Novel Unsymmetrically π-Elongated Porphyrin for Dye-Sensitized TiO_2 Cells

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General Procedure. All commercial reagents and solvents were used without further purification. ^{1}H NMR spectra were recorded on a JEOL EX270 KS and JEOL AL 300 NMR spectrometer. UV-visible absorption spectra of the porphyrins in CH_2Cl_2 and of the porphyrin monolayers on TiO_2 electrodes were recorded using a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer. Steady-state fluorescence spectra were acquired by a SPEX Fluoromax-3 spectrofluorometer. Spectroscopy grade CH_2Cl_2 was used for the measurements of UV-visible absorption and fluorescence spectra. Electrochemical measurements were made using an ALS 630a electrochemical analyzer. Redox potentials were determined in dichloromethane containing 0.1M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) at a scan rate of 0.1 V s^{-1}. A glassy carbon working electrode, Ag/$AgNO_3$ reference electrode, and Pt wire counter electrode were employed. Ferrocene (0.64 V vs NHE, for **Zn-1**) and decamethylferrocene (0.15 V vs NHE, for **fused-Zn-1**) were used as internal standards. Dichloromethane was purified just before use and Bu_4NPF_6 was recrystallized from methanol. MALDI-TOF mass spectra were measured with COMPACT MALDI II (SHIMAZU) mass spectrometer. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-HX 110A spectrometer.

Synthesis of Porphyrin Derivatives.

5-(4-Carbomethoxynaphth-1-yl)-10,15,20-tris(2,4,6-trimethylphenyl)porphyrin (H_2-1): To a solution of (2,4,6-trimethylphenyl)dipyrromethane (1.8 g, 6.8 mmol),[1] 4-carbomethoxynaphtaldehyde (720 mg, 3.4 mmol),[2] and 2,4,6-trimethylbenzaldehyde (503 mg, 3.4 mmol) in $CHCl_3$ (800 mL) was added BF_3OEt_2 (128 mg, 0.9 mmol). The solution was stirred at room temperature in dark for 2 h. Then, DDQ (681 mg, 3.0 mmol) was added and stirred at room temperature for 1 h. The solvent was evaporated and the product was isolated by column chromatography on silica gel (CH_2Cl_2 / hexane = 1 / 1 as an eluent): **H_2-1**; purple solid (264 mg, 0.31 mmol, 9%); δ_H (400 MHz; $CDCl_3$; Me_4Si) -2.43 (s, 2H, NH), 1.88 (s, 18 H, mesityl CH_3), 2.61 (s, 9 H, mesityl CH_3), 4.20 (s, 3 H, -COOMe), 7.13 (t, 1 H), 7.29 (s, 4 H), 7.61 (t, 1 H), 8.29 (d, 1 H), 8.43 (d, 1 H), 8.52 (d, 1 H), 8.58 (d, 1 H), 8.65 (m, 4 H), 9.17 (d, 1 H); MALDI-TOF MS: calcd for 848.41 ($C_{59}H_{52}N_4O_2$); found 848.46 (M^+).

5-(4-Carbomethoxynaphth-1-yl)-10,15,20-tris(2,4,6-trimethylphenyl)-porphyrinatonickel(II) (Ni-1): To a solution of **H_2-1** (200 mg, 0.24 mmol) in toluene was added Ni(acac)$_2$ (1.8 g). The solution was refluxed for 2 days. After the mixture was filtered, the solvent was evaporated. The mixture was extracted with CH_2Cl_2 and washed by H_2O. The organic layer was dried over Na_2SO_4 and concentrated. The product was isolated by column chromatography on silica gel (CH_2Cl_2 / hexane = 1 / 1 as an eluent): **Ni-1**; purple solid (174 mg, 0.19 mmol, 82%); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.74 (s, 6 H, mesityl CH_3), 1.89 (s, 12 H, mesityl CH_3), 2.55 (s, 9 H, mesityl CH_3), 4.16 (s, 3 H, -COOMe), 7.13-7.22 (m, 8 H), 8.59 (t, 1 H), 8.19 (d, 1 H), 8.36 (d, 2 H), 8.45-8.49 (m, 3 H), 8.55 (s, 4 H), 9.11 (d, 1 H); MALDI-TOF MS: calcd for 904.33 ($C_{59}H_{50}N_4NiO_2$); found 904.34 (M^+).

Fused-H_2-1: To a solution of **Ni-1** (170 mg, 0.19 mmol) in CH_2Cl_2 (20 mL) was added a solution of $FeCl_3$ (600 mg, 3.8 mmol) in nitromethane (10 mL). The solution was refluxed for 12 h. The reaction was quenched by addition of a saturated $NaHCO_3$ solution. The resulting mixture was extracted with CH_2Cl_2 and the organic layer was dried over Na_2SO_4. After the solvent was evaporated, the crude product was dissolved in a TFA (5.4 mL) / H_2SO_4 (0.9 mL) mixture and stirred at room temperature for 2 h. The mixture was poured to saturated $NaHCO_3$ solution and extracted by CH_2Cl_2. The organic layer was dried over Na_2SO_4 and solvent was evaporated. The product (**fused-H_2-1**) was isolated by column chromatography on silica gel (CH_2Cl_2 / hexane = 1 / 1 as an eluent): **fused-H_2-1**; green solid (25 mg, 0.03 mmol, 16%); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.90 (s, 6 H, mesityl CH_3), 1.93 (s, 6 H, mesityl CH_3), 2.60 (s, 3 H, mesityl CH_3), 2.64 (s, 3 H, mesityl CH_3), 2.67 (s, 3 H, mesityl CH_3), 4.15 (s, 3 H, -COOMe), 7.24 (s, 2 H, mesityl CH), 7.29 (s, 2 H, mesityl CH), 7.32 (s, 2 H, mesityl CH), 7.96 (dd, 1 H, naphthyl CH), 8.45, 8.46, 8.48, 8.62 ~ 8.72 (m, 3 H), 8.80 (d, 1 H), 9.04 (s, 1 H, β-porphyrin), 9.14 (d, 1 H), 9.25 (d, 2 H); MALDI-TOF MS: calcd for 846.39 ($C_{59}H_{50}N_4O_2$); found 846.42 (M+).

Fused-Zn-1: To a solution of **fused-H_2-1** (25 mg, 0.03 mmol) in THF (20 mL) / EtOH (20 mL) was added a solution of KOH (1 g) in H_2O (5 mL). The solution was refluxed for 2 h. After the reaction mixture was cooled to room temperature, 35% aqueous HCl (5 mL) was added. The mixture was extracted with CH_2Cl_2 and washed with saturated $NaHCO_3$ and H_2O. The organic layer was dried over Na_2SO_4, and then the solvent was removed. The hydrolyzed porphyrin was isolated by column chromatography on silica gel (CH_2Cl_2 / MeOH = 4 / 1 as an eluent). The hydrolyzed porphyrin in $CHCl_3$ (50 mL) was added a solution of $Zn(OAc)_2$ (250 mg) in MeOH (5 mL). The mixture was stirred at room temperature for 3 h. The reaction mixture was washed with H_2O, and organic layer was dried over Na_2SO_4. After the solvent was evaporated, the product was purified by column chromatography on silica gel (CH_2Cl_2 / MeOH = 4 / 1 as an eluent): **fused-Zn-1**; green solid (21 mg, 0.023 mmol, 77%); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.86-1.90 (m, 18 H, mesityl CH_3), 2.59-2.65 (m, 9 H, mesityl CH_3), 7.22-7.29 (br, 6 H, mesityl CH), 7.92 (t, 1 H, naphtyl CH), 8.52 (d, 4 H, β-porphyrin), 8.60 (d, 1 H), 8.72-8.77 (m, 2 H), 8.83 (d, 1 H), 9.60 (s, 1 H, β-porphyrin), 9.20-9.28 (m, 5 H, β-porphyrin and naphtyl CH); λ_{max} (CH_2Cl_2) / nm 482 (ε/dm^3 mol^{-1} cm^{-1} 124200), 682 (24600); HRMS (FAB, positive mode): calcd for 894.2912 ($C_{58}H_{46}N_4O_2Zn$); found 894.2939 (M^+).

5-(4-Carboxynaphth-1-yl)-10,15,20-tris(2,4,6-trimethylphenyl)porphyrinatozinc(II) (Zn-1): To a solution of **H_2-1** (60 mg, 0.071 mmol) in THF (20 mL) / EtOH (20 mL) was added a solution of KOH (1 g) in H_2O (5 mL). The solution was refluxed for 2 h. After the reaction mixture was cooled to room temperature, 35% aqueous HCl (5 mL) was added. The mixture was extracted with CH_2Cl_2 and washed with saturated $NaHCO_3$ and H_2O. The organic layer was dried over Na_2SO_4, and then the solvent was removed. The hydrolyzed porphyrin was isolated by column chromatography on silica gel (CH_2Cl_2 / MeOH = 4 / 1 as an eluent). To a solution of the hydrolyzed porphyrin (58 mg, 0.069 mmol) in $CHCl_3$ (50 mL) was added a solution of $Zn(OAc)_2$ (250 mg) in MeOH (5 mL). The mixture was stirred at room temperature for 3 h. The reaction mixture was washed with H_2O, and organic layer was dried over Na_2SO_4. After the solvent was evaporated, the product was purified by column chromatography on silica gel (CH_2Cl_2 / MeOH = 4 / 1 as an eluent): **Zn-1**; purple solid (58 mg, 0.065 mmol, 94%); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.79 (s, 6 H, mesityl CH_3), 1.81 (s, 3 H, mesityl CH_3), 1.85 (s, 6 H, mesityl CH_3), 1.88 (s, 3 H, mesityl CH_3), 2.58 (s, 6 H, mesityl CH_3), 2.60 (s, 3 H, mesityl CH_3), 7.09 (t, 1 H, naphtyl CH), 7.22 (s, 4 H, mesityl CH), 7.25 (s, 2 H, mesityl CH), 7.58 (t, 1 H, naphthyl CH), 8.32 (d, 1 H, naphtyl CH), 8.47 (d, 2 H, β-porphyrin), 8.62 (d, 2 H, β-porphyrin), 8.67-8.70 (m, 5 H, β-porphyrin and naphtyl CH), 9.25 (d, 2 H, naphtyl CH); λ_{max} (CH_2Cl_2) / nm 422 (ε/dm^3 mol^{-1} cm^{-1} 433000), 551 (20700); HRMS (FAB, positive mode): calcd for 896.3069 ($C_{58}H_{46}N_4O_2Zn$); found 896.3088 (M^+).

Density Functional Theory (DFT) Calculations. Geometry optimization and electronic structure calculations of the porphyrins were performed using B3LYP functional and 3-21G* basis set implemented in the Gaussian 03 program package. Molecular orbitals were visualized by Molstudio 3.0 software.

Preparation of Porphyrin-Modified TiO_2 Electrode. Nanoporous TiO_2 films were prepared from colloidal suspension of TiO_2 nanoparticles (P25, Nippon Aerogel) dispersed in deionized water and Triton X-100. The suspension was deposited on a transparent conducting glass (Asahi Glass, SnO_2: F, 9.4 ohm/sq) by using doctor blade technique. The films were annealed at 673 K for 10 min, followed by similar deposition and annealing (723 K, 2 h) for the 10-μm-thick TiO_2 films. The thickness of the films was determined using surface roughness/profile measuring instrument (SURFCOM 130A, ACCRETECH). The TiO_2 electrodes were immersed into each of the 0.2 mM methanol solution of the porphyrins at room temperature. After dye adsorption, the dye-coated electrodes were copiously rinsed with methanol. The amounts of the porphyrins adsorbed on the TiO_2 films were determined by measuring absorbance at the Soret band of the dye molecules that were dissolved from the dye-adsorbed TiO_2 films into DMF containing 0.1 M NaOH.

Photovoltaic Measurements. The photovoltaic measurements were performed in a sandwich cell consisting of the porphyrin-sensitized TiO_2 electrode as the working electrode and a platinum-coated conducting glass as the counter electrode. The two electrodes were placed on top of each other using a thin transparent film of Surlyn polymer (Dupont) as a spacer to form the electrolyte space. A thin layer of electrolyte (0.1 M LiI, 0.05 M I_2, 0.6 M 2,3-dimethyl-1-propylimidazolium iodide, and 0.5 M 4-*t*-butylpyridine in acetonitrile) was introduced into the interelectrode space. The IPCE values and photocurrent-voltage characteristics were determined by using a potentiostat (Bunko–Keiki Co., Ltd., Model HCSSP-25) irradiated with simulated AM 1.5 solar light (100 mW cm^{-2}, Bunko–Keiki Co., Ltd., Model CEP-2000). All the experimental values were given as an average from six independent measurements.

References

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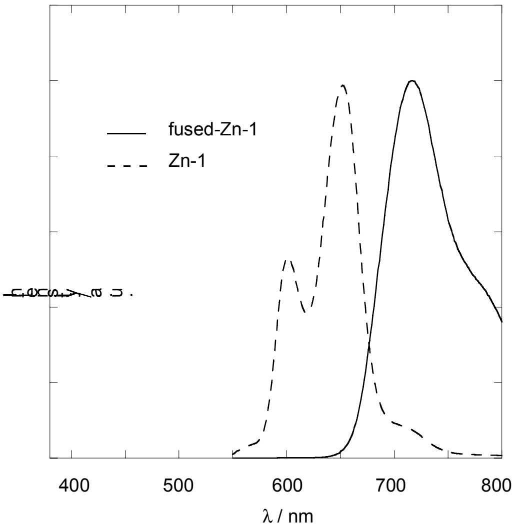
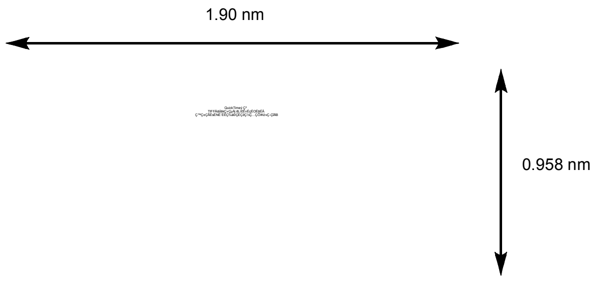
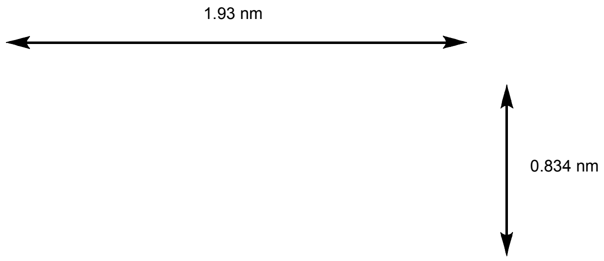


Fig. S1. Fluorescence spectra of **fused-Zn-1** (solid line) and **Zn-1** (dotted line) in CH_2Cl_2 solution excited at the peak position of the Soret band.



fused-Zn-1 side view

fused-Zn-1 top view



Zn-1 side view

Zn-1 top view

Fig. S2. Molecular structures of **fused-Zn-1** and **Zn-1** calculated at B3LYP/3-21G* level.

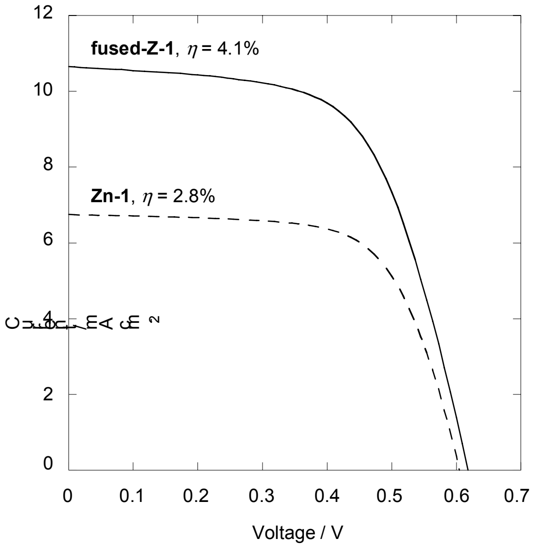


Fig. S3. Current-voltage characteristics of the **fused-Zn-1** (solid line) and **Zn-1** (dotted line)-sensitized cells. Conditions: Electrolyte: 0.1M LiI, 0.05M I_2, 0.5M 4-*t*-butylpyridine, and 0.6M 2,3-dimethyl-1-propylimidazolium iodide, in CH_3CN; Input power: AM1.5 under simulated solar light (100 mW cm^{-2}).

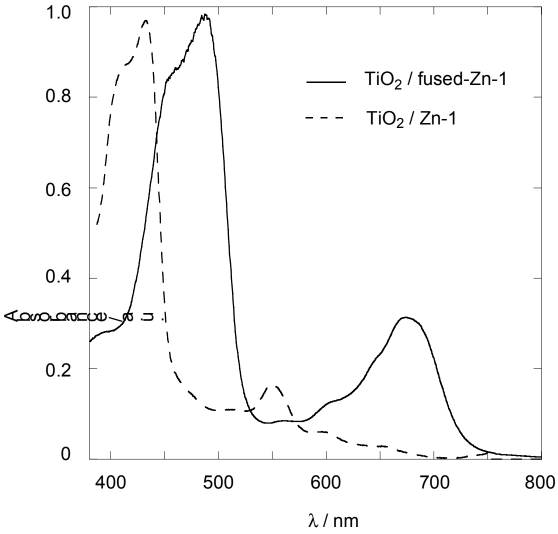


Fig. S4. UV-visible absorption spectra of **fused-Zn-1** (solid line) and **Zn-1** (dotted line) on TiO_2 electrodes. Thickness of the TiO_2 electrodes were adjusted to be 700-1000 nm to obtain the shape and peak position of the spectra accurately. The spectra are normalized at the Soret band for comparison.

Table S1. Optical and Electrochemical Data for Porphyrins.

	absorption[a] λ_{max} / nm	emission[b] λ_{max} / nm	E_{0-0}[c] / eV	E_{ox}[d] / V vs NHE	E_{ox}* /V
Zn-1	551	601	2.15	1.04	-1.11
Fused-Zn-1	682	716	1.77	0.99	-0.78

[a] In CH_2Cl_2. [b] By exciting at the peak position of the Soret band in CH_2Cl_2. [c] Determined from the intercept of the absorption and the emission spectra. [d] In CH_2Cl_2 containing 0.1 M Bu_4NPF_6; Pt wire working electrode, Ag/$AgNO_3$ reference electrode, Pt counter electrode; ferrocene (0.64 V vs NHE for **Zn-1**) and decamethylferrocene (0.15 V vs NHE for **fused-Zn-1**) were used as internal standards.