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Supporting Information

Highly Efficient Photosynthesis of Hydrogen Peroxide by a stable Zr(IV)-based MOF with a Diamino Functionalized Ligand

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1. Experimental Section

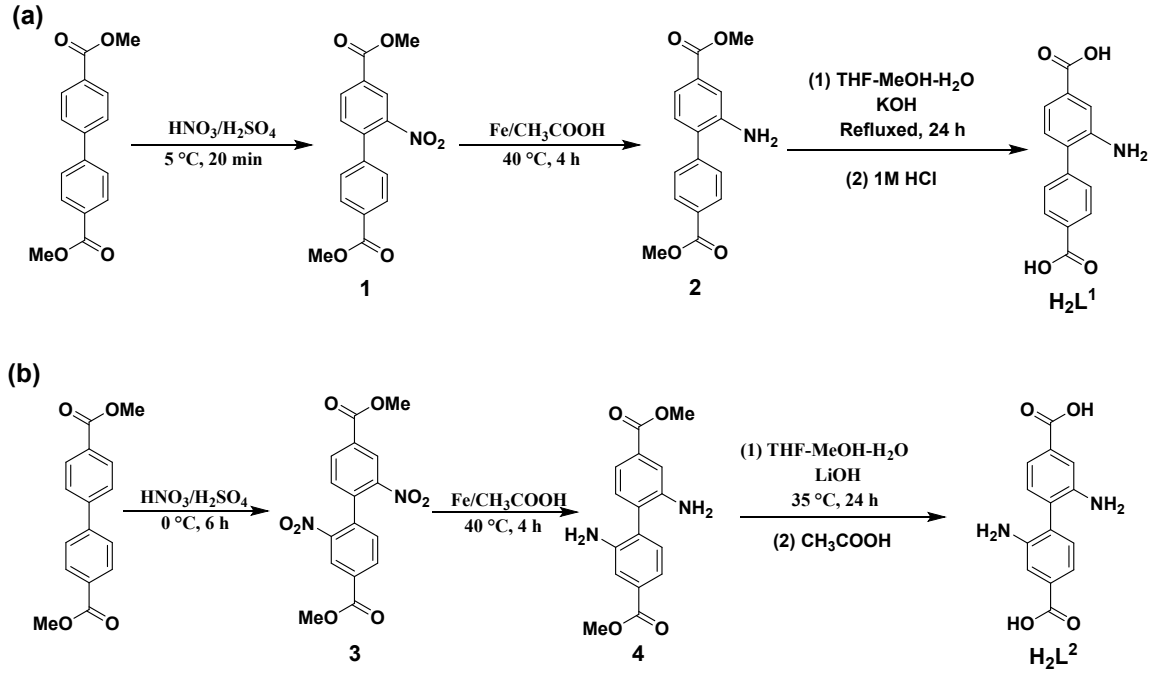
Materials and characterization methods

Organic reagents were purchased commercially and were used without further purification. 2-amino-4,4'-biphenyldicarboxylic acid (H_2L^1) and 2,2'-diamino-4,4'-biphenyldicarboxylic acid (H_2L^2) were synthesized according to the previously reported methods with slight modification (Scheme S1 and Fig. S1-S6).[1-4] ^1H and ^{13}C NMR were recorded on a Bruker Model AM-400 (400 MHz) spectrometer. Powder X-ray diffraction patterns were recorded with a Smartlab model X-ray diffractometer with Cu Kα radiation (λ=1.5406 Å). The morphology of samples was observed using a Hitachi SU8220 scanning electron microscope. Ultraviolet visible diffuse reflectance spectra were collected by a U-3010 spectrophotometer, barium sulfate ($BaSO_4$) was used as the reference. Thermogravimetric analyses experiments were collected on TGA 500. The Brunauer-Emmett-Teller specific surface area measurements were conducted by a Micromeritics ASAP 2460 at 77K and the pore size distribution was calculated from the nonlocal density functional theory method. The Mott-Schottky plots, electrochemical

impedance spectroscopy and photocurrent tests were completed by using the CHI 760E. X-ray photoelectron spectroscopy was obtained with a Thermo Scientific K-Alpha XPS. Electron paramagnetic resonance spectra were measured on a Bruker Elexsys-II E500 spectrometer.

Synthesis of Ligands

The synthesis route of 2-amino[1,1′-biphenyl]-4,4′-dicarboxylic acid (H_2L^1) and 2,2′-diamino[1,1′-biphenyl]-4,4′-dicarboxylic acid (H_2L^2) was shown in Scheme S1.



Scheme S1 Synthesis route of H_2L^1 and H_2L^2

4,4′-Dimethyl 2-nitro[1,1′-biphenyl]-4,4′-dicarboxylate (1) Dimethyl 4,4'-biphenyldicarboxylate (2 g, 7.40 mmol) was dissolved in 15 mL of concentrated H_2SO_4 and cooled to below 5 °C. A mixture of concentrated HNO_3 (482 μL, 7.40 mmol) and concentrated H_2SO_4 (3 mL) was added and the reaction was carried out at a controlled temperature below 5 °C for 20 min. After reaction, the solution was poured into ice water (500 ml) and the solid was washed with water until pH=7, dried under vacuum to obtain a white product (1.96 g, yield: 84%). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.55 (d, J = 1.7 Hz, 1H), 8.28 (dd, J = 8.0, 1.7 Hz, 1H), 8.11 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 8.4 Hz, 2H), 3.99 (s, 3H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.56, 164.81, 149.06, 141.18, 139.59,

133.23, 132.22, 131.14, 130.60, 130.16, 127.99, 125.61, 52.98, 52.44.

4,4′-Dimethyl 2-amino[1,1′-biphenyl]-4,4′-dicarboxylate (2) 4,4′-Dimethyl 2-nitro[1,1′-biphenyl]-4,4′-dicarboxylate (1.80 g, 5.70 mmol) was dissolved in 50 ml of glacial acetic acid, iron powder (6.40 g, 114 mmol) was added and stirred for 4 hours at 40 °C. The mixture was filtered through a Brinell funnel and extracted with ethyl acetate, the solvent was centrifuged, washed with water and saturated sodium carbonate solution and dried under vacuum to obtain the product (1.06 g, yield: 65%). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.12 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 7.9 Hz, 1H), 7.49 (s, 1H), 7.20 (d, J = 7.9 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.12, 166.89, 143.39, 143.16, 130.95, 130.89, 130.53, 130.37, 129.63, 129.04, 120.19, 117.08, 52.39, 52.31.

2-Amino[1,1′-biphenyl]-4,4′-dicarboxylic acid (H_2L^1) 4,4′-Dimethyl 2-amino[1,1′-biphenyl]-4,4′-dicarboxylate (990 mg, 3.47 mmol) was dissolved in a mixture of THF (35 mL) and MeOH (25 mL), and the above solution was mixed with KOH (2 g, 35.7 mmol) in 40 mL of water and refluxed overnight. The reaction solution was concentrated under vacuum and diluted with water, acidified with 1 **M** HCl to pH = 2, filtered, washed with water and dried to obtain H_2BPDC-NH_2 (839 mg, yield: 94%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.83 (s, 2H), 8.02 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.1 Hz, 2H), 7.41 (d, J = 1.6 Hz, 1H), 7.21 (dd, J = 8.0, 1.6 Hz, 1H), 7.11 (d, J = 7.9 Hz, 1H), 5.17 (s, 2H).

4,4′-Dimethyl 2,2′-dinitro[1,1′-biphenyl]-4,4′-dicarboxylate (3) Dimethyl 4,4'-biphenyldicarboxylate (2.7 g, 10 mmol) was dissolved in 25 mL of concentrated H_2SO_4 and cooled to below 5 ℃. A mixture of concentrated HNO_3 (1.4 mL) and concentrated H_2SO_4 (1.6 mL) was added and the reaction was carried out at a controlled temperature below 5 ℃ for 6 hours. After reaction, the solution was poured into ice water and the solid was washed with water until pH=7, dried under vacuum to obtain 4,4′-Dimethyl 2,2′-dinitro[1,1′-biphenyl]-4,4′-dicarboxylate (3.24 g, yield: 90%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.90 (d, *J* = 1.6 Hz, 2H), 8.36 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 4.02 (s, 6H).

4,4′-Dimethyl 2,2′-diamino[1,1′-biphenyl]-4,4′-dicarboxylate (4) 4,4′-Dimethyl 2,2′-dinitro[1,1′-biphenyl]-4,4′-dicarboxylate (1.81 g, 5 mmol) was dissolved in 50 ml of glacial

acetic acid, iron powder (8.42 g, 150 mmol) was added and stirred for 4 hours at 40 °C. The mixture was filtered through a Brinell funnel and extracted with ethyl acetate, the solvent was centrifuged, washed with water and saturated sodium carbonate solution and dried under vacuum to obtain the product (1.28 g, yield: 85%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.45 (d, J = 1.7 Hz, 2H), 7.23 (dd, J = 7.9, 1.7 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 5.00 (s, 4H), 3.83 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.05, 146.08, 131.28, 130.12, 128.06, 117.66, 116.28, 52.41.

2,2′-Diamino[1,1′-biphenyl]-4,4′-dicarboxylic acid (H_2L^2) 4,4′-Dimethyl 2,2′-diamino[1,1′-biphenyl]-4,4′-dicarboxylate (864 mg, 2.88 mmol), THF (36 mL), MeOH (18 mL) and 36 mL of aqueous LiOH (0.6 M) were added to a round-bottom flask. The mixture was reacted at 35°C for 24h. The reaction solution was concentrated under vacuum and diluted with water, acidified with glacial acetic acid, filtered, washed with water and dried to obtain H_2BPDC-$(NH_2)_2$ (671 mg, yield: 86%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.66 (s, 2H), 7.42 (d, J = 1.7 Hz, 2H), 7.22 (dd, J = 7.8, 1.7 Hz, 2H), 7.05 (d, J = 7.9 Hz, 2H), 4.93 (s, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.14, 145.90, 131.25, 131.10, 127.89, 117.98, 116.58.

Synthesis of UiO-67-NH_2 and UiO-67-$(NH_2)_2$

UiO-67-NH_2 and UiO-67-$(NH_2)_2$ were synthesized by following the previously reported methods with slight modification.[5] Specifically, $ZrCl_4$ (60 mg, 0.26 mmol), H_2L^1 (64.30 mg, 0.25 mmol) and benzoic acid (940 mg, 7.70 mmol) were dispersed in 10 mL of N, N-dimethylformamide (DMF), then the mixture was placed in a Teflon liner and sonicated for 10 minutes. After 24 h of reaction at 120 ℃, the powder was collected and washed with DMF and acetone. Finally, the product was dried under vacuum. The preparation method of UiO-67-$(NH_2)_2$ is similar to that of UiO-67-NH_2, except that ligand H_2L^2 is used instead of H_2L^1.

Photocatalytic H_2O_2 production

MOFs based Photocatalyst (5 mg) was suspended in deionized water (5 mL) and oxygen atmosphere was provided by an oxygen balloon. The dispersion liquid was stirred in the dark for 0.5 hour and then a blue LED (40 W) was used as the light source. The concentration of

H_2O_2 was measured by spectroscopic titration in an acidic solution of $Ce(SO_4)_2$.[6] To be specific, 2.5 mL of the reaction solution was centrifuged at 7500 rpm and then filtrated with a 0.22 μm filter to remove the photocatalyst. The sample was mixed with pre-prepared $Ce(SO_4)_2$ solution (1 mM), and the yellow solution of Ce^{4+} can be reduced by H_2O_2 to produce colorless Ce^{3+} (Eq. 1). The concentration of H_2O_2 could be calculated from the change of Ce^{4+} concentration (Eq. 2).

To get the calibration curve, $Ce(SO_4)_2$ of different mass was dissolved in 0.5 M H_2SO_4 and the absorption intensity was measured by UV-vis spectrometer (Fig. S7a). The linear relationship between absorption intensity and Ce^{4+} concentration can be found in Fig. S7b). The absorption peak used for the measurement is 316 nm.

$$2Ce^{4+} + H_2O_2 \rightarrow 2Ce^{3+} + 2H^+ + O_2 \qquad (1)$$

$$c(H_2O_2) = 1/2 \times c(Ce^{4+}) \qquad (2)$$

2. Characterization Results

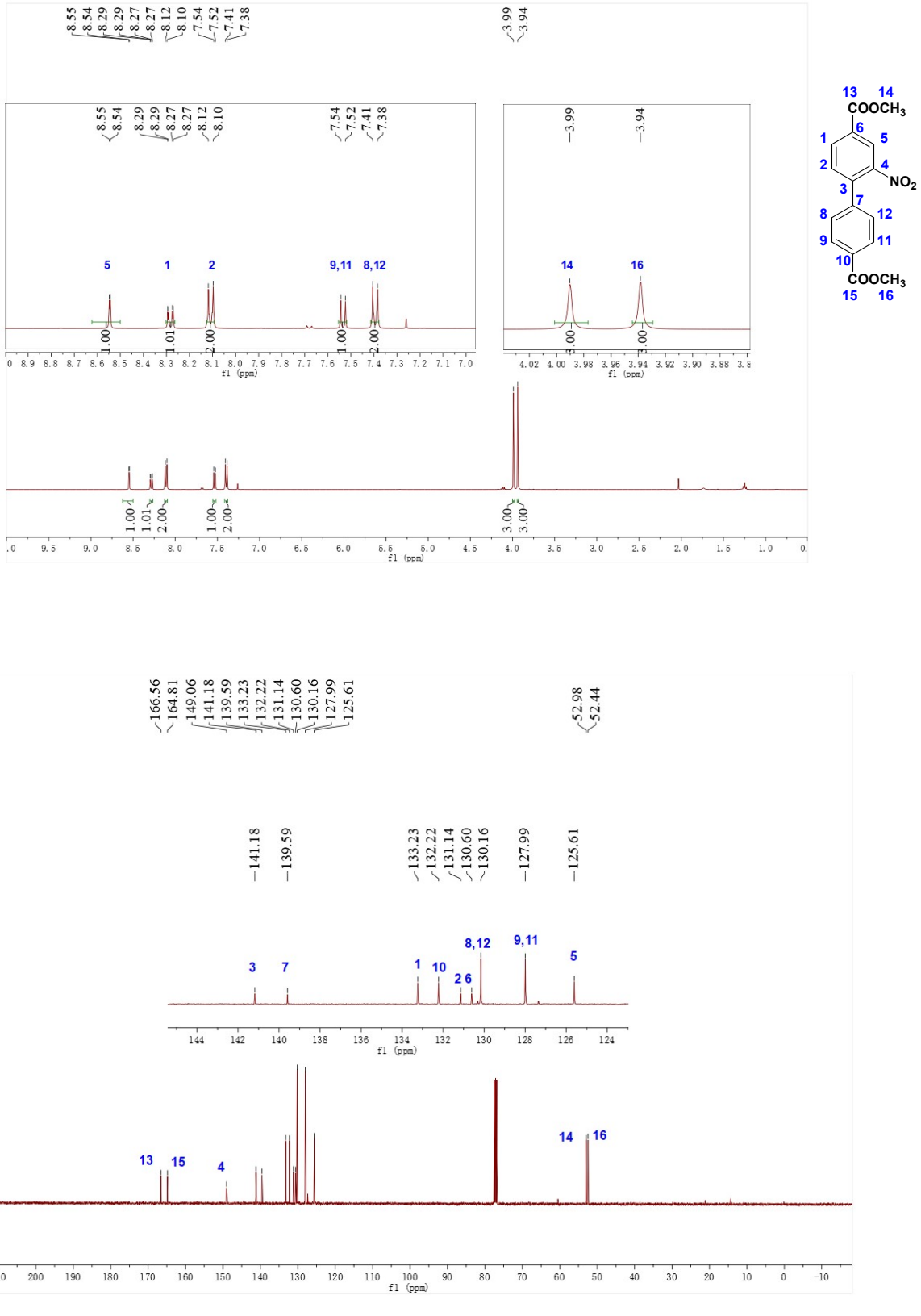
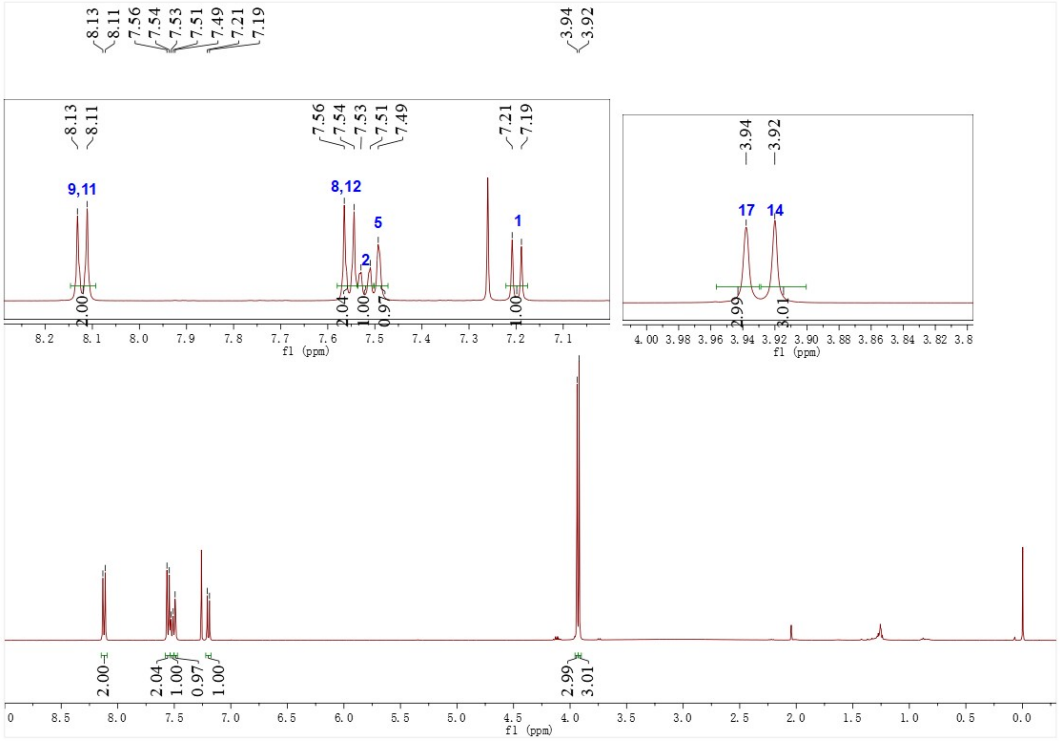


Fig. S1 ^{1}H NMR and ^{13}C NMR of **1**



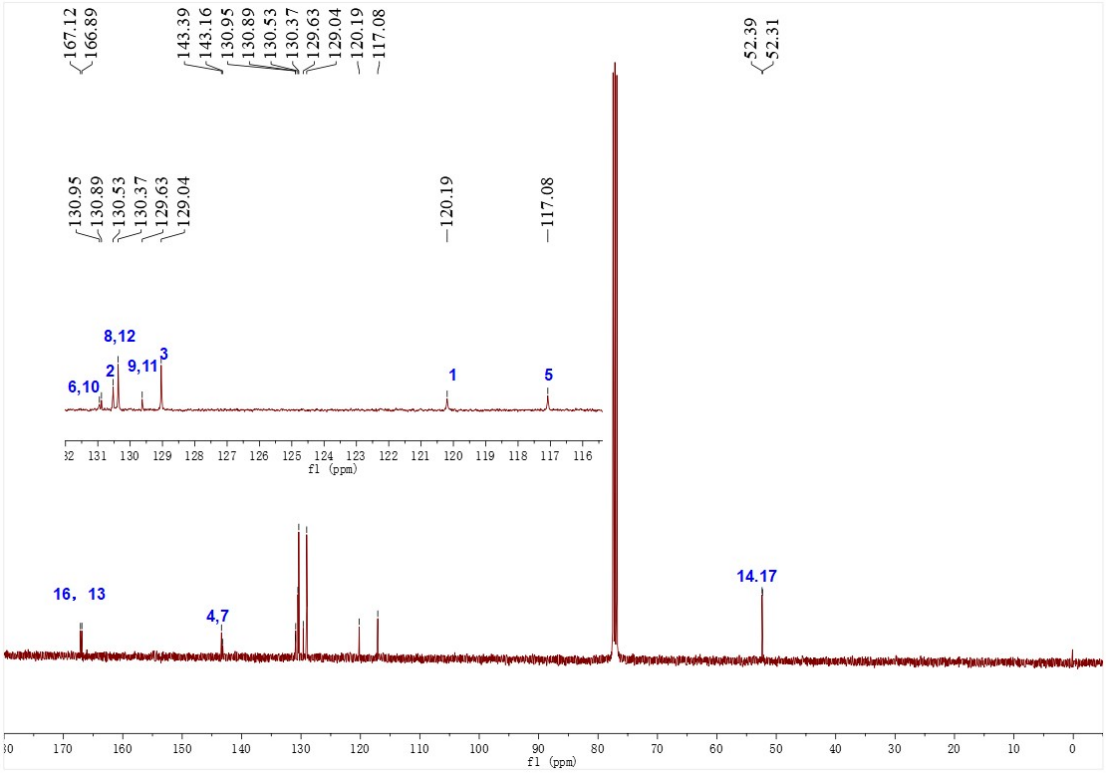


Fig. S2 ^{1}H NMR and ^{13}C NMR of **2**

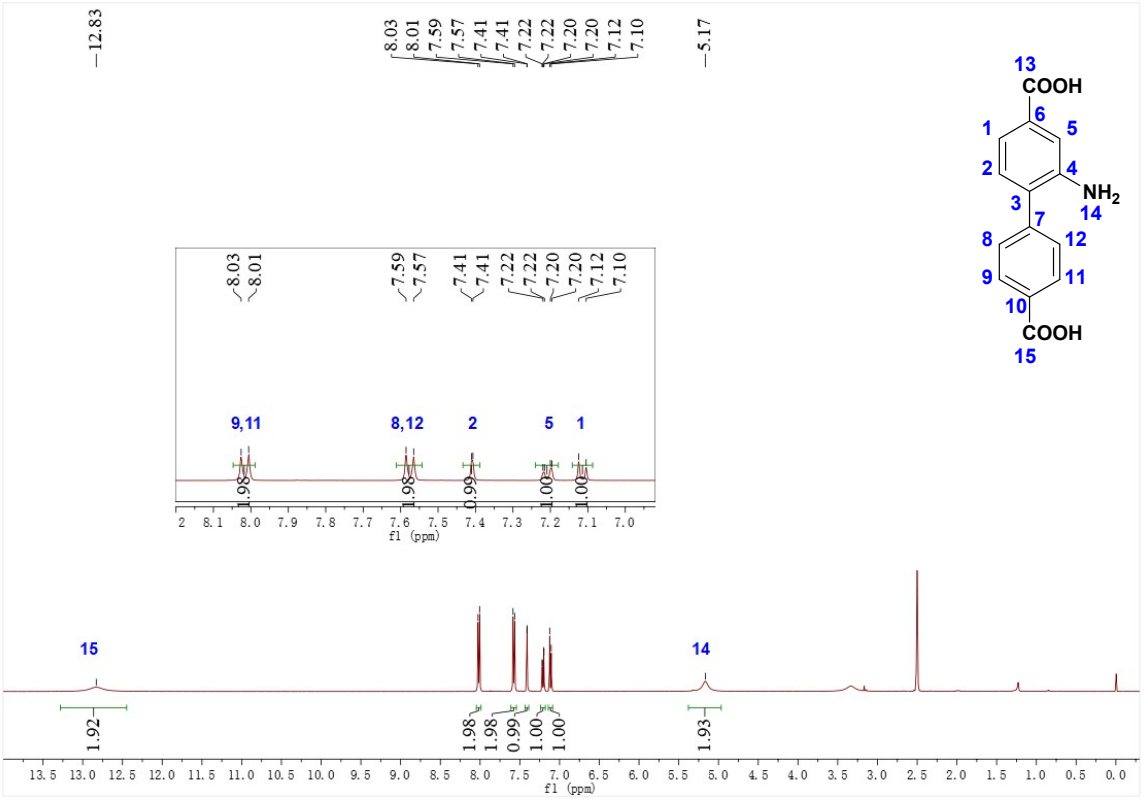


Fig. S3 ^{1}H NMR of $\mathbf{H_2L^1}$

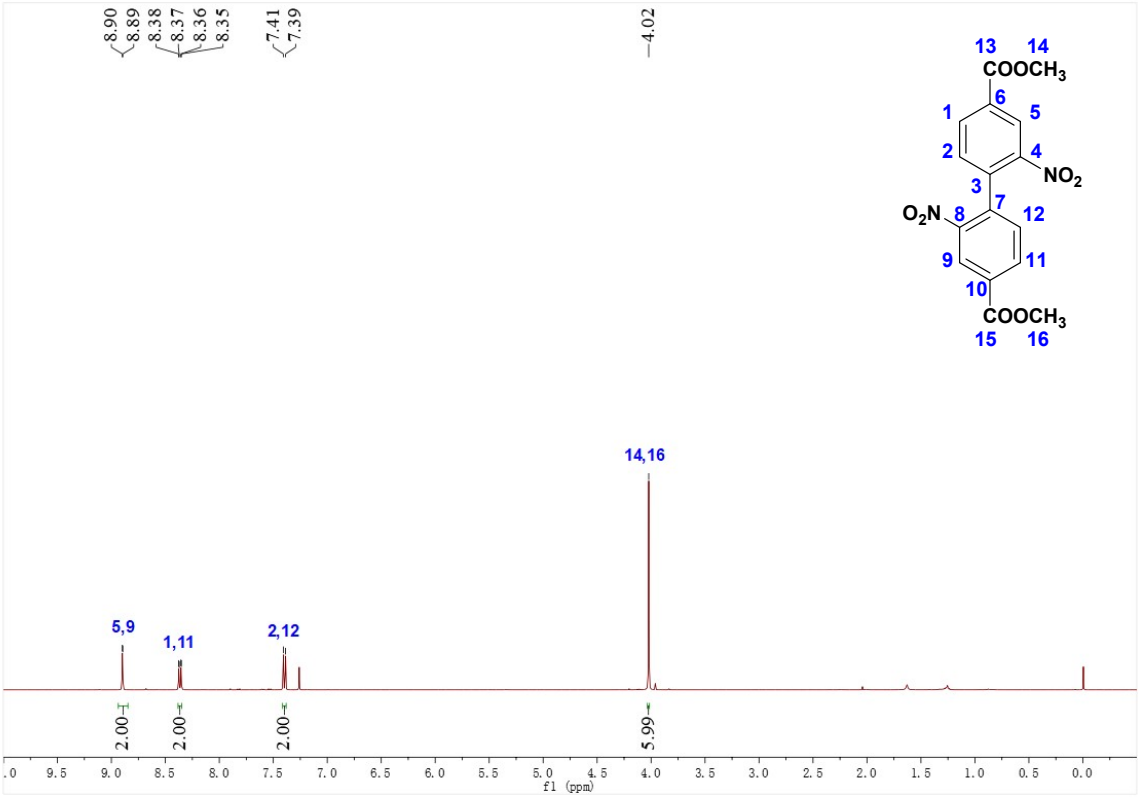


Fig. S4 ^{1}H NMR of **3**

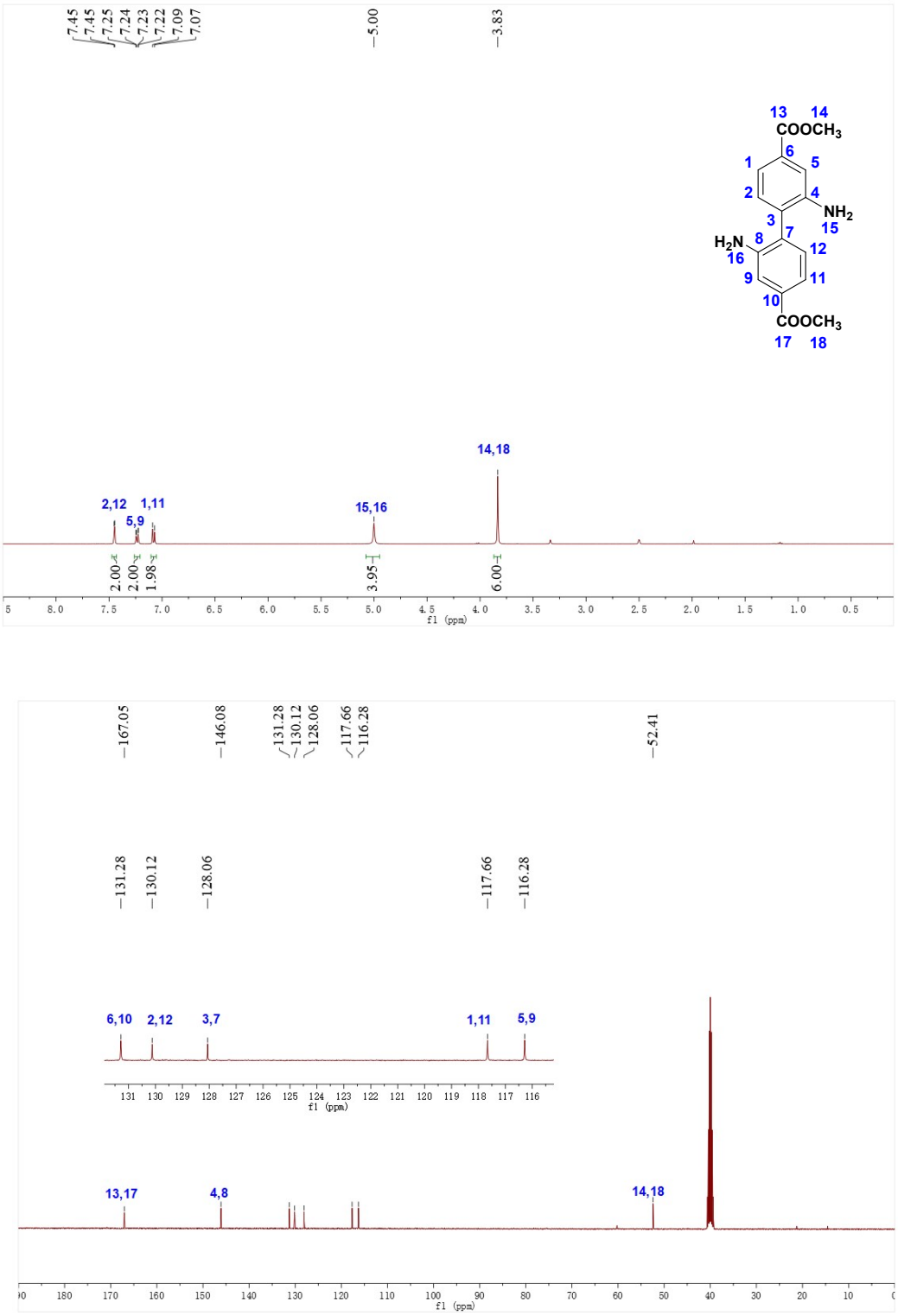
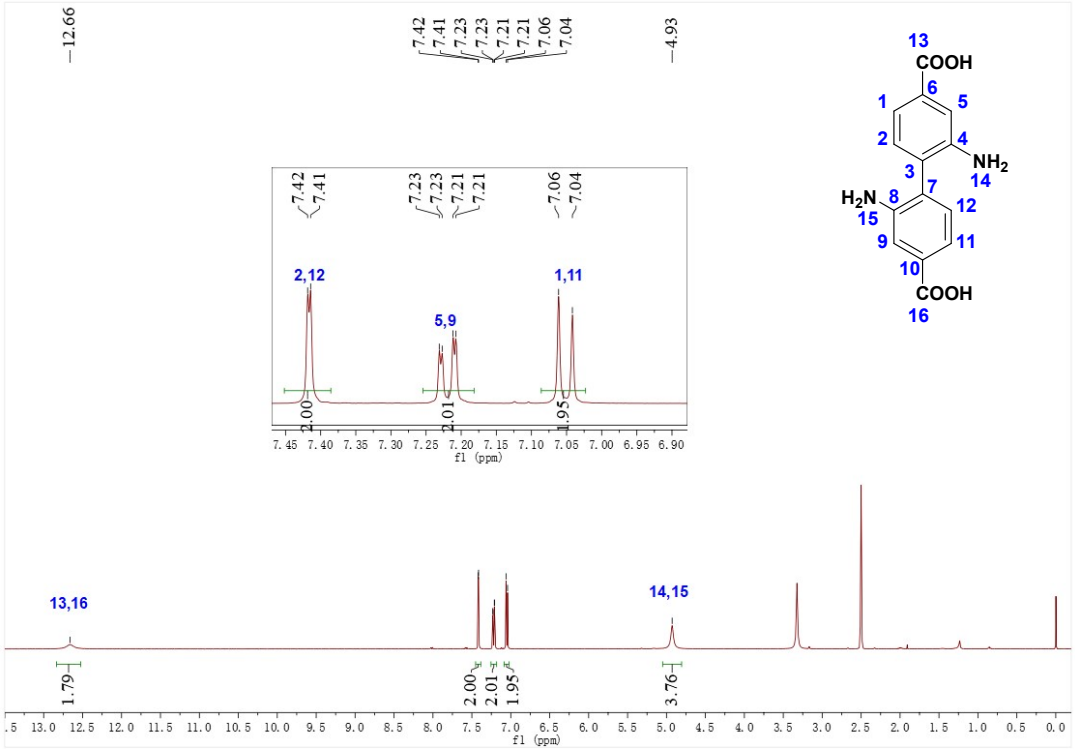


Fig. S5 ^{1}H NMR and ^{13}C NMR of **4**



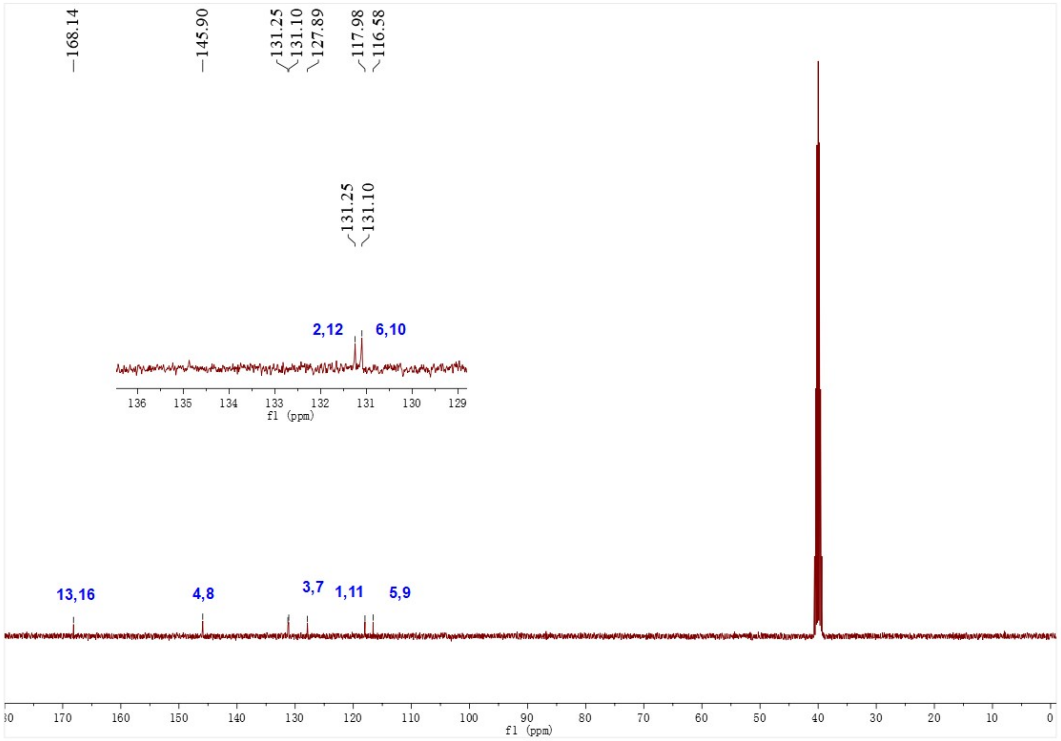


Fig. S6 ^{1}H NMR and ^{13}C NMR of $\mathbf{H_2L^2}$

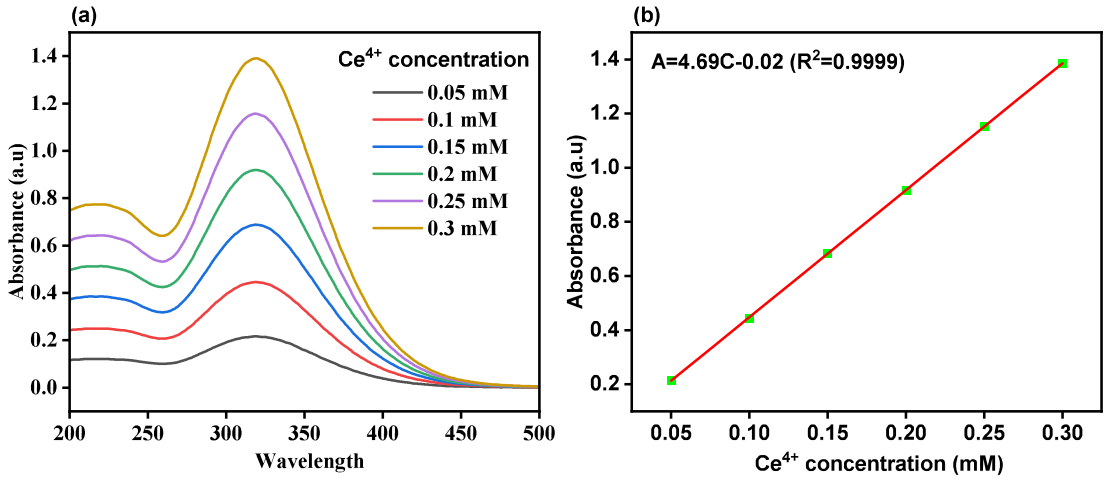


Fig. S7 (a) UV-vis absorption spectra of Ce^{4+} solutions with different concentrations. (b) Corresponding calibration curve at the absorption peak of 316 nm.

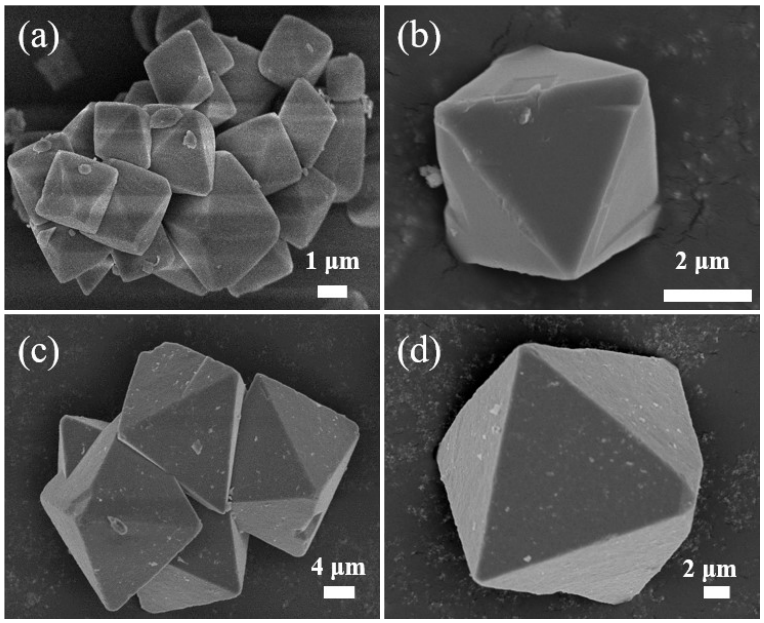


Fig. S8 The SEM of (a) the whole and (b) the single octahedron of UiO-67-$(NH_2)_2$, The SEM of (c) the whole and (d) the single octahedron of UiO-67-NH_2.

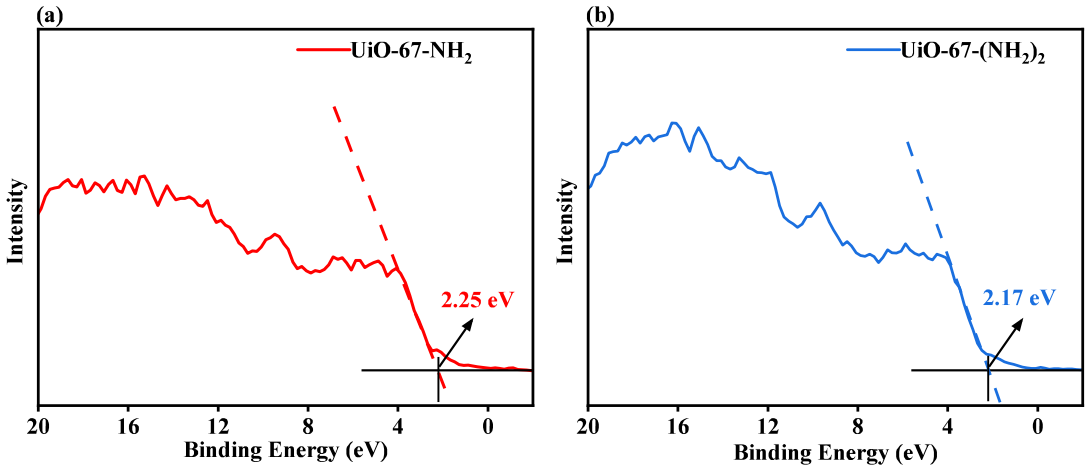


Fig. S9 The XPS valence band spectra of (a) UiO-67-NH_2 and (b) UiO-67-$(NH_2)_2$.

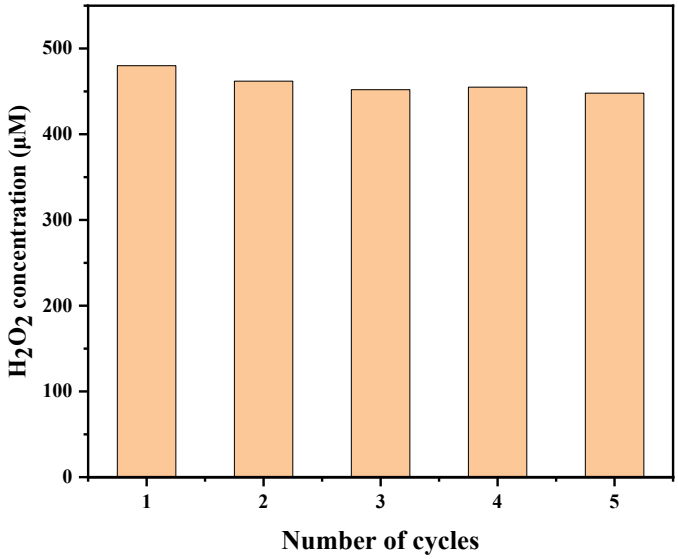


Fig. S10 Cycling tests of UiO-67-$(NH_2)_2$.

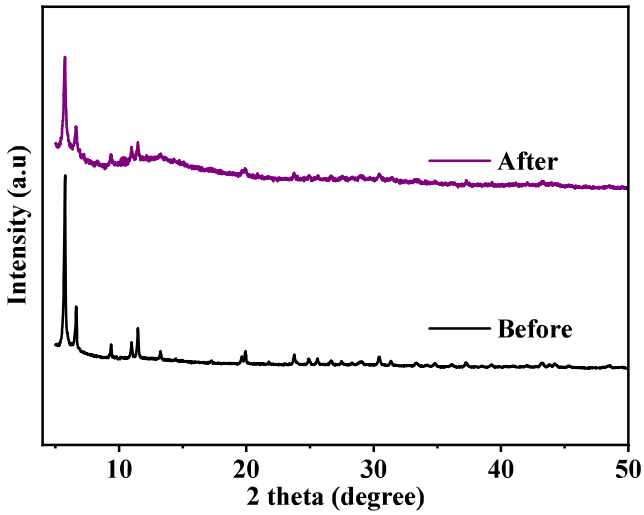


Fig. S11 The PXRD patterns of UiO-67-$(NH_2)_2$ before and after the reaction.

Photocatalyst	Light source	H_2O_2 yield ($mM \cdot g^{-1}_{cat} \cdot h^{-1}$)	Solvent	Gas	Catalyst amount ($g \cdot L^{-1}$)	Ref.
CTF-BDDBN	500 W Xe lamp λ>400 nm	1.94	water	O_2	0.6	7
MIL-111/001	500 W Xe lamp λ>400 nm	60.05	water	O_2	0.4	8
Ni-CAT-CN_{60}	Xe lamp λ>420 nm	120.07	water	air	0.67	9
COF-TfpBpy	300 W Xe lamp λ>420 nm	69.47	water	air	1.5	10
HEP-TAPT-COF	300 W Xe lamp λ>420 nm	16.9	water	O_2	0.5	11
C_5N_2	300 W Xe lamp λ>400 nm	15.5	water	O_2	10	12
PQTEE-COP	300 W Xe lamp λ≥400 nm	100.3	water	O_2	0.6	13
UiO-67-$(NH_2)_2$	40 W Blue LED λ=427 nm	96	water	O_2	1	**This work**

Table S1 Summary of the reaction condition of photocatalysts for H_2O_2 production.

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