

Electronic Supplementary Information

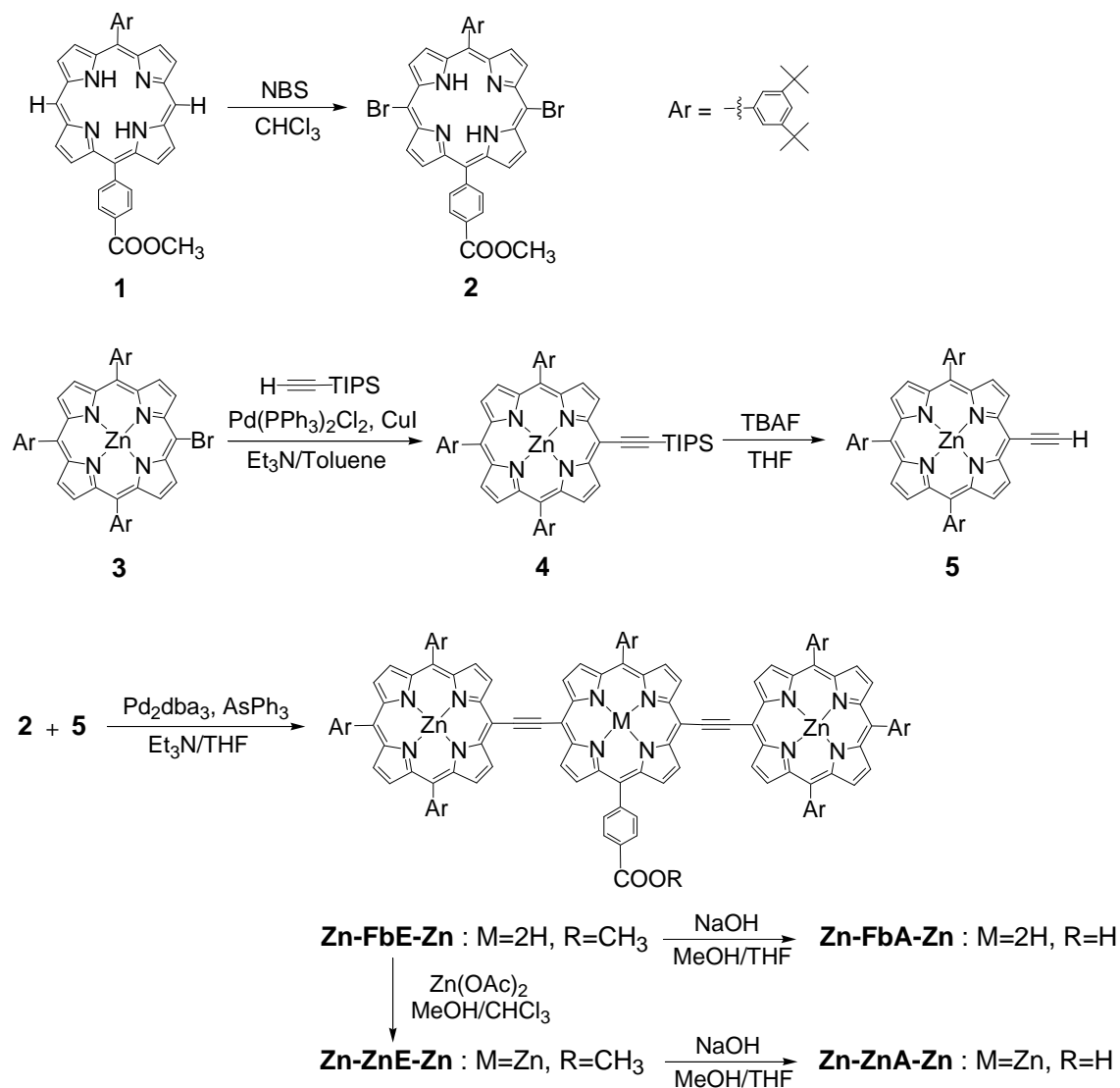
Dye-sensitized solar cells using ethynyl-linked porphyrin trimers

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Synthetic procedures

Scheme 1. Synthetic route of ethynyl-linked porphyrin trimers



General methods

¹H-NMR spectra were recorded on a JEOL AL-400 spectrometer using the sample solutions in chloroform-d (CDCl₃) or tetrahydrofuran-d₈ (C₄D₈O), where the chemical shifts were determined with residual CHCl₃ (δ 7.26) or C₄D₇HO (δ 3.58). Mass spectrometry was performed on a Bruker Autoflex system by the matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) method with dithranol as the matrix, or on a Shimadzu LCMS-IT-TOF system by the electrospray ionization (ESI) time-of-flight method with methanol as the solvent. High-resolution mass spectrometry was performed also on a Shimadzu LCMS-IT-TOF system. All reagents and solvents were purchased from Aldrich, Kanto Kagaku (Cica), Tokyo Kasei (TCI), or Wako Pure Chemicals, and were used without purification unless indicated otherwise. Triethylamine and pyrrole were distilled over CaH₂ under argon. All synthetic procedures were carried out under an argon atmosphere. Air-sensitive synthetic procedures were performed using Schlenk techniques. 3,5-Di-*tert*-butylbenzaldehyde,^{S1} 2,2'-dipyrrolylmethane,^{S2} 5-bromo-10,15,20-tris(3',5'-di-*tert*-butylphenyl)porphyrinatozinc(II)^{S3} (**3**) were synthesized according to the literatures.

5-(3',5'-Di-*tert*-butylphenyl)-15-(4'-methoxycarbonylphenyl)porphyrin (**1**)

To a CHCl₃ (750 mL) solution of 3,5-di-*tert*-butylbenzaldehyde (0.56 g, 2.6 mmol), 2,2'-dipyrrolylmethane (1.00 g, 6.8 mmol) and terephthalaldehydic acid methyl ester (0.70 g, 4.3 mmol), EtOH (4.0 mL) and trifluoroacetic acid (1.2 mL) were added. The solution was stirred for 2.5 h at room temperature in the dark. Chloranil (3.06 g) was added to the mixture, which was stirred overnight at room temperature. The reaction mixture was quenched with Et₃N (3.0 mL) and then evaporated to dryness. The crude product was purified by column chromatography on silica gel with hexane/CHCl₃ (2/3) as the eluent. The fraction containing the product was evaporated to dryness and was reprecipitated from CHCl₃ by the addition of MeOH. The mixture was filtered, to afford **1** (341 mg) as a purple solid in 21% yield. ¹H-NMR (400 MHz, CDCl₃): δ -3.08 (2H, s), 1.58 (18H, s), 4.14 (3H, s), 7.85 (1H, t, J = 1.6 Hz), 8.14 (2H, d, J = 1.7 Hz), 8.38 (2H, d, J = 2.0 Hz), 8.50 (2H, d, J = 2.0 Hz), 9.04 (2H, d, J = 4.6 Hz), 9.15 (2H, d, J = 4.6 Hz), 9.41 (2H, d, J = 4.4 Hz), 9.42 (2H, d, J = 4.4 Hz), 10.34 (2H, s). MS (ESI): m/z 633.3 ([M+H]⁺, calcd 633.3). UV-Vis (CHCl₃): λ_{\max} /nm 408, 504, 538, 576, 630.

5,15-Dibromo-10-(3',5'-di-*tert*-butylphenyl)-20-(4'-methoxycarbonylphenyl)porphyrin (**2**)

To a CHCl₃ (30 mL) solution of **1** (90 mg, 0.14 mmol) was added *N*-bromosuccinimide (NBS) (51 mg, 0.28 mmol) and pyridine (2.0 mL) at 0°C. After being stirred for 10 min, the reaction was terminated by the addition of acetone (30 mL), and evaporated to dryness. The residue was dissolved in CHCl₃, and reprecipitated by the addition of MeOH. The mixture was filtered, to afford **2** (112 mg) as a purple solid quantitatively. ¹H-NMR (400 MHz, CDCl₃): δ -2.70 (2H, s), 1.46 (18H, s), 4.14 (3H, s), 7.83 (1H, t, J = 2.1 Hz), 8.01 (2H, d, J = 2.0 Hz), 8.26 (2H, d, J = 8.3 Hz), 8.27 (2H, d, J = 8.1 Hz), 8.78 (2H, d, J = 4.6 Hz), 8.89 (2H, d, J = 4.6 Hz), 9.63 (2H, d, J = 4.4 Hz), 9.64 (2H, d, J = 4.4 Hz). MS (ESI): m/z 789.1 ([M+H]⁺, calcd 789.1). UV-Vis (CHCl₃): λ_{\max} /nm 422, 520, 556, 600, 658.

5-Ethynyl-10,15,20-tris(3',5'-di-*tert*-butylphenyl)porphyrinatozinc(II) (**5**)

5-Bromo-10,15,20-tris(3',5'-di-*tert*-butylphenyl)porphyrinatozinc(II) (**3**, 305 mg, 0.30 mmol) was dissolved in anhydrous toluene (60 mL) and distilled Et₃N (15 mL) under argon, and the mixture

was degassed by three freeze-pump-thaw cycles. To this solution were added Pd(PPh₃)₂Cl₂ (24.0 mg, 34 μmol), CuI (8.02 mg, 42 μmol), and triisopropylsilylacetylene (1.40 mL, 6.24 mmol). After being stirred for 3 h at 30°C, the reaction mixture was evaporated to dryness. The crude product was purified by column chromatography on silica gel with hexane/CHCl₃ (7/3) as the eluent. The product was reprecipitated from CHCl₃ solution by adding a small amount of MeOH, to afford 282 mg of purple solid (**4**). 280 mg of the solid was dissolved in 150 mL of tetrahydrofuran, and 1.0 M tetrabutylammonium fluoride in tetrahydrofuran (0.80 mL) was added. The mixture was stirred for 15 min, and evaporated to dryness. The residue dissolved in CHCl₃ was washed with water, and the organic phase was dried over Na₂SO₄. After removing the drying agent, the filtrate was evaporated to dryness, to afford **5** as purple-red solid. ¹H-NMR (400 MHz, CDCl₃): δ 1.52 (18H, s), 1.55 (36H, s), 4.09 (1H, s), 7.79 (1H, t, *J* = 1.8 Hz), 7.82 (2H, t, *J* = 1.8 Hz), 8.05 (2H, d, *J* = 2.0 Hz), 8.08 (4H, d, *J* = 1.7 Hz), 8.94 (4H, m), 9.04 (2H, d, *J* = 4.4 Hz), 9.73 (2H, d, *J* = 4.6 Hz). MS (ESI): *m/z* 1023.5 ([M+CH₃OH+CH₃O]⁻, calcd 1023.5). UV-Vis (CHCl₃): λ_{max}/nm 430, 560, 606.

5,15-Bis[[zinc(II)10',15',20'-tris(3'',5''-di-*tert*-butylphenyl)porphyrin-5'-yl]ethynyl]-10-(3',5'-di-*tert*-butylphenyl)-20-(4'-methoxycarbonylphenyl)porphyrin (Zn-FbE-Zn)

2 (8.4 mg, 10 μmol) and **5** (41 mg, 43 μmol) were dissolved in anhydrous tetrahydrofuran (60 mL) and distilled Et₃N (15 mL) under argon, and the mixture was degassed by three freeze-pump-thaw cycles. To this solution were added Pd₂(dba)₃ (1.7 mg, 1.9 μmol) and AsPh₃ (4.2 mg, 14 μmol). After being stirred for 18 h at 40°C, the reaction mixture was evaporated to dryness. The crude product was purified by silica gel chromatography with hexane/CHCl₃ (2/3) as the eluent. The fraction containing the product was evaporated to dryness, and dissolved in CHCl₃. The product was reprecipitated by adding a small amount of MeOH, to afford **Zn-FbE-Zn** (18 mg) as a black solid in 68% yield. ¹H-NMR (400 MHz, C₄D₈O): δ -2.00 (2H, br), 1.52 (18H, s), 1.55 (36H, s), 7.89 (2H, m), 7.94 (5H, m), 8.10 (4H, m), 8.18 (8H, m), 8.29 (2H, m), 8.53 (2H, d, *J* = 8.4 Hz), 8.57 (2H, d, *J* = 8.0 Hz), 8.83 (8H, m), 9.05 (2H, m), 9.10 (2H, m), 9.15 (4H, d, *J* = 4.4 Hz), 10.42 (8H, d, *J* = 4.6 Hz). MS (MALDI-TOF): *m/z* 2549.2 (M⁺, calcd 2549.3). UV-Vis (CH₂Cl₂): λ_{max}/nm (ε/10⁴ M⁻¹cm⁻¹) 435(33.2), 484(27.5), 581(3.10), 671(5.80), 789(14.6).

5,15-Bis[[zinc(II)10',15',20'-tris(3'',5''-di-*tert*-butylphenyl)porphyrin-5'-yl]ethynyl]-10-(3',5'-di-*tert*-butylphenyl)-20-(4'-methoxycarbonylphenyl)porphyrinatozinc(II) (Zn-ZnE-Zn)

To a CHCl₃ (180 mL) solution of **Zn-FbE-Zn** (45 mg, 18 μmol) was added saturated Zn(OAc)₂ in MeOH (2.5 mL), and the solution was stirred for 50 min at room temperature. The reaction mixture was quenched with a saturated NaHCO₃ aqueous solution, and was washed with water. The separated organic phase was dried over Na₂SO₄ and filtered. The filtrate was evaporated to dryness, to afford **Zn-ZnE-Zn** (43 mg) as a brown solid quantitatively. ¹H-NMR (400 MHz, C₄D₈O): δ 1.52 (18H, s), 1.55 (36H, s), 7.89 (2H, m), 7.91 (2H, m), 7.94 (2H, d), 7.94 (1H, s), 8.11 (4H, m), 8.20 (8H, m), 8.26 (2H, m), 8.51 (2H, d, *J* = 8.4 Hz), 8.55 (4H, m), 8.85 (4H, d, *J* = 4.2 Hz), 8.86 (4H, d, *J* = 4.6 Hz), 9.07 (2H, d, *J* = 4.6 Hz), 9.13 (2H, d, *J* = 4.4 Hz), 9.16 (4H, d, *J* = 4.4 Hz), 10.45 (2H, d, *J* = 4.6 Hz), 10.48 (6H, d, *J* = 4.6 Hz); MS (MALDI-TOF): *m/z* 2611.5 (M⁺, calcd 2611.2). UV-Vis (CH₂Cl₂): λ_{max}/nm (ε/10⁴ M⁻¹cm⁻¹) 418(32.0), 496(38.5), 552(3.7), 578(3.6), 778(17.2).

**5,15-Bis[[zinc(II)10',15',20'-tris(3'',5''-di-*tert*-butylphenyl)porphyrin-5'-yl]ethynyl]-10-(4'-c
arboxyphenyl)-20-(3',5'-di-*tert*-butylphenyl)porphyrin (Zn-FbA-Zn)**

To a THF/MeOH (24/12 mL) solution of **Zn-FbE-Zn** (7 mg, 3 μmol) was added 1.0 M NaOH aqueous solution (0.29 mL). After being refluxed for 15 h, the reaction mixture was evaporated to dryness. Water and 0.1 M HCl aqueous solution (2.9 mL) were added to the residue. The mixture was stirred for 1 h at room temperature, from which the product was extracted with CHCl_3 . The solution was dried over Na_2SO_4 , and filtered. After the filtrate was evaporated to dryness, the residue was purified by silica gel chromatography with CHCl_3 as the eluent, to afford **Zn-FbA-Zn** (3.8 mg) as a black solid in 55% yield. MS (MALDI-TOF): m/z 2535.5 (M^+ , calcd 2535.3). HRMS (ESI): m/z 1284.6496 ($[\text{M} - 2\text{H} + \text{CH}_3\text{OH}]^{2-}$, calcd for $\text{C}_{170}\text{H}_{178}\text{N}_{12}\text{O}_3\text{Zn}_2$ 1284.6459). UV-Vis (CHCl_3): $\lambda_{\text{max}}/\text{nm}$ 432, 486, 579, 670, 781.

**5,15-Bis[[zinc(II)10',15',20'-tris(3'',5''-di-*tert*-butylphenyl)porphyrin-5'-yl]ethynyl]-10-(4'-c
arboxyphenyl)-20-(3',5'-di-*tert*-butylphenyl)porphyrinatozinc(II) (Zn-ZnA-Zn)**

To a THF/MeOH (24/12 mL) solution of **Zn-ZnE-Zn** (12 mg, 4.6 μmol) was added 1.0 M NaOH aqueous solution (4.97 mL). After being refluxed for 15 h, the reaction mixture was evaporated to dryness. Water and 0.1 M HCl aqueous solution (9.55 mL) were added to the residue. The mixture was stirred for 1 h at room temperature, from which the product was extracted with CHCl_3 . The solution was dried over Na_2SO_4 , and filtered. The crude product was purified by silica gel chromatography with CHCl_3 as the eluent, to afford **Zn-ZnA-Zn** (10 mg) brown solid in 83% yield. MS (MALDI-TOF): m/z 2597.2 (M^+ , calcd 2597.2). HRMS (ESI): m/z 1316.6031 ($[\text{M} - 2\text{H} + \text{CH}_3\text{OH}]^{2-}$, calcd for $\text{C}_{170}\text{H}_{178}\text{N}_{12}\text{O}_3\text{Zn}_3$ 1316.6018). UV-Vis (CHCl_3): $\lambda_{\text{max}}/\text{nm}$ 418, 488, 550, 571, 768.

References

- ^{S1} M. J. Plater, S. Aiken and G. Bourhill, *Tetrahedron*, 2002, **58**, 2405.
^{S2} J. K. Laha, S. Dhanalekshmi, M. Taniguchi, A. Ambroise and J. S. Lindsey, *Org. Proc. Res. Dev.*, 2003, **7**, 799.
^{S3} J. T. Dy, K. Tamaki, Y. Sanehira, J. Nakazaki, S. Uchida, T. Kubo and H. Segawa, *Electrochemistry*, 2009, **77**, 206.

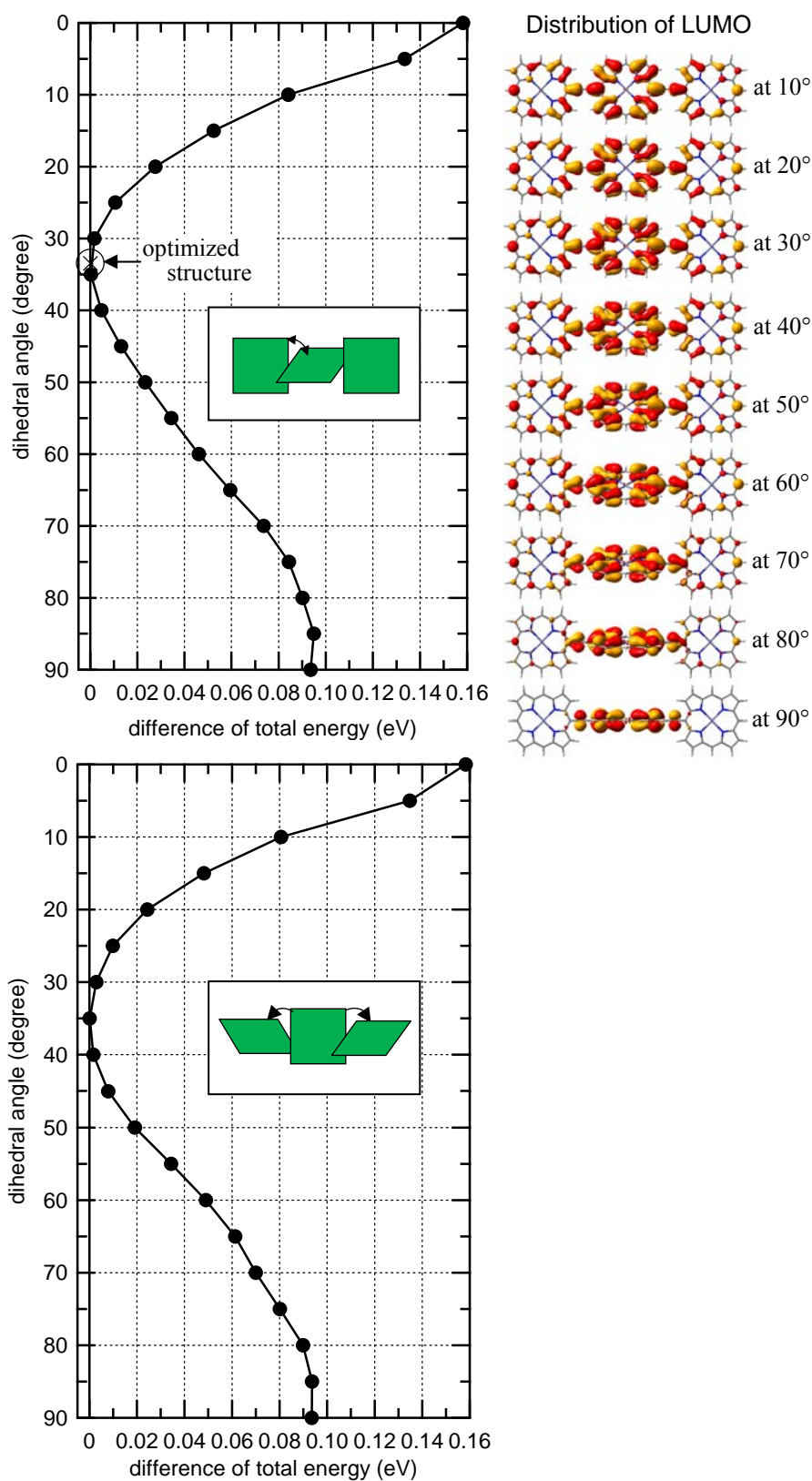


Figure S1. Calculated total energy for various conformer of the ethynyl-linked porphyrin trimer and the distribution of LUMO in each conformers. The total energy is given by the difference from the one in the fully optimized structure. The corresponding dihedral angles are indicated in the schematic drawing.

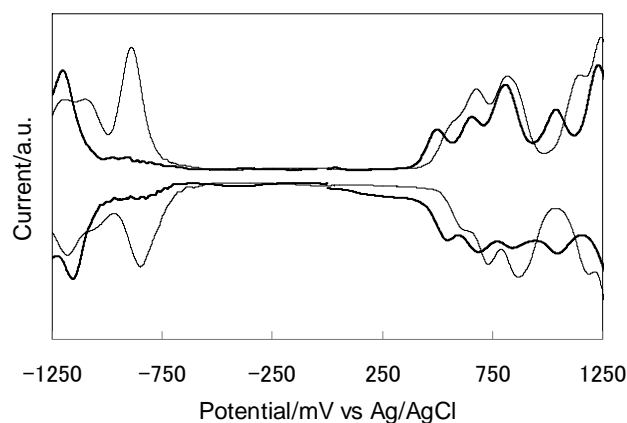


Figure S2. Differential pulse voltammetry curves of **Zn-ZnE-Zn** (thick line) and **Zn-FbE-Zn** (thin line) measured using 0.3 mM solutions of the compounds with 0.1 M $n\text{Bu}_4\text{NPF}_6$ in dehydrated CH_2Cl_2 as the supporting electrolyte

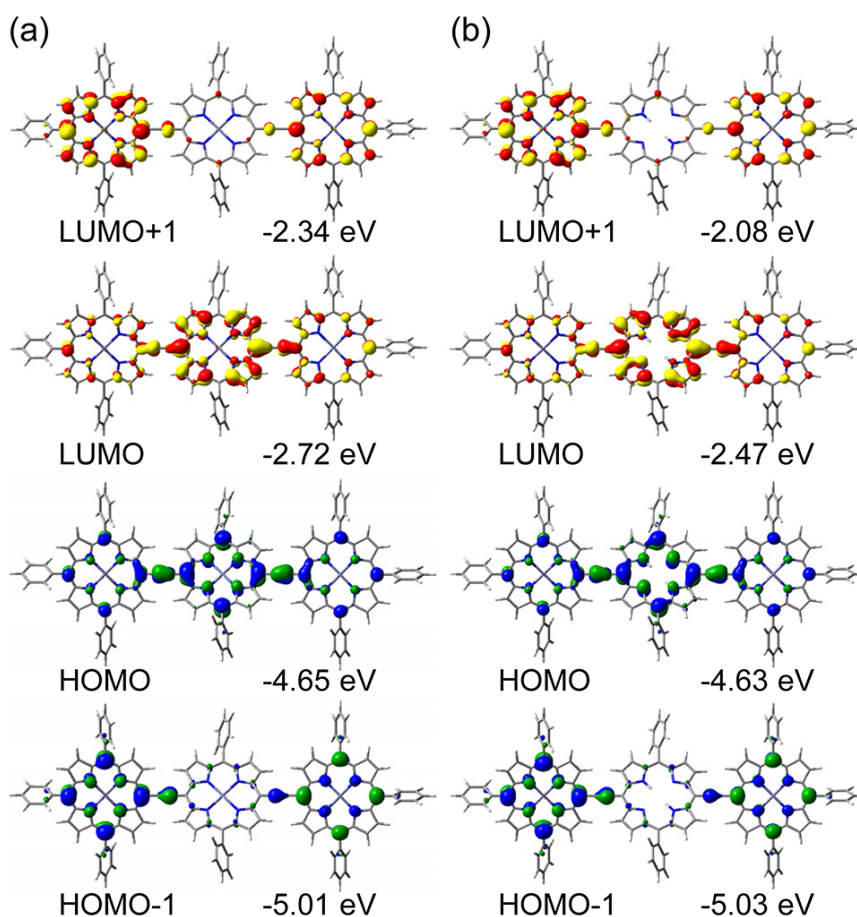


Figure S3. Molecular orbitals of ethynyl-linked porphyrin trimers calculated by Gaussian03 with B3LYP/6-31G. (a) all zinc trimer, (b) zinc-freebase-zinc trimer.

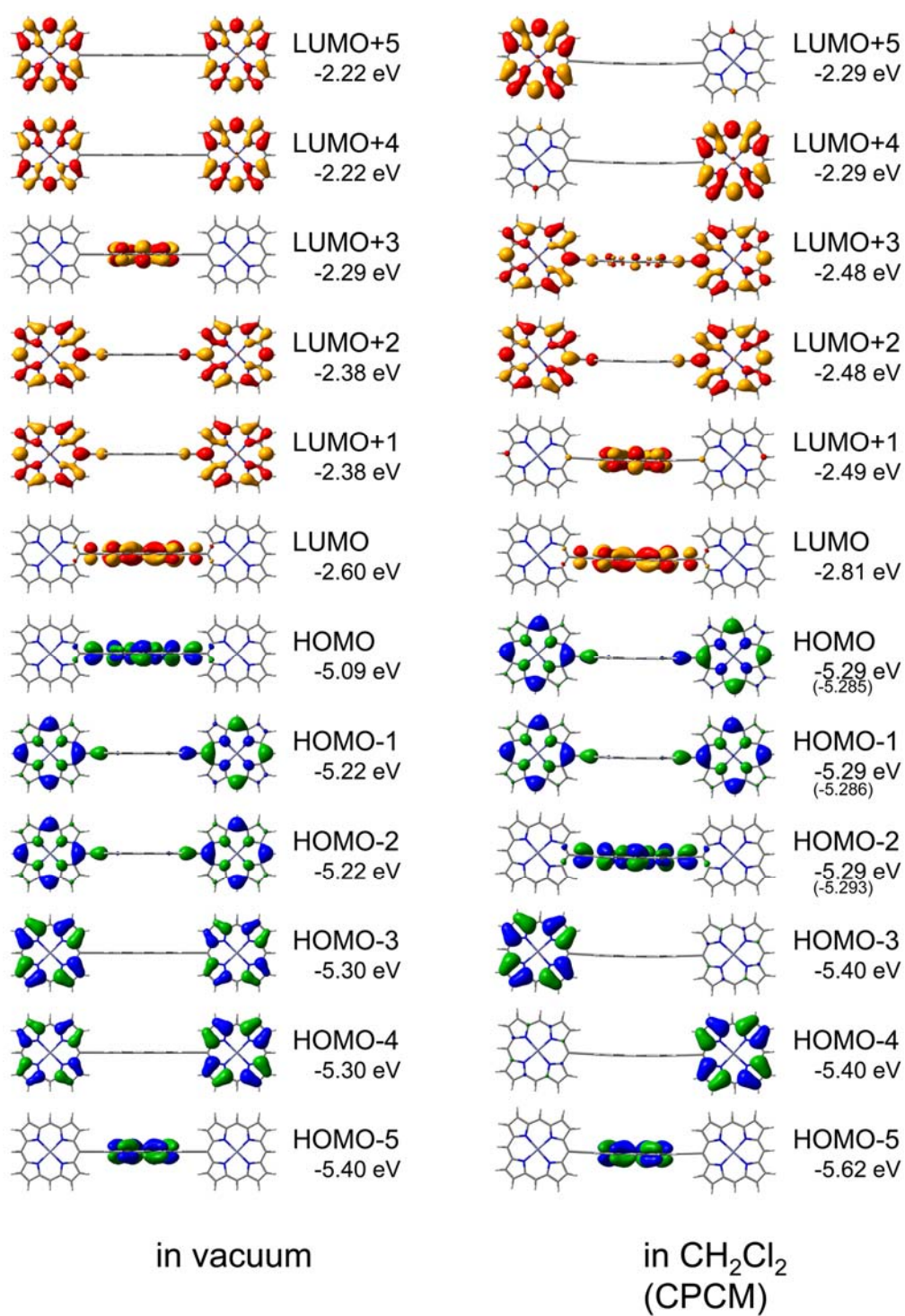


Figure S4. Calculated orbitals for the orthogonal conformer of the ethynyl-linked zinc-freebase-zinc porphyrin trimer obtained by B3LYP/6-31G(d) with and without consideration of the solvent effect.

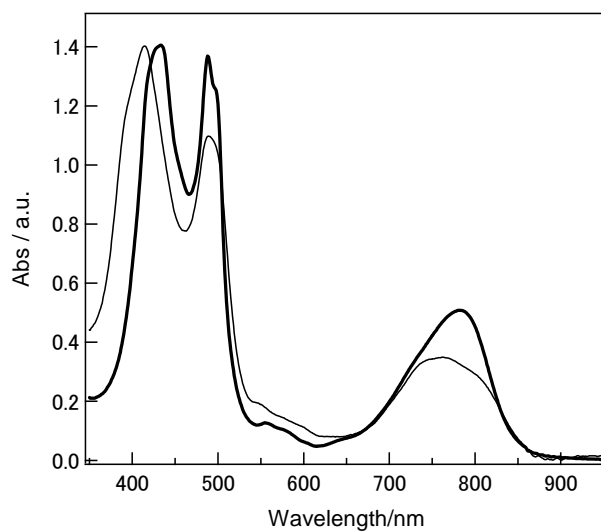


Figure S5. Absorption spectra of **Zn-ZnA-Zn** in 1:1 (v/v) CHCl₃-EtOH solution (solid line) and on a TiO₂ film (thin line).

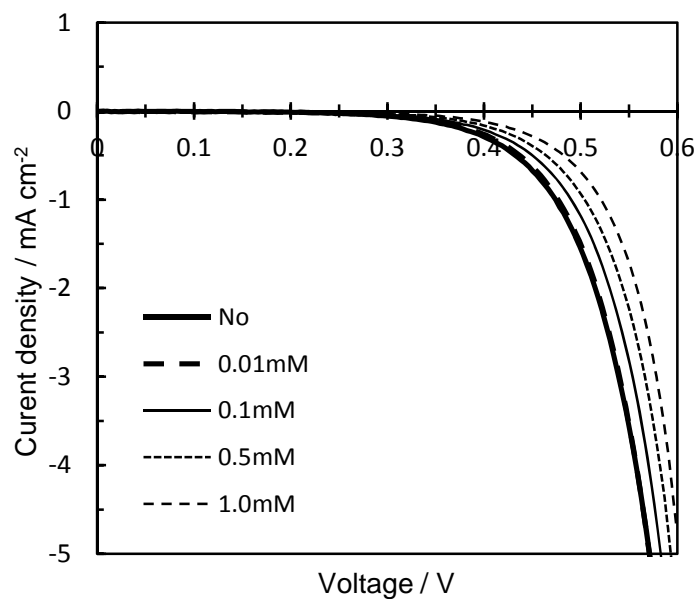


Figure S6 Current-voltage characteristics of the DSSCs using **Zn-ZnA-Zn** with various concentration of DCA in the dark.

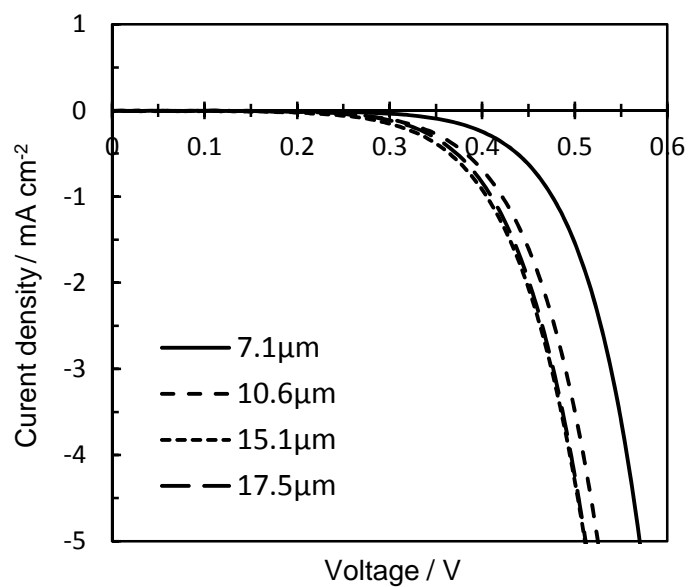


Figure S7 Current-voltage characteristics of the DSSCs using **Zn-ZnA-Zn** with various TiO₂ thickness in the dark.

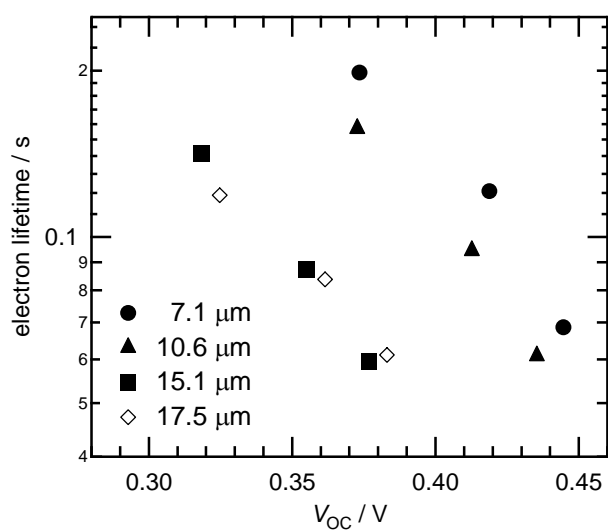


Figure S8 Electron lifetimes measured under different illumination intensities as a function of open-circuit voltage for the DSSCs with various TiO₂ film thicknesses.

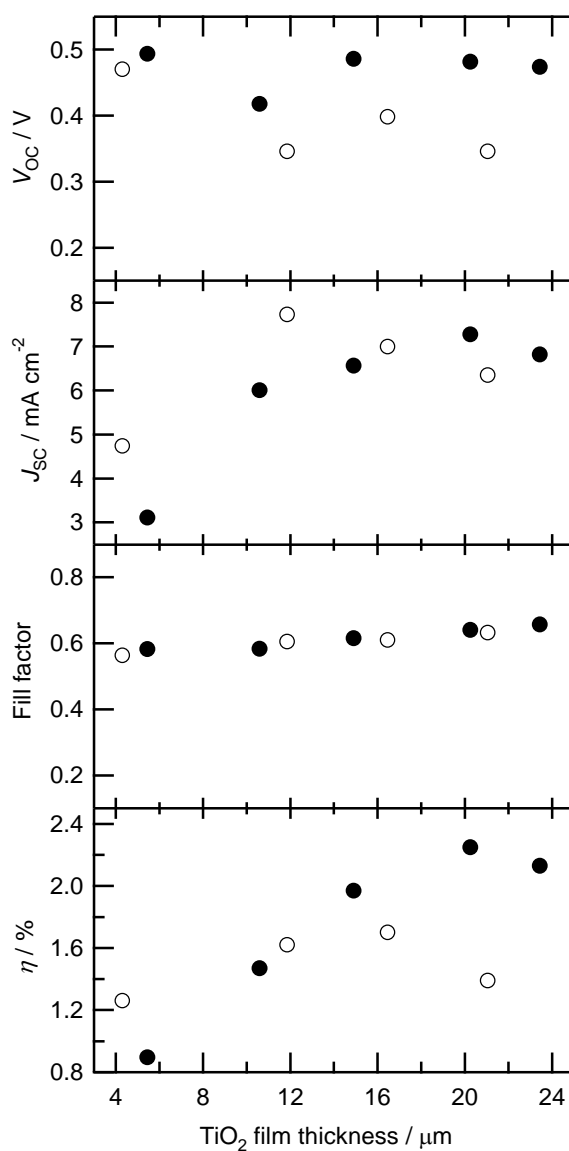


Figure S9 DSSC parameters [open circuit voltage (V_{oc}), current density (J_{sc}), fill factor, and efficiency (η)] of cells using 13 nm (open circles) and 37 nm (filled circles) TiO₂ nanoparticles and sensitized with **Zn-ZnA-Zn**.