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Supporting Information:

Novel D-π-A Structured Zn(II)-porphyrin Dyes Containing a Bis(3,3dimethylfluorenyl)amine Moiety for Dye-Sensitised 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 (BF₃·OEt₂), 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, Nbromosuccinimide (NBS) and 4-tert-butylpyridine (TBP), were purchased from Aldrich. 1,2-Dimethyl-3propylimidazolium iodide (DMPII) was purchased from Solaronix. Tetrahydrofuran (THF) and toluene were dried over and distilled from Na/benzophenone under a dry nitrogen atmosphere. Dichloromethane (CH₂Cl₂) was dried over and distilled from calcium hydride (CaH₂) 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. The ¹³C NMR spectroscopy study was conducted with a Bruker Biospin Gmbh AVANCE II 900 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as the internal standard. Chemical shifts for ¹³C NMR spectra were recorded on a Bruker Biospin Gmbh AVANCE II 900 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 sensitiser in solution and on the TiO_2 film (3) μ m) 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 analysing 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 $0.1-10^5$ Hz and an 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 1000 W cm⁻², the equivalent of one 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 doubled-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, then rinsed with water and ethanol. The FTO glass plates were immersed in 40 mM TiCl₄ (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 TiO₂ paste (Solaronix, 15-20 nm Ti-Nanoxide T/SP) six times, then drying for 2 h at 25°C. The TiO₂ 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 TiO₂ 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 12.5 μ m thickness of 15-20 nm TiO₂. The dye-deposited film was used as the working electrode. The electrode was then immersed in a porphyrin/EtOH solution (0.2 mM, 25°C, 6 h) containing chenodeoxycholic acid (CDCA; 0.4 mM) or porphyrin/EtOH/THF (EtOH:THF=2:1) solution (0.2 mM, 25°C, 6 h) containing 4-(3,6-bis(4-(2-ethylhexyloxy)phenyl)-9H-carbazol-9-yl)benzoic acid (HC-A; 0.1 mM) for dye loading onto the TiO₂ 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 H₂O, 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 \times 0.4 cm. The adsorbed amount of Zn(II)-porphyrin dyes on the TiO₂ film with CDCA or HC-A were calculated according to the literature.¹

Synthesis

Dipyrromethane, 5-(4-cyanophenyl)dipyrromethane and bis(9,9-dimethyl-9H-fluoren-2-yl)amine were synthesized according to the literature.²⁻⁴



1: Benzaldehyde (1.9 g, 17.9 mmol), dipyrromethane (1.31 g, 8.95 mmol) and 5-(4cyanophenyl)dipyrromethane (2.21 g, 8.95 mmol) were dissolved in 980 mL of chloroform. BF₃·OEt₂ (660 μ L, 5.37 mmol) was quickly added by syringe and the solution was stirred at room temperature for 2 h. After that, DDQ (6.1 g, 26.86 mmol) was added and the solution was stirred for further 12 hrs. The solvent was evaporated and the crude product was eluted through a short pad of silica gel by chloroform to remove most of the tar. The mixture was further purified by flash column chromatography twice using *n*-C₆H₁₄/CH₃Cl (volume ratio 1:3) as the eluent and reprecipitated over ethanol/H₂O (volume ratio 20:1) to give pure product 1 (0.6 g, 11 %) as a dark brown red solid. ¹H-NMR (300 MHz; CDCl₃; TMS) δ 10.248 (1 H, s, meso-Ar-H), 9.355 (2 H, d, *J*=4.8 Hz, Ar-H), 9.038 (2 H, d, *J*=4.5 Hz, Ar-H), 8.931 (2 H, d, *J*=4.8 Hz, Ar-H), 8.821 (2 H, d, *J*=4.8 Hz, Ar-H), 8.442 (2 H, d, *J*=4.8 Hz, Ar-H), 8.307 (2 H, d, *J*=4.8 Hz, Ar-H), 8.249 (4 H, m, Ar-H), 7.782 (6 H, m, Ar-H), -2.76 (2 H, s). FT-IR (KBr) [cm⁻¹] 2230 (-CN).



3: **1** (340 mg, 0.6 mmol) was dissolved in 150 mL of CHCl₃, to which NBS (161 mg, 0.9 mmol) was added and the reaction mixture was refluxed for 12 h before being quenched by distilled water. The organic layer was washed with brine several times and dried with anhydrous sodium sulphate. The solvent was evaporated under vacuum and the crude product was purified by column chromatography using chloroform as eluent to give **2** (350 mg, 90 %) as a darkish purple solid. Brominated porphyrin **2** was dissolved in 100 mL of THF and zinc acetate dihydrate (350 mg, 0.54 mmol) was added. The solution was refluxed for 12 hrs. The solvent was then evaporated and the crude product was extracted with CH₂Cl₂. The organic layer was washed with brine several times and dried with anhydrous sodium sulphate. The filtrate was then evaporated under vacuum to give **3** (360 mg, 94 %) as a purple solid. ¹H-NMR (300 MHz; CDCl₃; TMS) δ 9.778 (2 H, d, *J*=5.1 Hz, Ar-H), 9.00 (2 H, d, *J*=5.1 Hz, Ar-H), 8.93 (2 H, d, *J*=4.2 Hz, Ar-H), 8.775 (2 H, d, *J*=5.1 Hz, Ar-H), 8.302 (2 H, d, *J*=8.4 Hz, Ar-H), 8.184 (4 H, d, *J*=6 Hz, Ar-H), 8.05 (2 H, d, *J*=8.4 Hz, Ar-H), 7.766 (6 H, m, Ar-H). FT-IR (KBr) [cm⁻¹] 2230 (-CN). MS (FAB): m/z found: 705 (M⁺), calc.: 705.94.



4: **3** (500 mg, mmol), bis(9,9-dimethyl-9H-fluoren-2-yl)amine (1.14 g, 2.83 mmol), 60 % NaH (430 mg, 10.62 mmol), Pd(OAc)₂ (60 mg, 0.28 mmol) and DPEphos (270 mg, 0.51 mmol) was dissolved in 50 mL of anhydrous THF. The reaction mixture was refluxed for 48 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 **4** (200 mg, 28 %) as a darkish blue solid. ¹H-NMR (300 MHz; (CD₃)₂CO; TMS) δ 9.416 (2 H, d, *J*=4.5 Hz, Ar-H), 8.80 (6 H, m, Ar-H), 8.404 (2 H, d, *J*=7.8 Hz, Ar-H), 8.204 (6 H, m, Ar-H), 8.055 (2 H, s, Ar-H), 7.78 (6 H, m, Ar-H), 7.562 (2 H, m, Ar-H), 7.464 (4 H, d, *J*=8.5 Hz, Ar-H), 7.223 (4H, t, *J*=3.6 Hz, Ar-H), 6.844 (2H, d, *J*=8.7 Hz, Ar-H), 1.475 (12 H, s, -CH₃). FT-IR (KBr) [cm⁻¹] 2230 (-CN). MS (MALDI-TOF): m/z found: 1023.8 (M⁺), calc.: 1024.32.



2Flu-ZnP-COOH: **4** (80 mg, 0.08 mmol) and KOH (90 mg, 1.56 mmol) were dissolved in THF/2ethoxyethanol/H₂O (4:4:2, 100 mL) and the solution was refluxed for 1 day. The reaction mixture was then cooled to room temperature and then acidified with aqueous HCl (pH \approx 2) 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 2Flu-ZnP-COOH (60 mg, 74 %) as a darkish blue solid. ¹H-NMR (300 MHz; (CD₃)₂SO; TMS) δ 9.29 (2 H, d, *J*=4.2 Hz, Ar-H), 8.70 (6 H, m, Ar-H), 8.273 (4 H, m, Ar-H), 8.145 (4 H, m, Ar-H), 8.028 (2 H, s, Ar-H), 7.78 (6 H, m, Ar-H), 7.503 (6 H, m, Ar-H), 7.223 (4H, t, *J*=3.9 Hz, Ar-H), 6.671 (2H, d, *J*=9 Hz, Ar-H), 1.475 (12 H, s, -CH₃). ¹³C-NMR (900 MHz; (CD₃)₂SO; TMS) 189.504, 174.183, 167.680, 164.435, 155.699, 154.207, 152.741, 151.996, 151.452, 149.339, 149.015, 148.759, 148.326, 141.937, 140.911, 138.071, 133.823, 133.712, 133.622, 133.362, 133.179, 132.394, 131.464, 131.135, 129.878, 129.245, 129.005, 127.194, 126.830, 126.657, 126.273, 125.971, 125.851, 125.663, 125.460, 125.150, 123.887, 122.691, 122.427, 122.280, 122.198, 121.967, 121.433, 120.913, 120.524, 120.185, 118.842, 122.691, 122.427, 122.280, 122.198, 121.967, 121.433, 120.913, 120.524, 120.185, 118.842, 112.103, 46.166, 30.942. FT-IR (KBr) [cm⁻¹] 1690 (carboxylic acid, -C=O), 2400-3400 (carboxylic acid -OH). UV-vis (THF, nm): λ_{max} (log ε) 419 (253,788), 569 (9,169), 623 (10,273). PL (THF, nm): λ_{max} 671. MS (MALDI-TOF): m/z found: 1044 (M+H)⁺, calc.: 1043.32.



5: A solution of DIBAL-H (1 M in hexanes, 0.21 mL, 0.21 mmol) was added drop-wise to a solution of **4** (110 mg, 0.11 mmol) in anhydrous CH₂Cl₂ (50 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 the aqueous layer was removed. The organic layers were washed with brine and dried over Na₂SO₄. Column chromatography (silica, CHCl₃) afforded a dark blue solid (70 mg, 63 %). ¹H-NMR (300 MHz; (CD₃)₂CO; TMS) δ 10.423 (1 H, s, H-C=O), 9.413 (2 H, d, *J*=4.8 Hz, Ar-H), 8.793 (6 H, m, Ar-H), 8.372 (4 H, d, Ar-H), 8.178 (4 H, m, Ar-H), 8.065 (2 H, s, Ar-H), 7.78 (6 H, m, Ar-H), 7.562 (2 H, m, Ar-H), 7.464 (4 H, d, *J*=8.5 Hz, Ar-H), 7.227 (4 H, t, *J*=3.6 Hz, Ar-H), 6.845 (2 H, d, *J*=8.4 Hz, Ar-H), 1.476 (12 H, s, -CH₃). FT-IR (KBr) [cm⁻¹] 1700 (O=C-H). MS (MALDI-TOF): m/z found: 1026.9 (M⁺), calc.: 1027.32.



2Flu-ZnP-CN-COOH: **5** (70 mg, 0.07 mmol), several drops of piperidine and cyanoacetic acid (20 mg, 0.2 mmol) were dissolved in 50 mL of CH₃CN and the solution was refluxed for 1 day. The reaction mixture was then cooled to room temperature and extracted with CH_2Cl_2 . The organic phase was washed with water several times and dried with sodium sulphate. The filtrate was concentrated in vacuum to give 2Flu-ZnP-CN-COOH (60 mg, 80 %) as a dark blue solid. ¹H-NMR (300 MHz; (CD₃)₂SO; TMS) δ 9.29 (2 H, d, *J*=4.2 Hz, Ar-H), 8.723 (6 H, m, Ar-H), 8.273 (4 H, m, Ar-H), 8.145 (4 H, m, Ar-H), 8.028 (2 H, s, Ar-H), 7.78 (6 H, m, Ar-H), 7.48 (6 H, m, Ar-H), 7.223 (4H, m, Ar-H), 6.653 (2H, d, *J*=8.1 Hz, Ar-H), 1.445 (12 H, s, -CH₃). ¹³C-NMR (900 MHz; (CD₃)₂SO; TMS) 154.214, 152.731, 151.996, 151.444, 149.310, 148.751, 148.331, 141.934, 138.068, 134.351, 133.822, 133.092, 132.382, 132.135, 131.509, 131.245, 131.128, 129.849, 127.326, 127.187, 126.673, 126.266, 125.961, 122.418, 122.274, 121.513, 120.931, 120.531, 120.367, 120.221, 119.681, 118.839, 114.461, 46.159, 30.918. FT-IR (KBr) [cm⁻¹] 1600 (acrylic acid, -C=O), 2220 (cyano, -CN), 3150-3700 (acrylic acid -OH). UV-

vis (THF, nm): λ_{max} (log ε) 420 (201,508), 570 (8,065), 624 (10,271). PL (THF, nm): λ_{max} 667. MS (MALDI-TOF): m/z found: 1095.8 (M+H)⁺, calc.: 1094.33.



Fig. S1 UV-vis absorption spectra of Zn(II)-porphyrin dyes.

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Fig. S2 Normalised absorption and photoluminescence spectra of the Zn(II)-porphyrin dyes in THF.

Zn(II)-porphyrin derivatives generally show two typical emission bands corresponding to Q(0-0) and Q(0-1) near 600 and 650 nm, respectively. In this case, we assume that the emission shoulder near 620 nm may result from the overlap of two emission bands due to their broadness.⁵





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Fig. S4 MALDI-TOF-Mass spectra of Zn(II)-porphyrin dyes.





Chemical Formula: C₆₉H₄₉N₅O₂Zn Exact Mass: 1043.32 Molecular Weight: 1045.57





Chemical Formula: C₇₂H₅₀N₆O₂Zn Exact Mass: 1094.33 Molecular Weight: 1096.62



Fig. S5 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. S6 Calculated frontier orbital of Zn(II)-porphyrin dyes.



Fig. S7 a) Nyquist plots and b) fitted Bode-phase plots of electrochemical impedance spectra for the DSSCs based on Zn(II)-porphyrin dyes; the inset is an equivalent circuit.



Fig. S8 Chemical structure of the multi-functional co-adsorbent HC-A.

Table S1. Numerical values of the electrochemical impedance spectra for DSSCs based on Zn(II)-porphyrin dyes

Dye	$R_s(\Omega)$	$C_{\mu}(\mathbf{mF})$	$\mathbf{R}_{\mathrm{ct}}\left(\Omega ight)$	Life time ($R_{ct} \ge C_{\mu}$, ms)
2Flu-ZnP-COOH w/o CDCA	11.62	0. 667	15.22	10.15
2Flu-ZnP-CN-COOH w/o CDCA	7.51	0.722	28.15	20.33
2Flu-ZnP-COOH with CDCA	8.07	0.875	22.39	19.59
2Flu-ZnP-CN-COOH with CDCA	10.34	0.542	75.44	40.94
2Flu-ZnP-CN-COOH with HC-A	8.86	0.586	155.6	91.24

Dye	Coabsorbent	Dye adsorbed amount [10 ⁻⁷ mol cm ⁻²]
2Flu-ZnP-COOH	0.4 mM CDCA	0.113
2Flu-ZnP-CN-COOH	0.4 mM CDCA	0.991
2Flu-ZnP-CN-COOH	0.1 mM HC-A1	1.217

Table S2. Adsorbed amount of Zn(II)-porphyrin dyes on the TiO₂ film with CDCA or HC-A1.

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