

Supporting Information for

Quinoxaline-Fused Porphyrins for Dye-Sensitized Solar Cells

Seunghun Eu,[†] Shinya Hayashi,[†] Tomokazu Umeyama,[†] Yoshihiro Matano,[†] Yasuyuki Araki,[‡] and Hiroshi Imahori^{*,†,%,#}

[†]*Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan*

[‡]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai, 980-8577, Japan*

[%]*Institute for Integrated Cell-Material Sciences, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan*

[#]*Fukui Institute for Fundamental Chemistry, Kyoto University, 34-4, Takano-Nishihiraki-cho, Sakyo-ku, Kyoto 606-8103, Japan*

E-mail: imahori@scl.kyoto-u.ac.jp

General

All solvents and chemicals were of reagent grade quality, purchased, and used without further purification unless otherwise noted. All of the reactions were carried out under nitrogen atmosphere in the dark. Column chromatography and thin-layer chromatography (TLC) were performed with UltraPure Silica Gel (230-400 mesh, SiliCycle) and Silica gel 60 F₂₅₄ (Merck), respectively. ¹H-NMR spectra were measured on a JEOL EX-400 (400 MHz) or a JEOL AL300 (300 MHz) spectrometer. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were made on a Shimadzu KOMPACT MALDI II using CHCA as a matrix. UV-vis absorption spectra were measured using a Perkin-Elmer Lambda 900 UV/VIS/NIR Spectrometer with a spectroscopy grade methanol. FT-IR spectra were acquired using by a JASCO FT/IR-470 plus spectrometer with a KBr pellet.

5,10,15,20-Tetrakis(2,4,6-trimethylphenyl)porphyrin (1),

5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrinatocopper (II) (2),

5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrinatozinc (II) (ZnP), methyl

3,4-diaminobenzoate, and dimethyl 4,5-diaminophthalate were prepared according to the

known procedures.ⁱ

Electrochemical measurements were made using a BAS 50W electrochemical workstation. Redox potentials in solution were determined by differential pulse voltammetry (DPV) as well as cyclic voltammetry (CV) in dichloromethane containing 0.1M tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. A glassy carbon working electrode (3 mm diameter), Ag/AgNO₃ reference electrode, and Pt wire counter electrode were employed. Ferrocene/ferrocenium (+0.642 V vs NHE) was used as an internal standard for all measurements. For DPV measurements, scan rate of 50 mV s⁻¹, pulse amplitude of 50 mV, pulse width of 50 ms, and pulse period of 200 ms were employed, whereas scan rate of 100 mV s⁻¹ was used for CV measurements. Oxidation potentials for the adsorbed porphyrins on the TiO₂ films were measured by cyclic voltammetry in acetonitrile containing 0.1M TBAP at a scan rate of 100 mV s⁻¹. Porphyrin-modified TiO₂ was employed as a working electrode along with the Ag/AgCl reference electrode (+0.197 V vs NHE) and Pt wire counter electrode. All of the measured potentials were quoted with reference to NHE.

Synthesis

2-Nitro-5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrinatocopper (II) (3).

This procedure was based upon the literature protocol for similar compound.ⁱⁱ To a solution of **2** (1.69 g, 2.0 mmol) in chloroform (1.3 L) was added a solution of copper nitrate trihydrate (1.19 g, 4.9 mmol) in a mixed solution of acetic anhydride (160 mL) and acetic acid (30 mL). The reaction mixture was stirred at 35 ~ 40 °C for 2 h until the reactant was not detected by silica TLC (hexane/CH₂Cl₂ = 3:1). After cooling to room temperature, the reaction mixture was treated with Na₂CO₃ and washed with water, subsequently dried over anhydrous magnesium sulfate and then concentrated in vacuo. Purification by silica column chromatography (hexane/CH₂Cl₂ = 3:1), and subsequently reprecipitation from CH₂Cl₂/methanol afforded **3** as a deep red solid (1.3 g, 1.5 mmol, 73 % yield). UV-vis (CH₂Cl₂) λ_{max} (nm) 419.20, 544.81, 585.14 (lit.^{1b} 420, 546, 584); FT-IR (KBr) ν_{max} 3422, 2916, 1610, 1527 (NO₂), 1450, 1375, 1334, 999, 803 cm⁻¹; MS (MALDI-TOF) m/z 888.2 (M+H⁺).

2-Nitro-5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrin (4). This procedure

was based upon the literature protocol for similar compound.ⁱⁱⁱ To a vigorously stirred

solution of **3** (1.20 g, 1.35 mmol) in trifluoroacetic acid (91 mL) was added a concentrated sulfuric acid (98%, 20 mL). After 2.5 h of stirring, the reaction mixture was neutralized with saturated aqueous NaHCO₃ and extracted with chloroform. The extract was washed with water, dried over anhydrous magnesium sulfate, and concentrated in vacuo. Purification by silica column chromatography (hexane/CH₂Cl₂ = 3:1 ~ 2:1), and subsequently reprecipitation from CH₂Cl₂/hexane afforded **4** as a brownish violet solid (793 mg, 0.96 mmol, 71 % yield). ¹H NMR (300 MHz, CDCl₃) δ 8.84-8.53 (m, 7H, β-pyrrolic H), 7.27 (s, 6H, phenyl H), 7.17 (s, 2H, phenyl H), 2.62-2.58 (m, 12H, methyl H), 1.89-1.84 (m, 24H, methyl H), -2.48 (s, 2H, inner H); FT-IR (KBr) ν_{max} 3329, 2917, 1611, 1529 (NO₂), 1473, 1376, 1341, 983, 968, 851, 802 cm⁻¹; MS (MALDI-TOF) *m/z* 829.4 (M+H⁺).

2-Amino-5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrin (5). This procedure was based upon the literature protocol for similar compound.^{iv} All glassware used was oven dried at 100 °C for 2 h and cooled by the stream of nitrogen. Two-neck round-bottomed flask was charged with **4** (562 mg, 0.679 mmol), dry dichloromethane (120 mL), and dry methanol (30 mL). Palladium (10% on carbon, 590 mg) was added to

the solution and the flask was shielded from light. The solution was purged with nitrogen and stirred at room temperature for 1 h, and placed into the ice-bath. Sodium borohydride (640 mg, 16.9 mmol) was added to the solution in small portions over a 10 min period. Progress of the reaction was monitored by silica TLC (hexane/CH₂Cl₂ = 1:1), where the reactant (**4**) moved slightly faster than the amino product (**5**) on the plate, as described in the literature for similar compound.^{1b} The reactant seemed to be completely consumed after 1.2 h of the reaction. Solvent was removed by using rotary evaporator, and the residue was passed through a plug of Celite using dichloromethane as eluent in the dark. The crude product was concentrated in vacuo, and was directly used for the next reaction without further purification due to the unstability against photo-oxidation.^v (499 mg, 0.63 mmol, 92.0 % yield). MS (MALDI-TOF) *m/z* 799.2 (M+H⁺).

2,3-Dioxo-5,10,15,20-tetrakis(2,4,6-trimethylphenyl)chlorin (6). This procedure was based upon the literature protocol for similar compound.^{vi} To a solution of **5** (430 mg, 0.54 mmol) in a dichloromethane (140 mL) was added a Dess-martin periodinane (250 mg, 0.59 mmol). Progress of the reaction was monitored by mass spectrometry

(MALDI) due to the reactant and product showed indistinguishable color and R_f values on silica TLC (hexane:CH₂Cl₂ = various ratios).^{vii} The reaction mixture was stirred for 30 h in the dark. Hydrochloric acid (1.0 M, 90 mL) was added to the solution and stirred for 1 h to hydrolyze undesirable imine products. The reaction mixture was treated with saturated aqueous NaHCO₃ and washed with water. Organic layer was collected, dried over anhydrous magnesium sulfate, and then the solvent was removed in vacuo. Column chromatography on silica gel (hexane/CH₂Cl₂ = 3:2 ~ 1:1) afforded **6** as a greenish brown solid. (163 mg, 0.2 mmol, 37 % yield). Unstable product was directly employed for the next reaction. MS (MALDI-TOF) m/z 812.6 (M+H⁺).

5,10,15,20-Tetrakis(2,4,6-trimethylphenyl)-6'-methoxycarbonylquinoxalino[2,3- β]p

orphyrin (7a). This procedure was based upon the literature protocol for similar compound.^{viii} Methyl 3,4-diaminobenzoate (27 mg, 0.16 mmol) and **6** (120 mg, 0.15 mmol) were charged into the Schlenk tube. Dry pyridine (3.2 mL) was added and the solution was stirred at 110 °C. Progress of the reaction was monitored by silica TLC (hexane/CH₂Cl₂ = 3:2). Although the reactant seemed to be completely consumed after 1 h, the reaction was made to proceed for 14 h. The reaction mixture was cooled to room

temperature, dissolved in dichloromethane, and separated with brine and water. Collected organic layer was dried over anhydrous sodium sulfate and the solvent was removed in vacuo. Purification by silica column chromatography (hexane/CH₂Cl₂ = 1:1 ~ 2:3), and subsequently reprecipitation from CH₂Cl₂/MeOH gave **7a** as a deep violet solid. (102 mg, 0.11 mmol, 73 % yield). ¹H NMR (400 MHz, CDCl₃) δ 8.85 (d, *J*=4.9 Hz, 2H, β-pyrrolic H), 8.75 (d, *J*=4.9 Hz, 2H, β-pyrrolic H), 8.66 (d, ⁴*J*=2.0 Hz, 1H, quinoxaline H), 8.54 (s, 2H, β-pyrrolic H), 8.36 (dd, *J*=8.8 and 2.0 Hz, quinoxaline H), 7.97 (d, *J*=8.8 Hz, 1H, quinoxaline H), 7.35 (s, 2H, phenyl H), 7.33 (s, 2H, phenyl H), 7.28 (s, 4H, phenyl H), 2.76 (s, 3H, methyl H), 2.75 (s, 3H, methyl H), 2.63 (s, 6H, methyl H), 1.89 (s, 12H, methyl H), 1.75 (s, 12H, methyl H), -2.36 (s, 2H, inner H); FT-IR (KBr) ν_{max} 3348, 2917, 2859, 1728 (ester), 1611, 1437, 1341, 1304, 1254, 1140, 1119, 979, 851, 819, 803, 725 cm⁻¹; MS (MALDI-TOF) *m/z* 942.6 (M+H⁺).

5,10,15,20-Tetrakis(2,4,6-trimethylphenyl)-6'-carboxyquinoxalino[2,3-β]porphyrin

(8a). To a solution of **7a** (100 mg, 0.11 mmol) in 2-propanol (40 mL) was added a solution of potassium hydroxide (0.66 g, 11.8 mmol) in H₂O (10 mL). The solution was refluxed (80 °C) for 2 h. After cooling to room temperature, the reaction mixture was

treated with aqueous HCl (1M, 12 mL) solution. The solution was washed with saturated aqueous NaHCO₃ and water. Organic layer was collected, dried over anhydrous magnesium sulfate, and then the solvent was removed in vacuo. Reprecipitation from CH₂Cl₂/hexane gave **8a** as a deep violet solid (91 mg, 0.098 mmol, 89 %). Mp > 300 °C; ¹H NMR (400 MHz, acetone-d₆) δ 8.76 (d, *J*=4.9 Hz, 2H, β-pyrrolic H), 8.70 (d, *J*=4.9 Hz, 2H, β-pyrrolic H), 8.54 (d, ⁴*J*=2.0 Hz, 1H, quinoxaline H), 8.40 (s, 2H, β-pyrrolic H), 8.33 (dd, *J*=8.8 and 2.0 Hz, quinoxaline H), 7.90 (d, *J*=8.8 Hz, 1H, quinoxaline H), 7.27 (s, 2H, phenyl H), 7.26 (s, 2H, phenyl H), 7.23 (s, 4H, phenyl H), 2.61 (s, 3H, methyl H), 2.60 (s, 3H, methyl H), 2.49 (s, 6H, methyl H), 1.76 (s, 12H, methyl H), 1.65 (s, 6H, methyl H), 1.65 (s, 6H, methyl H), -2.35 (s, 2H, inner H); FT-IR (KBr) ν_{max} 3436, 3350, 2918, 2856, 1736, 1706, 1612, 1446, 1344, 1212, 1141, 1120, 980, 803, 725 cm⁻¹; MS (MALDI-TOF) *m/z* 926.2 (M+H⁺).

5,10,15,20-Tetrakis(2,4,6-trimethylphenyl)-6'-carboxyquinoxalino[2,3-β]porphyrin

atozinc (II) (ZnQMA). To a solution of **8a** (85 mg, 0.091 mmol) in chloroform (148 mL) was added a solution of zinc acetate dihydrate (300 mg, 1.37 mmol) in methanol (25 mL). The solution was stirred at reflux for 18 h. The solvent was removed by using a

rotary evaporator, and the residue dissolved in dichloromethane and passed through the filter paper (ADVANTEC). The filtrate was washed with water, dried over anhydrous sodium sulfate, and then the solvent was removed in vacuo. Reprecipitation from CH₂Cl₂/acetonitrile gave **ZnQMA** as a deep purple solid (57 mg, 0.057 mmol, 63 % yield). ¹H NMR (400 MHz, acetone-d₆ + CD₃OD) δ 8.73 (d, ⁴J=1.4 Hz, 1H, quinoxaline H), 8.70-8.66 (m, 4H, β-pyrrolic H), 8.56 (s, 2H, β-pyrrolic H), 8.46 (dd, J=8.8 and 1.4 Hz, quinoxaline H), 8.07 (d, J=8.8 Hz, 1H, quinoxaline H), 7.36 (s, 2H, phenyl H), 7.35 (s, 2H, phenyl H), 7.32 (s, 4H, phenyl H), 2.72 (s, 6H, methyl H), 2.61 (s, 6H, methyl H), 1.89 (s, 12H, methyl H), 1.78 (s, 6H, methyl H), 1.77 (s, 6H, methyl H); UV-vis (MeOH) λ_{max} (nm) 420.5, 578.0, 621.5; MS (MALDI-TOF) m/z found 991.3(M+H⁺).

5,10,15,20-Tetrakis(2,4,6-trimethylphenyl)-6',7'-bis(methoxycarbonyl)quinoxalino[2,3-β]porphyrin (7b). This procedure was based upon the literature protocol for similar compound.⁷ Dimethyl 4,5-diaminophthalate (37 mg, 0.17 mmol) and **6** (130 mg, 0.16 mg) were charged into the Schlenk tube. Dry pyridine (3.5 mL) was added and the solution was stirred at 110 °C. Progress of the reaction was monitored by silica TLC

(hexane/CH₂Cl₂ = 3:2). Although the reactant seemed to be completely consumed after 1 h, the reaction was made to proceed for 14 h. The reaction mixture was cooled to room temperature, dissolved in dichloromethane, and separated with brine and water. Collected organic layer was dried over anhydrous sodium sulfate and the solvent was removed in vacuo. Purification by silica column chromatography (hexane/CH₂Cl₂ = 3:2 ~ 1:1), and subsequently reprecipitation from CH₂Cl₂/MeOH gave **7b** as a deep violet solid. (130 mg, 0.13 mmol, 81 % yield). ¹H NMR (400 MHz, CDCl₃) δ 8.84 (d, *J*=4.9 Hz, 2H, β-pyrrolic H), 8.75 (d, *J*=4.9 Hz, 2H, β-pyrrolic H), 8.54 (s, 2H, β-pyrrolic H), 8.32 (s, 2H, quinoxaline H), 7.33 (s, 4H, phenyl H), 7.28 (s, 4H, phenyl H), 2.74 (s, 6H, methyl H), 2.63 (s, 6H, methyl H), 1.89 (s, 12H, methyl H), 1.73 (s, 12H, methyl H), -2.37 (s, 2H, inner H); FT-IR (KBr) ν_{max} 3450, 3350, 2949, 2917, 2856, 1735 (ester), 1611, 1437, 1342, 1261, 1215, 1135, 1057, 979, 970, 851, 802, 726, 714 cm⁻¹; MS (MALDI-TOF) *m/z* 999.6 (M+H⁺).

5,10,15,20-Tetrakis(2,4,6-trimethylphenyl)-6',7'-dicarboxyquinoxalino[2,3-β]porphyrin (8b). To a solution of **7b** (123 mg, 0.12 mmol) in 2-propanol (90 mL) was added a solution of potassium hydroxide (1.53 g, 27.3 mmol) in water (23 mL). The solution

was refluxed (80 °C) for 2h. After cooling to room temperature, the reaction mixture was treated with aqueous HCl (1M, 28mL) solution. The solution was washed with saturated aqueous NaHCO₃ and water. Collected organic layer was dried over anhydrous sodium sulfate, and then the solvent was removed in vacuo. Reprecipitation from CH₂Cl₂/hexane gave **8b** as a deep violet solid (104 mg, 0.11 mmol, 89 %). Mp > 300 °C; ¹H NMR (400 MHz, acetone-d₆) δ 8.87 (d, *J*=4.9 Hz, 2H, β-pyrrolic H), 8.82 (d, *J*=4.9 Hz, 2H, β-pyrrolic H), 8.52 (s, 2H, β-pyrrolic H), 8.47 (s, 2H, quinoxaline H), 7.38 (s, 4H, phenyl H), 7.35 (s, 4H, phenyl H), 2.71 (s, 6H, methyl H), 2.61 (s, 6H, methyl H), 1.88 (s, 12H, methyl H), 1.78 (s, 12H, methyl H), -2.23 (s, 2H, inner H); FT-IR (KBr) ν_{max} 3350, 2917, 2860, 1716, 1611, 1441, 1343, 1211, 1139, 979, 852, 821, 802, 725 cm⁻¹; MS (MALDI-TOF) *m/z* 971.9 (M+H⁺).

5,10,15,20-Tetrakis(2,4,6-trimethylphenyl)-6',7'-dicarboxyquinoxalino[2,3-β]porphyrinatozinc (II) (ZnQDA). To a solution of **8a** (90 mg, 0.092 mmol) in chloroform (150 mL) was added a solution of zinc acetate dihydrate (450 mg, 2.1 mmol) in methanol (30 mL). The solution was stirred at reflux (60 °C) for 18 h. The solvent was removed by using a rotary evaporator, and the residue dissolved in dichloromethane and passed

through the filter paper (ADVANTEC). The filtrate was washed with water, dried over anhydrous sodium sulfate, and then the solvent was removed in vacuo. Reprecipitation from CH₂Cl₂/hexane gave **ZnQDA** as a deep purple solid (77 mg, 0.075 mmol, 81 % yield). ¹H NMR (400 MHz, acetone-d₆ + CD₃OD) δ 8.70 and 8.67 (ABq, *J*=4.4 Hz, 4H, β-pyrrolic H), 8.57 (s, 2H, β-pyrrolic H), 8.42 (s, 2H, quinoxaline H), 7.36 (s, 4H, phenyl H), 7.32 (s, 4H, phenyl H), 2.71 (s, 6H, methyl H), 2.61 (s, 6H, methyl H), 1.88 (s, 12H, methyl H), 1.77 (s, 12H, methyl H); UV-vis (MeOH) λ_{max} (nm) 424.5, 583.5, 627.5; MS (MALDI-TOF) *m/z* 1034.0 (M+H⁺).

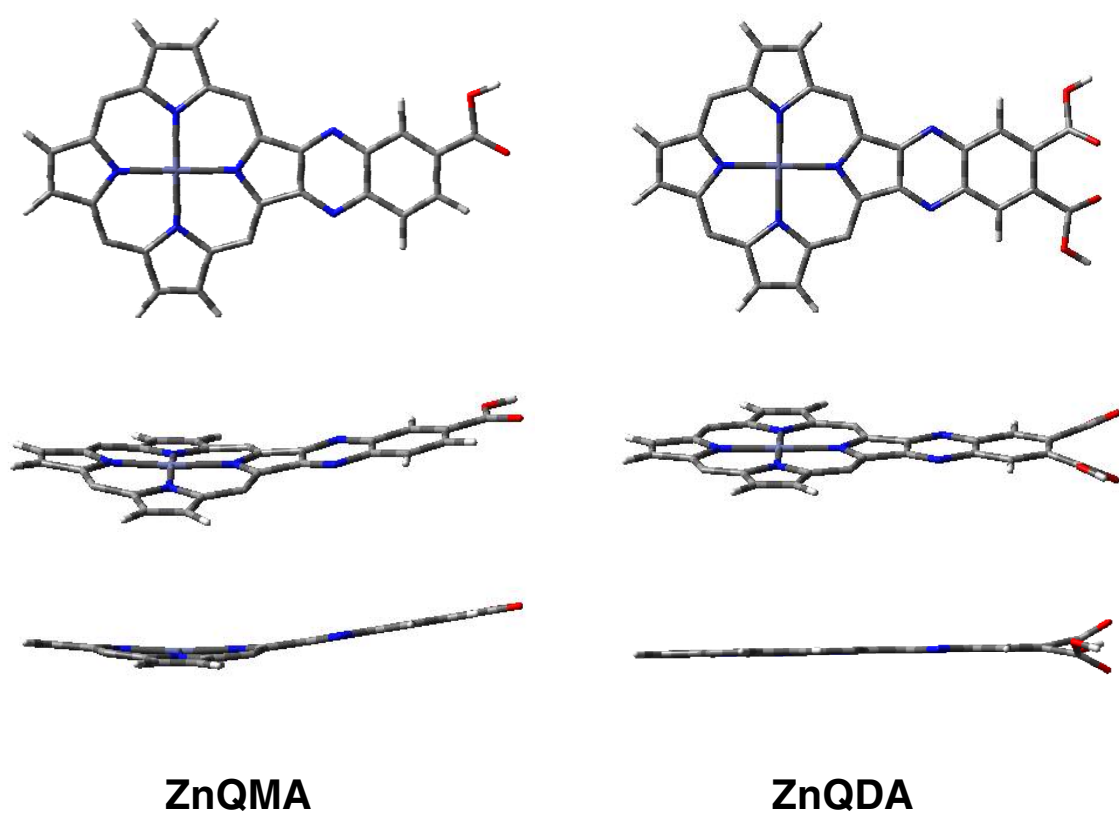


Figure S1. Optimized geometries for ZnQMA and ZnQDA estimated by DFT calculations with B3LYP/3-21G(d) with various viewing angles. *Meso* substituents are omitted for clarity.

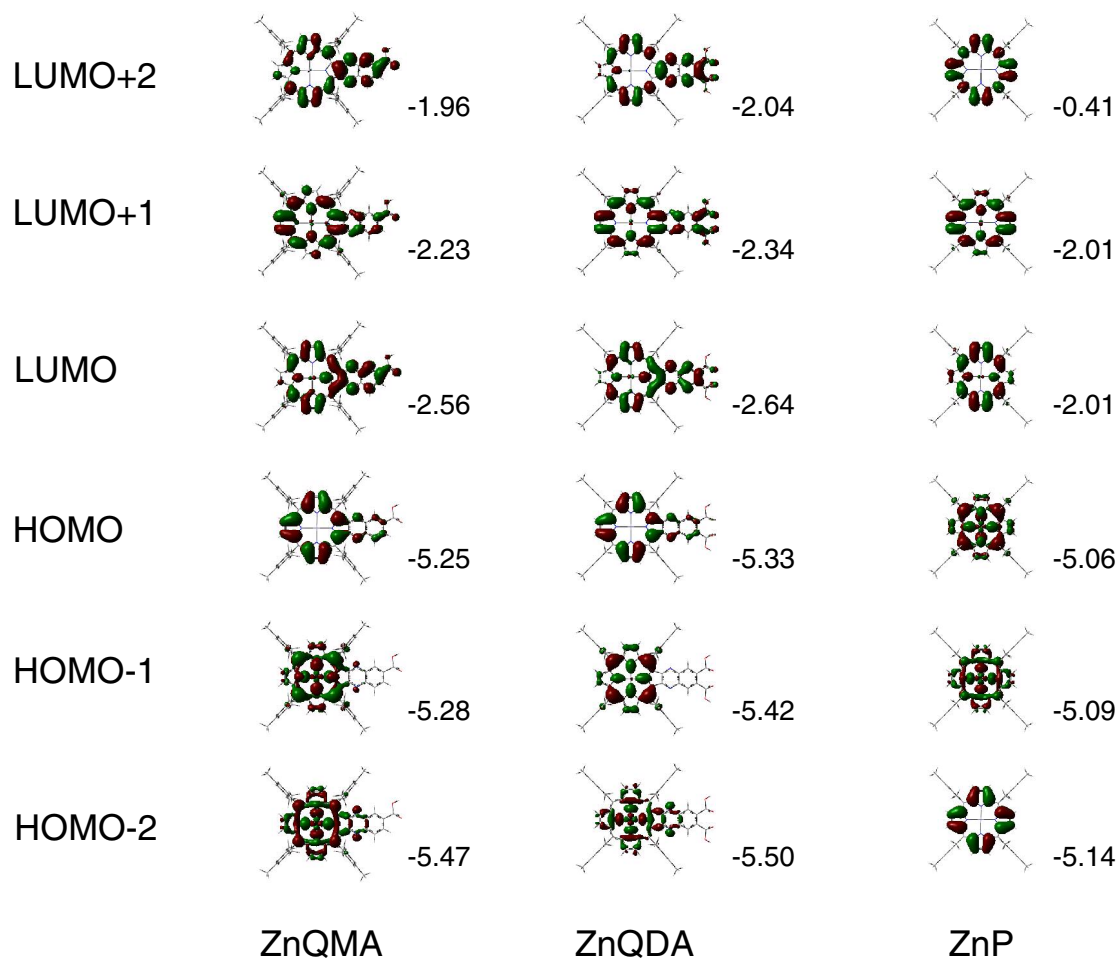


Figure S2. Some sets of molecular orbital diagrams and corresponding energies for ZnQMA, ZnQDA, and ZnP estimated by DFT calculations with B3LYP/3-21G(d). The energies in eV are quoted with respect to the vacuum (1 Hartree = 27.2116 eV).

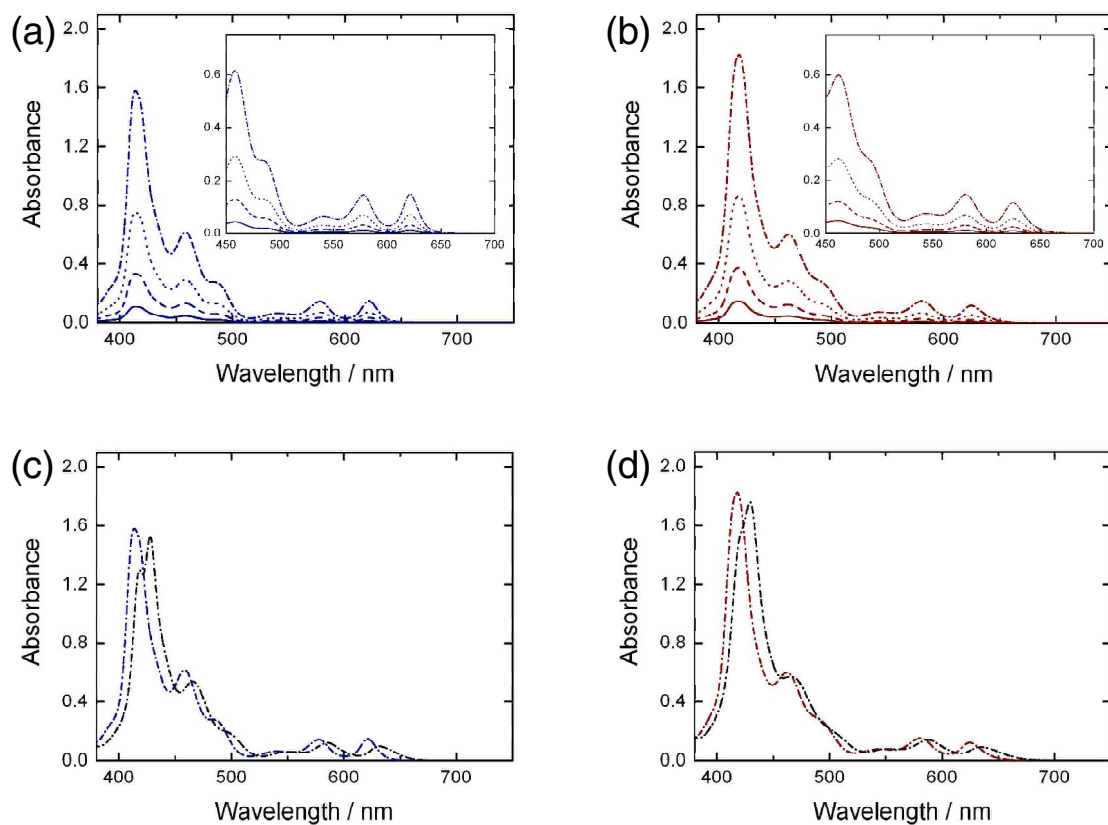


Figure S3. UV-visible absorption spectra of (a) ZnQMA and (b) ZnQDA measured in toluene solution with different concentrations of 1.0 μM (solid), 2.5 μM (dashed), 5.0 μM (dotted), and 10.0 μM (dashed dot). UV-visible absorption spectra of (c) ZnQMA and (d) ZnQDA measured in 10.0 μM with the addition of 2.5 mM of pyridine (black). Optical length = 1 cm.

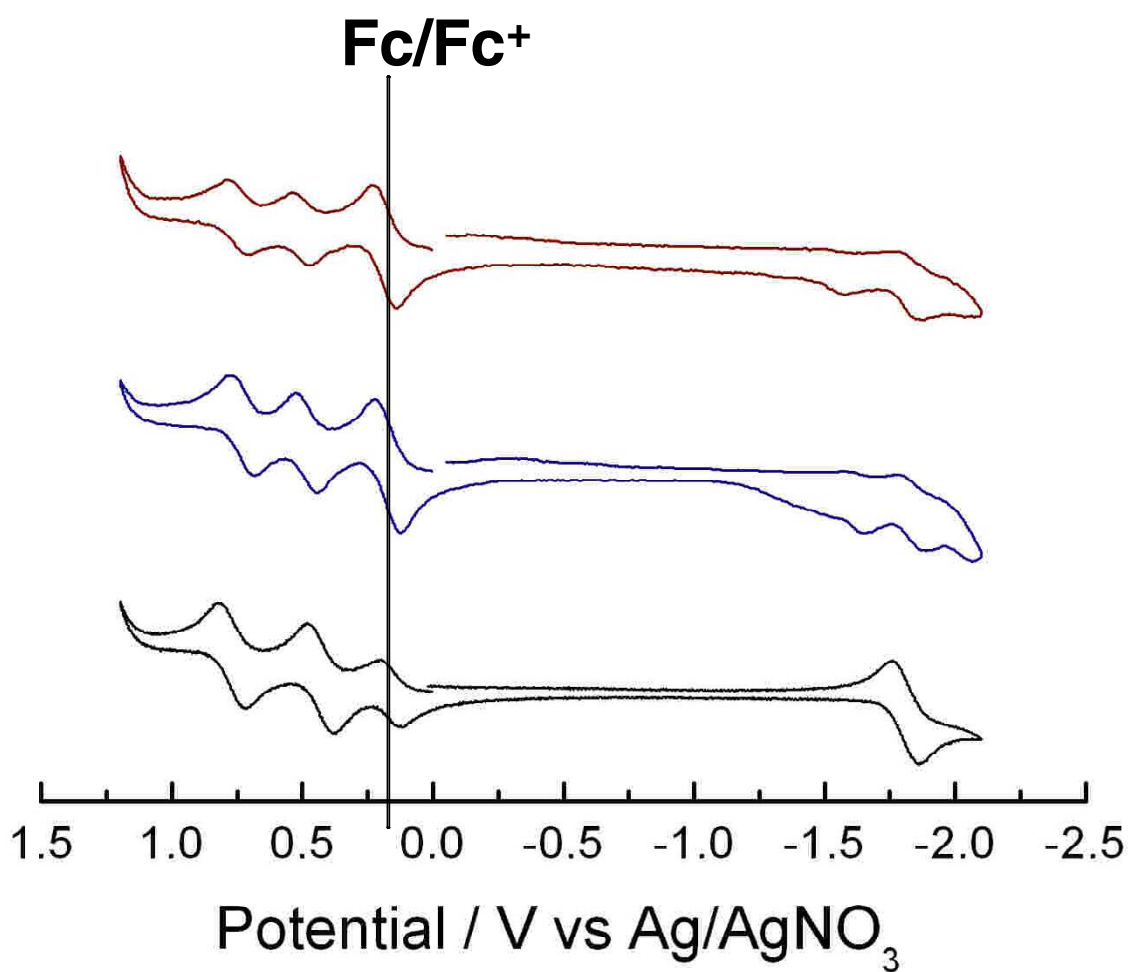


Figure S4. Cyclic voltammograms for ZnP (black), ZnQMA (blue), and ZnQDA (red) in CH_2Cl_2 containing 0.1M TBAP as a supporting electrolyte. A glassy carbon working electrode (3 mm diameter), Ag/AgNO_3 reference electrode, and Pt wire counter electrode were employed. Ferrocene/ferrocenium (+0.642 V vs NHE) was used as an internal standard for all measurements. Scan rate of 100 mV s^{-1} was used for the measurements.

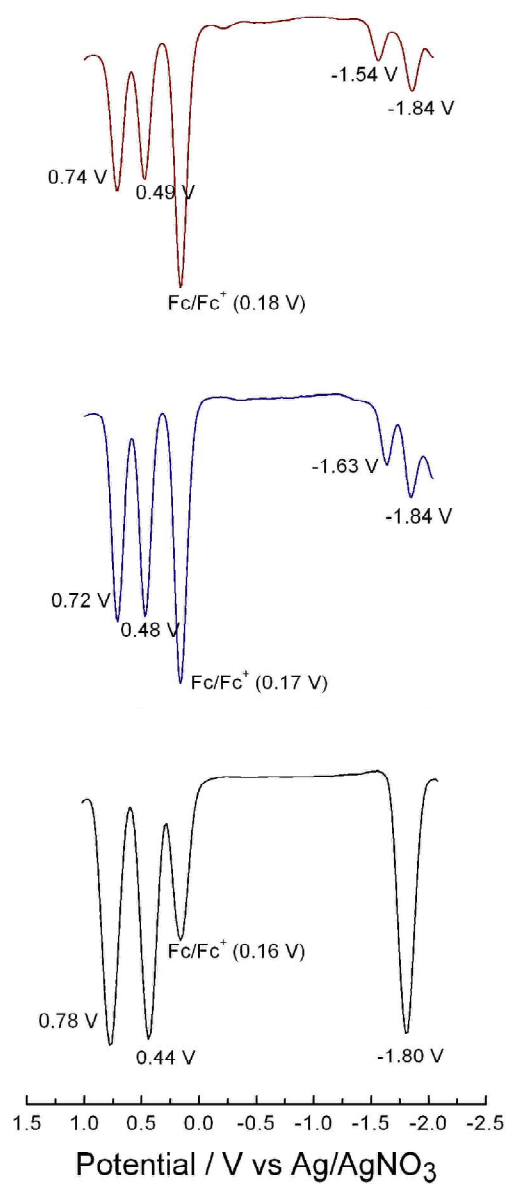


Figure S5. Differential pulse voltammograms for ZnP (black), ZnQMA (blue), and ZnQDA (red) in CH₂Cl₂ containing 0.1M TBAP as a supporting electrolyte. Scan rate of 50 mV s⁻¹ and pulse amplitude of 50 mV were used for measurements. Other conditions for measurements were the same for CV measurements.

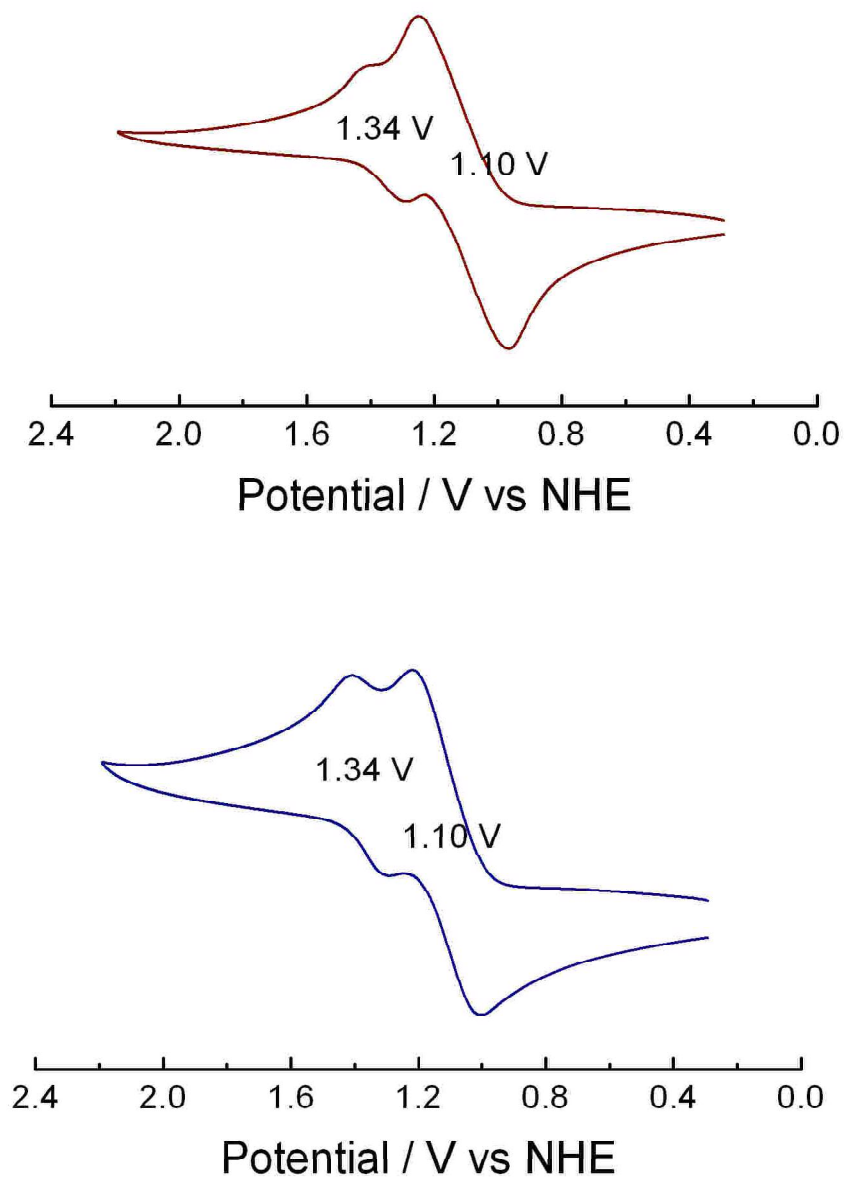


Figure S6. Cyclic voltammograms for TiO₂/ZnQMA (blue) and TiO₂/ZnQDA (red) in acetonitrile containing 0.1M TBAP at a scan rate of 100 mV s⁻¹. The porphyrin-modified TiO₂ was employed as a working electrode along with the Ag/AgCl reference electrode (+0.197 V vs NHE) and Pt wire counter electrode.

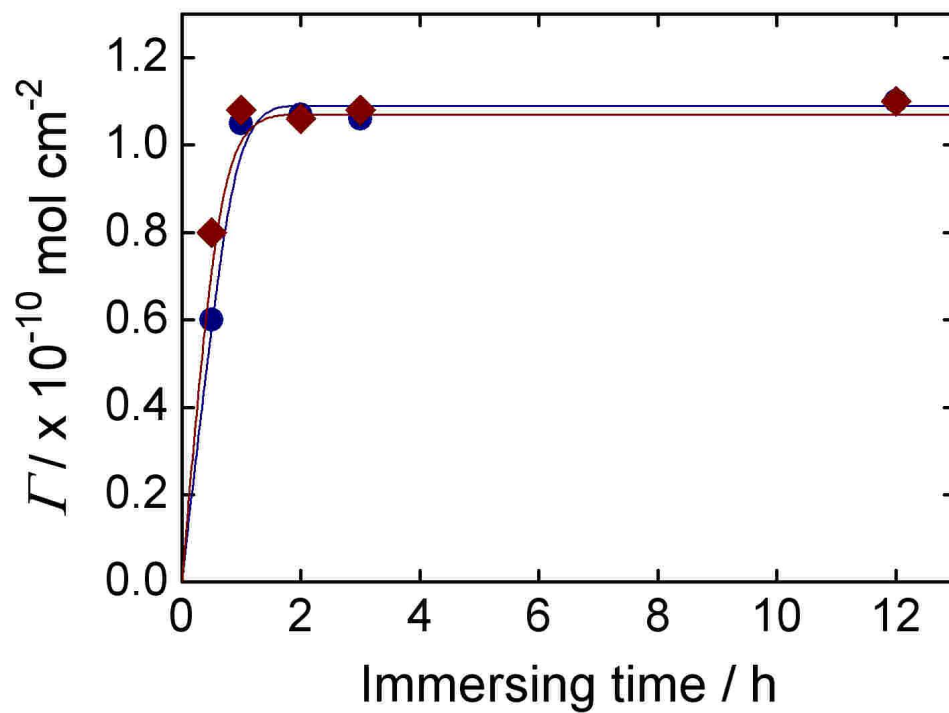


Figure S7. Time profiles of the surface coverage (Γ) of ZnQMA (blue) and ZnQDA (red) on the TiO_2 electrode for different immersing time in MeOH solution.

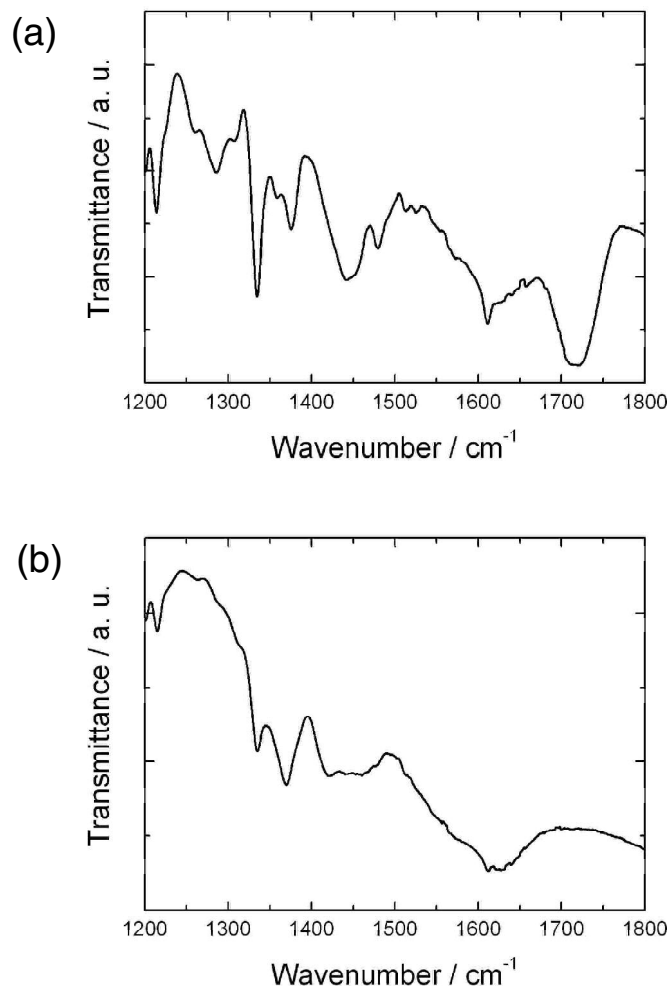


Figure S8. FTIR spectra of ZnQDA (a) before and (b) after being adsorbed on the TiO₂ electrodes. “Before” was measured for ZnQDA with powdered TiO₂ in a KBr pellet. “After” was measured for TiO₂/ZnQDA layer detached from FTO in a KBr pellet. The characteristic band of ν (C=O) of the carboxylic acid group at around 1700 cm⁻¹ disappeared due to the adsorption. Broadening of the symmetric (at around 1400 cm⁻¹) and asymmetric (at around 1600 cm⁻¹) carboxylates may result from the interactions between carboxylic acid group and TiO₂ surface.

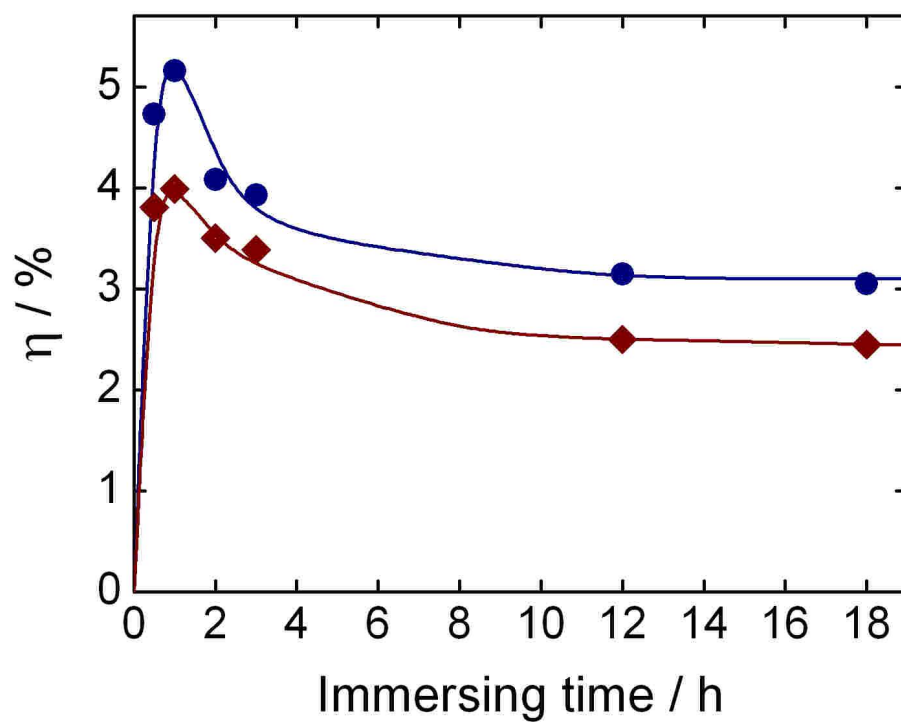


Figure S9. Time profiles of the η values of ZnQMA- (blue) and ZnQDA- (red) sensitized solar cells with the TiO_2 electrodes prepared under different immersing time for porphyrin adsorption in MeOH.

References and Notes

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