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A couple of new porphyrin photosensitizer and cobaloxime cocatalyst for highly efficient photocatalytic H_2 evolution

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Materials and Methods

All the chemicals used in this work were purchased from commercial sources and used as received. Solvents were dried by distilling over suitable dehydrating agents according to standard procedures. Purification of the compounds was performed by column chromatography with 100-200 mesh silica. ^{1}H and ^{13}C NMR spectra were recorded in an NMR spectrometer operating at 400.00 and 100.00 MHz respectively. The chemical shifts were calibrated from the residual peaks observed for the deuterated solvents chloroform ($CDCl_3$) at δ 7.26 ppm for ^{1}H and δ 77.0 ppm for ^{13}C, respectively. High-resolution matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained with a Bruker Autoflex MALDI-TOF mass spectrometer. The optical absorption and emission spectra of the porphyrins were measured for the freshly prepared air equilibrated solutions at room temperature by using UV-Vis spectrophotometer and spectrofluorimeter, respectively. Cyclic voltammetry (CV) was recorded on an electrochemical workstation in THF solution by using 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte. The experiments were performed at room temperature with a conventional three-electrode cell assembly consisting of a platinum wire as auxiliary electrode, a non-aqueous $Ag/AgNO_3$ reference electrode, ferrocene as internal standard and a glassy carbon working electrode.

Preparation of photocatalytic systems

A multichannel photochemical reaction system fixed with LED white light (PCX50B, 148.5 mW/cm^2) was used as the light source. The PHE evolution experiments were performed in a quartz vial reactor (20 mL) sealed with a rubber septum, gas-closed system, at ambient temperature and pressure. Initially, the prepared sample (10 μM) was dissolved in a mixture of 10 mL phosphate buffer/THF (9:1 v/v at pH 7.4) and ascorbic acid (AA) (0.4 M) under constant stirring. Then, chloro(pyridine)cobaloxime (CoPyCl) (2.0 mM) co-catalyst was added. The pH was determined by pH meter and adjusted to the required pH using conc. HCl or NaOH. The suspension was purged with argon gas for 15 min to ensure anaerobic conditions and then it was placed in a multichannel photochemical reaction system. After 1 h of irradiation, the released gas (400 μL) was collected by syringe from the headspace of the reactor and was analyzed by gas chromatography (Shimadzu, GC-2014, Japan, with ultrapure Ar as a carrier gas) equipped with a TDX-01(5 Å molecular sieve column) and a thermal conductivity detector (TCD). Eventually, the total content of PHE was calculated according to the standard curve. Continuous stirring was applied to the whole process to keep the photocatalyst particles in suspension state and to achieve uniform irradiation.

The apparent quantum efficiency (AQE) was measured under the similar photocatalytic reaction conditions except using 420 nm OLED light. The focused intensity and illuminated area LED light were ca. 68.0 mW/cm^2 and 9.04 cm^2, respectively. AQE was calculated via the following equation:

$$\text{AQE} = \left(\frac{2 \times \textit{number of hydrogen molecules}}{\textit{number of incident photons}}\right) \times 100\,\%$$

The turnover number (TON) was calculated by using the following formula;

$$\text{TON} = \frac{\textit{Number of moles of hydrogen produced in photocatalytic system}}{\textit{Number of moles of photocatalyst}}$$

Photoelectrochemical Measurement.

The photoelectrochemical tests were performed according to our previous report.[1] The transient photocurrent response (I–t curves) studies were performed using an electrochemical workstation (CHI660C Instruments, China) with Pt wire (counter electrode), a non-aqueous Ag/AgNO$_3$ (reference electrode) and fluorine-doped tin oxide (FTO) glass coated withthe porphyrins on the conductive surface (working electrode) upon irradiation of LED monochromatic point lamp (3 W, 420 nm). The light spot effective area on the working electrode was set as 28.26 mm^2. Typically, the working electrode was prepared by dissolving 100 μM of porphyrins in 200 μL of chlorobenzene (and then applied on the conductive surface of FTO glass using drop dispensing method. A 5 mL volume of 0.5 M Na$_2$SO$_4$ aqueous solution acted as the electrolyte. The open-circuit voltages were set as the initial bias voltages in the transient photocurrent responses tests.

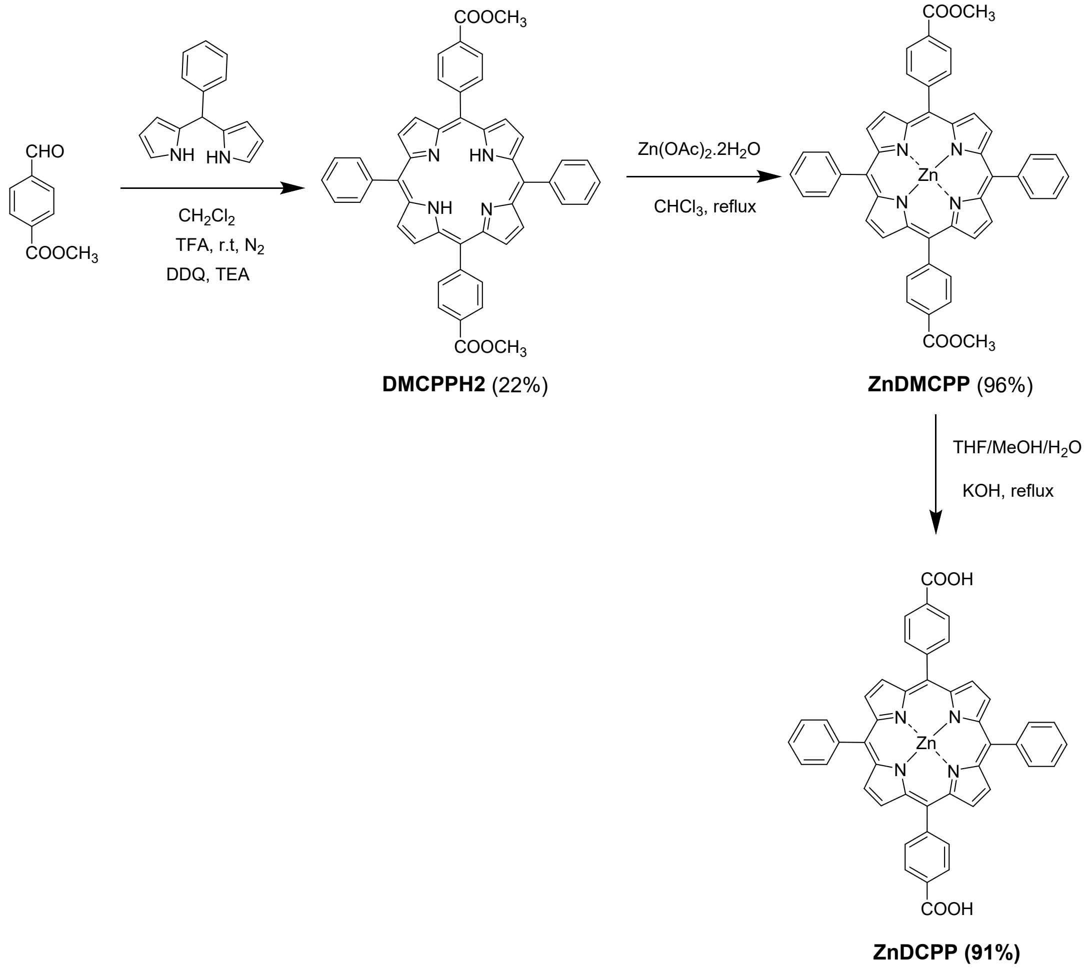
Fluorescence quantum yields (Φ_F). The Φ_F of the porphyrins in degassed phosphate buffer/THF (9:1 v/v, 1 μM) solution were calculated by comparing with that of 5,10,15,20-tetraphenylporphyrin (**TPP**). **TPP** was used as the fluorescence standard with Φ_F = 0.13 in degassed toluene. The Φ_F was calculated according to the following equation.

$$\Phi_F{}^{sample} = \Phi_F{}^{ref}\left(\frac{S_{sample}}{S_{ref}}\right)\left(\frac{A_{ref}}{A_{sample}}\right)\left(\frac{n_{sample_2}}{n_{ref}{}^{2}}\right)$$

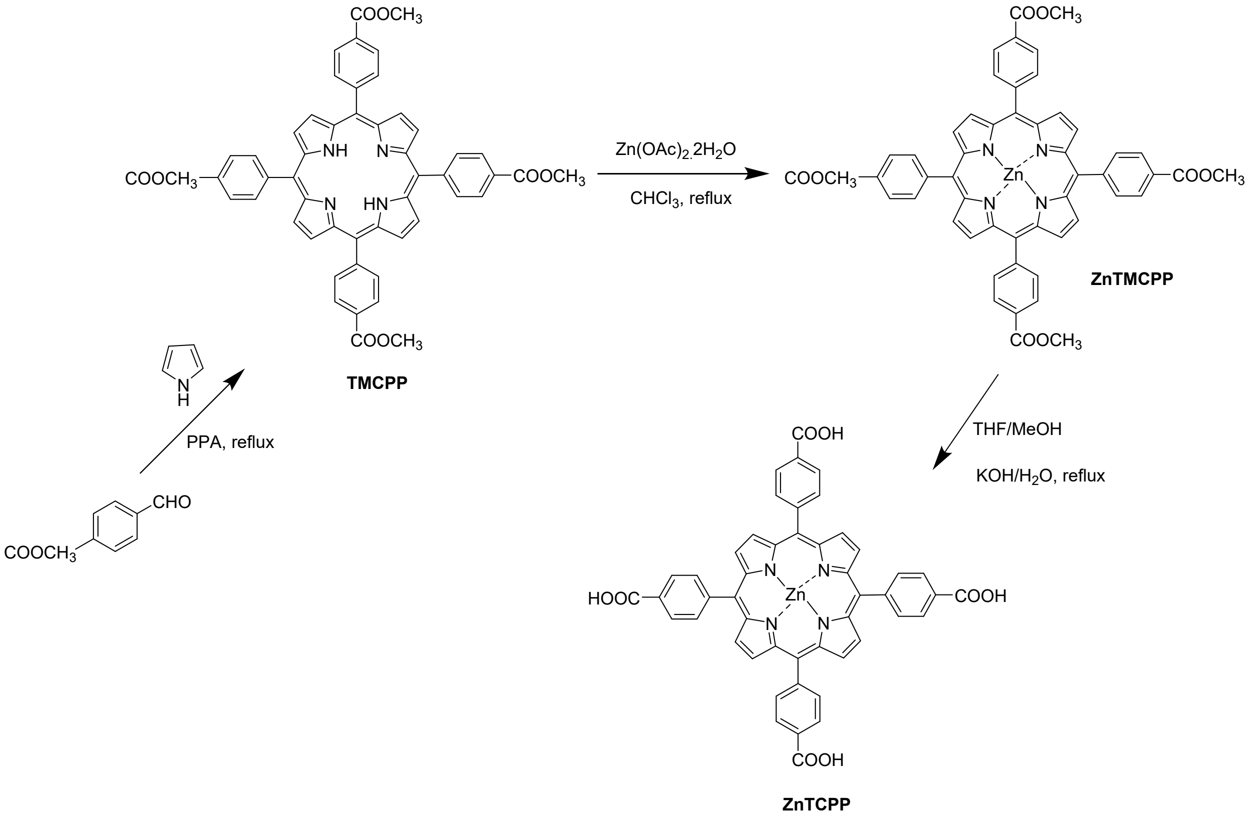
where A_{ref}, S_{ref}, n_{ref}, *and* A_{sample}, S_{sample}, n_{sample} represent the absorbance at the excited wavelength, integrated area under the fluorescence curves and the solvent refractive index of the standard and the sample solutions.

Synthesis

The porphyrin intermediate, **D(*p*-NI)PPH2** was synthesized and characterized according to our previous report.[1] Porphyrin **ZnTCPP** was synthesized according to the procedure described in literature.[2]



Scheme S1. Synthetic route for the preparation of **ZnDCPP** porphyrin.



Scheme S2. Synthetic route for the preparation of **ZnTCPP** porphyrin.

DiBrD(*p*-NI)PPH2:

In a 250 mL two-neck round-bottom flask, **D(*p*-NI)PPH2** (0.50 g, 0.46 mmol) and chloroform (200 mL) were taken and purged with nitrogen for 10 min. After NBS (0.18 g, 1.01 mmol) was added portion wise and the reaction mixture was stirred for 30 min at room temperature under nitrogen and dark. The reaction statues was monitored by TLC. After completion of reaction, the solvent was removed and the resulting crude product was purified by column chromatography with silica using chloroform/hexane (1:1, v/v) as eluent. Light green solid: yield 0.52 g, 92.0 %. ^{1}H NMR ($CDCl_3$, 400.00 MHz) δ – 2.70 (s, 2 H), 0.91-1.01 (m, 12 H), 1.37-1.47 (m, 12 H), 2.01-2.04 (m, 2 H), 4.15-4.23 (m, 4 H), 7.88-7.90 (m, 6 H), 8.04 (d, J = 7.6 Hz, 2 H), 8.33 (d, J =

8.0 Hz, 4 H), 8.66 (d, $J = 8.8$ Hz, 2 H), 8.71 (d, $J = 7.2$ Hz, 2 H), 8.79 (d, $J = 7.2$ Hz, 2 H), 8.97 (d, $J = 4.0$ Hz, 4 H), 9.69 (d, $J = 4.8$ Hz, 4 H).

DiBrZnD(*p*-NI)PP:

A mixture of **DiBrD(*p*-NI)PPH2** (0.5 g, 0.40 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (0.74 g, 4.0 mmol) and $CHCl_3$ (200 mL) was refluxed overnight. After completion of the reaction, solvent was removed and the resulting crude product was purified by column chromatography with silica using chloroform as eluant. Green color solid: yield 0.51 g, 98.0 %. ^{1}H NMR ($CDCl_3$, 400.00 MHz) δ 0.91-1.01 (m, 12 H), 1.35-1.47 (m, 12 H), 2.00-2.05 (m, 2 H), 4.14-4.25 (m, 4 H), 7.82-7.84 (m, 6 H), 8.01 (d, $J = 7.6$ Hz, 2 H), 8.31 (d, $J = 8.0$ Hz, 4 H), 8.63-8.69 (m, 4 H), 8.76 (d, $J = 7.6$ Hz, 2 H), 9.00 (d, $J = 4.4$ Hz, 4 H), 9.73 (d, $J = 4.8$ Hz, 4 H). ^{13}C NMR ($CDCl_3$, 100.00 MHz) δ 10.75, 14.18, 23.16, 24.15, 28.80, 30.85, 38.03, 44.25, 105.15, 121.02, 121.97, 123.03, 127.05, 128.04, 128.21, 128.83, 130.08, 130.96, 131.33, 132.55, 133.24, 134.88, 137.99, 142.97, 146.43, 150.27, 150.65, 164.52, 164.68.

ZnDC(*p*-NI)PP:

In a 100 mL two-neck round-bottom flask, **DiBrZnD(*p*-NI)PP** (0.20 g, 0.16 mmol), 4-carboxyphenylboronic acid (0.08 g, 0.46 mmol), potassium carbonate (0.14 g, 0.96 mmol) and 15 mL THF/H_2O (3:1, v/v) were taken and purged with nitrogen. After addition of $Pd(PPh_3)_4$ (50 mg, 2 mol %) the reaction mixture was refluxed for 12 h. After completion of reaction, it was diluted with chloroform and water. The organic layer was separated, dried over Na_2SO_4 and solvent removed under reduced pressure. The resulting crude reaction mixture containing product was purified by column chromatography with silica using chloroform/hexane (2:1, v/v) as eluent. Dark-red solid: yield 0.16 g, 74.0%; ^{1}H NMR ($CDCl_3$, 400.00 MHz) δ 0.87-0.94 (m, 12 H), 1.30-1.36 (m, 16 H), 1.91-1.95 (m, 2 H), 4.04-4.06 (m, 4 H), 7.81-7.87 (m, 5 H), 8.04-

8.10 (m, 5 H), 8.31-8.38 (m, 10 H), 8.62-8.70 (m, 5 H), 8.81 (d, *J* = 4.4 Hz, 4 H), 8.95 (s, 4 H), 12.68 (broad s, 2 H). (MALDI–TOF, m/z) calculated for $C_{86}H_{70}N_6O_8Zn$: 1380.455281 found 1380.442.

DMCPPH2:

In a 100 mL two-neck round-bottom flask, Methyl 4-formylbenzoate (0.5 g, 3.04 mmol), dipyrrolomethane (0.74 g, 3.34 mmol) and dichloromethane (100 mL) were taken and purged with nitrogen for 20 min. After TFA (500 μL) was added and the reaction mixture was stirred for 12 h at room temperature under nitrogen and dark. After 2,3-dichloro-5,6- dicyanobenzoquinone (DDQ) (1.38 g, 6.08 mmol) was added, and the reaction mixture was stirred for 30 min. The reaction was quenched by the addition of triethylamine (5 mL). After completion of reaction, the solvent was removed and the resulting crude product was purified by column chromatography with silica using dichloromethane/hexane (1:1, v/v) as eluent. Purple solid: yield 0.22 g, 10.0 %. ^{1}H NMR ($CDCl_3$, 400.00 MHz) δ – 2.79 (s, 2 H), 4.11 (s, 6 H), 7.73-7.79 (m, 6 H), 8.21 (dd, *J* = 8.0, 1.6 Hz, 4 H), 8.30 (d, *J* = 8.0 Hz, 4 H), 8.44 (d, *J* = 8.4 Hz, 4 H), 8.79 (d, *J* = 4.8 Hz, 4 H), 8.87 (d, *J* = 4.4 Hz, 4 H). ^{13}C NMR ($CDCl_3$, 100.00 MHz) δ 52.5, 118.84, 119.03, 126.82, 127.92, 128.00, 131.30, 132.25, 132.46, 134.59, 134.63, 141.97, 141.99, 146.98, 147.00, 167.38.

ZnDMCPP:

A mixture of **DMCPPH2** (0.2 g, 0.27 mmol), $Zn(OAc)_2 \cdot 2H_2O$ (0.50 g, 2.73 mmol) and $CHCl_3$ (100 mL) was refluxed overnight. After completion of the reaction, solvent was removed and the resulting crude product was purified by column chromatography with silica using chloroform as eluant. Purple solid: yield 0.20 g, 95.0 %. ^{1}H NMR ($CDCl_3$, 400.00 MHz) δ 4.10 (s, 1 H), 7.74-7.81 (m, 6 H), 8.22 (d, *J* = 6.4 Hz, 4 H), 8.31 (d, *J* = 8.0 Hz, 4 H), 8.42 (d, *J* = 8.0 Hz, 4 H), 8.90 (d, *J* = 4.8 Hz, 4 H), 8.97 (d, *J* = 4.8 Hz, 4 H). ^{13}C NMR ($CDCl_3$, 100.00 MHz) δ 52.39, 119.72, 119.89, 121.53, 121.71, 126.61, 127.62, 127.76, 129.31, 131.61, 131.67, 131.83, 132.27, 132.42, 132.48, 134.42, 134.43, 142.62, 147.69, 149.57, 149.64, 149.71, 150.28, 150.35, 150.43, 167.36.

ZnDCPP:

A mixture of **ZnDMCPP** (0.10 g, 0.13 mmol) and KOH (0.7 g, 13.00 mmol) in H_2O (10 mL), MeOH (10 mL), and THF (10 mL) was refluxed for 18 h under N_2. After completion, the solvents MeOH and THF were removed by flushing with air. The resulting reaction mixture was acidified to pH-5 by adding 1 M HCl. The resulted precipitate was collected by filtration and dried in vacuum for 1 h. Dark-red solid: yield 0.09 g, 91.0 %. ^{1}H NMR (DMSO-*d*6, 400.00 MHz) δ 7.80-7.81 (m, 6 H), 8.18-8.20 (m, 4 H), 8.30-8.38 (m, 4 H), 8.78-8.81 (m, 8 H) 13.25 (broad s, 2 H). (MALDI–TOF, m/z) calculated for $C_{46}H_{28}N_4O_4Zn$: 764.139649 found 764.1386.

TMCPP:

In a 250 mL round bottom flask, methyl 4-formylbenzoate (3.50 g, 21.31 mmol) was dissolved in 50 mL propionic acid. To this mixture, pyrrole (1.62 mL, 23.45 mmol) was added dropwise and the solution was refluxed at 140 °C for 12h. Then after the reaction mixture was cooled down to room temperature and the resulting purple color precipitate was collected by filtration and washed with methanol and water. Purple solid: yield 2.10 g, 1.2 %. ^{1}H NMR ($CDCl_3$, 400.00 MHz) δ – 2.80 (s, 2 H), 4.12 (s, 12 H), 8.30 (d, *J* = 8.4 Hz, 8 H), 8.46 (d, *J* = 8.0 Hz, 8 H), 8.83 (s, 8 H).

ZnTMCPP:

A mixture of **TMCPP** (1.0 g, 1.18 mmol), $Zn(OAc)_2 \cdot 2H_2O$ (2.59 g, 11.80 mmol) and $CHCl_3$ (100 mL) was refluxed overnight. After completion of the reaction, solvent was removed and the resulted crude product was purified by column chromatography with silica using chloroform as eluant. Purple solid: yield 1.23 g, 92.0 %. ^{1}H NMR ($CDCl_3$, 400.00 MHz) δ 4.08 (s, 12 H), 8.25 (d, *J* = 8.4 Hz, 8 H), 8.39 (d, *J* = 8.4 Hz, 8 H), 8.81 (s, 8 H).

ZnTCPP:

A mixture of **ZnTMCPP** (0.3 g, 0.33 mmol), KOH (2.63 g, 515.58 mmol) in H_2O (25 mL), MeOH (25 mL) and THF (25 mL) was refluxed for 18 h under N_2. After then the clear water solution was acidified to pH-5 by adding 1 M HCl. The resulting precipitate was collected by filtration and dried in vacuum for 1 h. Purple color solid: yield 0.25 g, 91.0 %. ^{1}H NMR ($CDCl_3$, 400.00 MHz) δ 8.28-8.37 (m, 16 H), 8.78 (s, 8 H).

Table S1. Photocatalytic hydrogen evolution properties of the reported photocatalytic systems comprising of porphyrin-based photosensitizer and photocatalyst.

Photosensitizer	Photocatalyst	ηH_2 (mmol g^{-1} h^{-1})	TON	Irradiating light	Reference
Zn(PyTBPP)}{Co(dmgH)$_2$Cl		-	22	Xe lamp (300 W)	3
[ZnTMPyP]$^{4+}$(Cl$^-$)$_4$,	[Co^{III}(dmgH)$_2$(py)Cl]	-	280	Xe lamp (175 W)	4
[ZnTMPyP]$^{4+}$(Cl$^-$)$_4$	[Co(dmgH)$_2$(N-methyl-imidazole)Cl]	-	1135	white LED light (40 W)	5
[ZnTMPyP]$^{4+}$(Cl$^-$)$_4$	Cobalt tetrapyridyl complex (1(BF$_4$)$_2$)		18.5	white LED light	6
PorFN	Pt	10.90	-	AM 1.5G, 100 mW cm^{-2}	7
ZnDC(*p*-NI)PP	Co^{III}(dmgH)$_2$(py)Cl]	35.70	5958	LED white light (148.5 mW/cm^2)	Our work

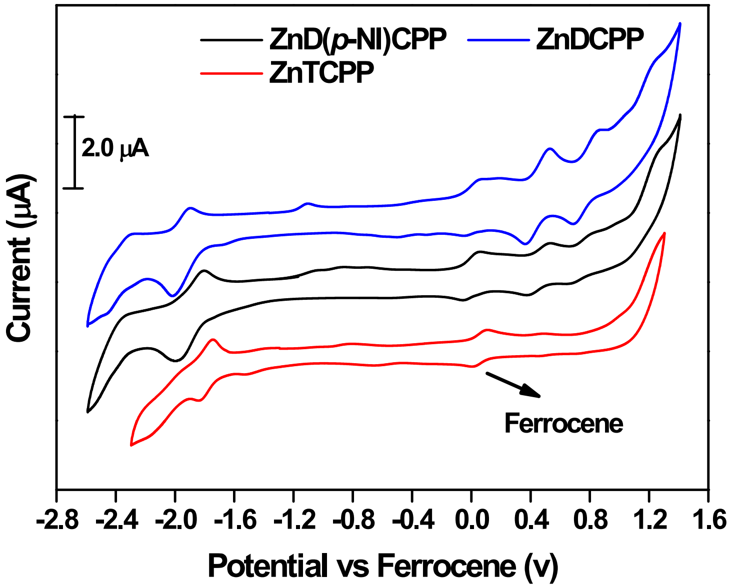


Fig. S1 Cyclic voltammograms of the porphyrins recorded in THF solution.

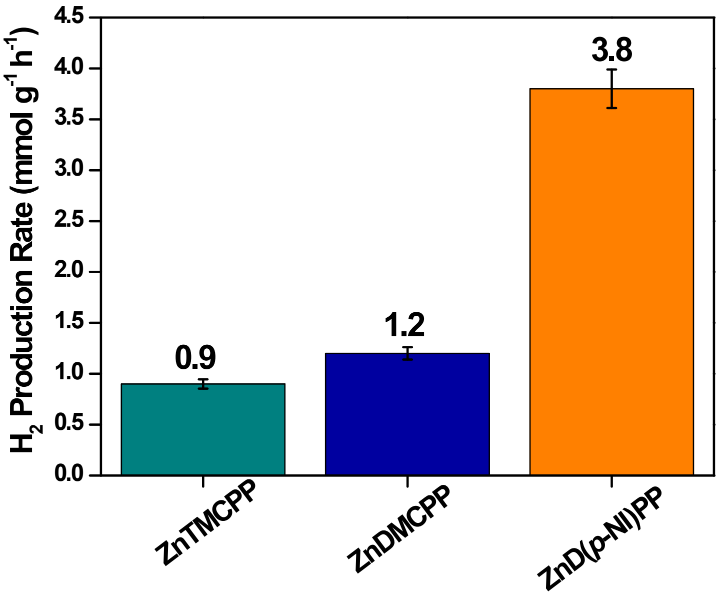


Fig. S2 H_2 production rate of photocatalytic systems under the irradiation for 5 h: (Porphyrin (10 μM) + CoPyCl (2.0 mM) + AA (0.4 M) + buffer/THF (9:1 v/v) at pH 7.4).

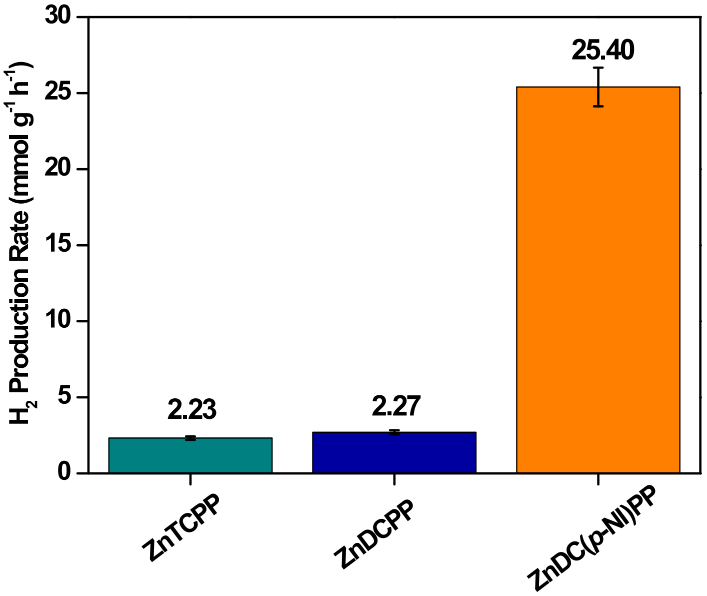


Fig. S3 H$_2$ production rate of photocatalytic systems under the irradiation for 5 h: (Porphyrin (10 μM) + Pt (2 wt%) + AA (0.4 M) + buffer/THF (9:1 v/v) at pH 7.4).

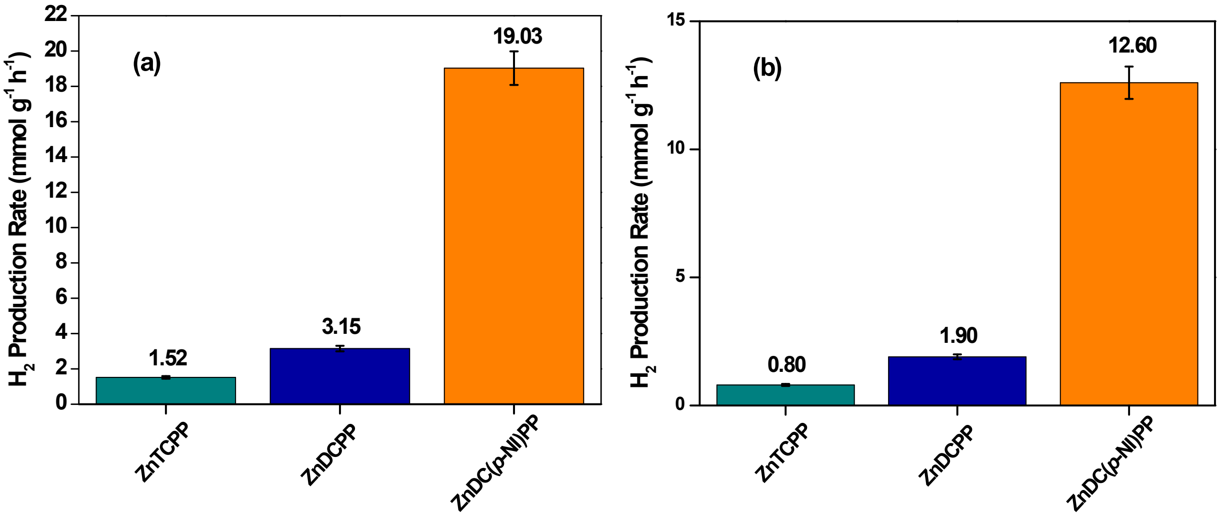


Fig. S4 H$_2$ production rate of photocatalytic systems under the irradiation for 5 h: (a) Porphyrin (100 μM) + CoPyCl (2.0 mM) + AA (0.4 M) + buffer/THF (9:1 v/v) at pH 7.4 and (b) Porphyrin (200 μM) + CoPyCl (2.0 mM) + AA (0.4 M) + buffer/THF (9:1 v/v) at pH 7.4

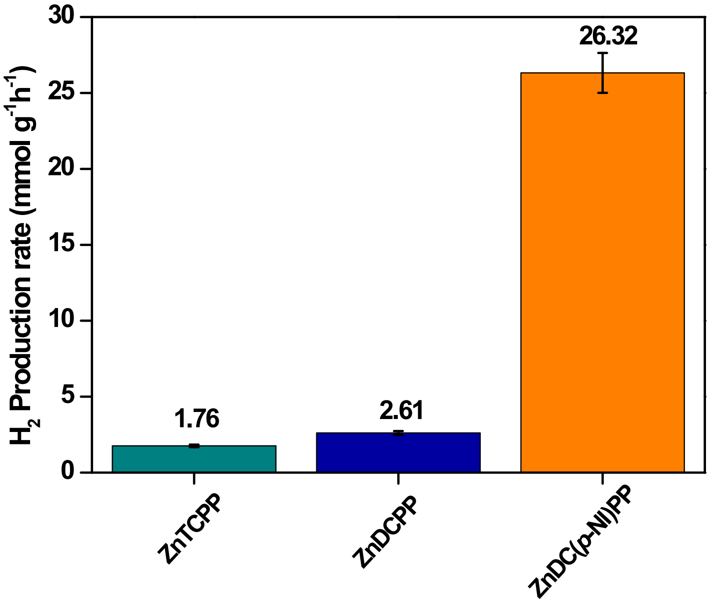


Fig. S5 H_2 production rate of photocatalytic systems under the irradiation for 5 h: (Porphyrin (10 μM) + CoPyCl (2.0 mM) + TEA (0.4 M) + buffer/THF (9:1 v/v) at pH 7.4).

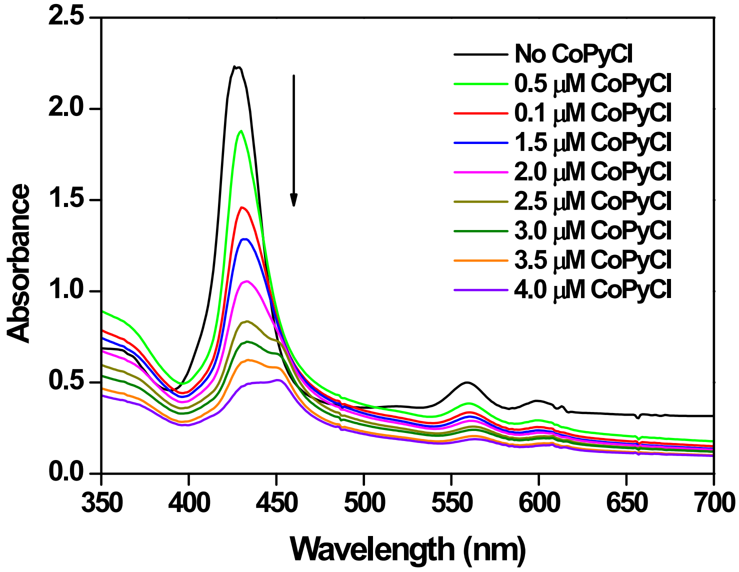


Fig. S6 Absorption spectra of **ZnDC(*p*-NI)PP** recorded in buffer/THF (9:1 v/v) at pH 7.4 in the presence of different concentrations of CoPyCl.

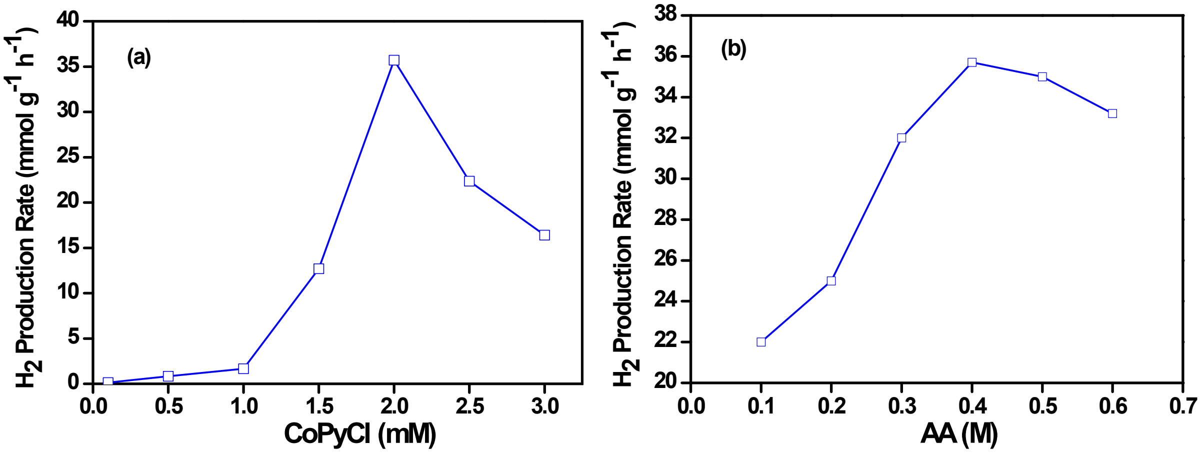


Fig. S7 H_2 production rate of photocatalytic systems at different concentration of (a) CoPyCl and (b) AA under the irradiation for 5 h: (Porphyrin (10 µM) + buffer/THF (9:1 v/v) at pH 7.4).

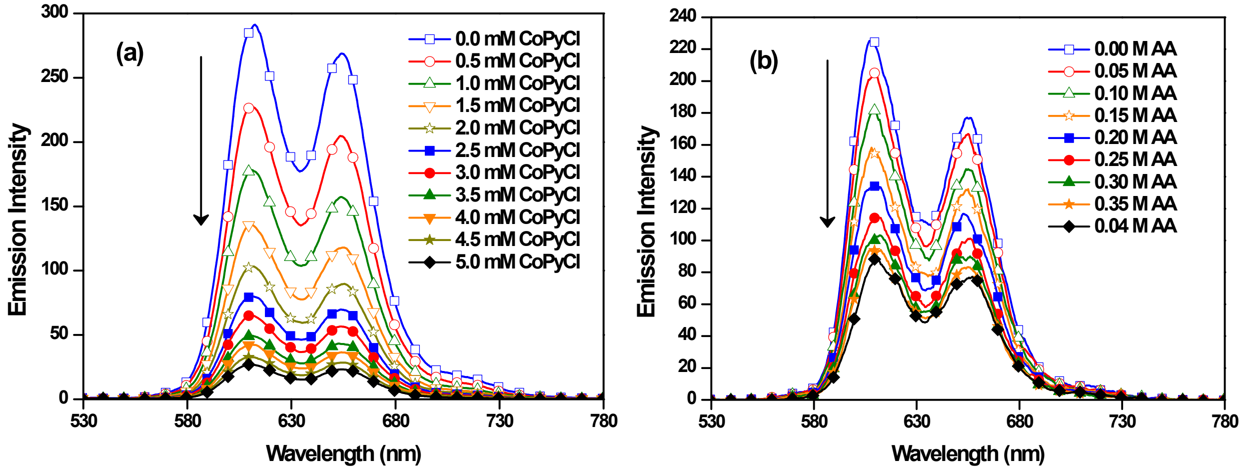


Fig. S8 Photoluminescence quenching of **ZnDC(*p*-NI)PP** (10 µM) with (a) CoPyCl and (b) AA as quencher in phosphate buffer/THF solution.

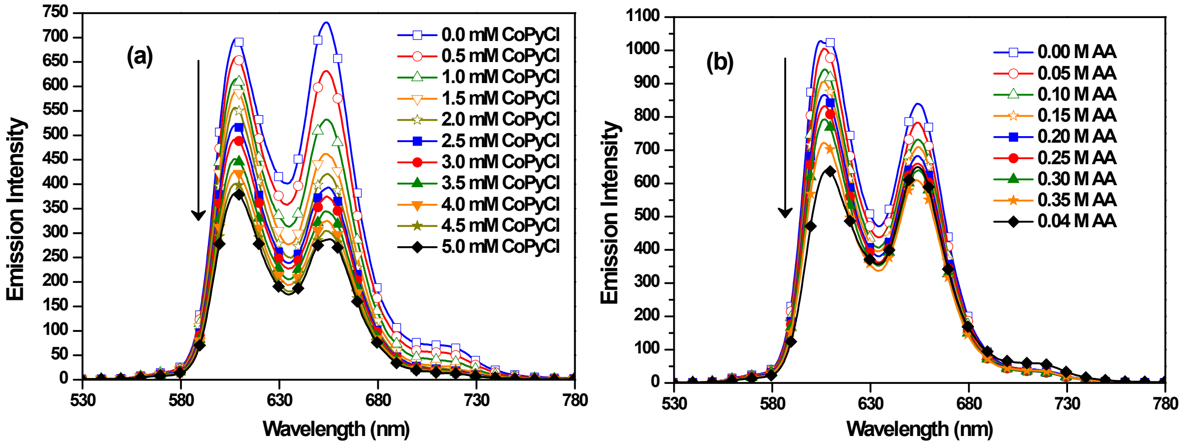


Fig. S9 Photoluminescence quenching of **ZnDCPP** (10 μM) with (a) CoPyCl and (b) AA as quencher in phosphate buffer/THF solution.

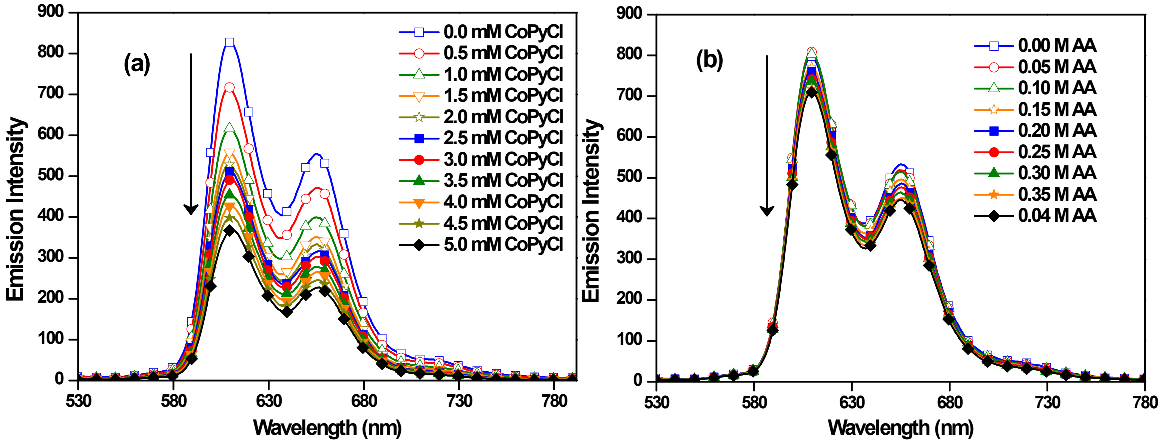


Fig. S10 Photoluminescence quenching of **ZnTCPP** (10 μM) with (a) CoPyCl and (b) AA as quencher in phosphate buffer/THF solution.

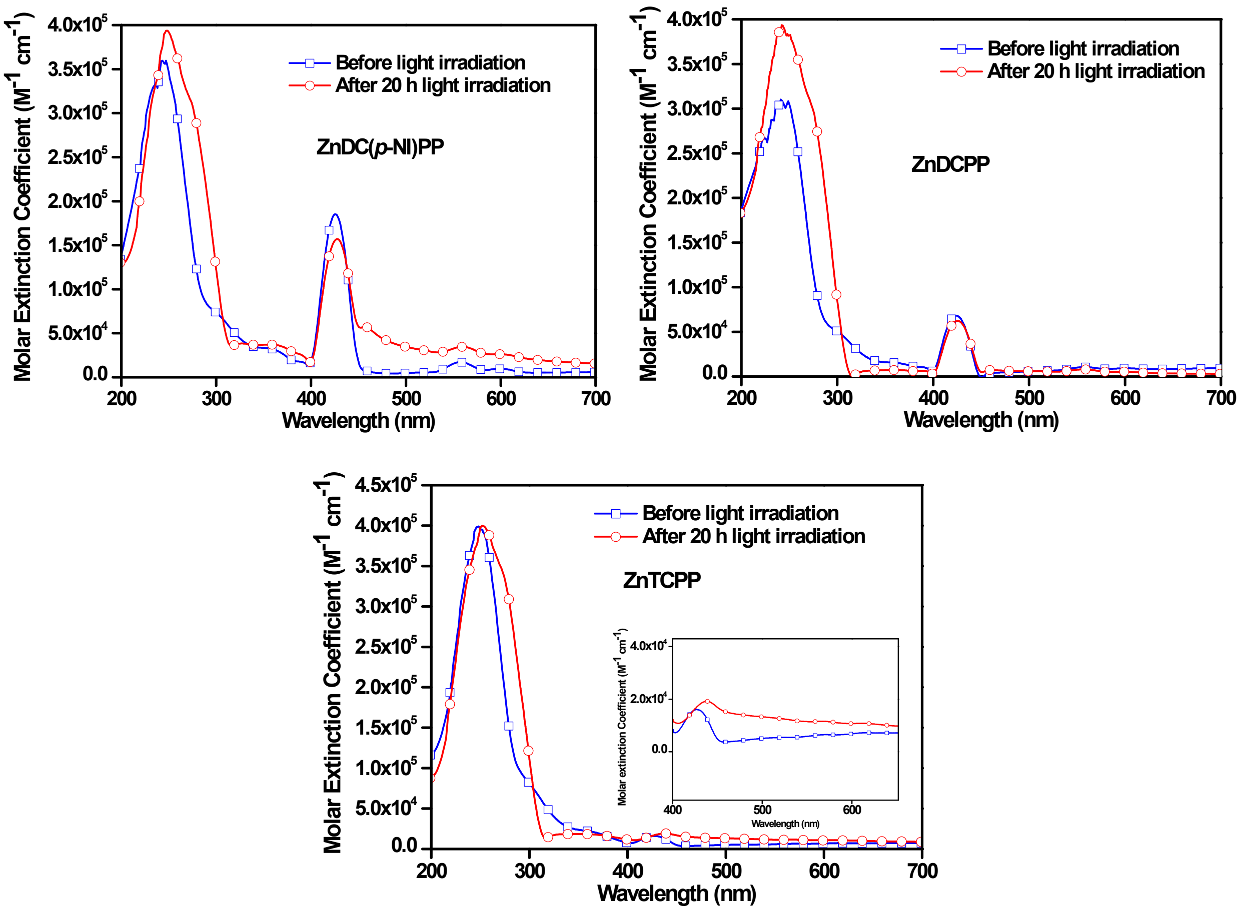


Fig. S11 Absorption spectra of photocatalytic systems before and after irradiation of light: Porphyrin (10 μM) + CoPyCl (2.0 mM) + AA (0.4 M) + buffer/THF (9:1 v/v) at pH 7.4.

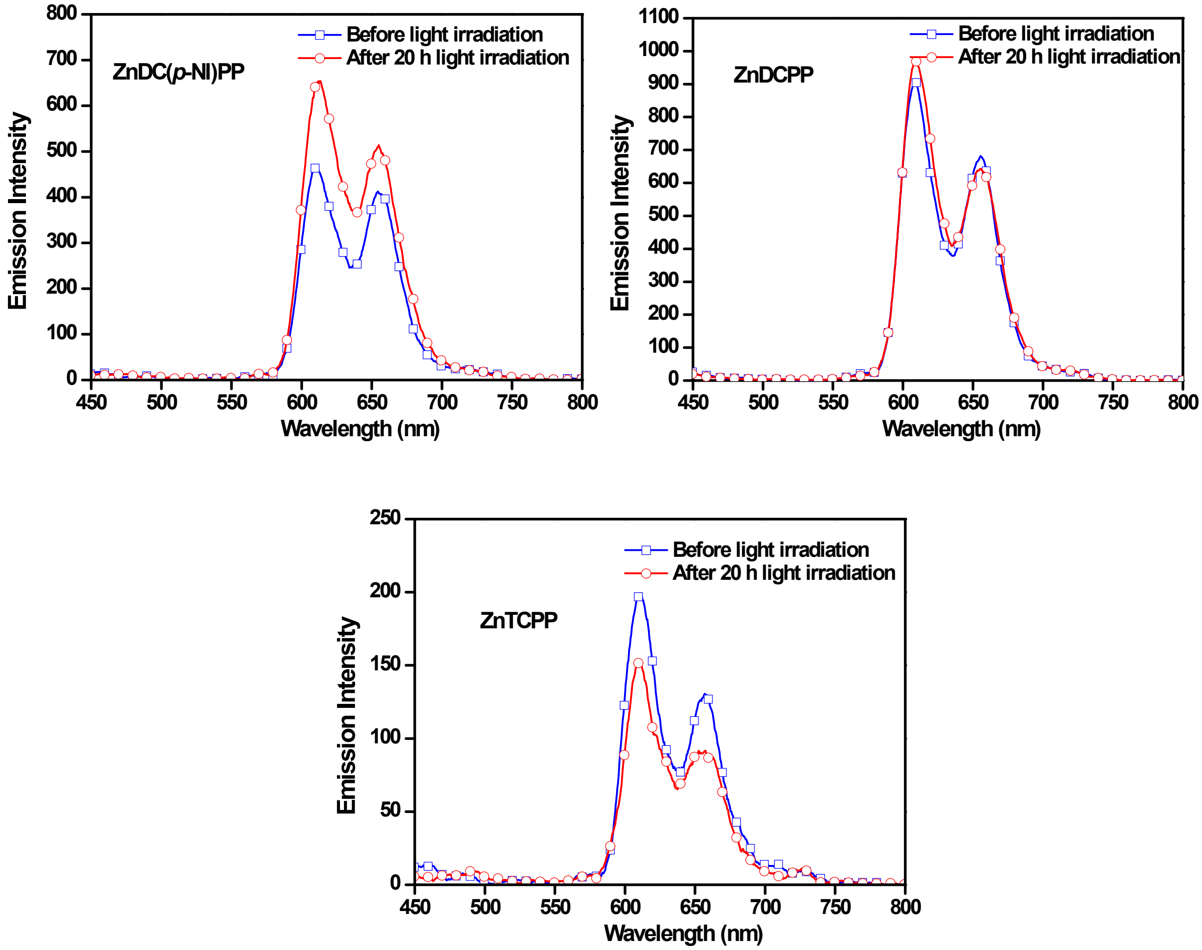


Fig. S12 Photoluminescence spectra of photocatalytic systems before and after light irradiation: Porphyrin (10 μM) + CoPyCl (2.0 mM) + AA (0.4 M) + buffer/THF (9:1 v/v) at pH 7.4.

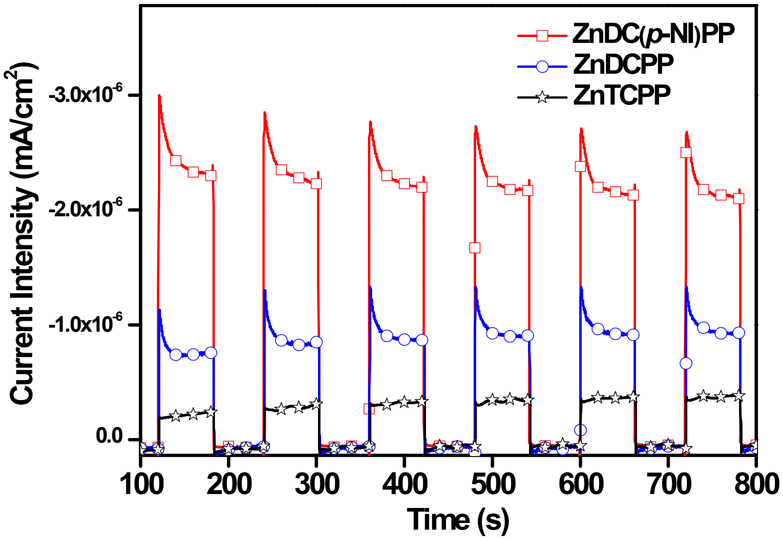


Fig. S13 Photocurrent response spectra of the porphyrins.

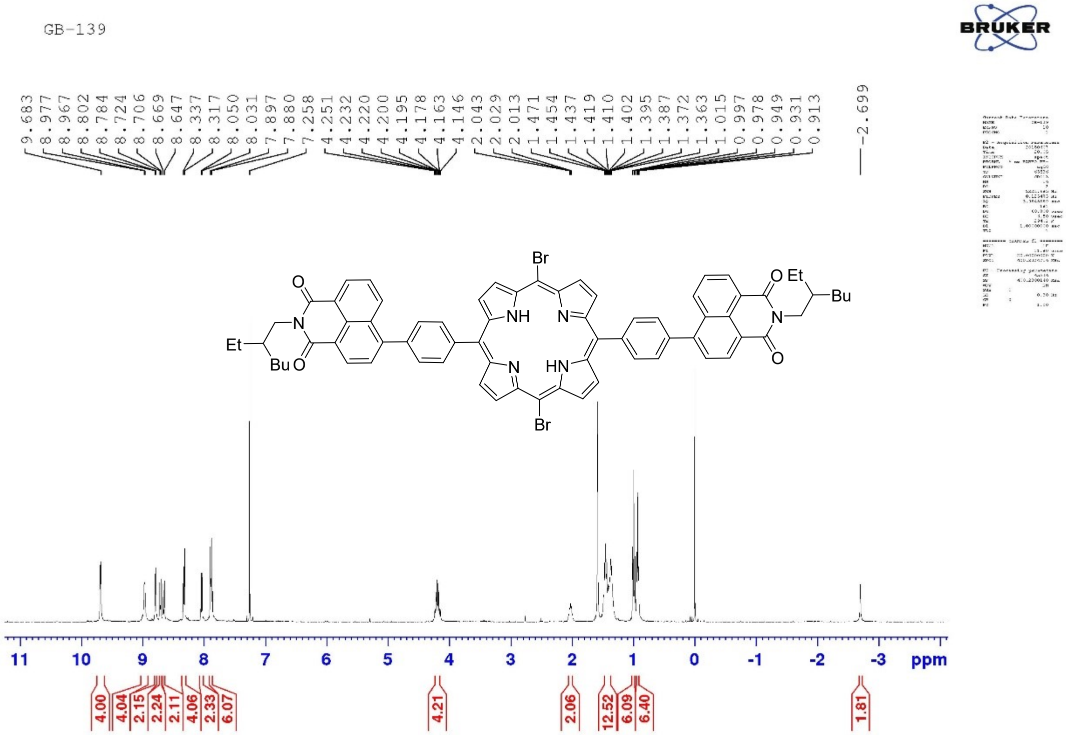


Fig. S14 ^{1}H NMR spectra of **DiBrD(*p*-NI)PPH2** recorded in $CDCl_3$.

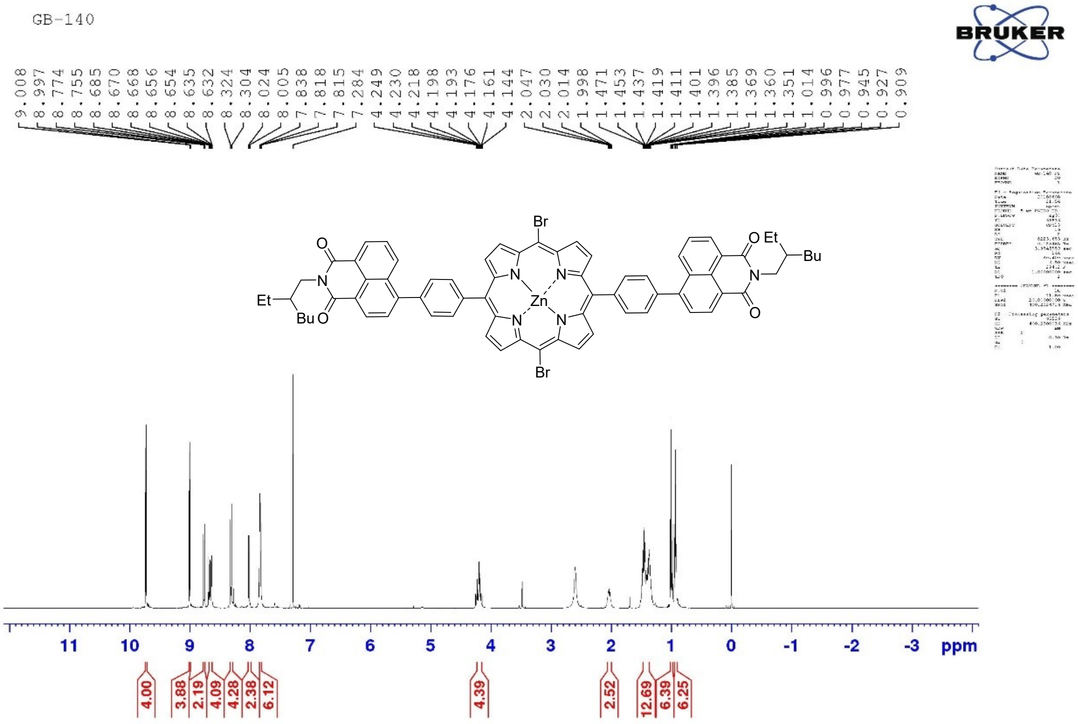


Fig. S15 ^{1}H NMR spectra of **DiBrZnD(*p*-NI)PPH2** recorded in $CDCl_3$.

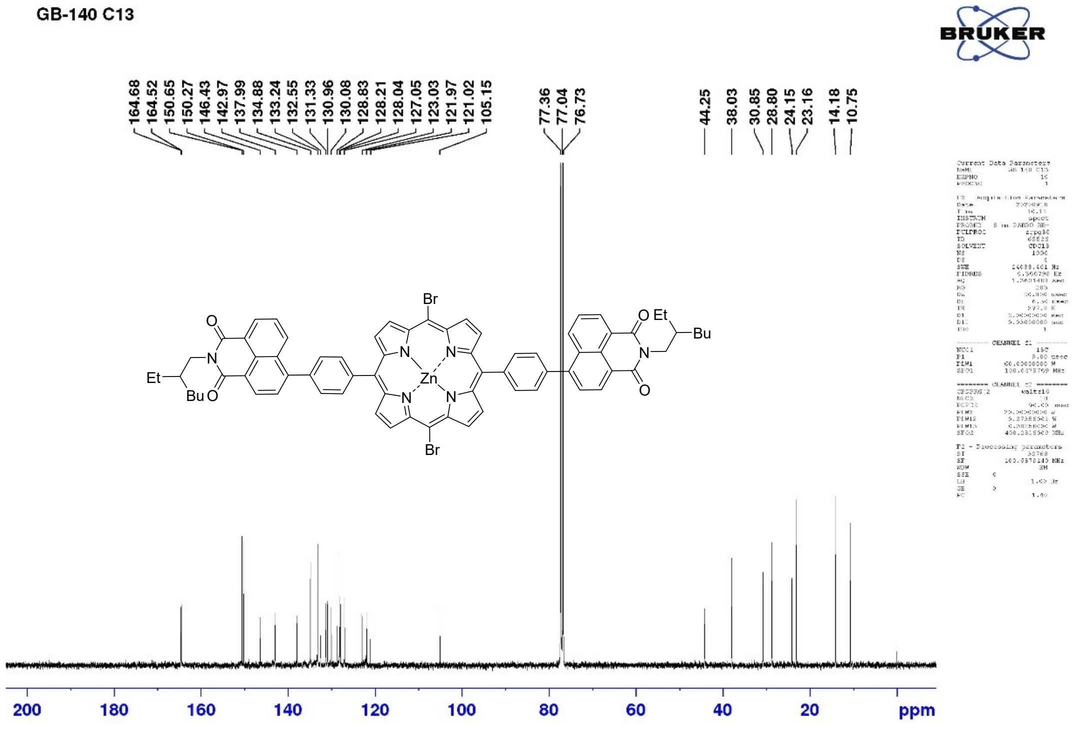


Fig. S16 ^{13}C NMR spectra of **DiBrZnD(*p*-NI)PPH2** recorded in $CDCl_3$.

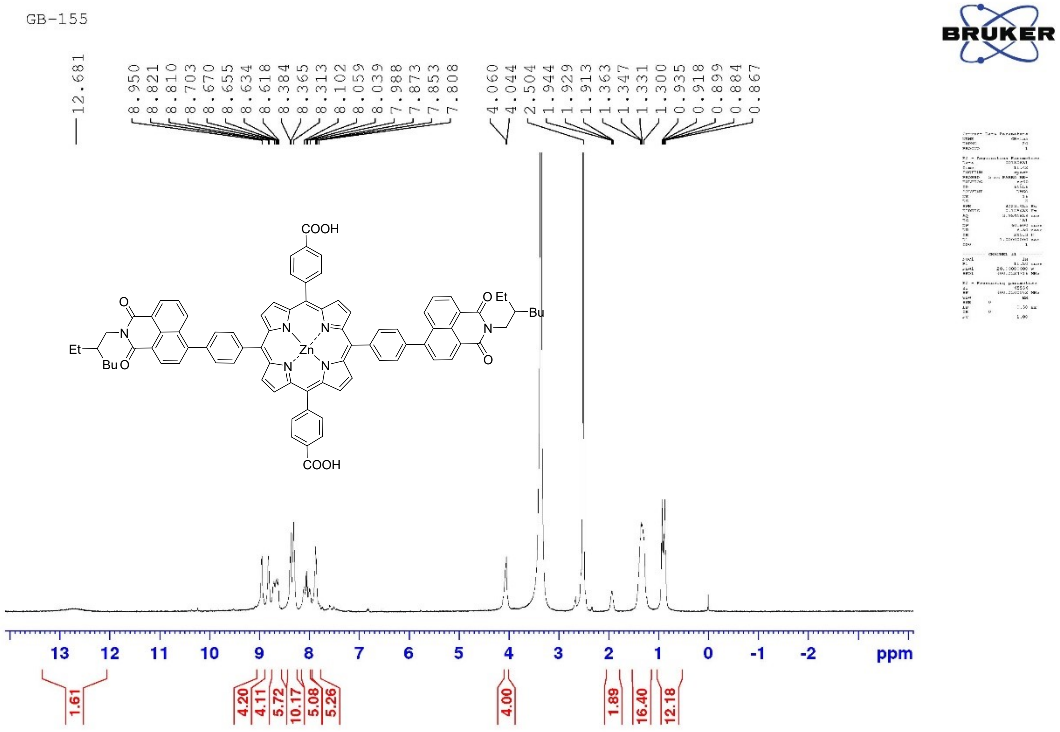


Fig. S17 ^{1}H NMR spectra of **ZnDC(*p*-NI)PP** recorded in DMSO-*d*6.

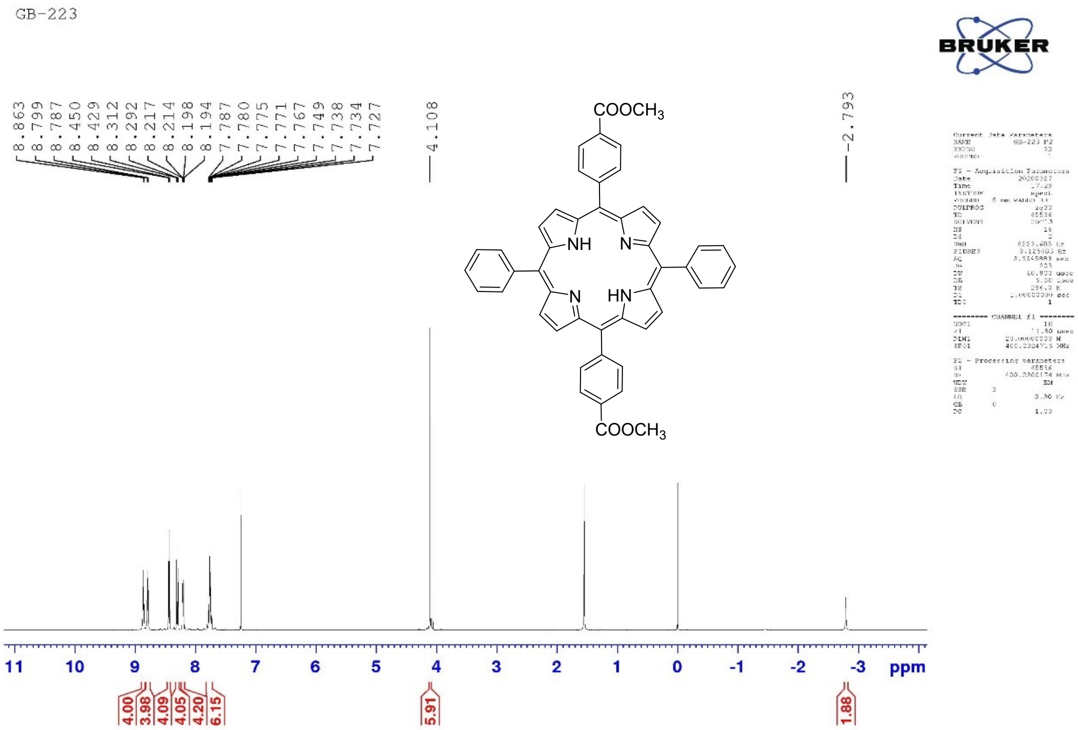


Fig. S18 ^{1}H NMR spectra of **DMCPPH2** recorded in CDCl$_3$.

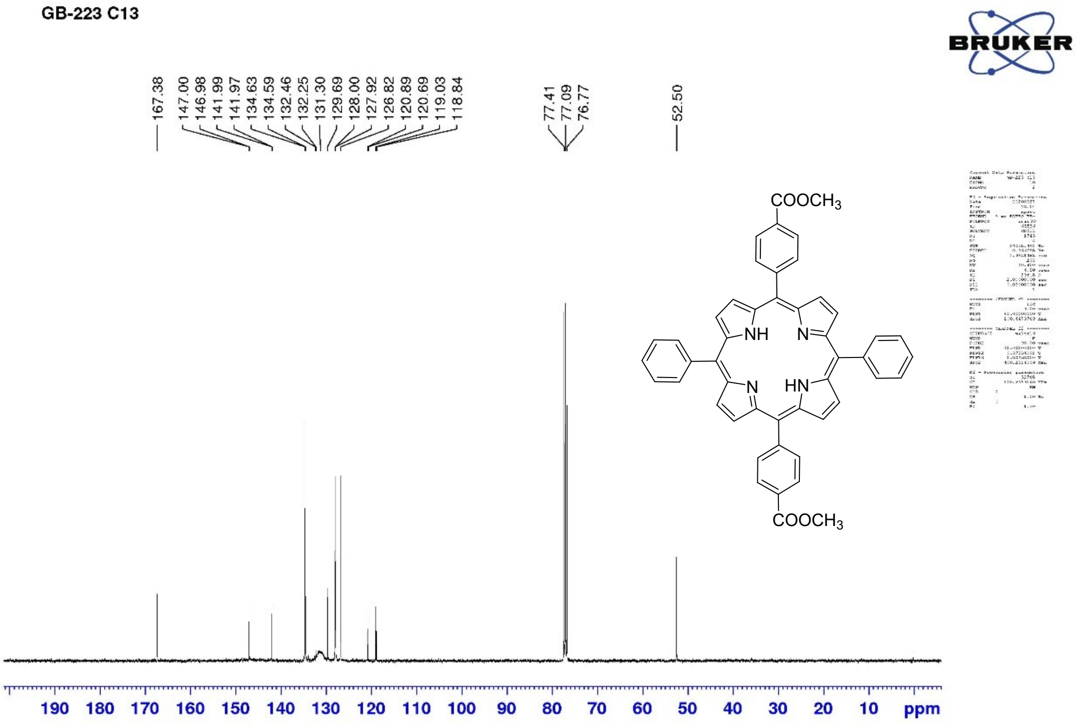


Fig. S19 ^{13}C NMR spectra of **DMCPPH2** recorded in $CDCl_3$.

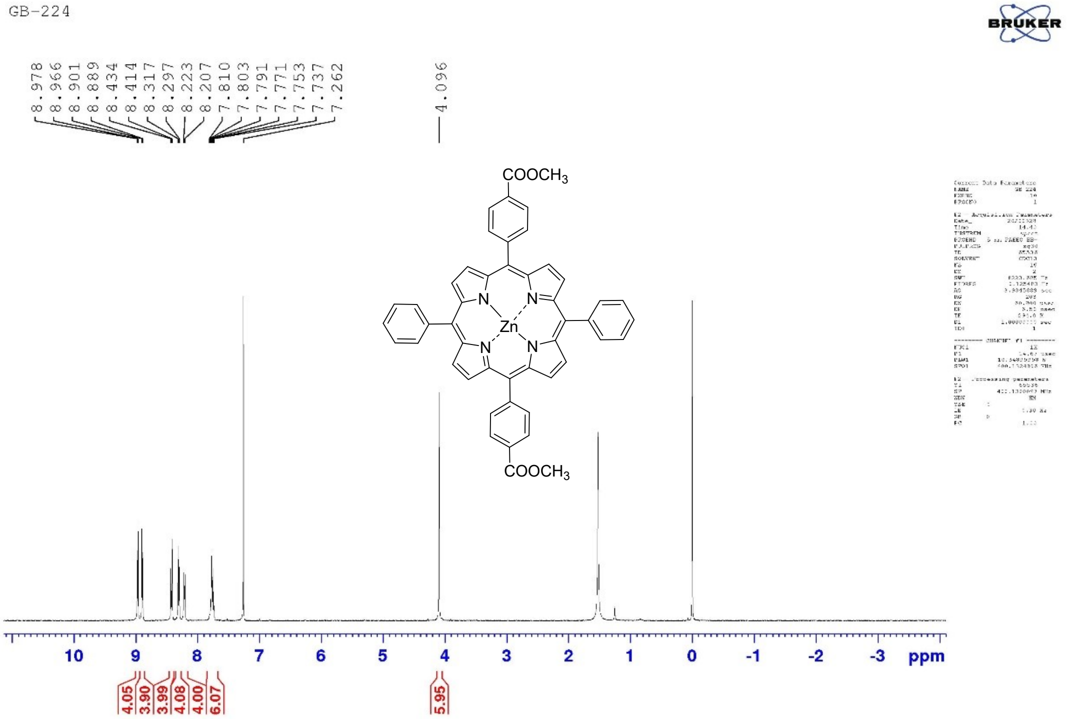


Fig. S20 ^{1}H NMR spectra of **ZnDMCPP** recorded in $CDCl_3$.

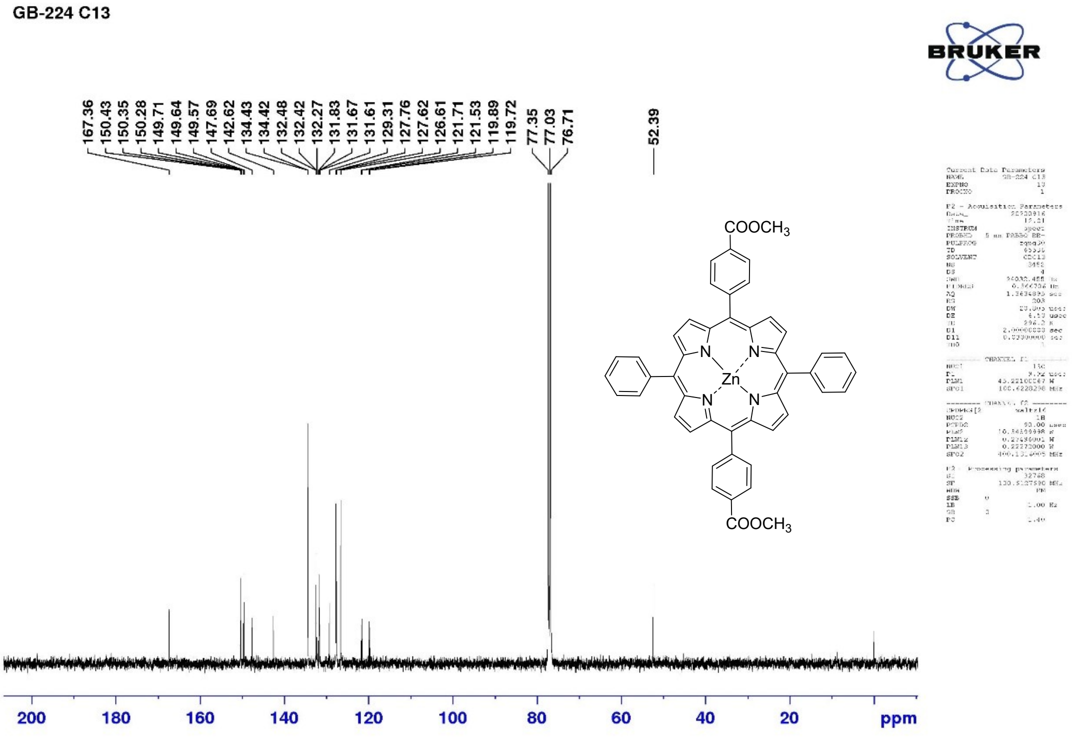


Fig. S21 ^{13}C NMR spectra of **ZnDMCPP** recorded in CDCl$_3$.

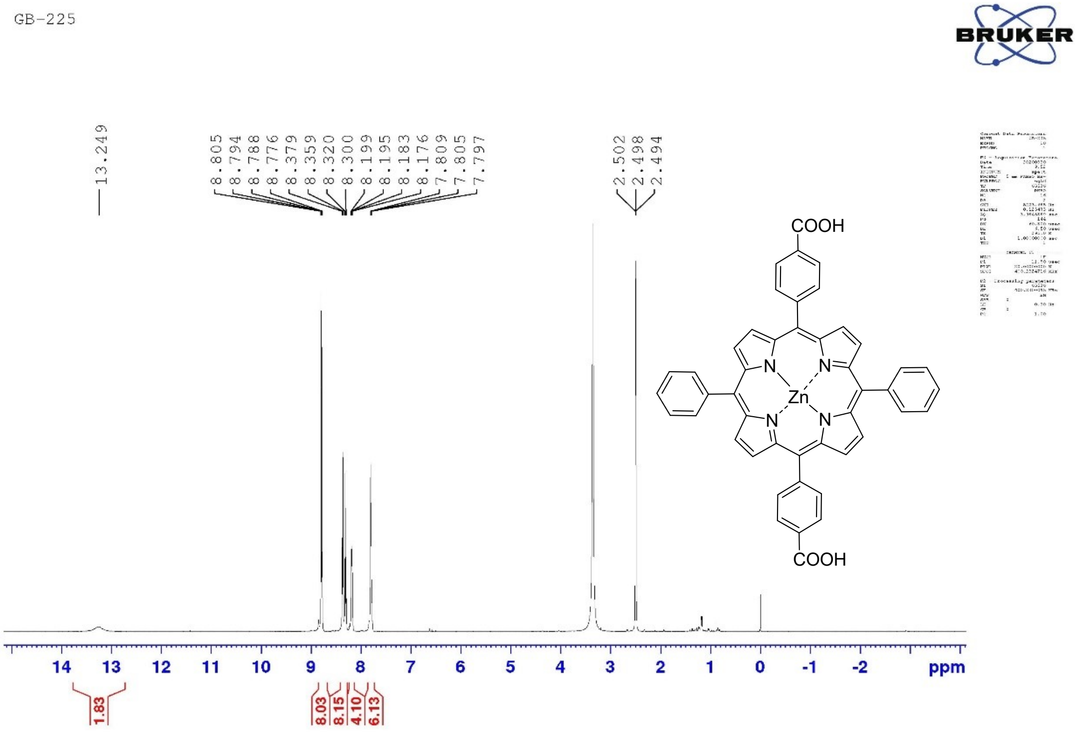


Fig. S22 ^{1}H NMR spectra of **ZnDCPP** recorded in DMSO-*d*6.

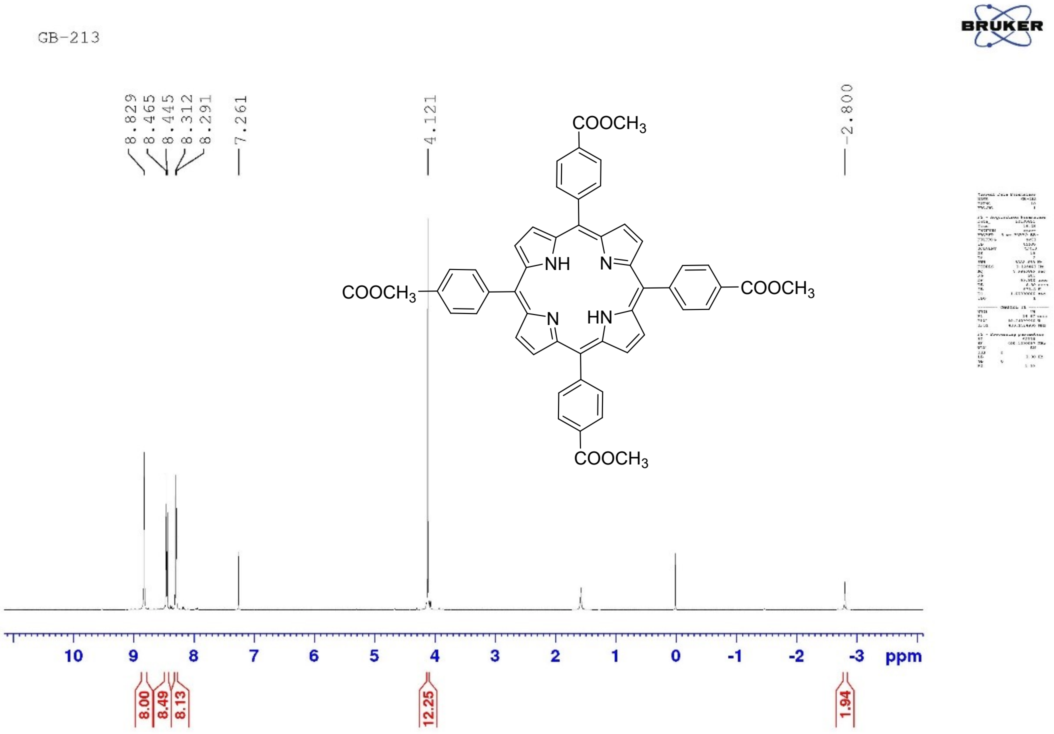


Fig. S23 ^{1}H NMR spectra of **TMCPP** recorded in $CDCl_3$.

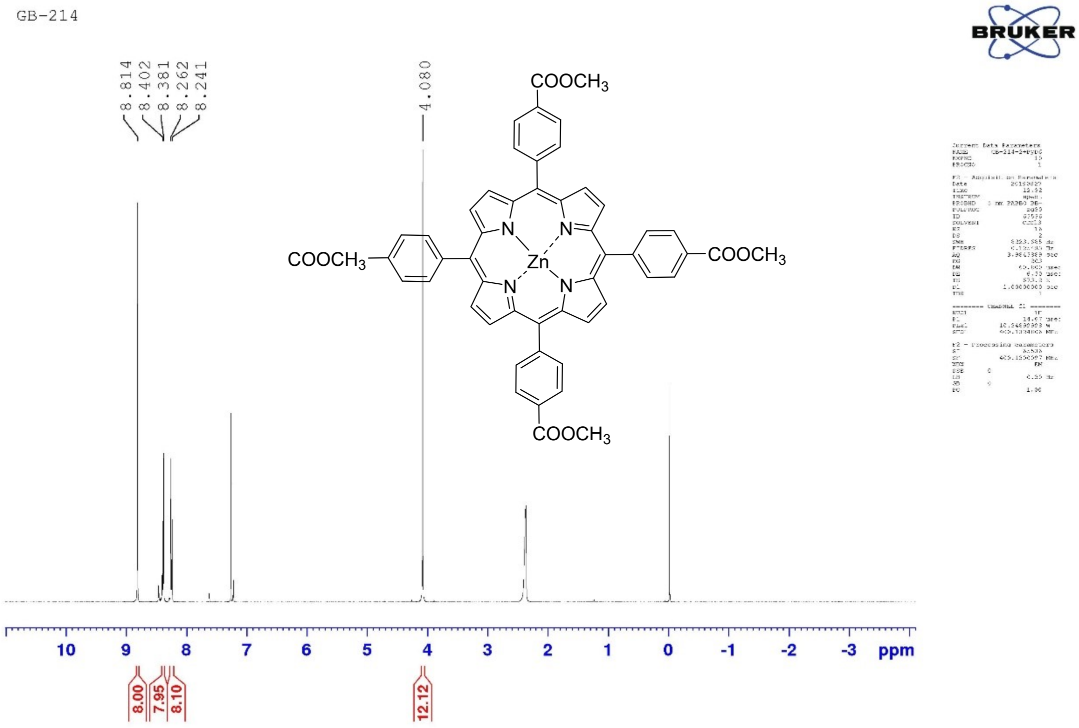


Fig. S24 ^{1}H NMR spectra of **ZnTMCPP** recorded in $CDCl_3$.

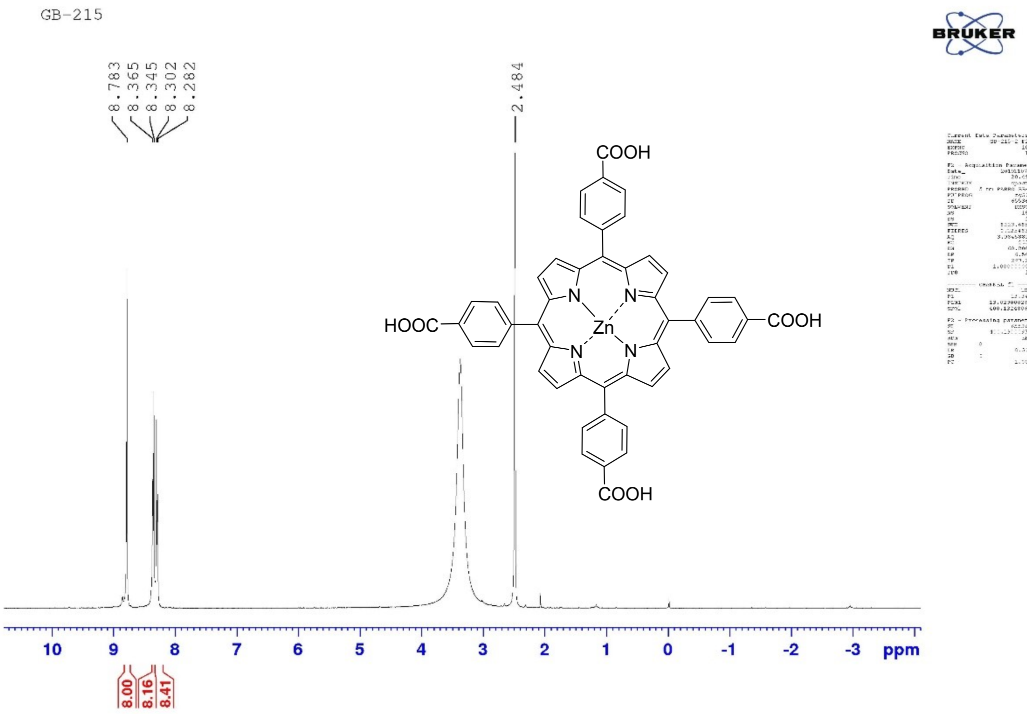
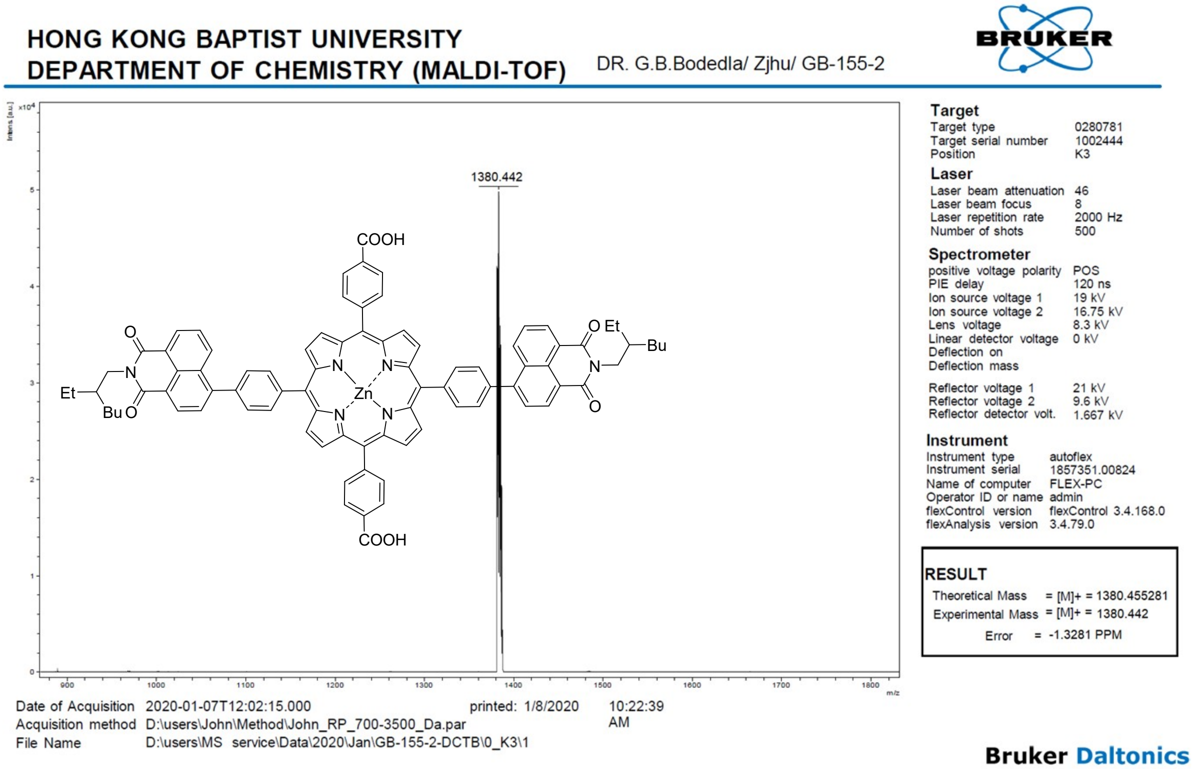


Fig. S25 ^{1}H NMR spectra of **ZnTCPP** recorded in DMSO-$d6$.


HONG KONG BAPTIST UNIVERSITY
DEPARTMENT OF CHEMISTRY (MALDI-TOF)
DR. G.B.Bodedla/ Zjhu/ GB-155-2

Target
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Target serial number 1002444
Position K3

Laser
Laser beam attenuation 46
Laser beam focus 8
Laser repetition rate 2000 Hz
Number of shots 500

Spectrometer
positive voltage polarity POS
PIE delay 120 ns
Ion source voltage 1 19 kV
Ion source voltage 2 16.75 kV
Lens voltage 8.3 kV
Linear detector voltage 0 kV
Deflection on
Deflection mass

Reflector voltage 1 21 kV
Reflector voltage 2 9.6 kV
Reflector detector volt. 1.667 kV

Instrument
Instrument type autoflex
Instrument serial 1857351.00824
Name of computer FLEX-PC
Operator ID or name admin
flexControl version flexControl 3.4.168.0
flexAnalysis version 3.4.79.0

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Experimental Mass = [M]+ = 1380.442
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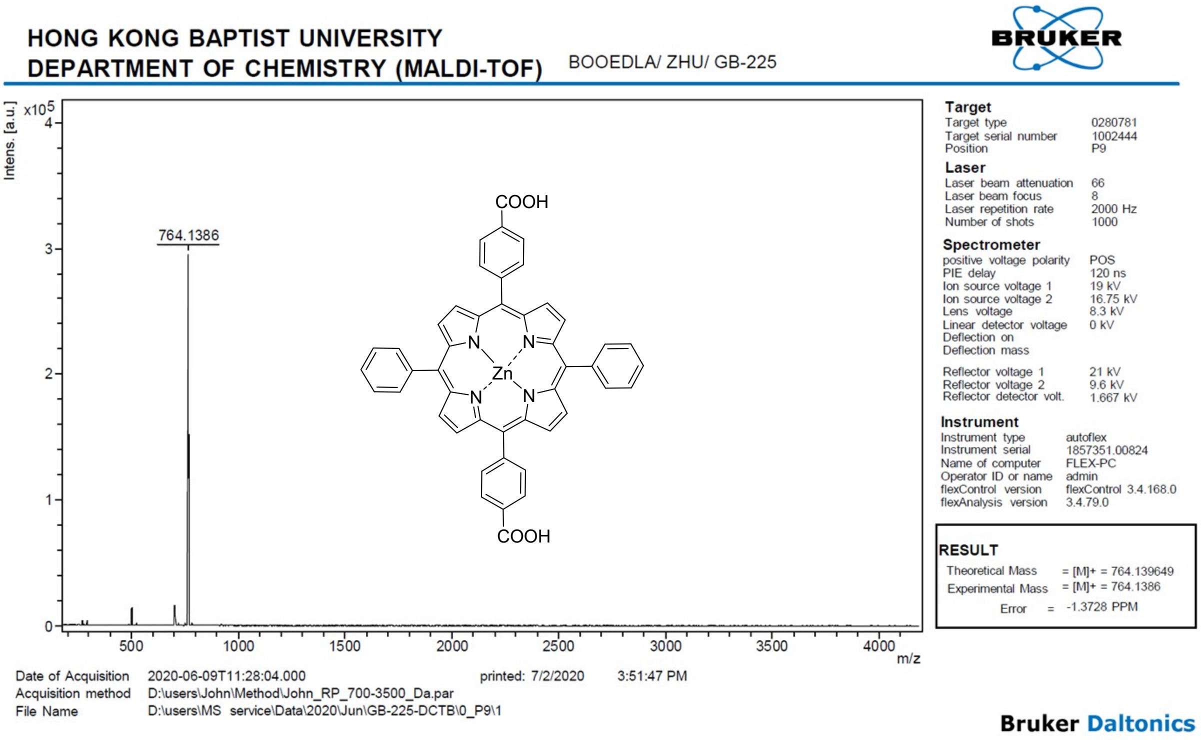
printed: 1/8/2020 10:22:39 AM

Bruker Daltonics

Fig. S26 MALDI−TOF spectrum of ZnDC(p-NI)PP.



HONG KONG BAPTIST UNIVERSITY
DEPARTMENT OF CHEMISTRY (MALDI-TOF) BOOEDLA/ ZHU/ GB-225

Target

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Target serial number	1002444
Position	P9

Laser

Laser beam attenuation	66
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Laser repetition rate	2000 Hz
Number of shots	1000

Spectrometer

positive voltage polarity	POS
PIE delay	120 ns
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Ion source voltage 2	16.75 kV
Lens voltage	8.3 kV
Linear detector voltage	0 kV
Deflection on	
Deflection mass	
Reflector voltage 1	21 kV
Reflector voltage 2	9.6 kV
Reflector detector volt.	1.667 kV

Instrument

Instrument type	autoflex
Instrument serial	1857351.00824
Name of computer	FLEX-PC
Operator ID or name	admin
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Fig. S27 MALDI–TOF spectrum of ZnDCPP.

References

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