

Supporting Information for

**Photoelectrochemical Properties of Doubly  $\beta$ -  
Functionalized Porphyrin Sensitizers for the Dye-  
Sensitized Nanocrystalline-TiO<sub>2</sub> Solar Cells**

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**This PDF file includes:**

(UV-vis absorption and emission, cyclic voltammogram, UV-vis absorption of **4b-FB**  
and **4b-Zn** in the dense solution and IPCE action spectra of **4b-FB** and **4b-Zn**.)

## (1) Details of synthetic procedure

### General Procedure 1 for Hydrolysis of Porphyrin Tetraacrylate to Tetraacid

The porphyrin tetraethyl ester (0.01 mmol) was dissolved in THF (1 mL). Then ethanol (1 mL) and NaOH aq. (2.0 M, 0.5 mL) were added. The solution was stirred at N<sub>2</sub> atmosphere at 70 °C (oil bath) for 24 h. The solvent was removed in vacuo, and the solid was dissolved in about 50 mL of water. The aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (×2) to get rid of the unreacted ester. The tetraacid was precipitated by the slow addition of HCl aq. (1.0 M) to the aqueous solution (pH = 3). The precipitate was filtered and washed with water and CH<sub>2</sub>Cl<sub>2</sub> thoroughly to give the product as dark powder. Yield 95~98%.

4b-FB: <sup>1</sup>H NMR (600 MHz, pyridine-d<sub>5</sub>): δ -1.91 (s, 2H, NH), 1.63 (s, 36H, *t*-Bu), 7.70–7.74 (d, 4H, *J* = 16.0 Hz, double bond CH), 8.15 (s, 2H, ArH), 8.51 (s, 4H, ArH), 9.76 (s, 4H, β-H), 9.94–9.97 (d, 4H, *J* = 15.5 Hz, double bond CH), 11.16 (s, 2H, *meso*-H).

4b-Zn: <sup>1</sup>H NMR (600 MHz, pyridine-d<sub>5</sub>): δ 1.56 (s, 36H, *t*-Bu) 7.65–7.68 (d, 4H, *J* = 15.6 Hz, double bond CH), 8.10 (s, 2H, ArH), 8.51 (s, 4H, ArH), 9.85 (s, 4H, β-H), 9.98–10.01 (d, 4H, *J* = 16.2 Hz, double bond CH), 11.11 (s, 2H, *meso*-H).

### General Procedure 2 for Hydrolysis of Porphyrin Diacrylate to Diacid

The porphyrin dihexyl ester (0.028 mmol) was dissolved in THF (2 mL). Then ethanol (2 mL) and NaOH aq. (2.0 M, 1.5 mL) were added. The solution was stirred at N<sub>2</sub> atmosphere at 70 °C (oil bath) for 40 h. The solvent was removed in vacuo, then add about 200 mL of water to the solid (colloid state). The green solid was precipitated by the slow addition of 1.0 M HCl aq. to the aqueous solution (pH = 3). The mixture was extracted with CHCl<sub>3</sub> (×5) and the organic layer was dried by Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent and precipitation from CHCl<sub>3</sub>/hexane gave the product as dark green powder. Yield 90~95%.

2b-FB:  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  -2.37 (s, 2H, NH), 1.52–1.59 (m, 54H, *t*-Bu), 7.21–7.22 (d, 2H,  $J = 15.6\text{Hz}$ , double bond CH), 7.81 (s, 1H, ArH), 7.89 (s, 2H, ArH), 8.04 (s, 2H, ArH), 8.11 (s, 4H, ArH), 8.87–8.91 (dd, 4H,  $\beta$ -H), 9.38 (s, 2H,  $\beta$ -H), 9.86–9.88 (d, 2H,  $J = 15.0\text{ Hz}$ , double bond CH), 10.64 (s, 1H, *meso*-H).

2b-Zn:  $^1\text{H}$  NMR (600MHz,  $\text{CDCl}_3$ ):  $\delta$  1.50–1.59 (m, 54H, *t*-Bu), 7.20–7.23 (d, 2H,  $J = 15.5\text{ Hz}$ , double bond CH), 7.80 (s, 1H, ArH), 7.89 (s, 2H, ArH), 8.05 (s, 2H, ArH), 8.12 (s, 4H, ArH), 8.97–9.01 (dd, 4H,  $\beta$ -H), 9.47 (s, 2H,  $\beta$ -H), 9.90–9.92 (d, 2H,  $J = 15.0\text{ Hz}$ , double bond CH), 10.71 (s, 1H, *meso*-H).

#### **Hydrolysis of Porphyrin Bisdienoate to 2b-bd-Zn.**

Follow the general procedure 2. After the organic layer was dried by  $\text{Na}_2\text{SO}_4$ , evaporation of the solvent and precipitation from hexane directly provided the product as dark green powder. Yield: 89%.

2b-bd-Zn:  $^1\text{H}$  NMR (600MHz,  $\text{CDCl}_3$ ):  $\delta$  1.43–1.59 (m, 54H, *t*-Bu), 6.28–6.31 (d,  $J = 15.1\text{ Hz}$ , 2H, double bond CH), 7.69–7.71 (dd, 2H, double bond CH), 7.79 (s, 1H, ArH), 7.87 (s, 2H, ArH), 8.04 (s, 2H, ArH), 8.12 (s, 4H, ArH), 8.30–8.35 (dd, 2H, double bond CH), 8.95–8.96 (d,  $J = 15.1\text{ Hz}$ , 2H, double bond CH), 8.96–8.97 (dd, 4H,  $\beta$ -H), 9.36 (s, 2H,  $\beta$ -H), 10.48 (s, 1H, *meso*-H).

#### **Hydrolysis of Porphyrin Dienoate to 1b-d-Zn.**

Follow the general procedure 2. After the organic layer was dried by  $\text{Na}_2\text{SO}_4$ , evaporation of the solvent and precipitation from acetone/water gave the product as red powder. Yield: 96%.

1b-d-Zn:  $^1\text{H}$  NMR(600MHz,  $\text{CDCl}_3$ ):  $\delta$  1.51–1.57 (m, 54H, *t*-Bu), 6.24–6.27 (d,  $J = 15.1\text{ Hz}$ , 1H, double bond CH), 7.60–7.65 (dd, 1H, double bond CH), 7.78 (s, 1H, ArH), 7.82 (s, 1H, ArH), 7.85 (s, 1H, ArH), 7.92–8.01 (dd, 1H, double bond CH), 8.06 (s, 2H, ArH), 8.11 (s, 2H, ArH), 8.12 (s, 2H, ArH), 8.72–8.75 (d,  $J = 15.2\text{ Hz}$ , 1H, double bond CH), 8.99–9.01 (m, 4H,  $\beta$ -H), 9.13–9.14 (d, 1H,  $\beta$ -H), 9.32 (s, 1H,  $\beta$ -H), 9.43 (d, 1H,  $\beta$ -H), 10.35 (s, 1H, *meso*-H).

### Hydrolysis of Porphyrin *meso*-Diester to 2m-s-Zn.

Follow the general procedure 2. After the organic layer was dried by Na<sub>2</sub>SO<sub>4</sub>, evaporation of the solvent and precipitation from CHCl<sub>3</sub>/hexane afforded the product as red powder. Yield: 98%.

2m-s-Zn: <sup>1</sup>H NMR (600 MHz, THF-d<sub>8</sub>): δ 3.46–3.48 (t, 4H, CH<sub>2</sub>), 5.40–5.43 (t, 4H, CH<sub>2</sub>), 7.90 (s, 2H, ArH), 8.11 (s, 4H, ArH), 8.92–8.92 (d, 4H, β-H), 9.60–9.61 (d, 4H, β-H), 10.97 (br, 2H, COOH).

### Preparation of 2b-bdta-Zn.

Diborylated Zn(II)-porphyrin (50.0 mg, 0.042mmol) and [Rh(cod)OH]<sub>2</sub> (2.5 mg, 0.0055 mmol) were added to the Schlenk flask and purged with argon, and then charged with 1,4-dioxane (1.0 mL), H<sub>2</sub>O (100 μL), and dimethyl 2-allylidene malonate (80.0μL, 0.47mmol). The mixture was stirred at room temperature for 48 h under argon. After removal of the solvent under vacuum, the crude product was passed through a short silica gel column (eluent: THF). After evaporation of the solvent, the residue was dissolved in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> and DDQ (20 mg) was added to the solution. The mixture was stirred for 15 min (the red color turn to green). The mixture was passed through a short alumina column (eluent: THF) and the crude product was separated by silica gel chromatography with hexane/THF = 10/1 to get dark green product (19.8 mg), which was precipitated from a mixture of CH<sub>2</sub>Cl<sub>2</sub>/MeOH. yield 39%; <sup>1</sup>H NMR (CDCl<sub>3</sub>): 1.51–1.57 (m, 54H, CH<sub>3</sub> *t*-Bu), 3.95–3.99 (d, 12H, OCH<sub>3</sub>), 7.79 (m, 1H, ArH), 7.84–7.85 (m, 2H, ArH), 8.02 (m, 2H, ArH), 8.03–8.09 (dd, 2H, double bond CH), 8.10 (m, 4H, ArH), 8.19–8.22 (d, *J* = 16.0 Hz, 2H, double bond CH), 8.87–8.90 (d, *J* = 15.1 Hz, 2H, double bond CH), 8.94–8.95 (d, 2H, β-H), 8.98–8.99 (d, 2H, β-H), 9.34 (s, 2H, β-H), 10.49 (s, 1H, *meso*-H).

### Hydrolysis to 2b-bdta-Zn.

The porphyrin bisdiene tetraester (19.8 mg, 0.0155 mmol) was dissolved in THF (2.0 mL). Then

ethanol (1.5 mL) and NaOH aq. (2.0 M, 2.0 mL) were added. The solution was stirred at N<sub>2</sub> atmosphere at 65~70 C (oil bath) for 24 h. The solvent was removed in vacuo, then add about 200 mL of water to the solid. The green solid was precipitated by the slow addition of HCl aq. (1.0 M) to the aqueous solution (pH = 3). After standing over night and filtration, dark green solid (19 mg) was obtained. Yield: 95%. The <sup>1</sup>H NMR for 2b-bdta-Zn in CDCl<sub>3</sub>, pyridine-d<sub>5</sub>, THF-d<sub>8</sub>, and DMSO-d<sub>6</sub> were almost unreadable.

## (2) UV-vis absorption and emission

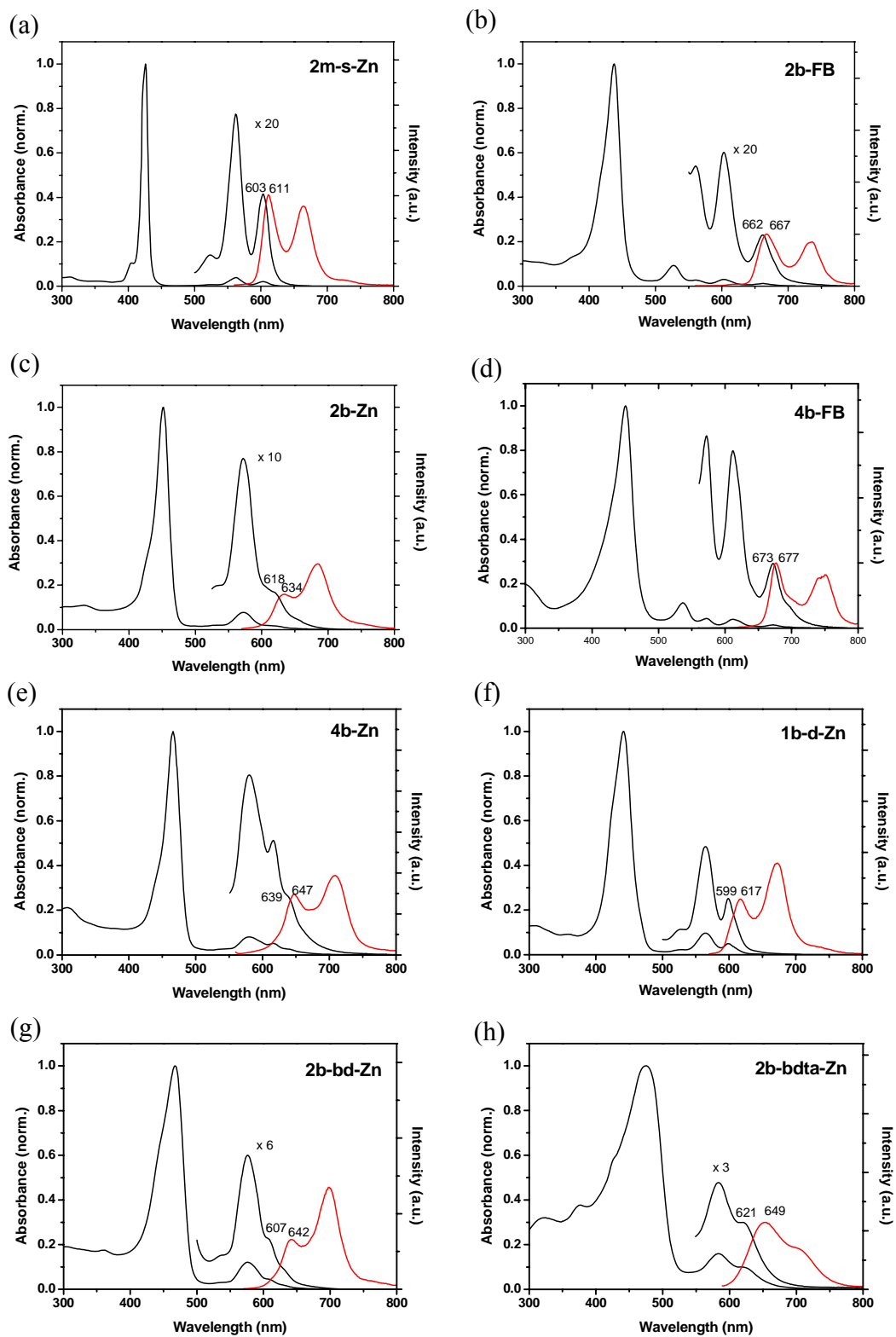
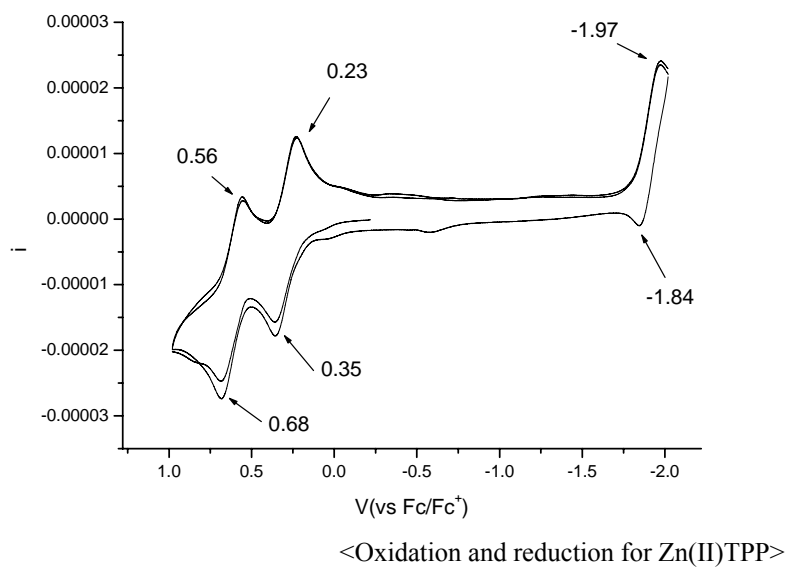


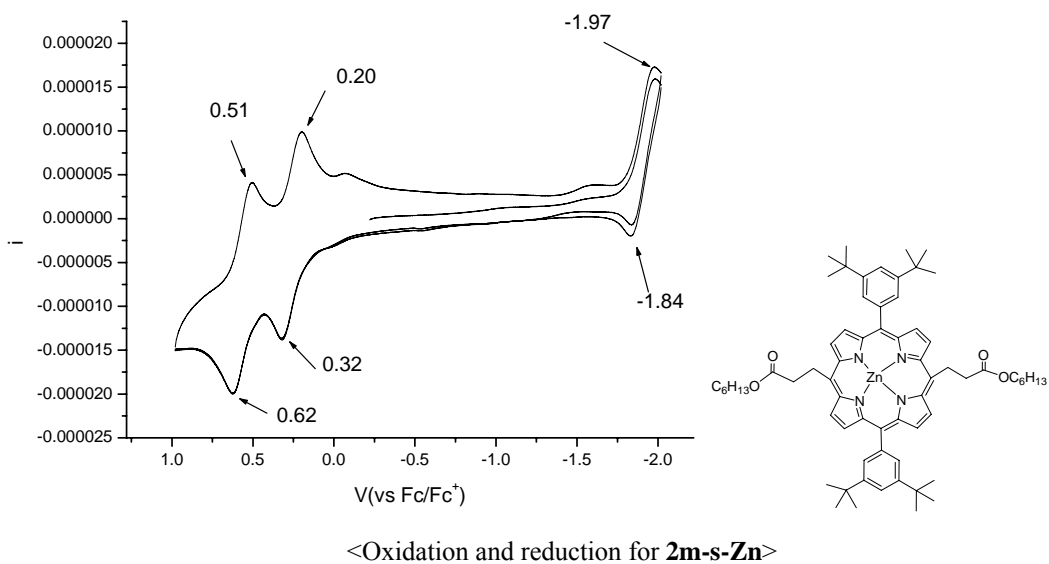
Figure S1. UV-vis absorption and emission for all porphyrins measured in ethanol.

### (3) Cyclic voltammetry

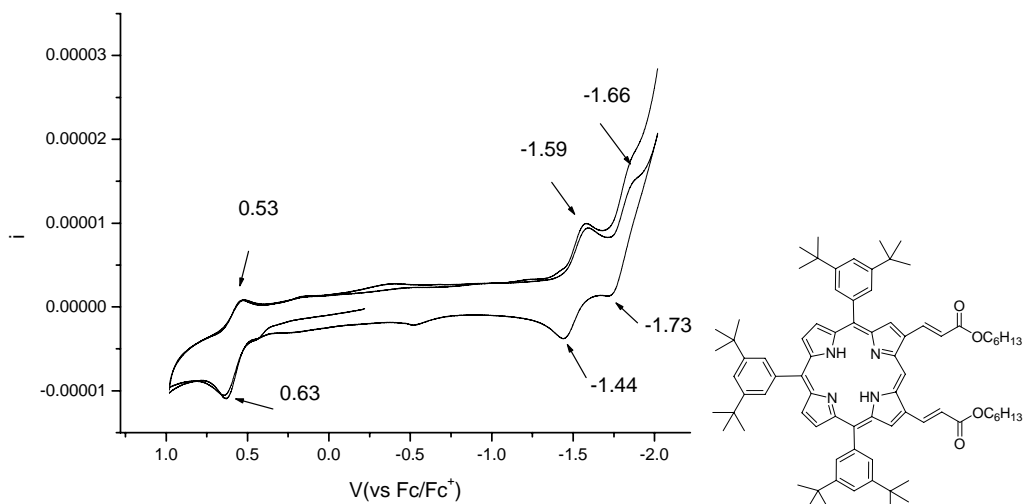
(a)



(b)

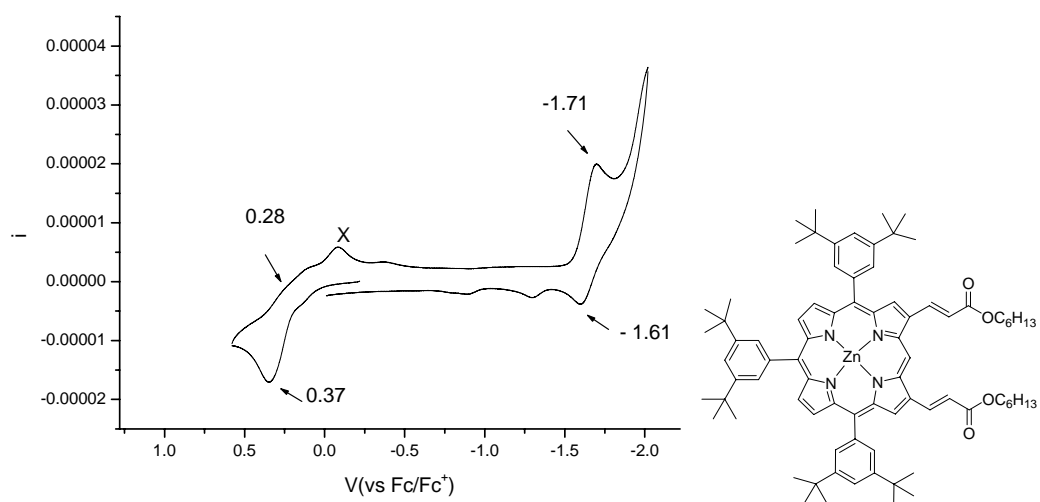


(c)



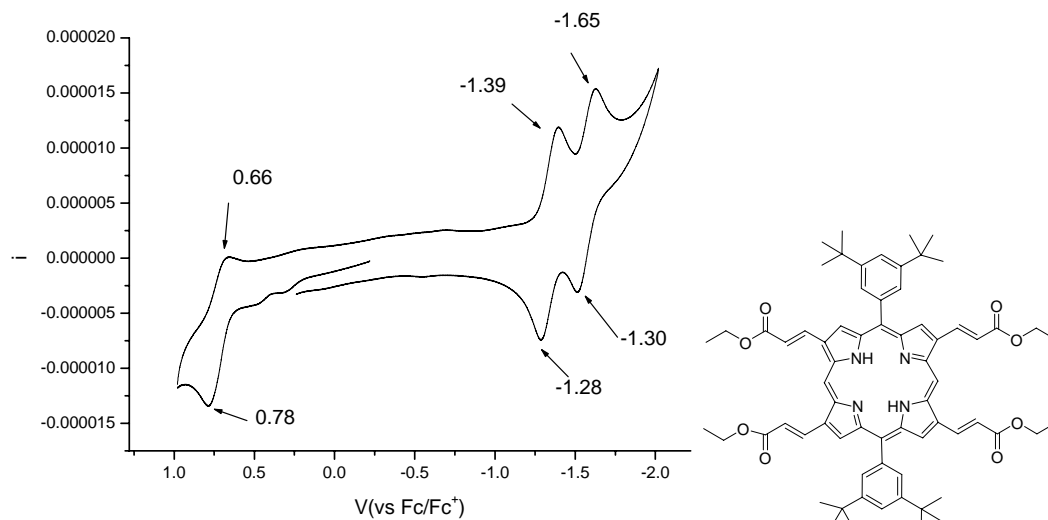
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(d)



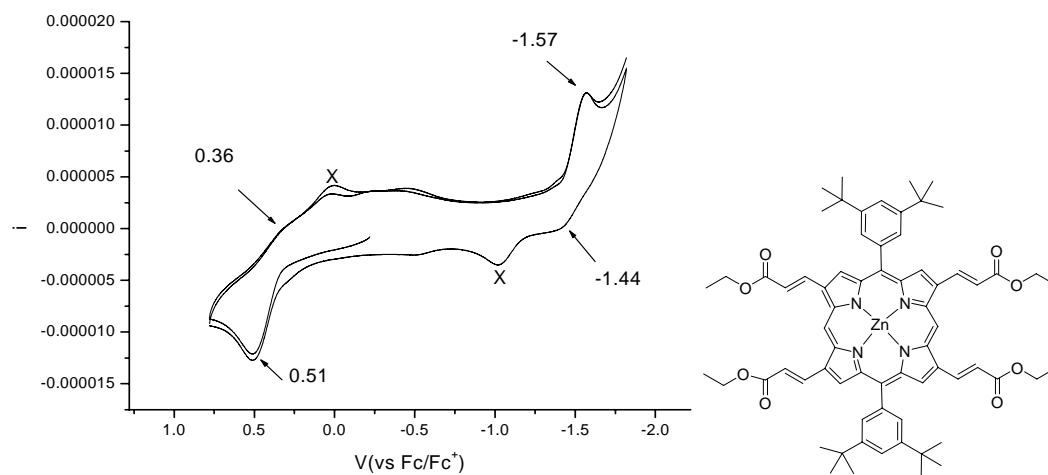
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(e)



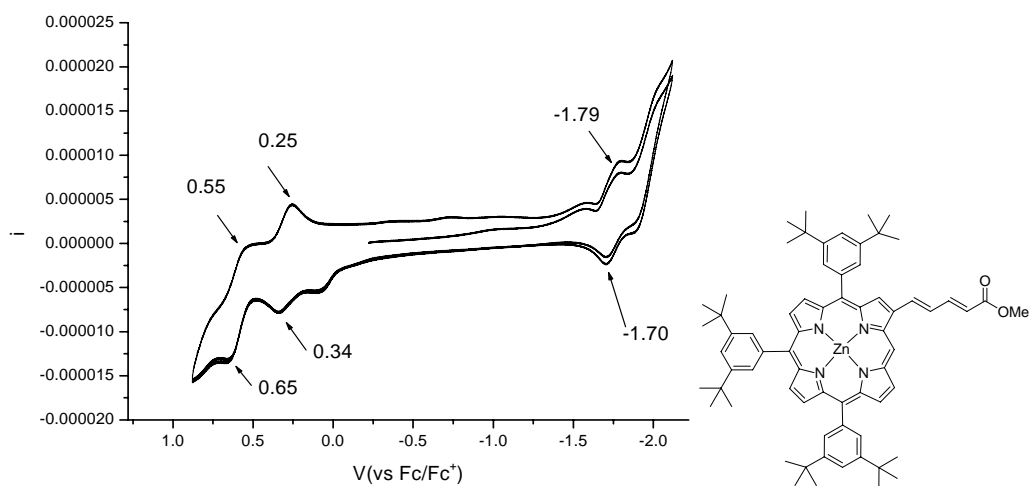
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(f)



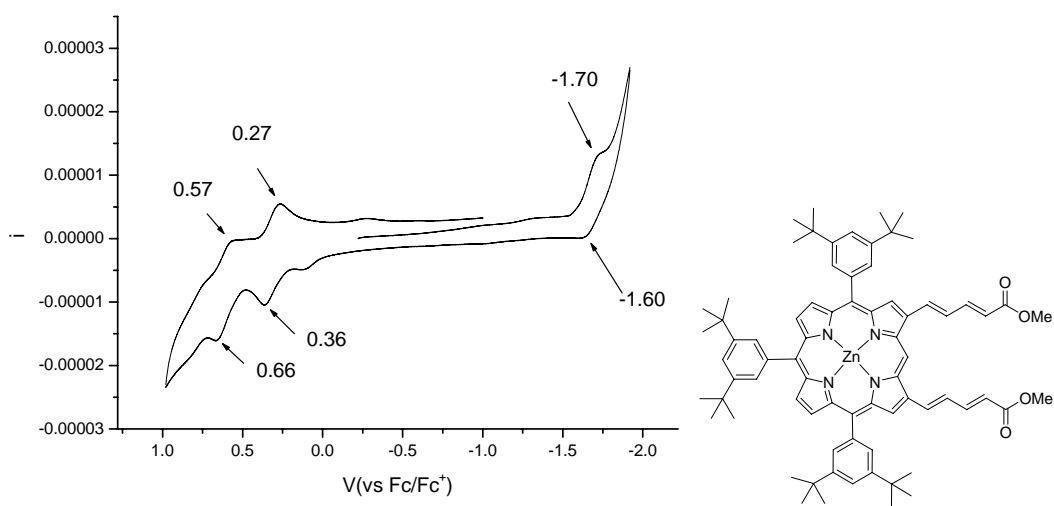
<Oxidation and reduction for **4b-Zn**>

(g)



<Oxidation and reduction for **1b-d-Zn**>

(h)



<Oxidation and reduction for **2b-bd-Zn**>

(i)

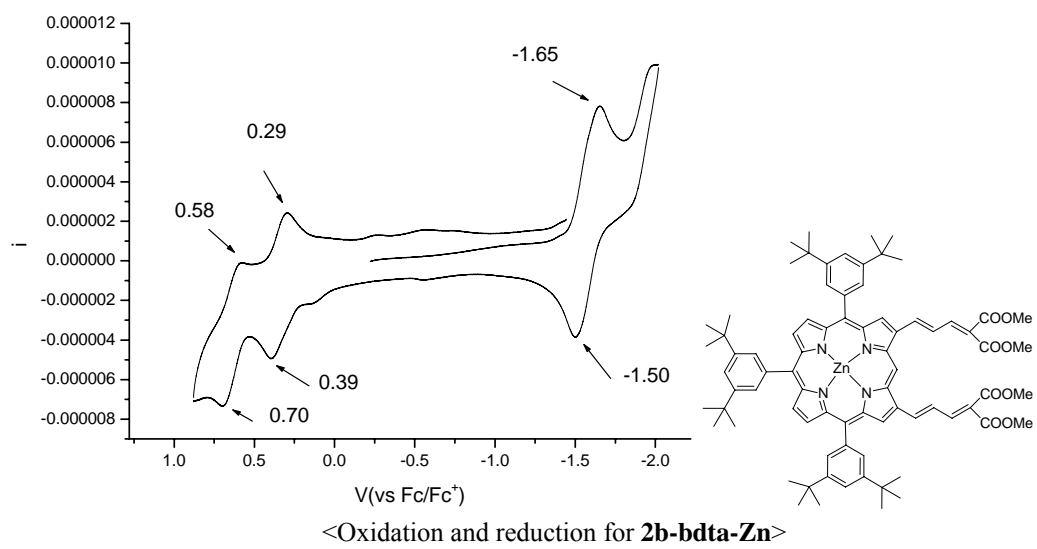
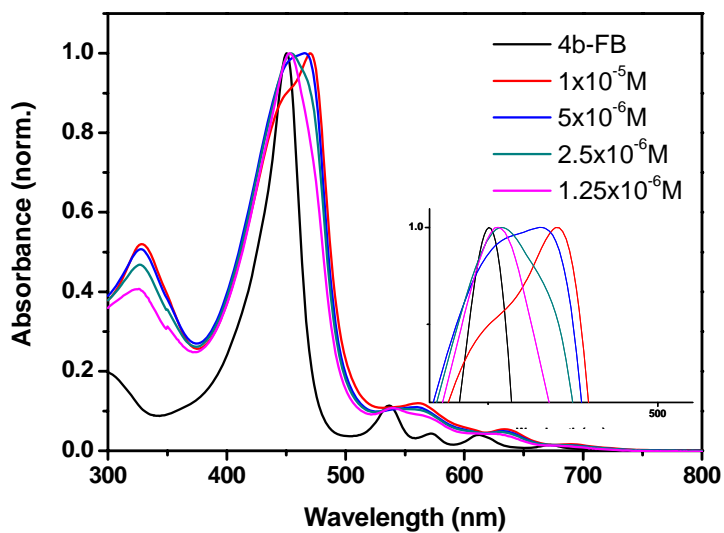


Figure S2. Cyclic voltammogram of all ester derivatives in dichloromethane reported versus  $Fc/Fc^+$  (V)

#### (4) Aggregation properties in solution

(a)



(b)

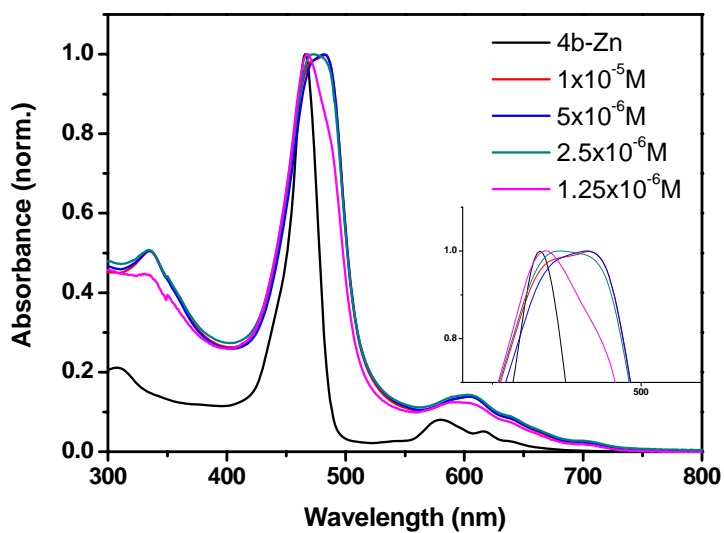
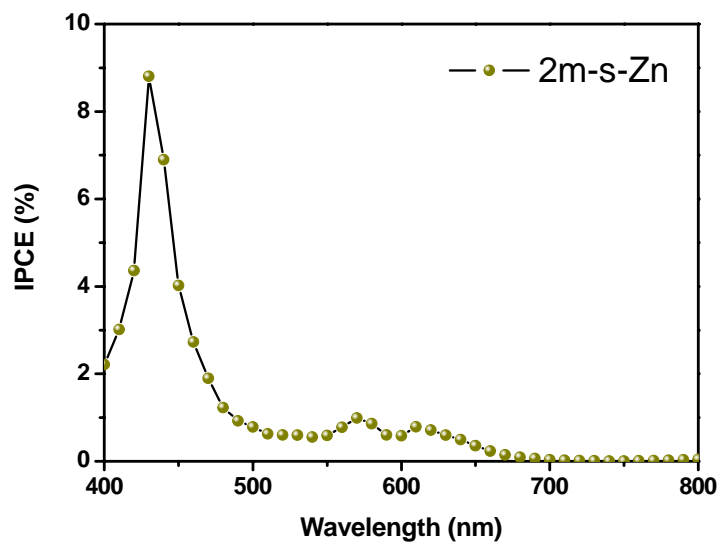


Figure S3. UV-vis spectra of (a) **4b-FB** and (b) **4b-Zn** in ethanol. Black line measured at  $\sim 10^{-6} \text{ M}$  concentration and the other spectra were measured in dilute solution from 0.2 mM standard solution.

## (5) IPCE spectrum

(a)



(b)

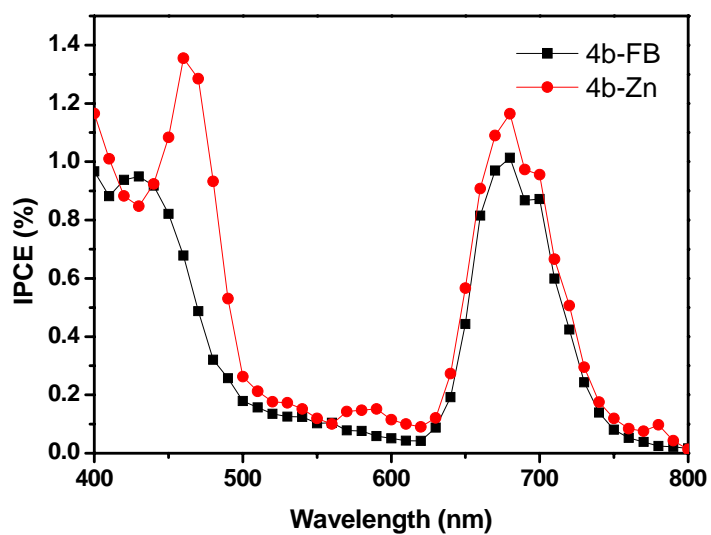


Figure S4. The photocurrent action spectra of FTO/TiO<sub>2</sub>/porphyrin cell.