

Supporting Information for

Dye Sensitized Solar Cells: Sensitizer-Dependent Injection into ZnO Nanotube Electrodes

by

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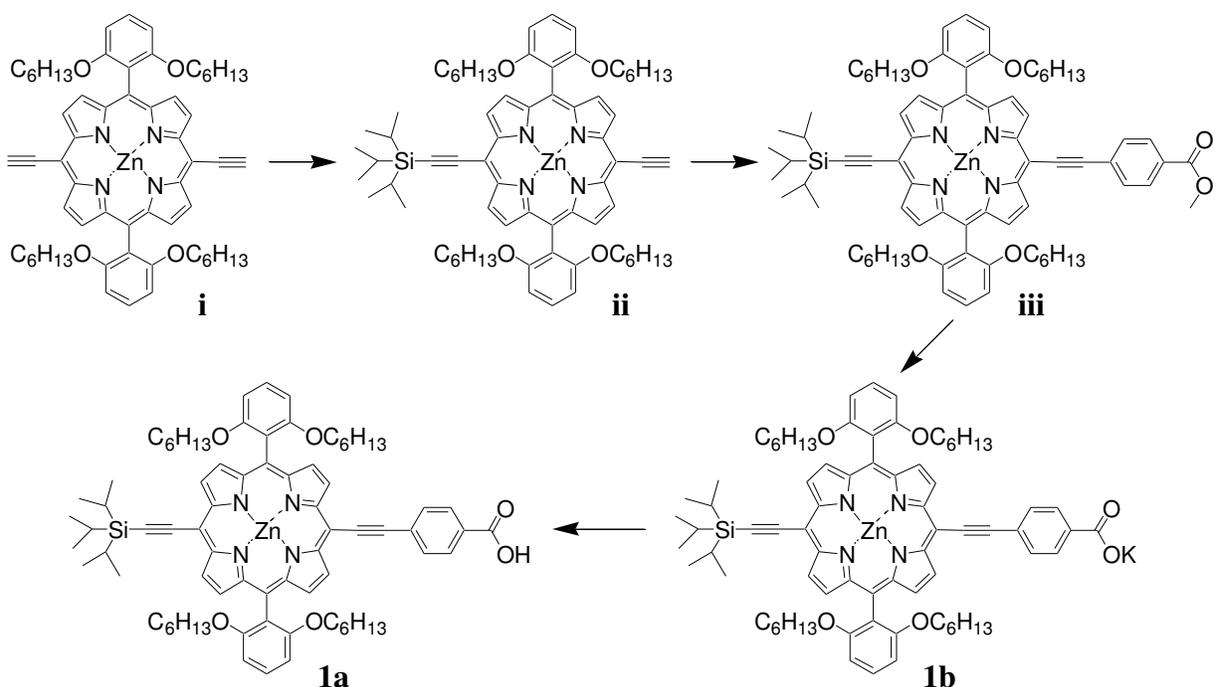
Experimental Section

Materials and General Procedures

Chemicals were obtained from commercial sources and used without further purification. All reactions were performed under nitrogen using inert-atmosphere and Schlenk techniques unless indicated otherwise. Solvents used in reactions were dried by standard procedures. Column chromatography was carried out with 230-400 mesh silica gel from Sorbent Technologies. Absorbance and fluorescence spectra were obtained using Varian Cary 5000 UV-Vis-NIR and ISA Instruments Fluorolog spectrophotometers, respectively. NMR spectra were recorded on either a Mercury 400 (400.168 MHz for ¹H) or an Inova 500 (499.773 for ¹H, and 125.669 MHz for ¹³C) spectrometer from the Integrated Molecular Structure Education Research Center (IMSERC) at Northwestern University. ¹H and ¹³C chemical shifts are reported in parts per million downfield from tetramethylsilane with solvent resonances as internal standards. Low-resolution laser desorption mass spectra were obtained on a Bruker Daltonics (Billerica, MA) AutoFlex III MALDI-ToF mass spectrometer as positive ions using the reflectron mode from the IMSERC facility with dithranol matrix. The instrument was equipped with Smartbeam™ laser technology operated at 69% power with a sampling speed of 200 Hz; 1000 spectra were averaged for the corresponding mass spectrum. The instrument was operated using the following parameters: ion source voltage 1 19 kV, ion source voltage 2 16.72 kV, lens voltage 8.3 kV, linear detector voltage 0.6 kV, deflection mass 500 Da. High-resolution mass spectra were analyzed on an Agilent (Wilmington, DE) 6210 ToF-LC/MS mass spectrometer from the

IMSERC facility. Analyses were performed in the positive ion ESI mode using the reflectron configuration. The instrument was calibrated with the Agilent ESI low concentration tune solution. Operational parameters are as follows: mass range 100-3000 m/z, VCap 3515 V, drying Gas 5.0 L/min, gas temperature 300 °C, skimmer 65 V, fragmentor 205 V, Ion Focus 108 V. Samples were injected using flow injection on an Agilent 1200 HPLC system with 90% MeOH, 10% H₂O with 0.1% TFA as the carrier stream. All solvents used were HPLC grade or better.

Porphyrin Synthesis



5,15-Bis(ethynyl)-10,20-bis(2,6-di(*n*-hexoxy)phenyl)porphyrinato zinc(II) (i). Meso-(2,6-di(*n*-hexoxy)phenyl)dipyrromethane¹ (1.00 g, 2.37 mmol), and trimethylsilylpropanal (0.350 mL, 2.38 mmol) were dissolved in 400 mL of dichloromethane. The resulting solution was degassed for 5 min at 0 °C. Boron trifluoride diethyl etherate (60.0 μL, 0.476 mmol) was added slowly and the reaction mixture was allowed to stir under nitrogen atmosphere for 5 min at 0 °C. 2,3-dicyano-5,6-dichloro-parabenzoquinone (0.570 g, 2.51 mmol) was then added and, after stirring for 30 min, 2.00 mL of pyridine was also added. The precipitates were filtered off and the volatiles were removed under reduced pressure. The resulting residue was purified by silica-

gel column chromatography (hexanes/dichloromethane (1:1 v/v)) to afford 10,20-bis(2,6-di(*n*-hexoxy)phenyl)-5,15-bis(trimethylsilyl)ethynylporphyrin which was further metallated with zinc(II) acetate according to literature procedure to afford 10,20-bis(2,6-di(*n*-hexoxy)phenyl)-5,15-bis(trimethylsilyl)ethynylporphyrinato zinc.

200 mg (0.179 mmol) of 10,20-bis(2,6-di(*n*-hexoxy)phenyl)-5,15-bis(trimethylsilyl)ethynylporphyrinato zinc obtained from the above reaction was treated with tetra-*n*-butylammonium fluoride (1 M in tetrahydrofuran, 0.400 mL, 0.400 mmol) in tetrahydrofuran (15 mL) for 20 min. After workup, the deep green crude product was purified by silica-gel column chromatography (hexanes/tetrahydrofuran (7:3 v/v)) to afford **i** (158 mg, 23.0 % overall yield). ¹H NMR (CDCl₃): 9.63 (d, 4 H, *J* = 3.8 Hz), 8.88 (d, 4 H, *J* = 3.8 Hz), 7.69 (t, 2 H, *J* = 8.5 Hz), 6.99 (d, 4 H, *J* = 8.5 Hz), 4.09 (s, 2 H), 3.83 (t, 8 H, *J* = 6.8 Hz), 0.92 (m, 8 H), 0.50 (m, 16 H), 0.36 (m, 8 H), 0.23 (t, 12 H, *J* = 6.8 Hz). MS (MALDI-ToF) *m/z* 972.2 (Calcd *m/z* 972.5 for M⁺).

10,20-Bis(2,6-di(*n*-hexoxy)phenyl)-5-ethynyl-15-(triisopropylsilyl)ethynylporphyrinato

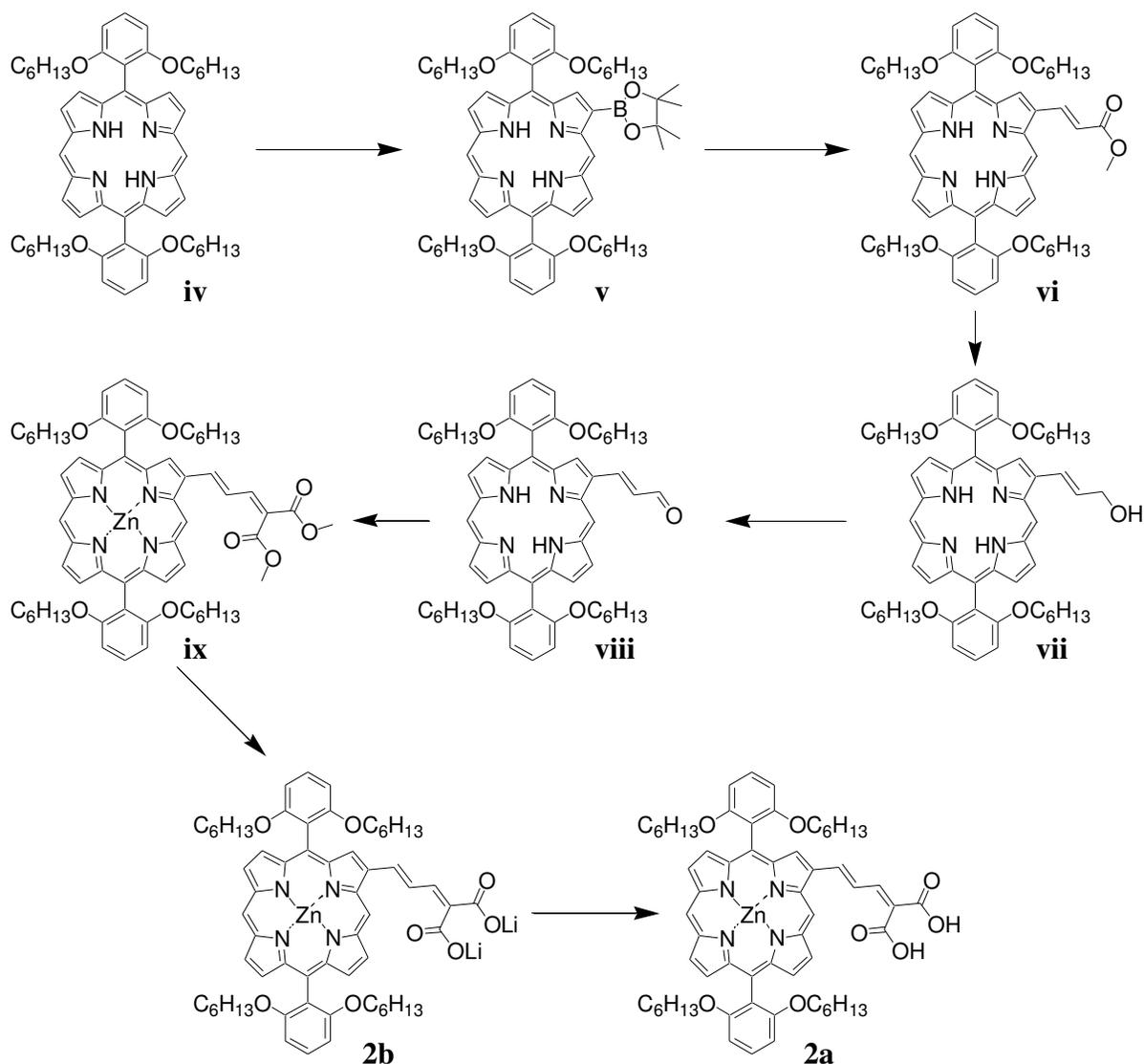
zinc(II) (ii). A solution of **i** (125 mg, 0.129 mmol) in tetrahydrofuran (8.00 mL) was allowed to cool to -78 °C and *n*-butyllithium (1.6 M in hexane, 80.0 μL, 0.128 mmol) was added slowly. After the addition was complete, the reaction mixture was allowed to warm to room temperature. The reaction mixture was again cooled to -78 °C and triisopropylsilylchloride (32.5 μL, 0.153 mmol) was added dropwise. After stirring for 15 min at -78 °C, the reaction mixture was warmed to room temperature and stirred for 6 h. The volatiles were removed under reduced pressure and the residue was extracted with dichloromethane. The extract was washed with water, dried over anhydrous magnesium sulfate and evaporated to dryness under reduced pressure to afford a deep green oily product which was purified by silica-gel column chromatography (hexanes/tetrahydrofuran (9:1 v/v)) to afford pure **ii** (67.0 mg, 46.0 %). ¹H NMR (CDCl₃): 9.66 (d, 2 H, *J* = 4.7 Hz), 9.61 (d, 2 H, *J* = 4.6 Hz), 8.86 (d, 4 H, *J* = 4.7 Hz), 7.68 (t, 2 H, *J* = 8.4 Hz), 6.98 (d, 4 H, *J* = 8.2 Hz), 4.08 (s, 1 H), 3.83 (t, 8 H, *J* = 6.5 Hz), 1.42 (m, 18 H), 1.01 (m, 3 H), 0.92 (m, 8 H), 0.52 (m, 16 H), 0.39 (m, 8 H), 0.27 (t, 12 H, *J* = 6.2 Hz). MS (MALDI-ToF) *m/z* 1128.1 (Calcd *m/z* 1128.6 for M⁺).

Methyl 4-(10,20-bis(2,6-di(*n*-hexoxy)phenyl)-5-ethynyl-15-(triisopropylsilyl)ethynylporphyrinato zinc(II))ethynylbenzoate (iii). A solution of **ii** (60.0 mg, 53.1 μmol) and methyl 4-

bromobenzoate (25.0 mg, 0.116 mmol) in toluene (25.0 mL) and triethylamine (5.00 mL) was degassed for 10 min. Tris(dibenzylideneacetone)dipalladium(0) (12.3 mg, 13.4 μmol) and triphenylphosphine (28.0 mg, 0.107 mmol) were added all at once and the mixture was warmed to 85 °C. After 1 h, the solution was cooled to room temperature and solvent was removed under reduced pressure. The product was purified and separated from a starting porphyrin dimer species using silica-gel column chromatography (hexanes/dichloromethane (4:6 v/v)) to afford **iii** as a dark green solid (15.6 mg, 23.2 %). ^1H NMR (CDCl_3): 9.68 (d, 2 H, $J = 4.3$ Hz), 9.67 (d, 2 H, $J = 4.3$ Hz), 8.90 (d, 2 H, $J = 4.7$ Hz), 8.88 (d, 2 H, $J = 4.7$ Hz), 8.18 (d, 2 H, $J = 8.2$ Hz), 8.02 (d, 2 H, $J = 8.2$ Hz), 7.69 (t, 2 H, $J = 8.4$ Hz), 6.99 (d, 4 H, $J = 8.4$ Hz), 3.99 (s, 3 H), 3.85 (t, 8 H, $J = 6.3$ Hz), 1.43 (m, 18 H), 0.97 (m, 3 H), 0.92 (m, 8 H), 0.51 (m, 16 H), 0.37 (m, 8 H), 0.22 (t, 12 H, $J = 7.0$ Hz). MS (MALDI-ToF) m/z 1262.2 (Calcd m/z 1262.6 for M^+).

4-(5-Ethynyl-10,20-bis(2,6-di(n-hexoxy)phenyl)-15-(triisopropylsilyl)ethynylporphyrinato zinc(II)ethynylbenzoic potassium salt (1b) and 4-(5-ethynyl-10,20-bis(2,6-di(n-hexoxy)phenyl)-15-(triisopropylsilyl)ethynylporphyrinato zinc(II)ethynylbenzoic acid (1a). Porphyrin **iii** (15.0 mg, 12.0 μmol) and potassium trimethylsilonate (4.60 mg, 35.9 μmol) were dissolved in tetrahydrofuran (2.50 mL) and allowed to stir at room temperature for 24 h. TLC analysis indicated that all starting material had been consumed. The mixture was diluted with dichloromethane (10.0 mL) and washed twice with water. Solvent was removed under reduced pressure to afford **1b** as a dark green solid (15.3 mg, 98.9 %). The ^1H NMR spectrum in CDCl_3 was identical to the acid form **1a** (see below). MS (MALDI-ToF) m/z 1287.0 (Calcd m/z 1286.7 for M^+). The product salt dissociated to acid form in the ESI ion source: MS (ESI) 1249.6127 (Calcd m/z 1249.6156 for $(\text{M}+\text{H})^+$).

Porphyrin salt **1b** (6.00 mg, 4.65 μmol) was dissolved in dichloromethane (5.00 mL) and washed three times with acidified water (67.6 mM aqueous phosphoric acid, 3 x 10 mL, pH ~ 2). Organic solvent was removed under reduced pressure to afford **1a** as a dark green solid (5.80 mg, 100 %). ^1H NMR (CDCl_3): 9.67 (d, 4 H, $J = 4.7$ Hz), 8.91 (d, 2 H, $J = 4.3$ Hz), 8.87 (d, 2 H, $J = 4.3$ Hz), 8.18 (d, 2 H, $J = 6.6$ Hz), 8.06 (d, 2 H, $J = 6.6$ Hz), 7.70 (t, 2 H, $J = 8.6$ Hz), 7.00 (d, 4 H, $J = 8.6$ Hz), 3.85 (t, 8 H, $J = 6.3$ Hz), 1.42 (m, 18 H), 0.95 (m, 11 H), 0.51 (m, 16 H), 0.37 (m, 8 H), 0.23 (t, 12 H, $J = 6.6$ Hz). MS (MALDI-ToF) m/z 1248.1 (Calcd m/z 1248.6 for M^+), MS (ESI) 1249.6116 (Calcd m/z 1249.6156 for $(\text{M}+\text{H})^+$).



5,15-Bis(2,6-di(n-hexoxy)phenyl)porphyrin (iv). Dipyrromethane² (1.00 g, 6.84 mmol) and 2,6-di(n-hexoxy)benzaldehyde¹ (2.10 g, 6.85 mmol) were dissolved in 1.20 L of dichloromethane. The resulting solution was degassed for 10 min at room temperature. Trifluoroacetic acid (330 μ L, 4.44 mmol) was slowly added and the resulting mixture was allowed to reflux for 8 h. Two grams (8.81 mmol) of 2,3-dicyano-5,6-dichloro-parabenzoquinone was then added and the reaction mixture was refluxed for an additional 1 h. After cooling, 7.00 mL of pyridine was added. The precipitate was filtered off and the volatiles were removed under reduced pressure. The resulting residue was purified by silica-gel column chromatography (hexanes/dichloromethane (1:1 v/v)) to afford pure **iv** as a purple solid (865 mg, 29.3 %). ¹H NMR (CDCl₃): 10.15 (s, 2 H), 9.26 (d, 4 H, *J* = 4.4 Hz), 8.97 (d, 4 H, *J* = 4.4 Hz),

7.71 (t, 2 H, $J = 8.4$ Hz), 7.02 (d, 4 H, $J = 9.5$ Hz), 3.83 (t, 8 H, $J = 6.2$ Hz), 0.90 (m, 8 H), 0.50 (m, 16 H), 0.40 (m, 8 H), 0.24 (m, 12 H), -3.00 (s, 2H). MS (MALDI-ToF) m/z 862.2 (Calcd m/z 862.5 for M^+).

5,15-Bis(2,6-di(*n*-hexoxy)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)porphyrin (v). Synthesis was conducted according to modified literature procedure.³ To a solution of **iv** (800 mg, 0.927 mmol) in 1,4-dioxane (8.00 mL) was added bis(pinacolato)diborane (117 mg, 0.463 mmol), 4,4'-di-*tert*-butyl-2,2'-bipyridyl (24.9 mg, 92.7 μ mol), and di- μ -methoxobis(1,5-cyclooctadiene)diiridium(I) (24.5 mg, 37.1 μ mol). The mixture was refluxed for 24 h and subsequently dried under reduced pressure. Silica-gel column chromatography (hexanes/tetrahydrofuran (9:1 v/v)) was used to separate unreacted **iv** and diborylated side product from the monoborylated product **v**, isolated as a dark purple solid. (318 mg, 34.7 %). ¹H NMR (CDCl₃): 10.88 (s, 1 H), 10.09 (s, 1 H), 9.54 (s, 1 H), 9.35 (d, 1 H, $J = 4.4$ Hz), 9.25 (d, 1 H, $J = 5.1$ Hz), 9.22 (d, 1 H, $J = 5.1$ Hz), 8.97 (d, 1 H, $J = 4.4$ Hz), 8.96 (d, 1 H, $J = 4.4$ Hz), 8.93 (d, 1 H, $J = 4.4$ Hz), 7.71 (t, 1 H, $J = 8.4$ Hz), 7.70 (t, 1 H, $J = 8.5$ Hz), 7.03 (d, 2 H, $J = 8.0$ Hz), 7.01 (d, 2 H, $J = 8.0$ Hz), 3.84 (t, 4 H, $J = 6.2$ Hz), 3.83 (t, 4 H, $J = 6.2$ Hz), 1.69 (s, 12 H), 0.92 (m, 8 H), 0.53 (m, 16 H), 0.43 (m, 8 H), 0.26 (m, 12 H), -2.86 (s, 2 H). MS (MALDI-ToF) m/z 988.3 (Calcd m/z 988.6 for M^+).

Methyl 3-*trans*-(5,15-bis(2,6-di(*n*-hexoxy)phenyl)porphyrin-2-yl)acrylate (vi). Synthesis was conducted according to modified literature procedure.⁴ Mono-borylated porphyrin **v** (300 mg, 0.303 mmol), methyl acrylate (55.0 μ L, 0.607 mmol), sodium carbonate (64.5 mg, 0.608 mmol), and palladium (II) acetate (6.80 mg, 30.3 μ mol) were dissolved in dimethylformamide (20 mL) and heated at 50 °C under O₂ for 12 h. The mixture was subsequently cooled to room temperature, diluted with ethyl acetate, washed with brine, dried over magnesium sulfate, filtered, and finally dried under reduced pressure. The resulting solid was purified by silica-gel column chromatography (hexanes/tetrahydrofuran (4:1 v/v)) to afford pure **vi** as a purple solid (160 mg, 55.7 %). ¹H NMR (CDCl₃): 10.34 (s, 1 H), 10.10 (s, 1 H), 9.42 (d, 1 H, $J = 15.4$ Hz), 9.36 (d, 1 H, $J = 5.1$ Hz), 9.27 (d, 1 H, $J = 4.4$ Hz), 9.22 (s, 1 H), 9.21 (d, 1 H, $J = 5.1$ Hz), 9.00 (d, 2 H, $J = 4.4$ Hz), 8.94 (d, 1 H, $J = 4.4$ Hz), 7.75 (t, 1 H, $J = 8.4$ Hz), 7.72 (t, 1 H, $J = 8.4$ Hz), 7.16 (d, 1 H, $J = 15.4$), 7.05 (d, 2 H, $J = 8.8$ Hz), 7.03 (d, 2 H, $J = 8.8$ Hz), 4.02 (s, 3 H), 3.87 (t,

4 H, $J = 5.9$ Hz), 3.86 (t, 4 H, $J = 5.9$ Hz), 0.93 (m, 8 H), 0.51 (m, 16 H), 0.43 (m, 8 H), 0.24 (m, 12 H), -2.75 (s, 2 H). MS (MALDI-ToF) m/z 947.2 (Calcd m/z 946.6 for M^+).

3-(5,15-Bis(2,6-di(*n*-hexoxy)phenyl)porphyrin-2-yl)allylhydroxide (vii). A solution of **vi** (150 mg, 0.158 mmol) in toluene (8.50 mL) was cooled to -78 °C and a 1 M solution of diisobutylaluminium hydride in toluene (555 μ L, 0.555 mmol) was added dropwise. After 1h at -78 °C, the mixture was warmed to room temperature and left for 3h. Methanol (2.50 mL) and a 10% solution of aqueous sodium hydroxide (8.50 mL) were added and the reaction mixture was subsequently diluted with ethyl acetate and washed three times with brine, dried over magnesium sulfate, filtered, and the solvents were removed under reduced pressure. The resulting solid was purified by silica-gel column chromatography (hexanes/tetrahydrofuran/dichloromethane (4:1:2 v/v)) to afford **vii** as a purple solid (63.0 mg, 43.4 %). ^1H NMR (CDCl_3): 10.25 (s, 1 H), 10.11 (s, 1 H), 9.29 (d, 1 H, $J = 4.3$ Hz), 9.25 (d, 2 H, $J = 5.1$ Hz), 9.00 (s, 1 H), 8.98 (d, 1 H, $J = 4.4$ Hz), 8.975 (d, 1 H, $J = 16.1$ Hz), 8.97 (d, 2 H, $J = 4.4$ Hz), 7.74 (t, 1 H, $J = 8.0$ Hz), 7.72 (t, 1 H, $J = 8.1$ Hz), 8.27 (d, 1 H, $J = 16.1$ Hz), 7.05 (d, 2 H, $J = 8.8$ Hz), 7.03 (d, 2 H, $J = 8.1$ Hz), 3.86 (t, 4 H, $J = 5.8$ Hz), 3.85 (t, 4 H, $J = 5.8$ Hz), 3.71 (t, 2 H, $J = 5.8$ Hz), 0.93 (m, 9 H), 0.53 (m, 16 H), 0.43 (m, 8 H), 0.25 (m, 12 H), -2.85 (s, 2 H). MS (MALDI-ToF) m/z 919.2 (Calcd m/z 918.6 for M^+).

3-(5,15-Bis(2,6-di(*n*-hexoxy)phenyl)porphyrin-2-yl)allylaldehyde (viii). A solution of **vii** (50.0 mg, 54.4 μ mol) and manganese dioxide (213 mg, 2.45 mmol) in toluene (6.50 mL) was heated at reflux. After 45 min the reaction was cooled to room temperature and the solution was filtered over celite, diluting with dichloromethane. Solvents were removed under reduced pressure and the resulting solid was purified by silica-gel column chromatography (hexanes/tetrahydrofuran/dichloromethane (5:1:1 v/v)) to afford **viii** as a purple solid (37.3 mg, 74.8 %). ^1H NMR (CDCl_3): 10.28 (s, 1 H), 10.18 (d, 1 H, $J = 8.1$ Hz), 10.08 (s, 1 H), 9.35 (d, 1 H, $J = 4.4$ Hz), 9.27 (d, 1 H, $J = 4.4$ Hz), 9.26 (s, 1H), 9.18 (d, 1 H, $J = 4.4$ Hz), 9.18 (d, 1 H, $J = 15.4$ Hz), 9.01 (d, 1 H, $J = 3.6$ Hz), 9.00 (d, 1H, $J = 3.6$ Hz), 8.90 (d, 1 H, $J = 4.4$ Hz), 7.75 (t, 1 H, $J = 8.4$ Hz), 7.71 (t, 1 H, $J = 8.4$ Hz), 7.44 (dd, 1 H, $J = 15.4$ Hz, $J = 8.1$ Hz), 7.03 (d, 2 H, $J = 8.0$ Hz), 7.02 (d, 2 H, $J = 8.0$ Hz), 3.86 (t, 4 H, $J = 6.2$ Hz), 3.85 (t, 4 H, $J = 6.2$ Hz), 0.91 (m, 8 H), 0.49

(m, 16 H), 0.40 (m, 8 H), 0.21 (m, 12 H), -2.69 (s, 2 H). MS (MALDI-ToF) m/z 917.3 (Calcd m/z 916.6 for M^+).

Methyl 5-(5,15-bis(2,6-di(*n*-hexoxy)phenyl)porphyrinato zinc(II)-2-yl)-2-methoxycarbonyl penta-2,4-dienoate (ix). A solution of **viii** (25.0 mg, 27.3 μ mol), dimethylmalonate (18.7 μ L, 0.164 mmol), and ammonium acetate (12.6 mg, 0.164 mmol) in 1:1 acetic acid and tetrahydrofuran (2.50 mL) was heated to 70 °C. After 2 d, zinc acetate (20.0 mg, 0.109 mmol) was added and, after an additional 30 min at 70 °C, the solution was cooled to room temperature, diluted with dichloromethane and washed twice with water. The organic layer was reduced under vacuum to a dark green solid which was then purified by silica-gel chromatography (hexanes/tetrahydrofuran/dichloromethane (5:1:1 v/v)) to afford pure **ix** (21.6 mg, 72.3 %). ^1H NMR (CDCl_3): 10.26 (s, 1 H), 10.08 (s, 1 H), 9.33 (d, 1 H, $J = 4.4$ Hz), 9.29 (s, 1H) 9.28 (d, 1 H, $J = 4.4$ Hz), 9.26 (d, 1 H, $J = 4.4$ Hz), 9.02 (d, 1 H, $J = 4.4$ Hz), 9.01 (d, 1 H, $J = 4.4$ Hz), 9.00 (d, 1 H, $J = 4.4$ Hz), 8.87 (d, 1H, $J = 15.4$ Hz), 8.12 (d, 1 H, $J = 11.8$ Hz), 7.96 (dd, 1 H, $J = 15.4$ Hz, $J = 11.8$ Hz), 7.74 (t, 1 H, $J = 8.4$ Hz), 7.71 (t, 1 H, $J = 8.4$ Hz), 7.05 (d, 2 H, $J = 8.8$ Hz), 7.02 (d, 2 H, $J = 8.8$ Hz), 4.01 (s, 3 H), 3.93 (s, 3 H), 3.86 (t, 4 H, $J = 6.6$ Hz), 3.84 (t, 4 H, $J = 6.6$ Hz), 0.90 (m, 8 H), 0.43 (m, 16 H), 0.32 (m, 8 H), 0.16 (m, 12 H). MS (MALDI-ToF) m/z 1092.2 (Calcd m/z 1092.5 for M^+).

5-(5,15-bis(2,6-di(*n*-hexoxy)phenyl)porphyrinato zinc(II)-2-yl)-2-carboxypenta-2,4-dienoic dilithium salt (2b) and 5-(5,15-Bis(2,6-di(*n*-hexoxy)phenyl)porphyrinato zinc(II)-2-yl)-2-carboxypenta-2,4-dienoic acid (2a). A mixture of **ix** (20.0 mg, 18.3 μ mol) dissolved in tetrahydrofuran (5.00 mL), and lithium hydroxide monohydrate (3.07 mg, 73.1 μ mol) in water (0.10 mL) were stirred overnight at room temperature. TLC analysis indicated that all starting material had been consumed. The mixture was diluted with dichloromethane (10.0 mL) and washed twice with water. Solvent was removed under reduced pressure to afford **2b** as a dark green solid (19.4 mg, 98.0 %). The ^1H NMR spectrum in d_6 -DMSO was identical to the acid form **2a** (see below). MS (MALDI-ToF) m/z 1076.7 (Calcd m/z 1076.5 for M^+). The product salt dissociated to acid form in the ESI ion source: MS (ESI) m/z 1064.4613 (Calcd m/z 1064.4642 for M^+).

Porphyrin salt **2b** (10.0 mg, 9.27 μmol) was dissolved in dichloromethane (5.00 mL) and washed three times with acidified water (67.6 mM aqueous phosphoric acid, 3 x 10 mL, pH ~ 2). Organic solvent was removed under reduced pressure to afford **2a** as a dark green solid (9.89 mg, 100 %). ^1H NMR (d_6 -DMSO): 10.43 (s, 1 H), 10.06 (s, 1 H), 9.29 (d, 1 H, $J = 4.7$ Hz), 9.27 (s, 1 H), 9.27 (d, 1 H, $J = 4.7$ Hz), 9.17 (d, 1 H, $J = 14.9$ Hz), 9.01 (m, 2 H), 8.76 (d, 1H, $J = 4.7$ Hz), 8.75 (d, 1 H, $J = 4.4$ Hz), 8.09 (d, 1 H, $J = 12.1$ Hz), 7.78 (t, 1 H, $J = 8.2$ Hz), 7.74 (t, 1 H, $J = 8.0$ Hz), 7.02 (appt t, 1 H, $J = 11.2$ Hz), 7.15 (d, 2 H, $J = 8.6$ Hz), 7.12 (d, 2 H, $J = 8.6$ Hz), 3.84 (t, 8 H, $J = 6.3$ Hz), 0.87 (m, 8 H), 0.49 (m, 24 H), 0.28 (m, 12 H). MS (MALDI-ToF) m/z 1064.1, MS (ESI) m/z 1064.4636 (Calcd m/z 1064.4642 for M^+).

Fluorescence Upconversion Measurements

A 100-250 kHz Coherent RegA system centered at 790 nm was used. Part of the light was frequency doubled to create the 395 nm pump light while another portion of the light was used as the 795 nm gate pulse. Both the 395 nm and 795 nm beams were directed into the Ultrafast System Halcyone fluorescence setup. The 790 nm beam was directed to a retroreflector attached to a variable translation stage. The 395 nm light was focused into a 2 mm cuvette containing the solutions studied. The solutions were stirred using a small magnetic stirrer to minimize effects such as heating and sample degradation. The solution samples were studied within a few hours of after they were dissolved. The fluorescence signals passed through a longpass filter with a 420 nm cutoff. The fluorescence light and the 790 nm light were then focused onto a BBO crystal cut to optimize the sum frequency generation (SFG) of the signal. The SFG signals were created when the fluorescence and gate pulses were combined in the crystals, and were directed into a monochromator and single photon counting PMT setup. The instrument response function was less than 500 fs. The kinetics traces were obtained by varying the time delay between the excitation pulse and the gate pulse through moving the variable translation stage connected with the gate pulse. The detection wavelengths were changed using the monochromator. Since the efficiency of the SFG changes as a function of the wavelength, the crystal angle is optimized for each kinetics trace at the different wavelengths.

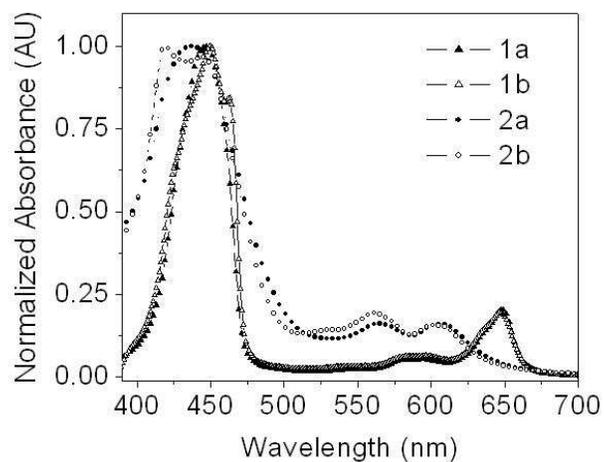


Figure S1. Absorption spectra of **1a**, **1b**, **2a**, **2b** adsorbed on ZnO nanotubes. The peaks in the 400 -500 nm region are Soret bands, and the peaks in the 550 – 680 nm are Q bands.

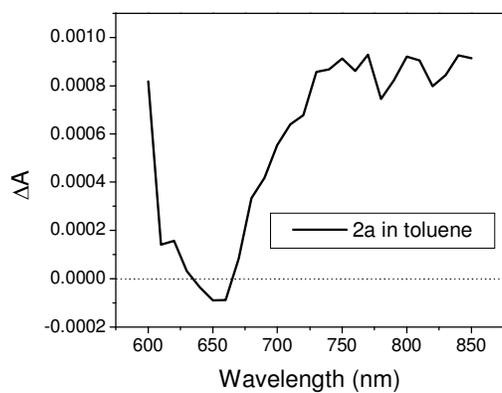


Figure S2. Transient absorption spectrum of **2a**, at 100 ps excited at 400 nm.

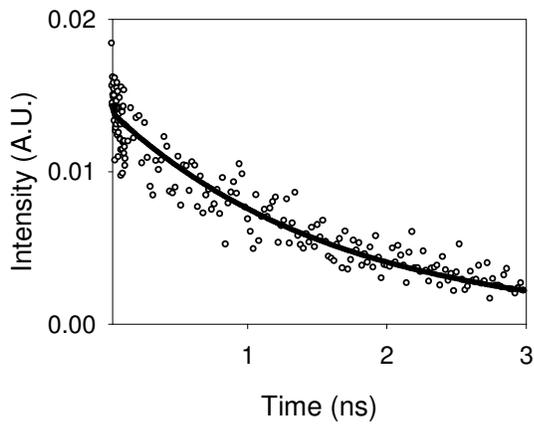


Figure S3. Fluorescence decay of 2a in toluene monitored at 660 nm by the upconversion technique. Dots are data and the solid line is a single exponential fit with a lifetime of 1.6 ns.

References

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