Supporting Information for

2-Diphenylaminothiophene as the donor of porphyrin sensitizers for dye-sensitized solar cells

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Synthetic details

5-Bromo-3-hexylthiophene-2-carbaldehyde: 2,5-Dibromo-3-dihexylthiophene (2.4 g, 7.36 mmol) was mixed with dry THF (75 mL), and n-butyllithium (3.1 mL, 2.4 M in hexane, 7.36 mmol) was added at -78 °C under nitrogen. After the addition was finished, the mixture was stirred for another 1 h and anhydrous DMF (0.6 g, 7.96 mmol) was added. The mixture was slowly warmed to room temperature overnight and poured into 2 N HCl. The organic layer was extracted with CH_2Cl_2 and dried over Na_2SO_4. After the solvent was removed under reduced pressure, the residue was purified on a silica gel column to give the product (1.2 g, yield 60%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.90 (t, *J* = 6.8 Hz, 3H), 1.29-1.37 (m, 6H), 1.56-1.65 (m, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 7.46 (s, 1H, thienyl), 9.76 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ 14.07, 22.56, 28.80, 29.48, 31.55, 122.13, 136.80, 142.88, 143.99, 181.90.

3-Hexyl-5-trimethylsilylthiophene-2-carbaldehyde: In a three-necked 250 ml-flask, 5-bromo-3-hexylthiophene-2-carbaldehyde (1.1 g, 4.1 mmol), $Pd(PPh_3)_2Cl_2$ (70 mg, 0.1 mmol) and CuI (38 mg, 0.2 mmol) were mixed in THF (40 ml) and Et_3N (40 mL) under nitrogen. Then trimethylsilylacetylene (442 mg, 4.5 mmol) was added. After stirring at 50 °C for 24 h, the solvent was removed under reduced pressure, and the residue was purified on a silica gel column to give the target compound (1.1 g, yield 87%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.27 (s, 9H), 0.89 (t, *J* = 6.8 Hz, 3H), 1.28-1.36 (m, 6H), 1.59-1.67 (m, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 7.51 (s, 1H, thienyl), 9.81 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ 14.36, 22.85, 29.09, 29.65, 30.14, 31.80, 96.61, 106.81, 128.35, 136.80, 142.33, 149.69, 182.85.

3-Hexyl-5-ethynylthiophene-2-carbaldehyde: 3-hexyl-5-trimethylsilylthiophene-2-carbaldehyde (1.1 g, 3.5 mmol), KOH (0.24 g, 4.2 mmol), a few drops of methanol and 40 ml THF were mixed in a 100 ml flask and stirred for 3 h at room temperature. Then the organic layer was extracted with CH_2Cl_2 and dried over Na_2SO_4. After the solvent was removed under reduced pressure, the residue was purified on a silica gel column to give the target compound (600 mg, yield 78%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.89 (t, *J* = 6.8 Hz, 3H), 1.27-1.34 (m, 6H), 1.59-1.68 (m, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 3.67 (s, 1H), 7.53 (s, 1H, thienyl), 9.83 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ 14.06, 22.55, 28.81, 29.32, 29.93, 31.52, 75.82, 87.68, 126.69, 136.40, 142.56, 149.83, 182.57.

2a: Dibromoporphyrin **1** (300 mg, 0.21 mmol), methyl 4-ethynylbenzoate (34 mg, 0.21 mmol), $Pd(PPh_3)_4$ (37 mg, 0.03 mmol), CuI (6 mg, 0.03 mmol) were placed in a Schlenk flask, flushed with nitrogen and then charged with dry THF (70 mL) and Et_3N (10 mL). The mixture was stirred at 50 °C for 18 h. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2, washed with water, dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified on a silica gel column. Recrystallization from CH_2Cl_2/CH_3OH gave the target compound (52 mg, yield 16%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.34-0.55 (m, 16H), 0.58-0.66 (m, 8H), 0.75-0.83 (m, 20H), 0.86-1.13 (m, 40H), 1.15-1.21 (m, 8H), 3.85 (t, *J* = 6.4 Hz, 8H), 3.99 (s, 3H, OMe), 7.01 (d, *J* = 8.8 Hz, 4H, phenyl), 7.70 (t, *J* = 8.4 Hz, 2H, phenyl), 8.01 (d, *J* = 7.6 Hz, 2H, phenyl), 8.19 (d, *J* = 8.0 Hz, 2H, phenyl), 8.84 (d, *J* = 4.8 Hz, 2H, pyrrolic), 8.91 (d, *J* = 4.4 Hz, 2H, pyrrolic), 9.60 (d, *J* = 4.4 Hz, 2H, pyrrolic), 9.66 (d, *J* = 4.4 Hz, 2H, pyrrolic). MS (MALDI-TOF, m/z): [M] calcd for $C_{90}H_{121}BrN_4O_6Zn$, 1496.78; found, 1496.71. IR (KBr pellet, cm^{-1}): 2922(s), 2852(m), 2183(w), 2030(w), 1958(m), 1727(m), 1660(m), 1589(w), 1455(m), 1434(w), 1272(m), 1248(w), 1100(s), 995(m), 792(m).

2b: It was prepared according to the procedure same as that for **2a**, except that

4-ethynylbenzaldehyde (30 mg, 0.23 mmol) was used instead of methyl 4-ethynylbenzoate. Yield: 53 mg, 17%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.35-0.54 (m, 16H), 0.57-0.65 (m, 8H), 0.74-0.83 (m, 20H), 0.86-1.11 (m, 40H), 1.13-1.21 (m, 8H), 3.85 (t, *J* = 6.4 Hz, 8H), 7.01 (d, *J* = 8.4 Hz, 4H, phenyl), 7.71 (t, *J* = 8.4 Hz, 2H, phenyl), 7.98 (d, *J* = 7.6 Hz, 2H, phenyl), 8.04 (d, *J* = 8.0 Hz, 2H, phenyl), 8.85 (d, *J* = 4.4 Hz, 2H, pyrrolic), 8.91 (d, *J* = 4.8 Hz, 2H, pyrrolic), 9.60 (d, *J* = 4.8 Hz, 2H, pyrrolic), 9.64 (d, *J* = 4.8 Hz, 2H, pyrrolic), 10.06 (s, 1H, CHO). MS (MALDI-TOF, m/z): [M] calcd for $C_{89}H_{119}BrN_4O_5Zn$, 1466.77; found, 1466.57. IR (KBr pellet, cm^{-1}): 2922(s), 2852(m), 2191(w), 2027(w), 1956(m), 1703(m), 1660(s), 1592(s), 1456(s), 1382(w), 1296(w), 1246(m), 1200(m), 1101(s), 995(s), 822(w), 789(m), 711(w).

2c: It was prepared according to the procedure same as that for **2a**, except that 5-ethynylthiophene-2-carbaldehyde (32 mg, 0.23 mmol) was used instead of methyl 4-ethynylbenzoate. Yield: 47 mg, 15%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.33-0.55 (m, 16H), 0.58-0.66 (m, 8H), 0.76-0.84 (m, 20H), 0.87-1.13 (m, 40H), 1.18-1.22 (m, 8H), 3.85 (t, *J* = 6.4 Hz, 8H), 7.01 (d, *J* = 8.4 Hz, 4H, phenyl), 7.60 (d, *J* = 4.0 Hz, 1H, thienyl), 7.70 (t, *J* = 8.4 Hz, 2H, phenyl), 7.78 (d, *J* = 3.6 Hz, 1H, thienyl), 8.83 (d, *J* = 4.4 Hz, 2H, pyrrolic), 8.93 (d, *J* = 4.8 Hz, 2H, pyrrolic), 9.17 (d, *J* = 4.8 Hz, 2H, pyrrolic), 9.60 (d, *J* = 4.8 Hz, 2H, pyrrolic), 9.97 (s, 1H, CHO). MS (MALDI-TOF, m/z): [M] calcd for $C_{87}H_{117}BrN_4O_5SZn$, 1472.22; found, 1472.55. IR (KBr pellet, cm^{-1}): 2922(s), 2852(m), 2183(w), 2027(w), 1956(m), 1669(s), 1589(m), 1456(s), 1429(w), 1247(w), 1223(w), 1205(w), 1100(s), 1064(w), 997(s), 930(w), 791(m), 719(m).

2d: It was prepared according to the procedure same as that for **2a**, except that 3-hexyl-5-ethynylthiophene-2-carbaldehyde (56 mg, 0.25 mmol) was used instead of methyl 4-ethynylbenzoate. Yield: 50 mg, 15%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.37-0.53 (m, 16H), 0.58-0.66 (m, 8H), 0.75-0.83 (m, 20H), 0.86-1.13 (m, 43H), 1.16-1.22 (m, 8H), 1.42-1.48 (m, 4H), 1.95-2.03 (m, 4H), 3.22 (t, *J* = 8.0 Hz, 2H), 3.85 (t, *J* = 6.4 Hz, 8H), 7.00 (d, *J* = 8.4 Hz, 4H, phenyl), 7.70 (t, *J* = 8.4 Hz, 2H, phenyl), 7.74 (s, 1H, thienyl), 8.83 (d, *J* = 4.4 Hz, 2H, pyrrolic), 8.89 (d, *J* = 4.8 Hz, 2H, pyrrolic), 9.57 (d, *J* = 4.8 Hz, 2H, pyrrolic), 9.59 (d, *J* = 4.4 Hz, 2H, pyrrolic), 9.94 (s, 1H, CHO). MS (MALDI-TOF, m/z): [M] calcd for $C_{93}H_{129}BrN_4O_5SZn$, 1556.82; found, 1556.81. IR (KBr pellet, cm^{-1}): 3359(br), 2922(s), 2852(s), 2175(w), 2027(w), 1956(m), 1660(s), 1588(w), 1456(s), 1425(w), 1245(m), 1200(w), 1162(w), 1097(m), 994(s), 790(m), 717(w).

3a: Compound **2a** (50 mg, 0.033 mmol), 2-diphenylamino-5-tributylstannylthiophene (20 mg, 0.037 mmol) and $Pd(PPh_3)_4$ (2 mg, 0.002 mmol) were dissolved in dry toluene (10 mL) and the reaction mixture was degassed with nitrogen. Then the mixture was heated at 80°C for 5 h. After cooling to room temperature, toluene was removed *in vacuo*, and the residue was purified by column chromatography on silica gel. Recrystallization from CH_2Cl_2/CH_3OH gave the target compound (33 mg, yield 60%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.34-0.53 (m, 16H), 0.56-0.63 (m, 8H), 0.73-0.81 (m, 20H), 0.84-1.09 (m, 40H), 1.11-1.18 (m, 8H), 3.83 (t, *J* = 6.0 Hz, 8H), 3.99 (s, 3H, OMe), 7.00 (d, *J* = 8.4 Hz, 4H, phenyl), 7.08-7.12 (m, 3H), 7.35-7.45 (m, 8H, phenyl), 7.61 (d, *J* = 3.2 Hz, 1H, thienyl), 7.70 (t, *J* = 8.0 Hz, 2H, phenyl), 8.04 (d, *J* = 8.0 Hz, 2H, phenyl), 8.20 (d, *J* = 8.0 Hz, 2H, phenyl), 8.85 (d, *J* = 4.4 Hz, 2H, pyrrolic), 8.93 (d, *J* = 4.4 Hz, 2H, pyrrolic), 9.18 (d, *J* = 4.4 Hz, 2H, pyrrolic), 9.71 (d, *J* = 4.4 Hz, 2H, pyrrolic). MS (MALDI-TOF, m/z): [M] calcd for $C_{106}H_{133}N_5O_6SZn$, 1667.93; found, 1667.82. IR (KBr pellet, cm^{-1}): 2923(s), 2852(m), 2191(w), 2027(w), 1956(m), 1723(m), 1664(m), 1590(m), 1494(w), 1455(m), 1272(m), 1242(w), 1175(w), 1100(s), 994(m), 960(w), 790(m).

3b: It was prepared according to the procedure same as that for **3a**, except that **2b** (50 mg, 0.034 mmol) was used instead of **2a**. Yield: 34 mg, 62%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.34-0.54 (m, 16H), 0.55-0.64 (m, 8H), 0.72-0.81 (m, 20H), 0.84-1.06 (m, 40H), 1.12-1.22 (m, 8H), 3.84 (t, *J* = 6.4 Hz, 8H), 7.00 (d, *J* = 8.4 Hz, 4H, phenyl), 7.07-7.12 (m, 3H), 7.35-7.45 (m, 8H, phenyl), 7.61 (d, *J* = 3.6 Hz, 1H, thienyl), 7.71 (t, *J* = 8.4 Hz, 2H, phenyl), 7.92 (d, *J* = 8.0 Hz, 2H, phenyl), 8.02 (d, *J* = 8.0 Hz, 2H, phenyl), 8.84 (d, *J* = 4.4 Hz, 2H, pyrrolic), 8.94 (d, *J* = 4.8 Hz, 2H, pyrrolic), 9.18 (d, *J* = 4.4 Hz, 2H, pyrrolic), 9.69 (d, *J* = 4.8 Hz, 2H, pyrrolic), 9.99 (s, 1H, CHO). MS (MALDI-TOF, m/z): [M] calcd for $C_{105}H_{131}N_5O_5SZn$, 1637.92; found, 1637.99. IR (KBr pellet, cm^{-1}): 3357(br), 2922(s), 2851(s), 2183(w), 2030(w), 1956(m), 1697(w), 1659(m), 1632(m), 1596(s), 1494(w), 1455(s), 1250(w), 1204(w), 1199(m), 995(m), 790(m).

3c: It was prepared according to the procedure same as that for **3a**, except that **2c** (47 mg, 0.033 mmol) was used instead of **2a**. Yield: 32 mg, 59%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.35-0.53 (m, 16H), 0.56-0.63 (m, 8H), 0.72-0.81 (m, 20H), 0.83-1.06 (m, 40H), 1.12-1.19 (m, 8H), 3.84 (t, *J* = 6.4 Hz, 8H), 7.01 (d, *J* = 8.4 Hz, 4H, phenyl), 7.08-7.12 (m, 3H), 7.35-7.45 (m, 8H, phenyl), 7.60 (d, *J* = 3.6 Hz, 1H, thienyl), 7.68-7.73 (m, 3H, phenyl), 7.85 (d, *J* = 4.0 Hz, 1H, thienyl), 8.89 (d, *J* = 4.4 Hz, 2H, pyrrolic), 8.93 (d, *J* = 4.4 Hz, 2H, pyrrolic), 9.53 (d, *J* = 4.4 Hz, 2H, pyrrolic), 9.59 (d, *J* = 4.4 Hz, 2H, pyrrolic), 9.90 (s, 1H, CHO). MS (MALDI-TOF, m/z): [M] calcd for $C_{103}H_{129}N_5O_5S_2Zn$, 1643.87; found, 1644.19. IR (KBr pellet, cm^{-1}): 2922(s), 2851(m), 2179(m), 2027(w), 1959(m), 1668(s), 1588(m), 1455(s), 1245(w), 1200(w), 1099(s), 995(m), 793(m), 752(w), 707(w), 697(m).

3d: It was prepared according to the procedure same as that for **3a**, except that **2d** (50 mg, 0.032 mmol) was used instead of **2a**.Yield: 36 mg, 65%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.34-0.54 (m, 16H), 0.55-0.63 (m, 8H), 0.70-0.82 (m, 20H), 0.83-1.07 (m, 43H), 1.12-1.19 (m, 8H), 1.57-1.67 (m, 4H), 1.96-2.07 (m, 4H), 3.24 (t, *J* = 8.0 Hz, 2H), 3.83 (t, *J* = 6.4 Hz, 8H), 7.00 (d, *J* = 8.4 Hz, 4H, phenyl), 7.08-7.12 (m, 3H), 7.35-7.45 (m, 8H), 7.60 (d, *J* = 3.6 Hz, 1H, thienyl), 7.70 (t, *J* = 8.4 Hz, 3H, phenyl), 7.75 (s, 1H, thienyl), 8.84 (d, *J* = 4.4 Hz, 2H, pyrrolic), 8.93 (d, *J* = 4.8 Hz, 2H, pyrrolic), 9.17 (d, *J* = 4.8 Hz, 2H, pyrrolic), 9.62 (d, *J* = 4.8 Hz, 2H, pyrrolic), 9.93 (s, 1H, CHO). MS (MALDI-TOF, m/z): [M] calcd for $C_{109}H_{141}N_5O_5S_2Zn$, 1727.97; found, 1728.02. IR (KBr pellet, cm^{-1}): 2922(s), 2852(s), 2174(m), 2030(w), 1956(m), 1667(s), 1591(m), 1495(m), 1455(s), 1248(m), 1178(w), 1099(m), 994(m), 790(m).

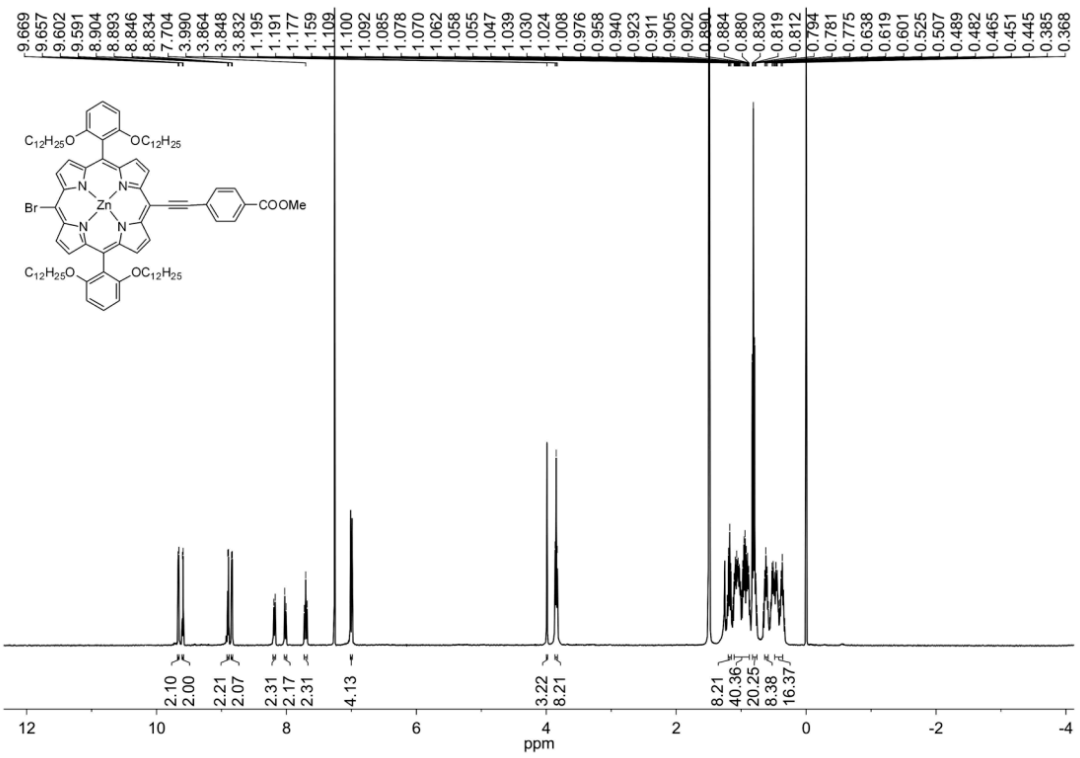

Fig. S1 The ^{1}H NMR spectrum of **2a** in $CDCl_3$

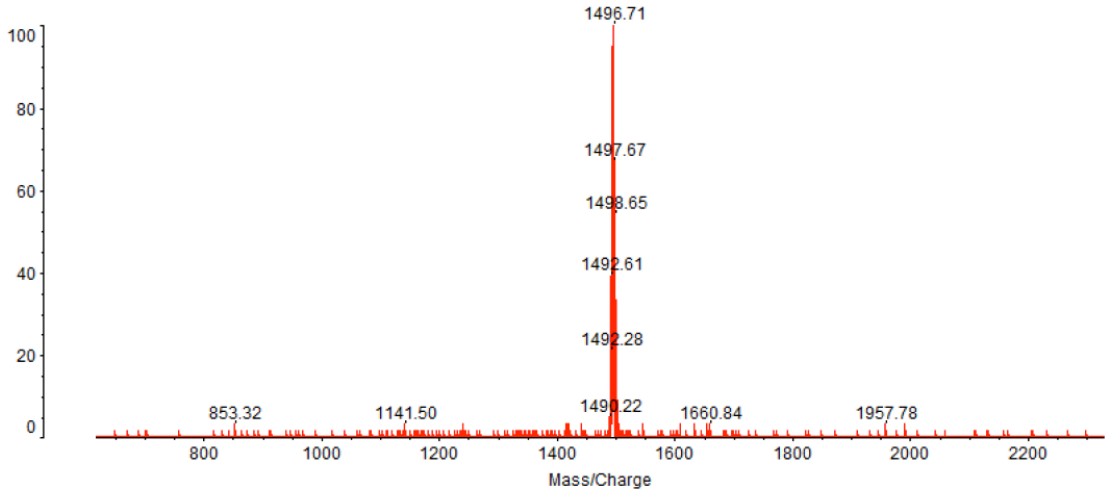

Fig. S2 MALDI-TOF MS of **2a**

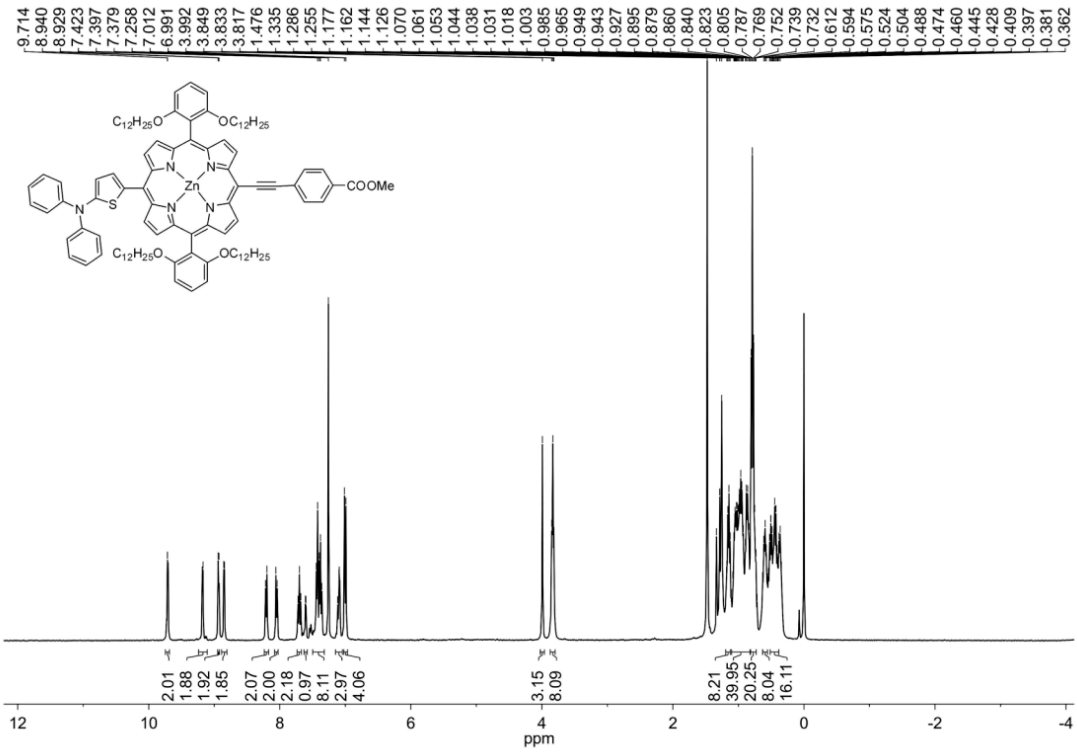

Fig. S3 The ^{1}H NMR spectrum of **3a** in $CDCl_3$

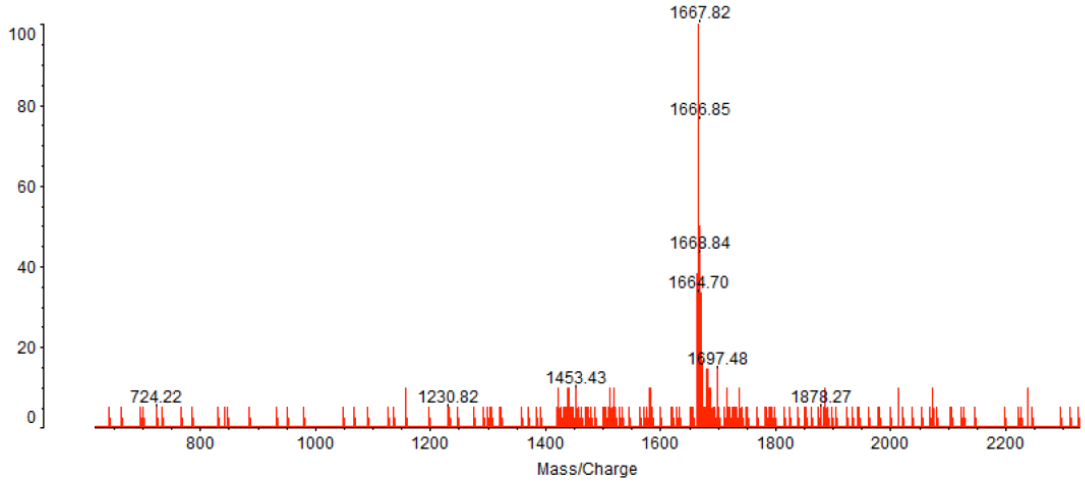

Fig. S4 MALDI-TOF MS of **3a**

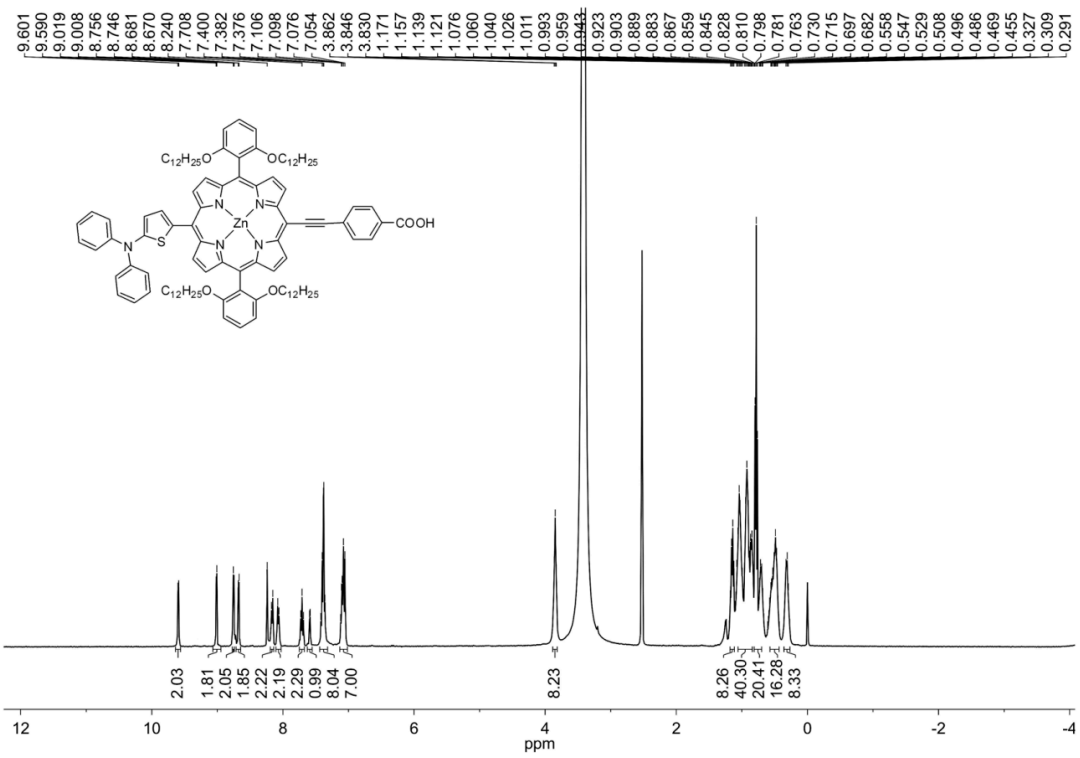

Fig. S5 The ^{1}H NMR spectrum of **YQ1** in $CDCl_3$: DMSO-d_6 = 1 : 2

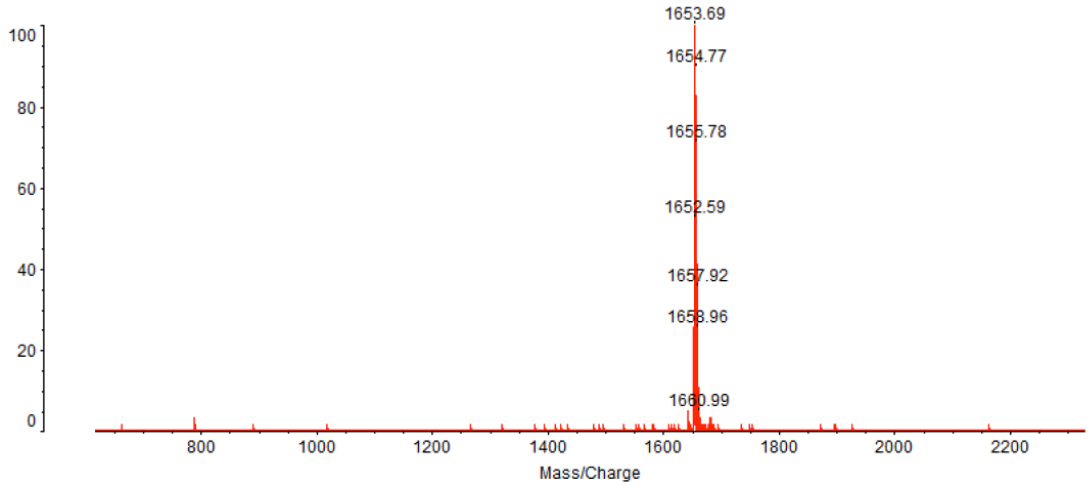

Fig. S6 MALDI-TOF MS of **YQ1**

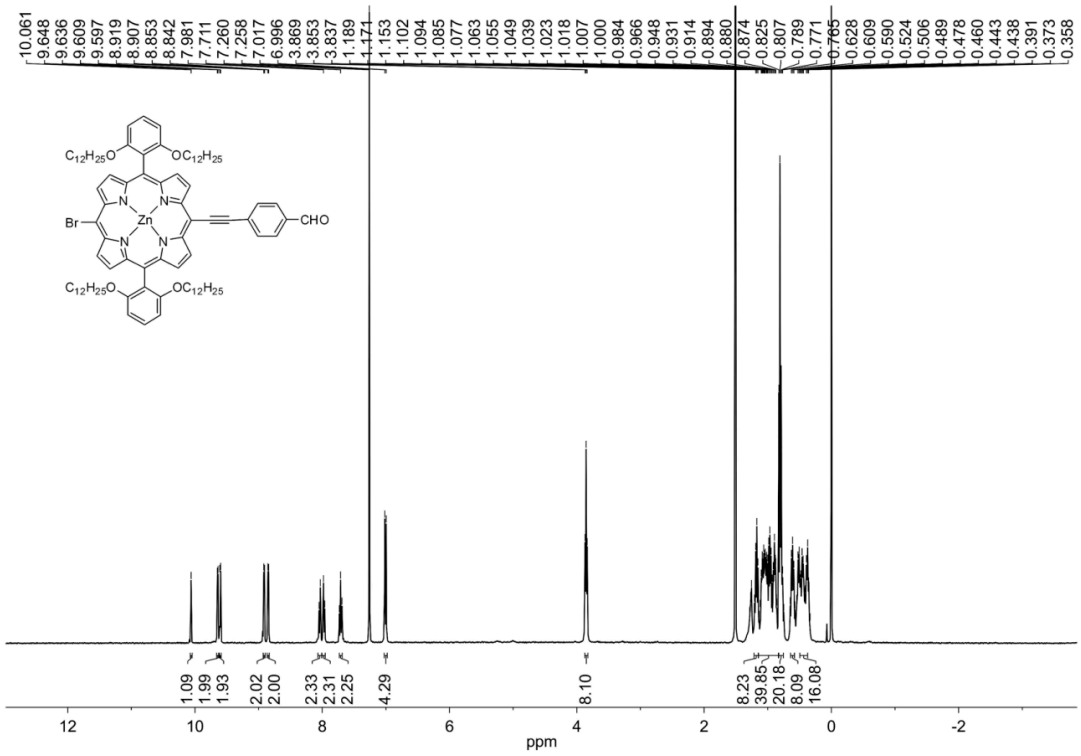

Fig. S7 The ^{1}H NMR spectrum of **2b** in $CDCl_3$

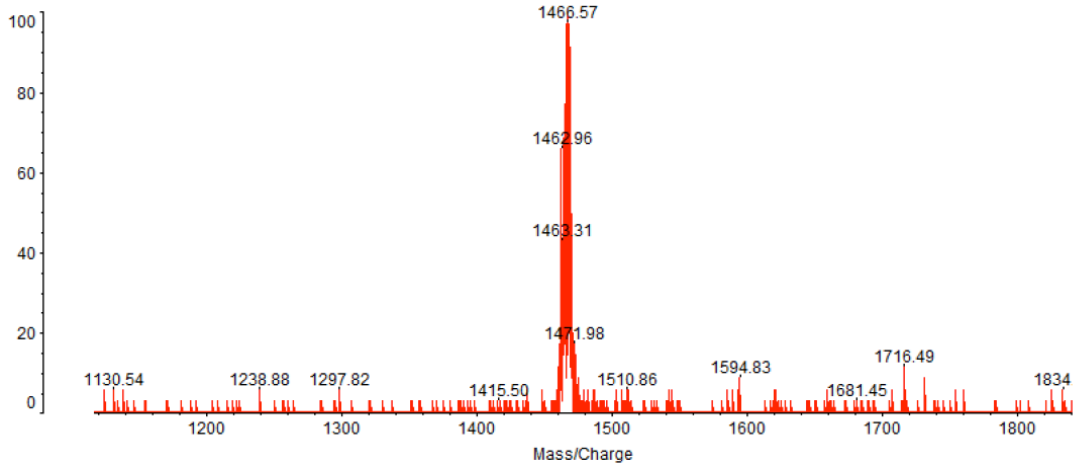

Fig. S8 MALDI-TOF MS of **2b**

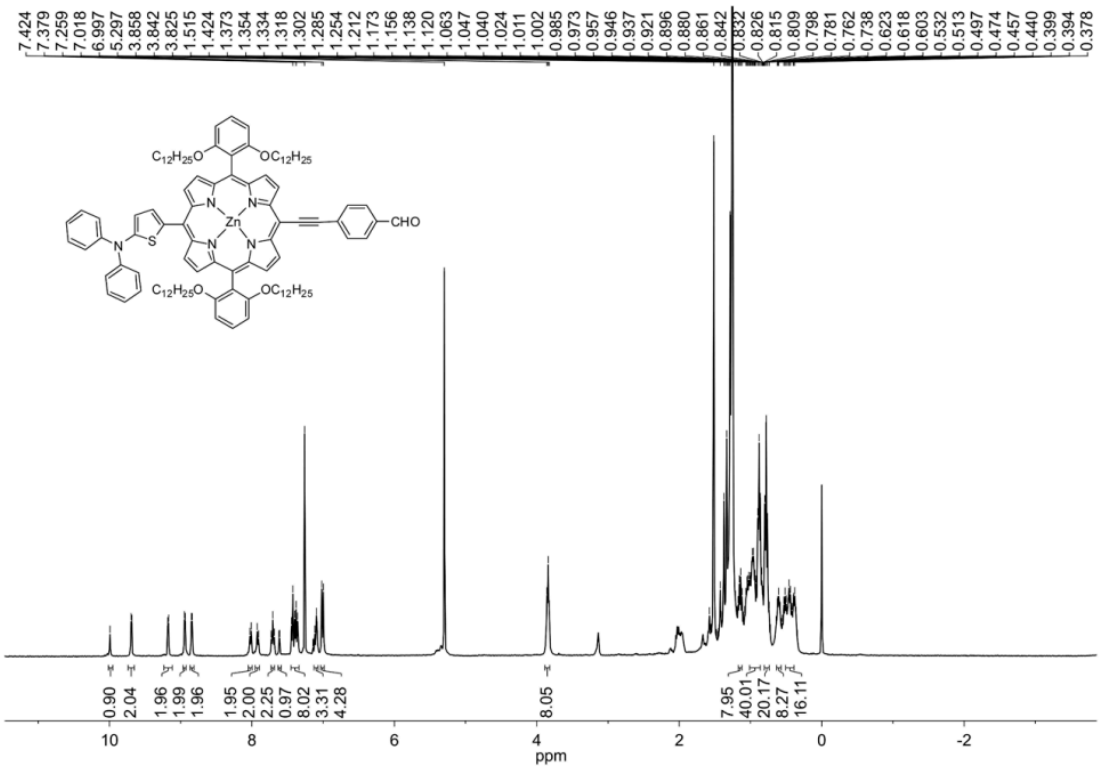

Fig. S9 The ^{1}H NMR spectrum of **3b** in $CDCl_3$

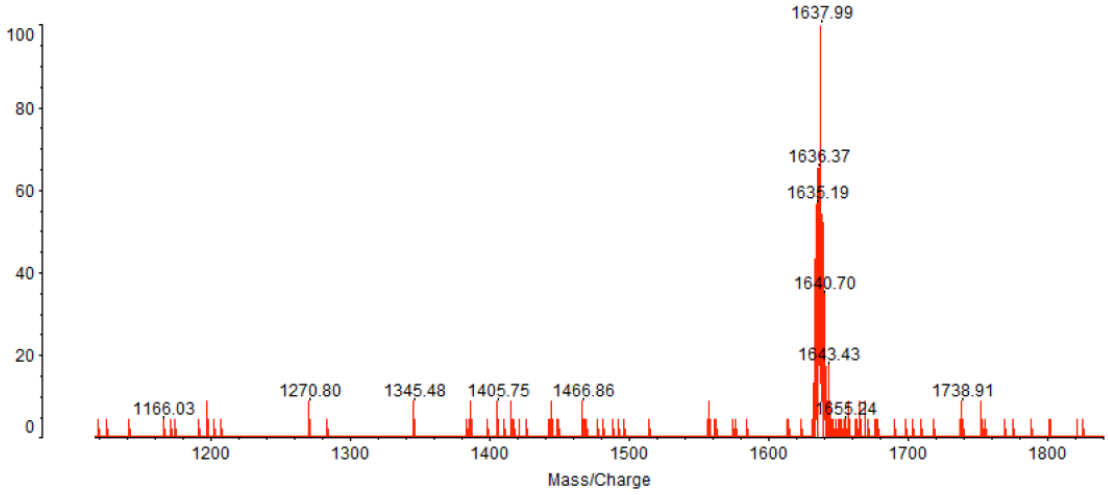

Fig. S10 MALDI-TOF MS of **3b**

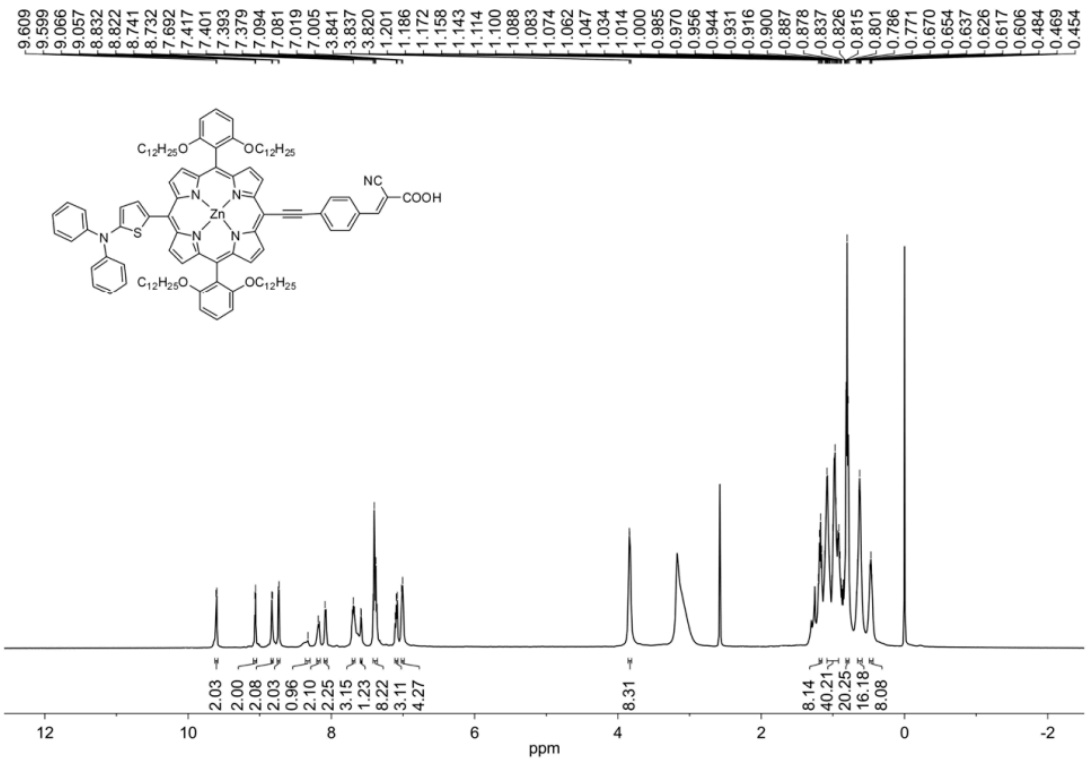

Fig. S11 The ^{1}H NMR spectrum of **YQ2** in $CDCl_3$: DMSO-d_6 = 1 : 2

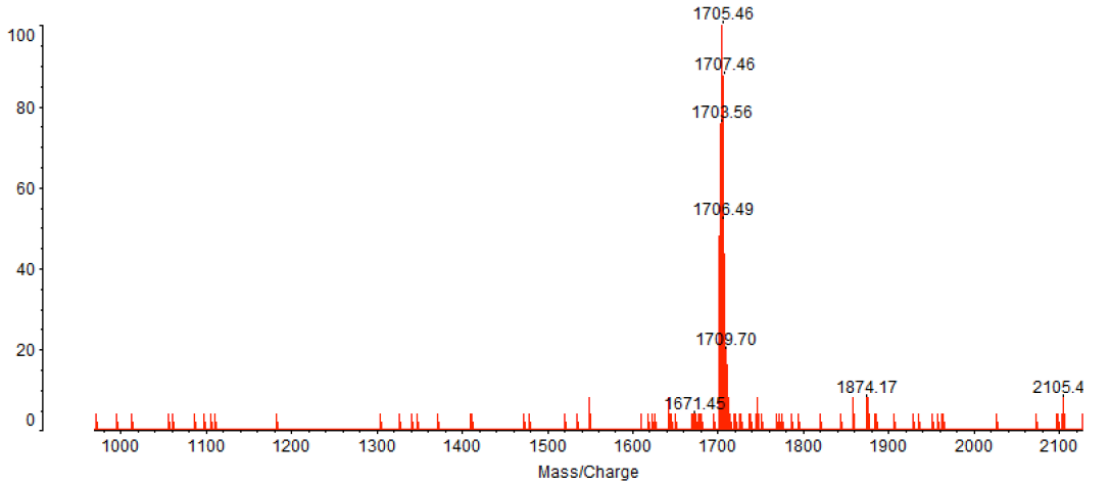

Fig. S12 MALDI-TOF MS of **YQ2**

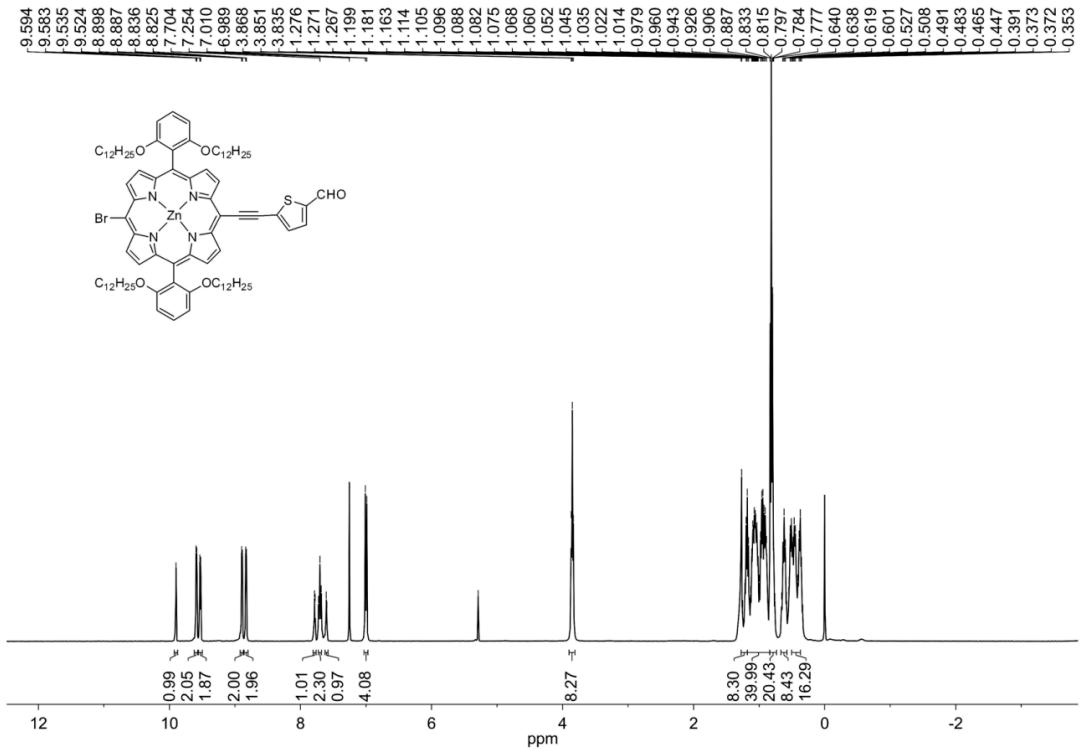

Fig. S13 The ^{1}H NMR spectrum of **2c** in $CDCl_3$

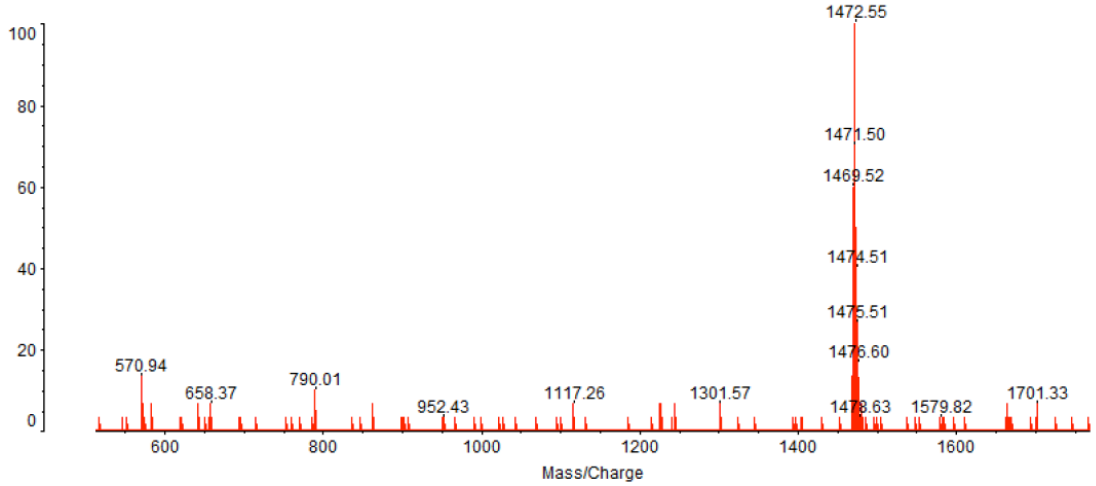

Fig. S14 MALDI-TOF MS of **2c**

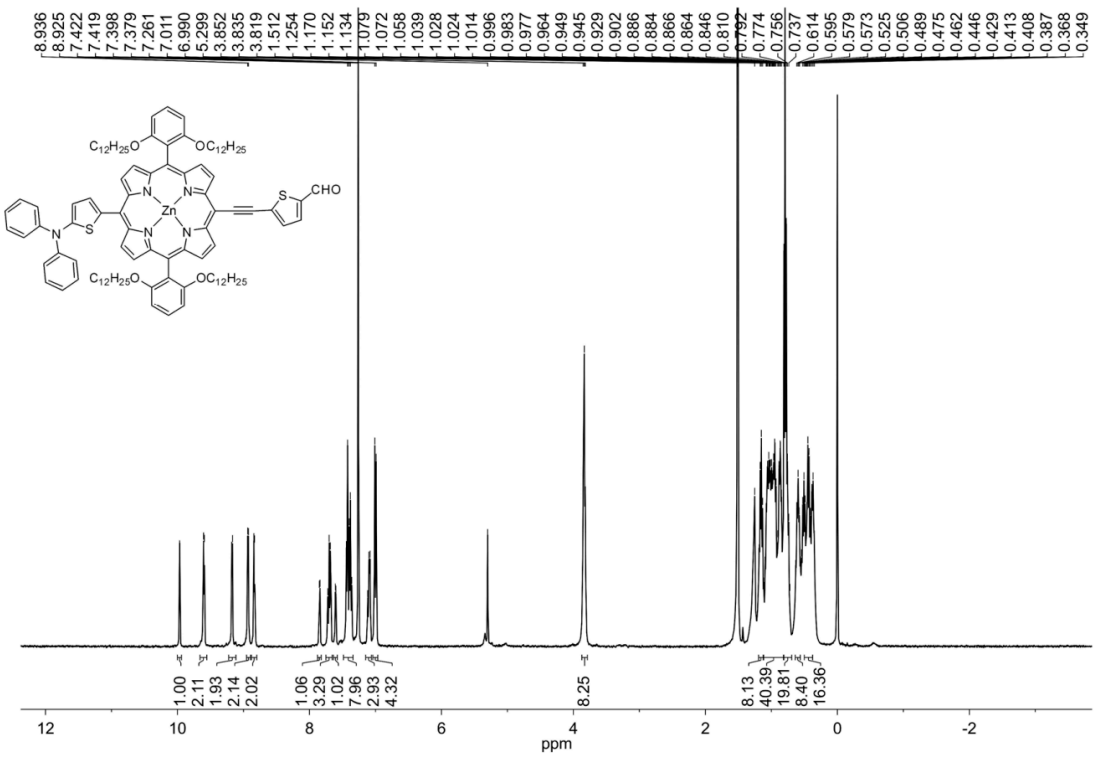

Fig. S15 The ^{1}H NMR spectrum of **3c** in $CDCl_3$

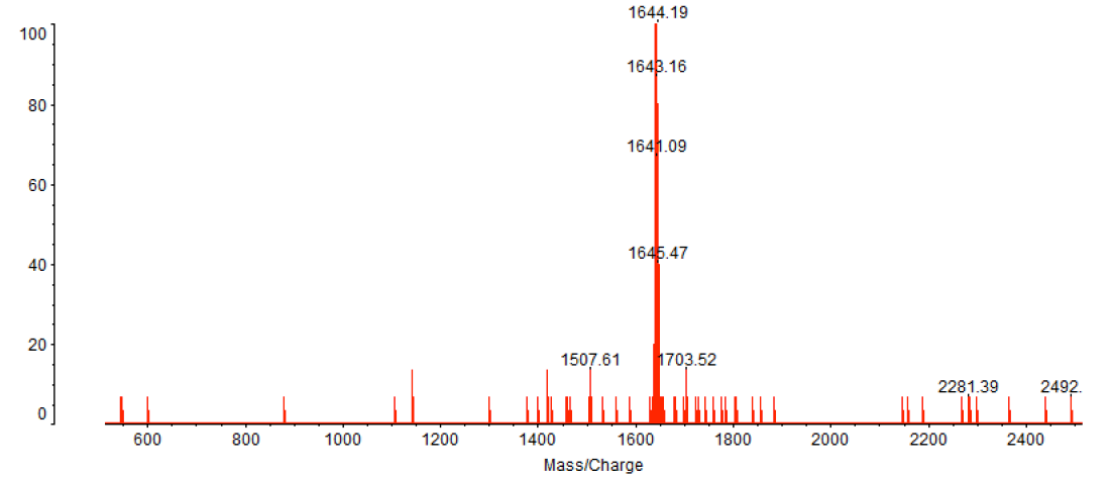

Fig. S16 MALDI-TOF MS of **3c**

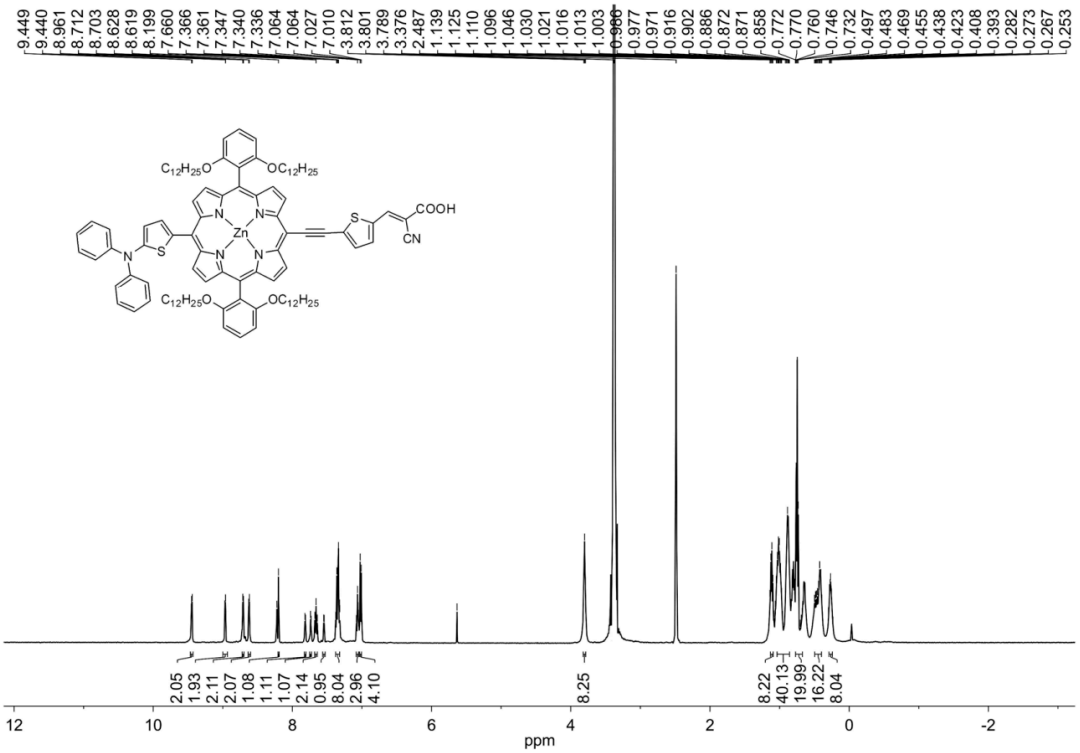

Fig. S17 The ^{1}H NMR spectrum of **YQ3** in $CDCl_3$: DMSO-d_6 = 1 : 2

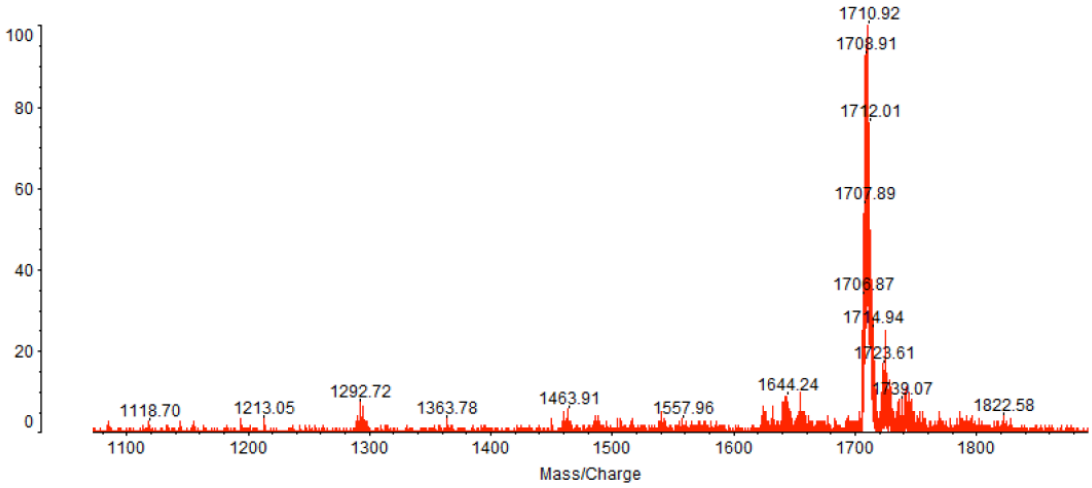

Fig. S18 MALDI-TOF MS of **YQ3**

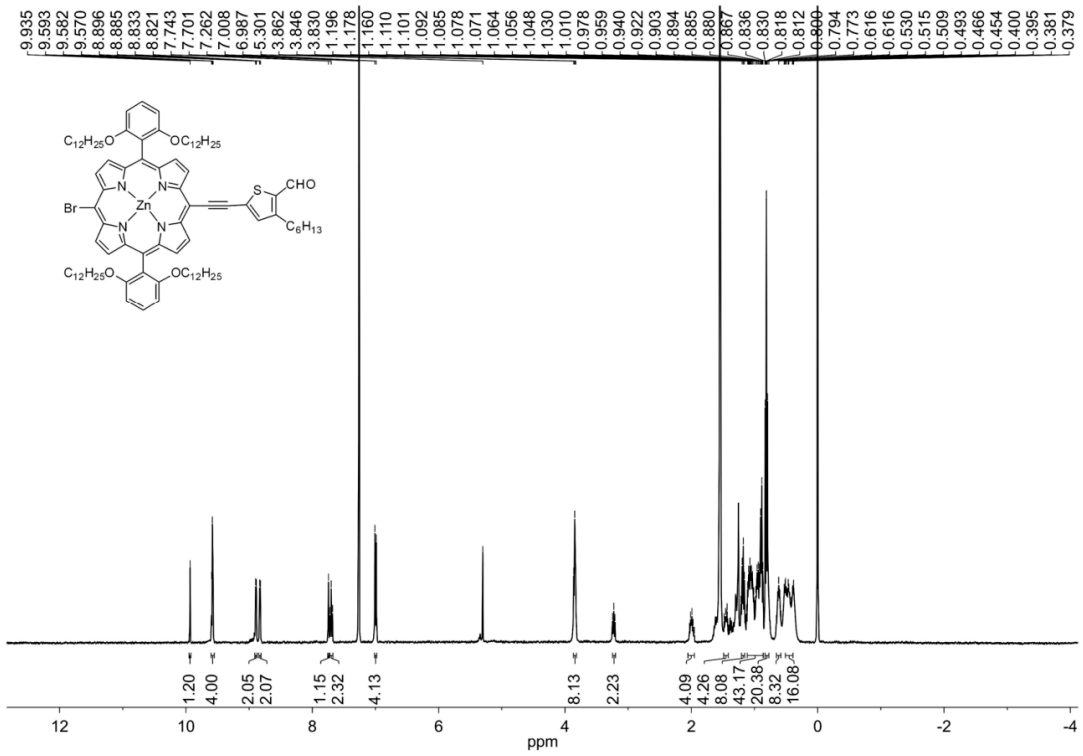

Fig. S19 The ^{1}H NMR spectrum of **2d** in $CDCl_3$

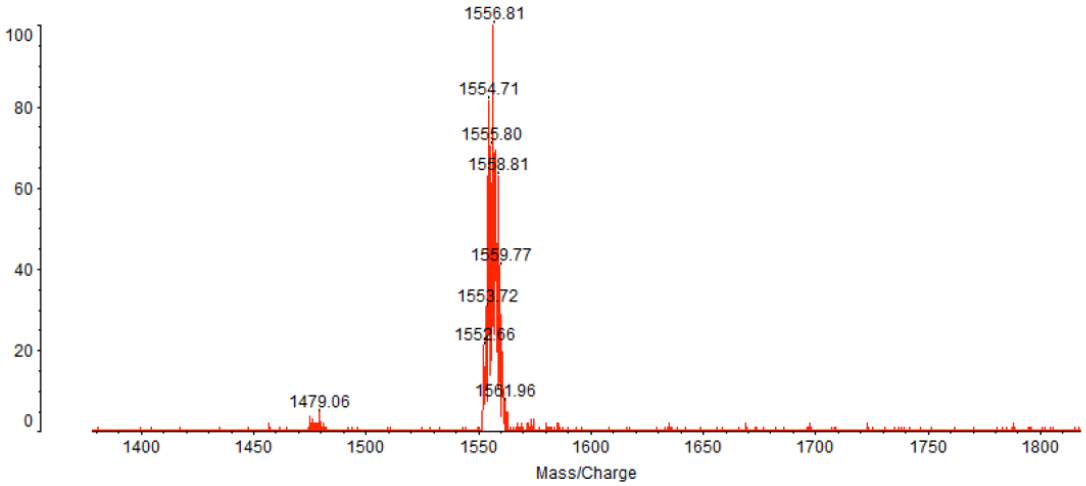

Fig. S20 MALDI-TOF MS of **2d**

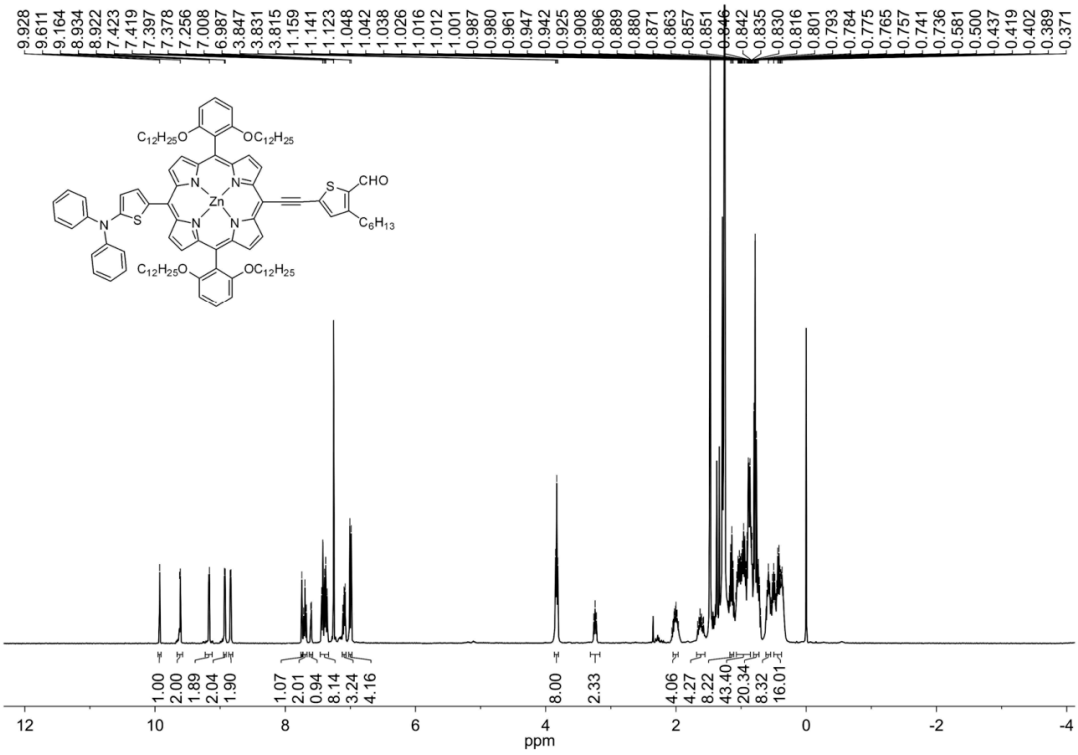

Fig. S21 The ^{1}H NMR spectrum of **3d** in $CDCl_3$

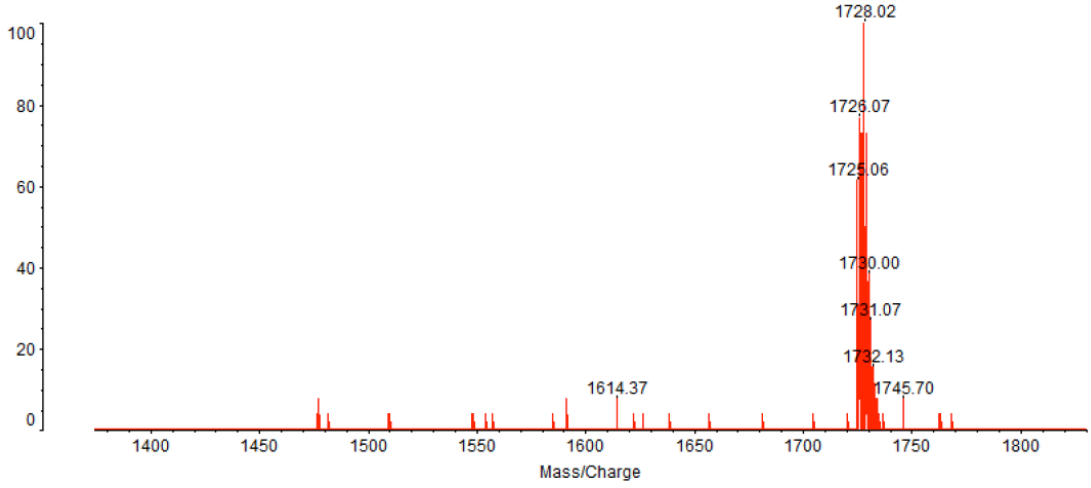

Fig. S22 MALDI-TOF MS of **3d**

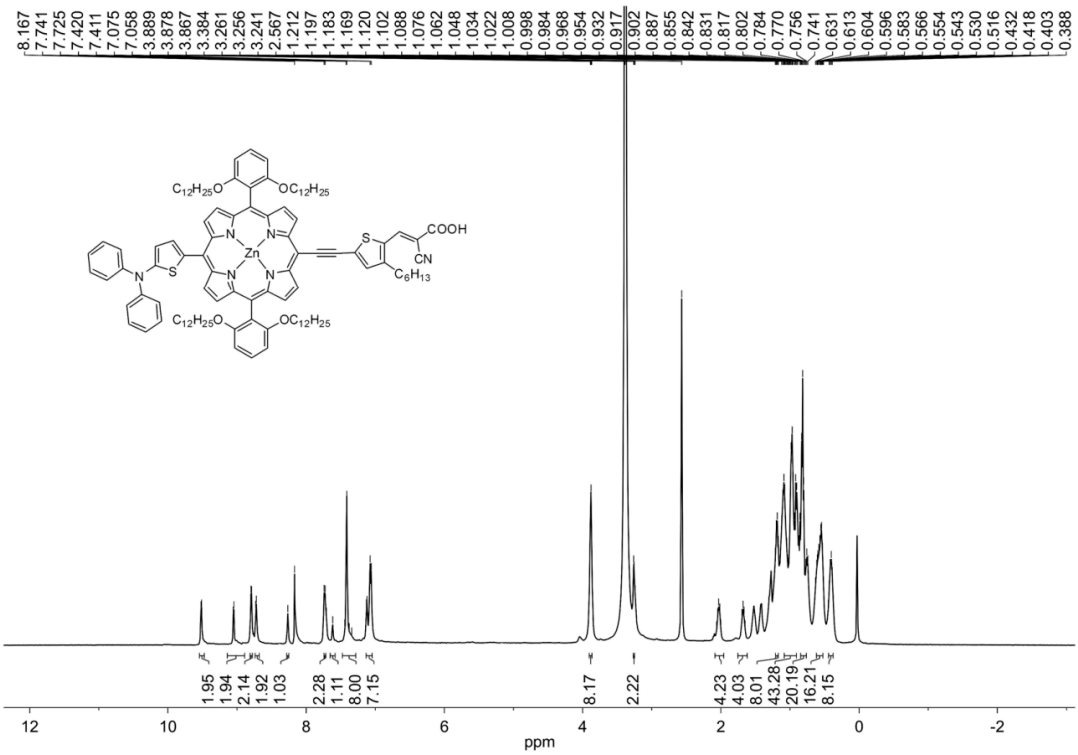

Fig. S23 The ^{1}H NMR spectrum of **YQ4** in $CDCl_3$: DMSO-d_6 = 1 : 2

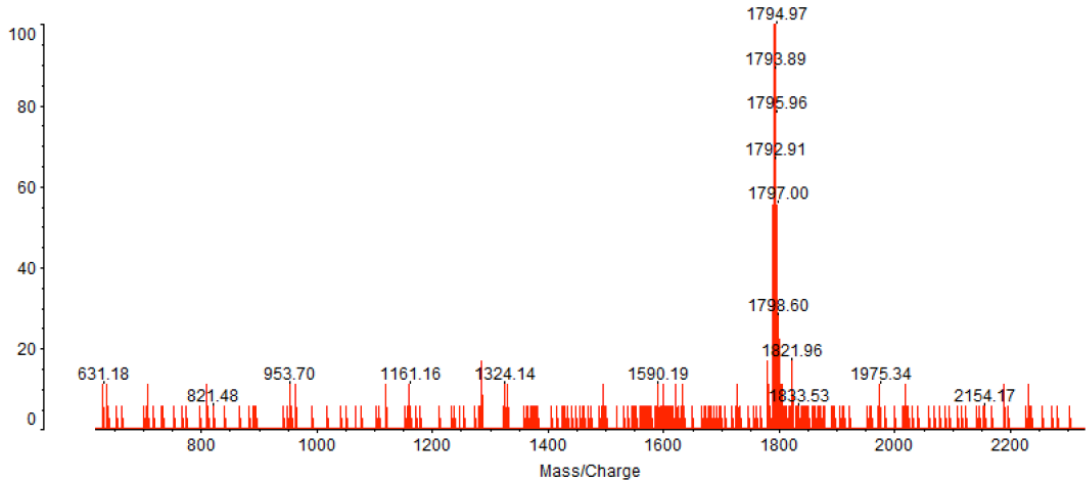

Fig. S24 MALDI-TOF MS of **YQ4**