

Supporting information for:

Synthesis and properties of push-pull porphyrins as sensitizers for NiO based dye-sensitized solar cells

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Synthesis of the dyes

General Remarks

¹H and ¹³C NMR spectra were recorded on an AVANCE 300 UltraShield BRUKER, AVANCE 400 BRUKER or AVANCE III 500 BRUKER. Chemical shifts for ¹H NMR spectra are referenced relative to residual protium in the deuterated solvent (**CDCl₃** δ = 7.26 ppm for ¹H and δ = 77.16 ppm for ¹³C; **THF-d₈** δ = 3.57, 1.72 ppm for ¹H and δ = 25.4, 67.6 ppm for ¹³C; **MeOD-d₄** δ = 3.31 ppm for ¹H and δ = 49.0 ppm for ¹³C. Spectra were recorded at room temperature, chemical shifts are written in ppm and coupling constants in Hz. High-resolution mass (HR-MS) spectra were obtained either by electrospray ionization coupled with high resolution ion trap orbitrap (LTDQ-Orbitrap, ThermoFisher Scientific,) or by MALDI-

TOF-TOF (Autoflex III, Bruker), both working in ion-positive mode and with 2,5-dihydroxybenzoic acid (DHB) or dithranol as matrix.

Electrochemical measurements were performed with a potentiostat-galvanostat *AutoLab PGSTAT 302N* controlled by resident GPES software (General Purpose Electrochemical System 4.9) using a conventional single-compartment three-electrode cell. The working electrode was a glassy carbon or a platinum electrode. The auxiliary electrode was a Pt plate of 1 cm² and the reference electrode was the saturated calomel electrode (SCE). The supporting electrolyte was 0.1 N *n*-Bu₄NPF₆ (TBAP) in adapted dry solvent and solutions were purged with argon before the measurements. All potentials are quoted relative to SCE. In all the experiments the scan rate was 100 mV/s.

UV-Visible absorption spectra were recorded on a *UV-2401PC Shimadzu* spectrophotometer. Fluorescence spectra were recorded on a *SPEX Fluoromax* fluorimeter.

Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with Merck 5735 Kieselgel 60F254. Column chromatography was carried out either with Merck 5735 Kieselgel 60F (0.040-0.063 mm mesh), or with CombiFlash[®]Rf. apparatus.

Compounds **2**, **4**, **5**, **8**, **10** and **18** were purchased from Sigma-Aldrich or Alfa Aesar and used as received.

General procedure for Suzuki's coupling

To a sealed tube containing the halogenated reactant, the boronic acid (5 eq.) and Ba(OH)₂·H₂O (2 eq.), a mixture of THF and H₂O (6.5 mM) (3/1 v/v) was added under argon. After the solution was degased using freeze-pump-thaw technic, Pd(PPh₃)₄ (5% mol) was added and the reaction was heated at 80 °C overnight. After being cooled down to room temperature, the crude mixture was filtrated over celite and solvents were evaporated. Purification on silica gel gave desired compound.

General procedure for Sonogashira's coupling

To a sealed tube containing the alkyne and the halogenated reactant (5eq), THF (6mM) and Et₃N (100 eq) were added under argon. After the solution was degased using freeze-pump-thaw technic, AsPh₃ (2eq) and Pd₂(dba)₃.CHCl₃ (5% mol) were added and the reaction was heated at 80 °C overnight. After being cooled down to room temperature, water was added. Organic phase was collected with DCM, washed with water and dried over Na₂SO₄. Evaporation of the solvents and purification on silica gel gave desired compound.

5-(4-nitro-phenyl)ethynyl-15-bromo-10,20-bis[2,6-di(dodecyloxy)phenyl] porphyrin – Compound 3

Under an argon atmosphere, porphyrin **1** (150 mg, 0.106 mmol), copper iodide (2.0 mg, 0.011 mmol) and 1-ethynyl-4-nitrobenzene **2** (15.5 mg, 0.106 mmol) were mixed in anhydrous tetrahydrofuran (21 ml) with triethylamine (8 ml). The resulting solution was freed from O₂ by three freeze-pump-thraw cycles and Pd(PPh₃)₄ (12.2 mg, 0.011 mmol) was added. Then the solution was heated to reflux for 1 h. Solvent was removed under vacuum and the crude was purified by flash column chromatography (silica gel, Petroleum ether/Dichloromethane, 7/3) to afford a purple solid (27.0 mg, 17%). ¹H NMR (400 MHz, THF-d₈): δ_H = 9.61 (d, *J* = 4.6 Hz, 2H), 9.49 (d, *J* = 4.6 Hz, 2H), 8.82 (d, *J* = 4.6 Hz, 2H), 8.73 (d, *J* = 4.6 Hz, 2H), 8.44 (d, *J* = 8.9 Hz, 2H), 8.21 (d, *J* = 8.8 Hz, 2H), 7.71 (t, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 4H), 3.89 (t, *J* = 6.5 Hz, 8H), 1.28-1.18 (8H, m), 1.18-1.09 (16H, m), 1.09-0.95 (16H, m), 0.95-0.89 (16H, m), 0.89-0.78 (8H, m and 12H, t, ³*J* = 7.1 Hz), 0.78-0.65 (8H, m), 0.65-0.54 (8H, m). ¹³C NMR (100 MHz, THF-d₈): δ_C = 161.0, 153.3, 152.6, 151.6, 149.5, 149.2, 147.8, 136.2, 134.4, 133.3, 132.9, 132.6, 130.8, 130.7, 129.2, 129.0, 128.3, 124.8, 124.6, 121.6, 116.3, 106.3, 105.5, 101.0, 97.1, 94.4, 82.3, 77.7, 69.1, 32.8, 30.5, 30.4, 30.3, 30.2, 30.1, 29.8, 29.7, 26.3, 23.5, 14.4. MALDI-TOF: *m/z* calculated for 1483.7552 [M]⁺, Found 1483.7584 [M]⁺, Δ = 2.2 ppm.

5-(4-nitro-phenyl)ethynyl-15-(4-carboxy-phenyl)ethynyl-10,20-bis[2,6-di(dodecyloxy)phenyl]

porphinato-zinc(II) – ZnP-eCO₂H-eNO₂

Following general procedure for Sonogashira's coupling, porphyrin **3** (35.0 mg, 0.027 mmol) was reacted with 4-ethynylbenzoic acid (15,6 mg, 0.107 mmol), AsPh₃ (25 mg, 0.080 mmol) and Pd₂dba₃.CHCl₃ (8.3 mg, 0.008 mmol, 3%) in 0.85 ml of Et₃N and 4 ml of THF at 80°C overnight in a sealed tube. Purification on a short column of silica (Dichloromethane/Methanol 98/2) gave the desired compound as a green solid (12 mg, 33%). ¹H NMR (400 MHz, THF-d₈): δ_H = 9.62 (d, *J* = 4.5 Hz, 2H), 9.61 (d, *J* = 4.5 Hz, 2H), 8.80 (d, *J* = 4.5 Hz, 2H), 8.78 (d, *J* = 4.5 Hz, 2H), 8.44 (d, *J* = 8.9 Hz, 2H), 8.23 (d, *J* = 8.9 Hz, 2H), 8.22 (d, *J* = 8.4 Hz, 2H), 8.09 (d, *J* = 8.5 Hz, 2H), 7.71 (t, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 4H), 3.89 (t, *J* = 6.6 Hz, 8H), 1.23-1.15 (8H, m), 1.15-1.04 (16H, m), 1.04-0.88 (24H, m), 0.88-0.77 (8H, m and 12H, t, ³*J* = 7.1 Hz), 0.77-0.65 (16H, m), 0.65-0.56 (8H, m). ¹³C NMR (100 MHz, THF-d₈): δ_C = 160.0, 151.4, 151.3, 150.9, 150.8, 146.9, 131.9, 131.8, 131.7, 131.5, 131.3, 130.9, 129.9, 129.8, 129.7, 129.6, 128.9, 128.2, 128.1, 123.8, 120.7, 115.8, 104.6, 96.7, 94.8, 68.1, 31.8, 29.5, 29.4, 29.3, 29.2, 28.8, 28.6, 25.4, 24.8, 24.7, 13.4. MALDI-TOF: *m/z* calculated for 1549.8658 [M]⁺, Found 1549.8614 [M]⁺, Δ = 2.8 ppm.

5-(4-nitro-phenyl)ethynyl-15-(4-methoxycarbonyl-phenyl)-10,20-bis[2,6-di(dodecyloxy)phenyl]

porphyrin – Compound 6

Following general procedure for Suzuki's coupling, porphyrin **3** (43 mg, 0.029 mmol), 4-methoxycarbonylphenylboronic acid **5** (26 mg, 0.14 mmol), barium hydroxide (18 mg, 0.060 mmol) and Pd(PPh₃)₄ (2 mg, 1.73 μmol) in 4 ml of a mixture of THF and H₂O (3/1 v/v) were reacted. After evaporation of the solvents, treatment with HCl conc. followed by neutralisation with H₂O permits to afford the crude free base porphyrin. Purification on silica gel (Petroleum ether/Dichloromethane, 7/3 to 5/5) gave compound **6** (22 mg, 51 %). ¹H NMR (400 MHz, CDCl₃): δ_H = 9.58 (d, *J* = 4.7 Hz, 2H), 8.91 (d, *J* = 4.7 Hz, 2H), 8.74 (d, *J* = 4.7 Hz, 2H), 8.62 (d, *J* = 4.7 Hz, 2H), 8.41 (d, *J* = 8.4 Hz, 2H), 8.29 (d, *J* = 8.4

Hz, 2H), 7.92 (bs, 2H), 7.72 (t, $J = 8.5$ Hz, 2H), 7.66 (bs, 2H), 7.02 (d, $J = 8.5$ Hz, 4H), 4.11 (s, 3H), 3.87 (t, $J = 6.5$ Hz, 8H), 1.17 (m, 8H), 1.05 (m, 26H), 0.93 (br, 8H), 0.84 (br, 12H), 0.80 (t, $J = 7.3$ Hz, 12H), 0.71 (br, 8H), 0.60 (br, 18H), 0.52 (br, 8H), -2.24 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): $\delta_{\text{C}} = 167.5, 160.2, 147.4, 146.3, 134.5, 131.4, 131.0, 130.4, 129.6, 127.9, 123.6, 120.1, 119.8, 114.7, 105.3, 98.9, 96.6, 94.2, 68.8, 32.0, 29.6, 29.5, 29.3, 29.2, 28.9, 28.8, 25.5, 22.5, 14.2$. MALDI-TOF: m/z calculated for 1478.9757 $[\text{M}]^+$, Found 1478.9801 $[\text{M}]^+$, $\Delta = 3.0$ ppm

5-(4-nitro-phenyl)ethynyl-15-(4-carboxy-phenyl)-10,20-bis[2,6-di(dodecyloxy)phenyl]porphinato-zinc(II) – ZnP-CO₂H-eNO₂

Compound **6** was dissolved in a mixture of DCM/MeOH (1/1) and $\text{Zn}(\text{OAc})_2$ (100 mg, excess) was added. The solution was then heated to reflux for 4h. After cooled down to RT, DCM and H_2O were added. The organic phase was washed with water, dried over Na_2SO_4 and solvents were evaporated giving us the desired zinc porphyrin. This latter was then dissolved in 9 ml of a mixture of THF/MeOH (8/1) and 1.4 ml of NaOH (1M) was added. The resulting solution was heated to reflux for 4h. After cooling down to RT, water was added followed by HCl (1M) until pH = 4. Extraction with DCM followed by washing of the organic phase with water gave desired porphyrin after the organic phase was dried over Na_2SO_4 and the solvents evaporated as a green powder (21 mg, 100%). ^1H NMR (400 MHz, THF-d₈): $\delta_{\text{H}} = 9.66$ (d, $J = 4.6$ Hz, 2H), 8.87 (d, $J = 4.6$ Hz, 2H), 8.71 (d, $J = 4.6$ Hz, 2H), 8.61 (d, $J = 4.6$ Hz, 2H), 8.39 (d, $J = 8.3$ Hz, 2H), 8.36 (d, $J = 8.6$ Hz, 2H), 8.25 (d, $J = 8.3$ Hz, 2H), 8.15 (d, $J = 8.6$ Hz, 2H), 7.69 (t, $J = 8.5$ Hz, 2H), 7.06 (d, $J = 8.5$ Hz, 4H), 3.88 (t, $J = 6.5$ Hz, 8H), 1.22 (m, 8H), 1.12 (m, 18H), 0.97 (m, 28H), 0.86 (br, 8H), 0.82 (t, $J = 7.3$ Hz, 12H), 0.71 (br, 18H), 0.60 (br, 8H). ^{13}C NMR (100 MHz, THF-d₈): $\delta_{\text{C}} = 167.7, 160.9, 152.7, 152.0, 151.19, 149.3, 149.0, 147.4, 134.9, 132.8, 132.5, 132.2, 131.5, 131.5, 130.7, 130.4, 130.2, 128.2, 124.5, 122.8, 121.4, 115.7, 105.4, 101.2, 96.4, 94.1, 68.9, 32.6, 30.4, 30.3, 30.2, 30.1, 30.0, 29.6, 29.5, 26.1, 23.3, 14.21$. MALDI-TOF: m/z calculated for 1525.8658 $[\text{M}]^+$, Found 1525.8608 $[\text{M}]^+$, $\Delta = 3.3$ ppm.

5-(tri-isopropylethynyl)-15-(4-nitro-phenyl)-10,20-bis[2,6-di(dodecyloxy)phenyl]porphyrin–

Compound 9

Following general procedure for Suzuki's coupling, porphyrin **7** (94 mg, 0.062 mmol) was reacted with 4-nitrophenylboronic acid **8** (52 mg, 0.310 mmol), Ba(OH)₂·H₂O (23 mg, 0.120 mmol) and Pd(PPh₃)₄ (4 mg, 3.5 μmol) in 9 ml of a mixture of THF/ H₂O (3/1). After the reaction mixture was heated at 80°C in a sealed tube for 12h, it was filtrated on celite and solvents were evaporated. Purification on silica column (Petroleum ether/Dichloromethane, 8/2) gave the desired compound (45 mg, 48 %). ¹H NMR (400 MHz, THF-d₈): δ_H = 9.60 (d, *J* = 4.7 Hz, 2H), 8.80 (d, *J* = 4.6 Hz, 2H), 8.74 (d, *J* = 4.7 Hz, 2H), 8.63 (d, *J* = 6.7 Hz, 2H), 8.60 (d, *J* = 4.6 Hz, 2H), 8.41 (d, *J* = 6.7 Hz, 2H), 7.70 (t, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 4H), 3.85 (t, *J* = 6.5 Hz, 8H), 1.50 (m, 18H), 1.19 (m, 8H), 1.07 (m, 18H), 0.93 (m, 8H), 0.88 (m, 8H), 0.82 (t, *J* = 7.1 Hz, 12H), 0.75 (m, 8H), 0.59 (m, 8H), 0.52 (m, 8H), 0.45 (m, 16H), -2.24 (s, 2H). ¹³C NMR (100 MHz, THF-d₈): δ_C = 160.8, 150.1, 148.6, 135.7, 131.0, 122.3, 120.6, 118.1, 115.2, 110.4, 105.7, 98.8, 97.4, 69.0, 32.6, 30.1, 30.0, 29.9, 29.8, 29.7, 29.3, 29.3, 25.9, 23.3, 19.4, 14.2, 12.7.

5-(4-carboxy-phenyl)ethynyl-15-(4-nitro-phenyl)-10,20-bis[2,6-di(dodecyloxy)phenyl]porphinato-zinc(II) – ZnP-eCO₂H-NO₂

Porphyrin **9** (45 mg, 0.030 mmol) was metallated by reaction with Zn(OAc)₂ (100 mg, excess) in 20 ml of a mixture of DCM/MeOH (1/1) at reflux. Water was added and the organic phase was isolated, washed with water, dried over Na₂SO₄ and solvents were evaporated. The triple bond was then deprotected by reaction of the porphyrin with TBAF (1M in THF) (45 ml, 0.045 μmol) in 5 ml THF at RT for 40 minutes. Water and DCM were added and the organic phase was isolated, washed with water and dried over Na₂SO₄ and solvents were evaporated.

Following general procedure for Sonogashira's coupling, porphyrin was reacted with 4-iodobenzoic acid **10** (15 mg, 0.060 mmol), AsPh₃ (18 mg, 0.060 mmol) and Pd₂dba₃·CHCl₃ (2 mg, 1.9 μmol) in 0.5 ml

of Et₃N and 5 ml of THF at 80°C overnight in a sealed tube. Purification on a short column of silica (Dichloromethane/Methanol, 99/1) gave the desired compound as a green solid (46 mg, 100%). ¹H NMR (400 MHz, THF-d₈): δ_H = 9.70 (d, *J* = 4.6 Hz, 2H), 8.87 (d, *J* = 4.6 Hz, 2H), 8.75 (d, *J* = 4.6 Hz, 2H), 8.62 (d, *J* = 4.5 Hz, 2H), 8.60 (m, 4H), 8.39 (d, *J* = 8.6 Hz, 2H), 8.24 (d, *J* = 8.3 Hz, 2H), 8.11 (d, *J* = 8.3 Hz, 2H), 7.70 (t, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 3.88 (t, *J* = 6.4 Hz, 8H), 1.22 (m, 8H), 1.12 (m, 18H), 0.95 (br, 28H), 0.84 (t, *J* = 7.1 Hz, 12H), 0.71 (br, 18H), 0.59 (br, 8H). ¹³C NMR (100 MHz, THF-d₈): δ_C = 167.2, 160.8, 152.7, 151.9, 151.6, 151.4, 148.9, 148.3, 135.7, 132.7, 131.9, 131.6, 131.0, 130.8, 130.6, 130.5, 129.8, 121.8, 121.7, 118.9, 115.6, 105.4, 98.1, 97.7, 95.1, 68.8, 32.6, 30.3, 30.2, 30.1, 30.0, 29.6, 29.5, 26.1, 23.3, 14.2. ESI+: *m/z* calculated for 1525.86576 [M]⁺, Found 1525.86597 [M]⁺, Δ = 0.14 ppm.

5-Bromo-15-(4-methoxycarbonyl-phenyl)-10,20-bis[2,6-di(dodecyloxy)phenyl] porphyrin –

Compound 13.

Porphyrin **12** (245 mg, 0.184 mmol) was dissolved in 75 ml of dry chloroform under argon atmosphere and freed from oxygen by argon bubbling while sonicating (15 min). Then the solution was cooled to 0°C and NBS (37.6 mg, 0.211 mmol) was added. After 1 hour of stirring at 0°C, 30 ml of acetone were added and the solvent was removed under reduced pressure. The concentrated crude was then purified by flash column chromatography (silica gel, Petroleum spirit/Dichloromethane, 6/4) to afford the title product as a purple solid (243 mg, 94%). ¹H NMR (400 MHz, CDCl₃): δ_H = 9.61 (2H, d, ³*J* = 4.8 Hz), 8.89 (2H, d, ³*J* = 4.7 Hz), 8.82 (2H, d, ³*J* = 4.7 Hz), 8.69 (2H, d, ³*J* = 4.7 Hz), 8.45 (2H, d, ³*J* = 8.1 Hz), 8.31 (2H, d, ³*J* = 8.1 Hz), 7.73 (2H, t, ³*J* = 8.4 Hz), 7.02 (4H, d, ³*J* = 8.4 Hz), 4.14 (3H, s), 3.87 (8H, t, ³*J* = 6.4 Hz), 1.33-1.07 (24H, m), 1.07-0.91 (24H, m), 0.91-0.83 (12H, t, ³*J* = 7.2 Hz), 0.82-0.69 (8H, m), 0.69-0.54 (16H, m), 0.54-0.40 (8H, m), -2.58 (2H, s). ¹³C NMR (100 MHz, CDCl₃): δ_C = 167.4, 160.1, 147.4, 134.5, 130.2, 129.4, 127.8, 120.3, 117.7, 113.7, 105.2, 102.0, 68.7, 52.3, 31.9, 29.5, 29.4, 29.3, 29.2, 29.1, 28.7, 28.6, 25.3, 22.7, 14.2. MALDI-TOF: *m/z* calculated for 1411.8699 [M+H]⁺, Found 1411.8668 [M+H]⁺, Δ = 2.2 ppm.

**5-(4-nitro-phenyl)-15-(4-methoxycarbonyl-phenyl)-10,20-bis[2,6-di(dodecyloxy)phenyl] porphyrin –
Compound 14.**

Following general procedure for Suzuki's coupling, porphyrin **13** (141 mg, 0.1 mmol) was reacted with 4-nitrophenylboronic acid (83 mg, 0.5 mmol), Ba(OH)₂·H₂O (38 mg, 0.2 mmol) and Pd(PPh₃)₄ (6 mg, 5.2 μmol) in 15 ml of a mixture of THF/H₂O (3/1). Purification on silica column (Dichloromethane/Petroleum ether, 25/75) gave the desired compound (94 mg, 0.065 mmol). ¹H NMR (400 MHz, CDCl₃): δ_H = 8.84 (d, *J* = 4.8 Hz, 2H), 8.81 (d, *J* = 4.7 Hz, 2H), 8.69 (d, *J* = 4.7 Hz, 2H), 8.63 (d, *J* = 4.8 Hz, 2H), 8.60 (d, *J* = 8.7 Hz, 2H), 8.41 (d, *J* = 8.4 Hz, 2H), 8.38 (d, *J* = 8.7 Hz, 2H), 8.28 (d, *J* = 8.4 Hz, 2H), 7.69 (t, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 4H), 4.10 (s, 3H), 3.82 (t, *J* = 6.3 Hz, 8H), 1.19 (m, 8H), 1.08 (br, 18H), 0.95 (m, 22H), 0.87 (br, 12H), 0.82 (t, *J* = 7.3 Hz, 12H), 0.73 (m, 8H), 0.59 (m, 18H), 0.47 (m, 8H), -2.64 (s, 2H). ¹H NMR (100 MHz, CDCl₃): δ_C = 167.5, 160.2, 150.0, 147.7, 147.6, 135.3, 134.7, 130.3, 129.5, 127.9, 121.8, 120.5, 118.0, 113.7, 105.3, 68.7, 52.5, 51.0, 32.0, 29.6, 29.5, 29.3, 29.2, 28.8, 28.7, 25.4, 22.76, 14.2. MALDI-TOF: *m/z* calculated for 1454.9757 [M]⁺, Found 1454.9767 [M]⁺, Δ = 0.7 ppm.

**5-(4-nitro-phenyl)-15-(4-carboxy-phenyl)-10,20-bis[2,6-di(dodecyloxy)phenyl] porphinato-zinc(II) –
ZnP-CO₂H-NO₂**

Porphyrin **14** (20 mg, 0.014 mmol) was dissolved in 10 ml of a mixture of THF/MeOH (9/1), 2 ml NaOH (1M) were added. The resulting solution was heated to reflux for 4h. After cooling down to room temperature, water was added followed by HCl (1M) until pH = 4. Addition of DCM permits to isolate organic phase that was washed with water and dried over Na₂SO₄. Evaporation of solvents permits to isolate free base porphyrin with a quantitative yield.

Porphyrin was dissolved in DCM/MeOH (1/1), Zn(OAc)₂ (50 mg, excess) was added and the solution was heated to reflux for 4h. After it was cooled down to room temperature, DCM and H₂O were added.

The organic phase was washed with water, dried over Na₂SO₄ and solvents were evaporated giving us the desired zinc porphyrin (18 mg, 86 %). ¹H NMR (400 MHz, CDCl₃): δ_H = 8.95 (d, *J* = 4.5 Hz, 2H), 8.94 (d, superposed, *J* = 4.5 Hz, 2H), 8.83 (d, *J* = 4.6 Hz, 2H), 8.75 (d, *J* = 4.6 Hz, 2H), 8.61 (d, *J* = 8.4 Hz, 2H), 8.59 (d, *J* = 8.0 Hz, 2H), 8.40 (d, *J* = 8.4 Hz, 2H), 8.36 (d, *J* = 8.0 Hz, 2H), 7.70 (t, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 4H), 3.84 (t, *J* = 6.4 Hz, 8H), 1.20 (m, 8H), 1.08 (m, 18H), 0.93 (m, 20H), 0.83 (t, *J* = 7.2 Hz, 12H), 0.79 (m, 8H), 0.67 (m, 8H), 0.53 (m, 18H), 0.42 (m, 8H). ¹³C NMR (100 MHz, THF-d₈): δ_C = 171.4, 160.1, 151.2, 151.0, 150.8, 149.4, 149.3, 148.9, 147.5, 135.2, 134.8, 132.1, 132.0, 131.4, 130.8, 130.0, 128.4, 128.2, 121.6, 121.3, 118.8, 116.8, 114.5, 105.4, 68.7, 32.0, 29.8, 29.6, 29.5, 29.3, 29.2, 28.8, 28.7, 25.3, 22.8, 14.2. MALDI-TOF: *m/z* calculated for 1501.8658 [M]⁺, Found 1501.8717 [M]⁺, Δ = 3.9 ppm.

5-Bromo-15-(4-carboxy-phenyl)-10,20-bis[2,6-di(dodecyloxy)phenyl]porphyrin – Compound 15.

Porphyrin **13** (140 mg, 0.100 mmol) was dissolved in 58 ml of dry THF and 8 ml of MeOH under argon atmosphere. Then 12 ml of 1 M NaOH aqueous solution was added by syringe. The resulting solution was refluxed under argon for 2.5 hours and cooled to room temperature. The pH value was adjusted to around 4 by 1 M HCl. The mixture was extracted with dichloromethane twice and dried over anhydrous Na₂SO₄. After removal of the solvent, the crude product was purified by flash chromatography (silica gel, Dichloromethane/Methanol, 98/2) and precipitated over methanol to give the title product as a purple solid (142 mg, 88%). ¹H NMR (400 MHz, CDCl₃): δ_H = 9.58 (2H, d, ³*J* = 6.4 Hz), 8.87 (2H, d, ³*J* = 6.4 Hz), 8.81 (2H, d, ³*J* = 6.4 Hz), 8.70 (2H, d, ³*J* = 6.4 Hz), 8.54 (2H, d, ³*J* = 10.9 Hz), 8.34 (2H, d, ³*J* = 10.6 Hz), 7.72 (2H, t, ³*J* = 11.2 Hz), 7.01 (4H, d, ³*J* = 11.3 Hz), 3.85 (8H, t, ³*J* = 8.4 Hz), 1.30-1.19 (8H, m), 1.19-1.05 (16H, m), 1.04-0.93 (16H, m), 0.92-0.81 (20H, m), 0.78-0.68 (8H, m), 0.65-0.52 (16H, m), 0.52-0.41 (8H, m), -2.60 (2H, s). ¹³C NMR (100 MHz, CDCl₃): δ_C = 171.4, 160.2, 148.5, 134.8, 130.3, 128.6, 128.5, 120.4, 117.7, 113.9, 105.3, 102.2, 68.8, 32.0, 29.6, 29.5, 29.4, 29.3, 29.2, 28.9, 28.8, 25.5, 22.8, 14.2. MALDI-TOF: *m/z* calculated for 1397.8542 [M+H]⁺, Found 1397.8546 [M+H]⁺, Δ = 0.3 ppm.

5-(N-4-ethynylphenyl,N'-dioctyl-1,8:4,5-naphthalenetetracarboxydiimide)-15-(4-carboxy-phenyl)-10,20-bis[2,6-di(dodecyloxy)phenyl]porphyrin – Compound ZnP-CO₂H-eNDI.

Zinc insertion in porphyrin **15** (41 mg, 0.029 mmol) was carried out as usual with Zn(OAc)₂, 2H₂O (29 mg, 0.162 mmol) in 7 ml of a mixture of methanol/dichloromethane (1/1) at reflux for 2 h. The reaction mixture was washed with H₂O twice and the organic layer was dried over Na₂SO₄. The solvent was removed under reduced pressure to give the corresponding zinc porphyrin as a purple solid (39 mg, 90%). ¹H NMR (400 MHz, CDCl₃): δ_H = 9.70 (2H, d, ³J = 4.7 Hz), 8.95 (2H, d, ³J = 4.7 Hz), 8.89 (2H, d, ³J = 4.7 Hz), 8.78 (2H, d, ³J = 4.7 Hz), 8.46 (2H, d, ³J = 8.2 Hz), 8.32 (2H, d, ³J = 8.1 Hz), 7.71 (2H, t, ³J = 8.4 Hz), 7.02 (4H, d, ³J = 8.5 Hz), 3.86 (8H, t, ³J = 6.4 Hz), 1.30-1.03 (24H, m), 1.03-0.90 (16H, m), 0.92-0.78 (20H, m), 0.75-0.63 (8H, m), 0.63-0.46 (16H, m), 0.46-0.33 (8H, m)

Under an argon atmosphere, the above zinc porphyrin (39 mg, 0.027 mmol), copper iodide (0.3 mg, 0.001 mmol) and **16** (54 mg, 0.112 mmol) were mixed in anhydrous tetrahydrofuran (4 ml) with triethylamine (2 ml). The resulting solution was freed from O₂ by three freeze-pump-thraw cycles and Pd(PPh₃)₄ (3.3 mg, 0.003 mmol) was added. Then the solution was heated to reflux for 3 h. Solvent was removed under vacuum and the crude was purified by flash column chromatography (silica gel, Dichloromethane/Methanol, 97/3) to afford a purple green solid (36.0 mg, 68%). ¹H NMR (400 MHz, CDCl₃): δ_H = 9.77 (2H, d, ³J = 4.5 Hz), 8.99 (2H, d, ³J = 4.5 Hz), 8.87 (2H, d, ³J = 4.4 Hz), 8.86 (2H, d, ³J = 7.5 Hz), 8.82 (2H, d, ³J = 7.5 Hz), 8.76 (2H, d, ³J = 4.6 Hz), 8.48 (2H, d, ³J = 7.8 Hz), 8.33 (2H, d, ³J = 8.0 Hz), 8.21 (2H, d, ³J = 8.2 Hz), 7.71 (2H, t, ³J = 8.4 Hz), 7.52 (2H, d, ³J = 8.2 Hz), 7.01 (4H, d, ³J = 7.5 Hz), 4.22 (2H, t, ³J = 7.5 Hz), 3.86 (8H, t, ³J = 6.3 Hz), 1.78 (2H, m), 1.50-1.25 (10H, m), 1.25-1.16 (8H, m), 1.16-1.02 (16H, m), 1.02-0.87 (19H, m), 0.82 (8H, m and 12H, t, ³J = 7.1 Hz), 0.70-0.60 (8H, m), 0.60-0.41 (24H, m) ¹³C NMR (100 MHz, CDCl₃): δ_C = 163.0, 162.8, 160.0, 152.1, 151.1, 150.6, 149.1, 148.8, 134.5, 134.1, 132.6, 132.4, 131.5, 131.2, 130.5, 129.9, 128.9, 128.3, 127.1, 126.9, 126.7, 125.8, 121.1, 119.8, 114.9, 105.3, 98.5, 94.5, 94.3, 68.7, 41.1, 31.9, 29.7, 29.4, 29.3, 29.2, 29.0, 28.7, 28.6, 28.1, 27.1, 25.2.

Fabrication and characterization of the dye-sensitized solar cells

Conductive glass substrates (F-doped SnO₂) were purchased from Pilkington (TEC8, sheet resistance 8 Ω/square). Conductive glass substrates were successively cleaned by sonication in soapy water, then ethanol for 10 min before being fired at 450 °C for 30 min. Once cooled down to room temperature, FTO plates were rinsed with ethanol and dried in ambient air. NiO electrodes were prepared by screen-printing of a NiO paste on clean FTO substrates, using a commercial semiautomatic screen printer. The NiO screen-printing paste was produced by preparing a slurry of 3 g of NiO nanopowder (Inframat) suspended in 10 mL of distilled ethanol and ball-milled (500 rpm) for 24 h. The resulting slurry was mixed in a round-bottom flask with 10 ml of 10 wt% ethanolic ethyl cellulose (Sigma Aldrich) solution and 20 ml terpineol, followed by slow ethanol removal by rotary evaporation. The dried film was first calcined in air at 400 °C for 0.5 h followed by sintering at 550 °C for 10 min. The prepared NiO electrodes were soaked while still hot (80 °C) in a 0.1 mM solution of each dye in a mixture of ethanol/toluene (1/1, v/v) for 16 h.

Electrolyte used are composed of: 0.5 M 1,2-dimethyl-3-butylimidazolium iodide, 0.5 M LiI, 0.1 M I₂, 0.5 M 4-tert-butylpyridine and 0.1 M guanidinium thiocyanate in acetonitrile for I₃⁻/I⁻ electrolyte and 0.1 M Co^{II}(dtb-bpy)₃(2ClO₄⁻) + 0.1 M Co^{III}(dtb-bpy)₃(3 ClO₄⁻) and 0.1 M LiClO₄ in propylene carbonate for cobalt complex as redox shuttle (dtb-bpy = 4,4'-ditertbutyl-2,2'-bipyridine). Counter electrode were prepared by chemical deposition of platinum from hexachloroplatinic acid in distilled isopropanol (2 mg per mL). The two electrodes were placed on top of each other using a thin transparent film of Surlyn polymer (DuPont, 25 μm) as a spacer to form the electrolyte space. The empty cell was tightly held, and the edges were heated to 110 °C to seal the two electrodes together. A drop of electrolyte was introduced through a predrilled hole in the counter electrode by vacuum backfilling, and was sealed afterward. The cell had an active area of ca. 0.25 cm².

The current-voltage characteristics were determined by applying an external potential bias to the cell and measuring the photocurrent using a Keithley model 2400 digital source meter. The solar simulator is an Oriel Lamp calibrated to 100 mW/cm^2 . The overall conversion efficiency (η) of the photovoltaic cell is calculated from the integral photocurrent density (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor of the cell (FF), and the intensity of the incident light (IPh).