

## Supplementary Information

### Study on a series of novel self-assembly supramolecular solar cells based on double-layer structured chromophore of Zn- porphyrins

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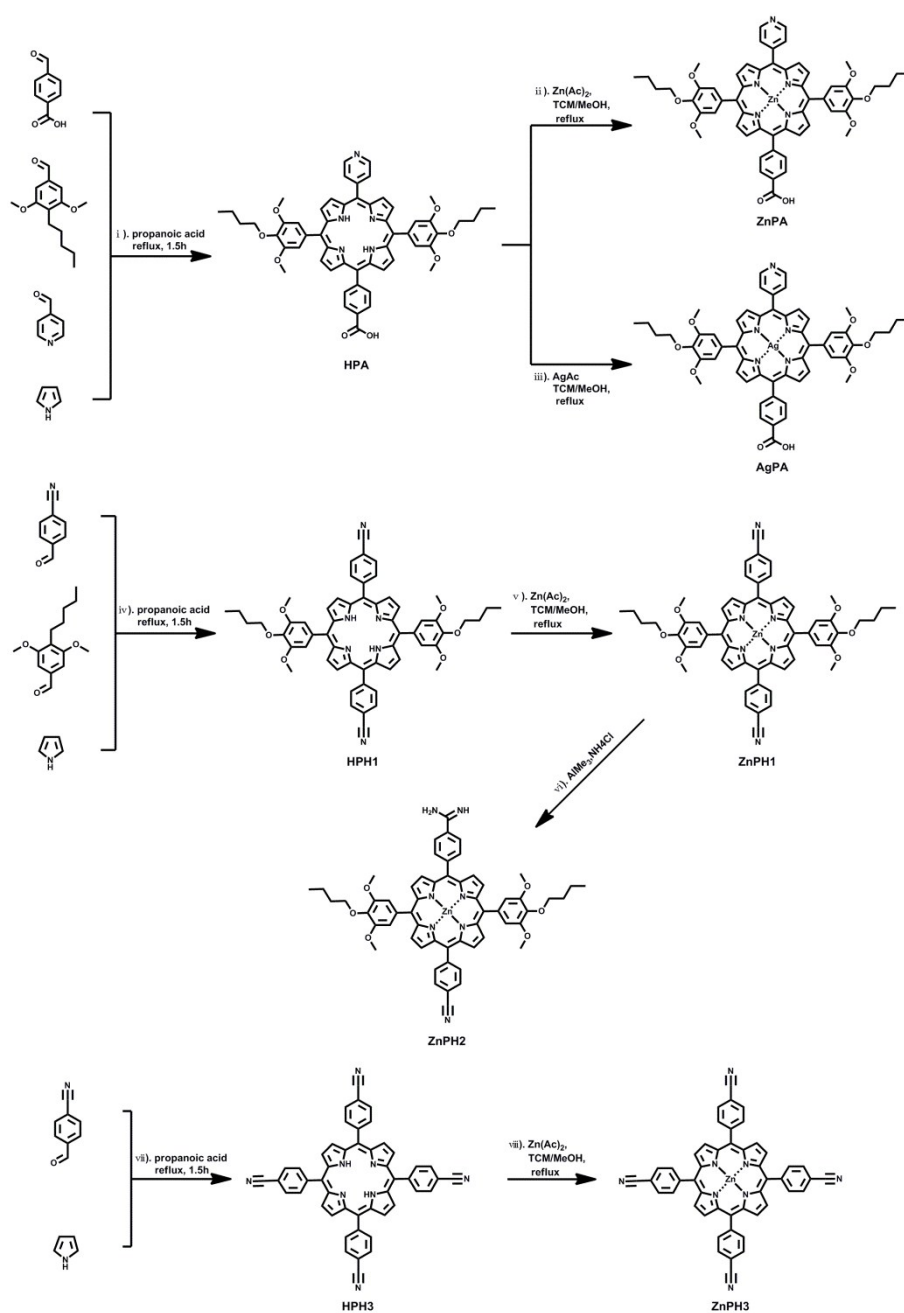
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## Experimental

### Materials synthesis

All solvents and starting materials were of commercially analytical grade and used directly without further purification, unless otherwise noted. All pyrrole in this work was distilled before use. The synthesis process is illustrated in **scheme. S1**.

**Synthesis of porphyrin HPA.** The Synthesis procedure was according to the reported literature.<sup>1</sup> Methyl 3,5-dimethoxy-4-pentylbenzaldehyde (4.73 g, 0.020 mol)



**Scheme S1.** Synthetic routes of the ZnPA, AgPA and ZnPH<sub>x</sub> (x=1, 2 and 3).

and 4-formylbenzoic acid (1.50 g, 0.010 mol) was added to a stirred solvent of propionic acid (180 mL). After dissolving and mixing, pyridine-4-carbaldehyde (0.95 mL, 0.010 mol) and pyrrole (5.54 mL, 0.080 mol) were slowly added to the solution successively. The resulting mixture was heated to 140 °C under reflux for 1.5 h. After slightly cooled to about 100 °C, the hot solution was evaporated to dryness under vacuum and then cooled to room temperature. The crude residue was dissolved in a dichloromethane-methanol mixture. After filtration and evaporation of the solvent, the crude product was purified by chromatography on silica with a CH<sub>2</sub>Cl<sub>2</sub>/MeOH eluent to afford the product 0.46 g. Yield, 5%. <sup>1</sup>H NMR (400 MHz, -CDCl<sub>3</sub>): 9.00-9.02 (two partially overlapping doublets, 6H; 2,6-PyH + β-H), 8.88 (d, 2H; β-H), 8.82 (d, 2H; β-H), 8.59 (d, 2H; 2,6-HOOCPhH), 8.37 (d, 2H; 3,5-PyH), 8.22 (d, 2H; 3,5-HOOCPhH), 7.47 (d, 4H; 2,6-(MeO)<sub>2</sub>(BuO)PhH), 4.33 (t, 4H; 1-OBuH), 3.96 (s, 12H; -OMeH), -2.80 (s, 2H; NH). ESI-MS (m/z): 924 [M+H]<sup>+</sup>.

**Synthesis of porphyrin HPH1.** Pyrrole (2.77 mL, 0.040 mol) were slowly added to a mixture of Methyl 3,5-dimethoxy-4-pentylbenzaldehyde (2.38 g, 0.010 mol) and 4-formylbenzotrile (1.31 g, 0.010 mol) in propionic acid (180 mL). The subsequent steps are carried out according to the synthesis of porphyrin HPA and the final product was purified by chromatography on silica using dichloromethane and petroleum ether as eluent, (1.40 g, 15%). ESI-MS (m/z): 929 [M+H]<sup>+</sup>.

**Synthesis of porphyrin ZnPA and ZnPH1.** The metallization was according to the reported method.<sup>2</sup> A solution of zinc acetate dihydrate (110 mg, 0.500 mmol) in methanol (10 mL) was added to a solution of free-base porphyrin HPA, HPH1 and HPH3 (0.100 mmol) in chloroform (30 mL) respectively. The mixture was heated to 60 °C under reflux in the dark overnight. The reaction solution was washed with saturated solution of sodium bicarbonate and dried over sodium sulfate. After filtration, the solvent was removed in vacuum to give the final products. ZnPA, (90 mg, 91%). <sup>1</sup>H NMR (400 MHz, -CDCl<sub>3</sub>): 8.90-8.91 (two partially overlapping doublets, 6H; 2,6-PyH + β-H), 8.80 (d, 2H; β-H), 8.74 (d, 2H; β-H), 8.35 (d, 2H; 2,6-

HOOCPhH), 8.17 (d, 2H; 3,5-PyH), 8.16 (d, 2H; 3,5-HOOCPhH), 7.40 (d, 4H; 2,6-(MeO)<sub>2</sub>(BuO)PhH), 4.18 (t, 4H; 1-OBuH), 3.87 (s, 12H; -OMeH), 1.82 (m, 4H; 2-OBuH), 1.61 (m, 4H; 3-OBuH), 0.82 (m, 6H; 4-OBuH). ESI-MS (m/z): 986 [M+H]<sup>+</sup>. ZnPH1, (90 mg, 91%). <sup>1</sup>H NMR (400 MHz, <sup>2</sup>-CDCl<sub>3</sub>): 9.10 (d, 4H; β-H), 8.85 (d, 4H; β-H), 8.34 (d, 4H; 2,6-NCPhH), 8.08 (d, 4H; 3,5-NCPhH), 7.44 (s, 4H; 2,6-(MeO)<sub>2</sub>(BuO)PhH), 4.31 (t, 4H; 1-OBuH), 3.94 (s, 12H; -OMeH), 1.97 (m, 4H; 2-OBuH), 1.68 (m, 4H; 3-OBuH), 1.10 (t, 6H; 4-OBuH). ESI-MS (m/z): 991 [M+H]<sup>+</sup>.

**Synthesis of porphyrin AgPA.** The silver coordination of HPA, labeled as AgPA, was synthesized in the same procedure as ZnPA when 0.500 mmol silver acetate was used instead of zinc acetate dihydrate. The quantity of AgPA we got finally was 92 mg. Yield, 89%. <sup>1</sup>H NMR (400 MHz, -CDCl<sub>3</sub>): 8.92-8.97 (two partially overlapping doublets, 6H; 2,6-PyH + β-H), 8.82 (m, 4H; β-H), 8.49 (d, 2H; 2,6-HOOCPhH), 8.38 (d, 2H; 3,5-PyH), 8.29 (d, 2H; 3,5-HOOCPhH), 7.26 (d, 4H; 2,6-(MeO)<sub>2</sub>(BuO)PhH), 4.26 (t, 4H; 1-OBuH), 3.94 (s, 12H; -OMeH), 1.93 (m, 4H; 2-OBuH), 1.64 (m, 4H; 3-OBuH), 0.86 (m, 6H; 4-OBuH). ESI-MS (m/z): 1029 [M+H]<sup>+</sup>.

**Synthesis of porphyrin ZnPH2.**<sup>3</sup> Under the strict condition of water-free and oxygen-free, a solution of AlMe<sub>3</sub> in hexane (2m, 0.30 mL) was added to a stirred suspension of NH<sub>4</sub>Cl (53 mg, 1.0 mmol) in toluene (10 mL). After the mixture stirred for 2 h at room temperature, a solution of ZnPH1 (311 mg, 0.40 mmol) in toluene (10 mL) was injected into the mixture rapidly. The stirred resulting solution was heated to 80 °C for 48 h in the dark. A silica gel suspension of CHCl<sub>3</sub> (10 g, 50 mL) was poured into the reaction mixture and stirred for 10 min. After filtered and the solvents evaporated, the crude product was purified by chromatography on silica gel with a CH<sub>2</sub>Cl<sub>2</sub>/MeOH eluent to obtain a purple solid 120 mg. Yield, 38%. <sup>1</sup>H NMR (400 MHz, -CDCl<sub>3</sub>): 9.64 (br.s, 3H; amidine-H), 9.10 (m, 4H; β-H), 8.92 (d, 2H; β-H), 8.70 (d, 2H; β-H), 8.36 (d, 2H; 2,6-H<sub>2</sub>N(HN=)CPhH), 8.30 (d, 2H; 2,6-NCPhH), 8.23 (d, 2H; 3,5-H<sub>2</sub>N(HN=)CPhH), 8.14 (d, 2H; 3,5-NCPhH), 7.38 (s, 4H; 2,6-(MeO)<sub>2</sub>(BuO)PhH), 4.18 (t, 4H; 1-OBuH), 3.87 (s, 12H; -OMeH), 1.83 (m, 4H; 2-

OBuH), 1.60 (m, 4H; 3-OBuH), 1.03 (t, 6H; 4-OBuH). ESI-MS (m/z): 1008 [M+H]<sup>+</sup>.

***Synthesis of porphyrin ZnPH3.*** The synthesis of porphyrin ZnPH3 was according to the preparation of porphyrin ZnPH1 and has been reported by literature method.<sup>4</sup> Yield, 18%. <sup>1</sup>H NMR (400 MHz, -CDCl<sub>3</sub>): 8.73 (s, 8H; β-H), 8.27 (d, 8H; 2,6-NCPH), 8.06 (d, 8H; 3,5-NCPH). ESI-MS (m/z): 777 [M+H]<sup>+</sup>.

**Fig. S1.** SEM-EDS spectra of AgPA-ZnPH3 immobilized on titania nanoparticles (the sample was attached on silicon substrate and without any spray-metal) . The inset tables give the data of elemental analyses.

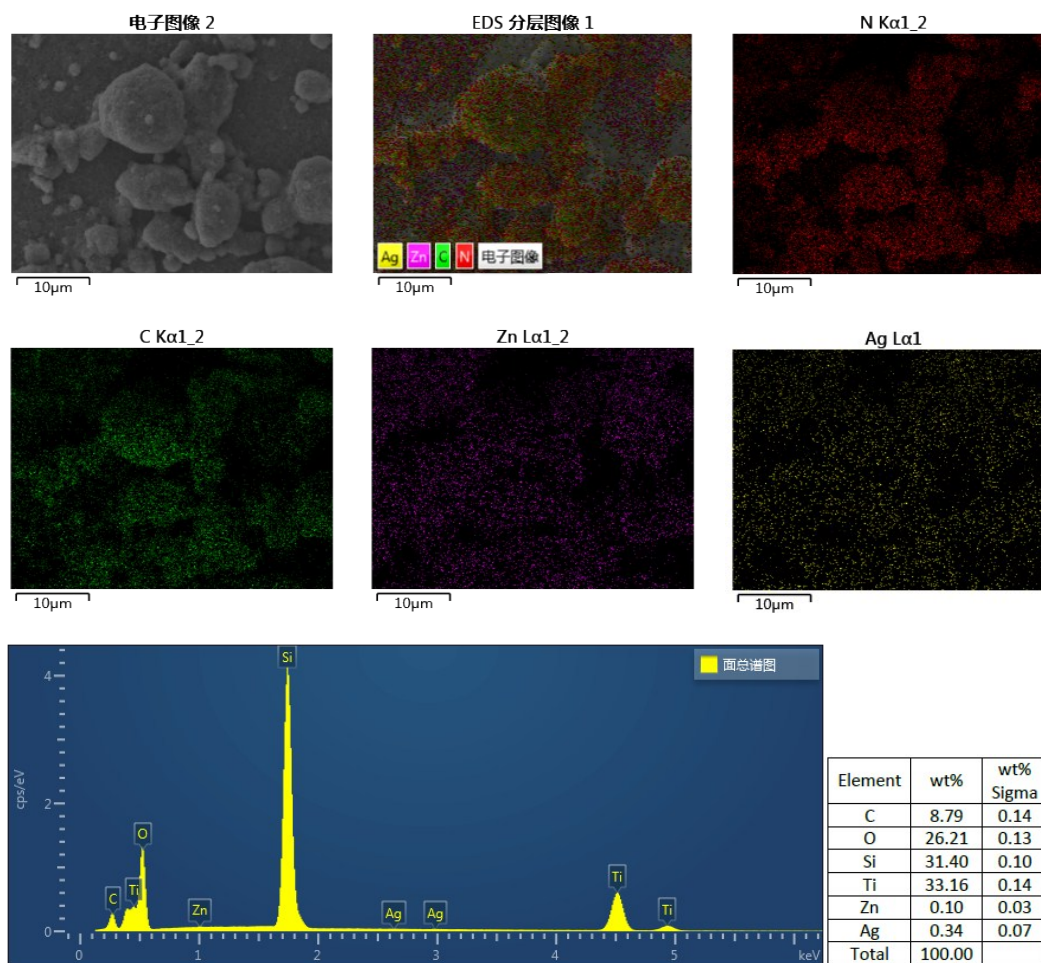
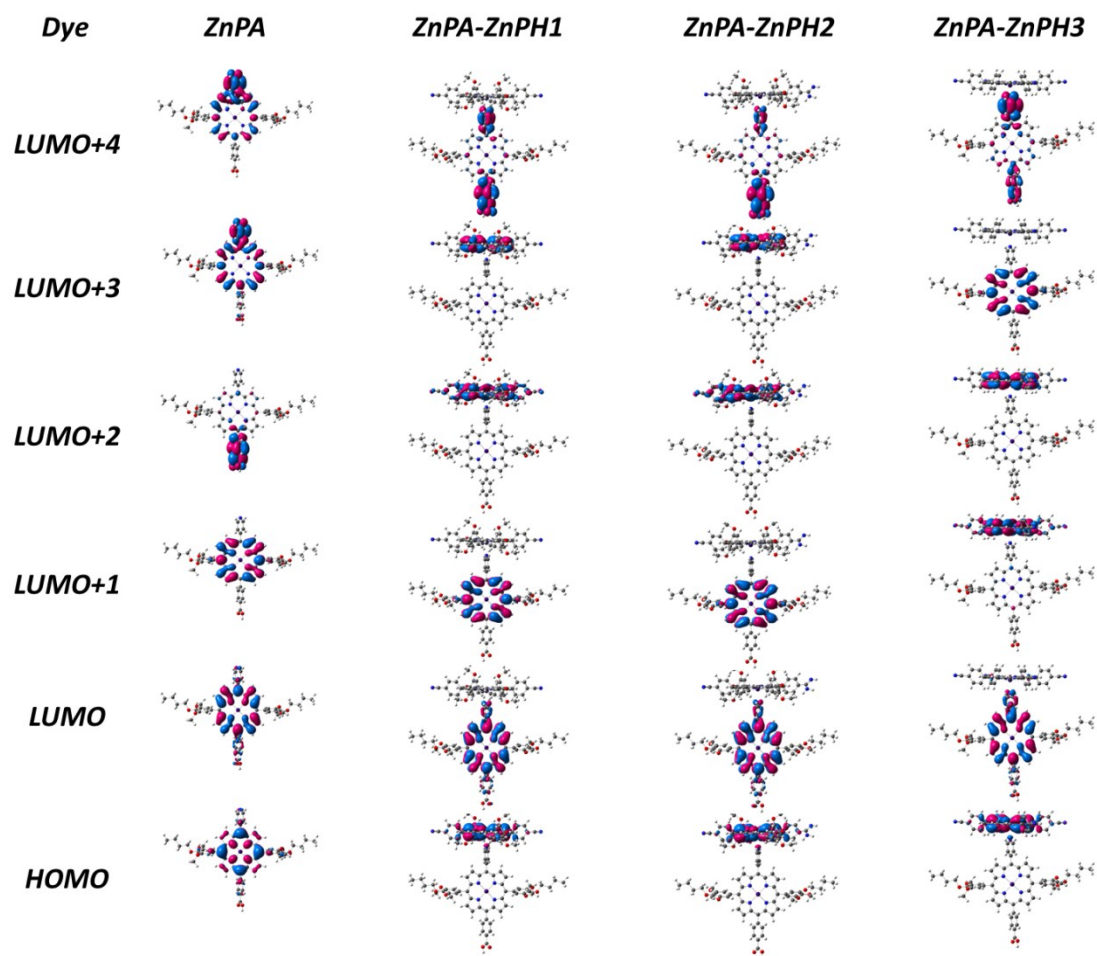


Fig. S2. The molecular orbital (MO) patterns of the anchoring porphyrin **ZnPA** and **ZnPA-ZnPH<sub>x</sub>** ( $x=1, 2$  and  $3$ ) assemblies.



**Table S1.** the UV-Vis absorption peak wavelength of **ZnPA**, **ZnPH<sub>x</sub>** and **ZnPA-ZnPH<sub>x</sub>** (**x=1, 2 and 3**). The tab “-s” and “-f” following the chemical species labels, “ZnPA-s” and “ZnPA-ZnPH1-f” for example, means the chemical species is in THF solution and on nanostructured TiO<sub>2</sub> thin films respectively.

<b>Dye</b>	<b>Absorption λ<sub>max</sub>/nm</b>
ZnPA-s	427, 560, 602
ZnPH1-s	430, 560, 601
ZnPH2-s	429, 561, 601
ZnPH3-s	428, 560, 600
ZnPA-f	435, 562, 605
ZnPA-ZnPH1-f	429, 560, 603
ZnPA-ZnPH2-f	432, 560, 603
ZnPA-ZnPH3-f	432, 558, 604

**Table S2.** the fluorescence spectra of **ZnPA**, **ZnPH<sub>x</sub>** and **ZnPA-ZnPH<sub>x</sub>** (**x=1, 2 and 3**). The tab “-s” and “-f” behind the labels of chemical species, “ZnPA-s” and “ZnPA-ZnPH1-f” for example, means the chemical species is in THF solution and on nanostructured TiO<sub>2</sub> thin films respectively.

<b>Dye</b>	<b>Emission/nm</b>
ZnPA-s	613.5
ZnPH1-f	606
ZnPH2-f	605
ZnPH3-f	600
ZnPA-f	611
ZnPA-ZnPH1-f	591
ZnPA-ZnPH2-f	593.5
ZnPA-ZnPH3-f	588



## Notes and references

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