

## Electronic Supplementary Information

### Visible-to-near-infrared light-harvesting A- $\pi$ -D- $\pi$ -A porphyrins for boosted photocatalytic hydrogen evolution

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## Experimental Section

### 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 the standard procedures. Purification of the compounds was performed by column chromatography with 100-200 mesh silica gel. <sup>1</sup>H NMR spectra were recorded on an NMR spectrometer operating at 400.00 MHz. The chemical shifts were calibrated from the residual

peaks observed for the deuterated solvent chloroform ( $\text{CDCl}_3$ ) at  $\delta$  7.26 ppm for  $^1\text{H}$  NMR spectra. 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 THF solutions (10  $\mu\text{M}$ ) at room temperature by using UV-Vis spectrophotometer and spectrofluorimeter, respectively. Cyclic voltammetry experiments were conducted on an electrochemical workstation (CHI660C Instruments, China) with standard three-electrode cell. A glassy carbon working electrode, a nonaqueous  $\text{Ag}/\text{Ag}^+$  reference electrode, and a platinum wire counter electrode were used for the measurements. Cyclic voltammetry experiments were measured at room temperature in THF solution (100  $\mu\text{M}$ ). Tetrabutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte and ferrocene (100  $\mu\text{M}$ ) was added as the internal reference.

### **Scanning electron microscopy (SEM)**

The samples were prepared by drying a solvent-based dispersion on silica substrates, followed by gold sputtering, and then transferred to a flat aluminum sample holder for SEM analysis. These samples were analyzed using a field emission scanning electron microscope (FESEM) (Tescan MAIA3) under an accelerating voltage of 5.0 kV.

### **Preparation of photocatalytic systems**

A multichannel photochemical reaction system fixed with LED white light (PCX50B, 148.5  $\text{mW}/\text{cm}^2$ ) 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, 100  $\mu\text{M}$  of porphyrins in THF/ $\text{H}_2\text{O}$  (2:1; v/v) solution sonicated for 5 min and 0.8 M of AA and 3 wt% of Pt were added. The resulting solution was purged with an argon gas for 15 min to ensure anaerobic conditions and then it was placed in

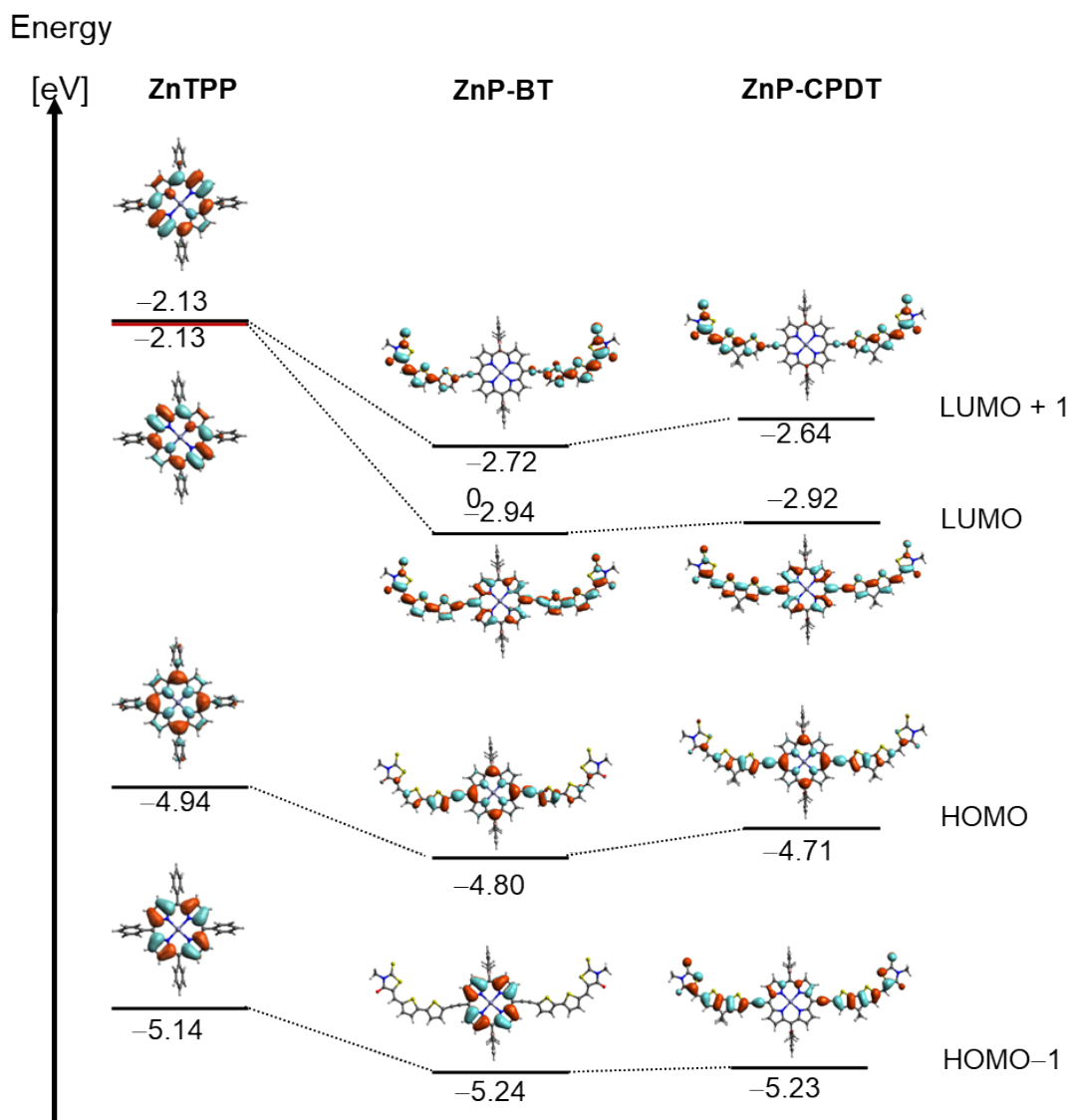
a multichannel photochemical reaction system. After 1 h of irradiation, the released gas (400  $\mu\text{L}$ ) was collected by syringe from the headspace of the reactor and was analyzed by gas chromatography (Shimadzu, GC-2014, Japan, with ultrapure Ar as a carrier gas) equipped with a TDX-01(5  $\text{\AA}$  molecular sieve column) and a thermal conductivity detector (TCD). Eventually, the total content of PHE was calculated according to the standard curve.

### **Photoelectrochemical measurement**

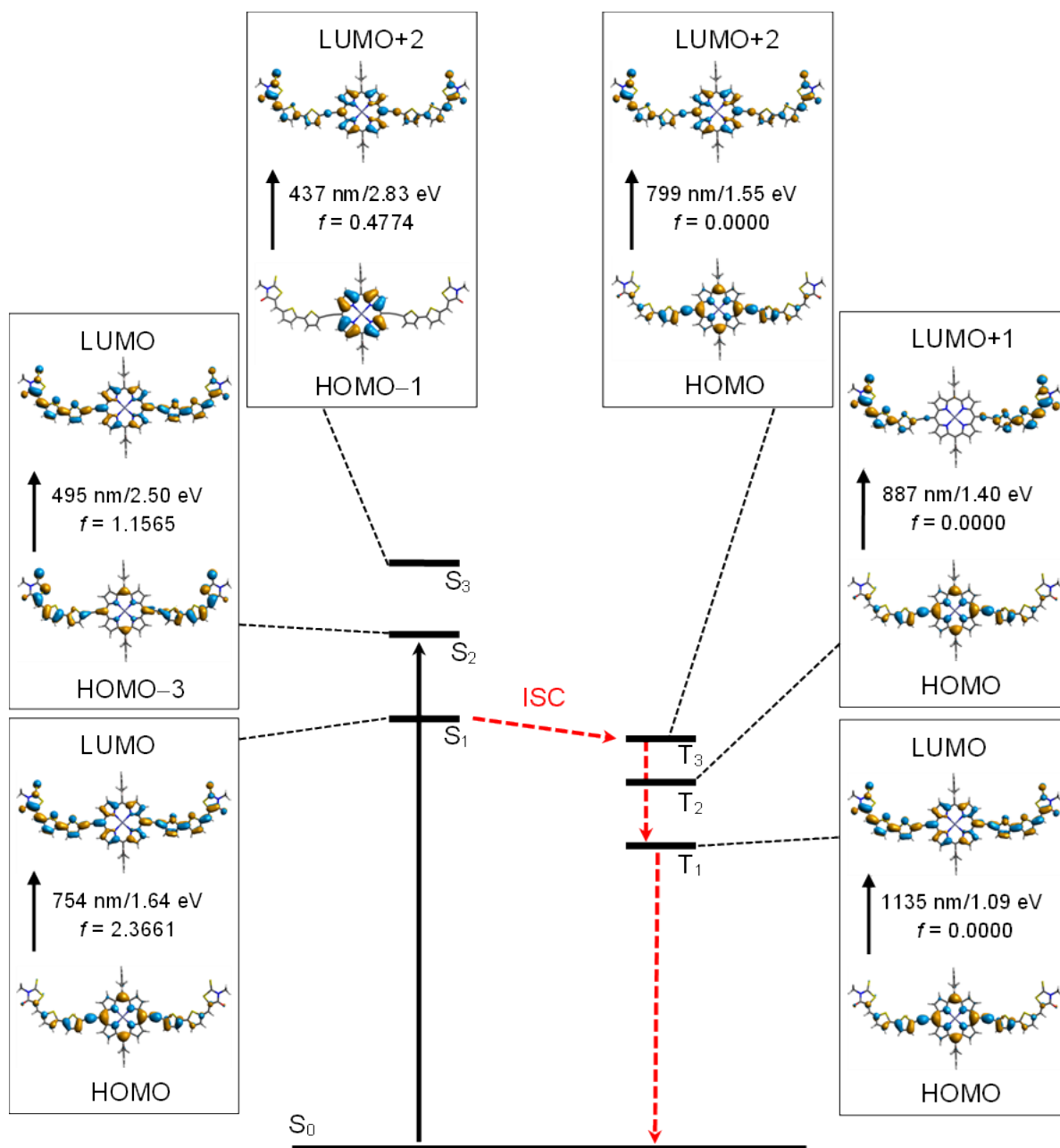
The transient photocurrent response ( $I-t$  curves) studies were performed using an electrochemical workstation (CHI660C Instruments, China) with a Pt wire (counter electrode), a non-aqueous Ag/AgNO<sub>3</sub> (reference electrode) and fluorine-doped tin oxide (FTO) glass coated with porphyrins on 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<sup>2</sup>. Typically, the working electrode was prepared by drop-casting a 100  $\mu\text{M}$  solution of porphyrins on the conductive surface of the FTO glass. A 5 mL volume of 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution acted as the electrolyte. The open-circuit voltages were set as the initial bias voltages in the transient photocurrent response tests.

### **Density functional theory calculations**

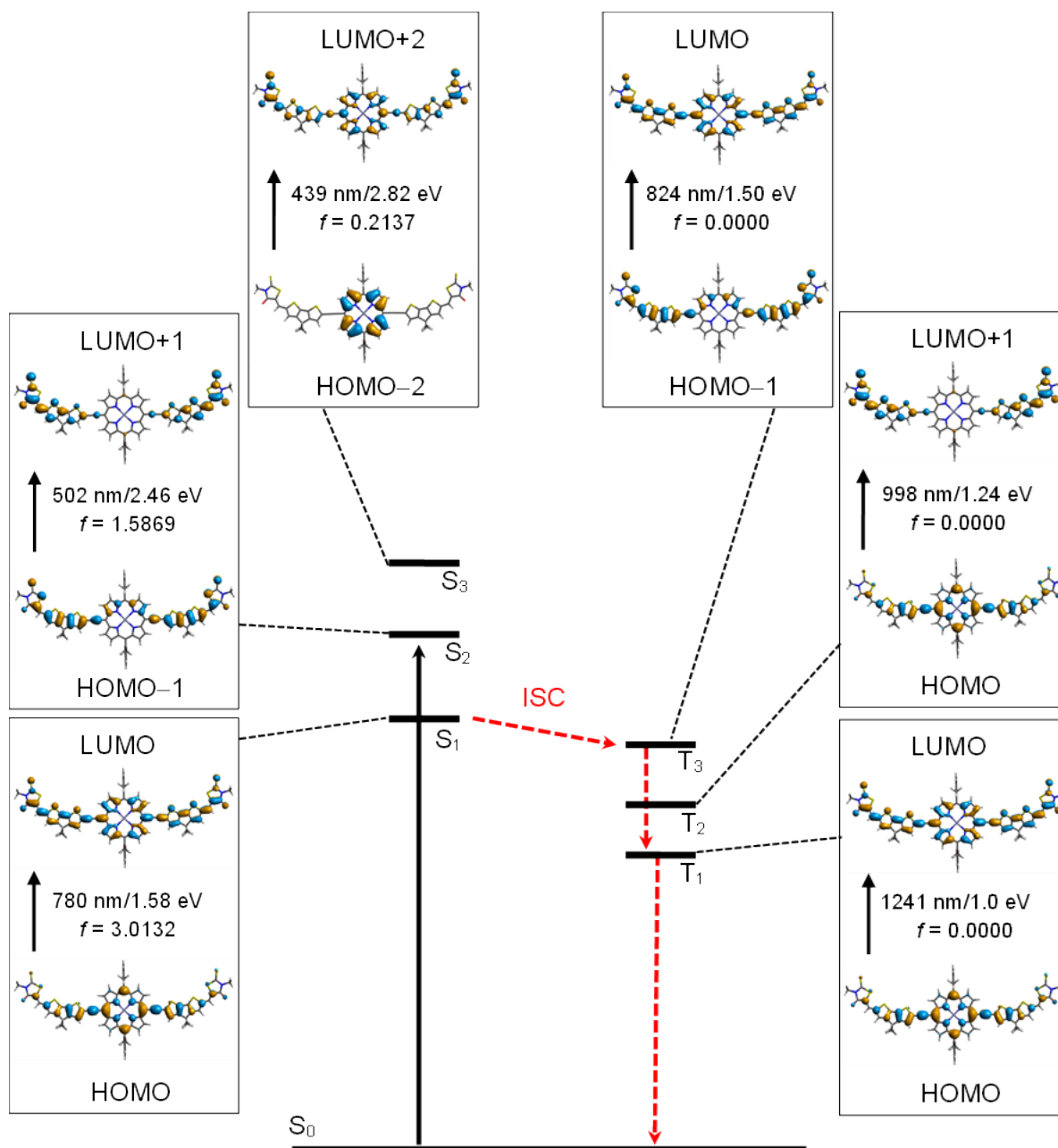
Density Functional Theory (DFT) calculations were used for geometry optimization and the frontier molecular orbitals (in a vacuum) of the complexes. All the calculations were performed with the Gaussian 09W program. The geometry optimization of the ground state was performed at the B3LYP/6-31G(d) level for C, H, N and O atoms. No imaginary frequency was observed for the computations.



**Fig. S1** Selected frontier molecular orbitals of **ZnTPP**, **ZnP-BT** and **ZnP-CPDT** calculated by DFT at the B3LYP/GENECP/LANL2DZ level with Gaussian 09 based on the optimized ground-state geometries. Iso value = 0.02.



**Fig. S2** Jablonski diagram of **ZnP-BT** calculated by DFT at the B3LYP/GENECP/LANL2DZ level with Gaussian 09 based on the optimized ground-state geometries. Iso value = 0.02.

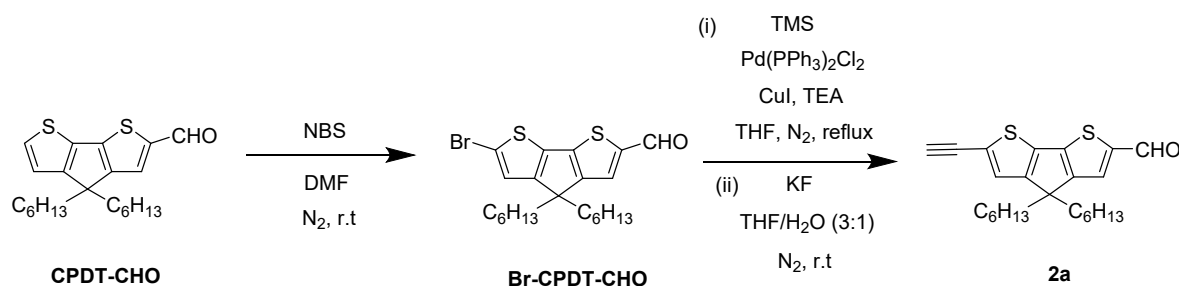


**Fig. S3** Jablonski diagram of **ZnP-CPDT** calculated by DFT at the B3LYP/GENECP/LANL2DZ level with Gaussian 09 based on the optimized ground-state geometries. Iso value = 0.02. Ethylhexyl chains were simplified to methyl groups for convenience.

## Synthesis

The di-bromo porphyrin scaffold (**1**),<sup>1</sup> ethynylbithiophene-aldehyde (**2b**) intermediate<sup>2</sup> and **ZnTPP**<sup>3</sup> were synthesized and characterized according to the previous reports. The synthetic

protocol used to synthesize ethynylcyclopentadithiophene-aldehyde (**2a**) is shown in Scheme S1. The cyclopentadithiophene-aldehyde, **CPDT-CHO** was synthesized and characterized according to the previous report.<sup>4</sup>



**Scheme S1.** Synthetic route of **2a**.

### **Br-CPDT-CHO:**

A mixture of **CPDT-CHO** (2.30 g, 6.13 mmol) and DMF (15 mL) was bubbled with N<sub>2</sub> for 20 min and to this mixture NBS (1.20 g, 6.70 mmol) in DMF (10 mL) was added dropwise at low-temperature (0 °C). Thereafter, the reaction mixture was allowed to stir at room temperature until the starting material disappeared. After completion of the reaction, the reaction mixture was poured into water and the organic content was extracted with dichloromethane (DCM). After evaporation of DCM solvent, the resulted crude solid containing the product was purified by column chromatography with silica using DCM/hexane (2:1, v/v) as eluant. Light-yellow color solid; yield: 2.37 g, 85.0 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.00 MHz) δ 0.81 (t, *J* = 6.8 Hz, 6 H), 0.88-0.93 (m, 4 H), 1.12-1.21 (m, 12 H), 1.60-1.86 (m, 4 H), 7.01 (s, 1 H), 7.55 (s, 1 H), 9.83 (s, 1 H).

### **2a:**

A mixture of **Br-CPDT-CHO** (1.00 g, 2.20 mmol), trimethylsilylacetylene (0.70 mL, 4.40 mmol), TEA (15 mL) and THF (60 mL) was bubbled with N<sub>2</sub> for 20 min and to this mixture CuI (20 mg) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (40 mg) were added. Then after, the reaction mixture was

refluxed until the starting materials disappeared. After completion of the reaction, THF and TEA were removed by flushing with air. The resulting crude light-yellow color liquid (1.00 g, 2.10 mmol) was dissolved in 50 ml of THF/H<sub>2</sub>O (3:1 v/v) and KF (0.90 g, 14.7 mmol) was added. This mixture was stirred for 0.5 h at room temperature. The reaction status was monitored by TLC. After completion of the reaction, THF was removed and the resulting black color liquid solution was poured into a mixture of water/DCM solution. The organic content was extracted with DCM. After evaporation of DCM solvent, the crude liquid containing the product was purified by column chromatography with silica using DCM/hexane (2:1, v/v) as eluant. Brown color solid; yield: 0.80 g, 92.0 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.00 MHz) δ 0.82 (t, *J* = 6.8 Hz, 6 H), 0.92-0.93 (m, 4 H), 1.12-1.21 (m, 12 H), 1.82-1.87 (m, 4 H), 3.54 (s, 1 H), 7.15 (s, 1 H), 7.57 (s, 1 H), 9.85 (s, 1 H).

### **3a:**

A mixture of **1** (0.30 g, 0.21 mmol), **2a** (0.21 g, 0.53 mmol), triethylamine (10 mL) and THF (30 mL) was bubbled with N<sub>2</sub> for 20 min and to this mixture CuI (15 mg) and Pd(PPh<sub>3</sub>)<sub>4</sub> (50 mg) were added. Then after, the reaction mixture was refluxed until the starting materials disappeared. After completion of the reaction, THF and TEA were removed by flushing with air. The resulting crude black solid containing the product was purified by column chromatography with silica using CHCl<sub>3</sub>/hexane (1:1, v/v) as eluent. Green color solid; yield: 0.40 g, 92.0 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.00 MHz) δ 0.41-0.64 (m, 24 H), 0.77-0.81 (m, 8 H), 0.83-1.25 (m, 104 H), 1.99 (t, *J* = 8.4 Hz, 8 H), 3.86 (d, *J* = 6.4 Hz, 8 H), 7.01 (d, *J* = 8.8 Hz, 4 H), 7.52 (s, 2 H), 7.64 (s, 2 H), 7.69-7.73 (m, 2 H), 8.85 (d, *J* = 4.4 Hz, 4 H), 9.56 (d, *J* = 4.8 Hz, 4 H), 9.89 (s, 2 H).

### **3b:**



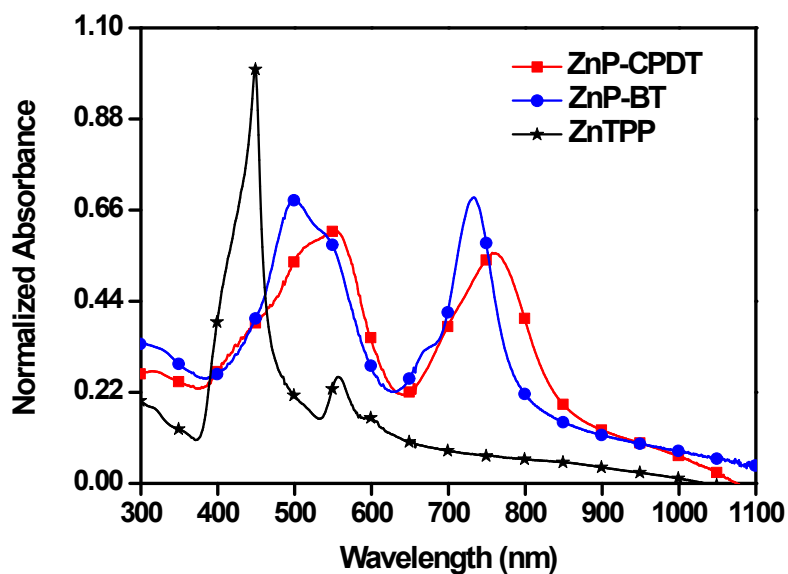
A mixture of **1** (0.20 g, 0.21 mmol), **2b** (0.12 g, 0.53 mmol), triethylamine (10 mL) and THF (30 mL) was bubbled with N<sub>2</sub> for 20 min and to this mixture CuI (15 mg) and Pd(PPh<sub>3</sub>)<sub>4</sub> (50 mg) were added. Then after, the reaction mixture was refluxed until the starting materials disappeared. After completion of the reaction, THF and TEA were removed by flushing with air. The resulting crude black solid containing the product was purified by column chromatography with silica using CHCl<sub>3</sub>/hexane (1:1, v/v) as eluent. Green color solid; yield: 0.28 g, 80.0 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.00 MHz) δ 0.42-0.53 (m, 8 H), 0.53-0.56 (m, 16 H), 0.73-0.89 (m, 22 H), 0.91-1.18 (m, 52 H), 3.86 (t, *J* = 6.4 Hz, 8 H), 7.01 (d, *J* = 8.4 Hz, 4 H), 7.16 (d, *J* = 4.0 Hz, 2 H), 7.23 (d, *J* = 12.4 Hz, 2 H), 7.44 (d, *J* = 4.0 Hz, 2 H), 7.61 (d, *J* = 4.0 Hz, 2 H), 7.68-7.70 (m, 2 H), 8.80 (d, *J* = 4.4 Hz, 4 H), 9.46 (d, *J* = 4.8 Hz, 4 H), 9.84 (s, 2 H).

#### **ZnP-CPDT:**

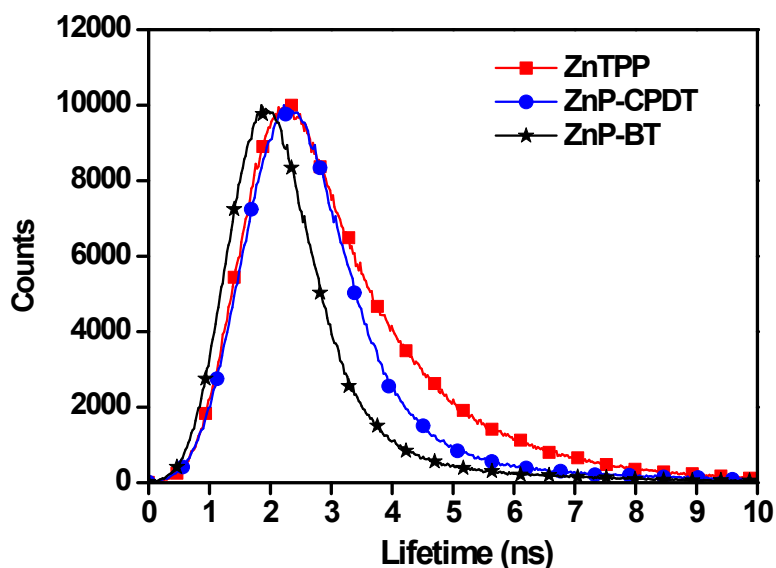
A mixture of **3a** (0.15 g, 0.07 mmol), 3-ethylrhodanine (0.12 g, 0.73 mmol), piperidine (100 μL) and CHCl<sub>3</sub> (20 mL) was bubbled with N<sub>2</sub> for 20 min and refluxed until the starting materials disappeared. After completion of the reaction, the reaction mass was poured into water and 50 mL chloroform was added. The organic layer was separated and the solvent was removed. The resulting crude product was purified by column chromatography with silica using CHCl<sub>3</sub>/hexane (1:1, v/v) as eluent. Black color solid; yield: 0.11 g, 65.0 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.00 MHz) δ 0.41-0.62 (m, 24 H), 0.41-0.62 (m, 24 H), 0.77-1.30 (m, 118 H), 1.97 (t, *J* = 8.0 Hz, 8 H), 3.87 (t, *J* = 6.4 Hz, 8 H), 4.1 (s-br, 4 H), 7.02 (d, *J* = 8.4 Hz, 4 H), 7.27 (s, 2 H), 7.26 (d, *J* = 8.4 Hz, 2 H), 7.52 (s, 2 H), 7.70-7.74 (m, 4 H), 7.86 (d, *J* = 4.4 Hz, 4 H), 7.58 (d, *J* = 4.4 Hz, 4 H). (MALDI-TOF, *m/z*) calculated for C<sub>138</sub>H<sub>182</sub>N<sub>6</sub>O<sub>6</sub>S<sub>8</sub>Zn: 2342.321; found 2342.321.

#### **ZnP-BT:**

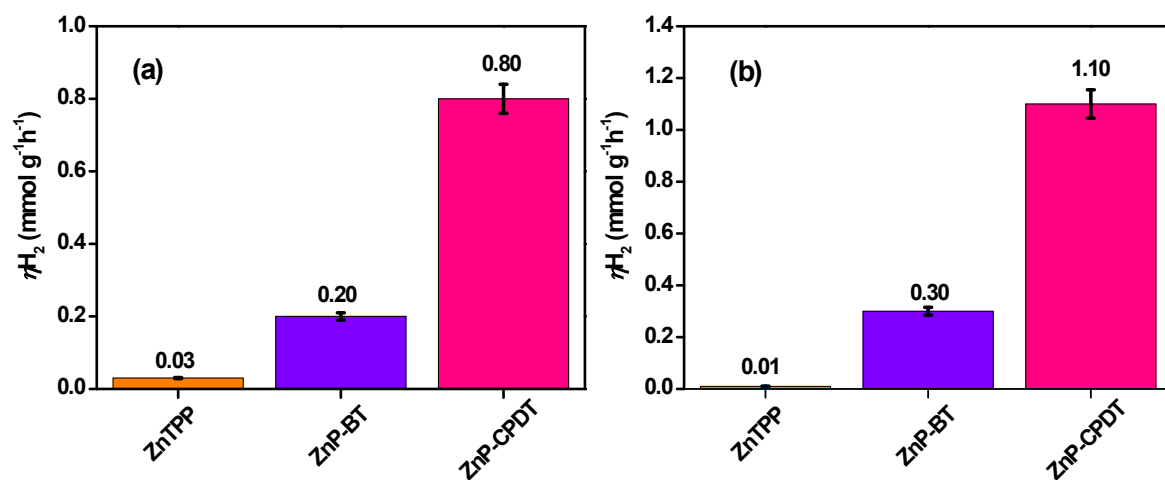
A mixture of **3b** (0.12 g, 0.07 mmol), 3-ethylrhodanine (0.12 g, 0.73 mmol), piperidine (100  $\mu$ L) and chloroform (20 mL) was bubbled with N<sub>2</sub> for 20 min and refluxed until the starting materials disappeared. After completion of the reaction, the reaction mass was poured into water and 50 mL chloroform was added. The organic layer was separated and the solvent was removed. The resulting crude product was purified by column chromatography with silica using chloroform/hexane (1:1, v/v) as eluent. Black color solid; yield: 0.10 g, 72.0 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.00 MHz)  $\delta$  0.55-0.90 (m, 44 H), 0.91-1.28 (m, 54 H), 3.93 (t,  $J$  = 6.4 Hz, 8 H), 4.16 (t,  $J$  = 7.6 Hz, 4 H), 6.64-6.75 (m, 4 H), 7.02-7.09 (m, 4 H), 7.16-7.22 (m, 2 H), 7.23-7.26 (m, 2 H), 7.60-7.65 (m, 2 H), 7.72-7.76 (m, 2 H), 8.11 (d,  $J$  = 4.4 Hz, 4 H), 9.43 (d,  $J$  = 4.8 Hz, 4 H). (MALDI-TOF,  $m/z$ ) calculated for C<sub>112</sub>H<sub>134</sub>N<sub>6</sub>O<sub>6</sub>S<sub>8</sub>Zn: 1984.908; found 1984.909.



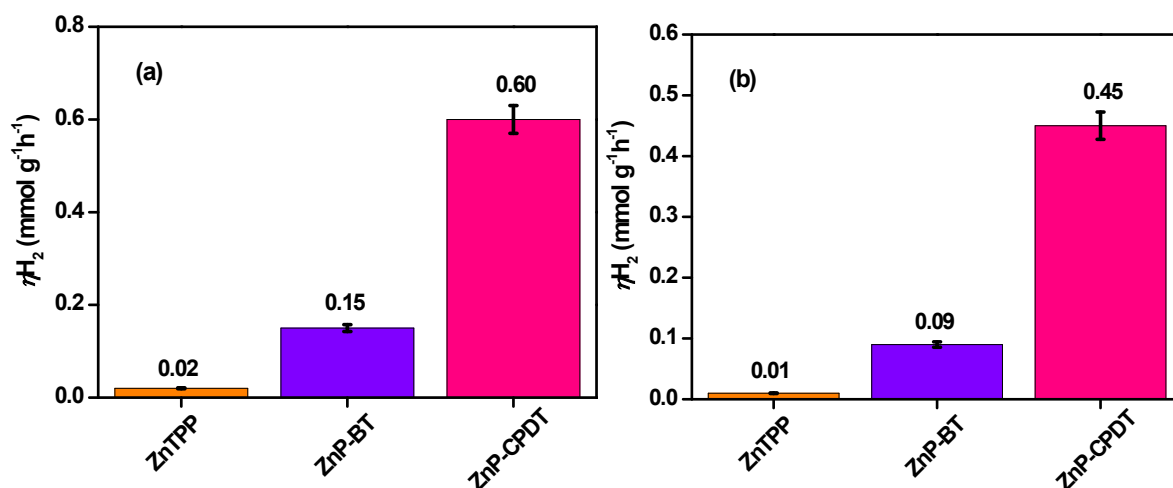
**Fig. S4** UV-Vis absorption spectrum of the porphyrins on drop-cast coated thin films (100  $\mu$ M) at room temperature.



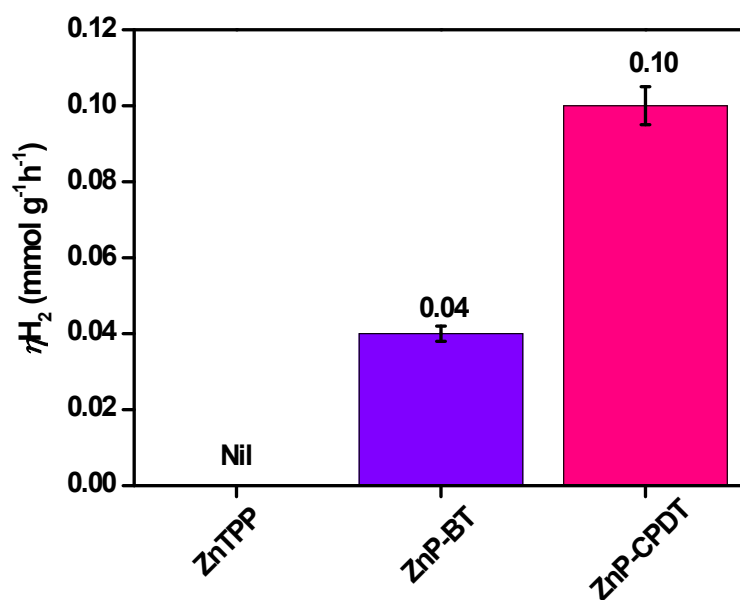
**Fig. S5** Photoluminescence lifetime decay spectrum of ZnTPP, ZnP-CPDT and ZnP-BT recorded ( $\lambda_{\text{ex}} = 380$  nm and lifetime monitored wavelength is 604 nm for ZnTPP, 778 nm for ZnP-CPDT and 756 nm for ZnP-BT) in THF solution (10  $\mu\text{M}$ ).



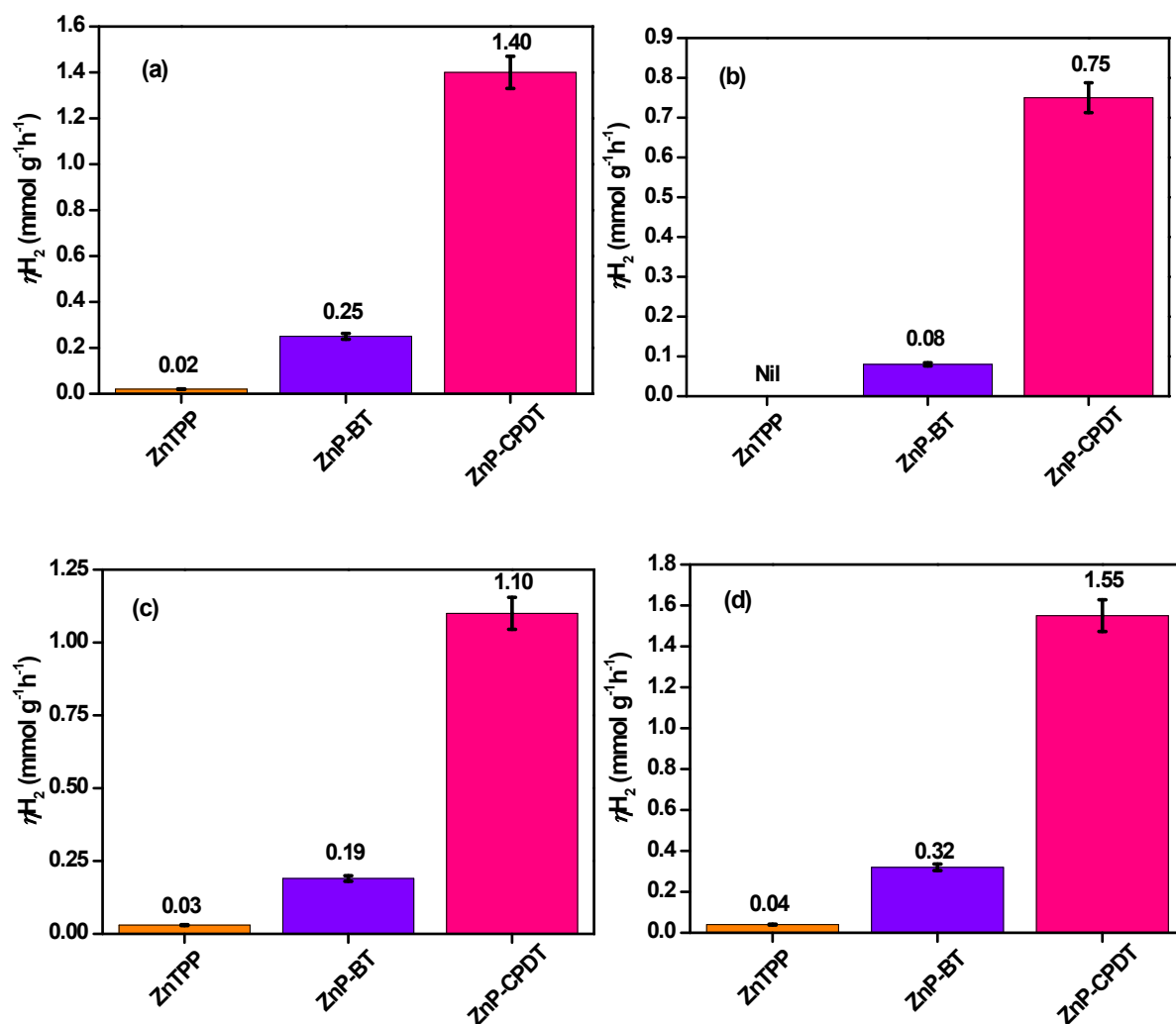
**Fig. S6** (a)  $\eta_{\text{H}_2}$  of photocatalytic systems of ZnTPP, ZnP-BT and ZnP-CPDT under irradiation for 5 h: Photosensitizer (100  $\mu\text{M}$ ) + TEA (0.8 M) + Pt (3 wt%) + THF/ $\text{H}_2\text{O}$  (2:1; v/v) and (b)  $\eta_{\text{H}_2}$  of photocatalytic systems of ZnTPP, ZnP-BT and ZnP-CPDT under irradiation for 5 h: Photosensitizer (100  $\mu\text{M}$ ) + TEOA (0.8 M) + Pt (3 wt%) + THF/ $\text{H}_2\text{O}$  (2:1; v/v).



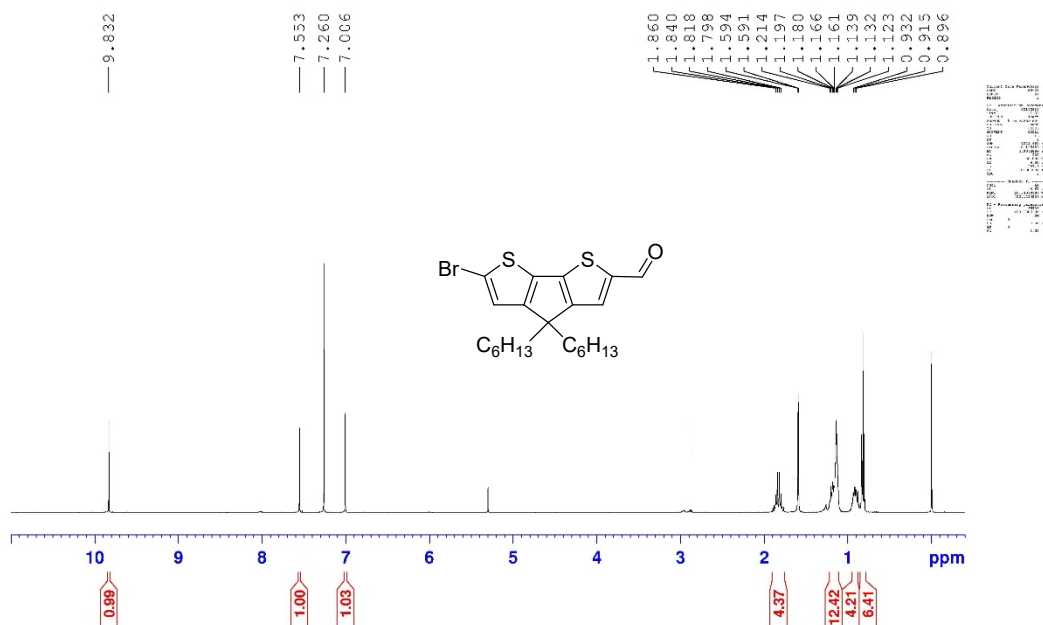
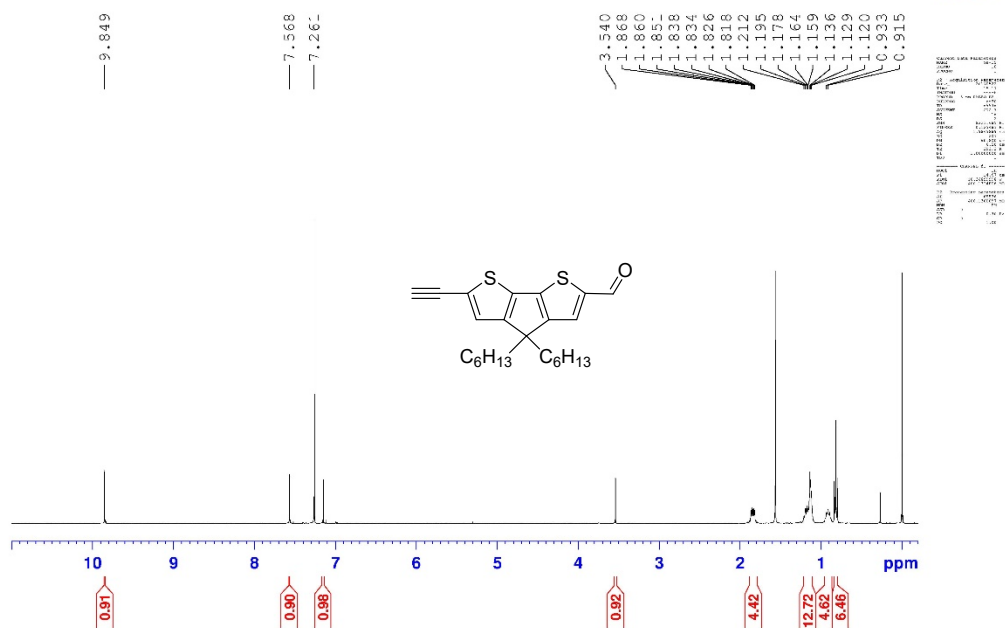
**Fig. S7** (a)  $\eta_{H_2}$  of photocatalytic systems of ZnTPP, ZnP-BT and ZnP-CPDT under irradiation for 5 h: Photosensitizer (100  $\mu\text{M}$ ) + AA (0.8 M) + Pt (3 wt%) + acetonitrile (ACN)/ $\text{H}_2\text{O}$  (2:1; v/v) and (b)  $\eta_{H_2}$  of photocatalytic systems of ZnTPP, ZnP-BT and ZnP-CPDT under irradiation for 5 h: Photosensitizer (100  $\mu\text{M}$ ) + AA (0.8 M) + Pt (3 wt%) + dimethylformamide (DMF)/ $\text{H}_2\text{O}$  (2:1; v/v).



**Fig. S8** (a)  $\eta_{H_2}$  of photocatalytic systems of ZnTPP, ZnP-BT and ZnP-CPDT under irradiation for 5 h: Photosensitizer (100  $\mu\text{M}$ ) + AA (0.8 M) + CoPyCl (400  $\mu\text{M}$ ) + THF/ $\text{H}_2\text{O}$  (2:1; v/v).



**Fig. S9**  $r_{H_2}$  of photocatalytic systems of ZnTPP, ZnP-BT and ZnP-CPDT under irradiation for 5 h (a) photosensitizer (100  $\mu\text{M}$ ) + AA (0.8 M) + Pt (3 wt%) + THF/ $\text{H}_2\text{O}$  (1:1; v/v), (b) photosensitizer (100  $\mu\text{M}$ ) + AA (0.8 M) + Pt (3 wt%) + THF/ $\text{H}_2\text{O}$  (1:9; v/v), (c) photosensitizer (100  $\mu\text{M}$ ) + AA (0.8 M) + Pt (3 wt%) + THF/ $\text{H}_2\text{O}$  (9:1; v/v) and (d) photosensitizer (100  $\mu\text{M}$ ) + AA (0.8 M) + Pt (3 wt%) + THF/ $\text{H}_2\text{O}$  (1:2; v/v).

Fig. S10 <sup>1</sup>H NMR spectrum of Br-CPDT-CHO.Fig. S11 <sup>1</sup>H NMR spectrum of 2a.

GB-27

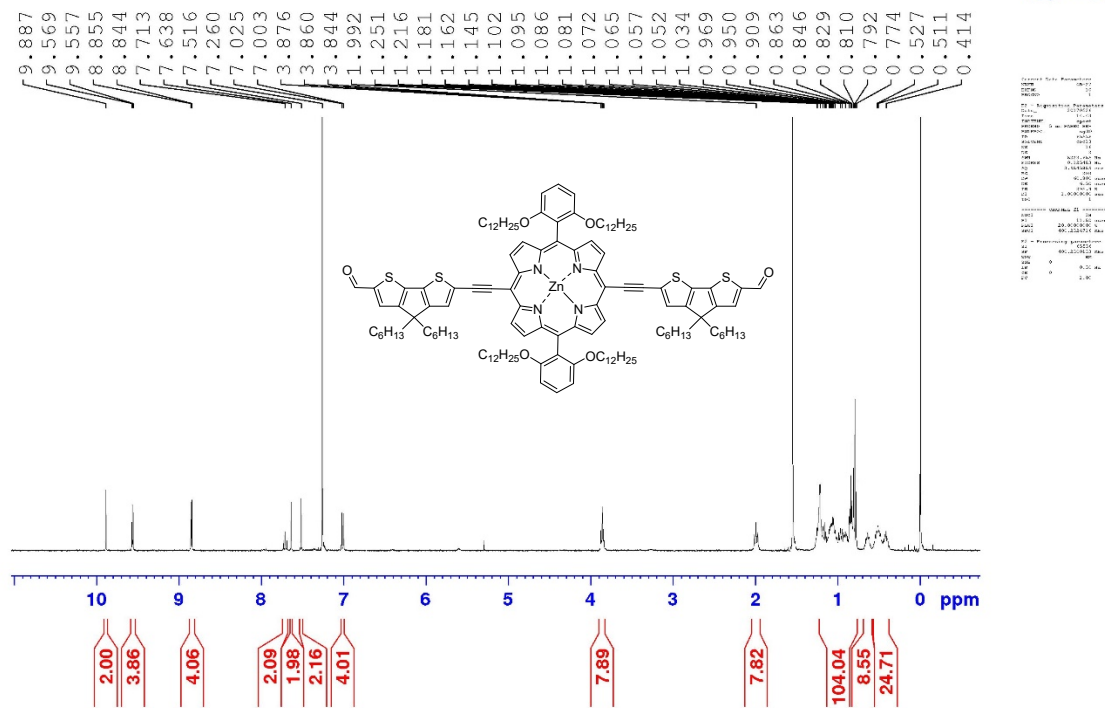


Fig. S12 <sup>1</sup>H NMR spectrum of 3a.

GB-42

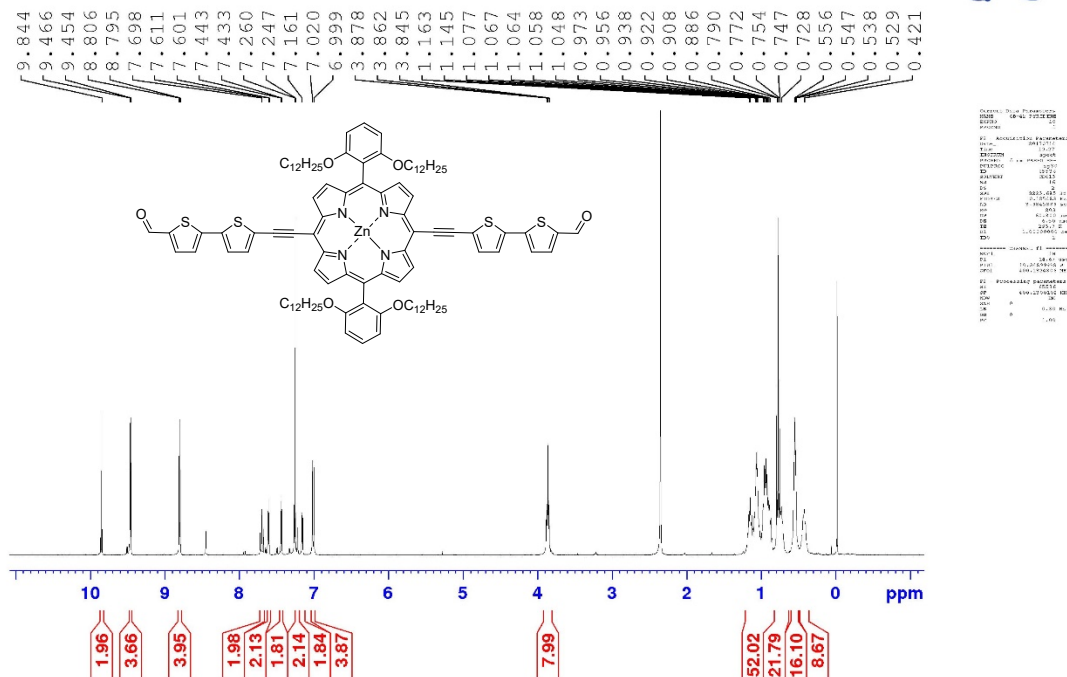


Fig. S13 <sup>1</sup>H NMR spectrum of 3b.

GB-30

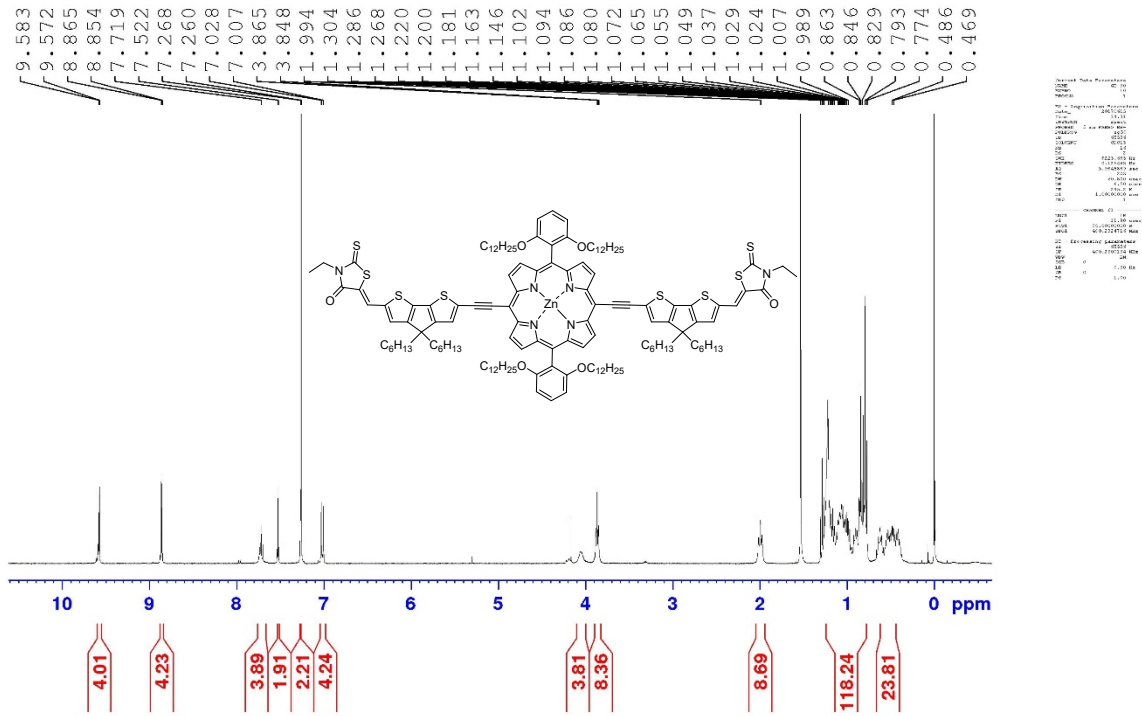


Fig. S14 <sup>1</sup>H NMR spectrum of ZnP-CPDT.

GB-47

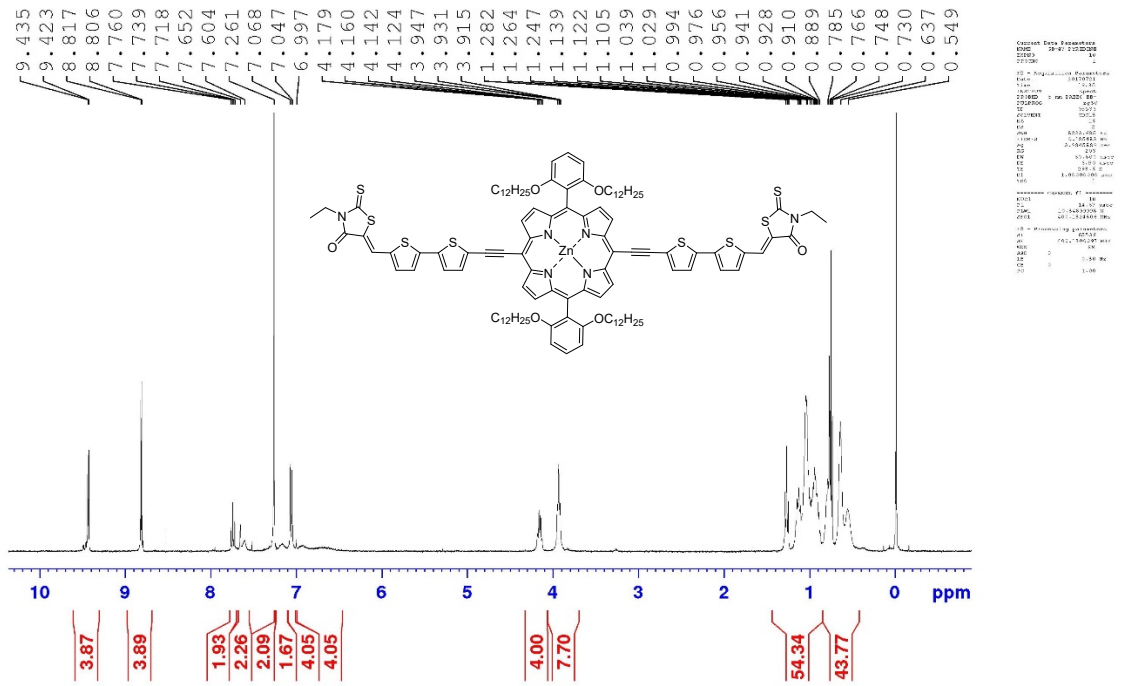
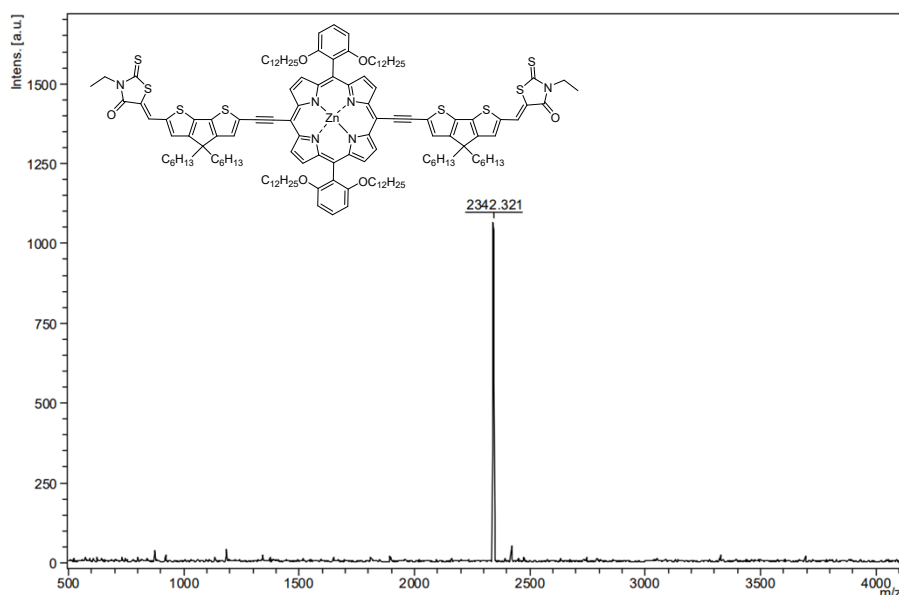


Fig. S15 <sup>1</sup>H NMR spectrum of ZnP-BT.





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Target serial number 0006489  
Position M3

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Laser beam focus 0  
Laser repetition rate 20 Hz  
Number of shots 500

**Spectrometer**  
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PIE delay 210 ns  
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ion source voltage 2 17.08 kV  
Lens voltage 8.1 kV  
Linear detector voltage 1.836 kV  
Deflection on  
Deflection mass  
Reflector voltage 1 20 kV  
Reflector voltage 2 0 kV  
Reflector detector volt. 1.781 kV

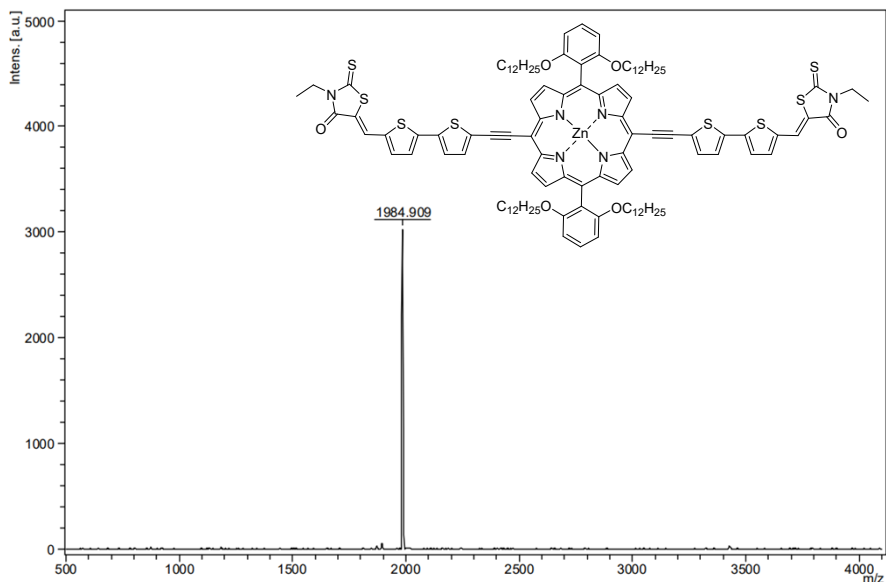
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Operator ID or name administrator  
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flexAnalysis version 3.4.79.0

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Error =

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File Name D:\Data (service)\AutoFlex\_T1207\_Data\MS\_Service\DATA 2017\JULY-AUG\GB-29P2-DCTB\0\_M3\1

Bruker Daltonics

Fig. S16 MALDI-TOF spectrum of ZnP-CPDT.



**Target**  
Target type 0026755  
Target serial number 0006489  
Position M5

**Laser**  
Laser beam attenuation 66  
Laser beam focus 0  
Laser repetition rate 20 Hz  
Number of shots 500

**Spectrometer**  
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ion source voltage 1 19.02 kV  
ion source voltage 2 17.08 kV  
Lens voltage 8.1 kV  
Linear detector voltage 1.836 kV  
Deflection on  
Deflection mass  
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Reflector voltage 2 0 kV  
Reflector detector volt. 1.781 kV

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**RESULT**  
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Bruker Daltonics

Fig. S17 MALDI-TOF spectrum of ZnP-BT.

## References

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