

Thiophene-linked Porphyrin derivatives for dye-sensitized solar cells

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Experimental Section

Materials and reagents. All starting materials were purchased from commercial suppliers (Pacific ChemSource and Alfa Aesar Corp.) in analytical grade. THF and toluene were refluxed over sodium and benzophenone and distilled. DMF was dried and distilled under reduced pressure. POCl₃, 1,2-dichloroethane were atmospheric distillation. All other solvents and chemicals used in this work were analytical grade without further purification. All chromatographic separation were carried out on silica gel (200~300 mesh).

Analytical measurements ¹H NMR and ¹³C NMR spectra were measured with Bruker Avance 400 (400 MHz) spectrometer using tetramethylsilane as internal standard. MALDI-TOF mass spectra were measured with Bruker Aupoflex-III mass spectrometer. FT-IR spectra were obtained on a Perkin-Elmer Spectra One spectrometer. The UV-vis spectra and the emission spectra of the three porphyrin dyes (10⁻⁶ M, in CHCl₃) were measured on a Perkin-Elmer Lamada 25 spectrometer and a Perkin-Elmer LS-50 luminescence spectrometer, respectively. Electrochemical redox potentials were obtained by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) using a

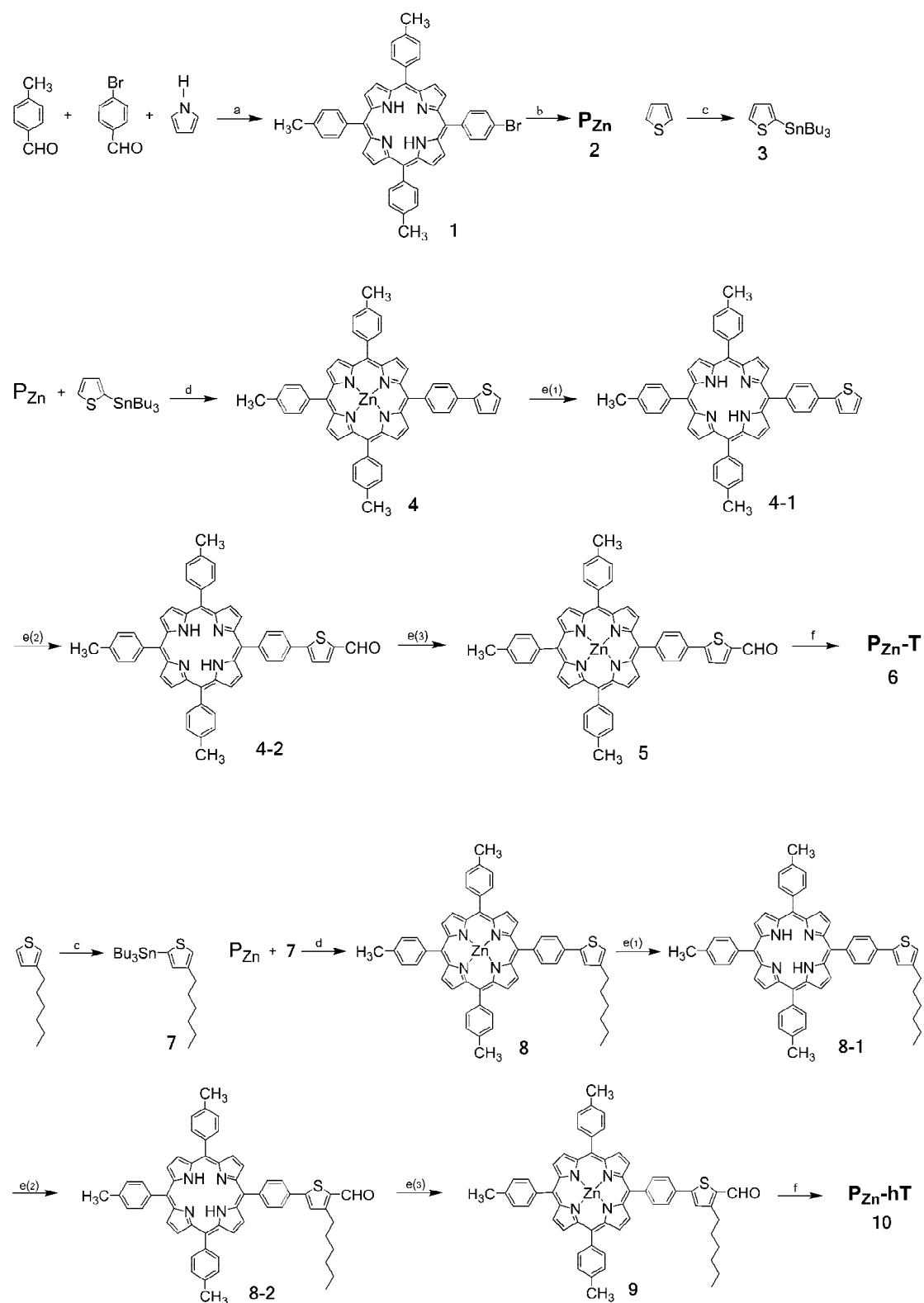
three-electrode cell and an electrochemistry workstation (CHI830B, Chenhua Shanghai). The three-electrode cell was composed of a platinum disk as the working electrode, a platinum wire as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate (TBAP) in DMF, which was degassed with N₂ (99.999%) for 15 min prior to scanning. Ferrocene was added to each sample solution at the end of the experiments, and the ferrocenium / ferrocene (Fc⁺ / Fc) redox couple was used as an internal potential reference. The potentials versus normal hydrogen electrode (NHE) were calibrated by addition of 0.642 V to the potentials versus Fc⁺ / Fc.

Synthesis of the three porphyrin dyes. The detailed synthetic pathways were shown in Scheme 1 and Scheme 2, respectively.

5-(4-Bromophenyl)-10,15,20-tris(4-methylphenyl)porphyrin (1). In a 250 mL one-necked round-bottomed flask, *p*-tolualdehyde (7.2 g, 60 mmol), 4-bromobenzaldehyde (3.7 g, 20 mmol) were dissolved in 200 mL propionic acid, and the solution was heated to reflux at 140 °C. Pyrrole (5.29 g, 80 mmol) was added dropwise and stirred for another 30 min. After cooling to room temperature (rt), the solvent was evaporated, the crude production was separated by column chromatography (petroleum ether / dichloromethane = 2 / 3 as an eluent). After recrystallization from CHCl₃ and CH₃OH, a desired purple solid of compound 1 was obtained (1.4 g, 9.5%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 8.88-8.79 (m, 8 H, pyrrolic-H), 8.1 (d, 8 H, Ar-H), 7.89 (d, 2 H, Ar-H), 7.55 (d, 6 H, Ar-H), 2.70 (s, 9 H, -CH₃), -2.75 (s, 2 H, -NH). MALDI-TOF MS (C₄₇H₃₅BrN₄) *m/z* : calcd for 734.20 ; found 734.22.

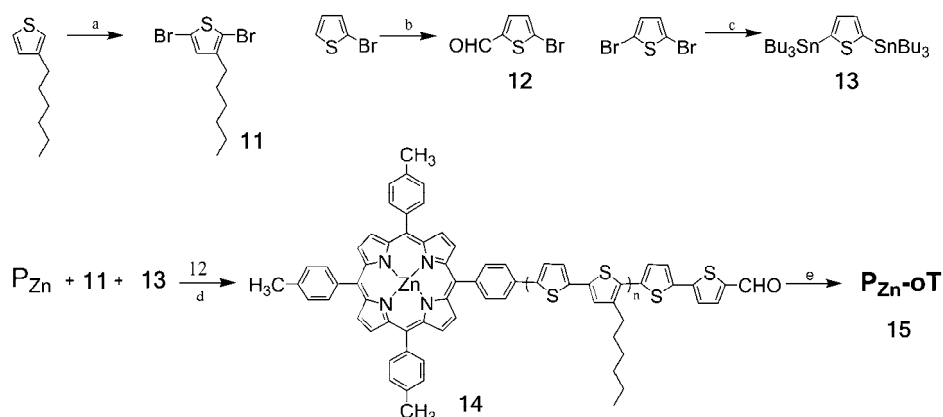
5-(4-Bromophenyl)-10,15,20-tris(4-methylphenyl)porphyrinzinc (2). A mixture of compound 1 (0.74 g, 1 mmol) and Zn (OAc)₂ (1.85 g, 10 mmol) in CHCl₃ (150 mL) and CH₃OH (10 mL) was refluxed for 4 h. After cooling to rt, the mixture was washed by water. The organic layer was dried over anhydrous MgSO₄ and concentrated. A purple solid of compound 2 was obtained (0.73 g, 91%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 8.99-8.89 (m, 8 H, pyrrolic-H), 8.1 (d, 8 H, Ar-H), 7.89 (d, 2 H, Ar-H), 7.55 (d, 6 H, Ar-H), 2.71 (s, 9 H, -CH₃). MALDI-TOF MS (C₄₇H₃₅BrN₄) *m/z* : calcd for 798.12 ; found 798.15.

Scheme 1: Synthetic routes to P_{Zn}-T, P_{Zn}-hT



Reagents and condition: (a). propionic acid, reflux; (b). CH₃OH, CHCl₃, Zn(OAc)₂; (c). n-BuLi, -78 °C; Bu₃SnCl, rt; (d). DMF, Pd[P(Ph₃)₄], reflux; (e). (1) H⁺, (2) ClCH₂CH₂Cl, DMF, 0 °C, then POCl₃, (3) CH₃OH, CHCl₃, Zn(OAc)₂; (f). CH₃CN, cyanoacetic acid, piperidine, reflux.

Scheme 2: Synthetic routes to $P_{Zn}\text{-oT}$



Reagents and conditions: (a). THF, NBS; (b). DMF, POCl_3 ; (c). *n*-BuLi, -78°C ; Bu_3SnCl , rt; (d). toluene, $\text{Pd}[\text{P}(\text{Ph}_3)]_4$, reflux; (e). CH_3CN , cyanoacetic acid, piperidine, reflux.

2-Tributylstannylthiophene (3). In a 100 mL three-necked flask, thiophene (2.52 g, 30 mmol) and dried THF (50 mL) were added under Ar atmosphere. *n*-Butyl lithium (12 mL, 2.5 M in hexane, 30 mmol) was added dropwise at -78°C and the solution was stirred for 1 h with the temperature maintained at -78°C . Then the mixture was warmed up to -40°C , stirred for 3 h and cooled to -78°C again, tributyltin chloride (7.8 mL, 30 mmol) was added in one portion. The mixture was warmed up to room temperature slowly and stirred for another 24 h. The mixture was poured into 100 mL of cooled water, and extracted by hexane. The organic layer was dried over anhydrous MgSO_4 . A light yellow liquid 3 (9.1 g, 81%) was obtained after evaporating the solvent by rotary evaporation. ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 7.65 (d, 1 H, Th-H), 7.23 (d, 1 H, Th-H), 7.19 (d, 1 H, Th-H), 1.67-1.58 (m, 6 H, $-\text{CH}_2$), 1.37-1.31 (m, 6 H, $-\text{CH}_2$), 1.12-1.08 (m, 6 H, $-\text{CH}_2$), 0.91-0.85 (m, 9 H, $-\text{CH}_3$).

5-(4-(2-Thienyl)-phenyl)-10,15,20-tris(4-methylphenyl)porphyrinatozinc(II) (4). In a 50 mL three-necked flask, porphyrin 2 (0.51 g, 0.64 mmol), 2-tributylstannylthiophene (0.24 g, 0.64 mmol) and $\text{Pd}[\text{P}(\text{Ph}_3)]_4$ (15.5 mg, 0.014 mmol) were dissolved in 25 mL of DMF under Ar atmosphere. The mixture was stirred for 6 days at 100°C . After cooling to rt, the solution was extracted with dichloromethane and dried over

anhydrous MgSO₄. The solvent was removed by rotary evaporation, and the residue was purified by silica gel column chromatography with petroleum ether / dichloromethane (2 / 3) as the eluent to yield 4 as a purple black solid (0.25 g, 49%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 9.02-8.95 (m, 8 H, pyrrolic-H), 8.24 (d, 2 H, Ar-H), 8.1 (d, 6 H, Ar-H), 8.01 (d, 2 H, Ar-H), 7.62 (s, 1 H, Th-H), 7.56 (d, 6 H, Ar-H), 7.43 (d, 1 H, Th-H), 7.23 (s, 1 H, Th-H), 2.70 (s, 9 H, -CH₃). MALDI-TOF MS (C₅₁H₃₆N₄SZn) *m/z* : calcd for 800.20 ; found 800.21.

5-(5-(4-Phenyl)-10,15,20-tris(4-methylphenyl)porphyrinatozinc-yl)-thiophene-2-carbaldehyde (5). In a 50 mL three-necked flask, porphyrin 4 (0.25 g, 0.31 mmol), DMF (0.49 mL, 6.2 mmol), 1,2-dichloroethane 15 mL were added sequentially under Ar atmosphere. POCl₃ (0.57 mL, 6.2 mmol) was added quickly at 0 °C. The mixture was heated to 80 °C and stirred for 12 h. After cooling to rt, diluted K₂CO₃ solution was added. The solution was extracted with dichloromethane, and washed by water and brine. The organic layer was dried over anhydrous MgSO₄. Solvent was removed by rotary evaporation, and the residue was purified by silica gel column chromatography with petroleum ether / dichloromethane (1 / 1) as the eluent to yield 5 as a purple-red solid (0.115 g, 45%). IR (KBr, *v*_{max}/cm⁻¹): 1671 (*v*_{C=O}). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 10.0 (s, 1 H, -CHO), 8.89-8.85 (m, 8 H, pyrrolic-H), 8.29 (d, 2 H, Ar-H), 8.1-8.05 (m, 8 H, Ar-H), 7.89 (d, 1 H, Th-H), 7.77 (d, 1 H, Th-H), 7.56 (d, 6 H, Ar-H), 2.70 (s, 9 H, -CH₃). ¹³C NMR (CHCl₃, 400 MHz, δ/ppm): 182.69, 150.49, 149.79, 144.47, 139.89, 137.36, 137.18, 135.21, 134.41, 132.28, 132.12, 131.42, 127.34, 124.61, 124.45, 121.39, 21.52. MALDI-TOF MS (C₅₂H₃₆N₄OSZn) *m/z* : calcd for 828.19; found 828.22.

2-Cyano-3-(5-(4-(2-thienyl)-phenyl)-10,15,20-tris(4-methylphenyl)porphyrinatozinc(II)-yl)-acrylic acid (P_{Zn}-T) (6). To a solution of acetonitrile (15 mL) and toluene (5 mL), porphyrin compound 5 (0.116 g, 0.14 mmol), cyanoacetic acid (35.4 mg, 0.42 mmol) and piperidine (0.5 mL) were added sequentially under Ar atmosphere, and the mixture was refluxed for 12 h. After cooling to rt, the solution was extracted with dichloromethane, and washed by water and 0.1 M HCl. The organic layer was dried over anhydrous MgSO₄. Solvent was removed by rotary evaporation, and the residue

was purified by silica gel column chromatography with methanol / dichloromethane (1 / 1) as eluent to yield a purple-black solid compound **6** (0.101 g, 81%). IR (KBr, ν_{max}/cm^{-1}): 2210 ($\nu_{\text{C}\equiv\text{N}}$). UV-vis λ_{max} (CHCl_3)/nm: 422.03, 549.91, 590.00. ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 8.98 (m, 8 H, pyrrolic-H), 8.3 (s, 1 H, -CH=C-), 8.25 (d, 2 H, Th-H), 8.1 (d, 8 H, Ar-H), 7.57 (d, 8 H, Ar-H), 2.72 (s, 9 H, -CH₃). ^{13}C NMR (DMSO, 400 MHz, δ/ppm): 148.98, 148.87, 148.41, 139.29, 136.06, 134.68, 133.52, 132.05, 131.24, 131.01, 130.81, 130.72, 129.31, 126.68, 125.15, 123.94, 122.75, 120.04, 119.87. Elem. Anal. For $\text{C}_{56}\text{H}_{40}\text{N}_5\text{O}_2\text{SZn}$ Calc: C, 73.72; H, 4.42; N, 7.68; S, 3.51. Found: C, 73.78; H, 4.43; N, 7.66; S, 3.50. MALDI-TOF MS ($\text{C}_{56}\text{H}_{40}\text{N}_5\text{O}_2\text{SZn}$) m/z : calcd for 910.22; found 910.25.

3-Hexyl-5-tributylstannyl-thiophene (7). The synthetic procedure for compound **7** was similar to that for **3**, except that 3-hexylthiophene was used instead of thiophene. ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 7.18 (s, 1 H, Th-H), 6.96 (s, 1 H, Th-H), 2.64 (t, 2 H, -CH₂), 1.62-1.54 (m, 6 H, -CH₂), 1.36-1.30 (m, 6 H, -CH₂), 1.11-1.06 (m, 6 H, -CH₂), 0.93-0.87 (m, 9 H, -CH₃).

5-(4-(3-Hexyl-2-thienyl)-phenyl)-10,15,20-tris(4-methylphenyl)porphyrinatozinc(II) (8). In a 50 mL three-necked flask, porphyrin **2** (0.5 g, 0.63 mmol), 3-hexyl-5-tributylstannyl-thiophene (0.29 g, 0.63 mmol) and $\text{Pd}[\text{P}(\text{Ph}_3)]_4$ (14 mg, 0.013 mmol) were dissolved in 20 mL DMF under Ar atmosphere. The mixture was stirred for 6 days at 100 °C. After cooling to rt, the solution was extracted with dichloromethane and washed by water. The organic layer was dried over anhydrous MgSO_4 . The solvent was removed by rotary evaporation, and the residue was purified by silica gel column chromatography with petroleum ether / dichloromethane (2 / 3) as the eluent to yield **8** as a purple black solid (0.234 g, 42%). ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 9.03-8.97 (m, 8 H, pyrrolic-H), 8.23 (d, 2 H, Ar-H), 8.12 (d, 6 H, Ar-H), 7.99 (d, 2 H, Ar-H), 7.57 (d, 6 H, Ar-H), 7.47 (s, 1 H, Th-H), 7.01 (s, 1 H, Th-H), 2.75 (t, 2 H, -CH₂), 1.76-1.26 (m, 6 H, -CH₂), 0.87 (t, 3 H, -CH₃). ^{13}C NMR (CDCl_3 , 400 MHz, δ/ppm): 150.29, 144.57, 139.97, 136.99, 134.91, 134.36, 132.02, 131.82, 131.64, 127.23, 124.93, 123.75, 121.14, 121.02, 119.85. MALDI-TOF MS ($\text{C}_{57}\text{H}_{48}\text{N}_4\text{SZn}$) m/z : calcd for 884.29; found

884.32.

5-(5-(4-Phenyl)-10,15,20-tris(4-methylphenyl)porphyrinatozinc-yl)-3-hexyl-thiophene-2-carbaldehyde (9). In a 50 mL three-necked flask, porphyrin 8 (0.225 g, 0.26 mmol), DMF (0.44 mL, 5.2 mmol), 1,2-dichloroethane of 15 mL were added sequentially under Ar atmosphere. POCl₃ (0.48 mL, 5.2 mmol) was added quickly at 0 °C, then the mixture was heated to 60 °C and stirred for 12 h. After the mixture was cooled to rt, diluted K₂CO₃ solution was added. The mixture was extracted with dichloromethane and washed by water and brine. The organic layer was dried over anhydrous MgSO₄, and the solvent was removed by rotary evaporation. The residue was purified by silica gel column chromatography with petroleum ether / dichloromethane (from 2 / 3 to 3 / 1) as the eluent to yield 9 as a purple-black solid (80 mg, 34%). IR (KBr, ν_{max}/cm^{-1}): 1653 ($\nu_{\text{C=O}}$). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 10.13 (s, 1 H, -CHO), 8.88-8.86 (m, 8 H, pyrrolic-H), 8.28 (d, 2 H, Ar-H), 8.1 (d, 6 H, Ar-H), 8.06 (d, 2 H, Ar-H), 7.56 (d, 6 H, Ar-H), 7.46 (s, 1 H, Th-H), 3.08 (t, 2 H, CH₂), 2.70 (s, 9 H, -CH₃), 1.83 (t, 2 H, -CH₂), 1.48-1.26 (m, 6 H, -CH₂), 0.87 (t, 3 H, -CH₃). ¹³C NMR (CDCl₃, 400 MHz, δ/ppm): 181.82, 150.34, 144.27, 139.86, 136.73, 135.13, 134.38, 132.24, 132.02, 131.43, 127.31, 126.82, 124.43, 121.51, 121.34, 119.53. MALDI-TOF MS (C₅₈H₄₈N₄OSZn) m/z : calcd for 912.28 ; found 912.31.

2-Cyano-3-(5-(4-(3-hexyl-2-thienyl)-phenyl)-10,15,20-tris(4-methylphenyl)porphyrinatozinc(II)yl)-acrylic acid (P_{Zn}-hT) (10). In a 50 mL three-necked flask, porphyrin compound 9 (0.08 g, 0.09 mmol) was dissolved in a solution of acetonitrile (15 mL) and toluene (5 mL), cyanoacetic acid (23 mg, 0.27 mmol) and piperidine (0.5 mL) were added sequentially under Ar atmosphere. The mixture was refluxed for 12 h and cooled to rt. The mixture was extracted with dichloromethane and washed by water and 0.1 M HCl. The organic layer was dried over anhydrous MgSO₄. The solvent was removed by rotary evaporation, and the residue was purified by silica gel column chromatography with methanol / dichloromethane (1 / 1) as the eluent to yield a purple-red solid compound 10 (71 mg, 80%). IR (KBr, ν_{max}/cm^{-1}): 2210 ($\nu_{\text{C}\equiv\text{N}}$). UV-vis λ_{max} (CHCl₃)/nm: 422.21, 549.71, 589.91. ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 8.97 (m, 8 H, pyrrolic-H),

8.52 (s, 1 H, -CH=C-), 8.3 (d, 2 H, Th-H), 8.1 (d, 8 H, Ar-H), 7.57 (d, 8 H, Ar-H) , 2.93 (t, 2 H, -CH₂), 2.72 (s, 9 H, -CH₃), 1.78 (m, 2 H, -CH₂), 1.49-1.26 (m, 6 H, -CH₂), 0.86 (t, 3 H, -CH₃). ¹³C NMR (CDCl₃, 400 MHz, δ/ppm): 149.46, 149.38, 149.31, 138.88, 136.08, 135.33, 134.21, 133.38, 131.24, 130.97, 130.36, 129.29, 126.28, 125.11, 123.62, 120.45, 120.30, 118.48. Elem. Anal. For C₆₂H₅₂N₅O₂SZn Calc: C, 74.72; H, 5.26; N, 7.03; S, 3.22. Found: C, 74.78; H, 5.28; N, 7.01; S, 3.21. MALDI-TOF MS (C₆₂H₅₂N₅O₂SZn) *m/z* : calcd for 994.31 ; found 994.35.

2,5-Dibromo-3-hexylthiophene (11). In a 100 mL two-necked flask, 3-hexylthiophene (1.67 g, 10 mmol) and THF (50 mL) were added, then a solution of *N*-bromosuccinimide (3.9 g, 21 mmol) in 10 mL of THF was added dropwise at 0 °C. The reaction mixture was stirred for 8 h with the temperature maintained at 0 °C in the dark. The solvent was removed by rotary evaporation, and the residue was purified by silica gel column chromatography with petroleum ether as the eluent to yield a colorless liquid of compound 11 (2.1 g, 64%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 6.77 (s, 1 H, Th-H), 2.5 (t, 3 H, -CH₂), 1.53 (d, 2 H, CH₂), 1.29 (s, 6 H, -CH₂), 0.88 (t, 3 H, -CH₃).

5-Bromothiophene-2-carbaldehyde (12). In a 50 mL three-necked flask, 2-bromothiophene (6.52 g, 40 mmol), dried DMF (4.64 mL, 60 mmol) and POCl₃ (5.66 mL, 60 mmol) were added sequentially. The reaction mixture was stirred at 25 °C for 30 min, then heated up to 90 °C and stirred for 4 h. After cooling to rt, 100 mL distilled water was added. The solution was extracted with dichloromethane and washed by water, aqueous KOH (10%) and brine. The organic layer was dried over anhydrous MgSO₄ and concentrated. The residue was purified by silica gel column chromatography with petroleum ether / dichloromethane (3 / 4) as the eluent to yield 12 as a yellow liquid (4.3 g, 56%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 9.81 (s, 1 H, Th-CHO), 7.53 (s, 1 H, Th-H), 7.20 (s, 1 H, Th-H).

2,5-Bis(tributylstannyl)thiophene (13). Under Ar atmosphere, 2,5-dibromothiophene (7.26 g, 30 mmol) and 150 mL freshly distilled dry THF were added in a 250 mL three-necked flask. *n*-Butyl lithium (32 mL, 2.5 M in hexane, 80 mmol) was added dropwise at -78 °C, and the solution was stirred for 1 h with the temperature maintained at -78 °C, then tributyltin chloride (32 mL, 120 mmol) was added in one portion. The mixture was

allowed up to room temperature slowly and stirred for another 24 h. Finally, the mixture was poured into 100 mL of cooled water, and extracted by hexane. The organic layer was dried over anhydrous MgSO_4 . Removal of the solvent by rotary evaporation, the residue was distilled under vacuum, a yellow-brown liquid stannylene derivative 13 (16.5 g, 83%) was obtained. The stannylene derivative was used in next step without further purified. ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 7.39 (s, 1 H, Th-H), 1.62-1.53 (m, 12 H, $-\text{CH}_2$), 1.38-1.29 (m, 12 H, $-\text{CH}_2$), 1.13-1.08 (m, 12 H, $-\text{CH}_2$), 0.94-0.84 (m, 18 H, $-\text{CH}_3$).

5-(5-(4-Phenyl)-10,15,20-tris(4-methylphenyl)porphyrinatozinc-yl)-oligthiophene-2-carbaldehyde (14). In a 100 mL three-necked flask, 2,5-dibromo-3-hexyl-thiophene (0.48 g, 1.46 mmol), 2,5-Bis(tributylstannyl)thiophene (1.32 g, 2 mmol), freshly distilled toluene (20 mL) and $\text{Pd}[\text{P}(\text{Ph}_3)]_4$ (44 mg, 0.04 mmol) were added under Ar atmosphere, and the solution was stirred at 100 °C for 36 h. Then porphyrin 2 (0.29 g, 0.365 mmol) was added and stirred for 48 h. Finally, 5-bromothiophene-2-carbaldehyde (0.133 g, 0.7 mmol) was added and stirred for another 12 h. After cooling to rt, the mixture was poured into CH_3OH to give a solid, recrystallized from petroleum ether and dried under vacuum. A red-black solid compound 14 was obtained (0.47 g, 6.8%). IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 1660 ($\nu_{\text{C=O}}$). ^1H NMR: 9.88 (s, 1 H, $-\text{CHO}$), 8.99-8.96 (d, 8 H, pyrrolic-H), 8.1 (b, 8 H, phenyl-H), 7.7-7.69 (d, 2 H, phenyl-H), 7.56 (b, 6 H, phenyl-H), 7.52 (s, 1 H, Th-H), 7.12-6.99 (m, 15 H, Th-H), 2.81-2.76(m, 8 H, $-\text{CH}_2$), 2.71 (s, 9 H, $-\text{CH}_3$), 1.72-1.64(m, 8 H, $-\text{CH}_2$), 1.42-1.34 (m, 24 H, $-\text{CH}_2$), 0.91 (m, 12 H, $-\text{CH}_3$).

2-Cyano-3-(5-(4-oligthiophene)-phenyl)-10,15,20-trimethylphenyl-porphyrinatozinc(II)yl-acrylic acid ($\text{P}_{\text{Zn}}\text{-oT}$) (15). In a 50 mL three-necked flask, the mixture of porphyrin compound 14 (0.125 g, 0.065 mmol), 15 mL of acetonitrile, cyanoacetic acid (14 mg, 0.165 mmol) and piperidine (0.5 mL) were refluxed for 12 h and then cooled to rt. The solution was extracted with petroleum ether and washed by water and 0.1 M HCl. After drying under vacuum, a brown solid compound 15 was obtained (0.08 g, 62%). UV-vis λ_{max} (CHCl_3)/nm: 422, 546, 590. IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 2216 ($\nu_{\text{C}\equiv\text{N}}$). ^1H NMR:

8.96-8.94 (d, 8 H, pyrrolic-H), 8.2 (s, 1 H, -CH=C-), 8.1-8.08 (m, 6 H, phenyl-H), 8.0-7.98 (m, 2 H, phenyl-H), 7.56-7.54 (m, 8 H, phenyl-H), 7.12-6.99 (m, 15 H, Th-H), 2.81-2.76 (m, 8 H, -CH₂), 2.71 (s, 9H, -CH₃), 1.81-1.76 (m, 8 H, -CH₂), 1.69-1.66 (m, 8 H, -CH₂), 1.45-1.33 (m, 18 H, -CH₂), 0.92 (m, 12 H, -CH₃). Elem. Anal. For C₁₁₆H₁₀₆N₅O₂S₁₀Zn: Calc: C, 70.08; H, 5.37; N, 3.52; S, 16.13. Found: C, 70.17; H, 5.39; N, 3.51; S, 16.09.

General procedure for preparing and testing solar cells. The TiO₂ suspension was prepared from P25 (Degussa AG, Germany) and 1 wt% magnesium acetate solution on following a literature procedure.¹ The suspension was deposited on a transparent conducting glass by using a doctor blade technique. The film was sintered at 450 °C for 30 min, then treated with 40 mM TiCl₄ aqueous solution at 70 °C for 30 min and annealed again at 450 °C for 30 min. After the film was cooled to rt, it was immersed into 1.0×10⁻³ M dye solution for 15 min in the dark. The sensitized electrode was then rinsed with ethanol, and dried. One drop of electrolyte solution was deposited onto the surface of the electrode and penetrated inside the TiO₂ film via capillary action. The photovoltaic measurements were performed in a sandwich cell consisting of the porphyrin-sensitized TiO₂ electrode as the working electrode and a Pt foil as the counter electrode. The electrolyte consists of 0.5 M LiI, 0.05 M I₂, and 0.5 M 4-*tert*-butylpyridine (TBP) in 3-methoxypropionitrile. The photocurrent- voltage (*J-V*) characteristics were recorded on Keithley 2602 Source meter. Porphyrin dyes and N719 (as reference) sensitized TiO₂ electrodes were measured under simulated AM 1.5 irradiation (100 mW cm⁻²). The solar-to-electricity conversion efficiency (η) of the DSSCs is calculated from short-circuit photocurrent (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor (ff) and the intensity of the incident light (P_{in}) according to the following equation:

$$\eta = \frac{J_{sc} (\text{mA cm}^{-2}) \times V_{oc} (\text{V}) \times ff}{P_{in} (\text{mW cm}^{-2})}$$

The IPCE values are plotted as a function of the excited wavelength and defined according to the following equation:²

$$\text{IPCE}(\lambda) = \frac{1240}{\lambda \text{ (nm)}} \times \frac{J_{\text{sc}} \text{ (mA cm}^{-2}\text{)}}{\Phi \text{ (mW cm}^{-2}\text{)}}$$

Where J_{sc} is the short-circuit photocurrent density generated by monochromatic light, λ is the wavelength of incident monochromatic light, and Φ is the incident light intensity.

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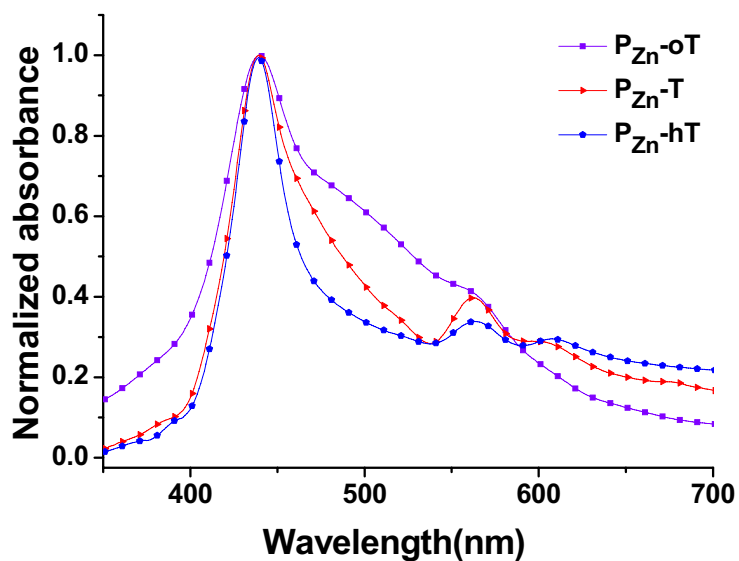


Fig. S1 Absorption spectra of the three porphyrin dyes on TiO₂ film.

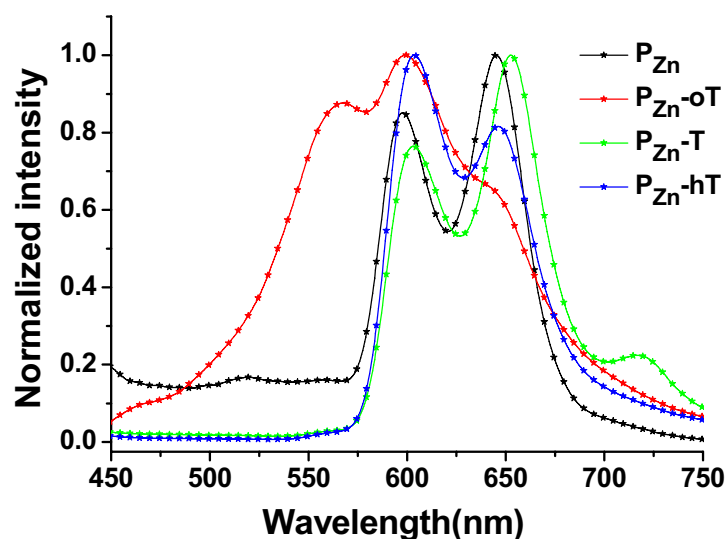


Fig. S2 Emission spectra of the three porphyrin dyes were obtained by exciting at the peaks of the Soret bands.

TABLE S1: UV-Vis absorption and emission data of the porphyrin dyes measured in CHCl₃ and on TiO₂ films

Dye	Soret / Q-band(s) ($\epsilon, 10^5 \text{M}^{-1} \text{cm}^{-1}$)	Soret/ Q-band (f)	E_{mi} (nm)	λ_{int} (nm)
P _{Zn} -oT	422 (1.2)	441/	568, 600	494
	546 (0.13), 590 (0.067)	560, 730		
P _{Zn} -T	422 (2.55)	440/	603, 653	563
	550 (0.18), 590 (0.091)	564, 605		
P _{Zn} -hT	422 (2.64)	440/	603, 646	563
	550 (0.16), 590 (0.04)	564, 607		
P _{Zn}	420 (2.21)		598, 645	448
	465 (0.07), 547 (0.07)			

TABLE S2: Electrochemical data for the porphyrin dyes

Dye	E_{0-0}^a (eV)	E_{ox}^b (V)	E_{red}^c (V)	E_{ox}^{*d} (V)	ΔG_{inj}^e (eV)	ΔG_{reg}^f (eV)
P _{Zn} -oT	2.51	1.29	-1.08	-1.22	-0.72	-0.79
P _{Zn} -T	2.2	1.26	-1.138	-0.94	-0.44	-0.76
P _{Zn} -hT	2.2	1.27	-1.128	-0.93	-0.43	-0.77
P _{Zn}	2.77	1.23	-1.19	-1.54		

a. Determined from the intercept of the normalized absorption and emission spectra. b. Ground state redox potentials (vs. NHE). c. Ground state redox potentials (vs. NHE). d. Excited-state oxidation potentials approximated from E_{ox} and E_{0-0} (vs. NHE). e. Driving forces for electron injection from the porphyrin singlet excited state (E_{ox}^*) to the CB of TiO₂ (-0.5 V vs. NHE). f. Driving forces for the regeneration of porphyrin radical cation (E_{ox}) by Γ / Γ^{3-} redox couple (+0.5 V vs. NHE).

TABLE. S3: Photovoltaic performance of P_{Zn}-hT on the durative illuminating time

Illumination time (min)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	ff	η (%)
2	5.41	0.63	0.74	2.53
4	5.63	0.63	0.74	2.63
8	8.88	0.63	0.70	3.93
10	9.44	0.63	0.69	4.13
20	10.46	0.61	0.69	4.40
30	10.96	0.61	0.68	4.55
40	12.10	0.61	0.67	4.92
60	12.65	0.61	0.66	5.06
80	12.79	0.60	0.66	5.09
100	12.95	0.60	0.66	5.14
120	12.95	0.60	0.66	5.14