Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

A supramolecular assembling of metal-free organic dye with zinc porphyrin chromophore for dye-sensitized solar cells

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General information

All solvents were treated by standard methods before use and all chemicals were purchased from commercial suppliers and used without further purification unless indicated otherwise. *N*, *N*-Dimethylformamide (DMF) and tetrahydrofuran (THF) were dried and distilled from CaH_2.

The ^1H NMR spectra were recorded on a Bruker DRX (400, 500 MHz) NMR spectrometer with tetramethylsilane (TMS) as the internal standard.

Fabrication of DSSCs

The photoanode was prepared by screen printing the TiO_2 paste on FTO glass plates (the TiO_2 paste, FTO glass plates and Pt counter electrode are all purchased from Dalian QiSeGuang solar technology development co., LTD, Dalian, P. R. China) The TiO_2 paste consists of 12 μm thick film (particle size, 20 nm, pore size 32 nm). The TiO_2 films were performed with a programmed procedure: (1) 80℃ for 15 min; (2) 135℃ for 10 min; (3) 325℃ for 30 min; (4) 375℃ for 5 min; (5) 450℃ for 15 min, and (6) 500℃ for 15 min. Then the films were treated again with $TiCl_4$ at 70℃ for 30 min and sintered at 500℃ for 30 min. Then the photoanodes were immersed into JH1 solution (0.3 mM of JH1, THF/EtOH=1/1) for 18 h at room temperature and washed with absolute ethanol. Immediately following, the photoanodes were immersed into P1 and P2 solution (0.2 mM, THF/EtOH=1/4) for 24 h, and supramolecular self-assembly was performed. The photoanode and the Pt counter electrode were then sealed with a Surlyn film (60 μm) by heating the sandwich-type cell at 120℃. The electrolyte was introduced through pre-drilled holes in the counter electrode and was driven into the cell via vacuum backfilling, and the hole was sealed with a Surlyn film and a thin glass (0.1 mm thickness) cover by heating. The electrolyte was composed of 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 50 mM I_2, 50 mM LiI, 0.5 M tert-butylpyridine and 0.1 M guanidiniumthiocyanate (GuNCS) in acetonitrile.

Characterizations of DSSCs

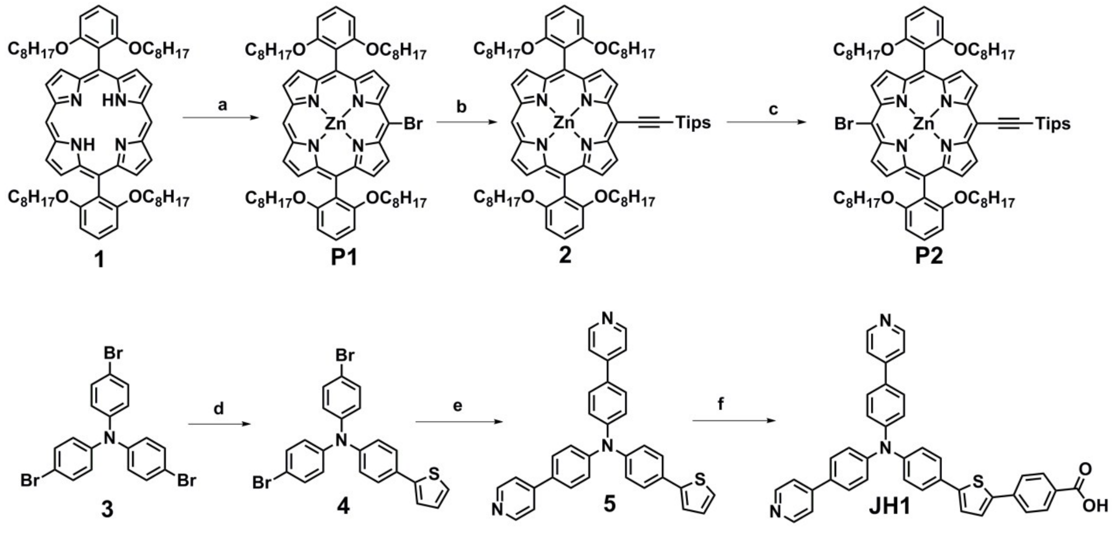
The photocurrent-voltage (I-V) curves of the DSSCs were measured on a Keithley 2400 source meter under standard global AM 1.5G solar irradiation supplied by a xenon light source (Oriel). The incident photo-to-electron conversion efficiency (IPCE) spectra of the DSSCs were measured by a DC method. The light source was a 300 W xenon lamp (Oriel 6258) coupled with a flux controller to improve the stability of the irradiance. The single wavelength was selected by a monochromator (Cornerstone 260 Oriel74125). Light intensity was measured by a NREL traceable Si detector (Oriel 71030NS) and the short circuit currents of the DSSCs were measured by an optical power meter (Oriel 70310).

UV-Vis spectra, electrochemical properties and measurement of dye loading

The UV-Vis absorption spectra were recorded on a Shimadzu UV-3600 spectrometer. The cyclic voltammograms and electrochemical impedance spectroscopy were studied using a Chenhua CHI660D model Electrochemical Workstation (Shanghai).

The dye loading on the TiO_2 films were measured by a Shimadzu UV-3600 spectrometer. The sensitized electrodes were immersed into a 0.1 M NaOH solution in a mixed solvent (H_2O/DMF=1/4), which resulted in desorption of each dye.

Synthesis



Scheme S1 synthesis procedure of **P1, P2** and **JH1**. Reagents and conditions: a) i: NBS, DCM; ii: $Zn(OAc)_2.2H_2O$, b) triisopropylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, THF, Et_3N, c) pyridine, NBS, DCM, d) 2-Thiopheneboronic acid, $Pd(PPh_3)_4$, K_2CO_3, H_2O, 1, 4-dioxane, e) Pyridine-4-boronic acid, $Pd(PPh_3)_4$, K_2CO_3, H_2O, 1, 4-dioxane, f) i: NBS, DMF; ii: Methyl 4-boronobenzoate, $Pd(PPh_3)_4$, K_2CO_3, H_2O, 1, 4-dioxane; ⅲ: EtOH, H_2O, NaOH.

Synthesis of P1

Compound 1 (7 g, 7.2 mmol) was dissolved in DCM (3 L), cooled the temperature to 0℃, then NBS (1.34 g, 7.5 mmol) was added in drops slowly.[S1] After 6 h, the reaction mixture was quenched by acetone, and the solvent was evaporated in vacuo. The residue was purified by silica gel column chromatography (DCM/PE=1/4) to give the intermediate, then dissolved in DCM (600 mL) and MeOH (300 mL), and added $Zn(OAc)_2.2H_2O$ (9.6 g, 43.6 mmol), the solution was stirred at room temperature for 3 h. Then, the mixture was extracted by DCM (3×100 mL), the combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo to give P1 (5 g, 63%)。 ^1H NMR ($CDCl_3$, 500 MHz): δ, [ppm]: 10.10 (s, 1H), 9.73 (d, *J* = 4.5Hz, 2H), 9.27 (d, *J* = 4.5Hz, 2H), 9.01 (t, *J* = 4.5Hz, 4H), 7.73 (t, *J* = 8.0Hz, 2H), 7.05 (d, *J* = 8.5Hz, 4H), 3.86 (t, *J* = 6.5Hz, 8H), 0.93-0.98 (m, 8H), 0.77-0.84 (m, 8H), 0.34-0.61 (m, 44H).

Synthesis of compound 2

Under an nitrogen, P1 (4.5 g, 4 mmol), Triisopropylsilylacetylene (1.8 mL, 10 mmol), and CuI (0.24 g, 1.2 mmol) were added in THF (150 mL) and Et_3N (25 mL), then $Pd(PPh_3)_2Cl_2$ (0.55 g, 0.8 mmol) was added. The mixture was heated under 80°C for 4 h. The reaction mixture was cooled to room temperature and extracted by EtOAc (3×50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography (DCM/PE=1/4) to give the compound 2 (4 g, 81%)。 ^1H NMR ($CDCl_3$, 400 MHz): δ, [ppm]: 10.08 (s, 1H), 9.78 (s, 2H), 9.24 (s, 2H), 8.96-8.99 (m, 4H), 7.65 (t, *J* = 8.4Hz, 2H), 6.97 (d, *J* = 8.8Hz, 4H), 3.81 (s, 8H), 1.39-1.572 (m, 21H), 0.90-0.93 (m, 8H), 0.71-0.74 (m, 8H), 0.33-0.52 (m, 44H).

Synthesis of P2

Compound 2 (4 g, 3.27 mmol) was dissolved in DCM (1 L), then added pyridine (50 mL) and NBS (0.68 g, 3.90 mmol), the mixture was stirred at room temperature for 1 h. The reaction mixture was quenched by acetone and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/DCM=4/1) to give P2 (3.2 g, 75%)。 ^1H NMR ($CDCl_3$, 500 MHz): δ, [ppm]: 9.71 (d, *J* = 4.5Hz, 2H), 9.64 (d, *J* = 4.5Hz, 2H), 8.92 (d, *J* = 4.5Hz, 2H), 8.89 (d, *J* = 4.5Hz, 2H), 7.71 (t, *J* = 8.5Hz, 2H), 7.02 (d, *J* = 8.5Hz, 4H), 3.85 (t, *J* = 6.5Hz, 8H), 1.43-1.53 (m, 21H), 0.94-1.00

(m, 8H), 0.77-0.82 (m, 8H), 0.37-0.59 (m, 44H).

Synthesis of compound 4

Under an nitrogen, compound 3 (6 g, 12.45 mmol), 2-Thiopheneboronic acid (1.6 g, 12.45 mmol), K_2CO_3 (5.16 g, 37.14 mmol) and $Pd(PPh_3)_4$ (0.5 g) were dissolved in 1, 4-dioxane (100 mL) and H_2O (20 mL). The mixture was heated under 90℃ for overnight. The reaction mixture was cooled to room temperature and extracted by CH_2Cl_2 (3×100 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo, the residue was purified by silica gel column chromatography (PE) to give compound 4 (3 g, 50%). ^1H NMR ($CDCl_3$, 400 MHz): δ, [ppm]: 7.47-7.51 (m, 2H), 7.33-7.37 (m, 4H), 7.23-7.25 (m, 2H), 7.02-7.07 (m, 3H), 6.94-6.98 (m, 4H).

Synthesis of compound 5

Under an nitrogen, compound 4 (3 g, 6.18 mmol), Pyridine-4-boronic acid (1.52 g, 12.37 mmol), K_2CO_3 (4.27 g, 30.91 mmol) and $Pd(PPh_3)_4$ (0.5 g) were dissolved in 1, 4-dioxane (50 mL) and H_2O (10 mL). The mixture was heated under 90℃ for overnight. The reaction mixture was cooled to room temperature and extracted by CH_2Cl_2 (3×100 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo, the residue was purified by silica gel column chromatography (EA) to give compound 5 (1.4 g, 47%). ^1H NMR ($CDCl_3$, 400 MHz): δ, [ppm]: 8.63-8.65 (m, 4H), 7.56-7.60 (m, 6H), 7.51-7.52 (m, 4H), 7.24-7.29 (m, 6H), 7.18-7.20 (m, 2H), 7.08-7.10 (m, 1H).

Synthesis of JH1

To a solution of compound 5 (1.2 g, 2.49 mmol) in DMF (10 mL) was added NBS (0.49 g, 2.74 mmol) in one portion, the mixture was stirred at room temperature for 12 h, then 100 mL H_2O was added, and extracted by CH_2Cl_2 (3×30 mL), the combined organic layers were evaporated in vacuo. Then, the residue, Methyl 4-boronobenzoate (0.67 g, 3.74 mmol), K_2CO_3 (1.03 g, 7.47 mmol) and $Pd(PPh_3)_4$ (0.4 g) were dissolved in 1, 4-dioxane (50 mL) and H_2O (10 mL) under N_2. The mixture was heated under 90℃ for overnight. The reaction mixture was cooled to room temperature and extracted by CH_2Cl_2 (3×50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo, the residue was purified by silica gel column chromatography (EA). Then the residue was added in EtOH (20 mL), THF (20 mL) and H_2O (30 mL), and then added NaOH (0.6 g). The mixture was heated under 90℃ for overnight. The reaction mixture was cooled to room temperature and the solvent was evaporated, the residue was acidified with diluted HCl, then filtered and recrystallization from MeOH/Ether to give JH1 (0.8 g, 53%). ^{1}H NMR (DMSO-*d6*, 400 MHz): δ, [ppm]: 8.60-8.61 (m, 4H), 7.93-7.95 (m, 2H), 7.87-7.89 (m, 2H), 7.81-7.83 (m, 3H), 7.73-7.75 (m, 2H), 7.69-7.71 (m, 4H), 7.29-7.41 (m, 3H), 7.17-7.23 (m, 4H), 7.07-7.09 (m, 2H).

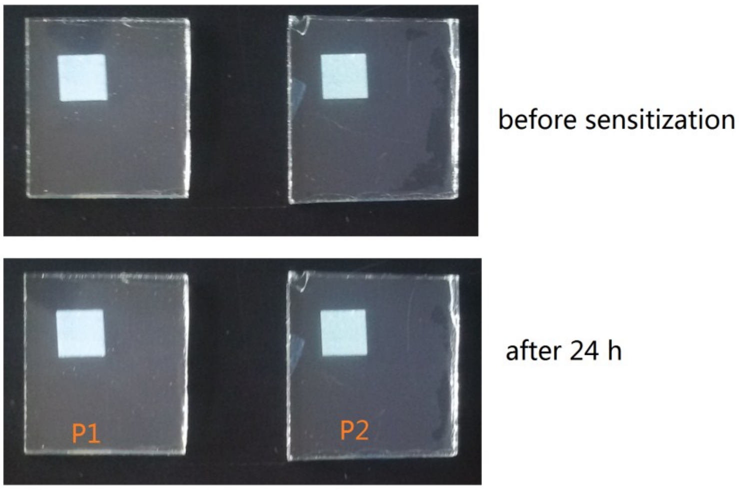


Fig. S1 Comparison of P1 and P2 before and after sensitization

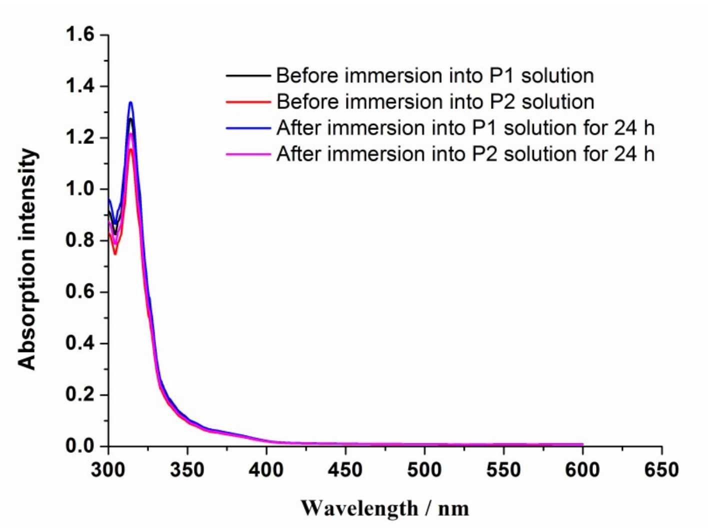


Fig. S2 Absorption spectra of TiO_2 before and after the immersion into P1 and P2 solutions

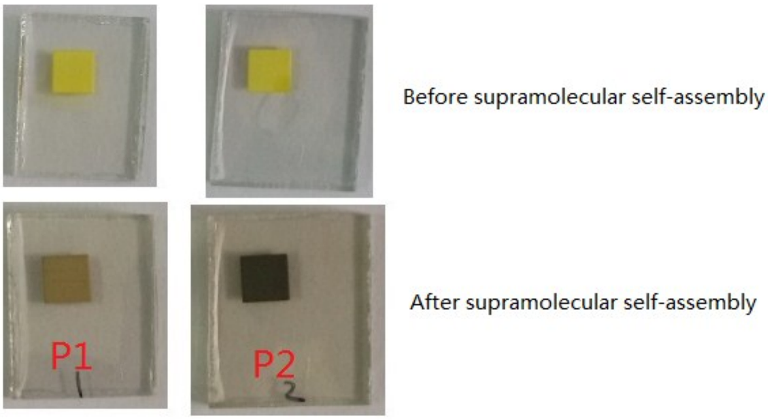


Fig. S3 Comparison of P1 and P2 before and after supramolecular self-assembly

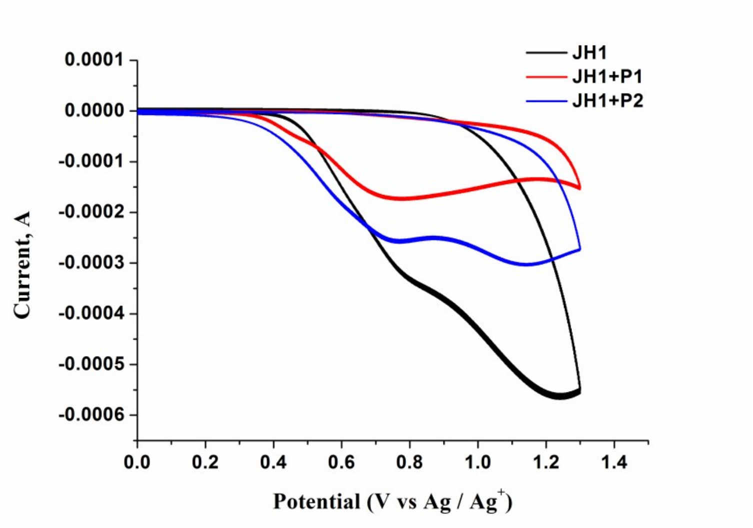


Fig. S4 Cyclic voltammogram of **JH1**, **JH1+P1** and **JH1+P2** in DMF, 0.1 M TBAPF$_6$, photoanode as working electrode, Pt as counter electrode, Ag/Ag$^+$ as reference electrode, scan rate: 100 mV s^{-1}, calibrated with ferrocene/ferrocenium (Fc/Fc$^+$) as an external reference.

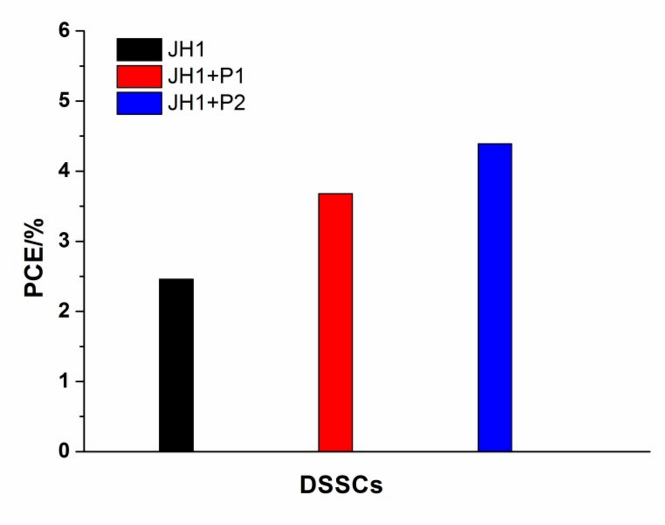


Fig. S5 Histogram of the power conversion efficiencies (PCE) of DSSCs

References

[S1] A. Yella, H. W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W. G. Diau, C. Y. Yeh, S. M. Zakeeruddin, M. Grätzel, *Science*, 2011, **334**, 629.