrum and (b) XPS spectra of Cu 2p of Cu-5-MOF.



Fig. S5. (a) SEM and (b) TEM images of Cu-5-MOF.

Entry	Photocatalyst	Zr (wt%)	Cu (wt%)	Zr/Cu
1	Cu-1-MOF	25.3	2.16	8.19
2	Cu-2-MOF	23.6	2.08	7.92
3	Cu-3-MOF	24.0	2.17	7.73
4	Cu-4-MOF	25.5	2.12	8.39
5	Cu-5-MOF	22.6	2.03	7.76

Table S1. ICP-MS results of Cu-MOFs.



Fig. S6. Photoluminescence spectra of UiO-67-bpy and Cu-MOFs, $\lambda_{ex} = 360$ nm.



Fig. S7. Photoluminescence lifetime of (a) Cu-1-MOF, (b) Cu-2-MOF, (c) Cu-3-MOF and (f) Cu-4-MOF, $\lambda_{ex} = 365$ nm, $\lambda_{em} = 486$ nm.



Fig. S8. Tauc plots of (a) UiO-67-bpy, (b) Cu-1-MOF, (c) Cu-2-MOF, (d) Cu-3-MOF, (e) Cu-4-MOF and (f) Cu-5-MOF.



Fig. S9. Mott-Schottky plots of (a) UiO-67-bpy, (b) Cu-1-MOF, (c) Cu-2-MOF, (d) Cu-3-MOF, (e) Cu-4-MOF and (f) Cu-5-MOF.



Fig. S10. The energy level diagram of UiO-67-bpy and Cu-MOFs.

Entry	photocatalyst	t (h)	Conv. (%)
1	UiO-67-bpy	1	3.6
2	Cu-1-MOF	1	8.2
3	Cu-2-MOF	1	17.2
4	Cu-3-MOF	1	38.9
5	Cu-4-MOF	1	51.2
6	Cu-5-MOF	1	90.2
7 ^a	-	1	trace
8 ^b	Cu-5-MOF	1	99.0
9°	Cu-5-MOF	1	trace
10 ^d	Cu-5-MOF	1	NR

Table S2. Catalytic activities with different catalysts for oxidative coupling of benzylamine.¹

Reaction conditions: 0.02 mmol benzylamine, 5.0 mg photocatalyst, irradiated with 300 W xenon lamp ($\lambda > 400$ nm, 100 mW/cm²), 1.5 mL CH₃CN/CH₂Cl₂ (1/1, v/v), air atmosphere and room temperature. The conversion rate was determined by ¹H NMR. ^aNo catalyst. ^bUnder O₂. ^cUnder Ar. ^dUnder the dark.



Fig. S11. Control experiments for oxidative coupling of benzylamine with Cu-5-MOF.



Fig. S12. (a) PXRD patterns and (b) SEM image of Cu-5-MOF after photocatalytic reation.



Fig. S13. (a) TGA curves and (b) UV-vis absorption spectra of Cu-5-MOF before and after photocatalytic reaction.



Fig. S14. Recycling experiments with (a) Cu-1-MOF and (b) Cu-3-MOF. Reaction conditions: 0.02 mmol benzylamine, 5.0 mg MOFs, 1.5 mL mixed solution (CH₃CN/CH₂Cl₂, 1/1, v/v), air atmosphere, room temperature, irradiated with 300 W xenon lamp ($\lambda > 400$ nm, 100 mW/cm²). The conversion was determined by ¹H NMR.



 Table S3. Substrate scope of photocatalytic oxidative coupling of benzylamines.

Reaction conditions: 0.02 mmol benzylamine, 5.0 mg Cu-5-MOF, irradiated with 300 W xenon lamp ($\lambda > 400$ nm, 100 mW/cm²), 1.5 mL CH₃CN/CH₂Cl₂ (1/1, v/v), air atmosphere and room temperature. The conversion rate was determined by ¹H NMR.

Entry	Control condition	Conv. (%)
1 ^a	HQ	9.6
2 ^b	KI	14.7
3°	AgNO ₃	37.8
4 ^d	BQ	31.6
5 ^e	NaN ₃	38.9
6 ^f	TPA	89.2
7 ^g	STD	90.5

Table S4. Control experiments for oxidative coupling of benzylamine with Cu-5-MOF.

Reaction conditions: 0.02 mmol benzylamine, 5.0 mg Cu-5-MOF, irradiated with 300 W xenon lamp ($\lambda > 400$ nm, 100 mW/cm²), 1.5 mL CH₃CN/CH₂Cl₂ (1/1, v/v), air atmosphere and room temperature. The conversion rate was determined by ¹H NMR. ^aHQ (hydroquinone) as free radical scavenger. ^bKI as hole scavenger. ^cAgNO₃ as electron scavenger. ^dBQ (p-benzoquinone) as O₂⁻ radical scavenger. ^eNaN₃ as ¹O₂ scavenger. ^fIPA (Isopropanol) as •OH radical scavenger. ^gSTD indicates the standard condition without scavengers.



Fig. S15. The absorption spectra of H_2O_2 . The inset shows the colors of the solutions with/without DPD and POD. Solution 1: Reaction solution (1 mL) was added into tube, following addition of 0.4 mL 0.5 M pH = 6 phosphate buffer to obtain. Solution 2: Solution 1 with 5 µL DPD and 5 µL POD solutions. Solution 3: 1 µL H_2O_2 (30 wt%) and 1 mL CH_3CN were added into tube, following addition of 0.4 mL 0.5 M pH = 6 phosphate buffer. Then, 5 µL DPD and 5 µL POD solutions were quickly added into above system.

Table S5. Photooxidation of CEES with different photocatalysts and different reaction conditions.

CI 🔨	$\sim \frac{8}{r}$ Air, C	Cat., hv ∴t	- CI	~ ["]
Entry	Photocatalyst	Light	t (h)	Conv. (%)
1	UiO-67-bpy	on	6	-
2	Cu-1-MOF	on	6	trace
3	Cu-2-MOF	on	6	53.7
4	Cu-5-MOF	on	6	100
5 ^a	-	on	6	trace
6 ^b	Cu-5-MOF	off	6	trace
7°	Cu-5-MOF	on	5	100
8 ^d	Cu-5-MOF	on	6	trace

Reaction conditions: CEES (0.02 mmol), photocatalyst (5.0 mg), 2 mL CH₃CN/CH₂Cl₂ (1/1, v/v), in air, irradiated with 300 W Xe lamp ($\lambda > 400$ nm, 100 mW/cm²). The crude product yields were determined by ¹H NMR spectrum. ^aNo catalyst. ^bUnder the dark. ^cUnder O₂. ^dUnder Ar.



Fig. S16. Control experiments for oxidative CEES with Cu-5-MOF.

Entry	Control condition	Conv. (%)
1ª	HQ	56.1
2 ^b	KI	26.4
3°	AgNO ₃	55.6
$4^{\rm d}$	BQ	59.2
5 ^e	NaN ₃	62.5
6 ^f	TPA	100
7g	STD	100

Table S6. Control experiments for oxidative CEES with Cu-5-MOF.

Reaction conditions: 0.02 mmol CEES, 5.0 mg Cu-5-MOF, irradiated with 300 W xenon lamp ($\lambda > 400$ nm, 100 mW/cm²), 2 mL CH₃CN/CH₂Cl₂ (1/1, v/v), in air and room temperature. The conversion rate was determined by ¹H NMR. ^aHQ (hydroquinone) as free radical scavenger. ^bKI as hole scavenger. ^cAgNO₃ as electron scavenger. ^dBQ (p-benzoquinone) as O₂⁻⁻ radical scavenger. ^eNaN₃ as ¹O₂ scavenger. ^fIPA (Isopropanol) as •OH radical scavenger. ^gSTD indicates the standard condition without scavengers.



Fig. S17. ESR spectra of Cu-5-MOF in the presence of (a) 4-oxo-TMP in CH_3CN and (b) DMPO in DMSO.



Fig. S18. Proposed mechanism for the photocatalytic oxidative CEES with O_2 using Cu-5-MOF as photocatalyst.

8. References

1 L. Huang, J. Zhao, S. Guo, C. Zhang, J. Ma, J. Org. Chem. 2013, 78, 5627-5637.