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NIR-II light-response porphyrin-heptazine-based conjugated organic polymers for highly efficient photooxidation

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Contents

1. Experimental Section

1.1 Reagents

All reagents were used as received unless otherwise noted. 5,10,15,20-Tetraphenylporphyrin (H_2TPP), melamine, cupric (II) acetate monohydrate, nickel (II) acetate tetrahydrate, phosphorus oxychloride, phosphorus pentachloride and aluminum chloride were purchased from Anhui Zesheng Technology Co., Ltd. Dichloromethane (DCM) was dried by distillation with CaH_2.

1.2 Materials Characterization

Solution-state ^{1}H NMR and ^{13}C NMR spectroscopies were recorded on a 400 MHz spectrometer (Bruker Ascend 400 Spectrometer) with tetramethylsilane as internal standard. Solid-state ^{13}C cross polarization magic angle spinning NMR spectroscopies (CP-MAS NMR) were performed by VANCE NEO 400 spectrometer, equipped with a 9.4 T magnet. Fourier transform infrared spectra (FT-IR) were recorded on a Thermofisher Scientific Nicolet iS50 spectrometer between 4000-400 cm^{-1}. Powder X-ray diffraction (PXRD) patterns were obtained on a Japan Rigaku SmartLab diffractometer. X-ray photoelectron spectroscopies (XPS) were performed on an Axis Ultra DLD spectrometer, equipped with a prereduction chamber. Scanning electron microscopies (SEM) were measured on a FEI Apreo S LoVac microscope. The UV-Vis absorption spectra were recorded on a UV-Vis DRS PE lambda 750 spectrophotometer, equipped with an integrating sphere assembly and BaSO4 was used as reflectance sample. Metal contents were measured by inductively coupled plasma optical emission spectrometer (ICP-OES, SpectroBlue, Germany). Nitrogen adsorption-desorption isotherms were obtained on a nitrogen adsorption apparatus (Surface Area and Pore Analyzer Micromeritics ASAP 2460) with all samples degassed at 373 K for 12 h prior to measurements. Steady-state photoluminescence (PL) spectra were collected by a HITACHI F-4600 spectrofluorometer.

1.3 Theoretical Calculation

Theoretical calculations were carried out using the Gaussian 09 software package.[1,2] All calculations were performed using the density functional theory (DFT) method. The geometries were optimized at the B3LYP-D3/6-31+G(d) level, and the energies were calculated at the same level.

1.4 Photocatalytic Oxidation

Photocatalytic oxidation reaction was performed according to the reported literatures with some modification.[3-6] Experiments were carried out at room temperature under air atmosphere, in a 50 mL quartz photoreactor with irradiation by a 300 W xenon lamp (30 mW cm^{-2}). The ethanol/water (v/v = 1/1) solution of 1,4-DHP (20 mL, 1×10^{-4} M or 1×10^{-3} M) and 20 mg photocatalyst was added to the photoreactor and then irradiated at $\lambda > 420$ nm. The reaction process was monitored by the spectral change of either the decreased absorption intensity of 1,4-DHP at 374 nm or the increased absorption intensity of the oxidative product at 280 nm.

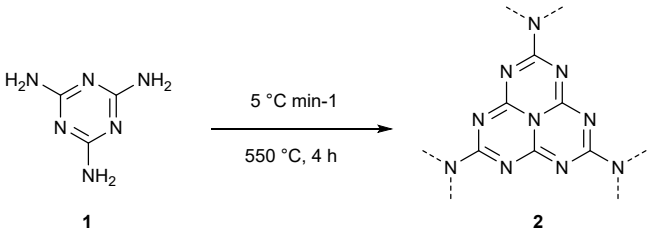
1.5 Electrochemical Experiments

Photocurrent response experiments and electrochemical impedance spectroscopy (EIS) were performed on a Zennium electrochemical workstation (ZAHNER, Germany) with a standard three-electrode cell using Ag/AgCl electrode as the reference electrode, a Pt wire as the counter electrode, sample deposited indium tin oxide (ITO) glass plate as the working electrode, and 0.1 M Na_2SO_4 aqueous solution as the electrolyte solution. The working electrode was manufactured as follows: 2.5 mg catalyst was dispersed in a mixture solution of 225 uL ethanol, 250 uL H_2O and 25 uL Nafion, and sonicated for 30 min. Then, the suspension was transferred onto a 1 cm × 2 cm ITO conductive glass and dried at 60°C. The exposure area of the catalyst is 1 cm^2. The photocurrent density measurements were performed at a 0.05 V bias potential under visible light ($\lambda > 420$ nm, 300 W Xenon light). The EIS datas were obtained using a frequency ranged from 10^6 Hz to 10^{-1} Hz with the open circuit potential at 0.01 V.

1.6 Electron Paramagnetic Resonance (EPR) Measurements

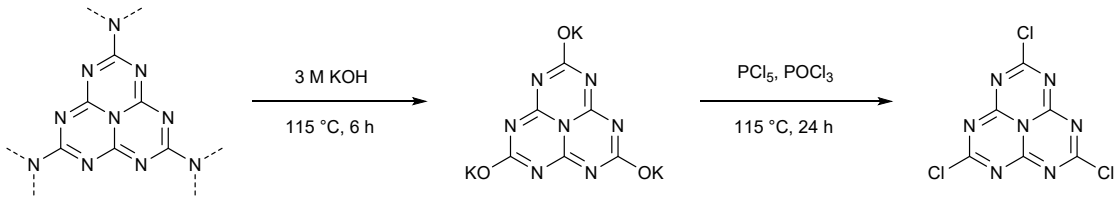
Spin trapping-EPR and unpaired electrons-EPR measurements were recorded using a Bruker EPR spectrometer operating at the X-band frequency (9.85 GHz). For Spin trapping-EPR measurements, 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) were used to detect superoxide anion radical ($O_2^{\bullet-}$). The detailed measurements were conducted as follows: catalysts (1 mg L^{-1}) were dispersed in a mixed solution of DMPO (20 mmol L^{-1}) and 1,4-DHP (5 mL, 1 x 10^{-3} mol L^{-1}). Before spin trapping-EPR tests, the mixture was stirred for 30 min under light (λ > 420 nm, 300 W Xenon light) or in darkness and then transported into quartz capillaries. For unpaired electrons-EPR measurements, catalyst (~5 mg) was injected into quartz capillaries without further treatment.

1.7 Synthetic Procedure



1 2

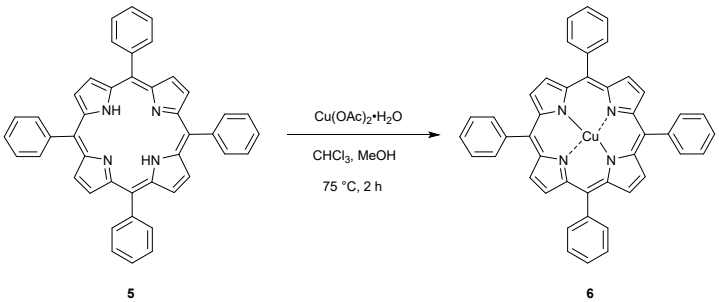
Synthesis of g-C_3N_4 (2).[7] Melamine (40.0 g, 317.2 mmol) was placed in a ceramic crucible and heated to 550°C at a rate of 5°C min^{-1} in a muffle furnace and stood for 4 h. After completed, the system was cooled to room temperature at an unrestricted rate and then the solid was ground to obtain compound **2** as a yellow powder.



2 3 4

Synthesis of Cymeluric Chloride (4).[8] Compound **2** (10 g) was dispersed in a aqueous solution of KOH (3 M, 150 mL) and then the mixture was heated at 115 °C for 6 h. The solution was filtered while hot and the filtrate was cooled in an ice-water bath. After that, the precipitated white crystals were collected by filtration and washed with ice ethanol. Finally, the products were dried in a vacuum oven at 80°C for 24 h without further treatment.

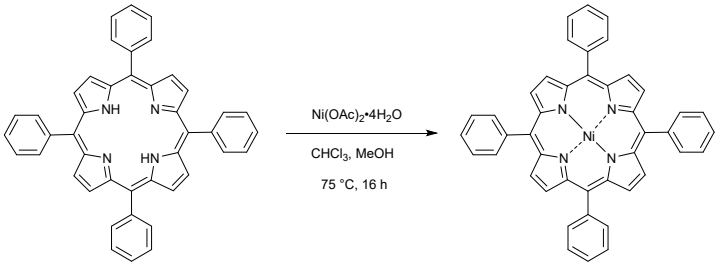
Compound **3** (6 g, 17.9 mmol) and PCl_5 (12 g, 57.7 mmol) was dispersed in $POCl_3$ (120 mL) in argon atmosphere. The mixture was heated at 115°C for 24 h. After completed, the mixture was filtered and the filtrate was removed by rotary evaporator. The residue was further treated by Soxhlet extraction with toluene for 24 h. Then, the solvent was removed by rotary evaporator and the residue dried under vacuum for 6 h, giving the final product **4** as a light-yellow solid (3.5 g, 72%). IR (KBr, cm^{-1}): 1643, 1608, 1502, 1451, 1377, 1302, 1199, 1095, 957, 831, 647, 452. ^{13}C NMR (400 MHz, benzene-d_6, ppm): δ 175.3 (N-C=N), 155.4 (C-Cl).



5 6

Synthesis of Cu(II)-Tetraphenylporphyrin (6, CuTPP).[9] Compound **5** (760 mg, 1.24 mmol) and $Cu(OAc)_2 \cdot H_2O$ (1.361 g, 6.2 mmol) were dissolved in a mixed solution of $CHCl_3$ and MeOH (300 mL, v/v = 2:1) and then the solution was refluxed at 75°C for 2 h. After completed, the mixture was cooled to room temperature and then poured into water, extracted with chloroform. The organic layer was dried over

Na_2SO_4. After filtered, the solvent was removed by rotary evaporator, giving compound **6** as a red and black solid (793 mg, 95%). FTIR (KBr, cm^{-1}): 3052, 2921, 1597, 1440, 1345, 1070, 1004, 793, 742, 697. MS (MALDI-TOF): m/z calcd for $CuC_{44}H_{28}N_4$, $[M+H]^+$:676.3; found: 677.1.



5 7

Synthesis of Ni(II)-Tetraphenylporphyrin (7, NiTPP).[10] Compound **5** (760 mg, 1.24 mmol) and $Ni(OAc)_2 \cdot 4H_2O$ (622 mg, 3.72 mmol) were dissolved in a mixed solution of $CHCl_3$ and MeOH (300 mL, v/v = 2:1) and then the solution was refluxed at 75°C for 16 h. When completed, the mixture was cooled to room temperature. After removal of the solvents under reduced pressure, the residue was purified via column chromatography over silica gel (eluent: from PE/DCM = 2:1, v/v to DCM), giving compound **7** as a purple and black solid (640 mg, 77%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.68 (d, 12H), 8.02 (d, 8H), 8.74 (s, 8H). The FTIR spectra of NiTPP is similar with CuTPP. MS (MALDI-TOF): m/z calcd for $C_{44}H_{28}N_4Ni$, $[M+H]^+$: 671.4; found: 671.7.

Synthesis of Heptazine-Based Polymers (MTPP-Cys). In general, free-base or metalated tetraphenylporphyrins (0.75 mmol) and Cy (1 mmol) were dissolved in anhydrous DCM (50 mL) in argon atmosphere. The system was kept at 25°C and anhydrous $AlCl_3$ (14.5 mmol) was added. Then, the mixture was refluxed with 55°C oil-bath for 72 h. After that, the system was cooled to room temperature and then filtered to obtain the crude product, which was washed successively with HCl (1 M), methanol and DCM. Further purification was carried out by Soxhlet extraction with the mixture of methanol and THF for 24 h. Finally, the products were dried in a vacuum oven at 80°C for 24 h.

2. Characterization

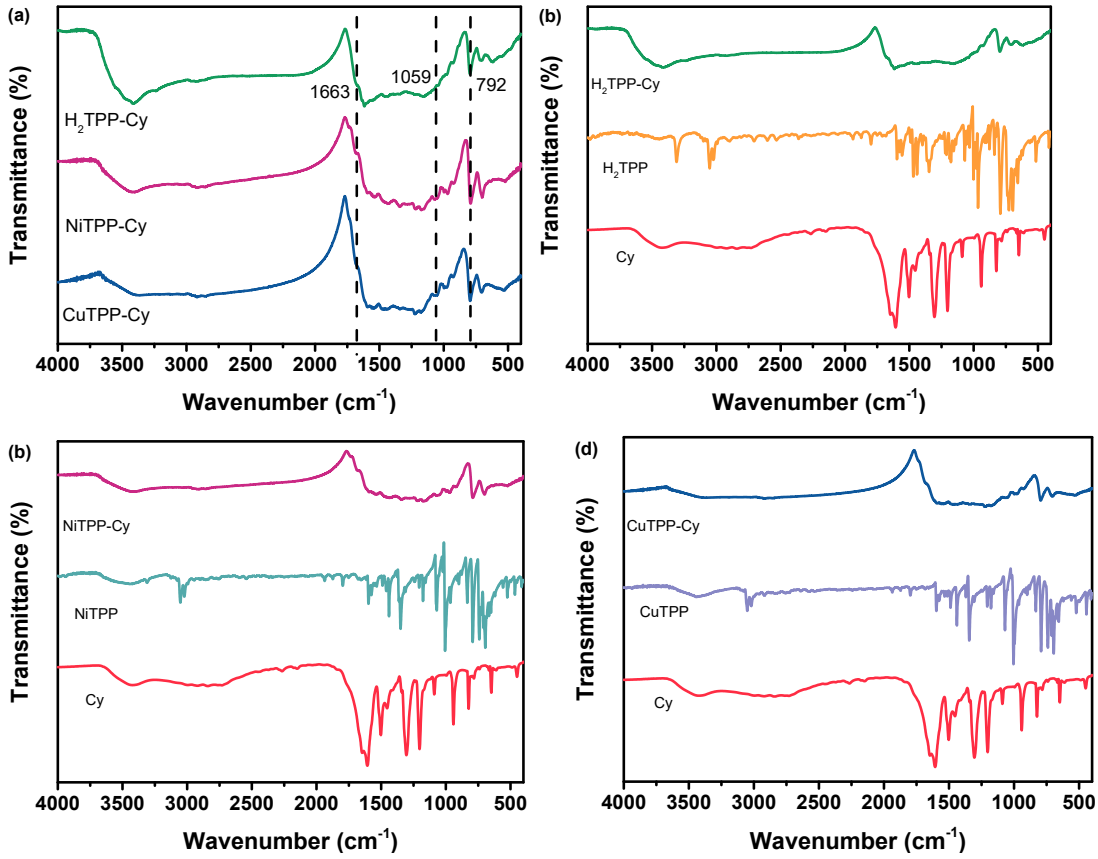


Figure S1. FT-IR spectra. (a) MTPP-Cys; (b) H_2TPP-Cy, (c) NiTPP-Cy, (d) CuTPP-Cy and their corresponding precursors.

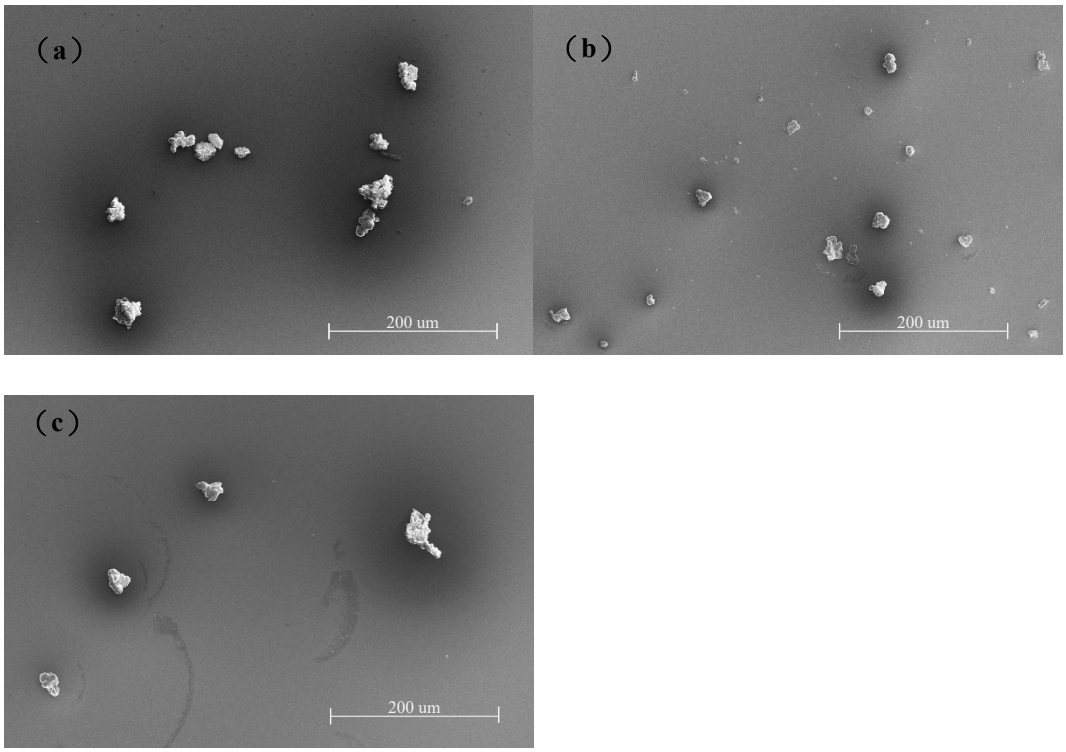


Figure S2. SEM spectra of MTPP-Cys. (a) H_2TPP-Cy; (b) NiTPP-Cy; (c) CuTPP-Cy.

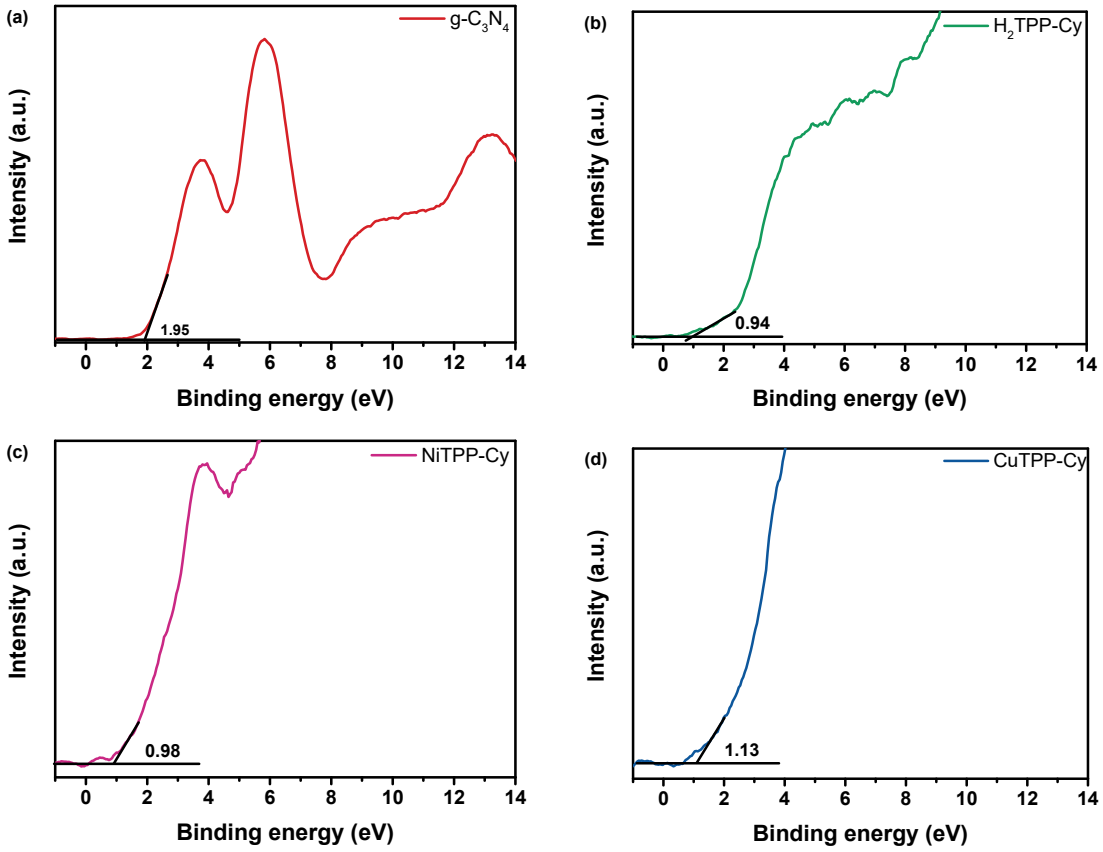


Figure S3. Valence band XPS spectra of g-C_3N_4 and MTPP-Cys. (a) g-C_3N_4; (b) H_2TPP-Cy; (c) NiTPP-Cy; (d) CuTPP-Cy.

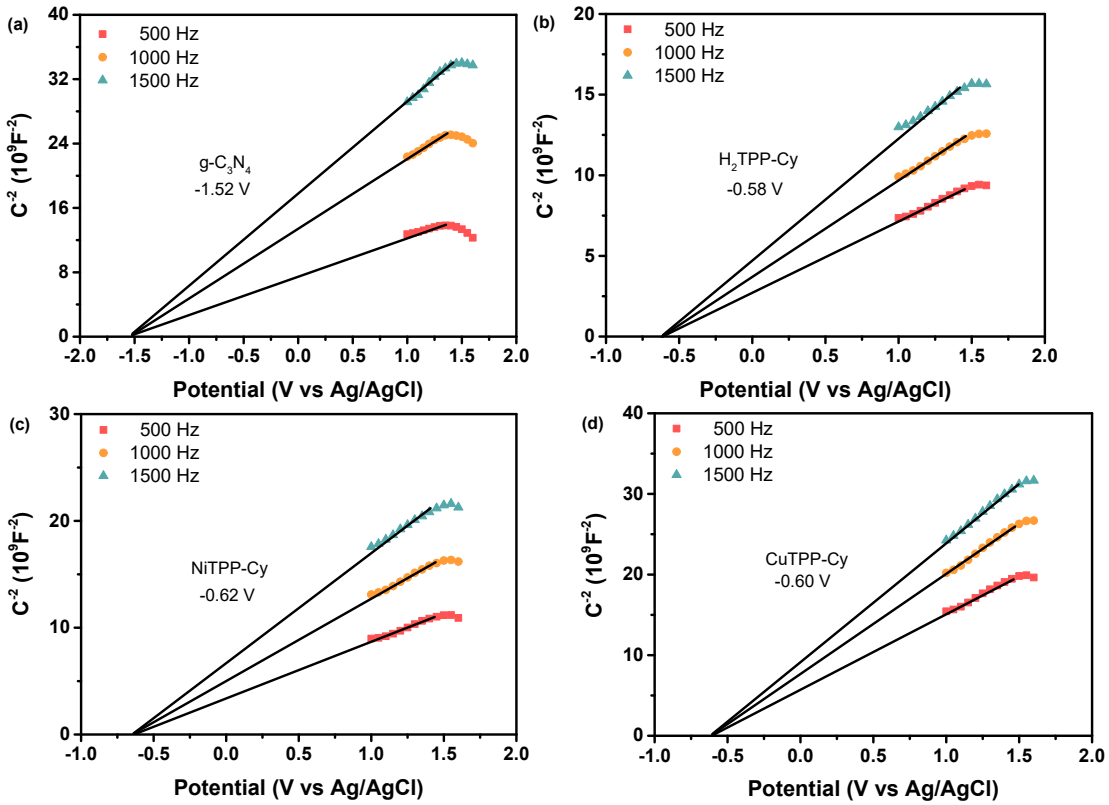


Fig S4. The determined flat-band potential of (a) g-C_3N_4, (b) H_2TPP-Cy, (c) NiTPP-Cy, (d) CuTPP-Cy by the Mott−Schottky method.

3. Structural optimization

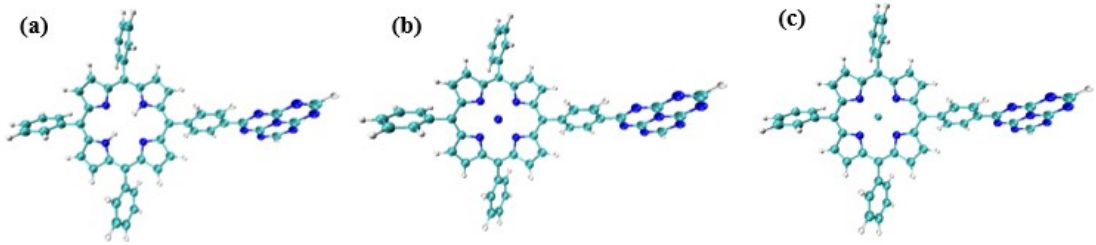


Figure S5. Structural optimization of MTPP-Cys by theoretical calculation. (a) H_2TPP-Cy; (b) NiTPP-Cy; (c) CuTPP-Cy.

4. Photooxidation of 1,4-DHP (10^{-4} M).

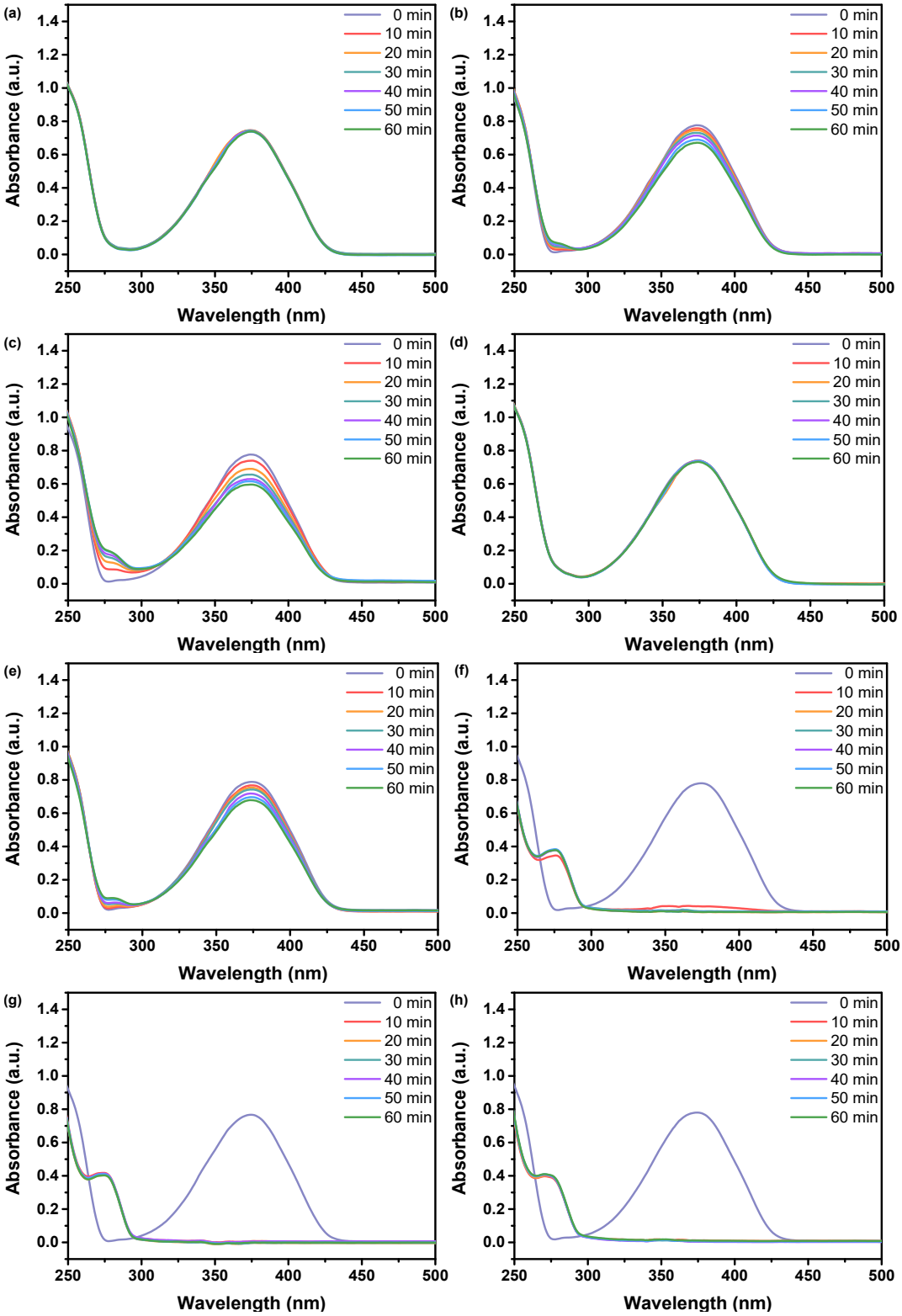


Figure S6. UV-vis absorption spectral change for the photooxidation of 1,4-DHP (10^{-4} M) catalyzed by different catalysts under irradiation with a xenon lamp ($\lambda > 420$ nm). (a) none; (b) g-C_3N_4; (c) CuTPP; (d) NiTPP; (e) H_2TPP; (f) CuTPP-Cy; (g) NiTPP-Cy; (h) H_2TPP-Cy.

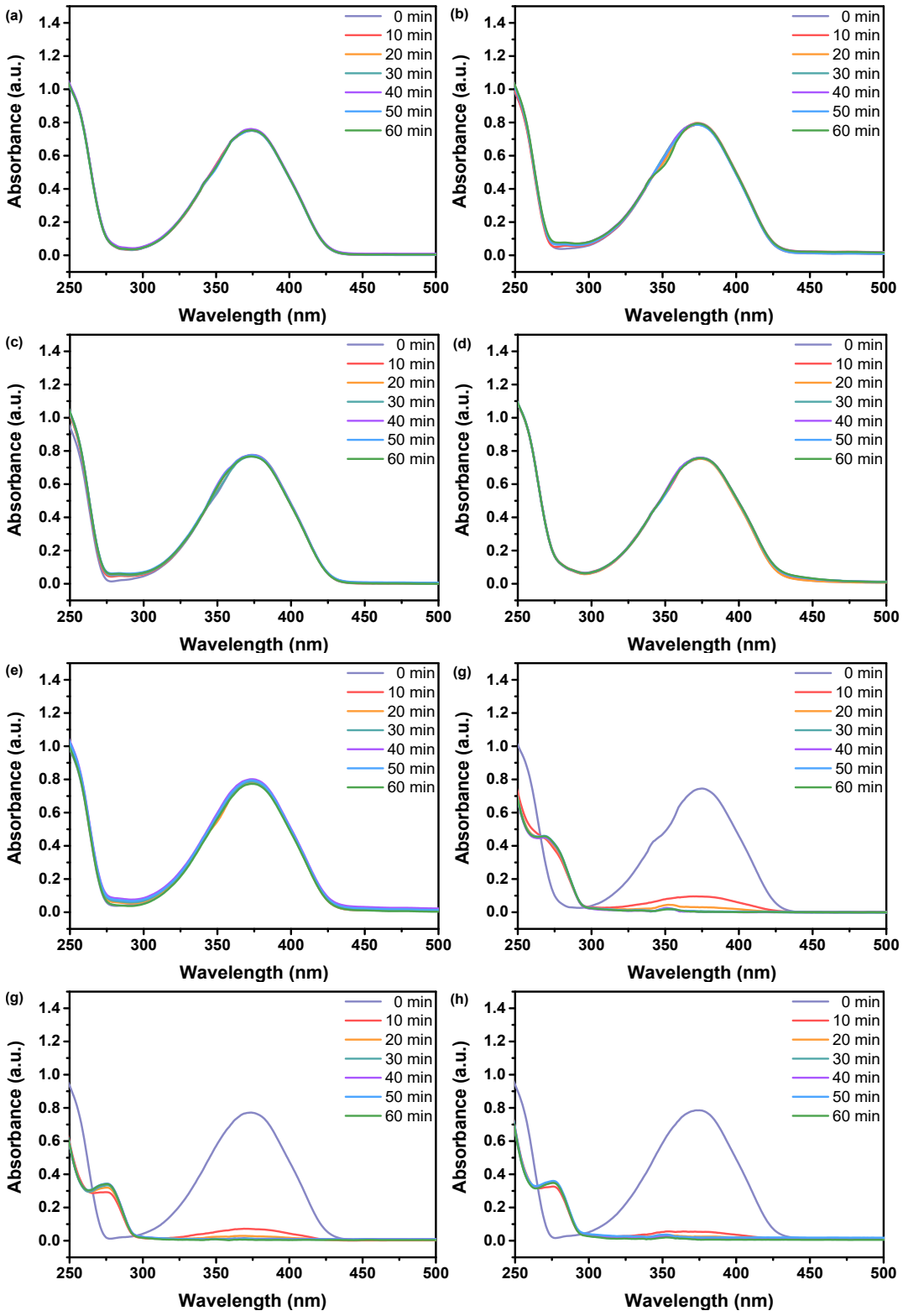
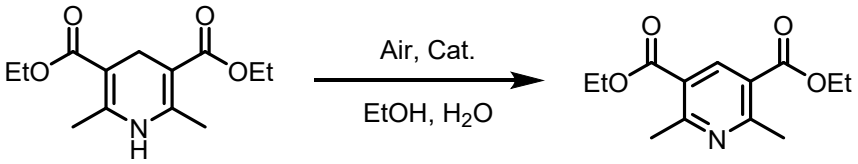


Figure S7. UV-vis absorption spectral change for the photooxidation of 1,4-DHP (10^{-4} M) catalyzed by different catalysts in darkness. (a) none; (b) g-C_3N_4; (c) CuTPP; (d) NiTPP; (e) H_2TPP; (f) CuTPP-Cy; (g) NiTPP-Cy; (h) H_2TPP-Cy.

Table S1. Phtooxidation of 1,4-DHP (10^{-4} M) catalyzed by different catalysts.



Entries[a]	Catalyst	Conditions[b]	Time/min	Conversion [c]/%
1	None	darkness	60	0
2		Light	60	0
3	$g\text{-}C_3N_4$	darkness	60	0
4		Light	60	14
5	CuTPP	darkness	60	0
6		Light	60	23
7	NiTPP	darkness	60	0
8		Light	60	0
9	H_2TPP	darkness	60	0
10		Light	60	14
11	CuTPP-Cy	darkness	≤30	>99
12		Light	≤20	>99
13	NiTPP-Cy	darkness	≤30	>99
14		Light	≤10	>99
15	H_2TPP-Cy	darkness	≤20	>99
16		Light	≤10	>99

[a] $C_{catalysts}$ = 1 mg mL^{-1}, $V_{solvent}$ = 20 mL (EtOH and H_2O, v/v = 1:1), $C_{1,4\text{-}DHP}$ = 10^{-4} M

[b] In darkness or under irradiation with a xenon lamp (λ > 420 nm).

[c] Determined by UV-Vis spectroscopy.

5. NMR spectra of the product.

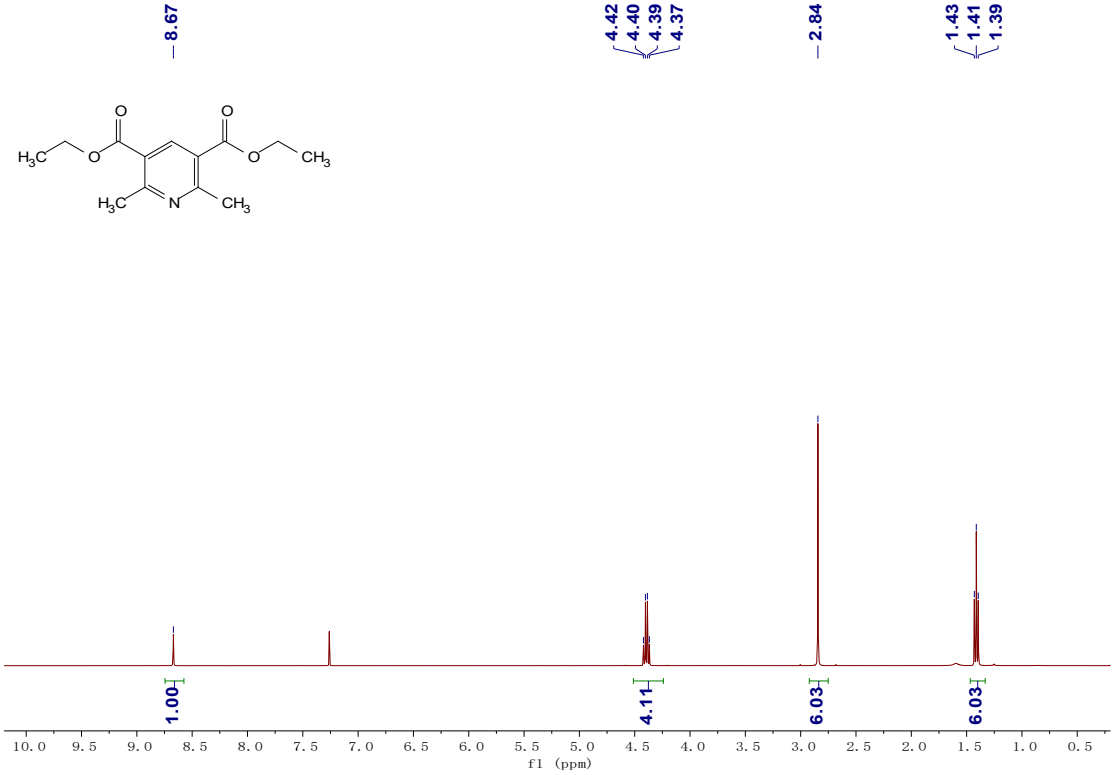


Figure S8. ^{1}H NMR spectrum of the product.

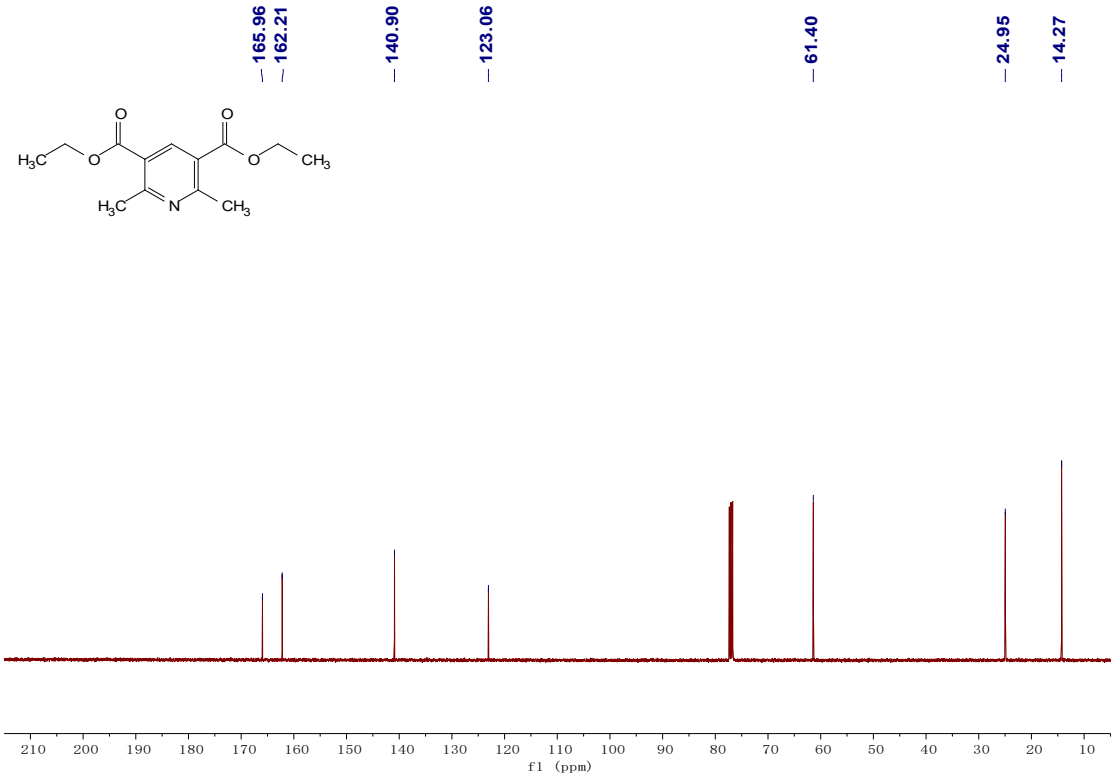


Figure S9. ^{13}C NMR spectrum of the product.

6. Photooxidation of 1,4-DHP (10^{-3} M).

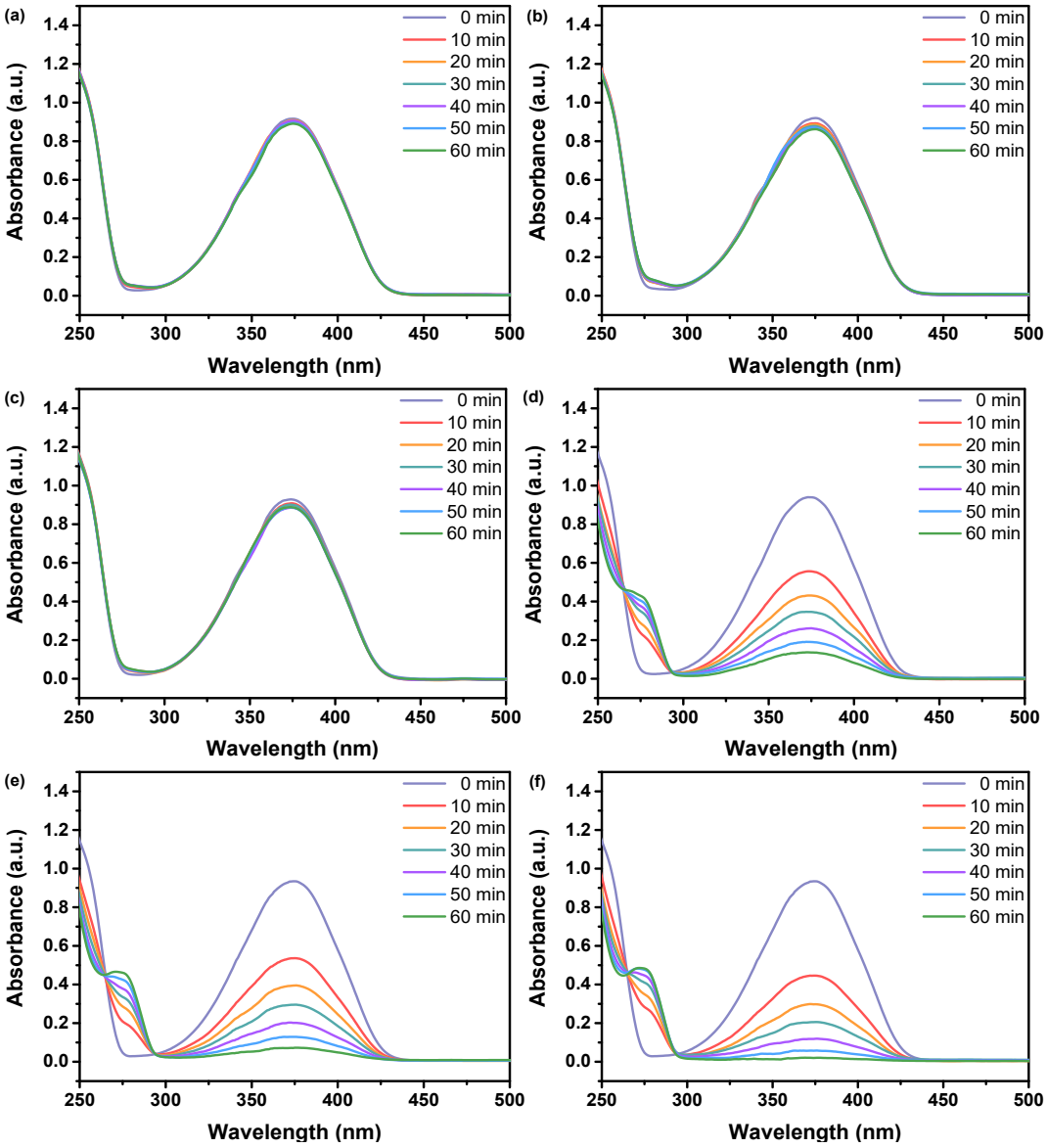


Figure S10. UV-vis absorption spectral change for the oxidation of 1,4-DHP (10^{-3} M) catalyzed by different catalysts under irradiation with a xenon lamp ($\lambda > 420$ nm). (a) g-C_3N_4; (b) CuTPP; (c) H_2TPP; (d) CuTPP-Cy; (e) NiTPP-Cy; (f) H_2TPP-Cy.

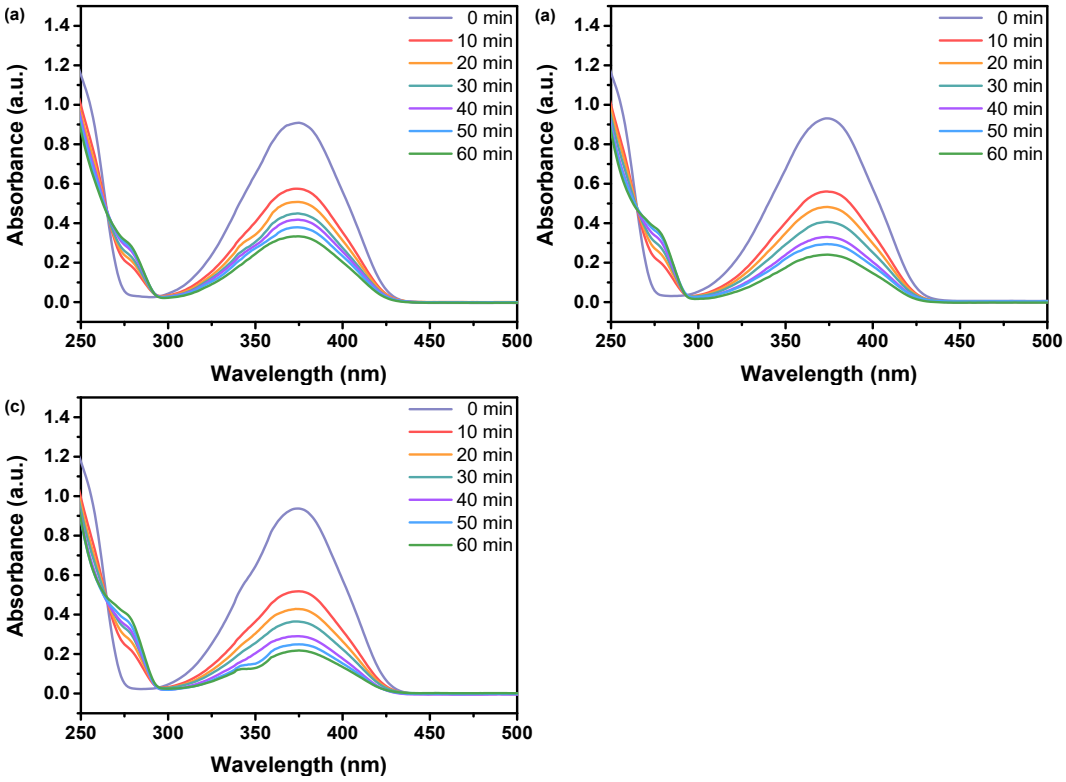


Figure S11. UV-vis absorption spectral change for the oxidation of 1,4-DHP (10^{-3} M) catalyzed by different catalysts in darkness. (a) CuTPP-Cy; (b) NiTPP-Cy; (c) H_2TPP-Cy.

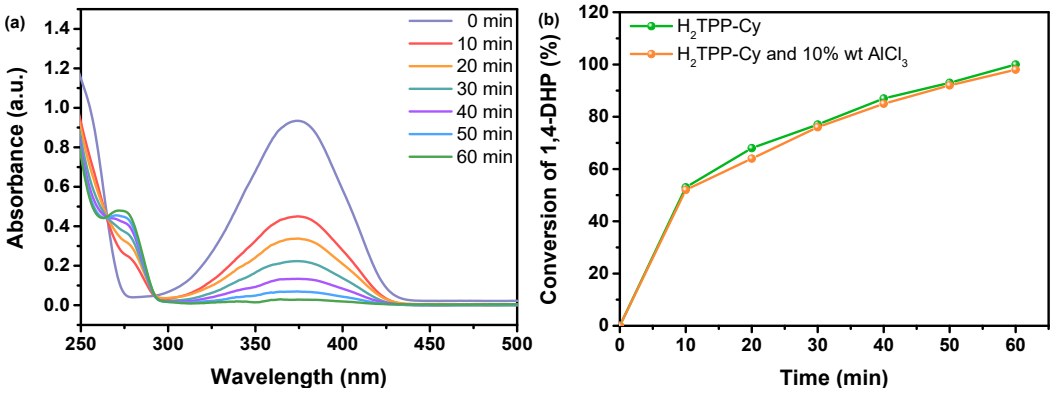


Figure S12. The oxidation of 1,4-DHP (10^{-3} M) catalyzed by H_2TPP-Cy and 10% wt $AlCl_3$ under irradiation with a xenon lamp (λ > 420 nm). (a) UV-vis absorption spectral change; (b) Comparison with H_2TPP-Cy.

7. ICP results of MTPP-Cys.

Table S2. ICP results of MTPP-Cys.

Catalysts	Al^{3+} contents (wt%)	Ni^{2+} contents (wt%)	Cu^{2+} contents (wt%)
H_2TPP-Cy	0.226	0	0
NiTPP-Cy	0.120	0.361	0
CuTPP-Cy	0.652	0	0.834

8. Cycling stability of H_2TPP-Cy.

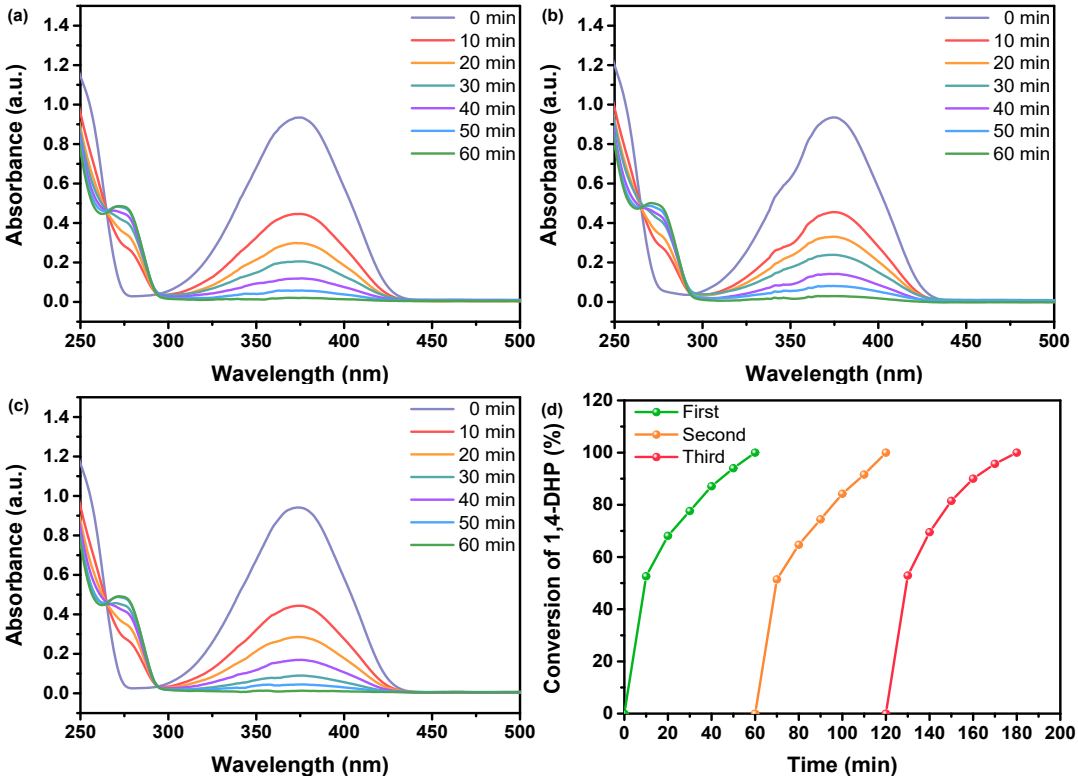


Figure S13. The durability of H_2TPP-Cy in photooxidation of 1,4-DHP (10^{-3} M) under irradiation with a xenon lamp ($\lambda > 420$ nm). (a) The first run; (b) The second run; (c) The third run; (d) The conversion of 1,4-DHP for three successive recycles.

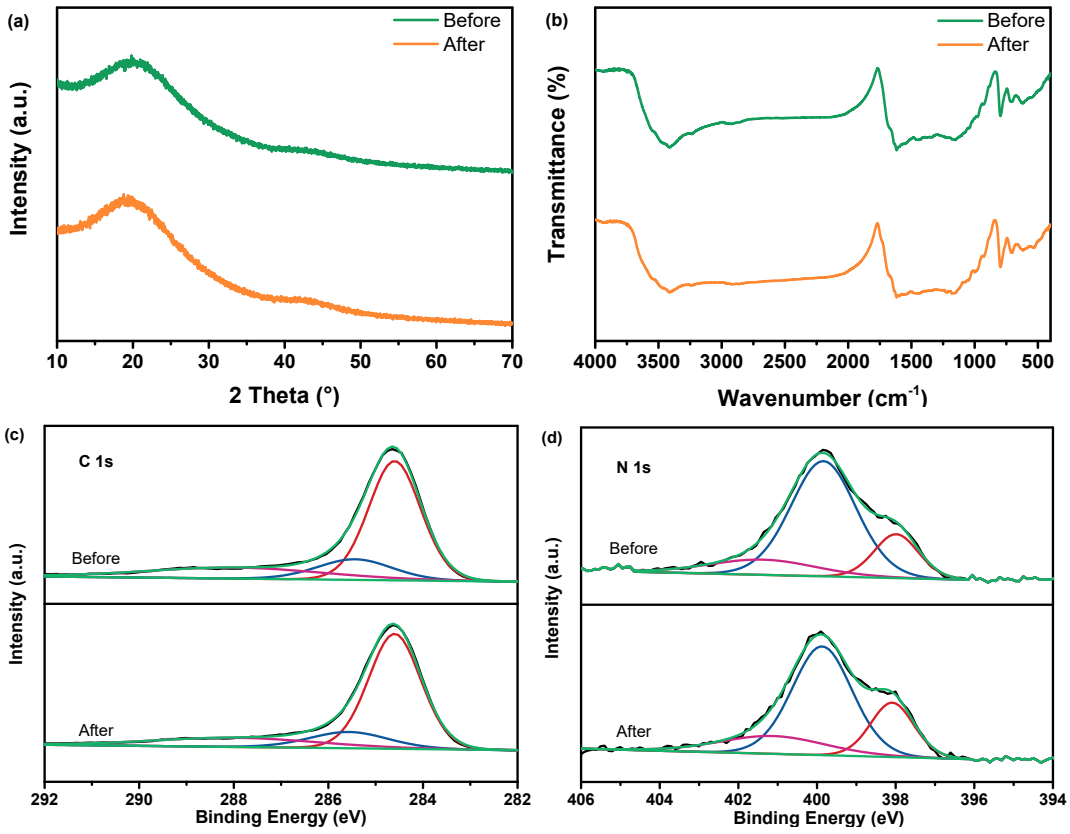


Figure S14. (a) XRD; (b) FT-IR; High-resolution (c) C 1s and (d) N 1s XPS spectra of H_2TPP-Cy before and after 3 times cycling experiments.

9. Summary of recently reported literatures for photooxidation of 1,4-DHP.

Table S3. Summary of oxidation of 1,4-DHP.

Catalyst	Conditions	$C_{1,4\text{-DHP}}$/M	Time/min	Con./%	Ref.
H_2TPP-Cy	darkness	10^{-4}	≤20	>99	This work
	Xenon lamp (30 mW/cm^2, λ>420 nm).	10^{-4}	≤10	>99	
	darkness	10^{-3}	60	77	
	Xenon lamp (30 mW/cm^2, λ>420 nm).	10^{-3}	≤60	>99	
C-120	Xenon lamp (60 mW/cm^2, λ> 385 nm)	10^{-4}	≤30	>99	11
P-CN	Xenon lamp (100 mW/m^2, λ>385 nm)	10^{-4}	≤40	>99	5
R-C_3N_4	Xenon lamp (100 mW/m^2, λ> 420 nm)	10^{-4}	≤40	>99	12
ZnCu-CDs-2	Xenon lamp (60 mW/cm^2, λ> 385 nm)	10^{-4}	≤90	93.93	4
350-FeCu-CDs	xenon lamp (60 mW/cm^2, λ> 385 nm)	10^{-4}	≤100	94.42	13
Cu-CDs-250	Xenon lamp (60 mW/cm^2, λ> 385 nm)	10^{-4}	160	60.8	14

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