Supporting information

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

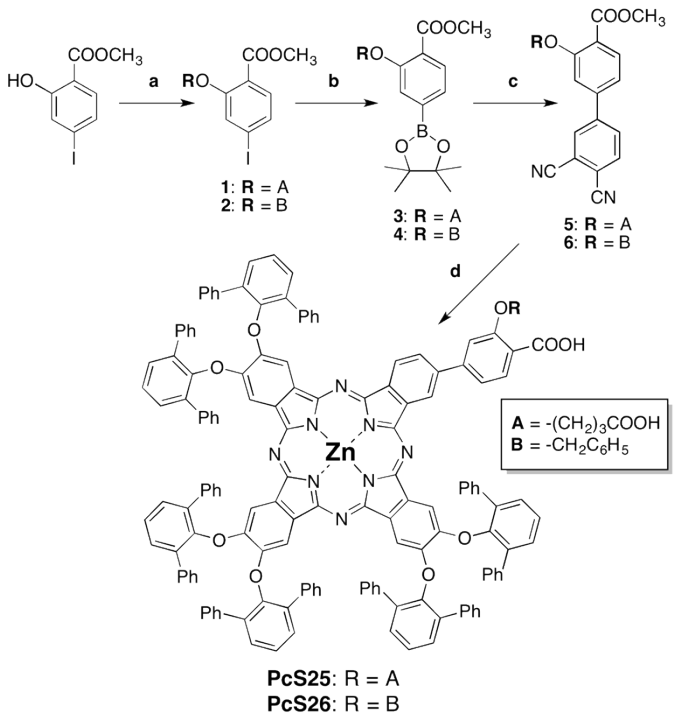
Mutsumi Kimura, Yuki Tohata, Takuro Ikeuchi, and Shogo Mori*

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^{o}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]

a) H. N. Tsao, C. Yi, T. Moehl, j. –H. Yum, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Grätzel, *ChemSusChem*, 2011, **4**, 591.



Scheme S1. Synthetic route of **PcS25** and **PcS26**.
Regents and conditions: **a**) K_2CO_3, **R**-Br, DMF, 80°C, **b**) $(Bpin)_2$, KOAc, $(PPh_3)_2PdCl_2$, *p*-dioxane 130°C, **c**) 3-bromo-1,2-dicyanobenzene, $Pd(PPh_3)_4$, toluene/2M K_2CO_3 aq, 80°C, **d**) 3,4-bis(2,6-diphenylphenoxy)-1,2-dicyanobenzene, $Zn(CH_3COO)_2$, DMAE, 150°C, and NaOH aq/THF 70°C.

Synthesis

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

[b]H. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gándara, A. C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O'Keefe, O. terasaki, J. F. Stoddart, O. M. Yaghi, *Science*, 2012, **336**, 1018.

[c]M. Kimura, H. Nomoto, H. Suzuki, T. Ikeuchi, H. Matsuzaki, T. N. Murakami, A. Furube, N. Masaki, M. J. Griffith, S. Mori, *Chem. Eur. J.*, 2013, **19**, 7496.

[d]S. Mori, M. Nagata, Y. Nakahata, K. Yasuta, R. Goto, M. Kimura, M. Taya, *J. Am. Chem. Soc.*, 2010, **132**, 4054.

1: K_2CO_3 (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 $MgSO_4$, the organic layer was

evaporated to give white solid. The product was purified by column chromatography on silica gel by eluting with CH_2Cl_2. Yield: 0.26g (93%). ^{1}H NMR ($CDCl_3$, 400.13MHz): δ (ppm) = 7.48 (1H, d, J = 8.0 Hz, Ar*H*), 7.32 (1H, d, J = 8.0 Hz, Ar*H*), 7.29 (1H, s, Ar*H*), 4.04-4.18 (4H, m, -CH_2-), 3.88 (3H, s, -CH_3), 2.55-2.63 (2H, m, -CH_2-), 2.12-2.16 (2H, m, -CH_2-), 1.35 (12H, s, -CH_3), 1.24-1.30 (5H, m, -CH_2-, -CH_3). ^{13}C NMR ($CDCl_3$, 100.61MHz): δ (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 $(PPh_3)_2PdCl_2$ (9 mg, 12.8 μmol) under an Ar atmosphere. Dry *p*-dioxane (4 ml) was added to the reaction vessel, and the mixture was refluxed at 130 ^{o}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 amd 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_2Cl_2. Yield: 0.25g (96%). ^{1}H NMR ($CDCl_3$, 400.13MHz): δ (ppm) = 7.75 (1H, d, J = 7.6 Hz, Ar*H*), 7.40 (1H, d, J = 7.6 Hz, Ar*H*), 7.39 (1H, s, Ar*H*), 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): δ (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 μmol) 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_2O 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_2O and diethylether. The crude product was purified using column chromatography on silica gel by eluting with CH_2Cl_2 and preparative HPLC. Yield: 0.14g (61%). ^{1}H NMR ($CDCl_3$, 400.13MHz): □ (ppm) = 8.06 (1H, s, Ar*H*), 7.88-7.96 (3H, m, Ar*H*), 7.17-7.20 (2H, m, Ar*H*), 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): □ (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%. ^{1}H NMR ($CDCl_3$, 400.13MHz): δ (ppm) = 7.87-7.96 (4H, m, Ar*H*), 7.51 (2H, d, *J* = 8.0 Hz, Ar*H*), 7.41 (2H, t, *J* = 6.8 Hz, Ar*H*), 7.34 (1H, t, *J* = 7.4 Hz, Ar*H*), 7.19 (1H, d, *J* = 8.0 Hz, Ar*H*), 7.16 (1H, s, Ar*H*), 5.27 (2H, s, -CH_2-), 3.93 (3H, s, -CH_3). ^{13}C NMR ($CDCl_3$, 100.61MHz): □ (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-diphenylphenoy)- 1,2-dicyanobenzene (100 mg, 0.17 mmol)**, 5** (17 mg, 42.8 μmol), $Zn(CH_3COO)_2$ (12 mg, 64.2 μmol) in 1.5 mL *N,N*-dimethylaminoethanol (DMAE) was heated at 150 ^{o}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 CH_2Cl_2 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 $C_{159}H_{116}N_{10}O_{11}Zn$: *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 ^{o}C for 24 h. The solvent was removed in vacuo and the residue was dissolved in water (10 mL). The aqueous solution was refluxed 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). ^{1}H NMR ($CDCl_3$, 400.13MHz): δ (ppm) = 13.4 (br, 1H, COO*H*), 9.3 (6H, br, Pc-*H*), 7.4-8.1 (48H, br, Pc-*H* and Ar*H*), 6.8-7.2 (36H, m, Ar*H*), 4.5 (2H, br, -CH_2-), 2.6 (2H, br, -CH_2-), 2.2 (2H, br, -CH_2-). MALDI-TOF Ms (dithranol): *m/z* 2262.960 (M+H), Calcd for $C_{151}H_{98}N_8O_{11}Zn$: *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). ^{1}H NMR ($CDCl_3$, 400.13MHz): δ (ppm) = 13.4 (br, 1H, COO*H*), 9.3-9.5 (6H, br, Pc-*H*), 7.6-8.0 (53H, br, Pc-*H* and Ar*H*), 6.8-7.0 (36H, m, Ar*H*), 5.4 (2H, br, -CH_2-), MALDI-

TOF Ms (dithranol): *m/z* 2265.987 (M+H), Calcd for $C_{154}H_{98}N_8O_9Zn$: *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 ^oC 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 400nm). 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 ^oC. 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).

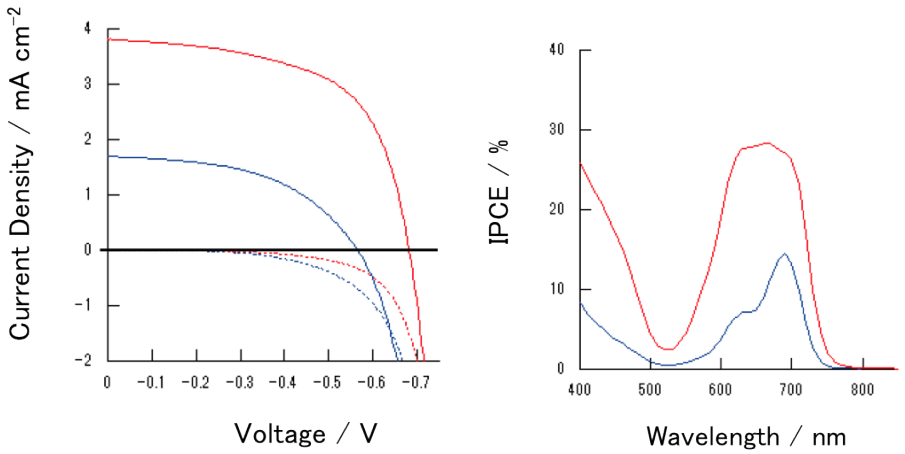


Fig. S1. *J-V* curves (left) obtained with DSSCs based on **PcS25** (blue) and **PcS26** (red) with $Co(bpy)_3^{2+/3+}$-based redox electrolyte under a standard global AM 1.5 solar condition (solid line) and dark current (dotted line). IPCE spectra (right) for DSSCs based on **PcS25** (blue) and **PcS26** (red). The photoanode used for $Co(bpy)_3^{2+/3+}$-based redox electrolyte consists of thin TiO_2 electrodes comprising a 4.9 μm mesoporous TiO_2 layer.