Supporting information

Zinc Phthalocyanine Sensitizer having Double Carboxylic Acid Anchoring Groups for Dye-Sensitized Solar Cells with Cobalt(II/III)-based Redox Electrolyte

Mutsumi Kimura*, Yuki Tohata, Takuro Ikeuchi, and Shogo Mori

Experimental Section

General procedures: NMR spectra were recorded on a Bruker AVANCE 400 FT NMR spectrometer at 399.65 MHz and 100.62 MHz for $^1$H and $^{13}$C in CDCl$_3$ solution. Chemical shifts are reported relative to internal TMS. IR spectra were obtained on a SHIMAZU IR Prestige-21 with DuraSample IR II. UV-Vis spectra and fluorescence spectra were measured on a JASCO V-650 and a JASCO FP-750. MALDI-TOF mass spectra were obtained on a Bruker autoflex spectrometer with dithranol as matrix. Differential pulse voltammetry (DPV) measurements of PcS25 and PcS26 were carried out in dry DMF containing 0.1 M tetraammonium hexafluorophosphate (TBAP) as an electrolyte at 25°C.

All chemicals were purchased from commercial suppliers and used without purification. Column chromatography was performed with activated alumina (Wako, 200 mesh) or silica gel (Wakogel C-200). Recycling preparative gel permeation chromatography was carried out by a JAI recycling preparative HPLC using CHCl$_3$ as an eluent. Analytical thin layer chromatography was performed with commercial Merck plates coated with silica gel 60 F$_{254}$ or aluminum oxide 60 F$_{254}$. [Co$^{II}$(bpy)$_3$](B(CN)$_4$)$_2$, and [Co$^{III}$(bpy)$_3$](B(CN)$_4$)$_3$ were prepared under modified condition of literature procedure.$^a$

Synthesis

Compounds 2 and 4, 4-bromo-1,2-dicyanobenzene, 3,4-bis(2,6-diphenylphenox)-1,2-dicyanobenzene were prepared by the literature procedures.b,c,d


1: K₂CO₃ (0.20g, 1.4 mmol) was added to a solution of methyl 4-iodosalicylate (0.20g, 0.72 mmol) and ethyl 4-bromobutylate (0.14g, 0.72 mmol), and the resulting reaction mixture was heated at 80 °C with stirring for 8 h. The reaction mixture was cooled to RT and poured into water (50 ml), and the aqueous layer was extracted with 3 x 50 mL of diethylether. After the mixture was dried over MgSO₄, the organic layer was
evaporated to give white solid. The product was purified by column chromatography on silica gel by eluting with CH$_2$Cl$_2$. Yield: 0.26g (93%). $^1$H NMR (CDCl$_3$, 400.13MHz): $\delta$ (ppm) = 7.48 (1H, d, $J$ = 8.0 Hz, ArH), 7.32 (1H, d, $J$ = 8.0 Hz, ArH), 7.29 (1H, s, ArH), 4.04-4.18 (4H, m, -C$_2$H$_5$), 3.88 (3H, s, -C$_3$H$_3$), 2.55-2.63 (2H, m, -CH$_2$-), 2.12-2.16 (2H, m, -CH$_2$-), 1.35 (12H, s, -C$_3$H$_3$), 1.24-1.30 (5H, m, -C$_2$H$_5$-).

$^{13}$C NMR (CDCl$_3$, 100.61MHz): $\delta$ (ppm) = 173.4, 166.4, 158.9, 133.2, 130.0, 123.0, 120.2, 100.2, 68.3, 60.9, 52.4, 30.8, 24.8, 14.6.

3: A Schlenk flask was charged with 1 (0.25g, 0.64mmol), bis(pinacolato)diboron (0.18g, 0.70 mmol), KOAc(0.19g, 1.92 mmol), and (PPh$_3$)$_2$PdCl$_2$ (9 mg, 12.8 $\mu$mol) under an Ar atmosphere. Dry p-dioxane (4 ml) was added to the reaction vessel, and the mixture was refluxed at 130 °C under Ar for 16 h. The reaction mixture was cooled to RT and filtered to remove insoluble salts. The filtrate was concentrated in vacuo and the residue was dissolved in EtOAc. Activated carbon was added to the solution and refluxed for 15 min. The insoluble materials were removed through a pad of Celite. The crude product was purified using column chromatography on silica gel by eluting with n-hexane/CH$_2$Cl$_2$. Yield: 0.25g (96%). $^1$H NMR (CDCl$_3$, 400.13MHz): $\delta$ (ppm) = 7.75 (1H, d, $J$ = 7.6 Hz, ArH), 7.40 (1H, d, $J$ = 7.6 Hz, ArH), 7.39 (1H, s, ArH), 4.16-4.21 (2H, m, -CH$_2$-), 4.02-4.08 (2H, m, -CH$_2$-), 3.87 (3H, s, -CH$_3$), 2.53-2.62 (2H, m, -CH$_2$-), 2.10-2.15 (2H, m, -CH$_2$-), 1.25 (3H, t, $J$ = 7.2Hz, -CH$_3$). $^{13}$C NMR (CDCl$_3$, 100.61MHz): $\delta$ (ppm) = 173.6, 167.1, 157.8, 130.9, 128.8, 126.9, 119.3, 84.4, 84.0, 83.7, 67.9, 63.1, 52.2, 30.8, 24.7, 14.5.

Phthalonitrile 5: A Schlenk flask was charged with 4-bromo-1, 2-dicyanobenzene (0.16 g, 0.76 mmol) and Pd(PPh$_3$)$_4$ (15.0 mg, 12.8 $\mu$mol) under an Ar atmosphere. Solution of 3 (0.25 g, 0.64 mmol) in THF (2 mL), toluene (1.5 ml), and NaCO$_3$ (2 M, 1 mL) in H$_2$O were prepared and deoxygenated with stream of Ar. This solution was added to the reaction vessel, and the mixture was refluxed under Ar for 48 h. The reaction mixture was poured into a mixture of H$_2$O and diethylether. The crude product was purified using column chromatography on silica gel by eluting with CH$_2$Cl$_2$ and preparative HPLC. Yield: 0.14g (61%). $^1$H NMR (CDCl$_3$, 400.13MHz): $\Box$ (ppm) = 8.06 (1H, s, ArH), 7.88-7.96 (3H, m, ArH), 7.17-7.20 (2H, m, ArH), 4.05-4.20 (4H, m, -CH$_2$-), 3.93 (3H, s, -CH$_3$), 2.55-2.63 (2H, m, -CH$_2$-), 2.12-2.16 (2H, m, -CH$_2$-), 1.35 (3H, t, $J$ = 7.2 Hz, -CH$_3$). $^{13}$C NMR (CDCl$_3$, 100.61MHz): $\Box$ (ppm) = 173.6, 166.5, 159.3, 145.7, 142.2, 134.4, 133.2, 132.6, 132.0, 121.8, 119.5, 117.0, 115.7, 115.2, 112.5,
68.3, 61.0, 52.6, 30.6, 24.7, 14.6.

Phthalonitrile 6 was synthesized from 4 and 4-bromo-1, 2-dicyanobenzene by the same procedure of 5.

6: Yield 77%. 1H NMR (CDCl3, 400.13MHz): δ(ppm) = 7.87-7.96 (4H, m, ArH), 7.51 (2H, d, J = 8.0 Hz, ArH), 7.41 (2H, t, J = 6.8 Hz, ArH), 7.34 (1H, t, J = 7.4 Hz, ArH), 7.19 (1H, d, J = 8.0 Hz, ArH), 7.16 (1H, s, ArH), 5.27 (2H, s, -CH2-), 3.93 (3H, s, -CH3).

13C NMR (CDCl3, 100.61MHz): δ (ppm) = 166.4, 159.1, 145.7, 142.1, 136.5, 134.5, 133.3, 132.6, 132.0, 129.1, 128.5, 127.3, 122.4, 120.0, 117.1, 115.7, 115.6, 115.3, 113.3, 71.5, 52.7.

Unsymmetrical ZnPcs PcS25 and PcS26

PcS25: A mixture of 3,4-bis(2,6-diphenylphenylo)- 1,2-dicyanobenzene (100 mg, 0.17 mmol), 5 (17 mg, 42.8 μmol), Zn(CH3COO)2 (12 mg, 64.2 μmol) in 1.5 mL N,N-dimethylaminoethanol (DMAE) was heated at 150 °C with stirring for 24 h. After the mixture was cooled, the solvent was removed and washed with methanol several time to remove excess Zn ion. The residue was purified by column chromatography on activated alumina by eluting with CH2Cl2 and recycling preparative HPLC to give unsymmetrical ZnPc having a 2-(dimethylamino)ethoxy ester. Yield: 9 mg (9 %). MALDI-TOF Ms (dithranol): m/z 2405.212 (M+H), Calcd for C159H116N10O11Zn: m/z 2404.82.

An aqueous solution of NaOH (3.0 M, 0.1 mL) was added to the solution of unsymmetrical ZnPc (9 mg, 3.7 μmol) in THF (1 mL). The mixture was stirred at 70 °C for 24 h. The solvent was removed in vacuo and the residue was dissolved in water (10 mL). The aqueous solution was refuxed for 1 h. The resulting green solution was filtered and neutralized with acetic acid. The precipitate was collected by filtration and dried in vacuo. Yield: 8 mg (89%). UV-Vis in THF (log ε / M⁻¹ cm⁻¹): 685 (5.05), 357 (4.59). 1H NMR (CDCl3, 400.13MHz): δ (ppm) = 13.4 (br, 1H, COOH), 9.3 (6H, br, Pc-H), 7.4-8.1 (48H, br, Pc-H and ArH), 6.8-7.2 (36H, m, ArH), 4.5 (2H, br, -CH2-), 2.6 (2H, br, -CH2-), 2.2 (2H, br, -CH2-). MALDI-TOF Ms (dithranol): m/z 2262.960 (M+H), Calcd for C151H98N8O11Zn: m/z 2263.67.

ZnPcs PcS26 was synthesized following the same procedure of PcS25.

PcS26: Yield: 8 %. UV-Vis in toluene (log ε / M⁻¹ cm⁻¹): 684 (5.01), 359 (4.67). 1H NMR (CDCl3, 400.13MHz): δ (ppm) = 13.4 (br, 1H, COOH), 9.3-9.5 (6H, br, Pc-H), 7.6-8.0 (53H, br, Pc-H and ArH), 6.8-7.0 (36H, m, ArH), 5.4 (2H, br, -CH2-), MALDI-
TOF Ms (dithranol): \( m/z \) 2265.987 (M+H), Calcd for C\(_{154}\)H\(_{98}\)N\(_{8}\)O\(_{9}\)Zn: \( m/z \) 2266.67.

**Fabrication and measurements for DSSCs using PcS25 and 26:** Double layered nanoporous TiO\(_2\) electrodes were prepared by applying pastes of TiO\(_2\) nanoparticles having two different diameters of 15-20 and 400 nm onto the transparent conducting glass substrates (SnO\(_2\):F, on 1.8 mm thick glass substrate, Asahi Glass) with the screen printing technique, and the electrodes were sintered at 550 °C for 30 min in air. TiCl\(_4\) treatment was applied to obtain high efficiency. The apparent surface area of the TiO\(_2\) electrode was 0.25 cm\(^2\) (0.5 x 0.5 cm). The TiO\(_2\) pastes for screen printing were supplied from Sumitomo Osaka Cement Co., Ltd. The TiO\(_2\) electrodes for iodide/triiodide redox electrolyte-based cells comprise a 12 μm thickness TiO\(_2\) transparent layer (particle size 20 nm) and a 6 μm thickness TiO\(_2\) scattering layer (particle size 400 nm). The TiO\(_2\) electrodes used for Co(bpy)\(_3^{2+/3+}\)-based redox electrolyte comprise a 9 μm thickness TiO\(_2\) transparent layer and a 4 μm thickness TiO\(_2\) scattering layer. A black mask (0.16 cm\(^2\)) was applied on the cell to reduce diffusive light. The adsorption of ZnPcs PcS25 and PcS26 to nanocrystalline TiO\(_2\) films was achieved by immersion of the performed metal oxide electrodes in 0.05 mM THF solutions of the dyes for 48 hr at 25 °C. The dye-adsorbed TiO\(_2\) electrodes were washed with THF to remove the physically adsorbed dye completely before measurements. Working and Pt counter electrodes were separated by a 50 μm thick hot melt ring (Surlyn, DuPont) and sealed by heating. Redox electrolytes (0.1 M LiI, 0.6 M 1,2-dimethyl-3-propylimidazolium iodide, 0.5 M 4-tert-butylpyridine, and 0.05 M I\(_2\) in dehydrated acetonitrile or 0.2 M [Co\(^{II}\)(bpy)\(_3\)](B(CN)\(_4\))\(_2\), 0.02M [Co\(^{III}\)(bpy)\(_3\)](B(CN)\(_4\))\(_3\), 0.5M TBP, and 0.1M LiClO\(_4\) in dehydrated acetonitrile.) were introduced into the space between the dye-adsorbed TiO\(_2\) electrode and the counter electrode, and then measured the photovoltaic performance under one sun conditions (AM 1.5, 100 mW/cm\(^2\)) by a solar simulator (YSS-100, Yamashita Denso).
Fig. S1. \(J-V\) curves (left) obtained with DSSCs based on \textbf{PcS25} (blue) and \textbf{PcS26} (red) with \(\text{Co(bpy)}_3^{2+/3+}\)-based redox electrolyte under a standard global AM 1.5 solar condition (solid line) and dark current (dotted line). IPCE spectra (right) for DSSCs based on \textbf{PcS25} (blue) and \textbf{PcS26} (red). The photoanode used for \(\text{Co(bpy)}_3^{2+/3+}\)-based redox electrolyte consists of thin TiO\(_2\) electrodes comprising a 4.9 \(\mu\)m mesoporous TiO\(_2\) layer.