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Supporting Information:

Novel D- π -A Structured Zn(II)-porphyrin Dyes with Bulky Fluorenyl Substituted Electron Donor Moieties for Dye-Sensitized Solar Cells

Min Soo Kang, In Taek Choi, Yeon Wook Kim, Ban Seok You, Sung Ho Kang, Ji Yeoun Hong, Myung Jong Ju and Hwan Kyu Kim*

GET-future Laboratory and Department of Advanced Materials Chemistry, Korea University, 2511 Sejong-Ro, Jochiwon, Sejong 339-700 Korea. Fax: +82-41-867-5396; Tel: +82-41-860-1493; E-mail: hkk777@korea.ac.kr

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 specifically 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 sulfate, 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), diisobutylaluminum hydride (DIBAL-H), sodium hydride, cyanoacetic acid, cesium 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. The silica (230 – 400 mesh) used for column chromatography was purchased from Merck. 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 purification. The ¹H NMR spectroscopy study was conducted on a Varian Mercury 300 spectrometer using tetramethylsilane (TMS; *d* = 0 ppm) as the internal standard. Chemical shifts for ¹H NMR spectra were recorded on a Varian Mercury 300 spectrometer using tetramethylsilane (TMS; *d* = 0 ppm) as the internal standard. The ¹³C NMR spectroscopy study was conducted on a Bruker Biospin Gmbh AVAVCE II 900 spectrometer using tetramethylsilane (TMS; *d* = 0 ppm) as the internal standard. Chemical shifts for ¹³C NMR spectra were recorded on a Bruker Biospin Gmbh AVAVCE II 900 spectrometer using tetramethylsilane (TMS; *d* = 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 analyzed with a Fluorolog FL-3-22 fluorometer from Horiba-Jobin-Yvon Ltd. equipped with a 450 W 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 externally with reference to the Fc⁺/Fc couple. Electrochemical impedance spectra (EIS) of DSSCs were measured with an impedance analyzer (*VersaSTAT3*, AMETEK) connected to a potentiostat under dark conditions at room temperature. The spectra were scanned in a frequency range of 0.1–10⁵ Hz and with the 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

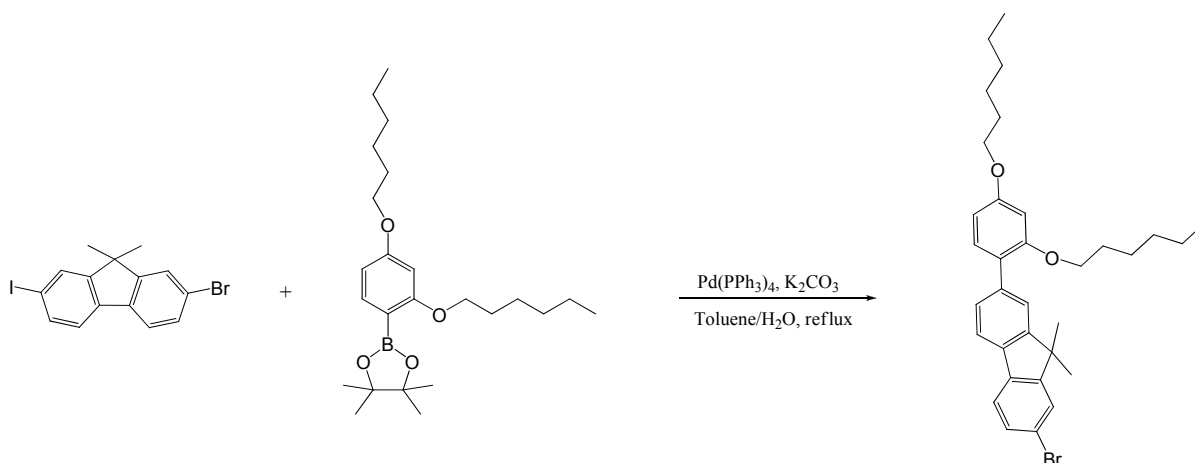
Mass (AM) 1.5 G, at the surface of the test cell. The light intensity was adjusted with a silicon solar cell that was doubled-checked with an NREL calibrated silicon solar cell (PV Measurement Inc.). The applied potential and measured cell current were measured using a Keithley model 2400 digital source 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. The photovoltaic performances were measured with non-reflective metal mask (0.16 cm^2).

Dye-sensitized Solar Cell Fabrication

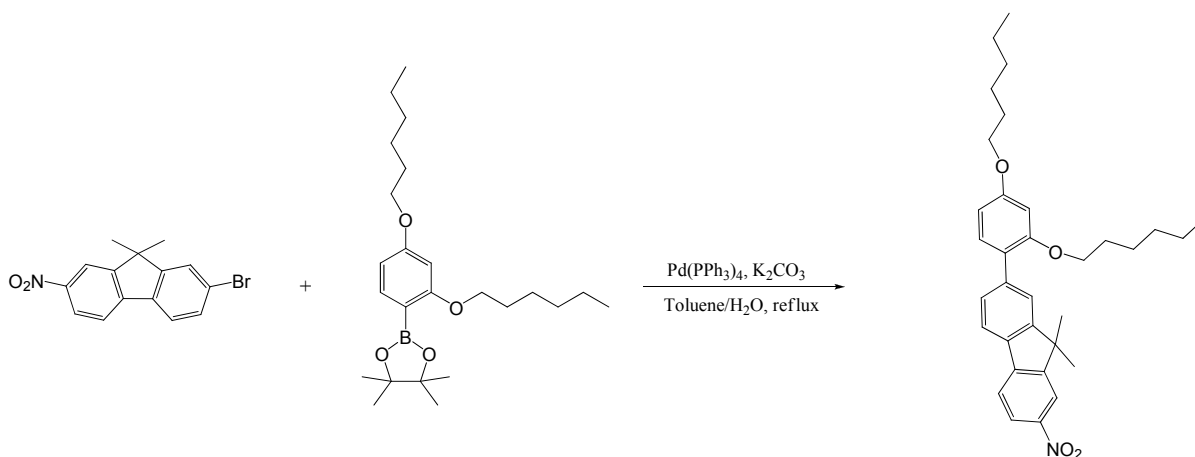
FTO glass plates (Pilkington TEC Glass-TEC 8, Solar 2.3 mm thickness) were cleaned in a mucasol liquid cleaner (Aldrich) in an ultrasonic bath for 30 min, then rinsed with deionized water and ethanol. The FTO glass plates were immersed in 40 mM TiCl_4 (aqueous) at 70°C for 30 min and washed with deionized water and ethanol. A transparent nanocrystalline layer on the FTO glass plate was prepared by repeated screen printing with TiO_2 paste (Solaronix, Ti-Nanoxide T/SP) six times (0.3 cm^2 , $14 \mu\text{m}$), 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 (ENB Korea, STP-500N) was deposited by screen 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 $14 \mu\text{m}$ thickness of 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 , 12 h) containing 4-(3,6-bis(4-(2-ethylhexyloxy)phenyl)-9H-carbazol-9-yl)benzoic acid (HC-A1; 0.4 mM) for dye loading onto the TiO_2 film except the 2,4-ZnP-CN-COOH/HC-A1 system utilized CHCl_3 instead of EtOH/THF. The FTO plate (Pilkington TEC Glass-TEC 8, 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 an 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 (Surllyn 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 I_2 , 0.1 M LiI and 0.5 M 4-*tert*-butylpyridine 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 Surllyn and a cover glass (0.1 mm thickness). The resulting cells had an active area of $0.4 \text{ cm} \times 0.4 \text{ cm}$.

Synthesis

Br-ZnP-CN,¹ 2-bromo-9,9-dimethyl-7-nitro-9H-fluorene,² 2-bromo-7-iodo-9,9-dimethyl-9H-fluorene,³ 2-(2,4-bis(hexyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane,⁴ 9,9-dimethyl-7-nitro-9H-fluoren-2-ol,^{2b} 7-bromo-9,9-dimethyl-9H-fluoren-2-ol,⁵ were synthesized according to the literature with slight modification.

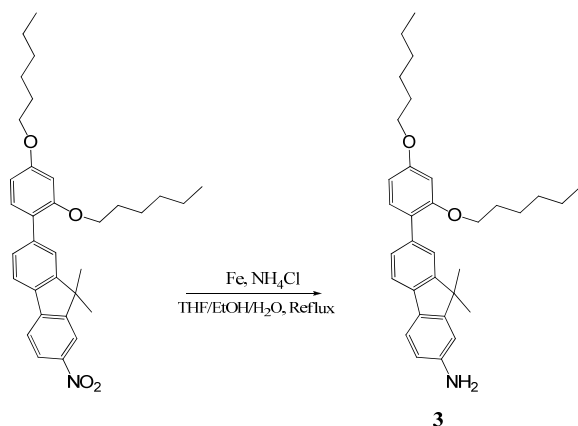


1: 2-bromo-7-iodo-9,9-dimethyl-9H-fluorene (4.14 g, 10.39 mmol), 2-(2,4-bis(hexyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4 g, 9.89 mmol), Pd(PPh₃)₄ (0.46 g, 0.4 mmol) and potassium carbonate (20.51 g, 148.37 mmol) were dissolved in anhydrous toluene/H₂O 1:1 solution (50 mL) under a nitrogen atmosphere. The reaction mixture was refluxed overnight. After the reaction, the reaction mixture was cooled to room temperature and extracted with CH₂Cl₂ and washed with brine several times. The organic layer was dried with anhydrous magnesium sulfate and filtered. The filtrate was then evaporated under vacuum and purified by column chromatography (silica, CH₂Cl₂ : *n*-hexane = 1 : 5) to give **1** (2.5 g, 46%). ¹H-NMR (300 MHz; CDCl₃; TMS) δ 7.58 (5H, m, Ar-H), 7.58 (5H, m, Ar-H), 6.57 (2H, m, Ar-H), 3.98 (4H, m, -OCH₂-), 1.76 (4H, m, -CH₂-), 1.49 (6H, s, -CH₃), 1.37 (6H, m, -CH₂CH₂CH₂-), 1.27 (6H, m, -CH₂CH₂CH₂-), 0.92 (3H, m, -CH₃), 0.87 (3H, m, -CH₃).

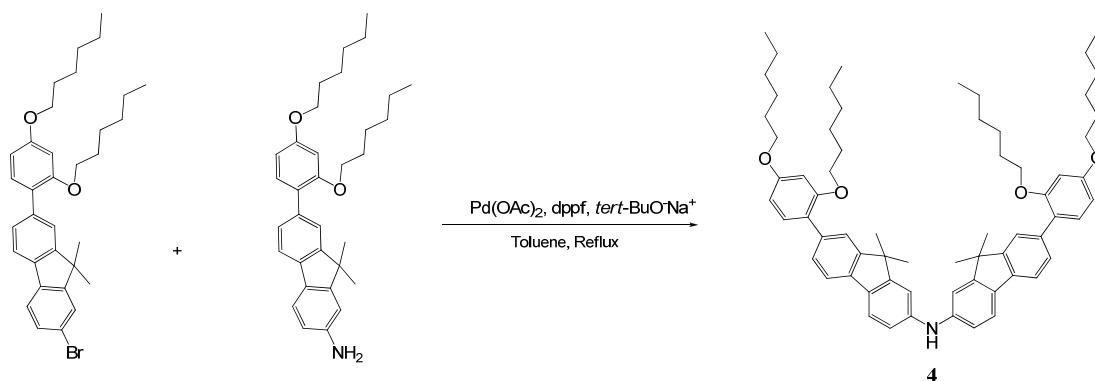


2: 2-bromo-7-nitro-9,9-dimethyl-9H-fluorene (2.97 g, 9.35 mmol), 2-(2,4-bis(hexyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.6 g, 8.9 mmol), Pd(PPh₃)₄ (0.41 g, 0.36 mmol) and potassium carbonate (18.46 g, 133.53 mmol) were dissolved in anhydrous toluene/H₂O 1:1 solution (30 mL) under a nitrogen atmosphere. The reaction mixture was refluxed overnight. After the reaction, the reaction mixture was cooled to room temperature and extracted with CH₂Cl₂ and washed with brine several times. The organic layer was dried with anhydrous magnesium sulfate and filtered. The filtrate was then evaporated under vacuum and purified by column chromatography (silica, CH₂Cl₂) to give **2** (4.2 g, 91%). ¹H-NMR (300 MHz; CDCl₃; TMS) δ 8.28 (1H, m, Ar-H), 8.25 (1H, d, *J* = 2.1 Hz Ar-H), 7.80 (2H, d, *J* = 8 Hz Ar-H), 7.70 (1H, s, Ar-H), 7.55 (1H, d, *J* = 8.1 Hz,

Ar-H), 7.31 (1H, d, $J=9$ Hz, Ar-H), 6.59 (2H, m, Ar-H), 4.00 (4H, m, -OCH₂-), 1.78 (4H, m, -CH₂-), 1.55 (6H, s, -CH₃), 1.37 (6H, m, -CH₂CH₂CH₂-), 1.28 (6H, m, -CH₂CH₂CH₂-), 0.92 (3H, m, -CH₃), 0.86 (3H, m, -CH₃). FT-IR (KBr) [cm⁻¹] 1510, 1338 (-NO₂).

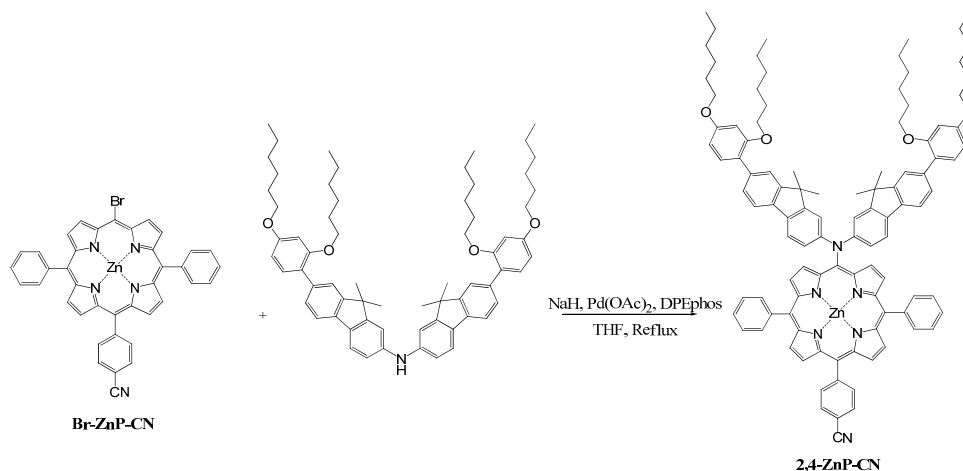


3: **2** (4.6 g, 8.92 mmol), Fe (2.49 g, 44.6 mmol) and NH₄Cl (4.77 g, 89.2 mmol) were dissolved in THF/EtOH/H₂O (50 mL) 4:4:2 solution under a nitrogen atmosphere. The reaction mixture was refluxed until all the starting materials disappeared. After cooling to room temperature, the solid was filtered off. The filtrate was extracted with CH₂Cl₂ (2 x 50 mL) and water (50 mL). The organic phase was combined and the solvent was removed by rotary evaporation. The product was purified by column chromatography (silica, CH₂Cl₂ : *n*-hexane = 3 : 2) to CH₂Cl₂ gradient to yield **3** (410 mg, 87%). ¹H-NMR (300 MHz; (CD₃)₂CO; TMS) δ 7.60 (1H, s, Ar-H), 7.56 (1H, d, $J=7.8$ Hz Ar-H), 7.48 (1H, d, $J=8.1$ Hz Ar-H), 7.37 (1H, d, $J=7.8$ Hz, Ar-H), 7.27 (1H, d, $J=8.7$ Hz, Ar-H), 6.82 (1H, d, $J=2.1$ Hz, Ar-H), 6.62 (3H, m, Ar-H), 4.03 (4H, q, $J=6$ Hz, -OCH₂-), 1.78 (4H, m, -CH₂-), 1.48 (6H, s, -CH₃), 1.40 (6H, m, -CH₂CH₂CH₂-), 1.30 (6H, m, -CH₂CH₂CH₂-), 0.92 (3H, m, -CH₃), 0.86 (3H, m, -CH₃). FT-IR (KBr) [cm⁻¹] 3464, 3476 (Ar-NH₂).

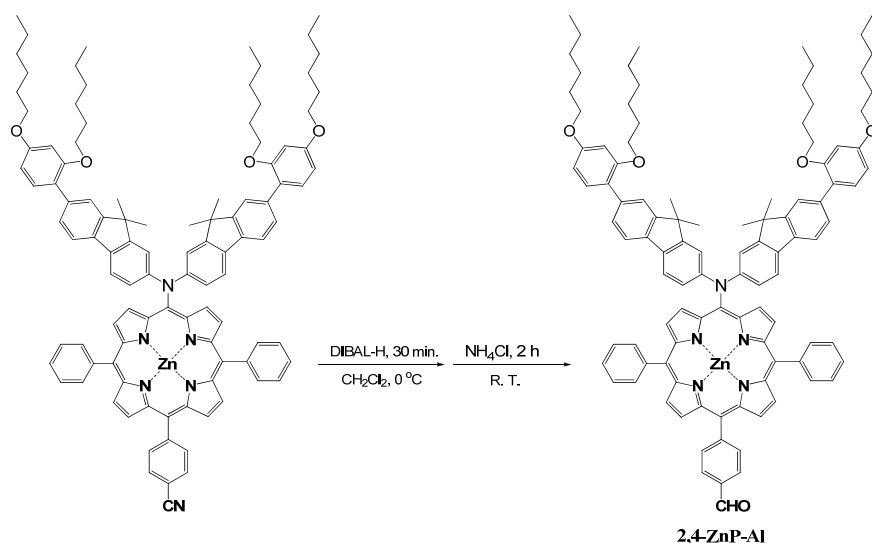


4: **1** (2.5 g, 4.55 mmol), **3** (2.32 g, 4.78 mmol), Pd(OAc)₂ (0.05 g, 0.23 mmol), dppf (0.25 g, 0.45 mmol) and *tert*-BuO⁻Na⁺ (1.31 g, 13.65 mmol) were dissolved in anhydrous toluene (50 mL) under a nitrogen atmosphere. The reaction mixture was refluxed overnight. After the reaction, the reaction mixture was cooled to room temperature and extracted with CH₂Cl₂ and washed with brine several times. The organic layer was dried with anhydrous magnesium sulfate and filtered. The filtrate was then evaporated under vacuum and purified by column chromatography (silica, CH₂Cl₂ : *n*-hexane = 3:1) to give **4** (3.5 g, 81%). ¹H-NMR (300 MHz; (CD₃)₂CO; TMS) δ 7.70 (8H, m, Ar-H), 7.43 (2H, d, $J=8.1$ Hz Ar-H), 7.31 (2H, d, $J=8.4$ Hz Ar-H), 7.17 (2H,

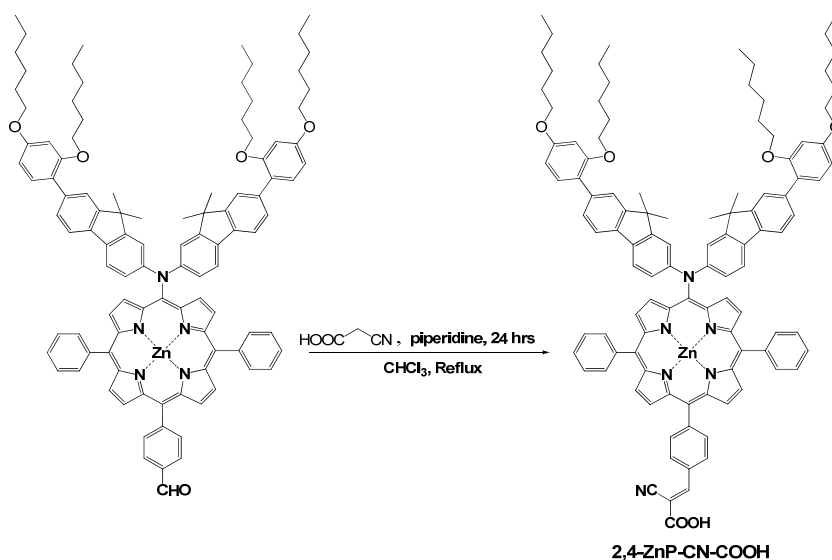
d, $J = 8.1$ Hz, Ar-H), 6.63 (4H, m, Ar-H), 4.04 (8H, q, $J = 6.6$ Hz, $-\text{OCH}_2-$), 1.78 (4H, m, $-\text{CH}_2-$), 1.52 (6H, s, $-\text{CH}_3$), 1.39 (6H, m, $-\text{CH}_2\text{CH}_2\text{CH}_2-$), 1.31 (6H, m, $-\text{CH}_2\text{CH}_2\text{CH}_2-$), 0.92 (3H, m, $-\text{CH}_3$), 0.86 (3H, m, $-\text{CH}_3$). FT-IR (KBr) [cm^{-1}] 3390 ($\text{Ar}_2\text{-NH}$). MS (MALDI-TOF): m/z found: 953.8 (M^+), calc.: 954.37.



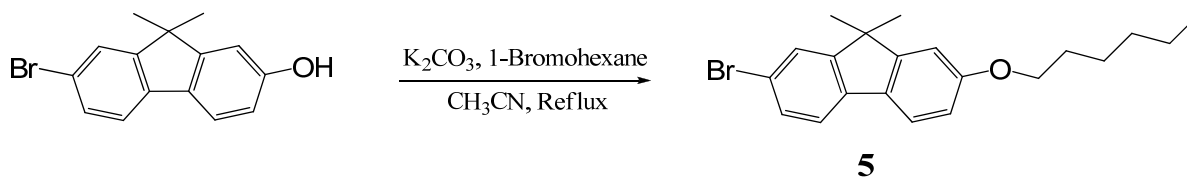
2,4-ZnP-CN: **Br-ZnP-CN** (200 mg, 0.28 mmol), **4** (0.95 g, 0.99 mmol), 60% NaH (140 mg, 3.4 mmol), Pd(OAc)₂ (30 mg, 0.11 mmol) and DPEphos (150 mg, 0.27 mmol) was dissolved in anhydrous THF (20 mL). The reaction mixture was refluxed for 24 h. After the reaction, the reaction mixture was extracted with CH₂Cl₂ and washed with brine several times. The organic layer was dried with anhydrous sodium sulfate and filtered. The filtrate was then evaporated under vacuum and purified by column chromatography (silica, EA : Hex = 1 : 6) to give **2,4-ZnP-CN** (130 mg, 29%). ¹H-NMR (300 MHz; (CDCl₃; TMS) δ 9.411 (2H, d, $J = 4.2$ Hz, Ar-H), 8.915 (2H, d, $J = 5.1$ Hz, Ar-H), 8.844 (2H, d, $J = 5.1$ Hz, Ar-H), 8.76 (2H, d, $J = 5.4$ Hz, Ar-H), 8.33 (2H, d, $J = 7.5$ Hz, Ar-H), 8.17 (4H, d, $J = 7.8$ Hz, Ar-H), 8.06 (2H, d, $J = 8.4$ Hz, Ar-H), 7.72 (6H, m, Ar-H), 7.59 (2H, s, Ar-H), 7.50 (2H, d, $J = 7.8$ Hz, Ar-H), 7.37 (6H, d, $J = 8.4$ Hz, Ar-H), 6.90 (2H, d, $J = 6$ Hz, Ar-H), 6.54 (4H, m, Ar-H), 3.96 (8H, m, $-\text{OCH}_2-$), 1.74 (8H, m, $-\text{CH}_2-$), 1.46 (12H, s, $-\text{CH}_3$), 1.36 (12H, m, $-\text{CH}_2\text{CH}_2\text{CH}_2-$), 1.26 (12H, m, $-\text{CH}_2\text{CH}_2\text{CH}_2-$), 0.87 (12H, m, $-\text{CH}_3$). FT-IR (KBr) [cm^{-1}] 2220 ($-\text{CN}$). MS (MALDI-TOF): m/z found: 1579.28 (M^+), calc.: 1579.40.



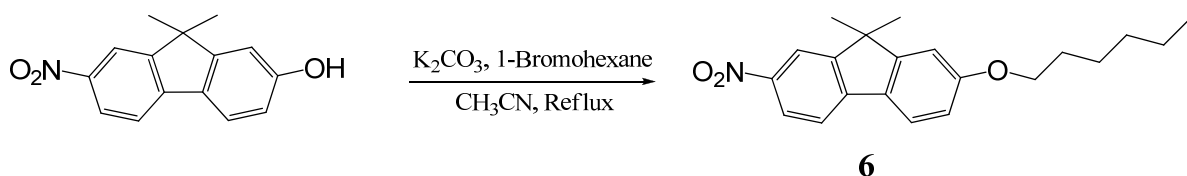
2,4-ZnP-Al: A solution of DIBAL-H (1 M in hexanes, 0.22 mL, 0.22 mmol) was added drop-wise to a solution of **2,4-ZnP-CN** (170 mg, 0.11 mmol) in anhydrous CH_2Cl_2 (50 mL) at 0°C under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 30 min and then quenched with 200 mL of saturated aq. NH_4Cl and stirred for another 2 h. After the reaction, the reaction mixture was extracted with CH_2Cl_2 and washed with brine several times. Column chromatography (silica, CHCl_3) afforded a dark blue solid (100 mg, 59%). $^1\text{H-NMR}$ (300 MHz; CDCl_3 ; TMS) δ 10.38 (1H, s, H-C=O), 9.38 (2H, d, $J = 5.1$ Hz, Ar-H), 8.78 (6H, m, Ar-H), 8.27 (8H, m, Ar-H), 7.89 (2H, s, Ar-H), 7.72 (6H, m, Ar-H), 8.06 (2H, d, $J = 8.4$ Hz, Ar-H), 7.72 (6H, m, Ar-H), 7.59 (2H, d, $J = 7.8$ Hz, Ar-H), 7.48 (2H, d, $J = 7.8$ Hz, Ar-H), 7.37 (6H, d, $J = 8.4$ Hz, Ar-H), 6.90 (2H, d, $J = 6$ Hz, Ar-H), 6.54 (4H, m, Ar-H), 3.96 (8H, m, $-\text{OCH}_2-$), 1.76 (8H, m, $-\text{CH}_2-$), 1.46 (12 H, s, $-\text{CH}_3$), 1.35 (12H, m, $-\text{CH}_2\text{CH}_2\text{CH}_2-$), 1.26 (12H, m, $-\text{CH}_2\text{CH}_2\text{CH}_2-$), 0.91 (6H, m, CH_3), 0.83 (6H, m, $-\text{CH}_3$). FT-IR (KBr) [cm^{-1}] 1700 ($-\text{C}=\text{O}$). MS (MALDI-TOF): m/z found: 1582.23 (M^+), calc.: 1582.40



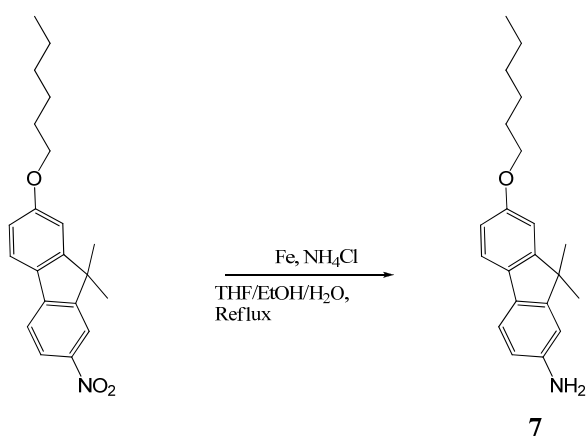
2,4-ZnP-CN-COOH: **2,4-ZnP-Al** (100 mg, 0.06 mmol), several drops of piperidine and cyanoacetic acid (20 mg, 0.19 mmol) were dissolved in CHCl_3 (50 mL) and the solution was refluxed for 1 day. The reaction mixture was then cooled to room temperature and extracted with CH_2Cl_2 and washed with H_2O several times. The organic phase was washed with water several times and dried with sodium sulfate. The filtrate was concentrated under vacuum and column chromatography (silica, $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH} = 1:1$) afforded **2,4-ZnP-CN-COOH** (80 mg, 77%) as a dark blue solid. $^1\text{H-NMR}$ (300 MHz; $(\text{CD}_3)_2\text{SO}$; TMS) δ 9.31 (2H, d, $J = 4.2$ Hz, Ar-H), 8.72 (6H, m, Ar-H), 8.27 (4H, m, Ar-H), 8.14 (2H, m, Ar-H), 8.07 (2H, m, Ar-H), 7.76 (6H, m, Ar-H), 7.64 (2H, s, Ar-H), 7.52 (2H, d, $J = 7.5$ Hz, Ar-H), 7.44 (2H, d, $J = 8.7$ Hz, Ar-H), 7.27 (4H, m, Ar-H), 6.61 (8H, m, Ar-H), 3.97 (8H, m, $-\text{OCH}_2-$), 1.68 (8H, m, $-\text{CH}_2-$), 1.48 (12H, s, $-\text{CH}_3$), 1.32 (12H, m, $-\text{CH}_2\text{CH}_2\text{CH}_2-$), 1.23 (12H, m, $-\text{CH}_2\text{CH}_2\text{CH}_2-$), 0.88 (6H, m, CH_3), 0.80 (6H, m, $-\text{CH}_3$). $^{13}\text{C-NMR}$ (225 MHz; $(\text{CD}_3)_2\text{SO}$; TMS) 159.27, 156.59, 154.753, 152.48, 152.22, 151.83, 149.68, 148.70, 142.39, 136.56, 136.19, 134.77, 134.18, 132.72, 131.90, 131.43, 130.81, 130.36, 127.86, 127.55, 126.62, 123.56, 122.93, 122.61, 120.76, 120.58, 118.77, 114.89, 105.89, 100.055, 67.86, 67.54, 56.05, 46.45, 31.03, 31.00, 28.75, 28.70, 26.967, 25.48, 22.01, 22.06, 18.56, 13.94, 13.89. 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: 1649.08 (M^+), calc.: 1649.44.



5: 7-bromo-9,9-dimethyl-9H-fluoren-2-ol (4.24 g, 14.66 mmol), 1-bromohexane (2.26 mL, 16.13 mmol) and potassium carbonate (5.26 g, 29.33 mmol) were dissolved in acetonitrile (30 mL). The reaction mixture was refluxed overnight. After the reaction, the reaction mixture was cooled to room temperature and extracted with CH_2Cl_2 and washed with brine several times. The organic layer was dried with anhydrous magnesium sulfate and filtered. The filtrate was then evaporated under vacuum and purified by column chromatography (silica, CH_2Cl_2 : *n*-hexane = 3:2) to give **5** (4.5 g, 82%). $^1\text{H-NMR}$ (300 MHz; $(\text{CD}_3)_2\text{CO}$; TMS) δ 7.67 (3H, m, Ar-H), 7.46 (1H, d, $J = 6.3$ Hz Ar-H), 7.13 (1H, d, $J = 2.1$ Hz, Ar-H), 6.92 (1H, d, $J = 8.8$ Hz, Ar-H), 4.06 (H, t, $J = 6.3$ Hz, $-\text{OCH}_2-$), 1.80 (2H, m, $-\text{CH}_2-$), 1.49 (8H, m, $-\text{CH}_3$, $-\text{CH}_2-$), 1.37 (4H, m, $-\text{CH}_2\text{CH}_2-$), 0.91 (3H, m, $-\text{CH}_3$).

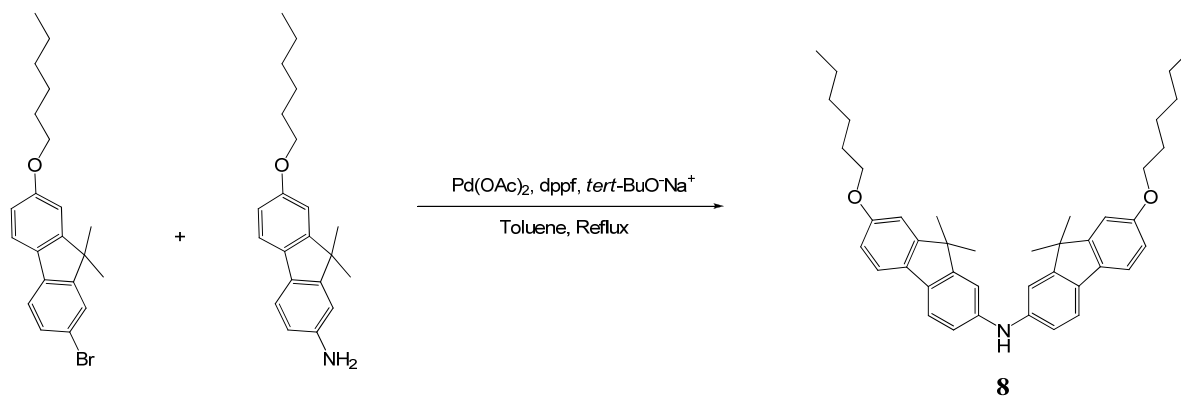


6: 9,9-dimethyl-7-nitro-9H-fluoren-2-ol (1.07 g, 4.19 mmol), 1-bromohexane (0.65 mL, 4.61 mmol) and potassium carbonate (1.50 g, 8.38 mmol) were dissolved in acetonitrile (30 mL). The reaction mixture was refluxed overnight. After the reaction, the reaction mixture was cooled to room temperature and extracted with CH_2Cl_2 and washed with brine several times. The organic layer was dried with anhydrous magnesium sulfate and filtered. The filtrate was then evaporated under vacuum and purified by column chromatography (silica, CH_2Cl_2 : *n*-hexane = 3:2) to give **6** (1.35 g, 95%). $^1\text{H-NMR}$ (300 MHz; $(\text{CD}_3)_2\text{CO}$; TMS) δ 8.35 (1H, d, $J = 2.1$ Hz, Ar-H), 8.24 (1H, d, $J = 8.4$ Hz Ar-H), 7.91 (2H, m, Ar-H), 7.234 (1H, d, $J = 2.1$ Hz, Ar-H), 7.01 (1H, d, $J = 8.7$ Hz, Ar-H), 4.11 (2H, t, $J = 6.3$ Hz, $-\text{OCH}_2-$), 1.81 (2H, m, $-\text{CH}_2-$), 1.54 (8H, m, $-\text{CH}_3$, $-\text{CH}_2-$), 1.36 (4H, m, $-\text{CH}_2\text{CH}_2-$), 0.91 (3 H, m, $-\text{CH}_3$).

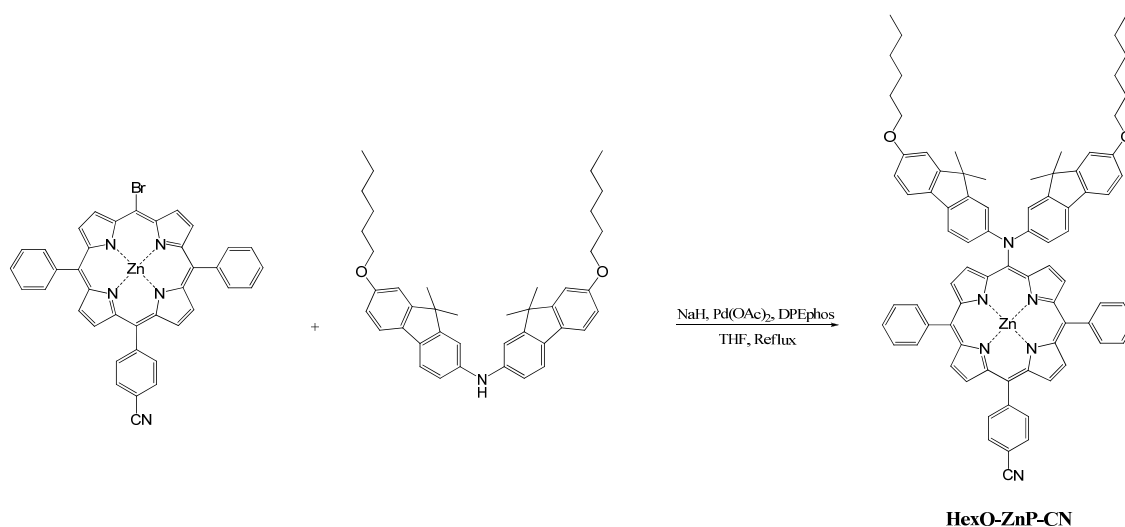


7: **6** (0.7 g, 2.06 mmol), Fe (0.58 g, 10.31 mmol) and NH_4Cl (1.10 g, 20.62 mmol) were dissolved in THF/EtOH/ H_2O 4:4:2 solution (50 mL) under a nitrogen atmosphere. The reaction mixture was refluxed until

all the starting materials disappeared. After cooling to room temperature, the solid was filtered off. The filtrate was extracted with CH_2Cl_2 (2 x 50 mL) and water (50 mL). The organic phase was combined and the solvent was removed by rotary evaporation. The product was purified by column chromatography (silica, CH_2Cl_2 : *n*-hexane = 3 : 2) to CH_2Cl_2 gradient to yield **7** (600 mg, 94%). $^1\text{H-NMR}$ (300 MHz; $(\text{CD}_3)_2\text{CO}$; TMS) δ 7.45 (1 H, d, $J = 8.1$ Hz, Ar-H), 7.37 (1H, d, $J = 8.1$ Hz Ar-H), 7.01 (1H, d, $J = 2.4$ Hz, Ar-H), 6.79 (2H, m, Ar-H), 6.61 (1H, d, $J = 7.2$ Hz, Ar-H), 4.00 (2H, q, $J=6.6$ Hz, $-\text{OCH}_2-$), 1.79 (2H, m, $-\text{CH}_2-$), 1.38 (12H, m, $-\text{CH}_3$, $-\text{CH}_2-\text{CH}_2\text{CH}_2-$), 0.92 (H, m, $-\text{CH}_3$). FT-IR (KBr) [cm^{-1}] 3460, 3370 (Ar-NH₂).

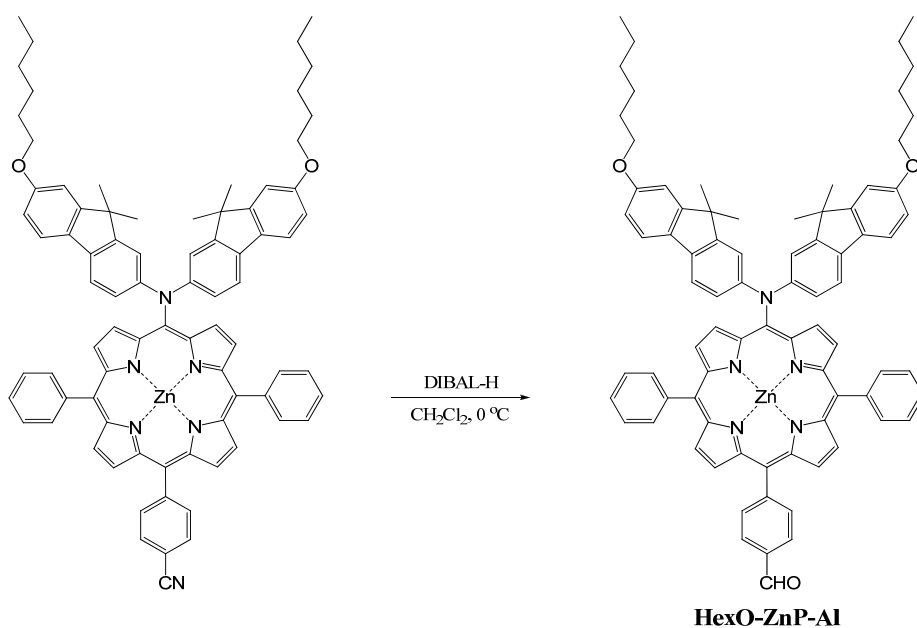


8: **5** (0.7 g, 1.83 mmol), **7** (0.58 g, 1.86 mmol), Pd(OAc)₂ (0.02 g, 0.009 mmol), dppf (0.1 g, 0.18 mmol) and *tert*-BuO⁻Na⁺ (0.53 g, 5.48 mmol) were dissolved in anhydrous toluene (50 mL) under a nitrogen atmosphere. The reaction mixture was refluxed overnight. After the reaction, the reaction mixture was cooled to room temperature and extracted with CH_2Cl_2 and washed with brine several times. The organic layer was dried with anhydrous magnesium sulfate and filtered. The filtrate was then evaporated under vacuum and purified by column chromatography (silica, CH_2Cl_2 : *n*-hexane = 3 : 1) to give **8** (0.7 g, 64%). $^1\text{H-NMR}$ (300 MHz; $(\text{CD}_3)_2\text{CO}$; TMS) δ 7.57 (4H, d, $J = 7.2$ Hz, Ar-H), 7.29 (2H, m, Ar-H), 7.09 (4H, m, Ar-H), 6.87 (2H, d, $J = 8.4$ Hz, Ar-H), 4.03 (4H, m, $-\text{OCH}_2-$), 1.84 (4H, m, $-\text{CH}_2-$), 1.45 (12H, s, $-\text{CH}_3$), 1.37 (12H, m, $-\text{CH}_2-\text{CH}_2\text{CH}_2-$), 0.91 (6H, m, $-\text{CH}_3$). FT-IR (KBr) [cm^{-1}] 3440 (Ar₂-NH), 3390 (hydrogen bonded Ar₂-NH).

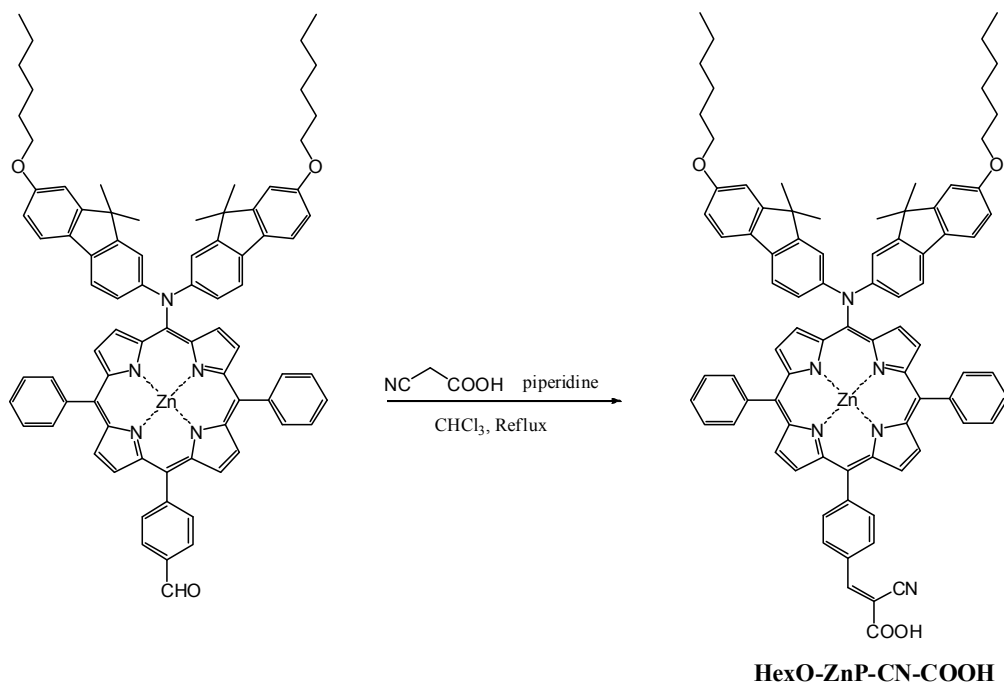


HexO-ZnP-CN: **Br-ZnP-CN** (200 mg, 0.28 mmol), **4** (600 mg, 0.99 mmol), 60% NaH (140 mg, 3.4 mmol),

$\text{Pd}(\text{OAc})_2$ (30 mg, 0.11 mmol) and DPEphos (150 mg, 0.27 mmol) was dissolved in anhydrous THF (20 mL). The reaction mixture was refluxed for 24 h. After the reaction, the reaction mixture was extracted with CH_2Cl_2 and washed with brine several times. The organic layer was dried with anhydrous sodium sulfate and filtered. The filtrate was then evaporated under vacuum and purified by column chromatography (silica, EA : Hex = 1 : 6) to give **HexO-ZnP-CN** (80 mg, 23%). $^1\text{H-NMR}$ (300 MHz; CDCl_3 ; TMS) δ 9.39 (2H, d, $J = 3.3$ Hz, Ar-H), 8.91 (2H, d, $J = 4.5$ Hz, Ar-H), 8.83 (2H, d, $J = 3.9$ Hz, Ar-H), 8.75 (2H, d, $J = 4.2$ Hz, Ar-H), 8.32 (2H, d, $J = 7.5$ Hz, Ar-H), 8.16 (4H, d, $J = 6$ Hz, Ar-H), 8.06 (2H, d, $J = 7.5$ Hz, Ar-H), 7.84 (2H, s, Ar-H), 7.72 (6H, m, Ar-H), 7.38 (4H, d, $J = 8.1$ Hz, Ar-H), 6.91 (2H, s, Ar-H), 6.84 (2H, d, $J = 8.7$ Hz, Ar-H), 6.77 (2H, d, $J = 7.2$ Hz, Ar-H), 3.96 (4H, m, $-\text{OCH}_2-$), 1.78 (4H, m, $-\text{CH}_2-$), 1.39 (24H, m, $-\text{CH}_3$, $-\text{CH}_2\text{CH}_2\text{CH}_2-$), 0.91 (6H, m, $-\text{CH}_3$). FT-IR (KBr) [cm^{-1}] 2220 ($-\text{CN}$). MS (MALDI-TOF): m/z found: 1224.7 (M^+), calc.: 1226.89.



HexO-ZnP-AL: A solution of DIBAL-H (1 M in hexanes, 0.22 mL, 0.22 mmol) was added drop-wise to a solution of **HexO-ZnP-CN** (170 mg, 0.11 mmol) in anhydrous CH_2Cl_2 (50 mL) at 0°C under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 30 min and then quenched with 200 mL of saturated aq. NH_4Cl and stirred for another 2 h. After the reaction, the reaction mixture was extracted with CH_2Cl_2 and washed with brine several times. Column chromatography (silica, CHCl_3) afforded a dark blue solid (50 mg, 62%). $^1\text{H-NMR}$ (300 MHz; CDCl_3 ; TMS) δ 10.38 (1H, s, H-C=O), 9.39 (2H, d, $J = 5.1$ Hz, Ar-H), 8.90 (2H, d, $J = 4.8$ Hz, Ar-H), 8.82 (4H, m, Ar-H), 8.37 (2H, m, Ar-H), 8.28 (2H, m, Ar-H), 8.17 (4H, m, Ar-H), 7.85 (2H, s, Ar-H), 7.72 (6H, m, Ar-H), 7.38 (4H, d, $J = 8.1$ Hz, Ar-H), 6.91 (2H, s, Ar-H), 6.85 (2H, m, Ar-H), 6.81 (2H, m, Ar-H), 3.97 (4H, m, $-\text{OCH}_2-$), 1.79 (4H, m, $-\text{CH}_2-$), 1.39 (24H, m, $-\text{CH}_3$, $-\text{CH}_2\text{CH}_2\text{CH}_2-$), 0.90 (6H, m, $-\text{CH}_3$). FT-IR (KBr) [cm^{-1}] 1701 ($-\text{C=O}$). MS (MALDI-TOF): m/z found: 1229.7 (M^+), calc.: 1229.89.



HexO-ZnP-CN-COOH: HexO-ZnP-Al (100 mg, 0.06 mmol), several drops of piperidine and cyanoacetic acid (20 mg, 0.19 mmol) were dissolved in CHCl_3 (50 mL) and the solution was refluxed for 1 day. The reaction mixture was then cooled to room temperature and extracted with CH_2Cl_2 and washed with H_2O several times. The organic phase was washed with water several times and dried with sodium sulfate. The filtrate was concentrated in under vacuum and column chromatography (silica, $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH} = 1:1$) afforded HexO-ZnP-CN-COOH (30 mg, 57%) as a dark blue solid. $^1\text{H-NMR}$ (300 MHz; $(\text{CD}_3)_2\text{SO}$; TMS) δ 9.26 (2H, m, Ar-H), 8.71 (H, m, Ar-H), 8.28 (2H, m, Ar-H), 8.16 (4H, m, Ar-H), 7.98 (2H, m, Ar-H), 7.83 (2H, s, Ar-H), 7.76 (6H, m, Ar-H), 7.42 (2H, d, $J = 7.8$ Hz, Ar-H), 7.31 (2H, d, $J = 7.8$ Hz, Ar-H), 7.10 (2H, s, Ar-H), 6.79 (2H, d, $J = 7.8$ Hz, Ar-H), 6.58 (2H, d, $J = 6.9$ Hz, Ar-H), 6.81 (2H, m, Ar-H), 3.97 (4H, m, $-\text{OCH}_2-$), 1.71 (4H, m, $-\text{CH}_2-$), 1.24 (24H, m, $-\text{CH}_3$, $-\text{CH}_2\text{CH}_2\text{CH}_2-$), 0.87 (6H, m, $-\text{CH}_3$). $^{13}\text{C-NMR}$ (225 MHz; $(\text{CD}_3)_2\text{SO}$; TMS) 158.13, 155.02, 154.11, 151.91, 151.52, 149.60, 149.02, 148.66, 142.30, 134.75, 134.16, 132.68, 131.87, 131.51, 131.04, 127.827, 127.53, 126.61, 122.79, 120.51, 119.87, 114.78, 112.95, 109.34, 67.60, 56.03, 31.21, 28.81, 27.01, 25.25, 22.08, 18.56, 13.92. FT-IR (KBr) $[\text{cm}^{-1}]$ 2218 ($-\text{CN}$), 1608 acrylic acid, $-\text{C}=\text{O}$), 3150-3700 (acrylic acid -OH). MS (MALDI-TOF): m/z found: 1296.75 (M^+), calc.: 1296.93.

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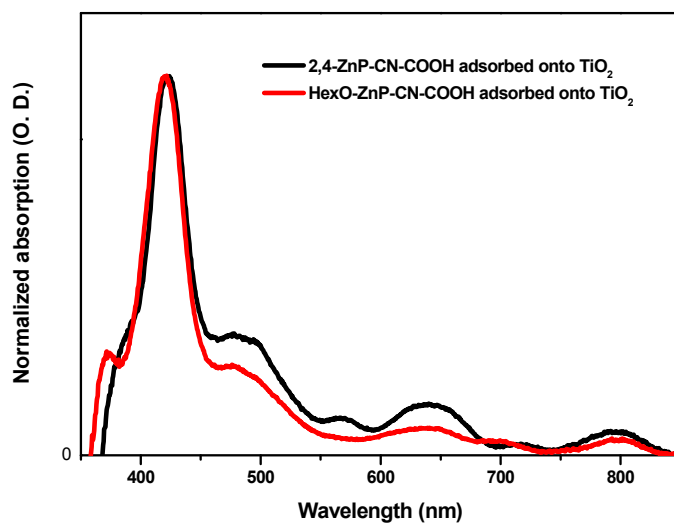


Fig. S1 UV-vis absorption spectra of Zn(II)-porphyrin sensitizers adsorbed onto TiO₂ Film.

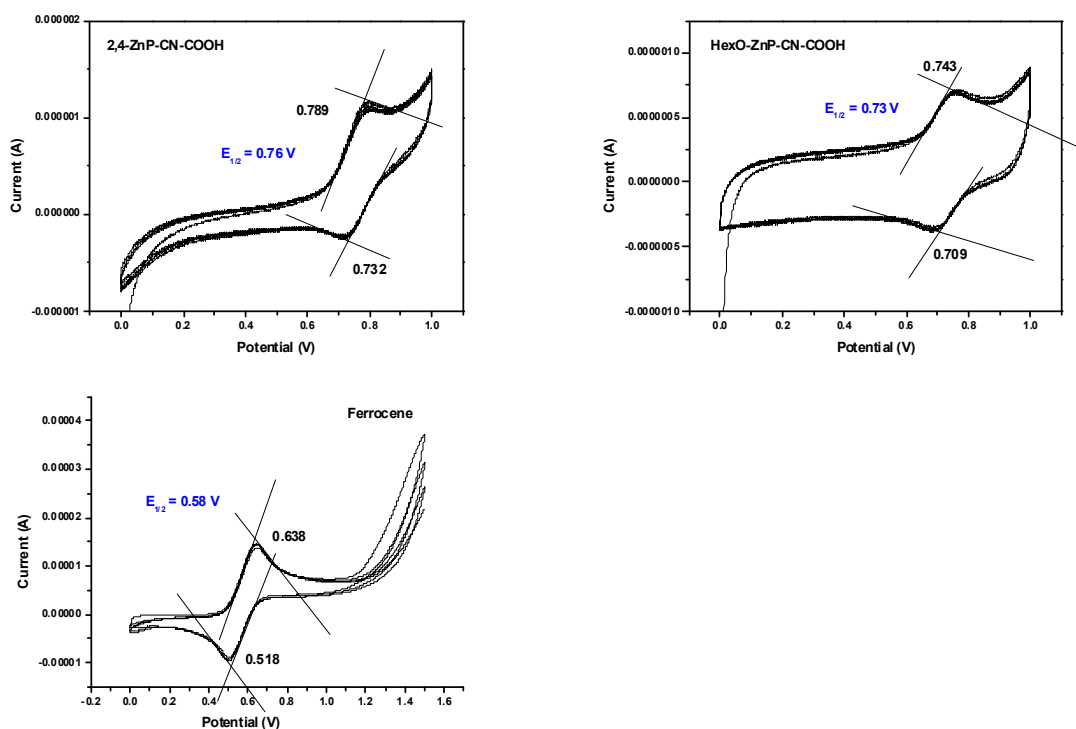
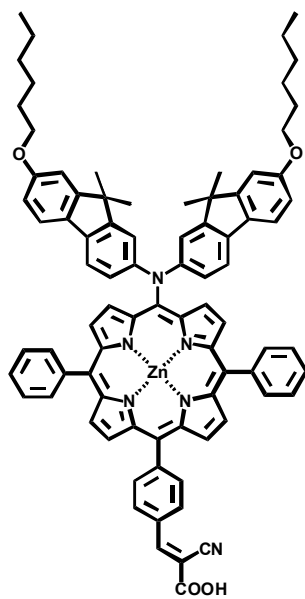
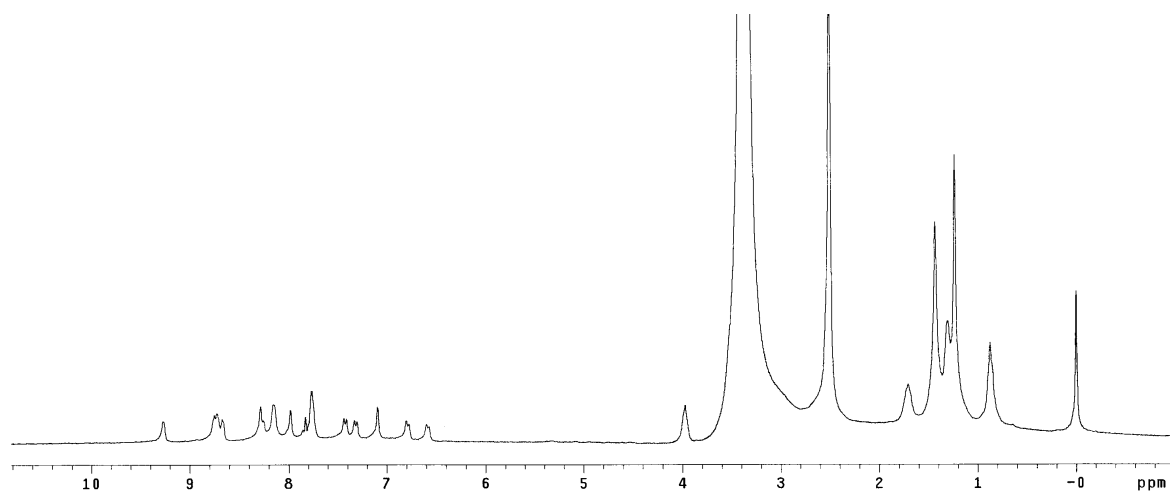
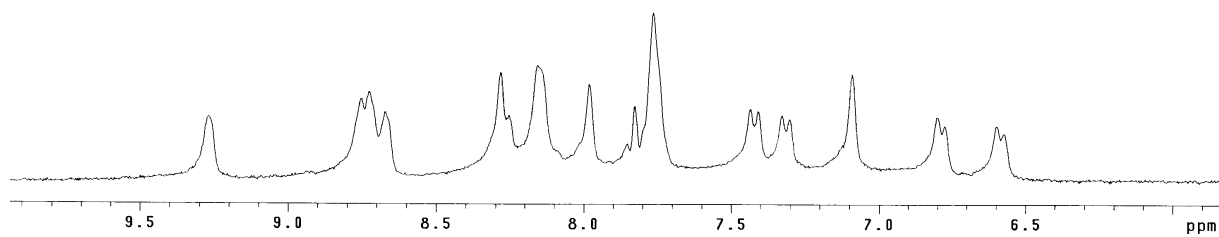


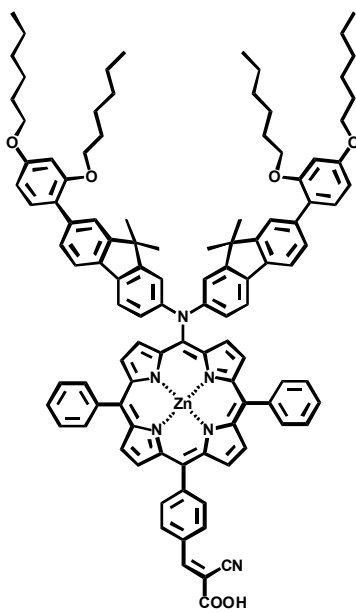
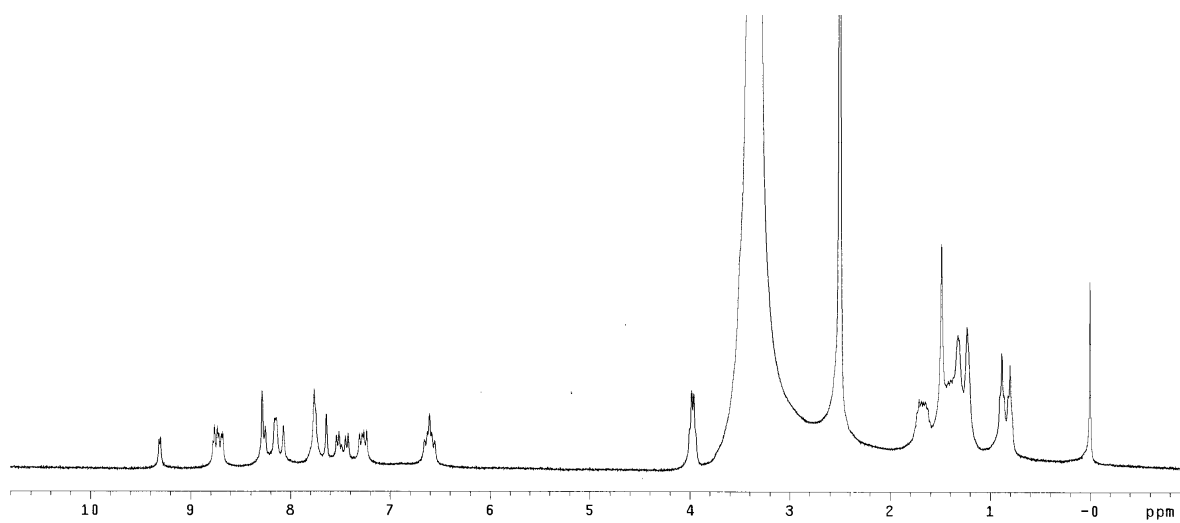
Fig. S2 Cyclic voltammograms of Zn(II)-porphyrin dyes and the Fc/Fc⁺ redox couple in THF at a scan rate of 50 mVs⁻¹ at room temperature with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. Pt working electrode, a Pt wire as the counter electrode and an Ag/AgCl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

Fig. S3 $^1\text{H-NMR}$ spectra of Zn(II)-porphyrin dyes.



Chemical Formula: $\text{C}_{60}\text{H}_{72}\text{N}_4\text{O}_2\text{Zn}$
Exact Mass: 1294.51
Molecular Weight: 1296.93





Chemical Formula: $C_{104}H_{106}N_8O_8Zn$
Exact Mass: 1646.75
Molecular Weight: 1649.44

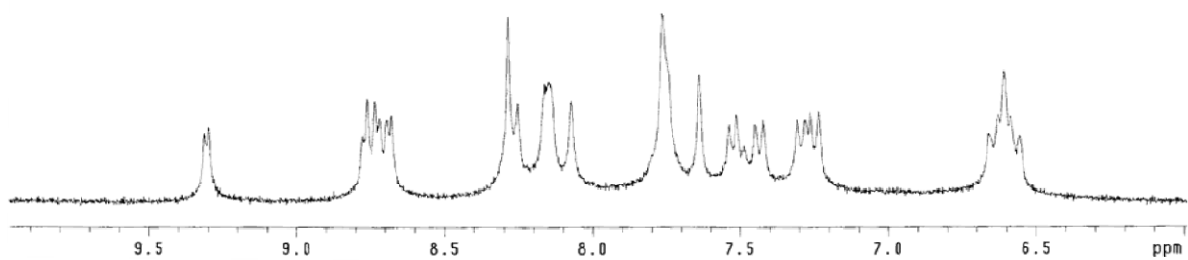
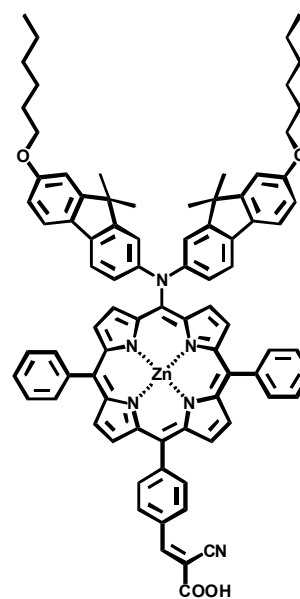
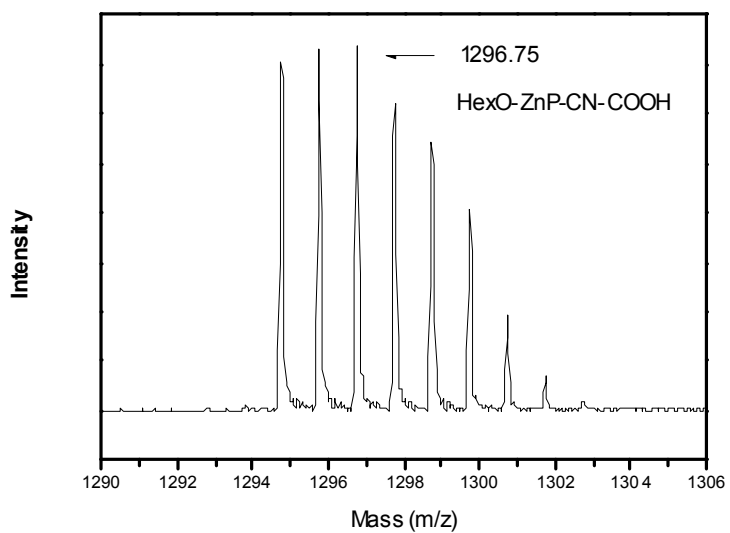
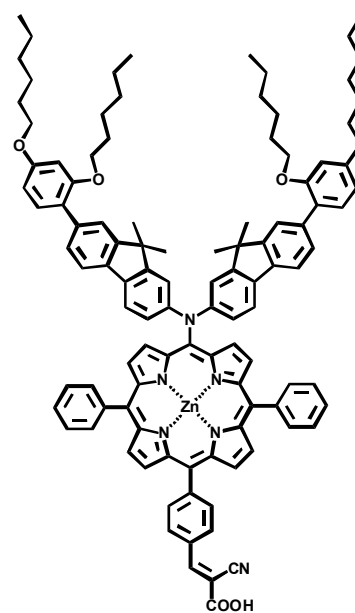
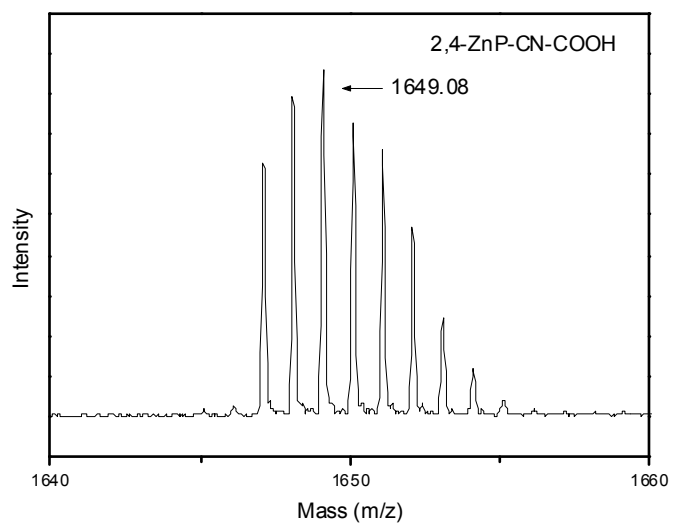


Fig. S4 $^1\text{H-NMR}$ spectra of Zn(II)-porphyrin dyes.



Chemical Formula: $\text{C}_{61}\text{H}_{72}\text{N}_4\text{O}_4\text{Zn}$
Exact Mass: 1294.51
Molecular Weight: 1296.93



Chemical Formula: $\text{C}_{108}\text{H}_{128}\text{N}_4\text{O}_4\text{Zn}$
Exact Mass: 1646.75
Molecular Weight: 1649.44

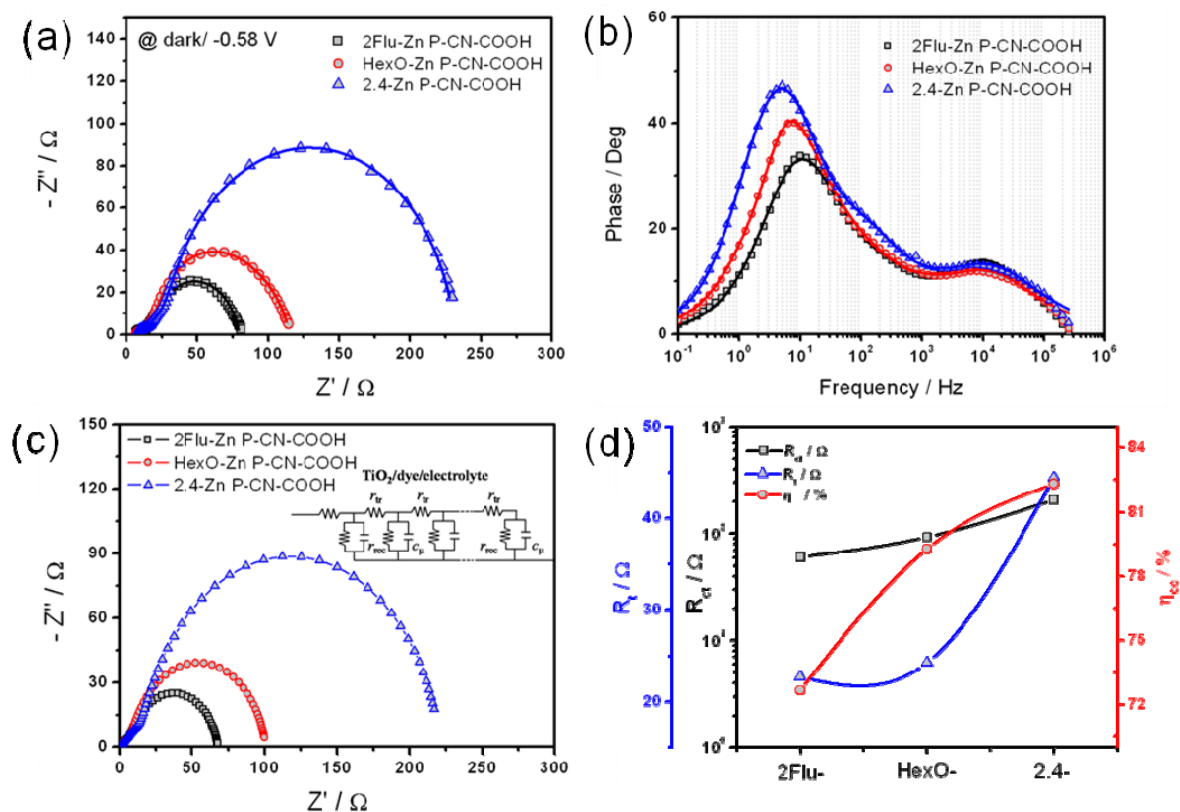


Fig. S5 (a) Nyquist and (b) Bode phase plots from EIS spectra for the DSSCs with porphyrin sensitizers. Solid lines are fitted lines. (c) Fitted curves from the EIS spectra of the DSSCs shown in Fig. S5(a) and the inset is the equivalent circuit used to fit the EIS spectra. (d) Charge collection efficiency, R_{ct} and R_s of the DSSCs.

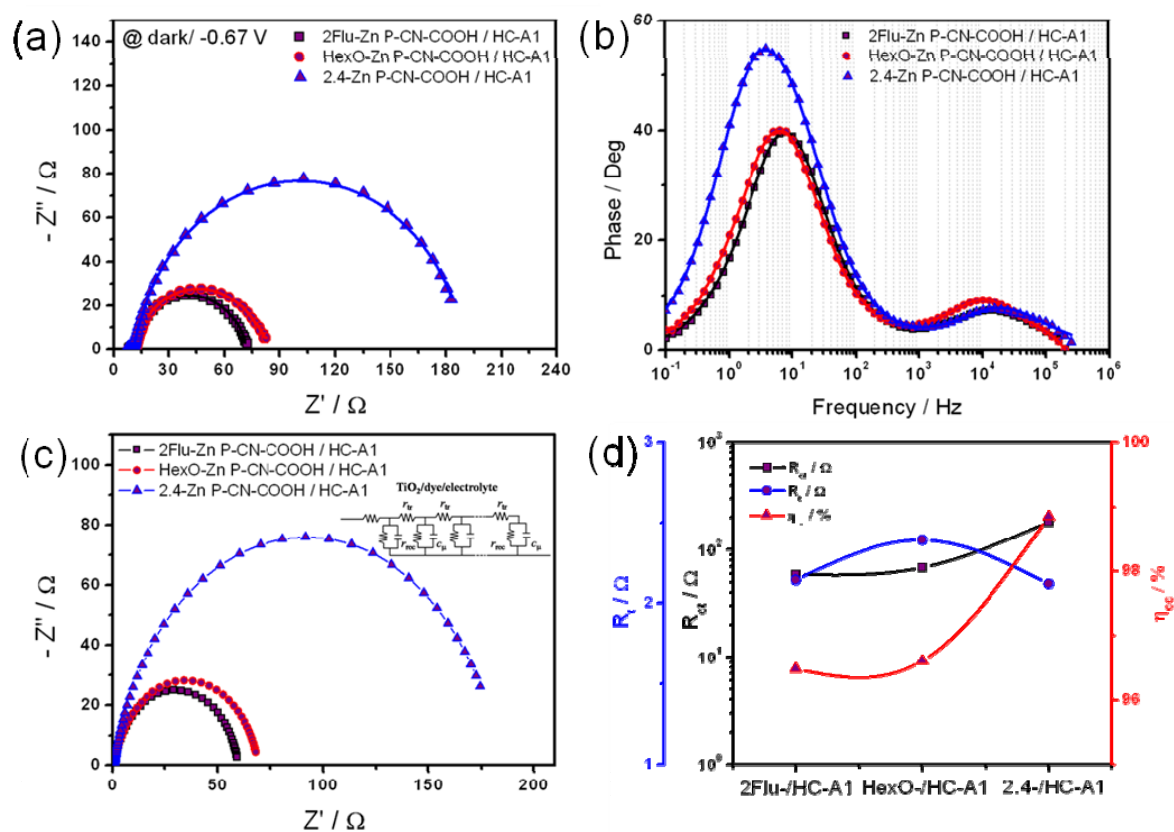


Fig. S6 (a) Nyquist and (b) Bode phase plots from EIS spectra for the DSSCs with porphyrin sensitizers and HCA1. Solid lines are fitted lines. (c) Fitted curves from the EIS spectra of the DSSCs shown in Fig. S6(a) and the inset is the equivalent circuit used to fit the EIS spectra. (d) Charge collection efficiency, R_{ct} and R_f of the DSSCs.

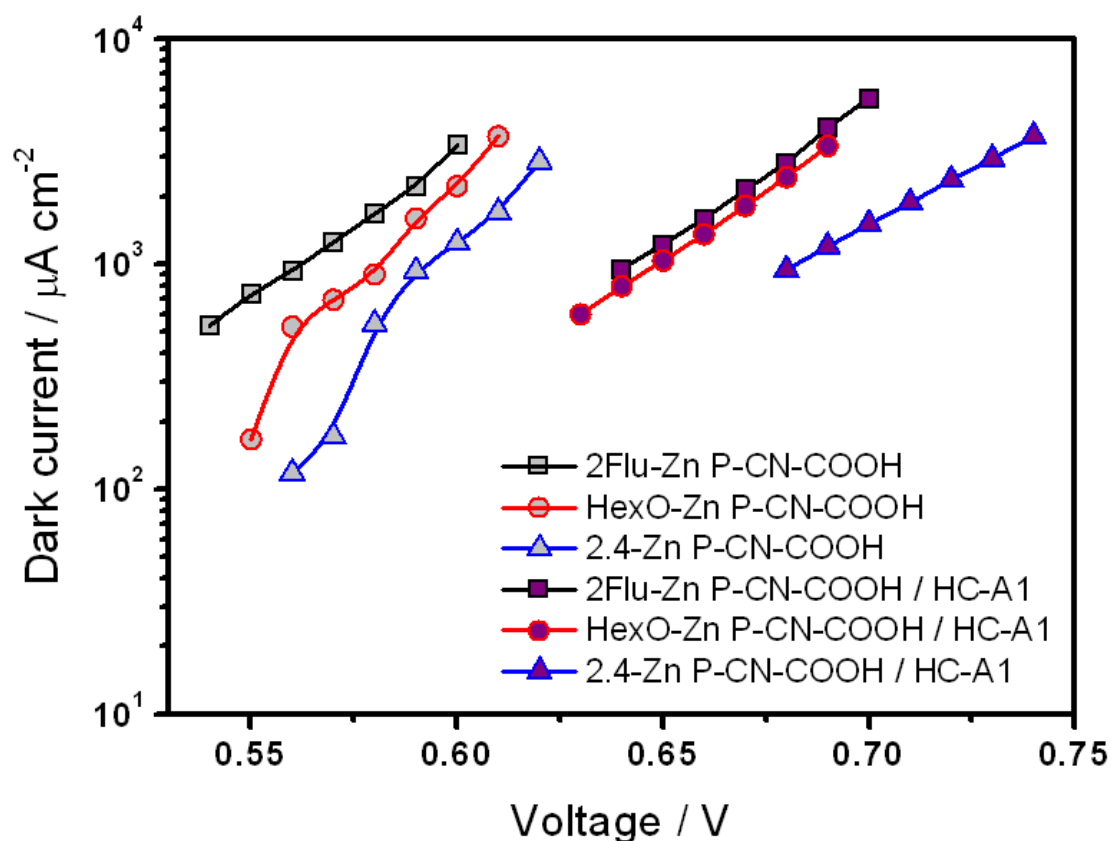


Fig. S7 Dark current obtained from EIS measurements of the DSSCs with porphyrin sensitizers and HC-A1. Based on the data from EIS, the dark current was assumed to be positive.

The difference in V_{OC} for the DSSCs with HC-A1 as the coadsorbent was plotted as a function of the $J-V$ curve obtained from the EIS measurements (Fig. S7). The dark current, measured from EIS, decreased with the co-adsorption of HC-A1. Higher dark current could reduce V_{OC} because it is governed by electron flow from the TiO_2 surface into the redox couple.

Table S1. EIS parameters and charge collection efficiency of the DSSCs.

Device	R_t/Ω	R_{ct}/Ω	C_{dl}/mF	τ_t/ms	τ_n/ms	η_{cc}
2Flu-Zn P-CN-COOH	22.7	60.4	0.86	19.5	52.1	0.72
HexO-Zn P-CN-COOH	24.2	92.8	0.83	20.2	77.3	0.79
2.4-Zn P-CN-COOH	44.4	206.8	0.66	29.4	137.1	0.82

Calculated values from EIS data measured at a forward bias of -0.58 V under dark conditions.

Table S2. EIS parameters and charge collection efficiency of the DSSCs.

Device	R_t/Ω	R_{ct}/Ω	C_{dl}/mF	τ_t/ms	τ_n/ms	η_{cc}
2Flu-Zn P-CN-COOH / HC-A1	2.14	58.8	1.30	2.80	76.7	0.96
HexO-Zn P-CN-COOH / HC-A1	2.39	68.1	1.53	3.67	104.5	0.97
2.4-Zn P-CN-COOH / HC-A1	2.16	144.6	1.39	3.00	201.1	0.98

Calculated values from EIS data measured at a forward bias of -0.67 V under dark conditions.