

Supporting Information

A *meso-meso* directly linked porphyrin dimer-based double D- π -A sensitizer for efficient dye-sensitized solar cells

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General

All solvents were purified according to standard methods. Other chemicals (AR) obtained from commercial sources were used without further purification. NMR solvents were used as received. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometer using TMS as the internal standard. UV-vis spectra were obtained on a Varian Cary 300 Conc UV-visible spectrophotometer. HR-MS data was measured on a Varian 7.0T FTMS. IR spectra were recorded on a Bio-rad FTS6000 spectrometer. Elementary analyses were performed using a Vario EL CUBE Analyzer. Cyclic voltammetry experiments and electrochemical impedance spectroscopy were recorded on a Zennium electrochemical workstation (Zahner, Germany). Electrochemical impedance spectroscopy was recorded in the dark under -0.60 V bias. The frequencies explored ranged from 100 mHz to 100 kHz. Cyclic voltammetry experiments were carried out using a conventional three-electrode system employing glassy carbon electrode as the working electrode, Ag/Ag⁺ electrode as the reference electrode, and Pt wire as the counter electrode. The redox potentials were measured in THF, using 0.1 M *n*-Bu₄NPF₆ as supporting electrolyte with a scan rate of 100 mV S⁻¹. Dipyrromethane,¹ 4-Octyloxyiodobenzene,² N,N-bis(4-octyloxyphenyl)aniline,² 4-(bis(4-(octyloxy)phenyl)amino)benzaldehyde,³ were synthesized according to literature methods.

Fabrication and characterization of DSSCs

The DSSCs were fabricated according to a previous literature procedure.⁴ A TiO₂ film (~10 μm) for the transparent nanocrystalline layer was prepared by doctor-blade method coating a commercial 20 nm TiO₂ sol (China National Academy of Nanotechnology & Engineering) onto the treated FTO conductive glass (Nippon Sheet Glass, Japan, fluorine-doped SnO₂ over layer, sheet resistance of 15 Ω/sq, treated with TiCl₄ (0.05 M) solution). The scattering layer (~4 μm) was applied over the transparent layer by doctor-blade method, then gradually heated to 500°C and sintered for 60 min. The resulting TiO₂ electrodes were treated by TiCl₄ and sintered again at 500°C for 60 min. The Pt electrode was obtained by thermal deposition of a platinum layer onto the surface of FTO at 450°C for 30 min. The TiO₂ thin film was dipped into the 0.3 mM dye solution in THF for at least 12 h. The electrolyte was composed of 0.3 M DMPII, 0.1 M LiI, 0.05 M I₂, and 0.5 M 4-*tert*-butylpyridine in acetonitrile. The DSSCs were illuminated by a solar simulator (Oriol® Sol2A, Newport Corporation) under 100 mW/cm² irradiation, which was calibrated by a standard silicon solar cell. The photocurrent intensity-voltage (*J-V*) characteristic curves of the DSSC under simulated sunlight were recorded using an IM6ex electrochemical workstation (Zahner, Germany). The measurement of the incident photon-to-current conversion efficiency (IPCE) was performed by using a commercial setup (QTest Station 2000 IPCE Measurement System, CROWNTech, USA).

Optical Spectroscopy

UV/Vis absorption spectra of the porphyrins in THF and adsorbed onto TiO₂ electrodes were recorded on a Varian Cary 300 Conc UV-visible spectrophotometer. For the absorption spectra of the thin films on TiO₂, TiO₂ films (area: 1×1 cm²) were prepared with thicknesses of about 1 μm to obtain comparable shapes and peak positions. The films were immersed in 0.3 mM solutions of the porphyrins in THF for 5 minutes and the films were rinsed with THF, dried, and the absorbance was measured (Transmittance UV spectra). Steady-state fluorescence spectra were

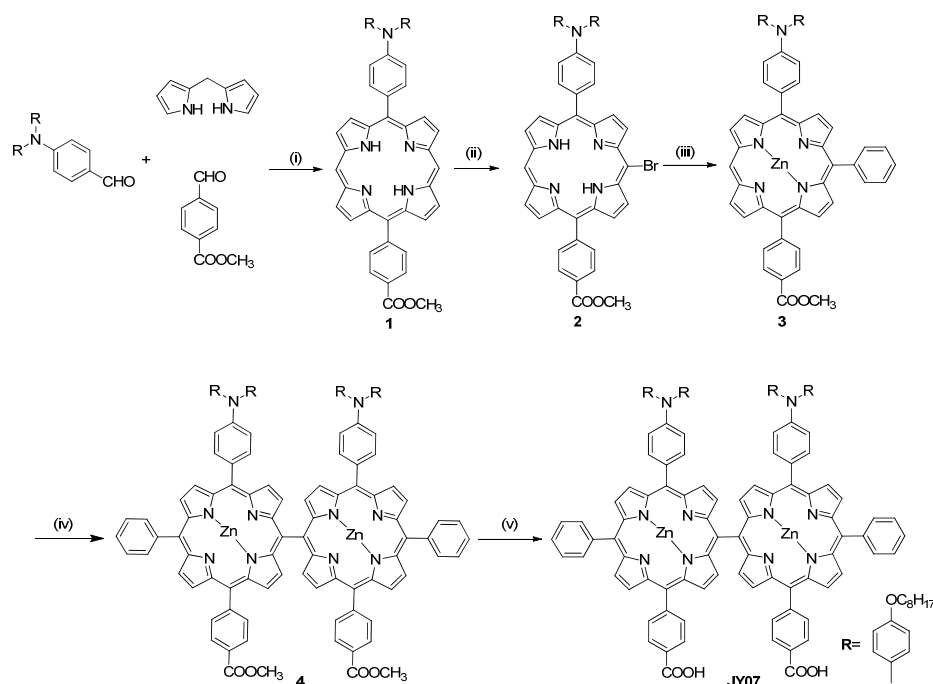
acquired on a Varian Cary Eclipse fluorescence spectrophotometer.

Dye-loading examination

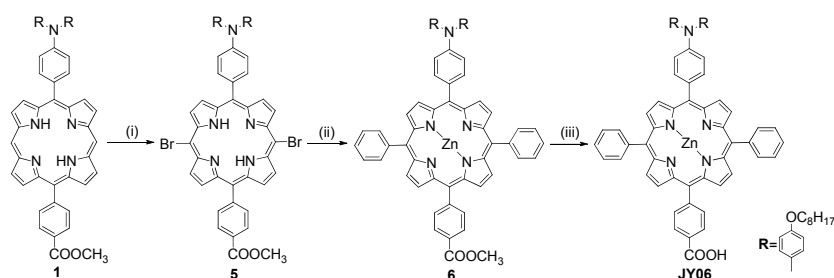
To determine the dye-loading amount of **JY06** and **JY07** on TiO₂ films, the dye adsorbed on TiO₂ (0.4 cm × 0.4 cm) was desorbed in 0.2 M KOH (aq) in THF (2:8, v/v). The calibration curves for **JY06** and **JY07** in 0.2 M KOH (aq) in THF (2:8, v/v) were derived to obtain the absorption coefficients. The amounts of dye-loading on TiO₂ films were obtained from the measured absorbances of the Soret bands in the spectra and the calibrated absorption coefficients at the same spectral position according to Beers' law.

In fact, more than 12 h exposure to commonly used 0.1 M aqueous solution of KOH in THF (2:8, v/v) was unable to completely desorb the dye **JY07** from TiO₂. Instead, a 0.2 M aqueous solution of KOH in THF (2:8, v/v) was used to desorb the dye from TiO₂. The requirement of a higher concentration of the base to desorb the dye from TiO₂ provides further evidence of a stronger adhesion of the double D- π -A dye than the porphyrin dye that possessed a single anchoring group.

Synthetic procedure



Reagents: (i) TFA, DDQ; (ii) NBS; (iii) a) Phenylboronic acid, Pd(PPh₃)₄, Cs₂CO₃; b) Zn(OAc)₂·2H₂O; (iv) PIFA; (v) KOH, EtOH/H₂O/THF.



Reagents: (i) NBS; (ii) a) Phenylboronic acid, Pd(PPh₃)₄, Cs₂CO₃; b) Zn(OAc)₂·2H₂O; (iii) KOH, EtOH/H₂O/THF.

Scheme S1. Syntheses of JY06 and JY07.

Synthesis of compound 1. To a degassed solution of dipyrromethane (731 mg, 5 mmol), 4-(bis(4-(octyloxy)phenyl)amino)benzaldehyde (1.32 g, 2.5 mmol), and methyl 4-formylbenzoate (410.5 mg, 2.5 mmol) in CH₂Cl₂ (500 mL) was added CF₃COOH (0.22 mL, 3 mmol). The mixture was stirred in the dark for 10 h and then DDQ (1.0 g, 4.5 mmol) was added. After another 1 h, Et₃N (5.0 mL) was added and the solvent was removed under reduced pressure. Purification by silica gel column chromatography (CH₂Cl₂/PE = 3/1) and recrystallization from CH₂Cl₂/MeOH afforded compound **1** as a purple red solid. Yield: 460 mg (19%). ¹H NMR (400 MHz, CDCl₃) δ 10.32 (s, 2H), 9.41 (t, *J* = 4.7 Hz, 4H), 9.25 (d, *J* = 4.6 Hz, 2H), 9.02 (d, *J* = 4.6 Hz, 2H), 8.49 (d, *J* = 8.0 Hz, 2H), 8.36 (d, *J* = 8.0 Hz, 2H), 8.06 (d, *J* = 8.3 Hz, 2H), 7.45–7.30 (m, 6H), 6.99 (d, *J* = 8.8 Hz, 4H), 4.14 (s, 3H), 4.01 (t, *J* = 6.5 Hz, 4H), 1.89–1.77 (m, 4H), 1.55–1.45 (m, 4H), 1.43–1.25 (m, 16H), 0.98–0.86 (m, 6H), –3.05 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 167.64, 156.07, 148.84, 147.86, 146.88, 146.57, 145.41, 145.26, 140.90, 135.98, 135.09, 132.80, 132.15, 131.73, 131.64, 130.63, 129.66, 128.39, 127.43, 120.47, 118.45, 117.31, 115.72, 105.62, 68.56, 52.67, 32.06, 29.63, 29.49, 26.35, 22.90, 14.34. HRMS (MALDI-TOF): *m/z* [M+H]⁺ calcd for C₆₂H₆₆N₅O₄, 944.5109; found, 944.5108. FT-IR (KBr) *v*_{max}: 3271, 3038, 2925, 2854, 1719, 1603, 1504, 1278, 1240, 1108 cm⁻¹.

Synthesis of compound 2. Porphyrin **1** (943 mg, 1.0 mmol) was dissolved in CH₂Cl₂/MeOH (*v/v* = 9:1, 200 mL) and NBS (196 mg, 1.1 mmol) was added. The reaction mixture was stirred under air at room temperature for 15 min and quenched with acetone (1.0 mL). The solvent was evaporated. After evaporation of the solvent, the product was isolated by column chromatography (silica gel) using CH₂Cl₂/PE = 3/1 as eluent. Recrystallization from CH₂Cl₂/CH₃OH gave a red solid. Yield: 562 mg (55%). ¹H NMR (400 MHz, CDCl₃) δ 10.16 (s, 1H), 9.74 (t, *J* = 4.3 Hz, 2H), 9.29 (t, *J* = 5.4 Hz, 2H), 9.12 (t, *J* = 5.1 Hz, 2H), 8.87 (t, *J* = 4.0 Hz, 2H), 8.47 (d, *J* = 8.0 Hz, 2H), 8.29 (d, *J* = 8.0 Hz, 2H), 7.98 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 4H), 7.32 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 4H), 4.13 (s, 3H), 4.00 (t, *J* = 6.5 Hz, 4H), 1.89–1.74 (m, 4H), 1.54–1.44 (m, 4H), 1.43–1.20 (m, 16H), 0.89 (t, *J* = 6.6 Hz, 6H), –2.97 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 167.32, 155.94, 148.77, 146.29, 140.58, 135.68, 134.69, 132.48, 129.67, 128.11, 127.31, 121.50, 118.24, 117.90, 115.53, 105.71, 103.79, 68.35, 52.49, 31.86, 29.43, 29.42, 29.29, 26.14, 22.70, 14.14. HRMS (MALDI-TOF): *m/z* [M+H]⁺ calcd for C₆₂H₆₅BrN₅O₄, 1022.4214; found, 1022.4216. FT-IR (KBr) *v*_{max}: 3301, 3038, 2925, 2855, 1718, 1603, 1504, 1279, 1239, 1109 cm⁻¹.

Synthesis of compound 3. A 100 mL round bottom flask containing porphyrin **2** (133 mg, 0.13 mmol), phenylboronic acid (50 mg, 0.41 mmol), Pd(PPh₃)₄ (18 mg, 0.016 mmol) and Cs₂CO₃ (251 mg, 0.77 mmol) was evacuated and flushed with nitrogen three times. Toluene/DMF (*v/v* = 5:1, 60 mL) was added. The reaction mixture was heated to 90 °C for 8 h with vigorous stirring. After addition of water and dichloromethane, the organic phase was separated, the aqueous layer was extracted three times with CH₂Cl₂, and the combined organic layer was dried over MgSO₄ and filtered. Then Zn(OAc)₂·2H₂O (283 mg, 1.29 mmol) in CH₃OH (10 mL) was added, the mixture was stirred at room temperature for 0.5 h. Then, the solvent was removed under reduced pressure. After addition of water and dichloromethane, the organic phase was separated, the aqueous layer was extracted three times with CH₂Cl₂, the combined organic layer was dried over

MgSO₄ and filtered. The product was isolated by column chromatography (silica gel) using CH₂Cl₂/PE = 3/1 as eluent. Recrystallization from CH₂Cl₂/CH₃OH gave a red solid. Yield: 118 mg (84%). ¹H NMR (400 MHz, CDCl₃) δ 10.22 (s, 1H), 9.39 (dd, *J* = 9.1, 4.5 Hz, 2H), 9.26 (d, *J* = 4.5 Hz, 1H), 9.16 (d, *J* = 4.6 Hz, 1H), 9.08–8.94 (m, 3H), 8.91 (d, *J* = 4.6 Hz, 1H), 8.43 (d, *J* = 8.1 Hz, 2H), 8.31 (d, *J* = 8.0 Hz, 2H), 8.22 (d, *J* = 6.3 Hz, 2H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.85–7.68 (m, 3H), 7.37 (d, *J* = 8.9 Hz, 4H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 4H), 4.10 (s, 3H), 3.99 (t, *J* = 6.5 Hz, 4H), 1.89–1.73 (m, 4H), 1.49–1.43 (m, 4H), 1.41–1.19 (m, 16H), 0.99–0.78 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 167.43, 155.70, 150.64, 150.62, 149.89, 149.71, 149.70, 149.65, 149.51, 148.35, 147.70, 142.86, 140.80, 135.34, 134.54, 134.44, 134.01, 133.00, 132.27, 131.98, 131.94, 131.63, 131.26, 129.22, 127.79, 127.53, 127.10, 126.52, 121.60, 121.56, 118.71, 117.95, 115.46, 105.94, 68.32, 52.38, 31.84, 29.40, 29.38, 29.27, 26.11, 22.68, 14.12. HRMS (MALDI-TOF): *m/z* [M+H]⁺ calcd for C₆₈H₆₈N₅O₄Zn, 1082.4557; found, 1082.4535. FT-IR (KBr) *v*_{max}: 3035, 2925, 2854, 1723, 1603, 1502, 1276, 1238, 997 cm⁻¹.

Synthesis of compound 4. To a degassed solution of porphyrin **3** (271 mg, 0.25 mmol) in CH₂Cl₂ (100 ml) was added PIFA (55 mg, 0.13 mmol). The mixture was stirred at room temperature for 1 min. The resulting yellow-brown mixture was then washed with water, dried with anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, CH₂Cl₂) to give **4** as a black solid. Yield: 219 mg (82%). ¹H NMR (400 MHz, CDCl₃) δ 9.17 (d, *J* = 4.7 Hz, 2H), 9.03 (t, *J* = 4.8 Hz, 4H), 8.91 (d, *J* = 4.7 Hz, 2H), 8.83 (d, *J* = 4.7 Hz, 2H), 8.58 (d, *J* = 4.7 Hz, 2H), 8.36–8.23 (m, 12H), 8.17–8.07 (m, 4H), 8.04–7.93 (m, 4H), 7.88–7.75 (m, 6H), 7.25–7.15 (m, 12H), 6.85 (d, *J* = 8.9 Hz, 8H), 3.94 (s, 6H), 3.90 (t, *J* = 6.5 Hz, 8H), 1.81–1.67 (m, 8H), 1.47–1.37 (m, 8H), 1.33–1.19 (m, 32H), 0.90–0.81 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 167.29, 155.62, 155.01, 154.80, 151.21, 150.32, 150.26, 150.06, 150.03, 149.23, 148.27, 147.72, 142.85, 140.70, 135.18, 135.11, 134.50, 134.40, 134.14, 134.04, 133.88, 132.42, 132.34, 132.28, 132.10, 131.40, 131.28, 129.16, 127.69, 127.64, 126.99, 126.65, 122.95, 122.01, 120.08, 119.59, 117.84, 115.37, 68.26, 52.26, 31.81, 29.36, 29.34, 29.23, 26.07, 22.65, 14.10. HRMS (MALDI-TOF): *m/z* [M+H]⁺ calcd for C₁₃₆H₁₃₃N₁₀O₈Zn₂, 2161.8885; found, 2161.8862. FT-IR (KBr) *v*_{max}: 3037, 2925, 2854, 1725, 1604, 1503, 1320, 1271, 1000 cm⁻¹.

Synthesis of compound JY07. A mixture of porphyrin **4** (65 mg, 0.03 mmol) and KOH (0.56 g, 10 mmol) in THF/EtOH/H₂O (1/1/0.1, 50 ml) was refluxed for 12 h. The mixture was then cooled to room temperature, acidified with 0.1 M HCl to PH = 5, 50 mL CH₂Cl₂ was added. The organic phase was separated, the aqueous layer was extracted three times with CH₂Cl₂, and the combined organic layer was dried over MgSO₄ and filtered. The residue was purified by flash column chromatography (silica gel, CH₂Cl₂/CH₃OH=5:1) to give **5** as a black solid. Yield: 60 mg (94%). ¹H NMR (400 MHz, THF-*d*₈) δ 11.48 (s, 2H), 8.93 (d, *J* = 4.6 Hz, 2H), 8.79 (dd, *J* = 4.6, 2.1 Hz, 4H), 8.73 (d, *J* = 4.7 Hz, 2H), 8.60 (d, *J* = 4.7 Hz, 2H), 8.36 (d, *J* = 4.7 Hz, 2H), 8.27–8.10 (m, 12H), 7.97 (d, *J* = 4.7 Hz, 2H), 7.88–7.85 (m, 6H), 7.76–7.58 (m, 6H), 7.18–6.99 (m, 12H), 6.75 (d, *J* = 9.0 Hz, 8H), 3.88 (t, *J* = 6.3 Hz, 8H), 1.50–1.36 (m, 8H), 1.36–1.12 (m, 40H), 0.90–0.76 (m, 12H). ¹³C NMR (101 MHz, THF-*d*₈) δ 167.98, 157.11, 156.15, 156.03, 152.04, 151.16, 151.13, 151.03, 150.96, 150.22, 149.37, 149.23, 144.82, 141.84, 136.19, 136.12, 135.93, 135.61, 135.40, 134.73, 134.45, 132.65, 132.56, 132.38, 132.28, 131.73, 131.59, 130.96, 128.63, 128.34, 128.03, 127.40, 123.38, 122.28, 120.93, 118.43, 116.24, 68.89, 32.97, 30.51, 30.41, 27.23,

23.70, 14.59, 14.58. HRMS (MALDI-TOF): m/z $[M+H]^+$ calcd for $C_{134}H_{129}N_{10}O_8Zn_2$, 2133.8572; found, 2133.8523. FT-IR (KBr) ν_{max} : 3038, 2926, 2856, 1731, 1694, 1603, 1502, 1237, 1000 cm^{-1} . Anal. Calcd. For $C_{134}H_{128}N_{10}O_8Zn_2$: C, 75.30; H, 6.04; N, 6.55. Found: C, 75.11; H, 6.31; N, 6.29.

Synthesis of compound 5. Porphyrin **1** (400 mg, 0.42 mmol) was dissolved in $CH_2Cl_2/MeOH$ ($v/v = 9:1$, 150 mL) and NBS (150 mg, 0.85 mmol) was added. The reaction mixture was stirred under air at room temperature for 15 min and quenched with acetone (1.0 mL). The solvent was evaporated. After evaporation of the solvent, the product was isolated by column chromatography (silica gel) using $CH_2Cl_2/PE = 3/1$ as eluent. Recrystallization from CH_2Cl_2/CH_3OH gave a red solid. Yield: 0.37 g (80%). 1H NMR (400 MHz, $CDCl_3$) δ 9.62 (t, $J = 4.4$ Hz, 4H), 9.01 (d, $J = 4.5$ Hz, 2H), 8.75 (d, $J = 4.1$ Hz, 2H), 8.45 (d, $J = 8.1$ Hz, 2H), 8.24 (d, $J = 7.8$ Hz, 2H), 7.92 (d, $J = 8.4$ Hz, 2H), 7.37 (d, $J = 8.9$ Hz, 4H), 7.29 (d, $J = 8.5$ Hz, 2H), 6.99 (d, $J = 8.9$ Hz, 4H), 4.13 (s, 3H), 4.01 (t, $J = 6.5$ Hz, 4H), 1.89–1.73 (m, 4H), 1.52–1.44 (m, 4H), 1.43–1.21 (m, 16H), 0.97–0.79 (m, 6H), -2.69 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.42, 156.24, 149.13, 146.45, 140.70, 135.80, 134.73, 132.62, 130.08, 128.25, 127.59, 122.93, 119.56, 117.82, 115.78, 104.12, 68.58, 52.70, 32.06, 29.63, 29.49, 26.35, 22.90, 14.33. HRMS (MALDI-TOF): m/z $[M+H]^+$ calcd for $C_{62}H_{64}Br_2N_5O_4$, 1100.3320; found, 1100.3335. FT-IR (KBr) ν_{max} : 3322, 3038, 2924, 2855, 1723, 1602, 1503, 1278, 1240, 1108 cm^{-1} .

Synthesis of compound 6. A 100 mL round bottom flask containing porphyrin **5** (143 mg, 0.13 mmol), phenylboronic acid (100 mg, 0.82 mmol), $Pd(PPh_3)_4$ (18 mg, 0.016 mmol) and Cs_2CO_3 (251 mg, 0.77 mmol) was evacuated and flushed with nitrogen three times. Toluene/DMF ($v/v = 5:1$, 60 mL) was added. The reaction mixture was heated to 90 °C for 8 h with vigorous stirring. After addition of water and dichloromethane, the organic phase was separated, the aqueous layer was extracted three times with CH_2Cl_2 , and the combined organic layer was dried over $MgSO_4$ and filtered. Then $Zn(OAc)_2 \cdot 2H_2O$ (283 mg, 1.29 mmol) in CH_3OH (10 mL) was added, the mixture was stirred at room temperature for 0.5 h. Then, the solvent was removed under reduced pressure. After addition of water and dichloromethane, the organic phase was separated, the aqueous layer was extracted three times with CH_2Cl_2 , the combined organic layer was dried over $MgSO_4$ and filtered. The product was isolated by column chromatography (silica gel) using CH_2Cl_2 as eluent. Recrystallization from CH_2Cl_2/CH_3OH gave a red solid. Yield: 115 mg (76%). 1H NMR (400 MHz, $CDCl_3$) δ 9.12 (d, $J = 4.6$ Hz, 2H), 8.96 (t, 4H), 8.87 (d, $J = 4.7$ Hz, 2H), 8.42 (d, $J = 8.2$ Hz, 2H), 8.30 (d, $J = 8.0$ Hz, 2H), 8.22 (d, $J = 6.4$ Hz, 4H), 7.99 (d, $J = 8.4$ Hz, 2H), 7.84–7.67 (m, 6H), 7.35 (d, $J = 8.8$ Hz, 4H), 7.29 (d, $J = 8.4$ Hz, 2H), 6.95 (d, $J = 8.9$ Hz, 4H), 4.10 (s, 3H), 3.98 (t, $J = 6.5$ Hz, 4H), 1.87–1.71 (m, 4H), 1.52–1.42 (m, 4H), 1.41–1.16 (m, 16H), 0.89 (t, $J = 6.6$ Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.64, 155.95, 150.94, 150.54, 150.30, 149.82, 148.58, 148.05, 142.99, 141.01, 135.46, 134.66, 134.35, 132.62, 132.49, 132.14, 131.61, 129.52, 127.99, 127.76, 127.33, 126.79, 122.37, 121.47, 119.48, 118.07, 115.69, 68.55, 52.59, 32.05, 29.62, 29.48, 26.34, 22.89, 14.33. HRMS (MALDI-TOF): m/z $[M]^+$ calcd for $C_{74}H_{71}N_5O_4Zn$, 1157.4792; found, 1157.4798. FT-IR (KBr) ν_{max} : 3042, 2926, 2855, 1725, 1603, 1502, 1278, 1237, 1001 cm^{-1} .

Synthesis of compound JY06. A mixture of porphyrin **6** (127 mg, 0.11 mmol) and KOH (0.56 g, 10 mmol) in THF/EtOH/ H_2O (1/1/0.1, 50 ml) was refluxed for 12 h. The mixture was

then cooled to room temperature, acidified with 0.1 M HCl to PH = 5, 50 mL CH₂Cl₂ was added. The solution was washed three times with water, and the combined organic layer was dried with MgSO₄ and removed by vacuo. The residue was purified by flash column chromatography (silica gel, CH₂Cl₂/CH₃OH=10:1) to give **JY06** as a red solid. Yield: 110 mg (87%). ¹H NMR (400 MHz, THF) δ 11.64 (s, 1H), 9.01 (d, *J* = 4.6 Hz, 2H), 8.91–8.73 (m, 6H), 8.42 (d, *J* = 8.1 Hz, 2H), 8.29 (d, *J* = 8.1 Hz, 2H), 8.26–8.11 (m, 4H), 7.98 (d, *J* = 8.5 Hz, 2H), 7.86–7.64 (m, 6H), 7.42–7.18 (m, 6H), 6.96 (d, *J* = 9.0 Hz, 4H), 3.99 (t, *J* = 6.4 Hz, 4H), 1.88–1.74 (m, 4H), 1.60–1.45 (m, 4H), 1.44–1.21 (m, 16H), 1.02–0.76 (m, 6H). ¹³C NMR (101 MHz, THF) δ 168.07, 157.21, 151.64, 151.23, 151.04, 150.67, 149.49, 149.25, 144.73, 141.93, 136.33, 135.93, 135.55, 135.47, 132.74, 132.61, 132.22, 131.91, 131.04, 128.71, 128.27, 128.15, 127.34, 122.56, 121.71, 120.08, 118.51, 116.35, 68.98, 33.00, 30.56, 30.54, 30.44, 27.28, 23.73, 14.60. HRMS (MALDI-TOF): *m/z* [M]⁺ calcd for C₇₃H₆₉N₅O₄Zn, 1143.4636; found, 1143.4638. FT-IR (KBr) *v*_{max}: 3041, 2925, 2854, 1734, 1693, 1604, 1502, 1237, 1001 cm⁻¹. Anal. Calcd. For C₇₃H₆₉N₅O₄Zn: C, 76.53; H, 6.07; N, 6.11. Found: C, 76.39; H, 6.02; N, 6.09.

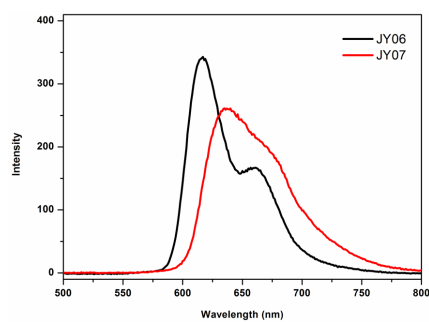


Fig. S1 Fluorescence spectra of **JY06** and **JY07** in THF.

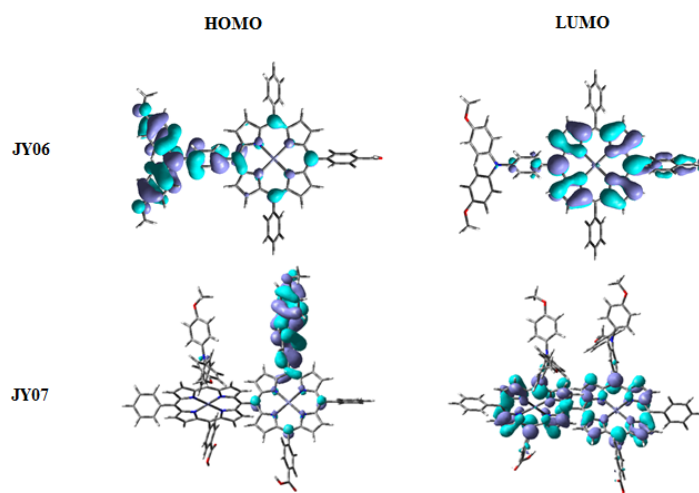


Fig. S2 Frontier orbitals of **JY06** and **JY07** (HOMO and LUMO).

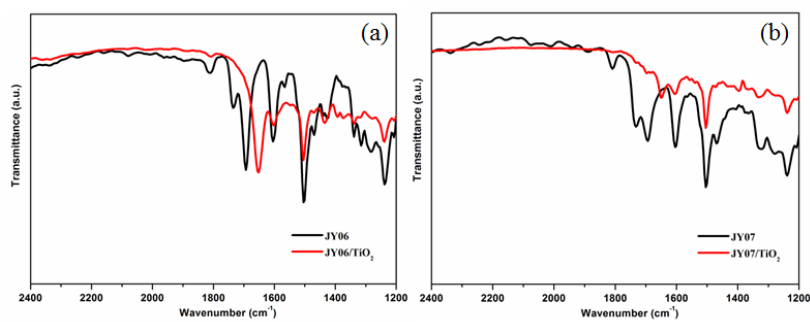


Fig. S3 FTIR spectra of (a) **JY06** and (b) **JY07** powders and stained TiO_2 films.

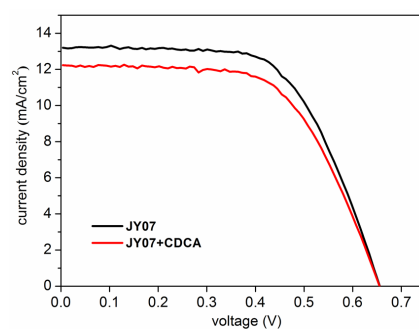


Fig. S4 The photocurrent density-voltage (J - V) curves based on **JY07** with and without CDCA.

Table S1 Photovoltaic performance for DSSCs based on **JY07**

dye	CDCA (mM)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η (%)	Γ (nmol cm ⁻²)
JY07	0	0.65	13.20	0.62	5.33	62
JY07	10	0.65	12.20	0.61	4.85	45

^aActive area: 0.16 cm²; Electrolyte is composed of 0.3 M 1,2-dimethyl-3-propylimidazolium iodide (DMPH), 0.1 M LiI, 0.05 M I₂, and 0.5 M 4-*tert*-butyl pyridine in acetonitrile.

Photostability study

The long-term stability of DSSCs is a critical requirement for their photovoltaic application. We have used a straightforward method reported in literature to examine the stability of studied dyes.⁵ For the stability study, TiO₂ thin films with areas of 1×1 cm² and thicknesses of 3-4 μm were used. The films were immersed in a 0.3 mM solution of the porphyrin in THF for 0.5 h, dried, and the absorbance was measured. Then, the same films were irradiated under standard one-sun illumination for 5 min and 30 min and the absorbance was measured again.

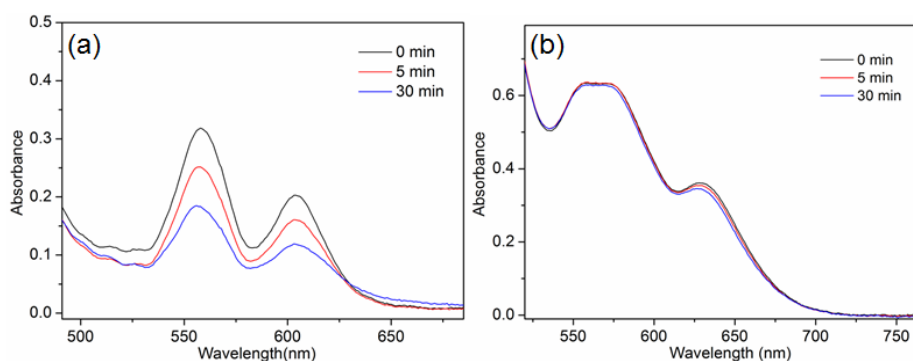


Fig. S5 Absorption spectra of (a) **JY06** and (b) **JY07** that were adsorbed onto TiO₂ films after irradiation for 0, 5, and 30 min.

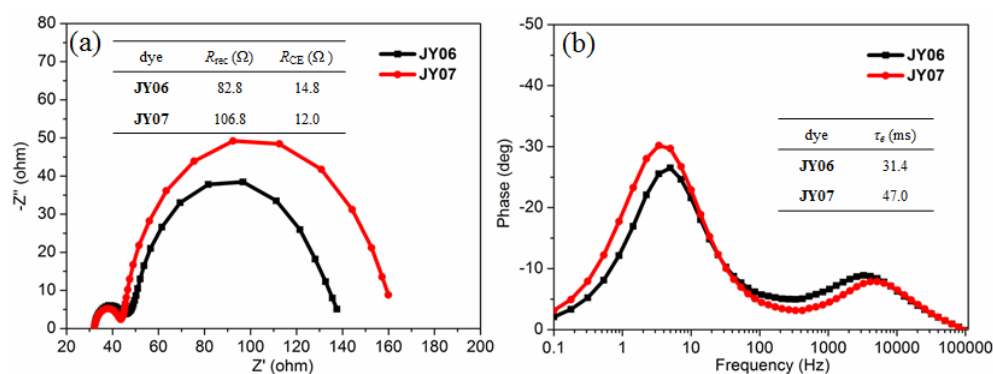


Fig. S6 EIS spectra of DSSCs tested at -0.6 V forward bias in the dark: (a) Nyquist and (b) Bode phase plots.

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^1H NMR and ^{13}C NMR spectra

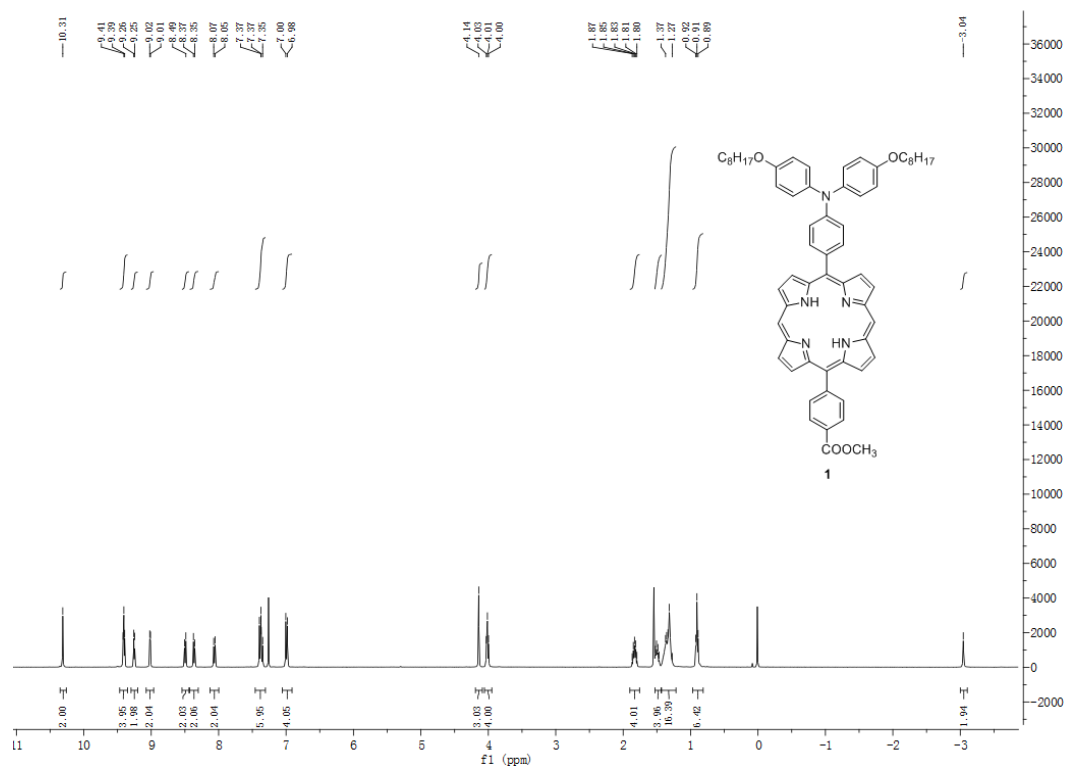


Fig. S7 ^1H NMR spectrum of compound **1** in CDCl_3 .

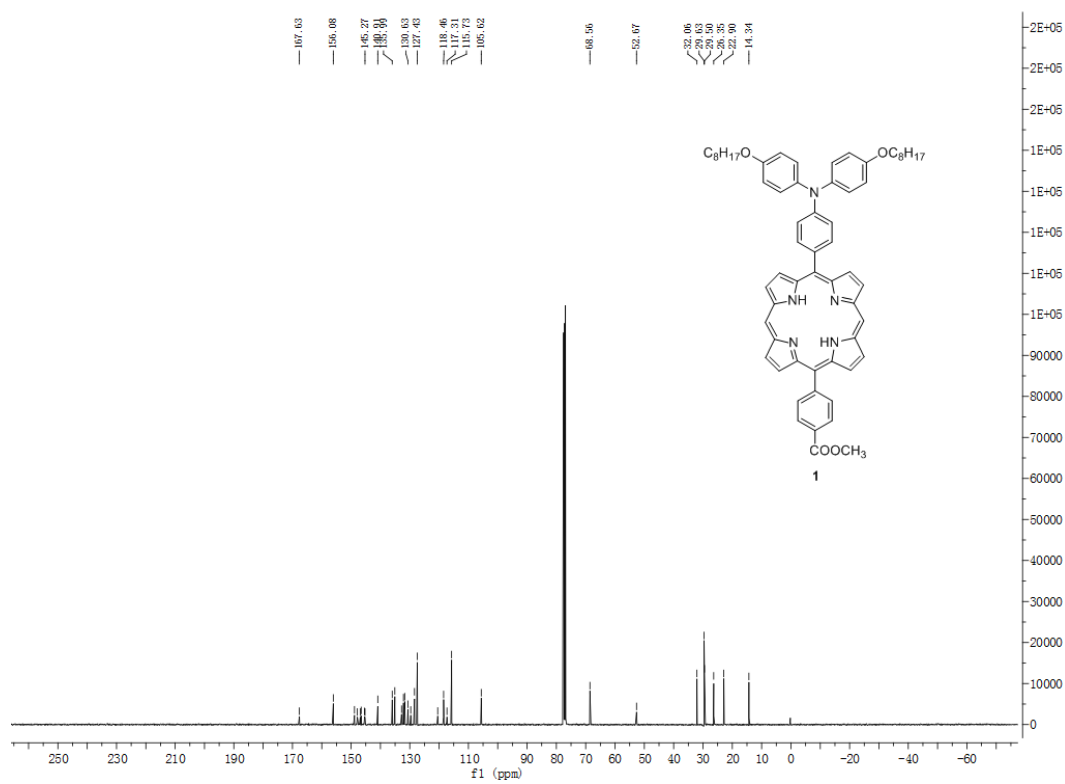


Fig. S8 ^{13}C NMR spectrum of compound **1** in CDCl_3 .

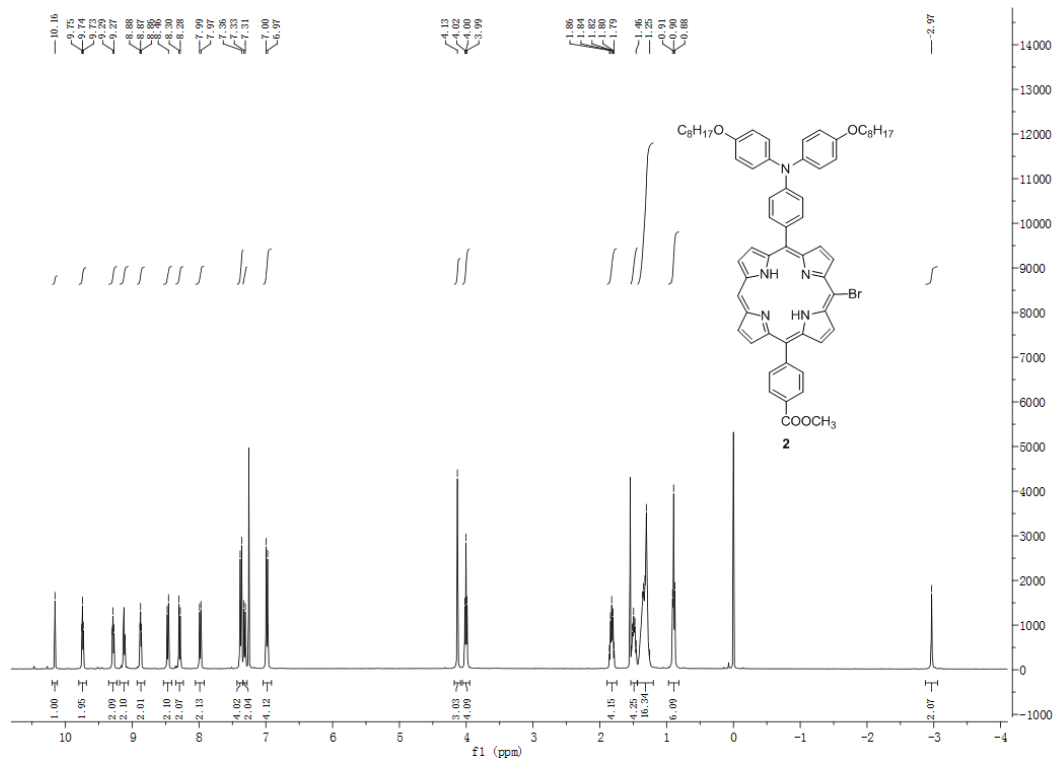


Fig. S9 ^1H NMR spectrum of compound **2** in CDCl_3 .

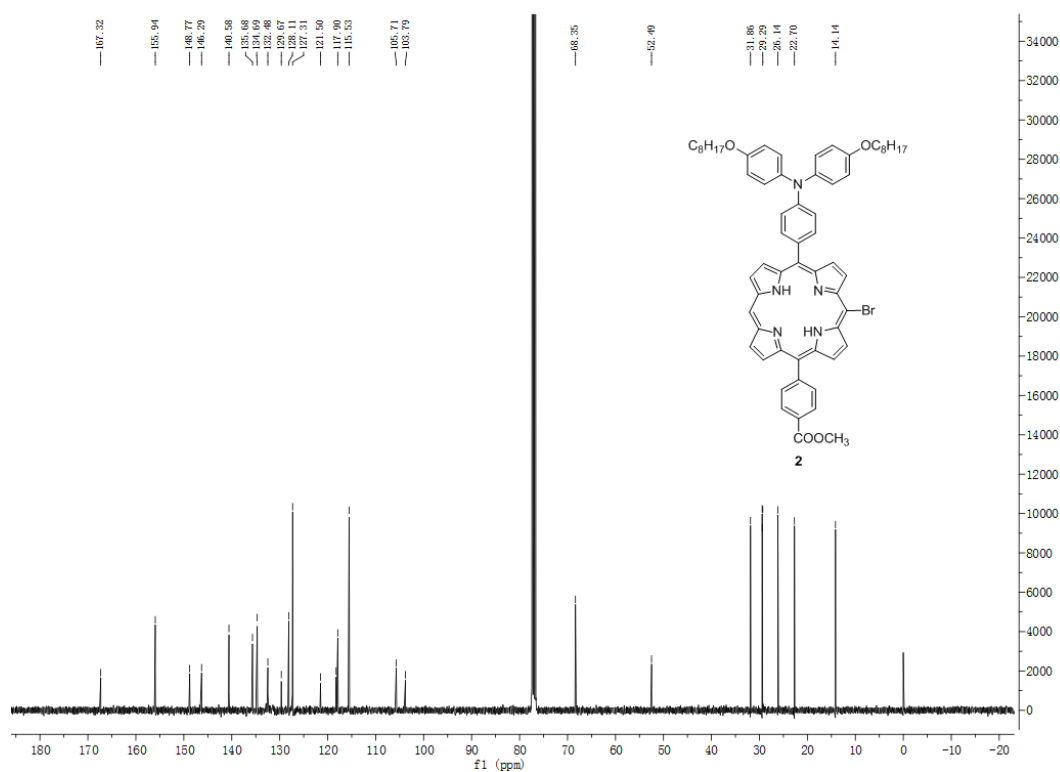


Fig. S10 ^{13}C NMR spectrum of compound **2** in CDCl_3 .

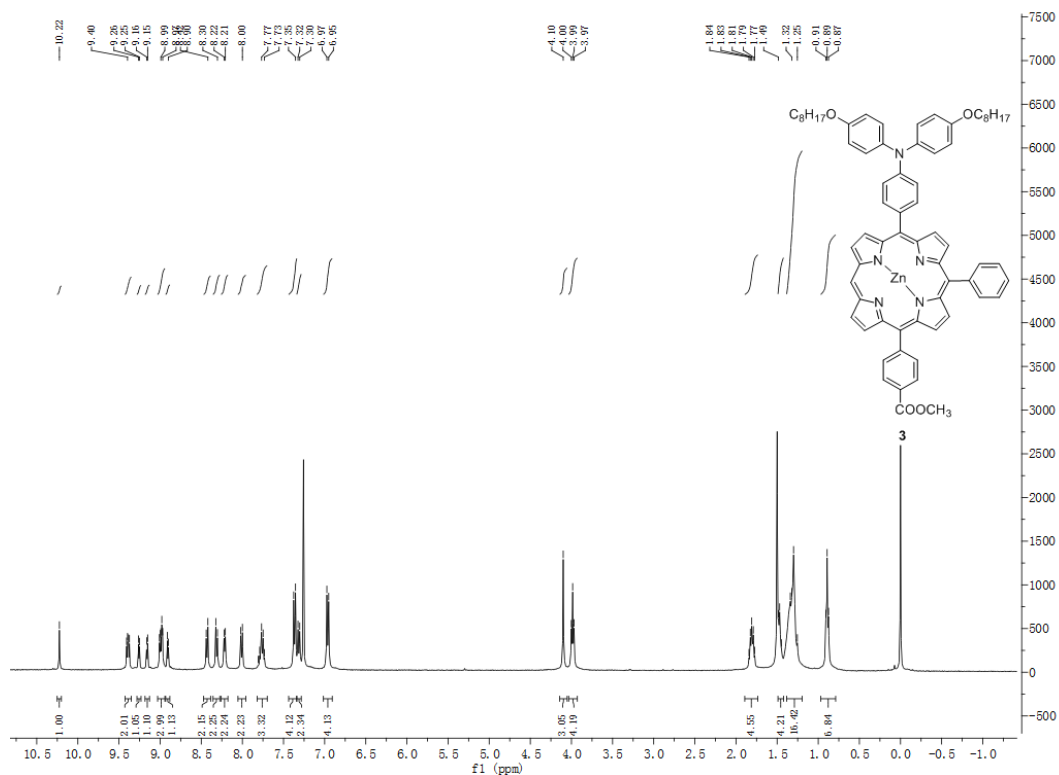


Fig. S11 ^1H NMR spectrum of compound **3** in CDCl_3 .

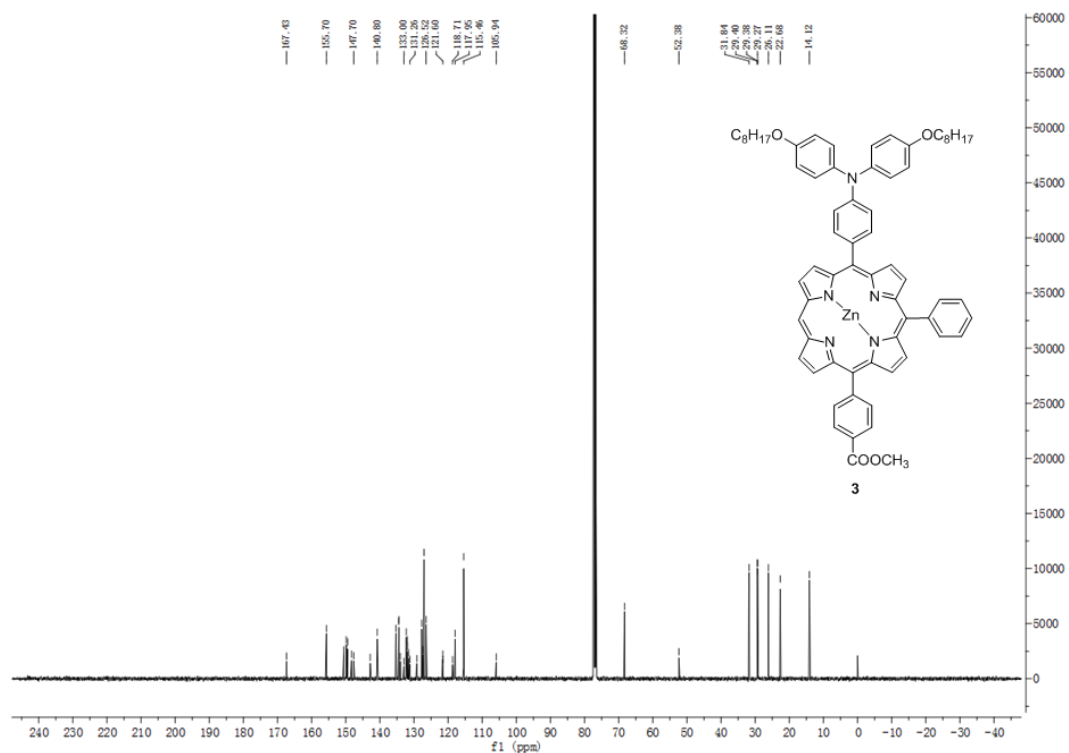


Fig. S12 ^{13}C NMR spectrum of compound **3** in CDCl_3 .

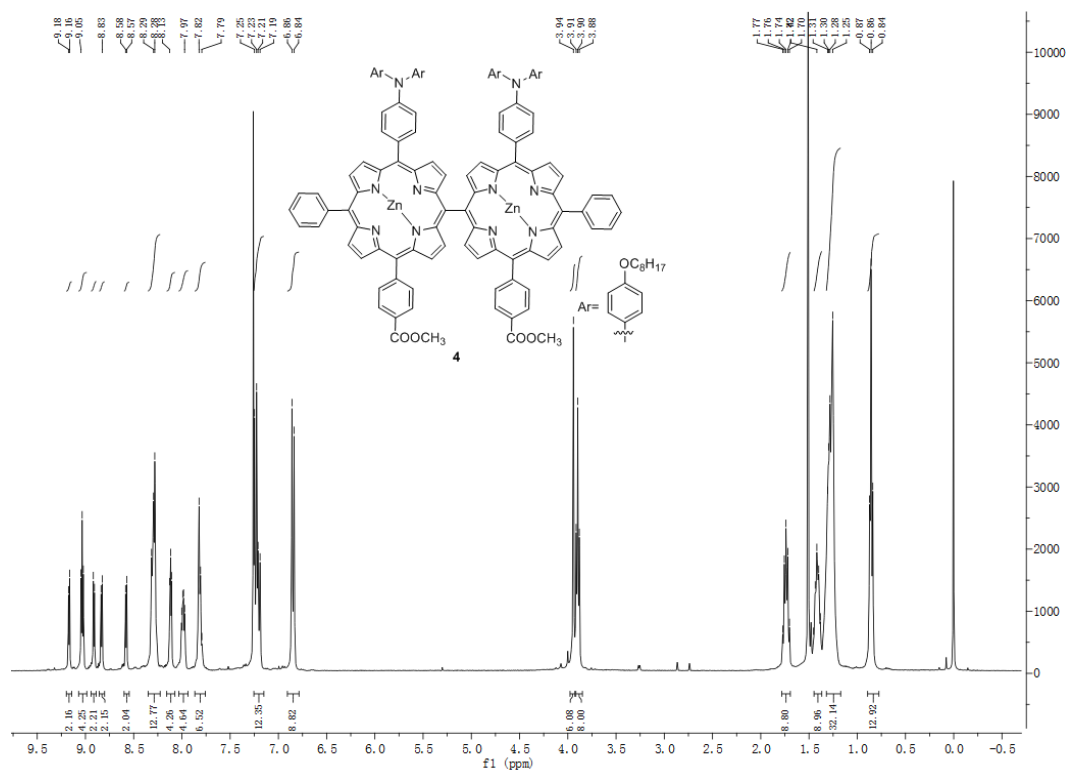


Fig. S13 ¹H NMR spectrum of compound 4 in CDCl₃.

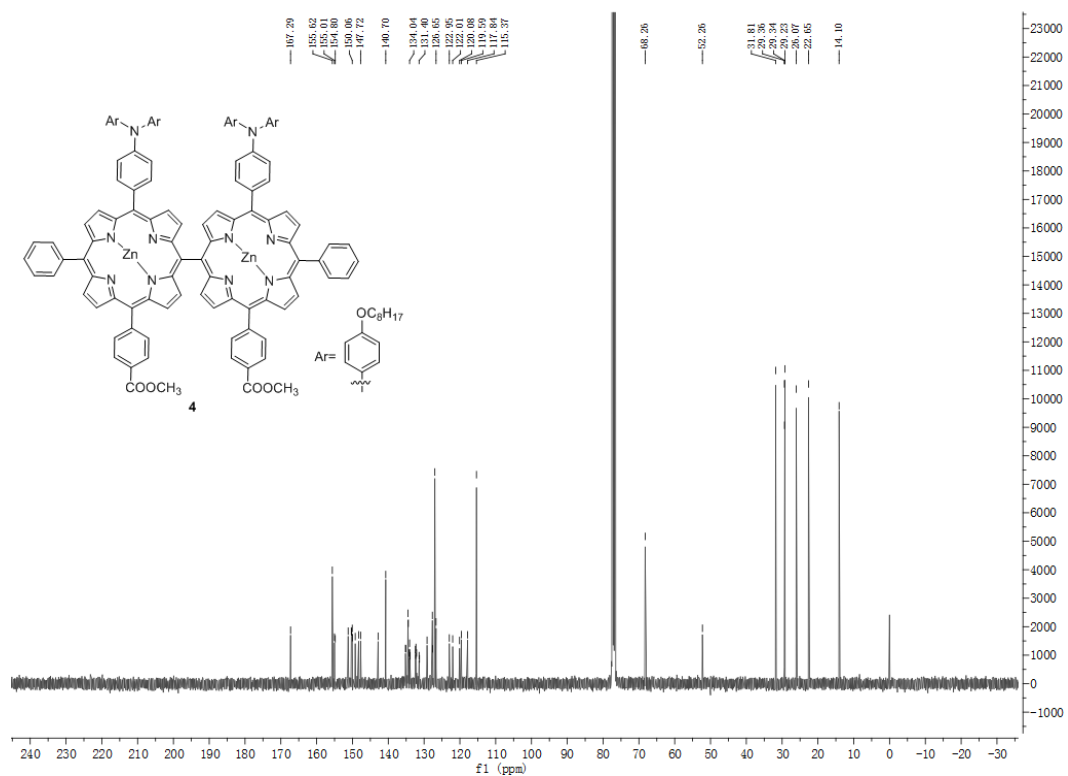


Fig. S14 ¹³C NMR spectrum of compound 4 in CDCl₃.

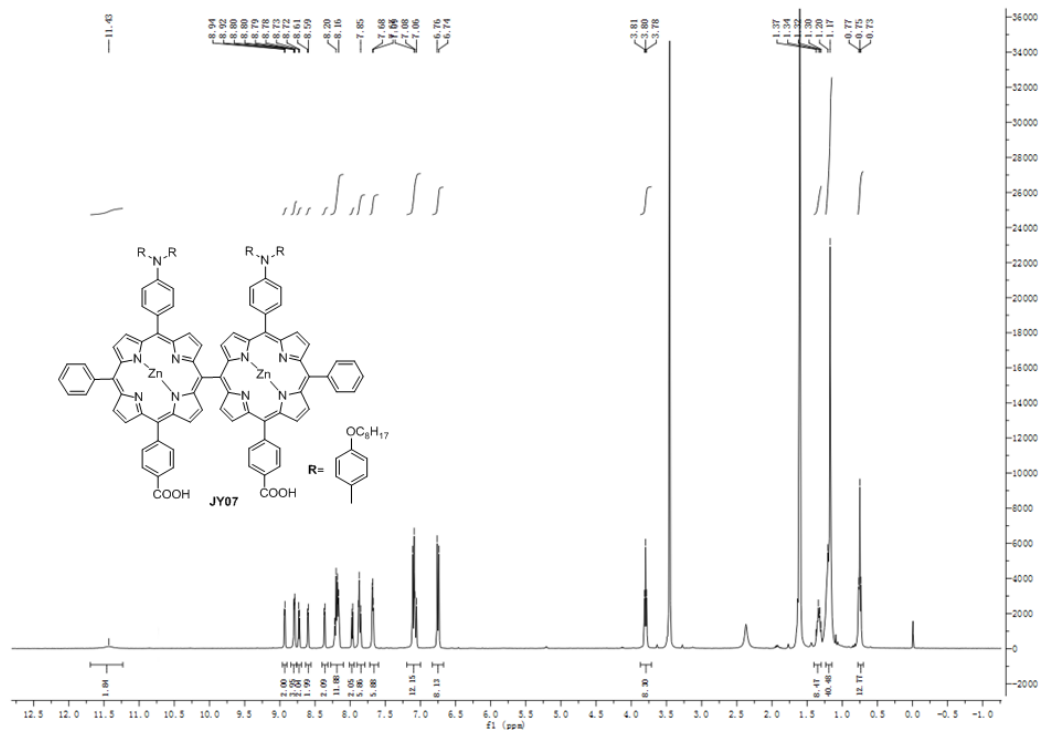


Fig. S15 ¹H NMR spectrum of compound JY07 in THF-*d*₈.

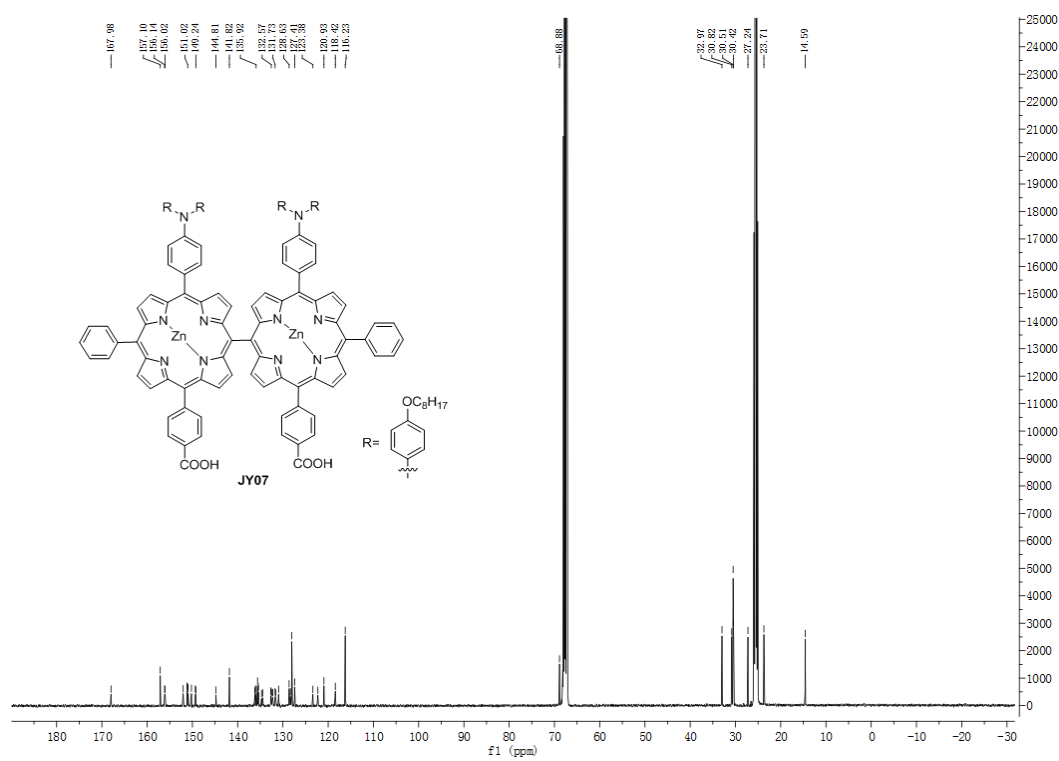


Fig. S16 ¹³C NMR spectrum of compound JY07 in THF-*d*₈.

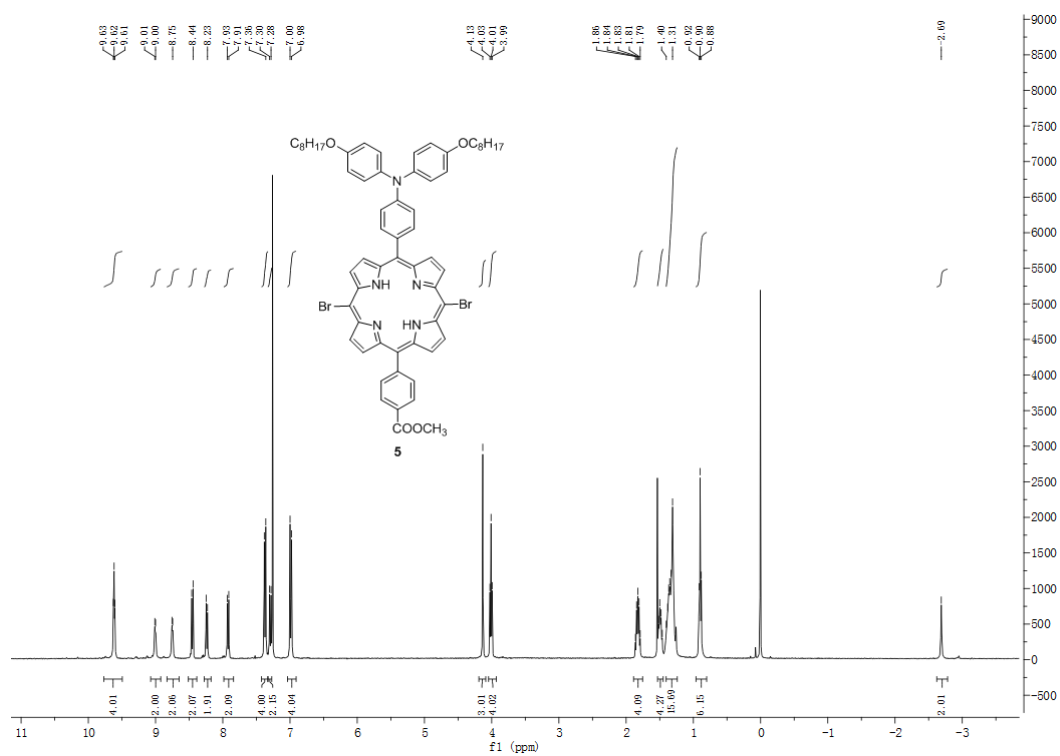


Fig. S17 ¹H NMR spectrum of compound **5** in CDCl₃.

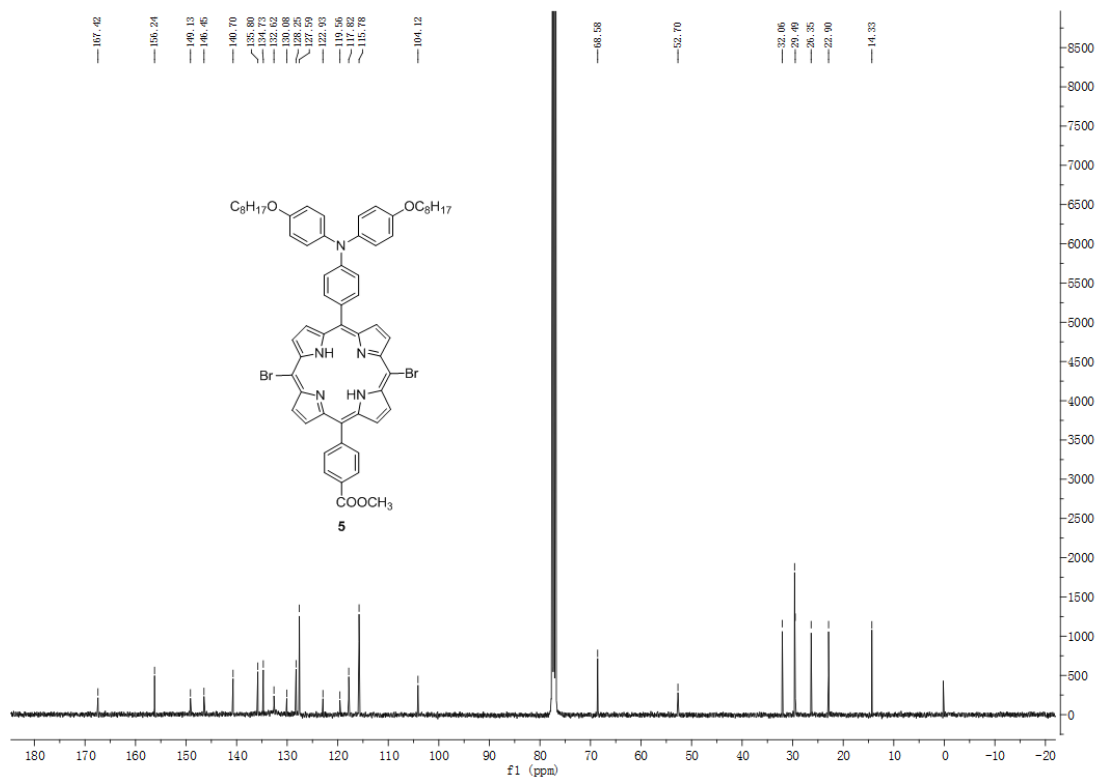


Fig. S18 ¹³C NMR spectrum of compound **5** in CDCl₃.

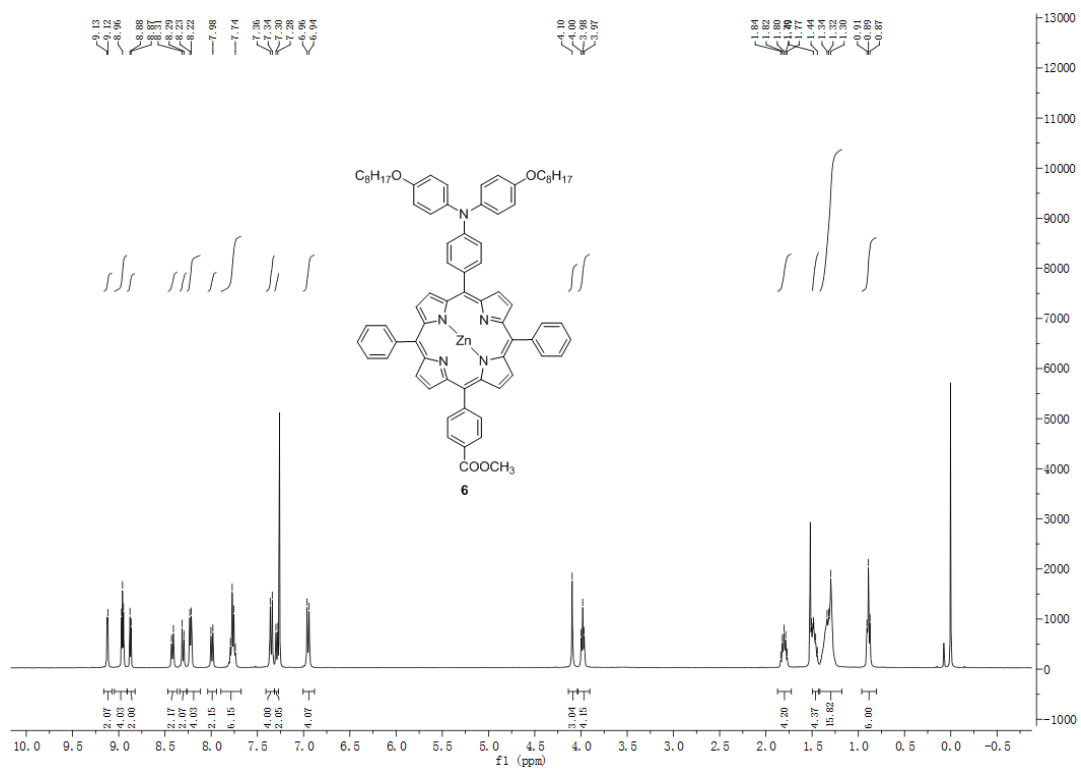


Fig. S19 ¹H NMR spectrum of compound **6** in CDCl₃.

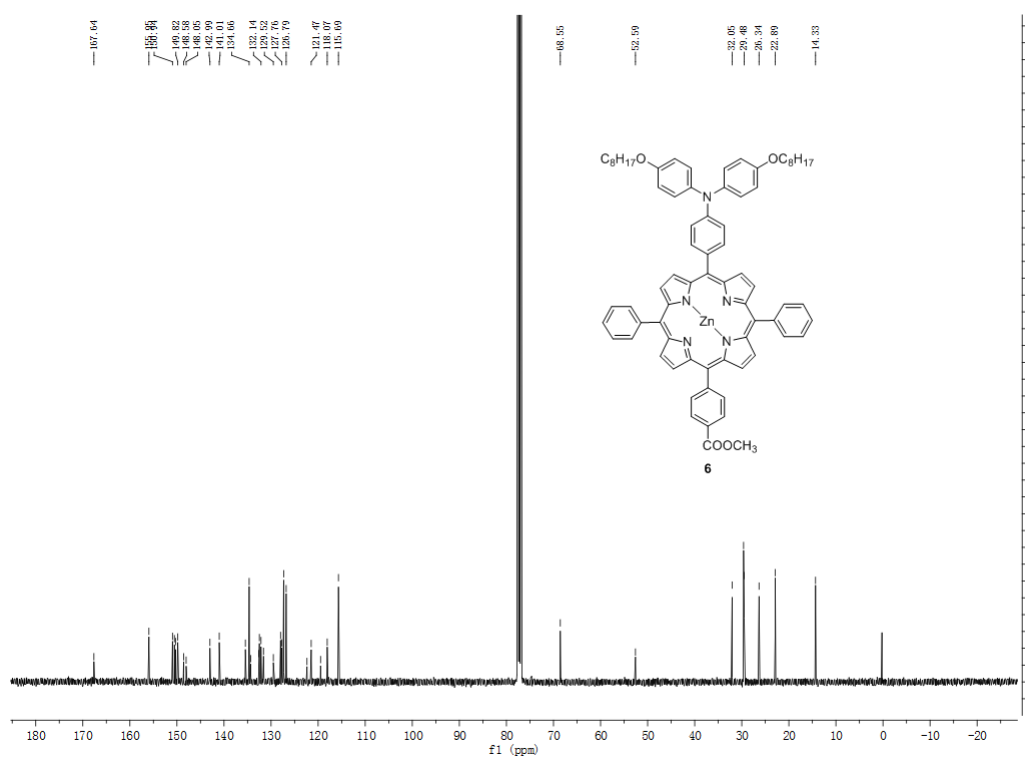


Fig. S20 ¹³C NMR spectrum of compound **6** in CDCl₃.

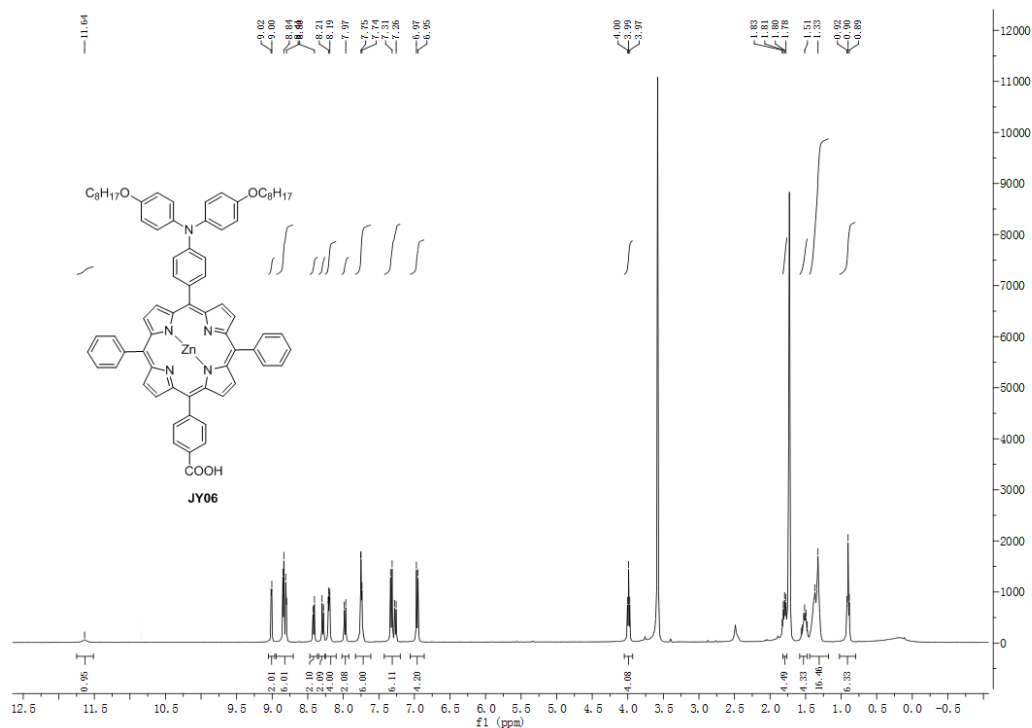


Fig. S21 ^1H NMR spectrum of compound **JY06** in $\text{THF-}d_8$.

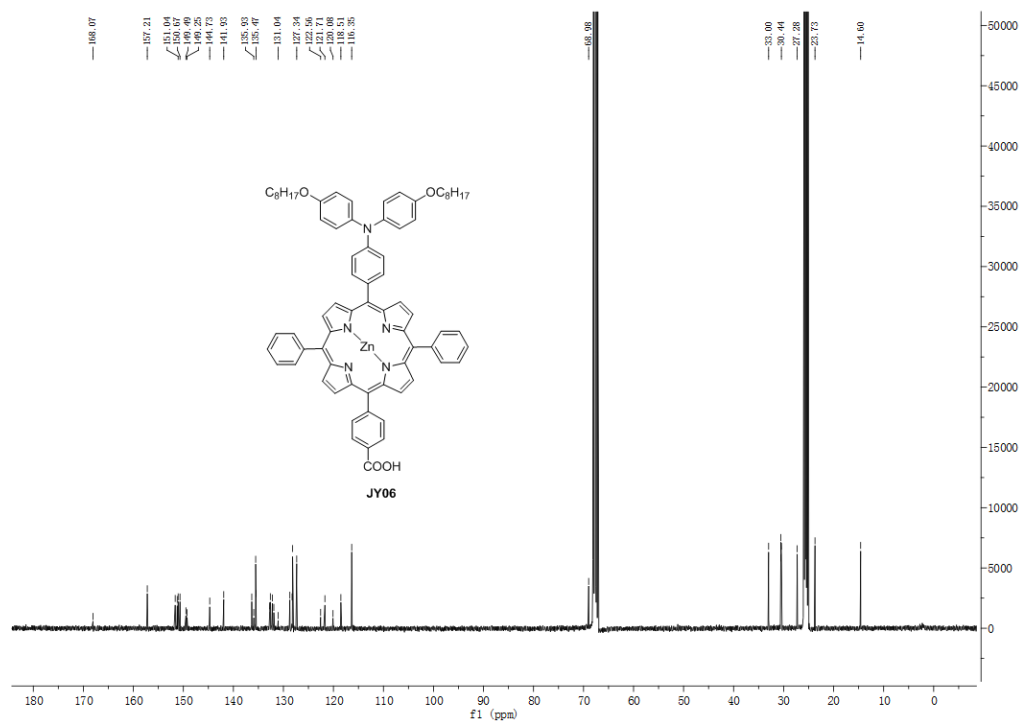


Fig. S22 ^{13}C NMR spectrum of compound **JY06** in $\text{THF-}d_8$.

HR-MS spectra

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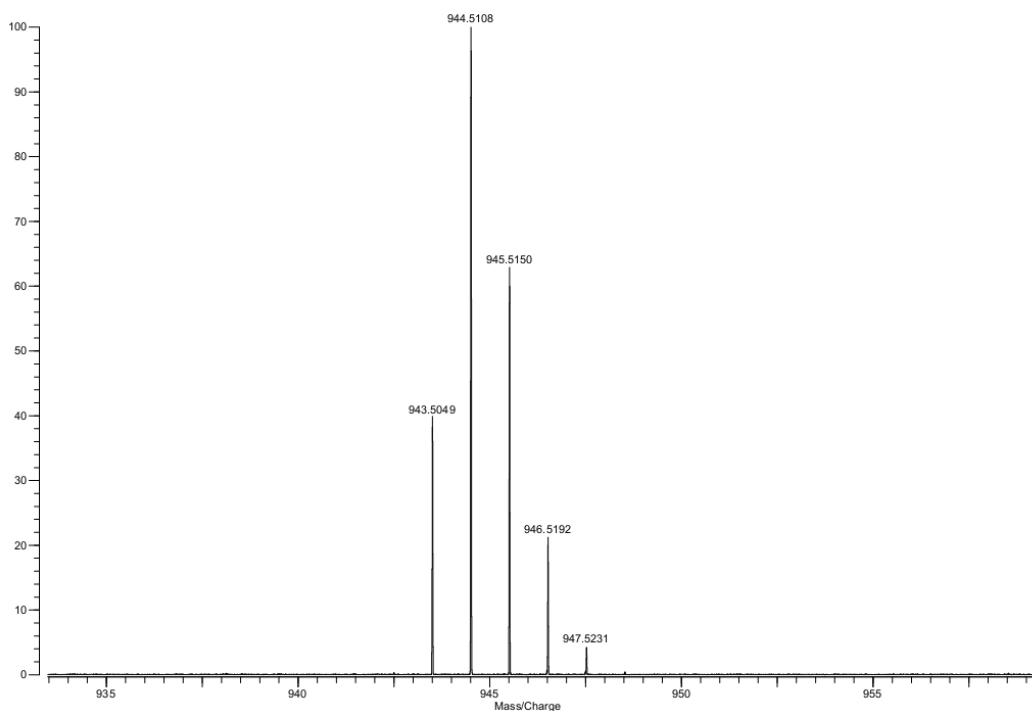


Fig. S23 HR-MS spectrum of compound 1.

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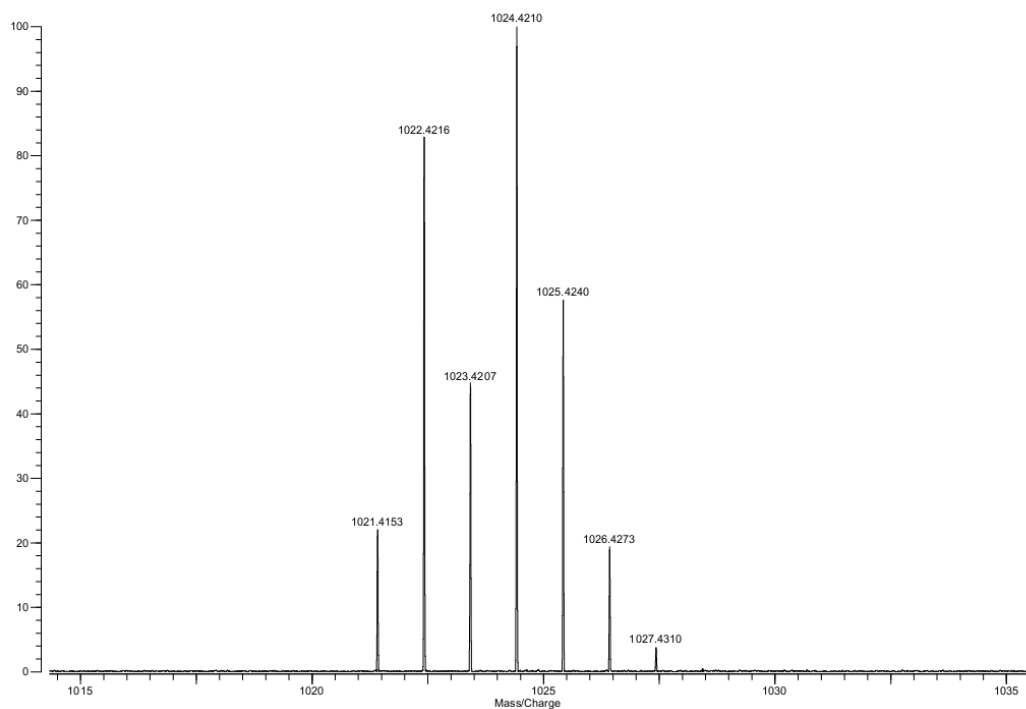


Fig. S24 HR-MS spectrum of compound 2.

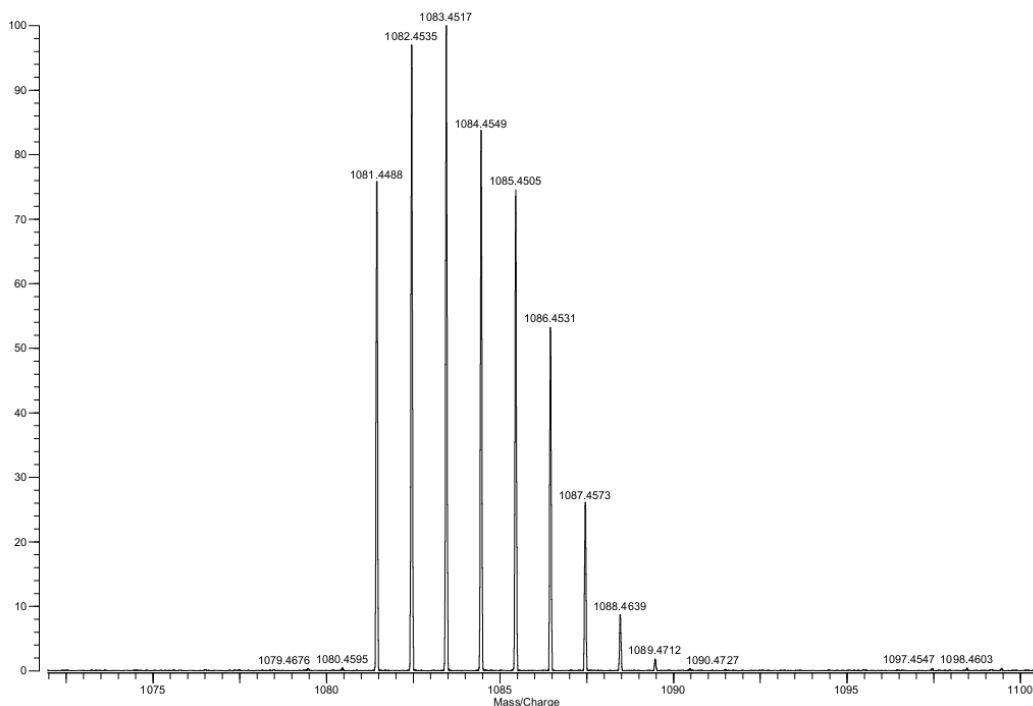


Fig. S25 HR-MS spectrum of compound 3.

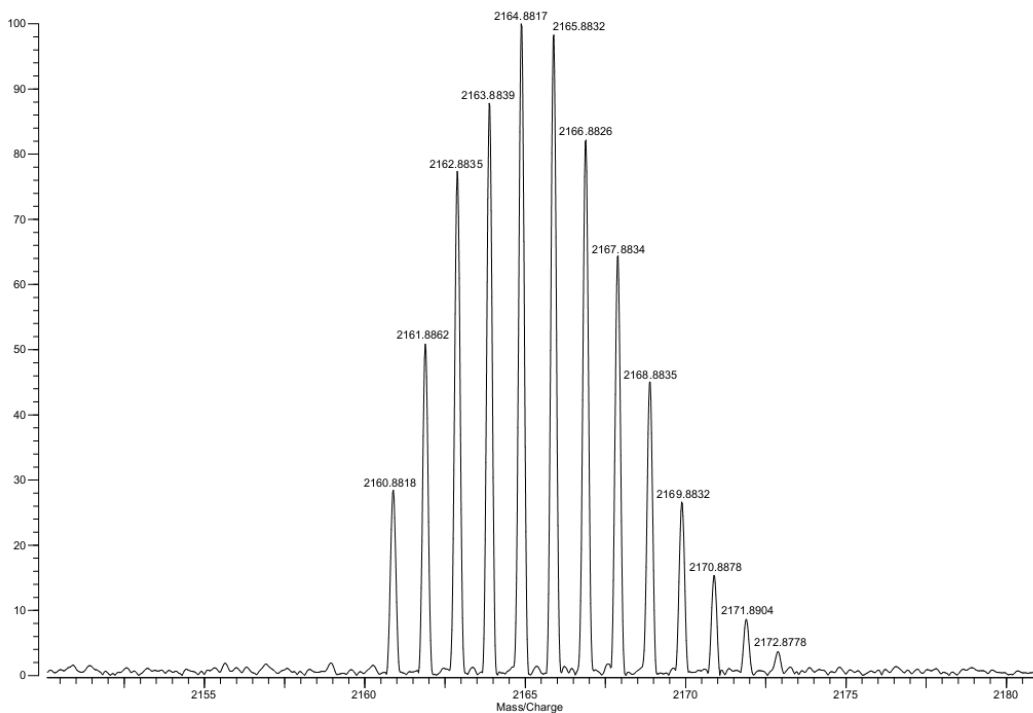


Fig. S26 HR-MS spectrum of compound 4.

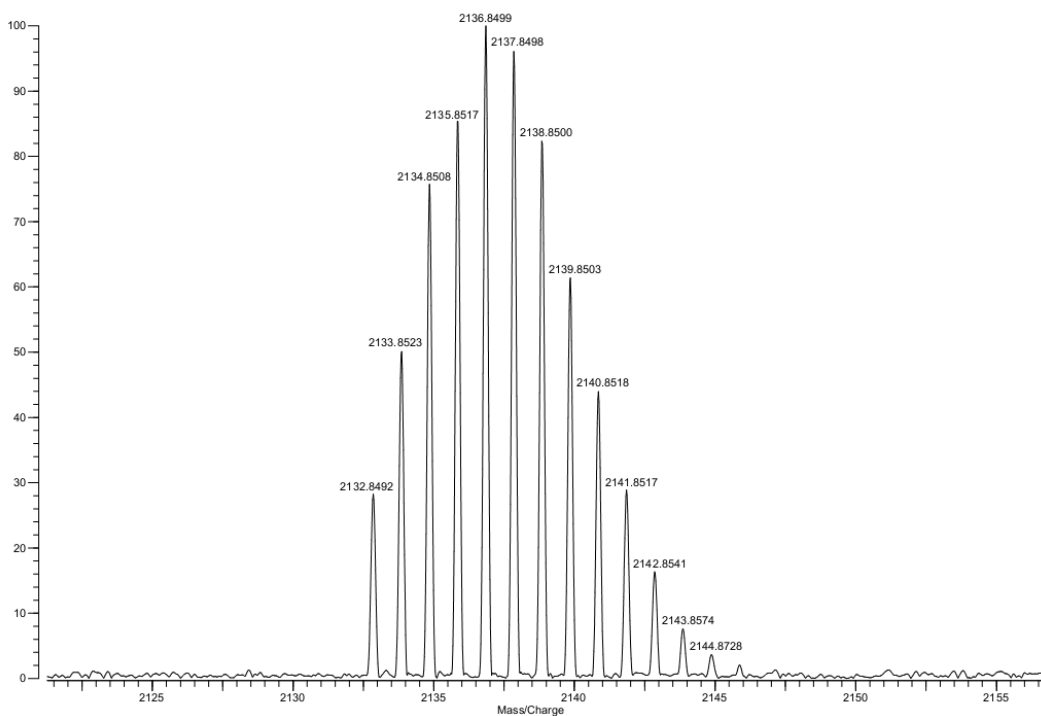


Fig. S27 HR-MS spectrum of compound JY07.

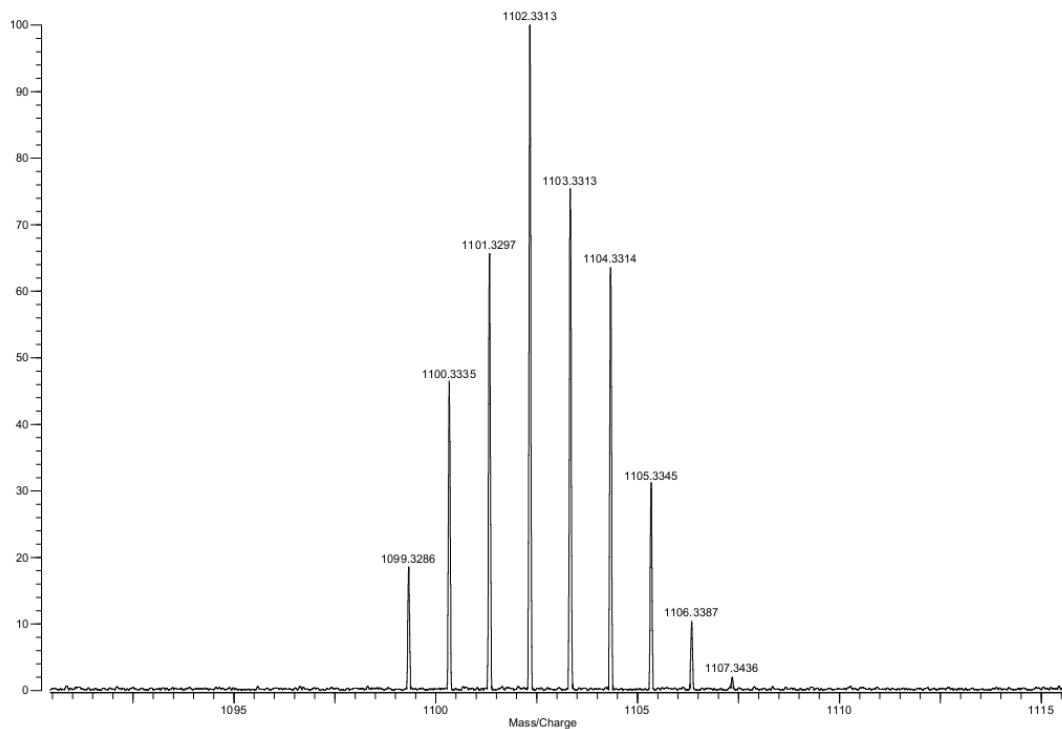


Fig. S28 HR-MS spectrum of compound 5.

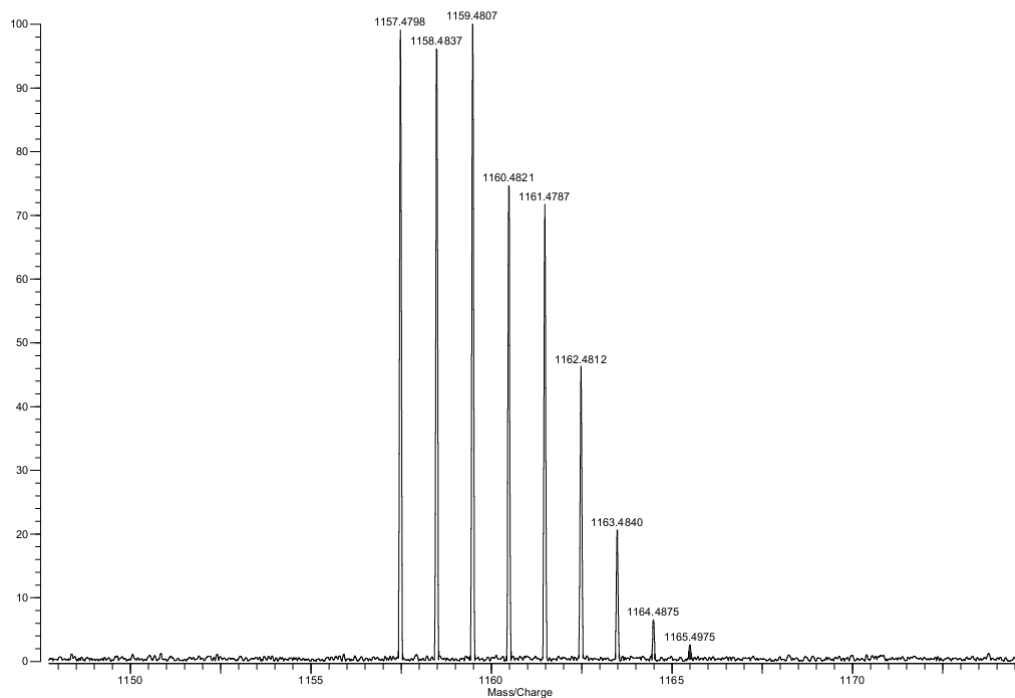


Fig. S29 HR-MS spectrum of compound **6**.

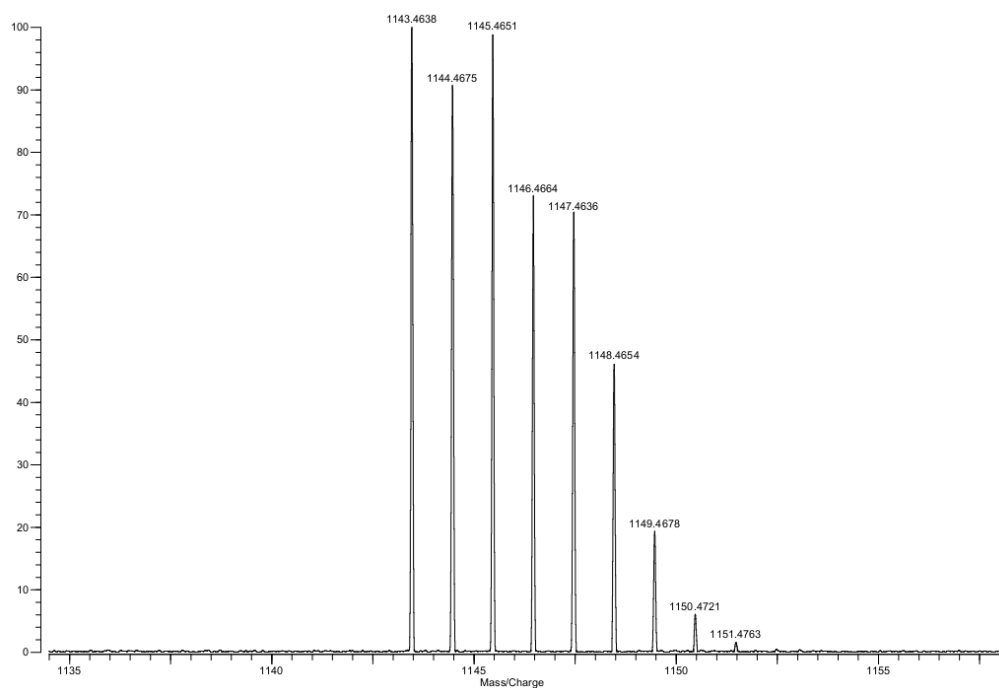


Fig. S30 HR-MS spectrum of compound **JY06**.