

Supporting information
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D- π -A Structured Porphyrins for Highly Efficient Dye-Sensitized Soar Cells

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1.1 Chemicals:

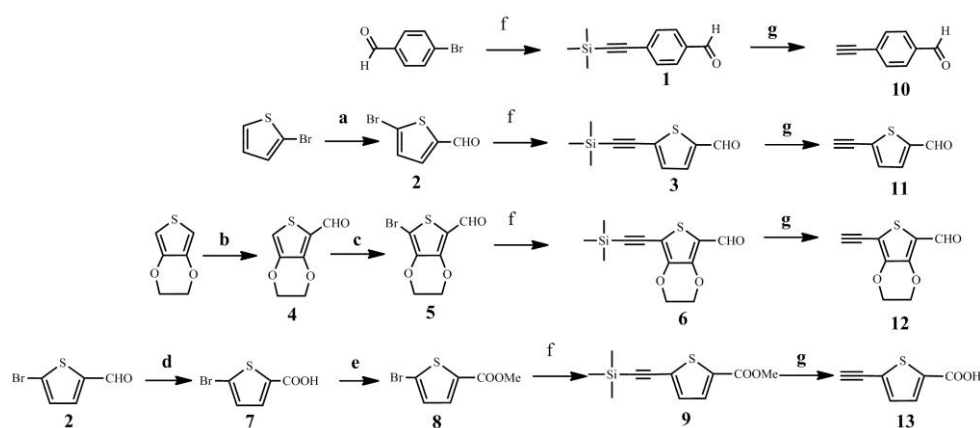
All solvents and reagents, unless otherwise stated, were of analytical grade quality and used as received. Standard Schlenk techniques were employed to manipulate oxygen- and moisture-sensitive chemicals. The starting reagents and 4-ethynyl-N,N-dimethylaniline were purchased from Aldrich and used as received.

5-bromo-15-(4-N,N-dimethylamino-phenyl)ethynyl-10,20-bis[2,6-di(dodecyloxy) phenyl]porphinato zinc(II) (coded as Por-1) was synthesized according to the literature. Tetrahydrofuran (THF) was dried with sodium sand, and benzophenone indicator, dichloromethane (DCM), ether, triethylamine (TEA) were dried out with calcium hydride before using. Reactions were carried out under a dry nitrogen atmosphere.

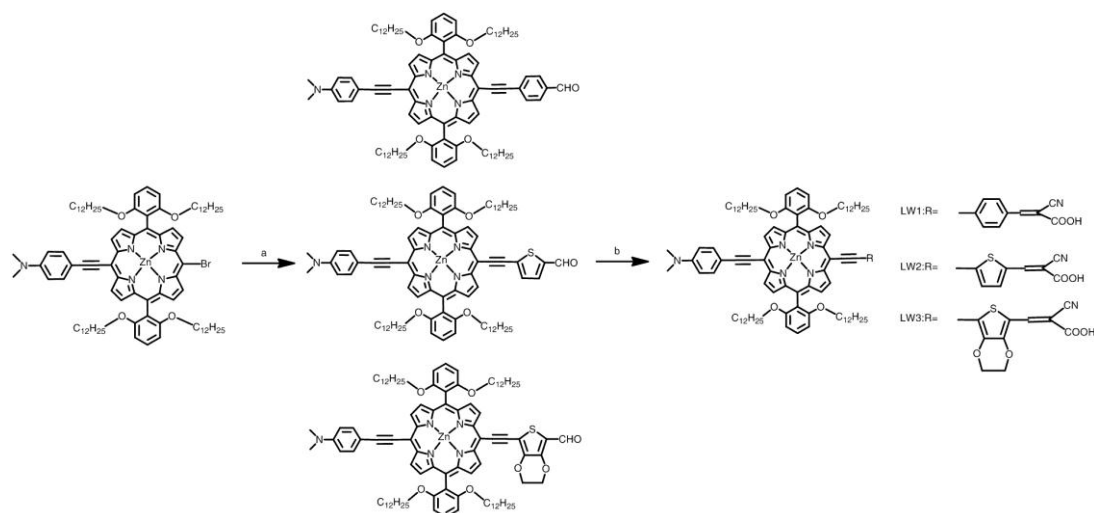
1.2 Synthesis of LW1-4

The preparation of Zn porphyrins dyes LW1-4 was achieved by a convergent synthesis (Scheme S1-3), which has been designed according to the Sonogashira coupling reactions.

1.2.1 Synthesis route of LW1-4



Scheme S1. a) POCl_3 , DMF, 0°C , 0.5h, 80°C , 4h; b) DMF, POCl_3 , CHCl_3 , -10°C , 1h, room temperature, overnight; c) MeCN, NBS, room temperature, 60h; d) Jones Reagent, room temperature, 2h; e) conc. H_2SO_4 , N_2 , reflux, MeOH, 12h; f) trimethylsilylacetylene, $\text{Pd}(\text{PPh}_3)_4$, CuI, TEA/THF, 18h, 45°C ; g) K_2CO_3 , MeOH, room temperature, 6h.



Scheme S2. a) por-1, Pd(PPh₃)₄, CuI, TEA/THF, 45 °C, 14 h; b) por-2/3/4, cyanoacetic acid, piperidine, CHCl₃, reflux, 8h.

Synthesis of 4-((trimethylsilyl)ethynyl)benzaldehyde (1). Compound **1** was prepared under modified conditions of literature procedure. ^[1] CuI (19 mg, 0.01 mmol) and Pd(PPh₃)₄ (115 mg, 0.11 mmol) were added into the solution of 4-bromobenzaldehyde (370 mg, 2.0 mmol) in freshly distilled triethylamine (10 mL) at 0 °C under nitrogen. After the solution was stirred for 30 min at 0 °C, trimethylsilylacetylene (0.85 mL, 6.0 mmol) was added and the mixture was stirred for 30 min in an ice bath before being warmed to room temperature. After reacting for 30 min at room temperature, the mixture was heated to 50 °C for 12 h. The solution was then allowed to cool to room temperature and the solvent mixture was evaporated in vacuum. The crude product was purified by column chromatography on silica gel with a solvent combination of CH₂Cl₂/hexane (1:1) as eluent to provide the target product as a white solid (330 mg, 82%). ¹H NMR (CDCl₃) δ 9.95 (s, 1H), 7.83 (d, J = 8.7 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 0.29 (s, 9H). MS (APCI) m/z: calcd for 202.32; found 202.6.

Synthesis of 5-Bromothiophene-2-carbaldehyde (2). Compound **2** was prepared with a modified condition according to the literature procedure. ^[2] POCl₃ (35 mL, 0.375 mol) was dropped into the DMF (27 mL, 0.35 mol) within an iced bath. The mixture was stirred for 0.5 h. Then 2-bromothiophene (25.7 g, 0.158 mol) was added to the mixture. The reaction solution was heated to 80 °C for 4 h. After the solution was cooled to room temperature, 50 mL of water was

added to hydrolyze the reaction mixture. Then the solution was extracted with CHCl_3 . The organic extracts were washed with water five times and with KOH (aqueous) twice. The colorless liquid was afforded by column chromatograph with petroleum ether/ethyl acetate (10:1) as an eluent (22.33 g, 74%). ^1H NMR (CDCl_3) δ 9.79 (s, 1H), 7.54 (s, $J=4.0$ Hz, 1H), 7.01 (s, $J=4.0$ Hz, 1H). MS (APCI) m/z : calcd for 191.05; found 191.3.

Synthesis of 2-formyl-5-((trimethylsilyl)ethynyl)thiophene (3). Compound **3** was prepared under modified conditions of literature procedure. ^[3] To a flask containing 5-bromo-2-thiophenecarboxaldehyde (9.55 g, 50.0 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.701 g, 1.00 mmol), CuI (0.096 g, 0.50 mmol), and Et_2NH (150 mL) were added (trimethylsilyl)acetylene (7.7 mL, 54.6 mmol). The resulting mixture was stirred at 0 °C for 30 min, allowed to warm to room temperature, and stirred for 12 h. The solvent was removed under vacuum, and the residue was extracted with Et_2O . Removal of Et_2O provided a brown-black oil, which was then chromatographed. Elution with CH_2Cl_2 /hexane (1:1) gave a yellow band from which powdery compound **3** was isolated (8.96 g, 86%) after removal of solvent. ^1H NMR (CDCl_3) δ 9.94 (s, 1H), 7.75 (s, $J=3.9$ Hz, 1H), 7.45 (s, $J=4.2$ Hz, 1H). 0.29 (s, 9 H). MS (APCI) m/z : calcd for 208.35; found 208.1.

Synthesis of 2-(3,4-Ethylenedioxythiophene) carbaldehyde (4). Compound **4** was prepared under modified conditions of literature procedure. ^[4] 3,4-Ethylenedioxythiophene (25 g, 0.1755 mmol) was dissolved in dry DMF (100 mL). The mixture was cooled to -10 °C and POCl_3 (17 mL, 0.18 mmol) was added drop-wise (15 min) in the cold solution. The mixture stirred 1 h at -10 °C, ice water (200 mL) was added and the mixture stirred overnight at room temperature. The aldehyde was filtered off, dissolved in CH_2Cl_2 (200 mL) and dried (Na_2SO_4). The CH_2Cl_2 filtrate was eluted through a short silica plug to remove colored byproducts, giving the dry product as white crystals (21g, 71%). ^1H NMR (CDCl_3) δ 9.84 (s, 1H), 6.80 (s, 1H), 4.38 (m, 2H), 4.36 (m, 2H). MS (APCI) m/z : calcd for 170.19; found 170.4.

Synthesis of 2-Bromo-(3,4-ethylenedioxythiophene)-5-carbaldehyde (5). Compound **5** was prepared under modified conditions of literature procedure. ^[4] Compound **4** (4.04 g, 23.7 mmol) was suspended in dry acetonitrile (100 mL) and cooled to 0 °C. NBS (4.36 g, 26.0 mmol), 1.1 equiv, was added and the

mixture was stirred for 60 h at room temperature, shielded from light and under nitrogen. The color changed from yellow to purple. The mixture was transferred with 150 mL of ethyl acetate to a separation funnel, washed with 10% aqueous Na_2CO_3 (2×200 mL), saturated $\text{Na}_2\text{S}_2\text{O}_3$ (2×200 mL) and water (2×200 mL), dried with MgSO_4 , and evaporated in vacuo. Recrystallization twice from ethanol (60 mL) of the bromide as yellow needles (5.35 g, 91%). ^1H NMR (CDCl_3) δ 9.84 (s, 1H), 4.38 (m, 2H), 4.36 (m, 2H). MS (APCI) m/z : calcd for 249.08; found 249.3.

Synthesis of 7-((trimethylsilyl)ethynyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine-5-carbaldehyde (6). Compound **6** was prepared under modified conditions of literature procedure.^[1] CuI (42 mg, 0.22 mmol), $\text{Pd}(\text{OAc})_2$ (49 mg, 0.22 mmol) and PPh_3 (173 mg, 0.66 mmol) were added into an ice-cooled mixture solution of compound **5** (0.837 g, 4.38 mmol) in freshly distilled TEA (20 mL) and THF (20 mL). After the solution was stirred for 30 min at 0 °C, trimethylsilylacetylene (1.85 mL, 13.14 mmol) was then added and the suspension was stirred for 30 min in an ice bath before being warmed to room temperature. After reacting for 30 min at room temperature, the mixture was stirred overnight at 45 °C. The solution was then allowed to cool to room temperature and the solvent mixture was evaporated in vacuum. The crude product was purified by column chromatography on silica gel with a solvent combination of CH_2Cl_2 /hexane (1:1) as eluent to provide **6** as a yellow solid (0.756 g, 83%). ^1H NMR δ (CDCl_3) 9.92 (s, 1H), 4.39 (s, 1H), 0.29 (s, 9H). MS (APCI) m/z : calcd for 266.39; found 266.1.

Synthesis of 5-Bromothiophene-2-carboxylic Acid (7). Compound **7** was prepared under modified conditions of literature procedure.^[5] To a stirred solution compound **3** (10g, 0.052mol) in 100 mL of acetone, 30.0 mL of 2.67 M Jones reagent was added drop-wise under nitrogen at 5 °C. Stirring was continued at 5 °C for 30 min followed by stirring at room temperature for 2 h. Methanol was added to the reaction mixture to destroy any excess oxidant, and the solids were filtered off. The filtrate was concentrated in vacuo, and the residue was partitioned between ether and water. The ether extract was washed with water twice and brine, dried with MgSO_4 and concentrated under reduced pressure. Trituration of the residue in hexanes and filtration then gave pure **7** as a pale yellow solid (10.8g, 99%). ^1H NMR (CDCl_3) δ 7.55 (d, $J=4.3$ Hz, 1H), 7.33 (d, $J=4.3$ Hz). MS (ESI) m/z : calcd for 207.05; found 206.8.

Synthesis of Methyl 5-Bromothiophene-2-carboxylate (8). Compound **8** was prepared under modified conditions of literature procedure.^[5] To a solution of **7** (1.00 g, 4.83 mmol) in MeOH (30.0 mL) was added conc. H₂SO₄ (1.00 mL). The reaction mixture was refluxed for 30 h. After removal of the solvent, the residue was poured into water, and extracted with AcOEt. The organic layer was washed with brine and dried over Na₂SO₄. Filtration, concentration in vacuo and purification by silica gel flash column chromatography (AcOEt/hexane = 1/10) gave 1.03 g (96 %) of **8** as a white solid. ¹H NMR (DMSO-d₆) δ 7.55 (d, J=4.3 Hz, 1H), 7.33 (d, J=4.3 Hz), 3.40 (3H, s). MS (APCI) m/z: calcd for 221.07; found 221.4.

Synthesis of methyl 5-((trimethylsilyl)ethynyl)thiophene-2-carboxylate (9). Compound **9** was prepared under modified conditions of literature procedure.^[5] (Trimethylsilyl)acetylene (687 mg, 6.99 mmol) was added into a solution of compound **8** (1.03 g, 4.66 mmol) obtained above, PdCl₂(PPh₃)₂ (32.7 mg, 46.6 μmol) and CuI (13.3 mg, 69.9 μmol) in diethylamine (15.5 ml). The mixture was stirred for 18 h at room temperature. After removal of the solvent, the residue was diluted with Et₂O and washed 1N aqueous HCl, saturated NaHCO₃, and brine, and was dried over Na₂SO₄. Concentration in vacuo and purification by silica gel flash column chromatography (AcOEt/hexane = 1/20) gave of **8** as a brown solid (895 mg, 81 %): ¹H NMR (CDCl₃) δ 7.63 (1H, d, J = 4.0 Hz), 7.16 (1H, d, J = 4.0 Hz), 3.88 (3H, s), 0.257 (9H, s). MS (APCI) m/z: calcd for 238.38; found 238.3.

Synthesis of 4-ethynylbenzaldehyde (10). Compound **10** was prepared under modified conditions of literature procedure.^[6] Compound **1** (0.34 g, 1.68 mmol) and K₂CO₃ (0.69 g, 5.04 mmol) were dissolved in 8 ml of MeOH. The reaction was stirred at room temperature for 6 h, and the solvent was removed under vacuum. The solid was redissolved in CH₂Cl₂ and was washed with aqueous NaHCO₃ three times. The organic layer was dried over Na₂SO₄ and evaporated under vacuum. The yellow residue was purified by column chromatography (CH₂Cl₂/hexane = 3/1) afforded product **10** (0.214 g, 98%). ¹H NMR (CDCl₃) δ 10.04 (s, 1H), 7.85 (d, J=8.3 Hz, 1H), 7.66 (d, J=8.3 Hz), 3.32 (s, 1H). MS (APCI) m/z: calcd for 130.14; found 130.1.

Synthesis of 5-ethynylthiophene-2-carbaldehyde (11). Compound **11** was prepared under modified conditions of literature procedure.^[3] To a solution of compound **3** (1.25 g, 6 mmol) in methanol (6 mL), as added K₂CO₃ (2.5 g, 18

mmol), the solution was allowed to stir for 5 h before being poured into water. The aqueous layer was extracted with dichloromethane, and the organic extracts were washed with brine. The combined organic layers were dried over MgSO_4 . The solvent was removed under vacuum. The crude product was chromatographed using CH_2Cl_2 /hexane (1:4) as eluent to afford a light brown powder **11** (0.75g, 92%). ^1H NMR (CDCl_3) δ 9.89 (s, 1H), 7.66 (d, $J=3.9$ Hz, 1H), 7.33 (d, $J=3.9$ Hz), 3.60 (s, 1H). MS (APCI) m/z : calcd for 136.17; found 135.9.

Synthesis of 7-ethynyl-2,3-dihydrothieno[3,4-b][1,4] dioxine-5-carbaldehyde (12). Compound **12** was prepared under modified conditions of literature procedure. ^[6] K_2CO_3 (2.5 g, 18 mmol) was added into a solution of compound **6** (1.6 g, 6 mmol) in methanol (10 mL). The solution was allowed to stir for 5 h before being poured into water. The aqueous layer was extracted with CH_2Cl_2 , and the organic extracts were washed with brine. The combined organic layers were dried over Na_2SO_4 . The solvent was removed under vacuum. No further purification was necessary to afford the title compound of **12** as a light brown liquid (1.12 g, 96%). ^1H NMR (CDCl_3) δ 9.92 (s, 1H), 4.39 (s, 4H), 3.71 (s, 1H). MS (APCI) m/z : calcd for 194.21; found 194.0.

Synthesis of 5-ethynylthiophene-2-carboxylic acid (13). Compound **13** was prepared under modified conditions of literature procedure. ^[5] 2M aqueous NaOH (3.75 mL, 7.50 mmol) was added into a solution of compound **9** (895 mg, 3.75 mmol) in MeOH (10.0 mL) at 0 °C. The reaction mixture was stirred for 5 h at room temperature. The mixture was neutralized and concentration in vacuo. The residue was poured into water and extracted with AcOEt. The organic layer was washed with brine, and dried over Na_2SO_4 . Filtration and concentration in vacuo gave **13** as a brown solid (552 mg, 97 %). ^1H NMR (DMSO-d_6) δ 7.64 (d, $J = 4.0$ Hz, 1H), 7.40 (d, $J = 3.7$ Hz, 1H), 4.80 (s, 1H). MS (ESI) m/z : calcd for 152.17; found 152.3.

Synthesis of compound Por-2. Compound **Por-2** was prepared under modified conditions of literature procedure. ^[7] $\text{Pd}(\text{PPh}_3)_4$ (11.6 mg, 0.01 mmol) and CuI (1.9 mg, 0.01 mmol) was added into a solution of **Por-1** (149 mg, 0.1 mmol) and compound **10** (40 mg, 0.3 mmol) in fresh distilled THF (70.0 mL) and anhydrous TEA (6 mL) under N_2 . The reaction was stirred at 45 °C for 14 h.

The progress of the reaction was monitored with TLC. The solvent was removed under vacuum. The residue was purified on silica chromatograph using THF/hexane=1/15 as eluent. The product was re-crystallized from CH₂Cl₂/MeOH to give green solid of **Por-2** (103 mg, 66%). ¹H NMR (CDCl₃/pyridine-d₅) δ 10.05 (s, 1H), δH 9.55 (d, J = 4.5Hz, 2H), 9.51 (d, J = 4.5Hz, 2H), 8.79 (d, J = 4.5Hz, 2H), 8.75 (d, J = 4.5Hz, 2H), 8.05 (d, J = 8.1Hz, 2H), 7.97 (d, J = 8.1Hz, 2H), 7.80 (d, J = 8.2Hz, 2H), 7.68 (t, J = 8.5Hz, 2H), 7.00(d, J = 8.5Hz, 4H), 6.81 (d, J = 8.7Hz, 2H), 3.84 (t, J =6.9Hz, 8H), 3.46 (s, 6H), 1.21-1.04(m, 26H), 0.98-0.88(m, 22H), 0.81(t, J=7.3Hz, 12H), 0.78-0.71(br, 8H), 0.61-0.53 (br, 16H), 0.47-0.40(br, 8H). MS (APCI) m/z: calcd for 1534.49; found 1534.1.

Synthesis of compound Por-3. The reaction and purification were performed in the same manner as for Compound **Por-2** (113mg, 73%). ¹H NMR (CDCl₃/pyridine-d₅) δH 10.03 (s, 1H), 9.55 (d, J = 4.5Hz, 2H), 9.51 (d, J = 4.5Hz, 2H), 8.92 (d, J = 4.5Hz, 2H), 8.86 (d, J = 4.5Hz, 2H), 7.98 (d, J = 8.5Hz, 2H), 7.80 (d, J = 3.8Hz, 1H), 7.78 (t, J = 8.8Hz, 2H), 7.71 (d, J = 3.8Hz, 1H), 7.00(d, J = 8.5Hz, 4H), 6.81 (d, J = 8.7Hz, 2H), 3.84 (t, J =6.9Hz, 8H), 3.46 (s, 6H), 1.21-1.04(m, 26H), 0.98-0.88(m, 22H), 0.81(t, J=7.3Hz, 12H), 0.78-0.71(br, 8H), 0.61-0.53 (br, 16H), 0.47-0.40(br, 8H). MS (APCI) m/z: calcd for 1540.52; found 1540.1.

Synthesis of compound Por-4. The reaction and purification were performed in the same manner as for **Por-2** (115mg, 72%). ¹H NMR (CDCl₃/pyridine-d₅) δ 10.02 (s, 1H), δH 9.55 (d, J = 4.5Hz, 2H), 9.51 (d, J = 4.5Hz, 2H), 8.92 (d, J = 4.5Hz, 2H), 8.86 (d, J = 4.5Hz, 2H), 7.92 (d, J = 8.5Hz, 2H), 7.78 (t, J = 8.8Hz, 2H), 7.00(d, J = 8.5Hz, 4H), 6.81 (d, J = 8.7Hz, 2H), 4.53 (m, 4H), 3.84 (t, J =6.9Hz, 8H), 3.46 (s, 6H), 1.21-1.04(m, 26H), 0.98-0.88(m, 22H), 0.81(t, J=7.3Hz, 12H), 0.78-0.71(br, 8H), 0.61-0.53 (br, 16H), 0.47-0.40(br, 8H). MS (APCI) m/z: calcd for 1598.56.52; found 1598.1.

Synthesis of compound LW1. **LW1** were prepared under modified conditions of literature procedure.^[8] 2-cyanoacetic acid (2.6 mg, 0.03 mmol) and piperidine (0.014 mL) in 4 mL of dry THF were added into a solution of **Por-2** (15.3 mg, 0.01 mmol) and heated to reflux under argon N₂ for 8 h. After cooling to room temperature, H₂O was added and the crude product was extracted with dichloromethane. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude was purified by column

chromatography (silica gel, methanol/dichloromethane, 1/9) twice, and recrystallized from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give green solid (8 mg, 50%). ^1H NMR ($\text{CDCl}_3/\text{pyridine-d}_5$) δ 9.58 (d, $J = 4.5\text{Hz}$, 2H), 9.48 (d, $J = 4.5\text{Hz}$, 2H), 8.79 (m, 4H), 8.25 (s, 1H), 8.00 (d, $J = 3.3\text{Hz}$, 2H), 7.91 (d, $J = 8.6\text{Hz}$, 2H), 7.74 (d, $J = 8.8\text{Hz}$, 2H), 7.60 (t, $J = 8.7\text{Hz}$, 2H), 6.92 (d, $J = 8.5\text{Hz}$, 4H), 6.73 (d, $J = 8.7\text{Hz}$, 2H), 3.74 (t, $J = 6.9\text{Hz}$, 8H), 3.06 (s, 6H), 1.21-1.04 (m, 26H), 0.98-0.88 (m, 22H), 0.81 (t, $J = 7.3\text{Hz}$, 12H), 0.78-0.71 (br, 8H), 0.61-0.53 (br, 16H), 0.47-0.40 (br, 8H). ^{13}C NMR ($\text{CDCl}_3/\text{pyridine-d}_5$) 160.0, 151.8, 151.2, 150.5, 150.3, 150.0, 132.6, 131.7, 131.4, 130.7, 130.4, 129.8, 129.5, 121.5, 115.0, 112.1, 111.7, 105.2, 102.0, 97.6, 96.8, 94.9, 91.8, 68.6, 45.2, 40.2, 31.8, 29.5, 29.4, 29.3, 29.2, 29.1, 28.7, 25.2, 22.6, 14.0. MS (ESI) m/z : calcd for 1601.54; found 1601.0.

Synthesis of compound LW2. The reaction and purification were performed in the same manner as for **LW1** (115 mg, 72%). ^1H NMR ($\text{CDCl}_3/\text{pyridine-d}_5$) δ 9.58 (d, $J = 4.5\text{Hz}$, 2H), 9.48 (d, $J = 4.5\text{Hz}$, 2H), 8.79 (m, 4H), 8.26 (s, 1H), 7.70 (d, $J = 7.7\text{Hz}$, 2H), 7.65 (s, 1H), 7.58 (t, $J = 8.8\text{Hz}$, 2H), 7.46 (d, $J = 3.8\text{Hz}$, 1H), 6.91 (d, $J = 8.5\text{Hz}$, 4H), 6.70 (d, $J = 8.7\text{Hz}$, 2H), 3.76 (t, $J = 6.9\text{Hz}$, 8H), 2.90 (s, 6H), 1.21-1.04 (m, 26H), 0.98-0.88 (m, 22H), 0.81 (t, $J = 7.3\text{Hz}$, 12H), 0.78-0.71 (br, 8H), 0.61-0.53 (br, 16H), 0.47-0.40 (br, 8H). ^{13}C NMR ($\text{CDCl}_3/\text{pyridine-d}_5$) 160.0, 151.5, 151.0, 150.6, 150.2, 150.0, 132.9, 132.6, 131.1, 130.5, 129.6, 121.4, 115.4, 112.1, 105.2, 102.1, 100.5, 97.2, 96.8, 91.8, 87.8, 68.6, 65.0, 40.3, 31.8, 29.5, 29.4, 29.3, 29.2, 29.1, 28.8, 25.2, 22.6, 14.0. MS (ESI) m/z : calcd for 1607.57; found 1607.5.

Synthesis of compound LW3. The reaction and purification were performed in the same manner as for **LW1** (115 mg, 72%). ^1H NMR ($\text{CDCl}_3/\text{pyridine-d}_5$) δ 9.58 (d, $J = 4.5\text{Hz}$, 2H), 9.48 (d, $J = 4.5\text{Hz}$, 2H), 8.79 (m, 4H), 8.52 (s, 1H), 7.84 (d, $J = 7.7\text{Hz}$, 2H), 7.69 (d, $J = 8.6\text{Hz}$, 2H), 7.58 (t, $J = 8.8\text{Hz}$, 2H), 7.46 (d, $J = 3.8\text{Hz}$, 1H), 7.01 (d, $J = 8.5\text{Hz}$, 4H), 6.85 (d, $J = 8.7\text{Hz}$, 2H), 4.50 (m, 4H), 3.76 (t, $J = 6.9\text{Hz}$, 8H), 2.90 (s, 6H), 1.21-1.04 (m, 26H), 0.98-0.88 (m, 22H), 0.81 (t, $J = 7.3\text{Hz}$, 12H), 0.78-0.71 (br, 8H), 0.61-0.53 (br, 16H), 0.47-0.40 (br, 8H). ^{13}C NMR ($\text{CDCl}_3/\text{pyridine-d}_5$) 160.0, 151.5, 151.1, 150.6, 150.3, 150.1, 146.9, 143.2, 140.3, 132.6, 131.1, 130.4, 129.5, 121.5, 115.3, 112.3, 112.1, 105.2, 102.5, 97.1, 96.9, 91.8, 86.3, 68.6, 67.9, 65.4, 65.0, 40.3, 31.8, 29.5, 29.4, 29.3, 29.2, 29.1, 28.8, 25.2, 22.6, 14.0. MS (ESI) m/z : calcd for 1665.60; found 1665.6.

Synthesis of compound LW4. LW4 was prepared under modified conditions of literature procedure.^[7] Pd(PPh₃)₄ (11.6 mg, 0.01 mmol) and CuI (1.9 mg, 0.01 mmol) was added into a solution of **Por-1** (149 mg, 0.1 mmol) and compound **13** (46 mg, 0.3 mmol) in fresh distilled THF (70.0 mL) and anhydrous TEA (6 mL) under N₂. The reaction was stirred at 45 °C for 20 h. The progress of the reaction was monitored with TLC. The solvent was removed under vacuo. The residue was purified on silica chromatograph using CH₂Cl₂/MeOH=25/1 as eluent. The product was re-crystallized from CH₂Cl₂/MeOH to give green solid of **LW4** (87 mg, 55%). ¹H NMR (CDCl₃/pyridine-d₅) δ 9.58 (d, J = 4.5Hz, 2H), 9.48 (d, J = 4.5Hz, 2H), 8.79 (m, 4H), 7.87 (d, J = 3.3Hz, 1H), 7.82 (d, J = 8.6Hz, 2H), 7.68 (t, J = 8.8Hz, 2H), 7.55 (d, J = 3.8Hz, 1H), 7.01 (d, J = 8.5Hz, 4H), 6.83 (d, J = 8.7Hz, 2H), 3.84 (t, J = 6.9Hz, 8H), 3.06 (s, 6H), 1.21-1.04 (m, 26H), 0.98-0.88 (m, 22H), 0.81 (t, J = 7.3Hz, 12H), 0.78-0.71 (br, 8H), 0.61-0.53 (br, 16H), 0.47-0.40 (br, 8H). ¹³C NMR (CDCl₃/pyridine-d₅) 160.0, 151.5, 151.2, 150.6, 150.3, 150.1, 132.9, 132.6, 131.8, 131.1, 130.4, 129.8, 129.5, 121.6, 115.0, 112.1, 111.8, 105.2, 102.1, 100.6, 97.2, 96.8, 91.9, 87.8, 68.6, 40.3, 31.8, 29.5, 29.4, 29.3, 29.2, 29.1, 28.8, 25.3, 22.6, 14.0. MS (ESI) m/z: calcd for 1556.52; found 1556.3.

1.2.2 NMR and MS characterization of compounds

¹H NMR and ¹³C NMR spectra were recorded on a Bruker AV400 400 MHz with tetramethylsilane as an internal standard. Mass Spectrometry was carried out on Agilent (1100 LC/MSD Trap).

Figure S1-S9 present the NMR spectra and MS of the prepared LW1-4 dyes.

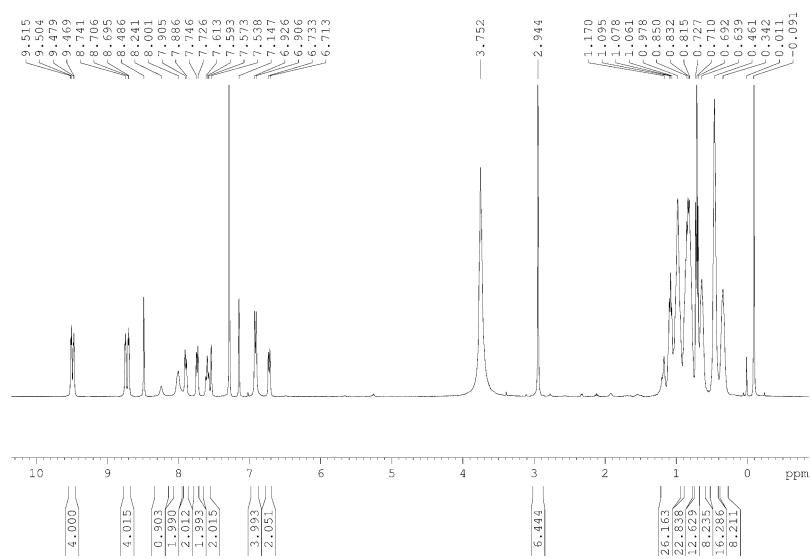


Figure S1. ¹H NMR spectrum of LW1 (400 MHz, CDCl₃/pyridine-d₅, 298 K).

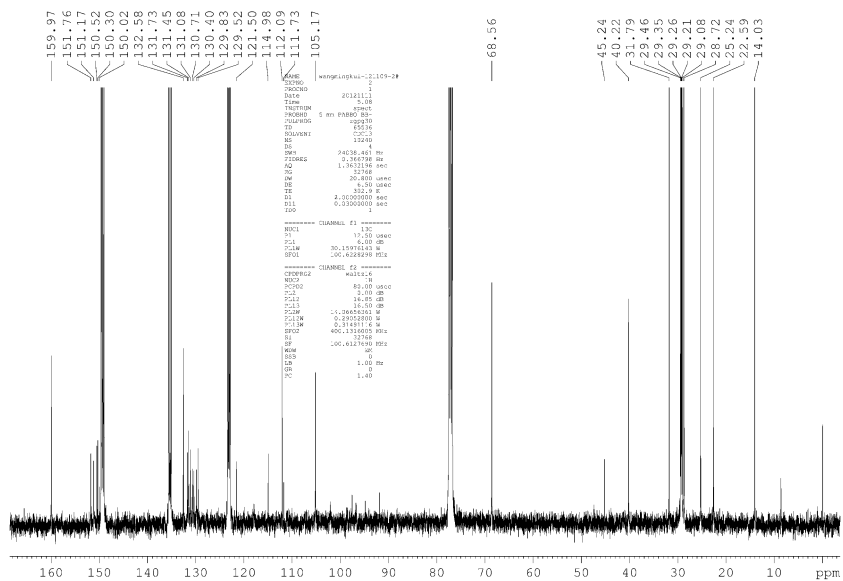


Figure S2. ¹³C NMR spectrum of LW1 (400 MHz, CDCl₃/pyridine-d₅, 298 K).

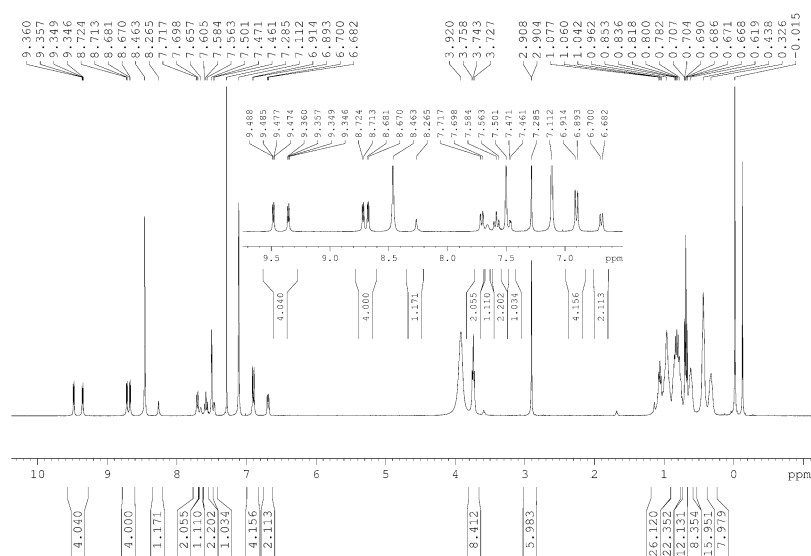


Figure S3. ^1H NMR spectrum of LW2 (400 MHz, $\text{CDCl}_3/\text{pyridine-d}_5$, 298 K).

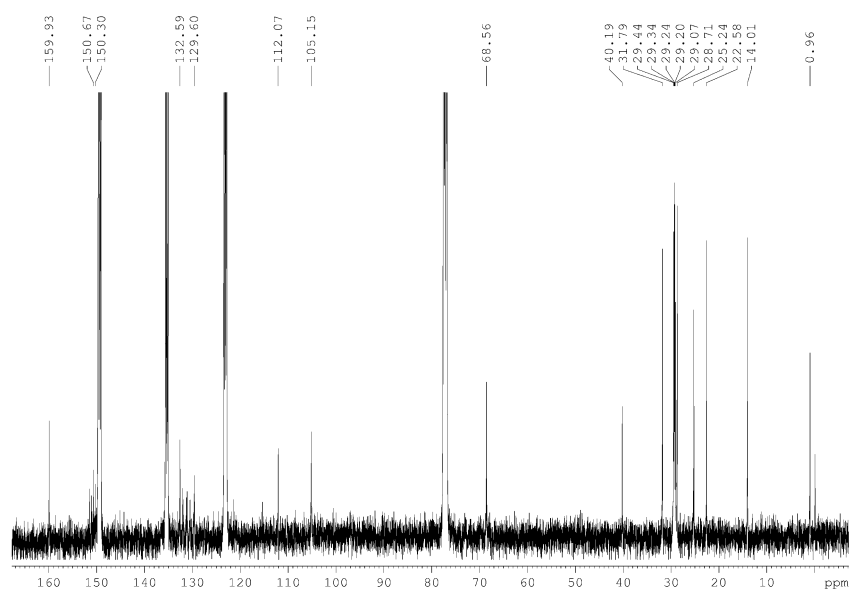


Figure S4. ^{13}C NMR spectrum of LW2 (400 MHz, $\text{CDCl}_3/\text{pyridine-d}_5$, 298 K).

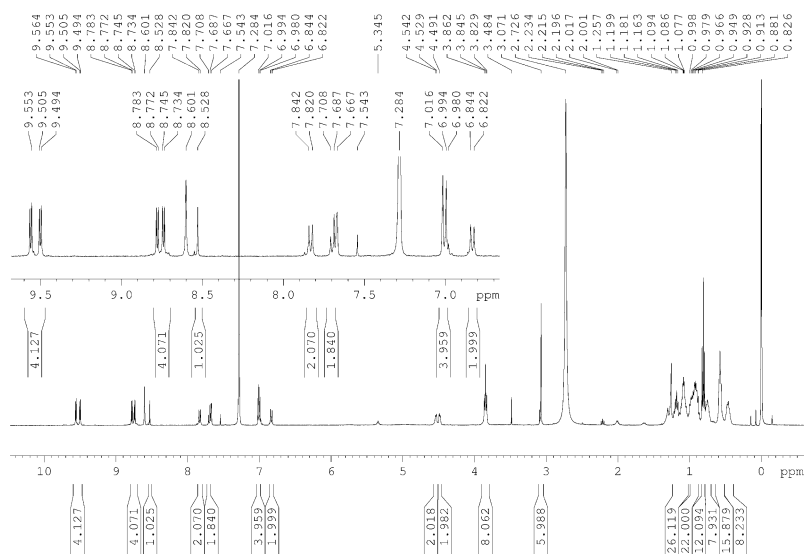


Figure S5. ¹H NMR spectrum of LW3 (400 MHz, CDCl₃/pyridine-d₅, 298 K).

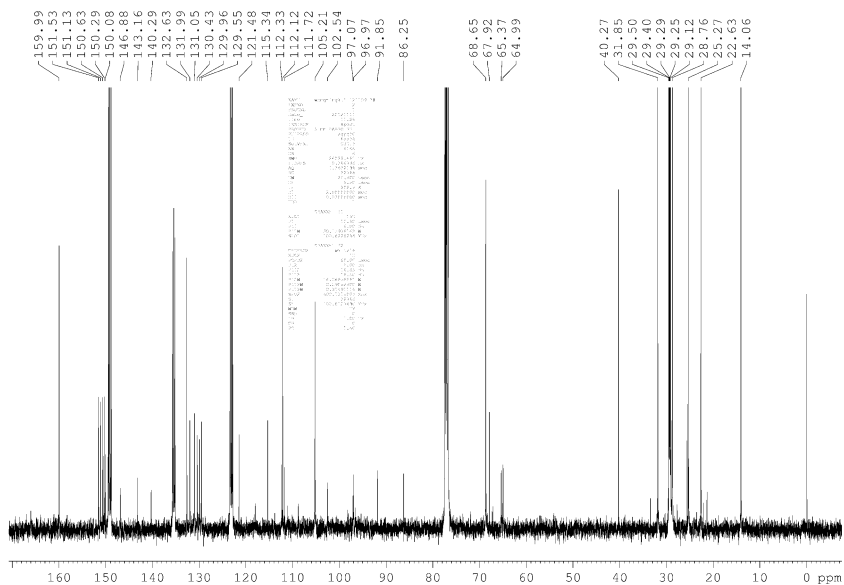


Figure S6. ¹³C NMR spectrum of LW3 (400 MHz, CDCl₃/pyridine-d₅, 298 K).

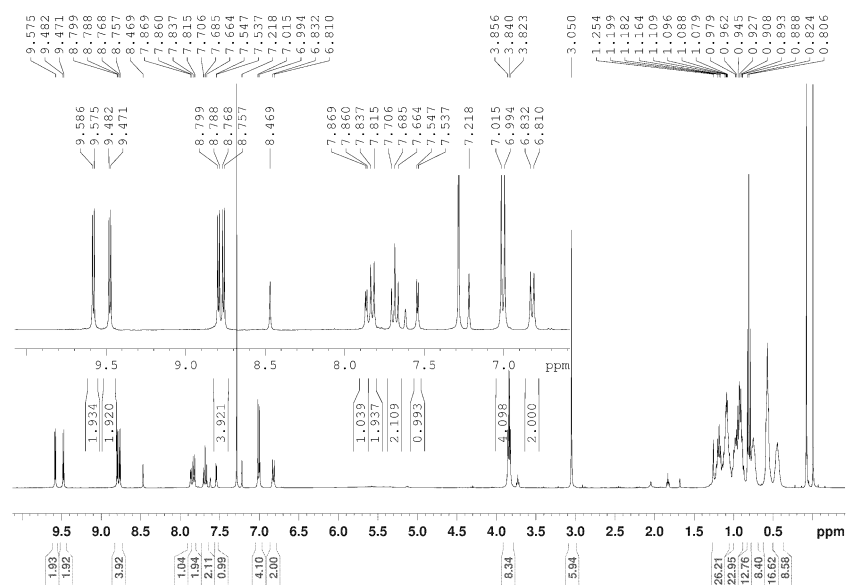


Figure S7. ¹H NMR spectrum of LW4 (400 MHz, CDCl₃/pyridine-d₅, 298 K).

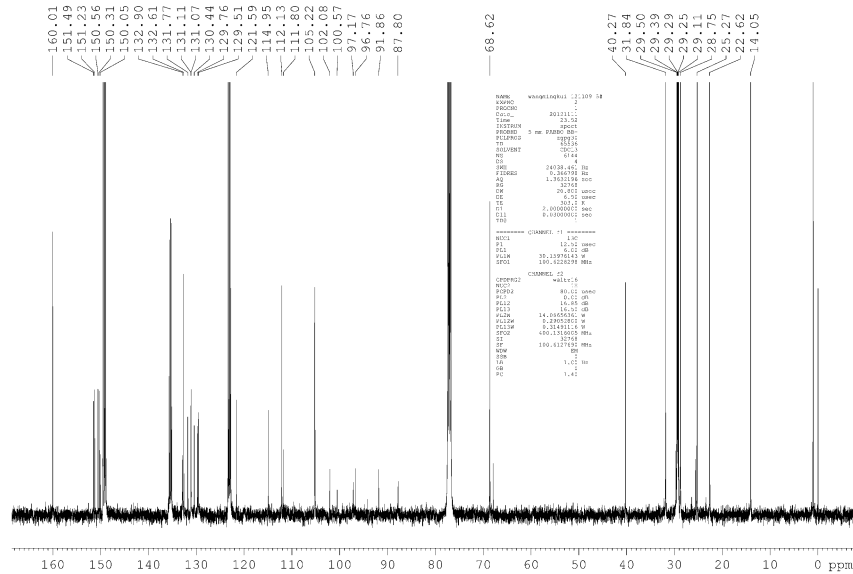


Figure S8. ¹³C NMR spectrum of LW4 (400 MHz, CDCl₃/pyridine-d₅, 298 K).

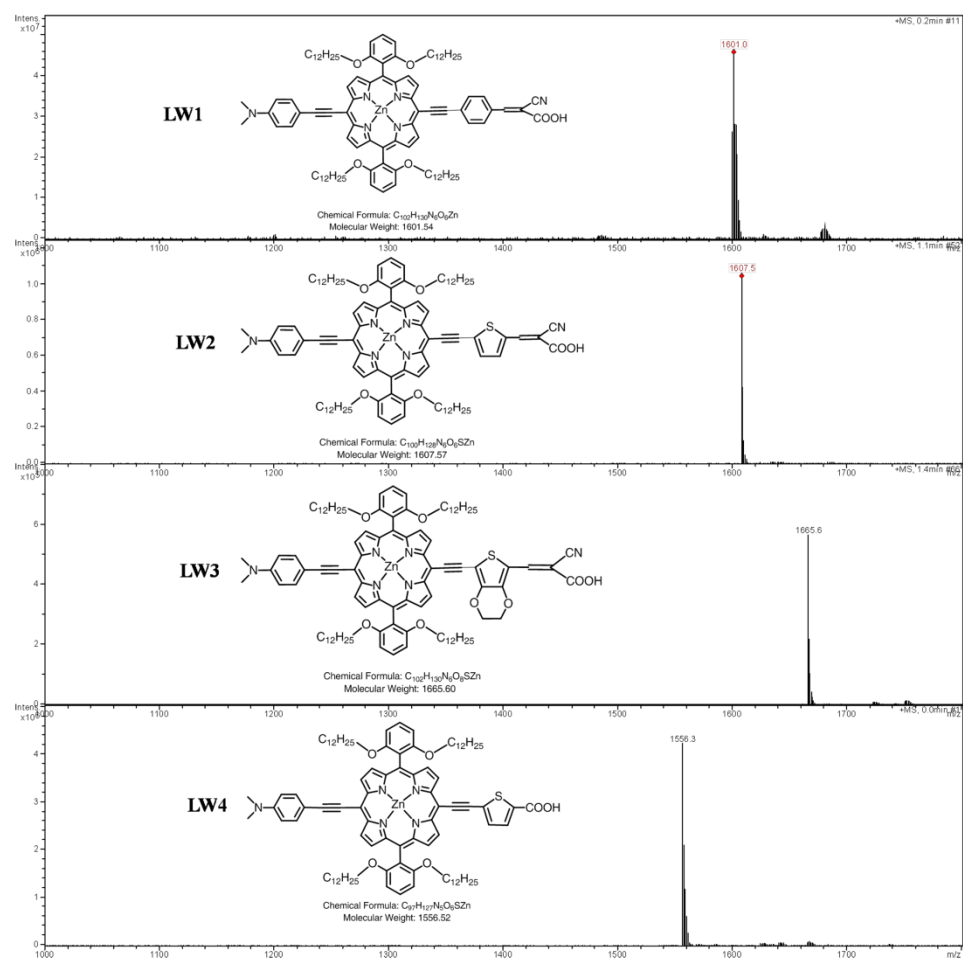


Figure S9. MS (ESI) of LW1-4

2. Electrochemical characterization of LW1-4

Square-wave voltammograms of various dyes were measured on a CHI660C electrochemical workstation. Glassy carbon electrode was used as the working electrode a platinum wire as the counter electrode, and Ag/AgCl (2 M LiCl in EtOH) as the reference electrode.

Figure S10 presents the cyclic voltammograms of LW series dyes.

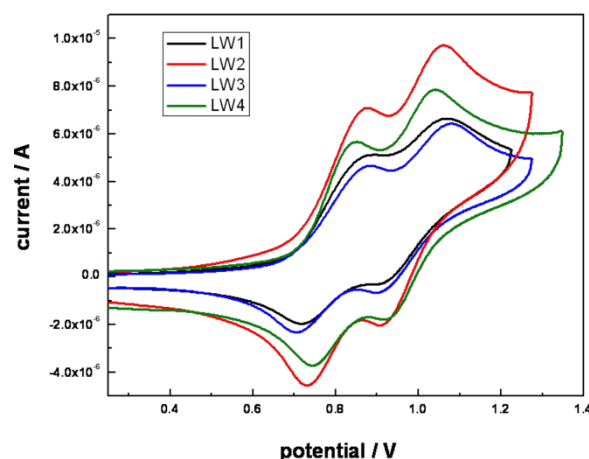


Figure S10. Cyclic voltammograms of Zn(II)-porphyrin dyes in THF at a scan rate of 50 mV/s at room temperature with 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. GC working electrode, Pt wire counter electrode, and Ag/AgCl reference electrode were used.

3. The schematic energy-level diagram

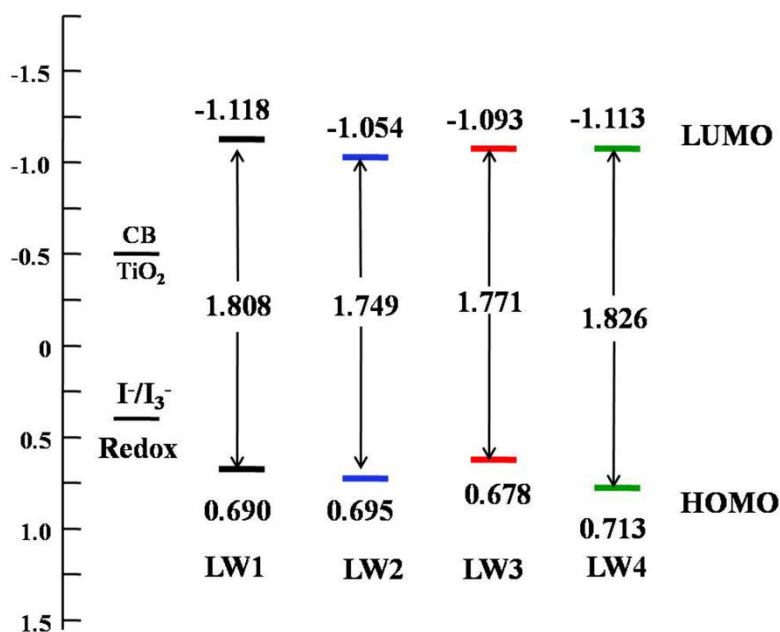


Figure S11. A schematic energy-level diagram of porphyrins LW1-4.

4. Spectroscopy measurements of LW1-4

The UV-visible absorption spectra were observed with a PE950 spectrophotometer and Fluorescent emission spectra were obtained with a Jasco FP-6500 spectrophotometer. Time-resolved luminescence of the porphyrins was recorded on Edinburgh instruments (FLSP920 spectrometers). The excitation light source centers at 445 nm, operated at a frequency of 10 MHz.

Figures S12 compares the UV-visible spectra of LW1-4 in THF solution and the colored transparent layers (4 μm thick) of 20 nm TiO_2 particles.

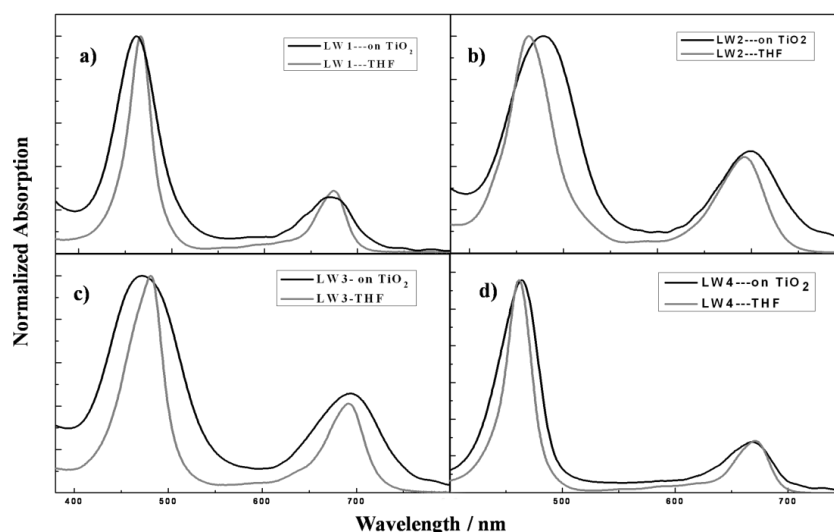


Figure S11. Normalized UV-visible spectra of LW1-4 in THF (grey curve) and on TiO_2 films in air (dark curve)

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