

Electronic Supporting Information

Novel D- π -A structured porphyrin dyes

with diphenylamine derived electron-donating substituents

for highly efficient dye-sensitized solar cells

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Experimental

General

Standard Schlenk techniques were employed to manipulate oxygen- and moisture-sensitive chemicals. Starting materials were all commercially available and used as received if not specially mentioned. Solvents for reactions including dichloromethane, toluene, chloroform, tetrahydrofuran (THF) and solvents for column chromatography including *n*-hexane, dichloromethane, chloroform, ethyl acetate, methanol as well as granular neutral silica gel for column chromatography, were purchased from Samchun Chemical. The 12 M HCl solution, sodium hydroxide, anhydrous sodium sulphate, calcium hydride and trifluoroacetic acid (TFA) were also purchased from Samchun Chemical. Bis(2-diphenylphosphinophenyl)ether (DPEphos) was purchased from Tokyo Chemical Industry. Dehydrated solvents for DSC preparation, acetonitrile and ethanol, were purchased from Aldrich and Merck, respectively. Reagents, including pyrrole, boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{OEt}_2$), benzaldehyde, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), diisobutylaluminium hydride (DIBAL-H), sodium hydride, cyanoacetic acid, caesium carbonate, palladium(II) acetate, lithium iodide, *N*bromosuccinimide (NBS) and 4-*tert*-butylpyridine (TBP), were purchased from Aldrich. 1,2-Dimethyl-3-propylimidazolium iodide (DMPII) was purchased from Solaronix. Tetrahydrofuran (THF) and toluene were dried over and distilled from Na/benzophenone under a dry nitrogen atmosphere. Dichloromethane (CH_2Cl_2) was dried over and distilled from calcium hydride (CaH_2) under a dry nitrogen atmosphere. Other chemicals and reagents were used as received without further purifications. The ^1H NMR spectroscopy study was conducted with a Varian Mercury 300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as the internal standard. Chemical shifts for ^1H NMR spectra were recorded on a

Varian Mercury 300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as the internal standard. MALDI-TOF mass spectra were recorded by a Voyager-DETM STR biospectrometry workstation. High-resolution mass spectra were recorded by a JEOL JMS-600W mass spectroscope. FT-IR spectra were acquired using a Jasco FT/IR-4200 spectrometer with a KBr pellet. UV-vis absorption spectra of the sensitizer in solution and on the TiO₂ film (3 μm) were measured by a Shimadzu UV-2401PC spectrophotometer. Photoluminescence spectra were analysed with a Fluorolog FL-3-22 fluorometer from Horiba-Jobin-Yvon Ltd. equipped with a 450W Xe-lamp and two analyzing monochromators. Visible emission spectra were detected with a Hamamatsu R928 photomultiplier. Cyclic voltammetry (CV) measurements were carried out with *VersaSTAT3* (AMETEK) using a typical three electrode electrochemical cell in a solution with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte in water-free THF at a scan rate of 50 mVs⁻¹ at room temperature; the sample was degassed with argon gas for 10 min prior to the scan. Potentials were calibrated with reference to the Fc/Fc⁺ couple. Electrochemical impedance spectra (EIS) of DSSCs were measured with an impedance analyser (*VersaSTAT3*, AMETEK) connected to a potentiostat under dark conditions at room temperature. The spectra were scanned in a frequency range of 0.1–10⁶ Hz and AC amplitude of 10 mV at room temperature. Photoelectrochemical data were measured using a 1000 W xenon light source (Oriel, 91193) that was focused to give 100 mW cm⁻², the equivalent of 1 sun at Air Mass (AM) 1.5G, at the surface of the test cell. The light intensity was adjusted with a silicon solar cell that was double-checked with an NREL calibrated silicon solar cell (PV Measurement Inc.). The applied potential and measured cell current were measured using a Keithley model 2400 digital source meter. The current-voltage characteristics of the cell under these conditions were determined by biasing the cell externally and measuring the generated photocurrent. This process was fully automated using Wave metrics software.

Dye-sensitized Solar Cell Fabrication

FTO glass plates (Pilkington TEC Glass-TEC 8, Solar 2.3 mm thickness) were cleaned in a detergent solution in an ultrasonic bath for 30 min, and then rinsed with water and ethanol. The FTO glass plates were immersed in 40 mM TiCl_4 (aqueous) at 70°C for 30 min and washed with water and ethanol. A transparent nanocrystalline layer on the FTO glass plate was prepared by repeated screen printing with TiO_2 paste (Solaronix, 25 nm Ti-Nanoxide T/SP) six times, then drying for 2 h at 25°C. The TiO_2 electrodes were gradually heated under an air flow at 325°C for 5 min, at 375°C for 5 min, at 450°C for 15 min and at 500°C for 15 min. The thickness of the transparent layer was measured using an Alpha-step 250 surface profilometer (Tencor Instruments, San Jose, CA). A paste for the scattering layer containing 400 nm anatase particles (CCIC, PST-400C) was deposited by doctor blade printing and then dried for 2 h at 25°C. The TiO_2 electrodes were gradually heated under an air flow at 325°C for 5 min, at 375°C for 5 min, at 450°C for 15 min and at 500°C for 15 min. The resulting layer was composed of a 14 μm thickness of 15-20 nm TiO_2 . The dye-deposited film was used as the working electrode. The electrode was then immersed in a porphyrin/EtOH/THF (EtOH:THF=2:1) solution (0.2 mM, 25°C, 6 h) containing CDCA=0.1mM or porphyrin/EtOH/THF (EtOH:THF=2:1) solution (0.2 mM, 25°C, 6h) containing HCA1=0.1 mM containing PTZ1=0.1 mM for dye loading onto the TiO_2 film. The FTO plate (Pilkington TEC Glass-TEC 8 Ω , solar 2.3 mm thickness) used as the counter electrode was cleaned in an ultrasonic bath in H_2O , acetone and 0.1 M HCl *aq*. Counter electrodes were prepared by coating with a drop of H_2PtCl_6 solution (2 mg of Pt in 1 mL of ethanol) on a FTO plate and heating at 400°C for 15 min. The dye-adsorbed TiO_2 electrode and Pt-counter electrode were assembled into a sealed sandwich-type cell by heating at 80°C

with a hot-melt ionomer film (Surlyn SX 1170-25, Solaronix) as a spacer between the electrodes. A drop of electrolyte solution (the electrolyte was 0.6 M DMPII, 0.05 M I₂, 0.1 M LiI and 0.5 M tertbutylpyridine in acetonitrile) was placed in a hole drilled in the counter electrode of the assembled cell and was driven into the cell via vacuum backfilling. Finally, the hole was sealed using additional Surlyn and a cover glass (0.1 mm thickness). The resulting cells had an active area of 0.4 cm × 0.4 cm. The adsorbed amount of Zn(II)-porphyrin dyes on the TiO₂ film with CDCA or HCA1 were calculated according to the literature.¹

Synthesis

Dipyrromethane, 5-(4-cyanophenyl)dipyrromethane and compound **1,2,3,4** were synthesized according to the literature.²⁻⁴

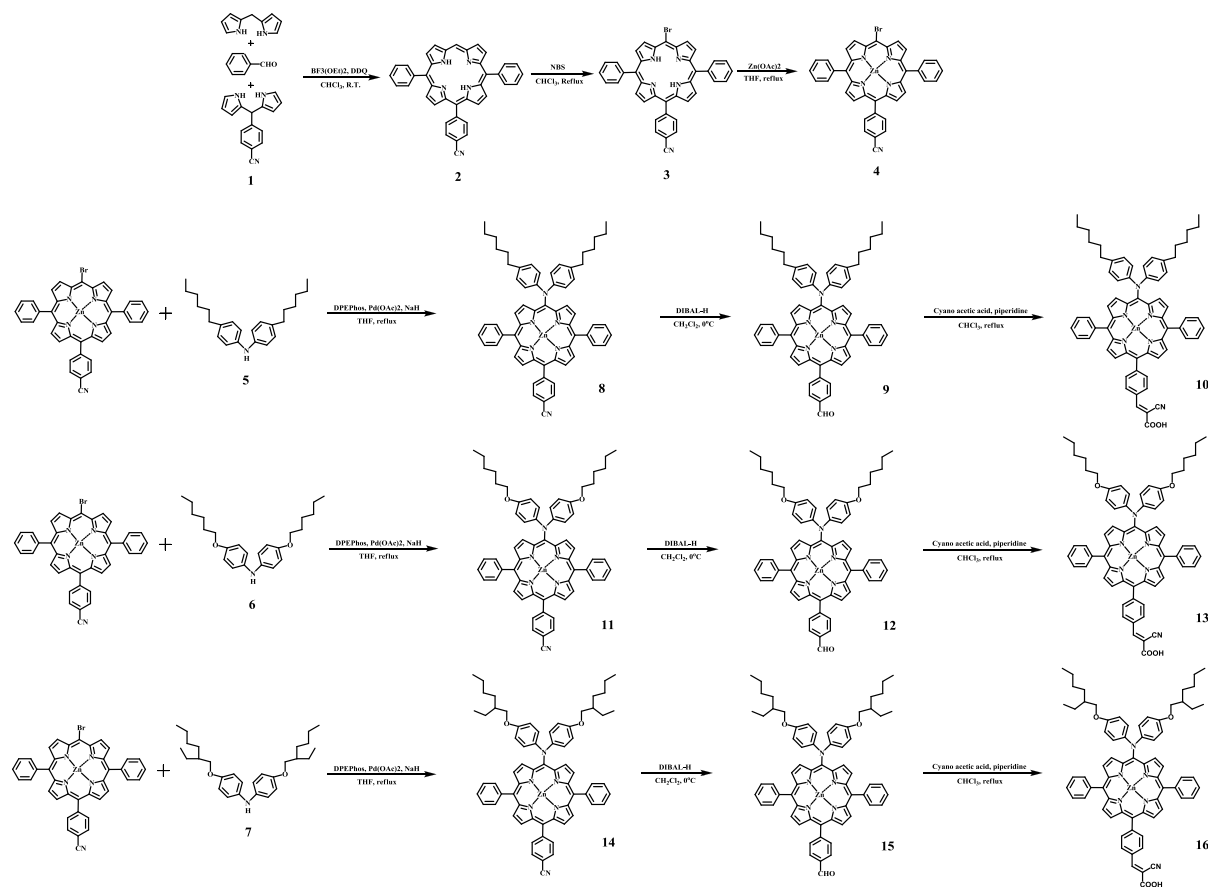


Fig. S1. Scheme of synthetic procedures of porphyrin dyes.

Compound 5

To a 100 ml Schlenk flask containing 4-*n*-hexyl-bromobenzene (2.5 g, 10.37 mmol), 4-*n*-hexylaniline (3.43 g, 11.40 mmol), Pd(OAc)₂ (116 mg, 0.52 mmol), 1,1'-Bis(diphenylphosphino) ferrocene (575 mg, 1.04 mmol), sodium *t*-butoxide (2.98 g, 31.10 mmol) and 70 mL of anhydrous toluene were added under argon atmosphere. The suspension was refluxed for 24h. The mixture was concentrated under reduced pressure. The crude product was purified by silica column chromatography eluted with toluene to give a liquid.

(2.40 g, 69 %). ¹H-NMR (300 MHz; (CDCl₃; TMS) δ 7.103-7.075 (4 H, d, J= 8.4 Hz, Ar-H), 7.004-6.975 (4 H, d, J= 8.7 Hz, Ar-H), 5.546 (H, Br-S, N-H), 2.593-2.542 (4 H, t), 1.639-1.568 (4 H, m), 1.334 (12 H, m), 0.918 (6 H, m, -CH₃). FT-IR (KBr) [cm⁻¹] 3400 (-NH).

Compound 6

To a 100 mL Schlenk flask containing 4-*n*-hexyloxy-bromobenzene (2.5 g, 9.72 mmol), 4-*n*-hexyloxyaniline (3.51 g, 10.69 mmol), Pd(OAc)₂ (109 mg, 0.49 mmol), 1,1'-Bis(diphenylphosphino) ferrocene (539 mg, 0.97 mmol), sodium *t*-butoxide (2.80 g, 29.16 mmol) and 70 mL of anhydrous toluene were added under argon atmosphere. The suspension was refluxed for 24h. The mixture was concentrated under reduced pressure. The crude product was purified by silica column chromatography eluted with toluene to give a liquid. (2.20g, 67 %). ¹H-NMR (300 MHz; ((CD₃)₂CO; TMS) δ 6.968-6.938 (4 H, d, J= 9 Hz, Ar-H), 6.822-6.792 (4 H, d, J= 9 Hz, Ar-H), 6.743 (H, Br-S, N-H), 3.939-3.897 (4 H, t), 1.755-1.686 (4 H, m), 1.485-1.325 (12 H, m), 0.918 (6 H, m). FT-IR (KBr) [cm⁻¹] 3400 (-NH).

Compound 7

To a 100 ml Schlenk flask containing 4-*n*-hexyl-bromobenzene (2.00 g, 7.01 mmol), 4-*n*-hexylaniline (2.90 g, 7.71 mmol), Pd(OAc)₂ (79 mg, 0.35 mmol), 1,1'-Bis(diphenylphosphino) ferrocene (0.39 mg, 0.70 mmol), sodium *t*-butoxide (2.02 g, 21.04 mmol) and 70 mL of anhydrous toluene were added under argon atmosphere. The suspension was refluxed for 24h. The mixture was concentrated under reduced pressure. The crude product was purified by silica column chromatography eluted with toluene to give a liquid. (1.50 g, 63 %). ¹H-NMR (300 MHz; (CDCl₃; TMS) δ 6.944 (4 H, d, J= 8.4 Hz, Ar-H), 6.870-6.841 (4 H, d, J= 8.7 Hz, Ar-H), 5.240 (H, S, N-H), 3.854-3.834 (4 H, d), 1.756 (2 H, m), 1.525-1.326 (16 H, m), 0.953 (12 H, t, -CH₃). FT-IR (KBr) [cm⁻¹] 3400 (-NH).

Compound 8

Compound 4 (500 mg, 0.71 mmol), Di(4-*n*-hexyl-phenyl) amine (0.95 g, 2.83 mmol), 60 % NaH (578 mg, 14.17 mmol), Pd(OAc)₂ (64 mg, 0.28 mmol) and DPEphos (305 mg, 0.57 mmol) was dissolved in 50 mL of anhydrous THF. The reaction mixture was refluxed for 24 h. The solvent was evaporated and the mixture was extracted with CH₂Cl₂ and brine several times. The organic layer was dried with anhydrous sodium sulphate. The filtrate was then evaporated under vacuum and purified by flash column chromatography using chloroform as the eluent to give **Compound 8** (170 mg, 25 %) as a darkish green solid. ¹H-NMR (300 MHz; CDCl₃; TMS) δ 9.373-9.356 (2 H, d, J=5.1 Hz, Ar-H), 8.912-8.895 (2 H, d, J=5.1 Hz, Ar-H), 8.852-8.835 (2 H, d, J=5.1 Hz, Ar-H), 8.761-8.744 (2 H, d, J=5.1 Hz, Ar-H), 8.336-8.308 (2 H, d, J=8.4 Hz, Ar-H), 8.171-8.151(4H, m, Ar-H), 8.066-8.037(2H, d, J=8.7 Hz, Ar-H), 7.761-7.713 (6 H, m, Ar-H), 7.226-7.197 (4 H, d, J=8.7 Hz, Ar-H), 6.987-6.958 (4 H, d, J=8.7 Hz Ar-H), 2.504 (4 H, t), 1.542 (4 H, m), 1.257 (12H, m), 0.867(6H, m, -CH₃). FT-IR (KBr) [cm⁻¹] 2230 (-CN).

Compound 9

A solution of DIBAL-H (1 M in hexanes, 0.27 mL, 0.27 mmol) was added drop-wise to a solution of **Compound 8** (130 mg, 0.14 mmol) in anhydrous CH₂Cl₂ (25 mL) under N₂ atmosphere. The reaction mixture was stirred at room temperature for 4 h and then quenched with 200 mL of saturated aq. NH₄Cl and stirred for another 2 hrs. After removing the aqueous layer, the organic layers were washed with brine and dried over Na₂SO₄. Column chromatography (silica, CHCl₃) afforded a dark green solid **Compound 9** (100 mg, 77 %). ¹H-NMR (300 MHz; CDCl₃; TMS) δ 10.325 (1H, s, -CHO), 9.371-9.356 (2 H, d, J=4.5 Hz, Ar-H), 8.904-8.889 (2 H, d, J=4.5 Hz, Ar-H), 8.850-8.836 (2 H, d, J=4.2 Hz, Ar-H), 8.810-

8.795 (2 H, d, J=4.5 Hz, Ar-H), 8.398-8.371 (2 H, d, J=8.1 Hz, Ar-H), 8.277-8.249(2H, d, J=8.4 Hz, Ar-H), 8.178-8.158(4H, m, Ar-H), 7.754 (6 H, m, Ar-H), 7.232-7.203 (4 H, d, J=8.7 Hz, Ar-H), 6.988-6.960 (4 H, d, J=8.4 Hz, Ar-H), 2.481 (4 H, t), 1.489 (4 H, m), 1.280 (12H, m), 0.867(6H, m, -CH₃). FT-IR (KBr) [cm⁻¹] 2230 (-CN). MS (MALDI-TOF): m/z found: 963.2 (M⁺), calc.: 963.39.

Compound 10

Compound 9 (100 mg, 0.10 mmol), several drops of piperidine and cyanoacetic acid (36 mg, 0.36 mmol) were dissolved in 50 mL of CHCl₃ and the solution was refluxed for 1 day. The reaction mixture was then cooled to room temperature and extracted with CH₂Cl₂. The organic phase was washed with water several times and dried with sodium sulphate. The filtrate was concentrated in vacuum to give **Compound 10** (80 mg, 75 %) as a dark blue solid. ¹H-NMR (300 MHz; (CD₃)₂SO ; TMS) δ 9.172 (2 H, d, Ar-H), 8.733 (2 H, d, Ar-H), 8.703 (2 H, d, Ar-H), 8.650 (2 H, d, Ar-H), 8.286 (4 H, m, Ar-H), 8.144 (4H, m, Ar-H), 7.765 (6 H, m, Ar-H), 7.116-7.089 (4 H, d, Ar-H), 7.006-6.983 (4 H, d, Ar-H), 3.321 (4 H, t), 1.468 (4 H, m), 1.224 (12H, m), 0.800(6H, m, -CH₃). ¹³C-NMR (900 MHz; (CD₃)₂SO; TMS) 163.172, 151.922, 150.247, 149.593, 149.043, 148.592, 147.159, 145.069, 142.358, 134.708, 134.114, 132.528, 132.421, 131.795, 131.484, 130.274, 128.873, 127.641, 127.527, 126.579, 122.062, 121.517, 120.417, 120.340, 119.858, 119.537, 67.472, 34.418, 31.069, 28.408, 22.009, 13.903. FT-IR (KBr) [cm⁻¹] 2230 (-CN). MS (MALDI-TOF): m/z found: 1032.0 (M⁺), calc.: 1030.39.

Compound 11

Compound 11 The preparation method was the same as that of **Compound 8**, ¹H-NMR (300 MHz; CDCl₃; TMS) δ 9.350-9.334 (2 H, d, J=4.8 Hz, Ar-H), 8.890-8.874 (2 H, d, J=4.8 Hz,

Ar-H), 8.826-8.810 (2 H, d, J=4.8 Hz, Ar-H), 8.736-8.721 (2 H, d, J=4.5 Hz, Ar-H), 8.325-8.298 (2 H, d, J=8.1 Hz, Ar-H), 8.167-8.144(4H, m, J=6.9 Hz, Ar-H), 8.040-8.015 (2H, d, J=7.5 Hz, Ar-H), 7.753-7.707 (6 H, m, Ar-H), 7.210-7.180 (2 H, d, J=9 Hz, Ar-H), 6.672-6.645 (2H, d, J=8.1 Hz, Ar-H) 3.802-3.749 (4 H, t), 1.705-1.618 (4H, m), 1.334 (12 H, m), 0.896 (6H, m, -CH₃). FT-IR (KBr) [cm⁻¹] 2230 (-CN).

Compound 12

Compound 12 The preparation method was the same as that of **Compound 9**. ¹H-NMR (300 MHz; CDCl₃; TMS) δ 10.352 (1H, s, -CHO), 9.360-9.343 (2 H, d, J=5.1 Hz, Ar-H), 8.887-8.873 (2 H, d, J=4.2 Hz, Ar-H), 8.830-8.816 (2 H, d, J=4.2 Hz, Ar-H), 8.792-8.775 (2 H, d, J=5.1 Hz, Ar-H), 8.386-8.361 (2 H, d, J=7.5 Hz, Ar-H), 8.269-8.242(2H, m, Ar-H), 8.150-8.143 (4H, d, J=2.1 Hz, Ar-H), 7.753-7.707 (6 H, m, Ar-H), 7.224-7.195 (2 H, d, J=8.7 Hz, Ar-H), 6.722-6.692 (2H, d, J=9 Hz, Ar-H) 3.832-3.789 (4 H, J=12.9 Hz, d), 1.702-1.653 (4 H, m), 1.295-1.259 (12 H, m), 0.856(6H, m, -CH₃). FT-IR (KBr) [cm⁻¹] 1700 (O=C-H).

Compound 13

Compound 13 The preparation method was the same as that of **Compound 10**. ¹H-NMR (300 MHz; (CD₃)₂SO; TMS) δ 9.200-9.186 (2 H, d, J=4.2 Hz, Ar-H), 8.726 (2 H, d, Ar-H), 8.702-8.686 (2 H, d, J=4.8 Hz, Ar-H), 8.653-8.639 (2 H, d, J=4.2 Hz, Ar-H), 8.282 (4 H, m, Ar-H), 8.152-8.127 (4H, m, Ar-H), 7.773-7.754 (6 H, m, Ar-H), 7.128-7.100 (2 H, d, J=8.4 Hz, Ar-H), 6.801-6.770 (2H, d, J=9.3 Hz, Ar-H) 3.841-3.798 (4 H, d, J=12.9 Hz), 1.617-1.590 (4 H, m), 1.330-1.237 (12 H, m), 0.826 (6H, m, -CH₃). ¹³C-NMR (900 MHz; (CD₃)₂SO; TMS) 163.567, 152.362, 152.112, 149.534, 149.079, 148.479, 147.681, 146.534, 145.262, 142.352, 134.754, 134.094, 132.408, 132.280, 131.799, 131.402, 130.322, 127.742, 127.508, 126.566, 122.762, 120.387, 119.611, 119.302, 115.102, 113.411, 67.529, 30.948,

28.711, 25.177, 22.026, 13.867. FT-IR (KBr) [cm^{-1}] 1600 (acrylic acid, $-\text{C}=\text{O}$), 2220 (cyano, $-\text{CN}$), 3150-3700 (acrylic acid $-\text{OH}$). MS (MALDI-TOF): m/z found: 1062.2 (M^+), calc.: 1062.38.

Compound 14

Compound 14 The preparation method was the same as that of **Compound 8**, $^1\text{H-NMR}$ (300 MHz; CDCl_3 ; TMS) δ 9.366-9.350 (2 H, d, $J=4.8$ Hz, Ar-H), 8.896-8.879 (2 H, d, $J=5.1$ Hz, Ar-H), 8.832-8.816 (2 H, d, $J=4.8$ Hz, Ar-H), 8.741-8.725 (2 H, d, $J=4.8$ Hz, Ar-H), 8.301 (2 H, d, Ar-H), 8.164-8.144 (4H, m, Ar-H), 8.063-8.035 (2H, d, $J=8.4$ Hz, Ar-H), 7.734-7.713 (6 H, m, Ar-H), 7.224-7.195 (2 H, d, $J=8.7$ Hz, Ar-H), 6.743-6.713 (2H, d, $J=9$ Hz, Ar-H) 3.726-3.709 (4 H, d, $J=5.1$ Hz), 1.482 (2 H, m), 1.271 (20 H, m), 0.884 (12H, m, $-\text{CH}_3$). FT-IR (KBr) [cm^{-1}] 2230 ($-\text{CN}$). MS (MALDI-TOF): m/z found: 1048.1 (M^+), calc.: 1048.44

Compound 15

Compound 15 The preparation method was the same as that of **Compound 9**. $^1\text{H-NMR}$ (300 MHz; CDCl_3 ; TMS) δ 10.348 (1H, s, $-\text{CHO}$), 9.367-9.351 (2 H, d, $J=4.8$ Hz, Ar-H), 8.890-8.874 (2 H, d, $J=4.8$ Hz, Ar-H), 8.835-8.819 (2 H, d, $J=4.8$ Hz, Ar-H), 8.792-8.776 (2 H, d, $J=4.8$ Hz, Ar-H), 8.389-8.362 (2 H, d, $J=8.1$ Hz, Ar-H), 8.268-8.242 (2H, m, Ar-H), 8.173-8.147 (4H, d, $J=7.8$ Hz, Ar-H), 7.753-7.708 (6 H, m, Ar-H), 7.230-7.200 (2 H, d, $J=9$ Hz, Ar-H), 6.735-6.706 (2H, d, $J=8.7$ Hz, Ar-H) 3.716-3.698 (4 H, $J=5.4$ Hz, d), 1.482 (2 H, m), 1.357-1.259 (20 H, m), 0.862 (12H, m, $-\text{CH}_3$). FT-IR (KBr) [cm^{-1}] 1700 ($\text{O}=\text{C}-\text{H}$). MS (MALDI-TOF): m/z found: 1051.1 (M^+), calc.: 1051.44.

Compound 16

Compound 16 The preparation method was the same as that of **Compound 10**. $^1\text{H-NMR}$ (300 MHz; $(\text{CD}_3)_2\text{SO}$; TMS) δ 9.200-9.184 (2 H, d, $J=4.8$ Hz, Ar-H), 8.740-8.724 (2 H, d, $J=4.8$ Hz, Ar-H), 8.700-8.685 (2 H, d, $J=4.5$ Hz, Ar-H), 8.652-8.636 (2 H, d, $J=4.8$ Hz, Ar-H), 8.304 (4 H, m, Ar-H), 8.146-8.127 (4H, m, Ar-H), 7.768-7.746 (6 H, m, Ar-H), 7.127-7.097 (2 H, d, $J=9$ Hz, Ar-H), 6.807-6.777 (2H, d, $J=9$ Hz, Ar-H) 3.723-3.704 (4 H, d, $J=5.7$ Hz), 1.579 (2 H, m), 1.380-1.233 (20 H, m), 0.823 (12H, m, $-\text{CH}_3$). $^{13}\text{C-NMR}$ (900 MHz; $(\text{CD}_3)_2\text{SO}$; TMS) 163.384, 152.561, 152.106, 149.531, 149.083, 148.469, 147.482, 146.573, 145.197, 142.354, 134.732, 134.100, 132.414, 132.315, 131.802, 131.411, 130.316, 127.705, 127.520, 126.575, 122.780, 120.388, 119.621, 119.356, 115.128, 113.640, 69.999, 38.735, 29.918, 28.412, 23.292, 22.465, 13.902, 10.894. FT-IR (KBr) $[\text{cm}^{-1}]$ 1600 (acrylic acid, $\text{C}=\text{O}$), 2220 (cyano, $-\text{CN}$), 3150-3700 (acrylic acid $-\text{OH}$). MS (MALDI-TOF): m/z found: 1120.3 (M^+), calc.: 1118.44.

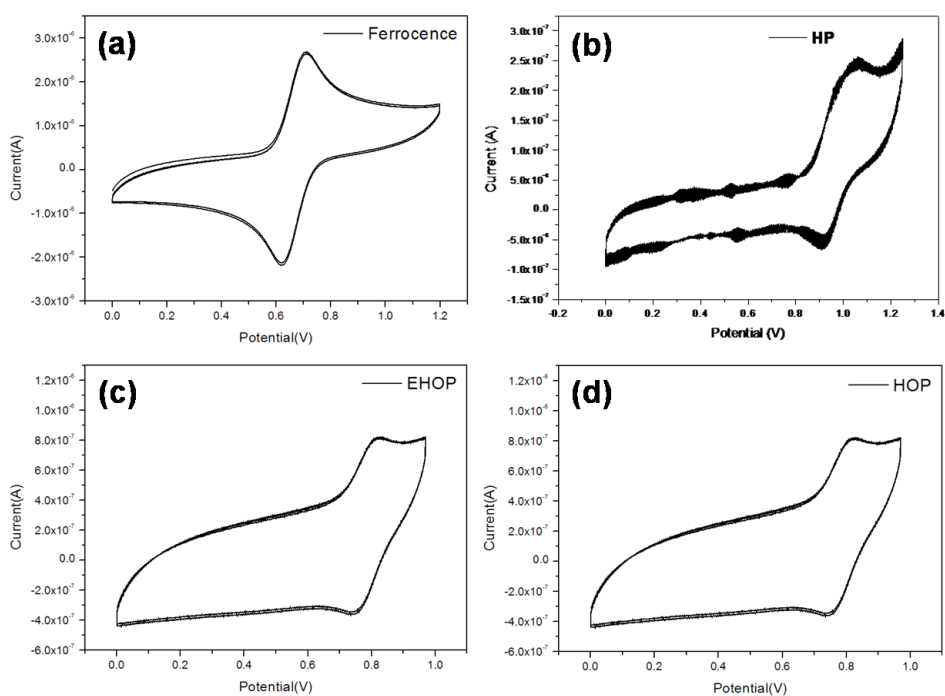


Fig.S2. Cyclic voltammograms of Zn(II)-porphyrin dyes and the Fc/Fc⁺ redox couple in THF at a scan rate of 50 mVs⁻¹ at room temperature with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. Pt working electrode, a Pt wire as the counter electrode, and an Ag/AgCl electrode saturated with KCl as the reference electrode were used.

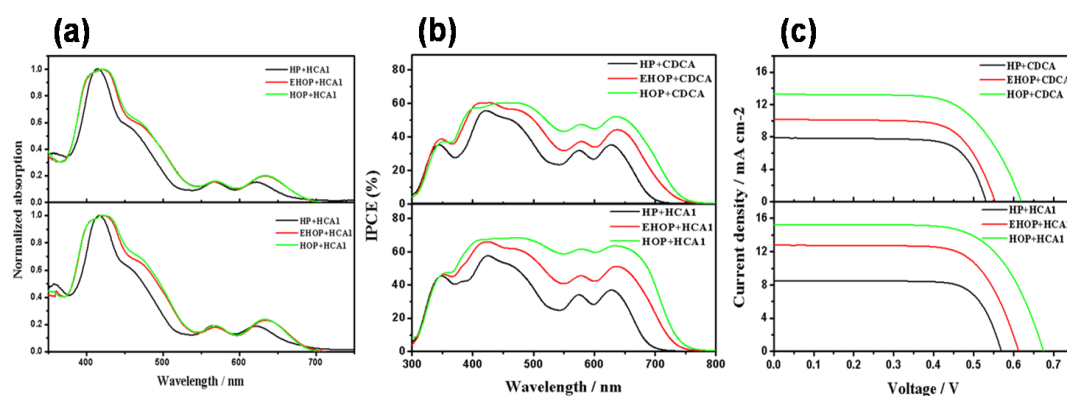


Fig. S3. (a) UV-visible absorption spectra of the TiO₂ films adsorbed with dyes only and the CDCA and HCA1 as co-absorbents with no coated scattering layer (film thickness ~ 2 μm), (b) IPCE spectra of the DSSCs fabricated with dye and the CDCA and HCA1 as a co-absorbent, and (c) current–voltage characteristics of the same devices (film thickness (14+5 μm)).

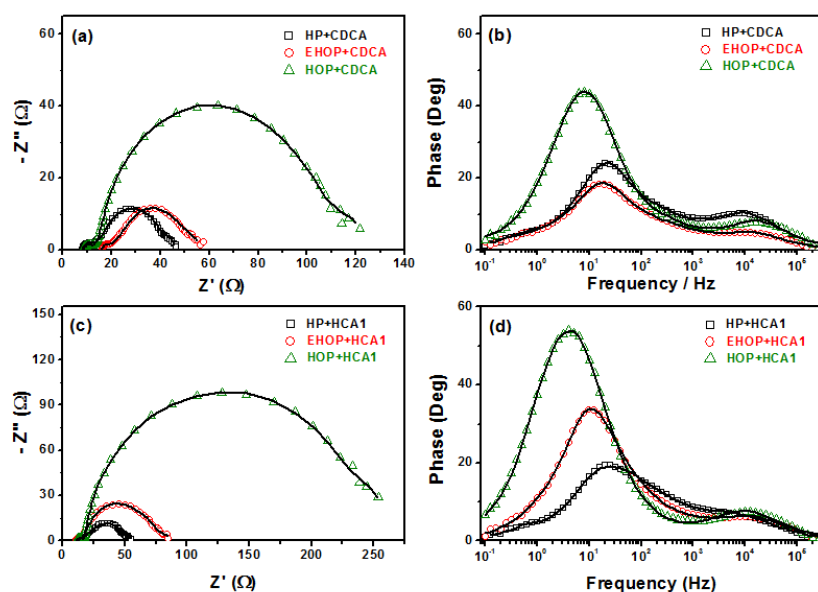


Fig. S4. Nyquist and Bode plots of electrochemical impedance spectra measured at a forward bias of -0.6 V under dark condition from 10⁶ to 0.1 Hz on the DSSCs with dye and CDCA (a, b), dye and HCA1 as co-absorbents (c, d), and solid lines were fitted to the equivalent circuit inserted in Fig 5(b).

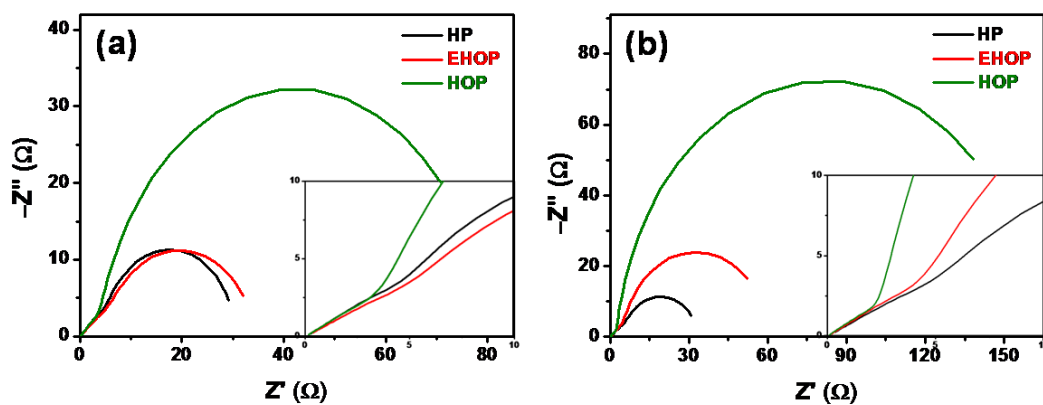


Fig. S5. Fitted curves of second circles from the impedance spectra of the DSSCs based dyes only (a) and **CDCA** and **HCA1** as co-absorbents (b). The insets are at high frequency regions.

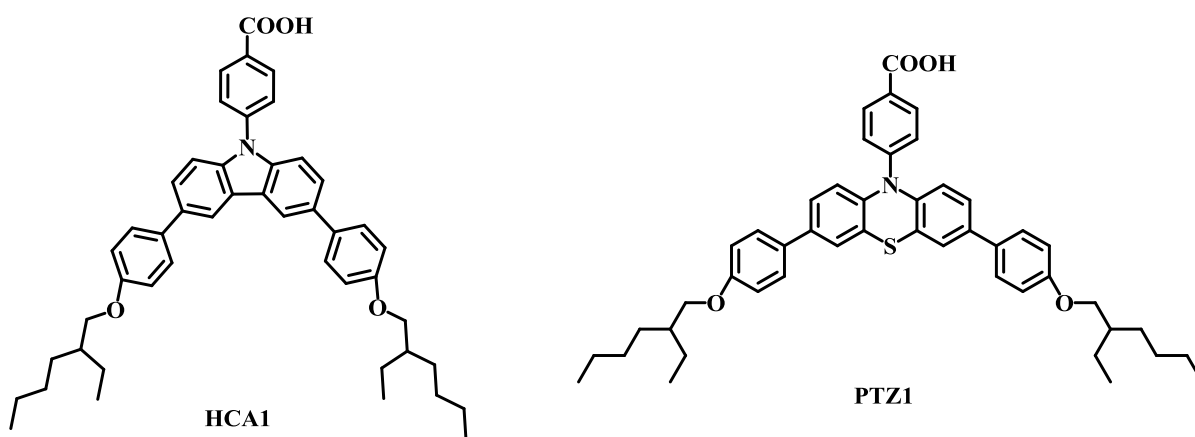


Fig. S6. Chemical structure of HCA1 and PTZ1.

Table S1. Characteristics of the DSSCs with dyes only and **PTZ1** as a co-absorbent

Dye	Dye adsorbed amount [10^{-7} mol cm^{-2}]	J_{SC} [mAcm^{-2}]	V_{OC} [mV]	FF [%]	η [%]
HP+CDCA	1.52	7.8	531	74.0	3.1
EHOP+CDCA	2.14	10.1	554	70.5	4.0
HOP+CDCA	2.39	13.2	620	66.2	5.4
HP+HCA1	1.24	8.5	569	75.9	3.7
EHOP+HCA1	1.61	12.7	613	70.6	5.5
HOP+HCA1	1.89	15.2	675	67.5	6.9

Table S2 Charge collection efficiencies calculated from the EIS parameters of the DSSCs with dyes and **CDCA** and **HCA1** as co-absorbents

Dye	Co-absorbent	R_t^a/Ω	R_{rec}^b/Ω	C_{it}/mF	τ_t/ms	τ_r/ms	η_{cc}
HP ^c	CDCA	-	-	-	-	-	-
	HCA1	-	-	-	-	-	-
EHOP	CDCA	17.6	25.3	0.84	14.8	21.3	0.59
	HCA1	13.1	54.8	0.78	10.2	42.7	0.81
HOP	CDCA	7.8	74.7	0.80	6.2	59.8	0.91
	HCA1	4.9	179.7	0.84	4.1	151.1	0.97

^a Charge transport resistance (R_t) and ^b recombination resistance (R_{rec}) at a forward bias of -0.60 V under dark condition, respectively. ^c DSSC with HP shows Gerischer impedance type to inefficient collection of electron which occurred when substantial electrons recombined back with I_3^- before these are even collected by the back electrode.

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