Electronic Supplementary Information

Engineering Conjugation in *Para*-Phenylene-Bridged Porphyrin Tapes

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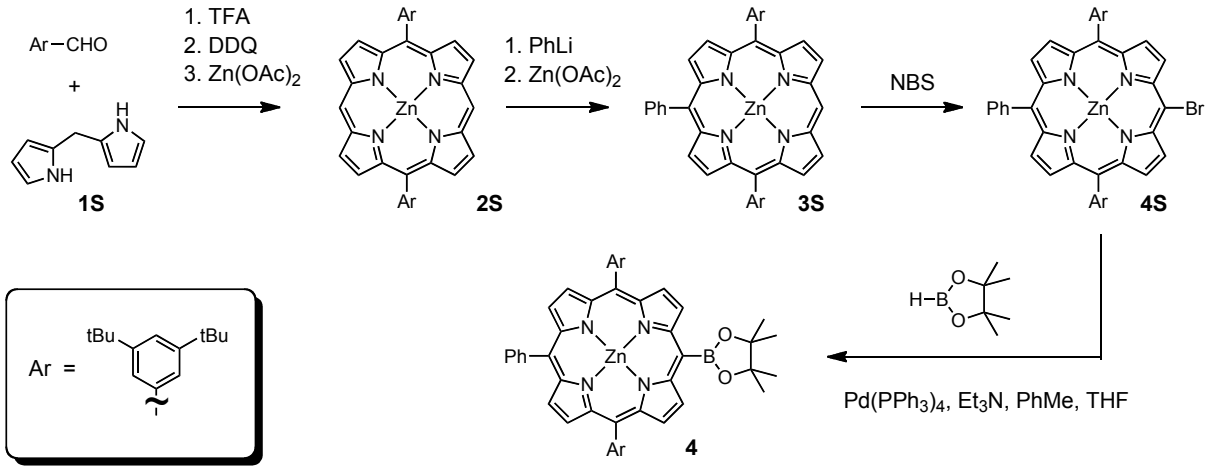
1. General Information

The handling of all air/water sensitive materials was carried out using standard high vacuum techniques. Freeze-thaw degassing was affected by freezing under vacuum, saturating with nitrogen then re-freezing and pumping under vacuum. Dried CH_2Cl_2, toluene and THF were obtained by passing through alumina under nitrogen, then further dried over activated molecular sieves (3 Å, 8–12 mesh). Triethylamine was distilled from CaH_2. Unless specified otherwise, all other solvents were used as commercially supplied. Where mixtures of solvents were used, ratios are reported by volume. Flash chromatography was carried out on silica gel 60 under positive pressure. Size-exclusion chromatography was carried out under gravity using cross-linked polystyrene (Bio-Beads® SX-1; 200–400 mesh) in THF. All UV-vis spectra were recorded in solution using a Perkin-Elmer Lambda 20 spectrometer (1.0 cm path length, silica cell). NMR spectra were recorded at room temperature using Brüker DPX400 (400 MHz), Brüker AV400 (400/100 MHz), Brüker AVC500 (500/125 MHz) instruments. ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm) referenced to the residual signal of the solvent (chloroform, methanol); coupling constants (*J*) are given in Hz and are accurate to ±0.4 Hz. MALDI-TOF mass spectrometry was carried out using a Micromass MALDI micro MX spectrometer. FT-IR spectra were recorded on Brüker Tensor 27 spectrometer.

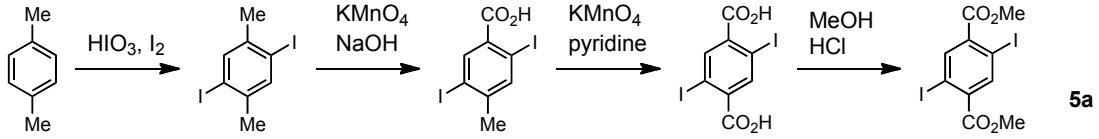
2. Synthesis of Known Compounds

The general synthetic approach to the following known compounds is presented at Scheme S1: dipyrromethane (**1S**),[1] porphyrin derivatives: 5,15-bis-(3,5-di-*tert*-butylphenyl) (**2S**),[2] 5,15-bis-(3,5-di-*tert*-butylphenyl)-10-phenyl- (**3S**),[3] 5-bromo-10,20-bis-(3,5-di-*tert*-butylphenyl)-15-phenyl- (**4S**),[4] 5-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-10,20-bis-(3,5-di-*tert*-butylphenyl)-10-phenyl- (**7**).[5]



Scheme S1. Synthesis of porphyrin boronate ester **7**.[5]

Dimethyl-2,5-diiodoterephthalate, **8b**, was synthesized according to previously described procedure[6] (Scheme S2), while 1,4-dibromo-2,5-diiodobenzene **8a** was purchased from Aldrich,



Scheme S2. Synthesis of dimethyl-2,5-diiodoterephthalate **8b**.[6]

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3. Synthesis of New Compounds

[5-(2,5-dibromo-4-iodophenyl)-10,20-bis-(3,5-di-*tert*-butylphenyl)-15-phenylporphyrinato]zinc(II) (**9a**). Porphyrin boronic ester **7** (142 mg, 0.149 mmol) was placed in a round bottom flask together with 1,4-dibromo-2,5-diiodobenzene **5b** (290 mg, 0.595 mmol), Cs_2CO_3 (523 mg, 1.49 mmol) and $Pd(PPh_3)_4$ (17.2 mg, 0.015 mmol). All solid ingredients were dried overnight under vacuum. Dry toluene/DMF (1:1) (6 mL) was added. The resulting solution was degassed by the freeze-pump-thaw and stirred at 90–95 °C for 1 h. Then all solvents were removed and the residue was chromatographed on silica column (eluting with CH_2Cl_2/60-80 petroleum ether, 1:1 volume ratio) to give the desired product as the second red band. Recrystallization by layered addition (CH_2Cl_2/MeOH) gave **9a** as a dark red solid (106 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) 9.02 (d, 2H, ^3J = 4.7 Hz), 8.98 (d, 2H, ^3J = 4.7 Hz), 8.94 (d, 2H, ^3J = 4.7 Hz), 8.79 (d, 2H, ^3J = 4.7 Hz), 8.50 (s, 1H), 8.45 (s, 1H), 8.25–8.20 (m, 2H), 8.13 (t, 2H, J = 1.6 Hz), 8.04 (t, 2H, J = 1.6 Hz), 7.81 (t, 2H, J = 1.6 Hz), 7.78–7.72 (m, 3H), 1.55 (s, 18H), 1.53 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) 150.8, 150.4, 150.0, 148.9, 148.5, 145.6, 143.0, 141.7, 141.6, 138.0, 134.4, 134.3, 133.1, 132.3, 132.0, 130.3, 130.0, 129.7, 127.4, 127.3, 126.6, 126.5, 126.4, 122.8, 121.8, 120.8, 115.7, 101.4, 35.1, 35.0, 31.8, 31.7; λ_{max} / nm ($CHCl_3$) (log ε) 423 (5.82), 549 (4.40); *m/z* (MALDI TOF MS+) 1186.41 ($C_{60}H_{57}N_4ZnBr_2I$; $[M]^+$ requires 1186.13).

p*-Phenylene Porphyrin Dimer 3a**. Boronic ester **7** (39 mg, 0.04 mmol) was placed in a round bottom flask together with porphyrin **9a** (32 mg, 0.027 mmol), Cs_2CO_3 (87 mg, 0.27 mmol) and $Pd(PPh_3)_4$ (5.0 mg, 0.0043 mmol). All solid ingredients were dried overnight under vacuum. Dry toluene/DMF (1:1) (4 mL) was added. The resulting solution was degassed by freeze-pump-thaw technique (4 times), and stirred at 90–95 °C for 1.5 h. Then all solvents were removed and residue was chromatographed on a silica column (eluting with CH_2Cl_2/60-80 petroleum ether, 1:1 volume ratio) to give the desired product as the second red band (after elution of **10**). Recrystallization by layered addition (CH_2Cl_2/MeOH) gave **3a** as a dark red solid (30 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) 9.31 (d, 4H, ^3J = 4.7 Hz), 9.25 (d, 4H, ^3J = 4.7 Hz), 9.06 (d, 4H, ^3J = 4.7 Hz), 9.01 (d, 4H, ^3J = 4.7 Hz), 8.87 (s, 2H), 8.30–8.25 (m, 4H), 8.24 (t, 4H, J = 1.6 Hz), 8.16 (t, 4H, J = 1.6 Hz), 7.87 (t, 4H, J = 1.6 Hz), 7.82–7.76 (m, 6H), 1.61 (s, 36H), 1.60 (s, 36H); ^{13}C NMR (125 MHz, $CDCl_3$) 162.4, 150.9, 150.7, 150.2, 149.5, 148.7, 145.2, 142.9, 141.7, 137.4, 134.4, 134.3, 133.4, 132.4, 132.1, 130.8, 130.0, 129.8, 127.5, 126.5, 125.0, 122.9, 121.8, 120.9, 117.0, 35.1, 35.0, 31.82, 31.81; λ_{max} / nm ($CHCl_3$) (log ε) 420 (5.82), 430 (5.93), 550 (4.69); ***m/z (MALDI TOF MS+) 1884.60 ($C_{114}H_{112}N_8Zn_2Br_2$; $[M]^+$ requires 1884.59).

Singly-Fused Dimer 10. This compound was obtained as a byproduct in the synthesis of **3a**. The first brown fraction observed on a silica column was collected and chromatographed on a size-exclusion column to give **10** (10 mg, 15%), as a brown-yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) 9.46 (d, 2H, ^3J = 4.7 Hz), 9.41 (d, 1H, ^3J = 4.7 Hz), 9.11 (d, 2H, ^3J = 4.7 Hz), 9.01 (d, 2H, ^3J = 4.7 Hz), 8.96 (d, 2H, ^3J = 4.7 Hz), 8.89 (d, 1H, ^3J = 4.7 Hz) 8.74 (s, 1H), 8.61 (d, 1H, ^3J = 5.0 Hz), 8.59 (d, 1H, ^3J =5.0 Hz), 8.55 (d, 1H, ^3J = 4.4 Hz), 8.46 (d, 1H, ^3J = 4.4 Hz), 8.28–8.24 (m, 2H), 8.19 (t, 2H, J = 1.6 Hz), 8.18 (s, 1H), 8.12–8.08 (m, 4H), 8.03 (d, 2H, J = 1.6 Hz), 8.01 (s, 1H), 7.91 (d, 2H, ^3J = 1.6 Hz), 7.81–7.79 (m, 4H), 7.78–7.68 (m, 6H), 7.60 (t, 1H, ^3J = 1.6 Hz), 1.57 (s, 18H), 1.56 (s, 18H), 1.52 (s, 18H), 1.39 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) 161.4, 154.9, 153.0, 152.6, 151.9, 151.2, 150.7, 150.6, 150.0, 149.8, 149.6, 148.9, 148.8, 148.6, 148.5, 145.2, 143.0, 142.2, 141.7, 141.1, 139.7, 136.6, 136.1, 134.4, 134.3, 133.7, 133.0, 132.2, 131.8, 131.7, 131.7, 131.1, 131.0, 130.4, 130.0, 129.8, 129.6, 129.4, 127.8, 127.6, 127.5, 127.4, 126.7, 126.5, 126.4, 125.2, 123.0, 122.5, 121.3, 121.0, 120.8, 119.0, 111.3, 35.1, 35.0, 34.9, 31.7 (3×), 31.6; λ_{max}/nm (benzene, 1% pyridine) (log ε) 429 (5.06), 489 (4.85) 567 (4.08), 611 (4.08), 722 (3.51); *m/z* (MALDI TOF MS+) 1723.28, 1803.02 ($C_{114}H_{111}N_8Zn_2Br$; $[M\text{-}Br]^+$ requires 1723.75, $[M]^+$ requires 1802.67).

Fully Fused Dimer 4. Dimer **3a** (30 mg, 0.016 mmol) was placed in a round bottom flask together with $Pd(PPh_3)_4$ (8.0 mg, 0.0069 mmol) and K_3PO_4 (34 mg, 0.16 mmol). All solid ingredients were dried overnight under vacuum, then DMF (10 mL) was added. The resulting solution was degassed by freeze-pump-thaw technique (4 times), and stirred at 152 °C for 24 h, protected from the light. Then all solvents were removed. The crude product was dried under vacuum for 1 h, then was washed with petrol ether (40–60); it is completely insoluble in this solvent. Recrystallization from CH_2Cl_2/MeOH yielded **4** (5.5 mg, 20%). ^{1}H NMR (500 MHz,

$CDCl_3$ + 1% pyridine-d_5) 9.04 (d, 4H, ^3J = 4.5 Hz), 8.56 (d, 4H, ^3J = 4.5 Hz), 8.34 (s, 4H), 8.32 (d, 4H, ^3J = 4.5 Hz), 8.23 (d, 4H, ^3J = 4.5 Hz), 8.01–7.98 (m, 4H) 7.95 (s, 2H), 7.91 (d, 4H, ^4J = 1.7 Hz), 7.85 (d, 4H, ^4J = 1.7 Hz), 7.84 (s, 2H), 7.72 (t, 4H, ^4J = 1.7 Hz), 7.69 (t, 4H, ^4J = 1.7 Hz), 7.64–7.58 (m, 6H), 1.52 (s, 36H), 1.48 (s, 36H); λ_{max} / nm (C_6H_6 + 1% pyridine) (log ε) 417 (5.17), 519 (4.69), 553 (5.03), 594 (5.05), 677 (4.47), 744 (4.06), 843 (3.78), 939 (3.87), 1077 (3.70); *m/z* (MALDI TOF MS+) 1722.56 ($C_{114}H_{110}N_8Zn_2$; $[M]^+$ requires 1722.74).

[5-(2,5-dibromo-4-iodophenyl)-10,20-bis-(3,5-di-*tert*-butylphenyl)-15-phenylporphyrinato]zinc(II) (**9b**). Porphyrin boronic ester **7** (200 mg, 0.21 mmol) was placed in a round bottom flask together with 2,5-diiododimethylterephthalate **8b** (280 mg, 0.63 mmol), Cs_2CO_3 (1.3 g, 4.2 mmol) and $Pd(PPh_3)_4$ (121 mg, 0.11 mmol). All solid ingredients were dried overnight under vacuum. Dry toluene/DMF (1:1) (20 mL) was added. The resulting solution was degassed by freeze-pump-thaw, and stirred at 90–95 °C for 1 h. Then all solvents were removed and the residue was chromatographed on a silica column (eluting with CH_2Cl_2/40–60 petroleum ether, 1:1 volume ratio) to give the desired product as the second red band. Recrystallization by layered addition (CH_2Cl_2/MeOH) gave **9b** as a purple solid (153 mg, 62%). ^{1}H NMR (500 MHz, $CDCl_3$) 9.00 (d, 2H, ^3J = 4.6 Hz), 8.99 (d, 2H, ^3J = 4.7 Hz), 8.98 (s, 1H), 8.94 (d, 2H, ^3J = 4.6 Hz), 8.73 (d, 2H, ^3J = 4.6 Hz), 8.63 (s, 1H), 8.25–8.21 (m, 2H), 8.13 (t, 2H, ^3J = 1.6 Hz), 8.05 (t, 2H, ^3J = 1.6 Hz), 7.81 (t, 2H, ^3J = 1.6 Hz), 7.78–7.72 (m, 3H), 3.91 (s, 3H), 3.00 (s, 3H), 1.55 (s, 18H), 1.53 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) 166.4, 165.5, 150.6, 150.3, 150.1, 149.0, 148.6, 143.7, 142.9, 141.8, 141.7, 137.2, 136.5, 135.5, 134.4, 134.3, 132.9, 132.3, 131.9, 130.3, 129.9, 129,7, 127.5, 126.5, 122.7, 121.3, 120.8, 116.7, 107.8, 97.7, 93.2, 52.8, 52.1, 35.1, 35.0, 31.8, 31.7; λ_{max} / nm ($CHCl_3$) (log ε) 424 (5.81), 551 (4.50); *m/z* (MALDI TOF MS+) 1142.46 ($C_{64}H_{63}N_4O_4ZnI$; $[M]^+$ requires 1142.32).

***p*-Phenylene Porphyrin Dimer 3b**. Porphyrin boronic ester **7** (120 mg, 0.13 mmol) was placed in a round bottom flask together with porphyrin **9b** (120 mg, 0.11 mmol), Cs_2CO_3 (0.34 g, 1.0 mmol) and $Pd(PPh_3)_4$ (12 mg, 0.011 mmol). All solid ingredients were dried overnight under vacuum. Dry toluene/DMF (1:1) (9 mL) was added. The resulting solution was degassed by freeze-pump-thaw and stirred at 90–95 °C for 1 h. Then all solvents were removed and the residue was chromatographed on a silica column (eluting with CH_2Cl_2/40–60 petroleum ether/pyridine, 15:15:1 volume ratio) to give the desired product as the second red band. Recrystallization by layer addition (CH_2Cl_2/MeOH) gave **3b** as a purple solid (176 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$ with 5 vol% pyridine-d_5): δ = 9.15 (d, ^3J = 4.4 Hz, 4H; pyrrole-β), 9.14 (s, 2H; Ar of terephthalate), 9.08 (d, ^3J = 4.4 Hz, 4H; pyrrole-β), 8.94 (d, J = 4.4 Hz, 4H; pyrrole-β), 8.90 (d, J = 4.4 Hz, 4H; pyrrole-β), 8.27 (m, 4H; Ph), 8.12 (m, 4H; *o*-Ar), 8.08 (m, 4H; *o*-Ar), 7.79 (t, ^4J = 1.8 Hz, 4H; *p*-Ar), 7.73–7.75 (m, 6H; Ph), 2.90 (s, 6H; Me), 1.56 (s, 36H; *t*-Bu), 1.54 ppm (s, 36H; *t*-Bu); ^{13}C NMR (125 MHz, $CDCl_3$) 167.0, 150.7, 150.5, 150.2, 149.6, 148.6, 143.6, 143.0, 141.8, 136.1, 134.4, 134.3, 133.8, 133.0, 132.4, 131.9, 130.9, 130.6, 130.0, 129.8, 127.4, 126.5, 122.8, 121.2, 120.8, 117.7, 107.8, 97.9, 52.0, 35.1 (×2), 31.8 (×2); λ_{max} / nm ($CHCl_3$) (log ε) 423 (5.81), 431 (5.84), 552 (4.74). *m/z* (MALDI TOF MS+) 1838.82 ($C_{118}H_{118}N_8O_4Zn_2$; $[M]^+$ requires 1838.79). IR (KBr disc): 1720 cm^{-1}.

Diketo dimer 5. Boron tribromide (20 mL, 1.0 M solution in CH_2Cl_2) was added to porphyrin dimer **3b** (100 mg, 0.054 mmol) as a dry solid. The porphyrin immediately dissolved to form a green solution. The mixture was stirred at room temperature for 48 h, then poured into saturated aqueous $NaHCO_3$ with vigorous stirring. After stirring for 30 min, the organic layer was separated, and chromatographed (flash silica). The first orange band (eluted with dichloromethane) was the desired product (free-base). The second band (eluted with 10:1 dichloromethane/methanol) included partially reacted material; it was dried under vacuum and treated with further BBr_3 (10 mL, 1.0 M solution in CH_2Cl_2). The work-up procedure was repeated. The combined product was treated with zinc acetate (100 mg) in methanol (3.0 mL) and passed through a silica plug, eluting with dichloromethane. Recrystallization from dichloromethane/*n*-heptane afforded **5** as a brown solid (70 mg, 72%). ^{1}H NMR (500 MHz, $CDCl_3$ with 1 vol% pyridine-d_5): δ = 9.57 (d, ^3J = 5.0 Hz, 2H; pyrrole-β), 9.54 (s, 2H; bridging Ar), 9.30 (s, 2H; pyrrole-β), 8.65 (d, ^3J = 5.0 Hz, 2H; pyrrole-β), 8.53–8.54 (m, 6H; pyrrole-β ×3), 8.44 (d, J = 5.0 Hz, 2H; pyrrole-β), 8.06 (dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 4H; *o*-Ph), 7.96 (d, ^4J = 2.0 Hz, 4H; *o*-Ar), 7.93

(d, ^4J = 2.0 Hz, 4H; *o*-Ar), 7.76 (t, ^4J = 2.0 Hz, 4H; *p*-Ar), 7.65–7.68 (m, 6H; Ph), 1.54 (s, 36H; *t*-Bu), 1.51 ppm (s, 36H; *t*-Bu). ^{13}C NMR (125 MHz, $CDCl_3$ with 1 vol% pyridine-d_5): δ = 184.5, 153.7, 153.3, 152.5, 151.2, 150.8, 150.8, 149.7, 148.7, 148.4, 147.0, 142.4, 141.6, 141.4, 140.9, 137.2, 136.9, 135.7, 133.8, 133.6, 133.2, 133.1, 133.0, 132.8, 132.5, 131.3, 130.3, 129.8, 129.5, 129.4, 127.4, 126.6, 123.4, 123.4, 121.2, 120.9, 110.8, 35.0, 34.9, 31.8, 31.7 ppm. λ_{max}/nm (log ε) (benzene with 5% pyridine): 430 (5.10), 535 (5.09), 636 (4.14), 695 (4.16), 821 (4.30), 910 (4.67). *m/z* (MALDI TOF MS+) 1777.9 ($C_{116}H_{110}N_8O_2Zn_2$; $[M]^+$ requires 1778.9). IR (KBr disc): 1647 cm^{-1}.

Porphyrin diol 11. Terephthalate-bridged porphyrin dimer **3b** (60 mg, 32 μmol) was placed in a round bottom flask and dried under vacuum for 1 h. The porphyrin was dissolved in THF (5 mL) and degassed by freeze-pump-thaw cycles. The solution was cooled to –78 °C. Phenyllithium in dibutylether (2.0 mL, 1.8 M, 3.6 mmol) was added dropwise to the solution with stirring. The red mixture turned greenish blue immediately following addition of phenyllithium. The solution was slowly allowed to warm room temperature with stirring. After 20 h, the reaction was quenched by addition of brine (20 mL). The greenish solution turned dark red following addition of brine. The crude mixture was extracted with dichloromethane. During the reaction with phenyllithium, the central zinc seems to be partially replaced by lithium. Then, the residue was treated with saturate zinc(II) acetate in methanol (100 mg in 3 mL) to introduce central zinc. After removal of the solvent, the residue was passed through a silica-gel chromatography with dichloromethane as the eluent. The first red fraction was dissolved in dichloromethane and reprecipitated from methanol and 40–60 petroleum ether to yield porphyrin **11** as a purple solid (45 mg, 67%). ^{1}H NMR (500 MHz, $CDCl_3$ with 1 % pyridine-d_5): δ = 9.02 (d, J = 4.5 Hz, 4H; pyrrole-β), 8.96 (d, J = 4.5 Hz, 4H; pyrrole-β), 8.95 (d, J = 4.5 Hz, 4H; pyrrole-β), 8.92 (d, J = 4.5 Hz, 4H; pyrrole-β), 8.32–8.34 (m, 2H; *o*-Ph), 8.24 (t, 2Hz, 4H; *o*-Ar), 8.22 (s, 2H; bridging Ar), 8.18 (br s, 1H; *o*-Ph), 8.17 (br s, 1H; *o*-Ph), 8.07 (t, 2Hz, 4H; *o*-Ar), 7.88 (t, 2Hz, 4H; *p*-Ar), 7.74–7.79 (m, 6H; *m,p*-Ph), 6.97–6.99 (m, 8H; Ph), 6.87–6.88 (m, 12H; Ph), 1.74 (s, 2H; OH), 1.67 (s, 18H; *t*-Bu), 1.60 ppm (s, 18H; *t*-Bu). ^{13}C NMR (125 MHz, $CDCl_3$ with 1 % pyridine-d_5): δ = 150.6, 150.3, 150.0, 149.9, 148.6, 148.5, 146.1, 144.1, 142.9, 141.8, 139.8, 137.6, 134.3, 132.3, 132.2, 131.8, 131.2, 129.9, 129.8, 127.6, 127.5, 126.7, 126.5, 122.7, 121.3, 120.8, 118.1, 84.2, 67.7, 35.15, 35.08, 31.9, 31.8 ppm. λ_{max}/nm (logε) (benzene with 1% pyridine): 432 (5.90), 535 (6.00), 566 (4.71), 607 (4.45). *m/z* (MALDI TOF MS+) 2091.9 ($C_{140}H_{134}N_8O_2Zn_2$; $[M]^+$ requires 2091.9).

Porphyrin Dimer 6. A solution of porphyrin dimer **11** (45 mg, 22 μmol) in dichloromethane (6 mL) was treated with boron trifluoride diethyl etherate (0.6 mL) with stirring at room temperature. The red solution turned brown immediately. After 10 min, methanol (10 mL) and degassed saturated aqueous sodium hydrogen carbonate (20 mL) was added to quench the reaction. The solution turned green immediately after addition of saturated aqueous sodium hydrogen carbonate. The organic layer was separated and then treated with saturate zinc(II) acetate in methanol (100 mg in 3 mL) after removal of the solvent. The solution was washed with saturated aqueous sodium hydrogen carbonate, and the organic layer was separated. The target material was eluted from a silica-gel chromatography as the first green fraction with dichloromethane as the eluent. The residue was passed through a Nylon membrane filter (pore diameter 0.2 μm) to remove any dust or silica particles. The porphyrin was precipitated by layer addition of the solution in dissolved in dichloromethane from methanol, and then from 40–60 petroleum ether to yield porphyrin dimer **6** as a dark green solid (32 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$ with 1 % pyridine-d_5): δ = 8.83 (d, ^3J = 4.5 Hz, 2H; pyrrole-β), 8.79 (d, ^3J = 4.5 Hz, 2H; pyrrole-β), 8.75 (d, ^3J = 4.5 Hz, 2H; pyrrole-β), 8.71 (d, ^3J = 4.5 Hz, 2H; pyrrole-β), 8.70 (d, ^3J = 4.5 Hz, 2H; pyrrole-β), 8.67 (s, 2H; bridging Ph), 8.64 (s, 2H; pyrrole-β), 8.50 (d, ^3J = 4.5 Hz, 2H; pyrrole-β), 8.14–8.16 (m, 4H; *o*-Ph), 8.13 (d, J = 1.9 Hz, 4H, *o*-Ar), 7.99 (d, J = 1.9 Hz, 4H; *o*-Ar), 7.79 (t, J = 1.9 Hz, 2H; *p*-Ar), 7.72 (t, J = 1.9 Hz, 2H; *p*-Ar), 7.69–7.65 (m, 6H; *m,p*-Ph), 7.59 (br d, J = 7.0 Hz, 8H; tetrahedral Ph), 7.81–7.13 (m, 12H; tetrahedral Ph), 1.59 (s, 36H; *t*-Bu), 1.54 ppm (s, 36H; *t*-Bu). ^{13}C NMR (125 MHz, $CDCl_3$ with 1 % pyridine-d_5): δ = 149.7, 148.8, 148.4, 148.2, 148.1, 147.8, 146.9, 146.8, 143.6, 142.4, 142.3, 141.9, 141.6, 135.9, 134.3, 131.8, 131.7, 131.6, 131.4, 130.9, 130.3, 130.2, 130.0, 128.6, 127.9, 127.0, 126.2, 123.9, 122.0, 121.0, 120.4, 120.2, 111.7, 59.2, 35.02, 35.01, 31.8 ppm. λ_{max}/nm (logε) (benzene with 1% pyridine): 429 (5.22), 451 (5.02), 467 (4.98),

500 (5.51), 581 (4.31), 657 (4.41), 716 (5.05). *m/z* (MALDI TOF MS+) 2056.6 ($C_{140}H_{130}N_8Zn_2$; $[M]^+$ requires 2055.9).

Porphyrin Dimer 12. Bis-keto porphyrin dimer **5** (15 mg, 8.4 μmol) and malononitrile (0.60 g, 9.0 mmol) were dissolved in dichloromethane (10 mL). The solution was cooled to 0 °C and then $TiCl_4$ (0.30 mL, 2.7 mmol) was added with stirring. The dark brown solution turned black. After stirring the mixture for 60 min. at 0 °C, pyridine (1.0 mL, 12 mmol) was added. The mixture was stirred for 20 h at 20 °C, then the solvent was removed under reduced pressure. The crude product was purified by chromatography (silica, dichloromethane, 1% methanol) to yield compound **12** as a black solid (3.5 mg, 21%). ^{1}H NMR (500 MHz, $CDCl_3$ with 1% pyridine-d_5): δ = 11.0 (s, 2H, bridging Ar), 10.1 (d, J = 4.55 Hz, 2H; β), 9.11 (d, J = 4.55 Hz, 2H; β), 8.66 (d, J = 4.60 Hz, 2H; β), 8.62 (d, J = 4.50 Hz, 2H; β), 8.60 (d, J = 4.60 Hz, 2H; β), 8.58 (d, J = 2.35 Hz, 6H, β and *o*-Ar), 8.21 (d, J = 1.6 Hz, 4H, *o*-Ar), 8.13 (dd, J = 6.2, 1.4 Hz, 4H; *o*-Ph), 8.07 (d, J = 1.25 Hz, 4H; *o*-Ph), 7.78 (d, J = 1.3 Hz, 4H; *o*-Ph), 7.71–7.70 (m, 8H; *m,p*-Ph and *o*-Ph), 7.66 (s, 2H; *p*-Ph), 5.83 (brs, 4H; NH_2), 1.57 (s, 36H; *t*-Bu), 1.51 ppm (s, 36H; *t*-Bu). ^{13}C NMR (125 MHz, $CDCl_3$ with 1% pyridine-d_5): δ = 154.1, 153.5, 150.7, 150.4, 148.6, 142.9, 142.7, 141.8, 141.6, 141.1, 139.7, 136.2, 136.1, 134.8, 134.1, 133.8, 132.2, 131.8, 131.4, 130.8, 129.8, 128.5, 127.8, 127.4, 126.5, 125.4, 123.8, 121.9, 120.9, 118.9, 106.6, 92.6, 88.5, 67.9, 35.2, 35.0, 31.8, 31.6 ppm. λ_{max}/nm (log ε) (benzene with 5% pyridine): 458 (5.28), 618 (4.20), 680 (4.30), 745 (4.28), 825 (4.74), 931 (3.61). *m/z* (MALDI TOF MS+) 1952.79 ($C_{126}H_{112}N_{14}Zn_2$; $[M]^+$ requires 1953.0).

4. NMR Spectra

4.1. *^{1}H and ^{13}C NMR Spectra of 9a*

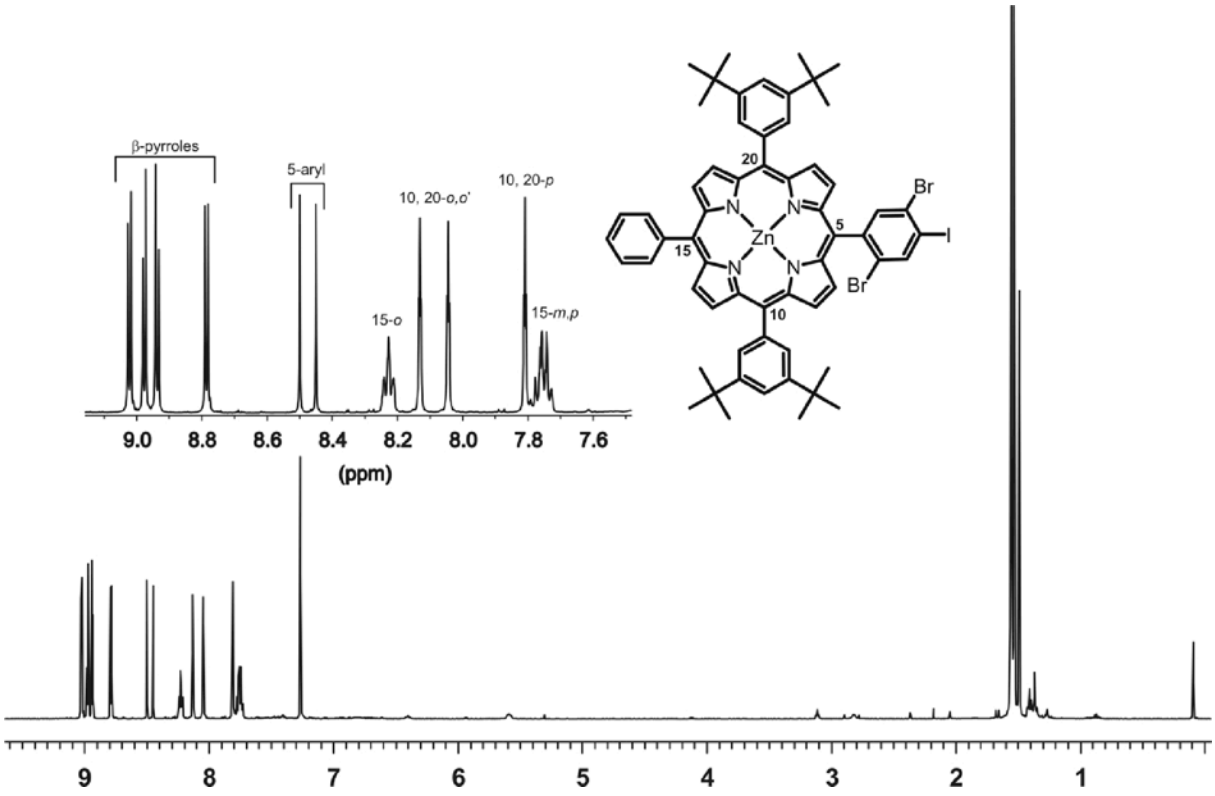

Figure S1. ^{1}H NMR spectrum of **9a** (298 K, $CDCl_3$, 500 MHz).

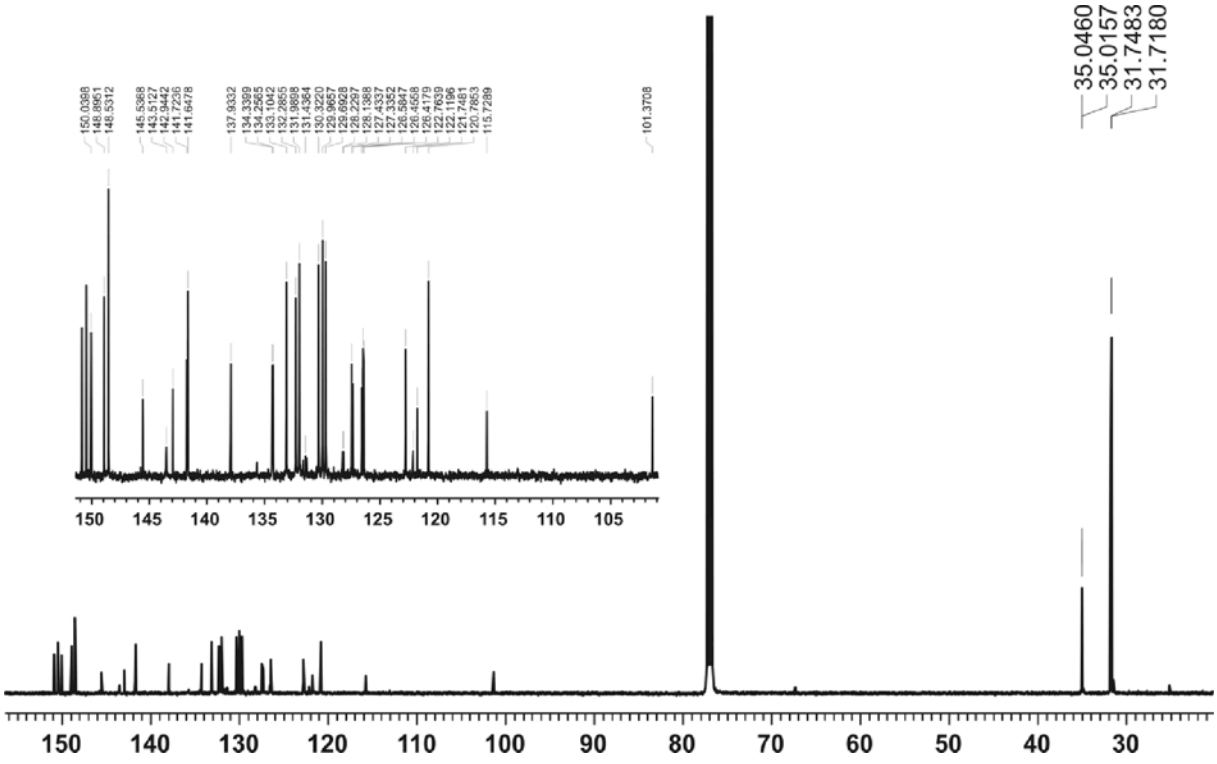

Figure S2. ^{13}C NMR spectrum of **9a** (298 K, $CDCl_3$, 125 MHz).

4.2. *^{1}H and ^{13}C NMR Spectra of 9b*

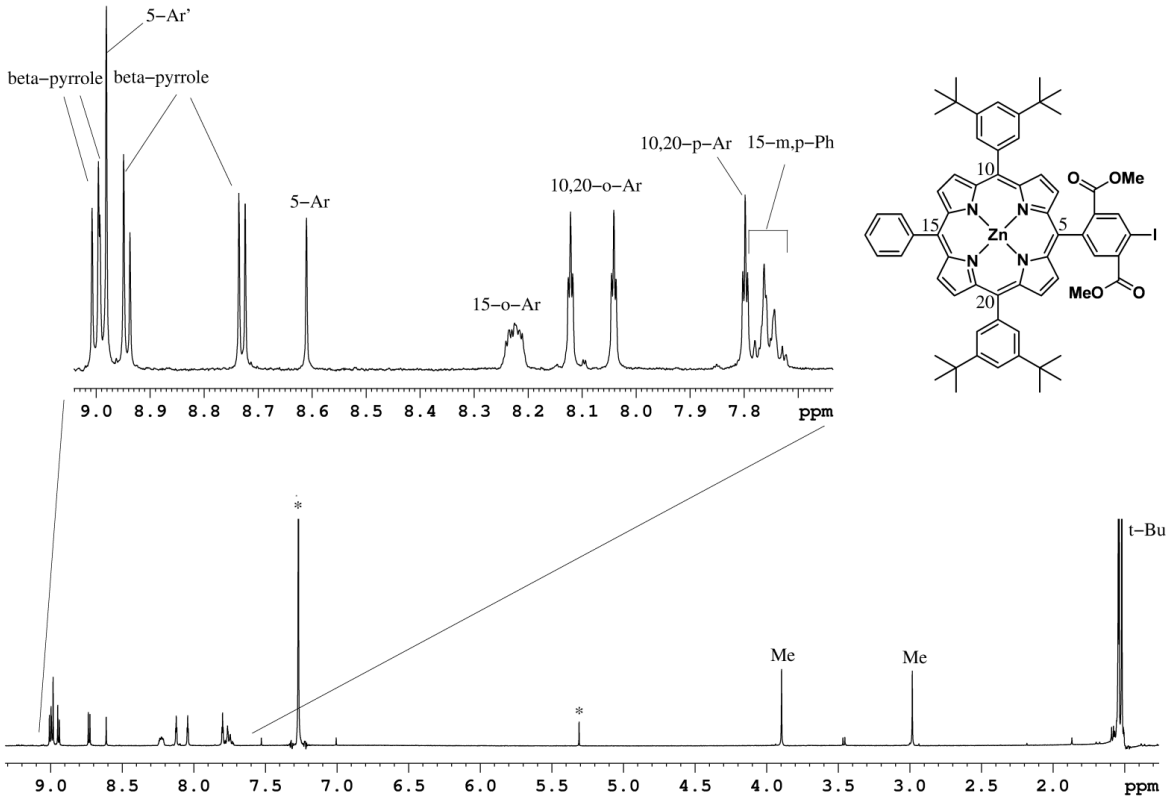

Figure S3. ^{1}H NMR spectrum of **9b** (298 K, $CDCl_3$, 500 MHz).

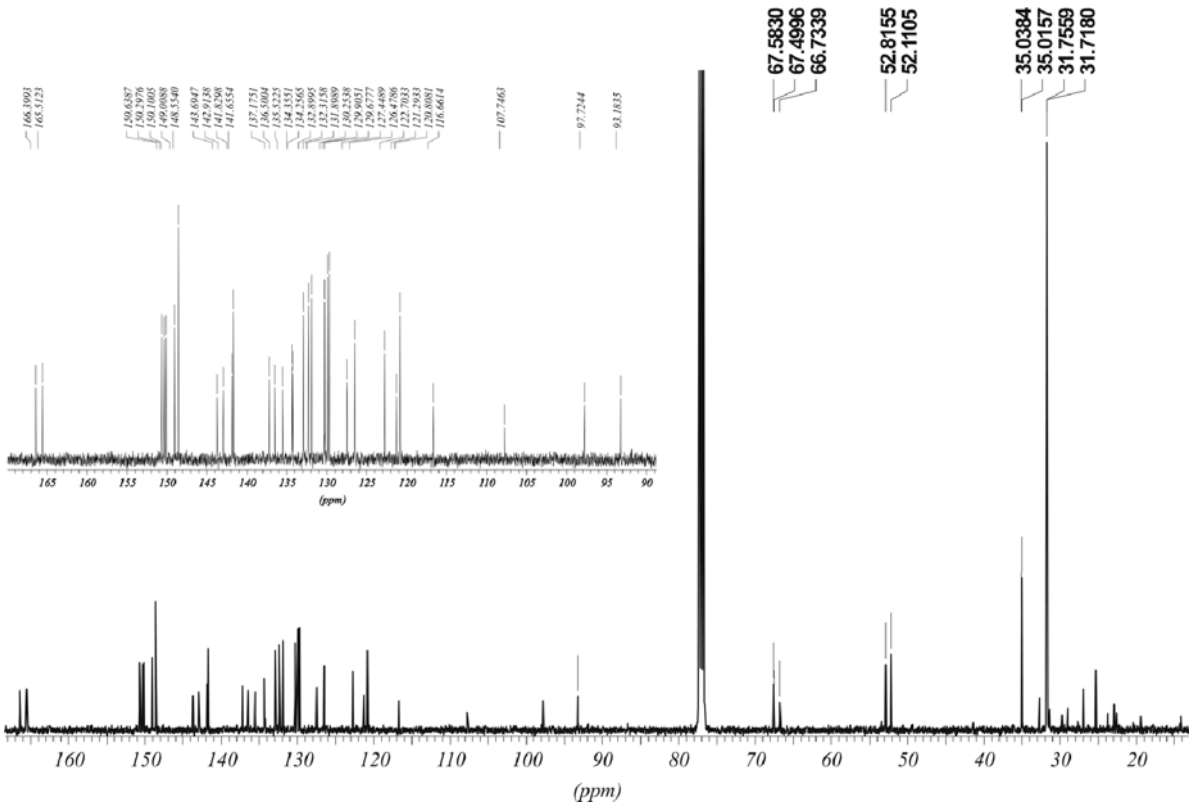

Figure S4. ^{13}C NMR spectrum of **9b** (298 K, $CDCl_3$, 125 MHz).

4.3. *^{1}H and ^{13}C NMR Spectra of 3a*

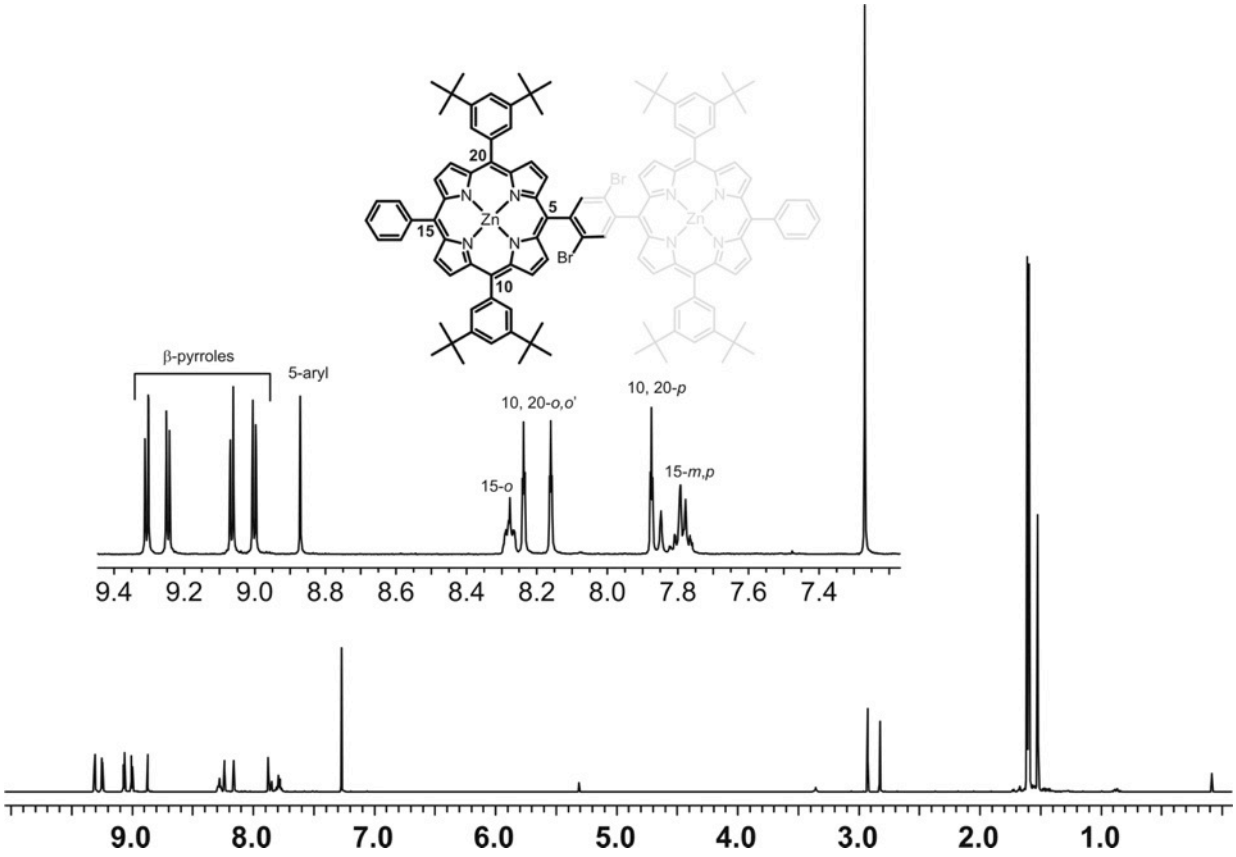

Figure S5. ^{1}H NMR spectra of **3a** (298 K, $CDCl_3$, 500 MHz).

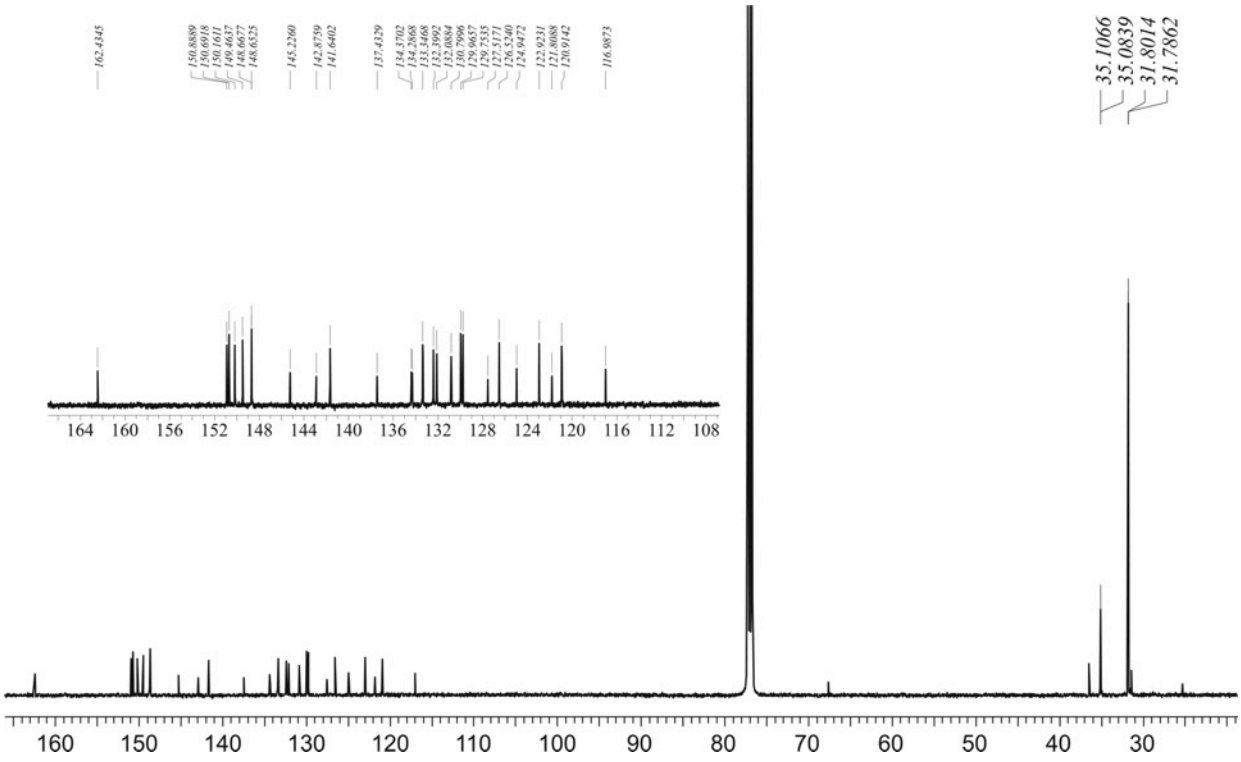

Figure S6. ^{13}C NMR spectrum of **3a** (298 K, $CDCl_3$, 125 MHz).

4.4. *[1]H and [13]C NMR Spectra of 3b*

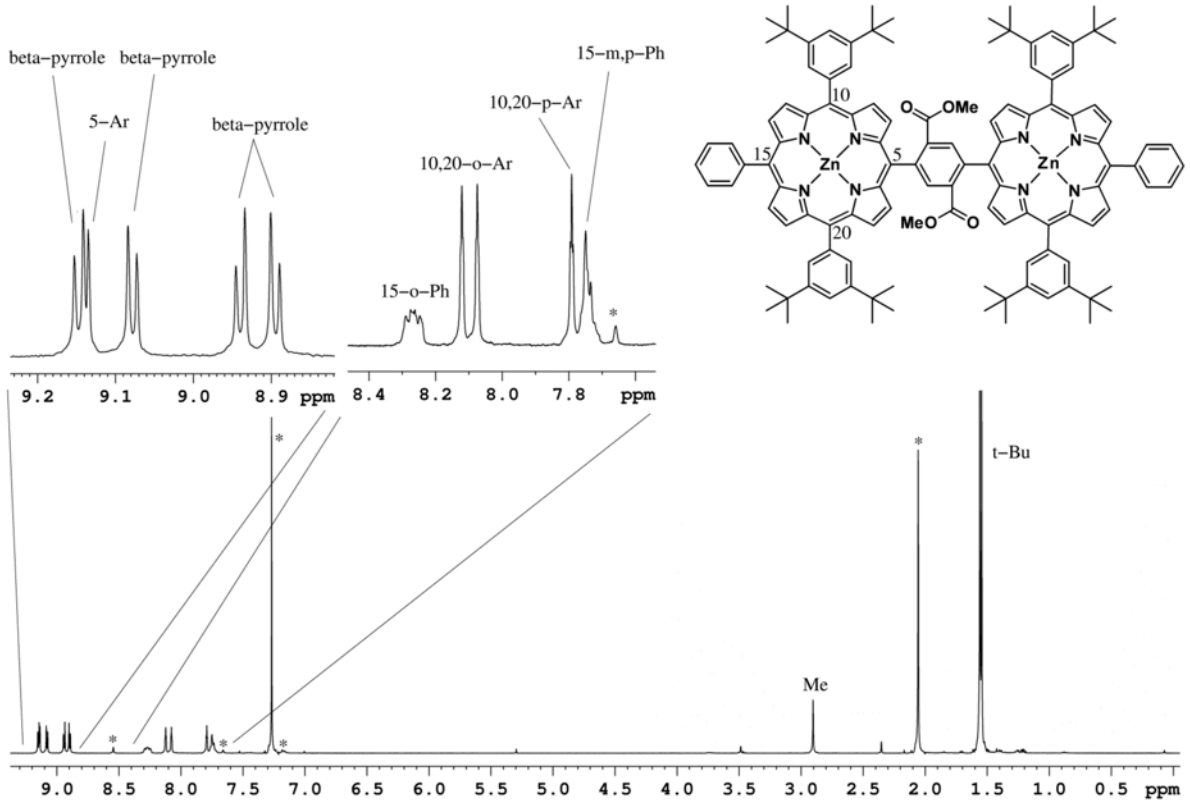

Figure S7. [1]H NMR spectrum of **3b** (298 K, $CDCl_3$, with 5% pyridine-d_5, 400 MHz). Asterisk indicates residual solvents.

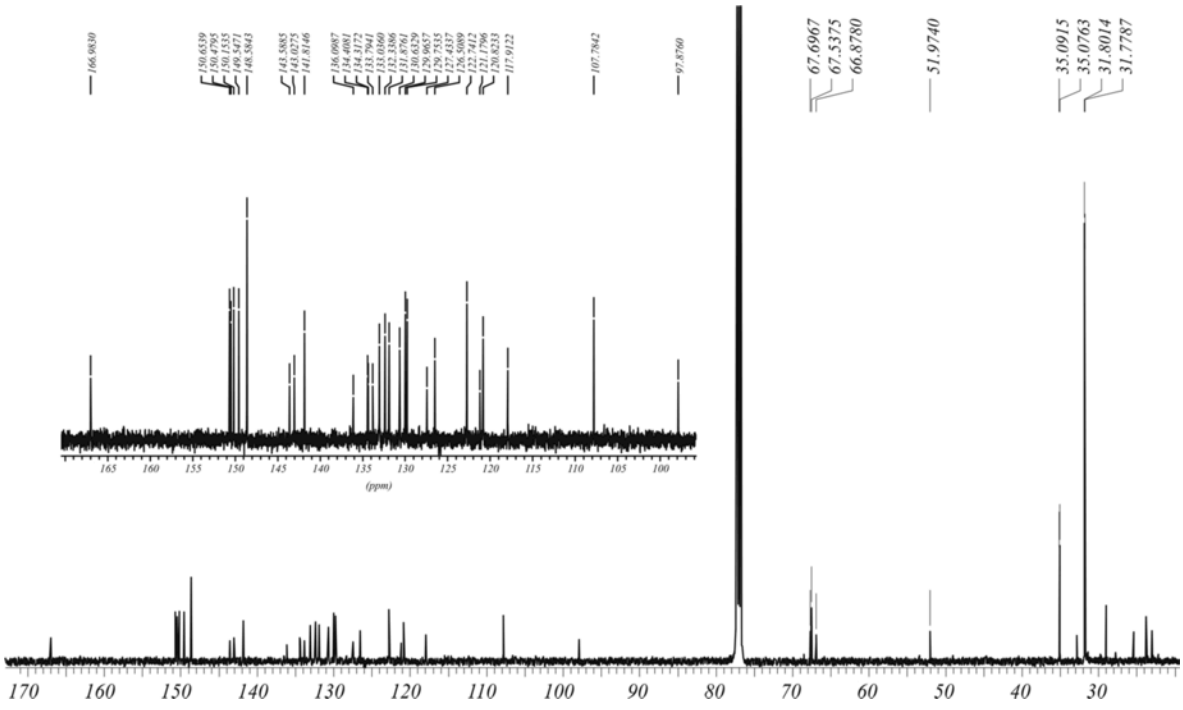

Figure S8. [13]C NMR spectrum of **3b** (298 K, $CDCl_3$, 125 MHz).

4.5. *NMR Spectra of Partially-Fused Dimer 10*

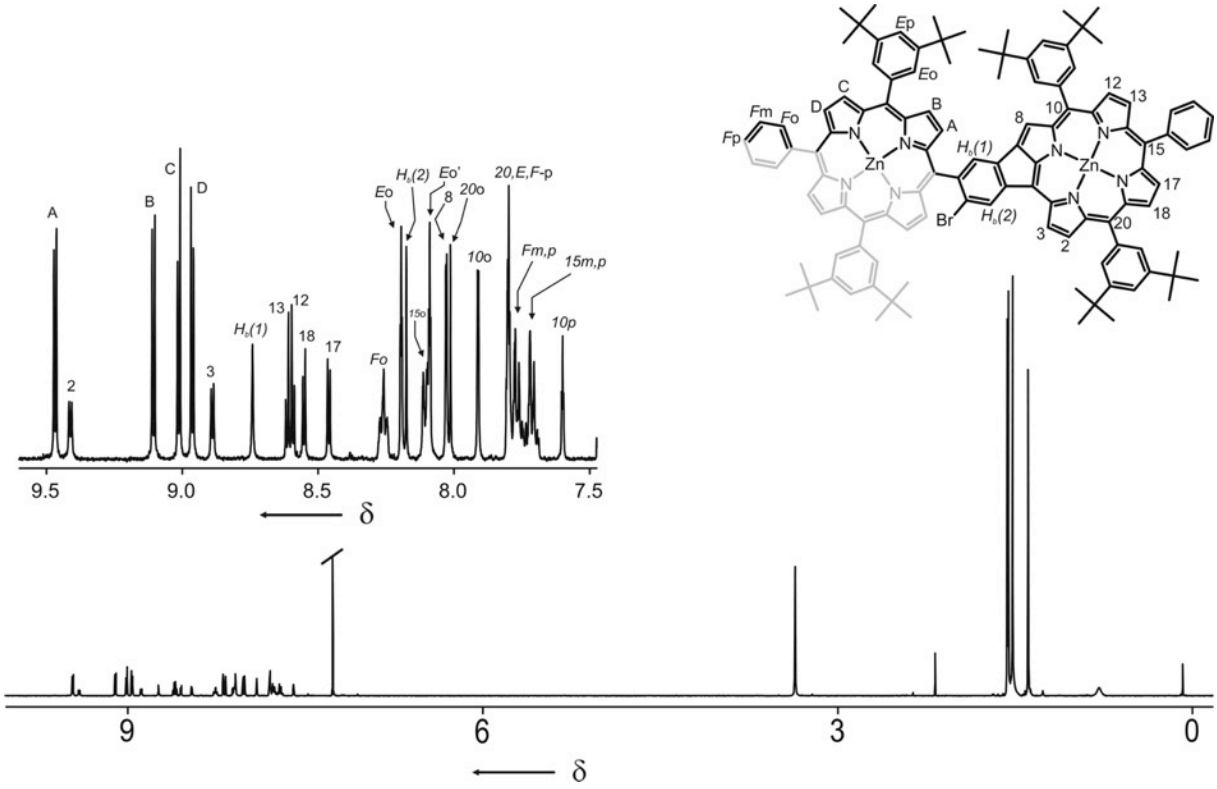

Figure S9. ^{1}H NMR spectrum of **10** (500 MHz, 298 K, $CDCl_3$).

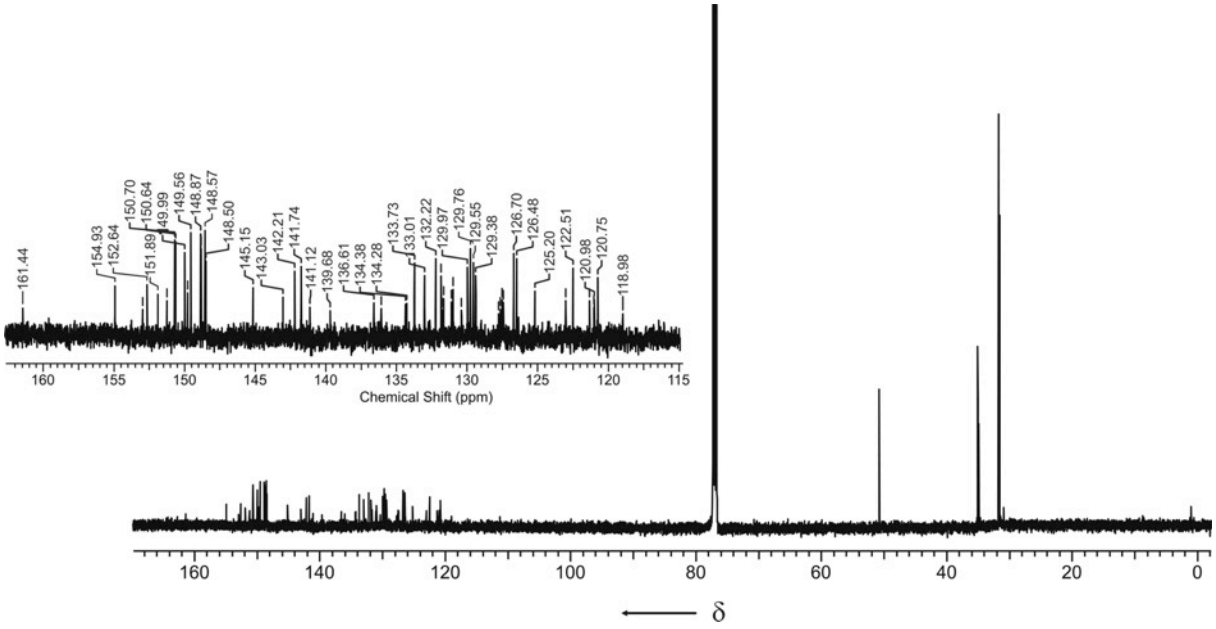

Figure S10. ^{13}C NMR spectrum of **10** (125 MHz, 298 K, $CDCl_3$).

4.6. *^{1}H NMR Spectra of Planarized Porphyrin Dimers 4 and 5*

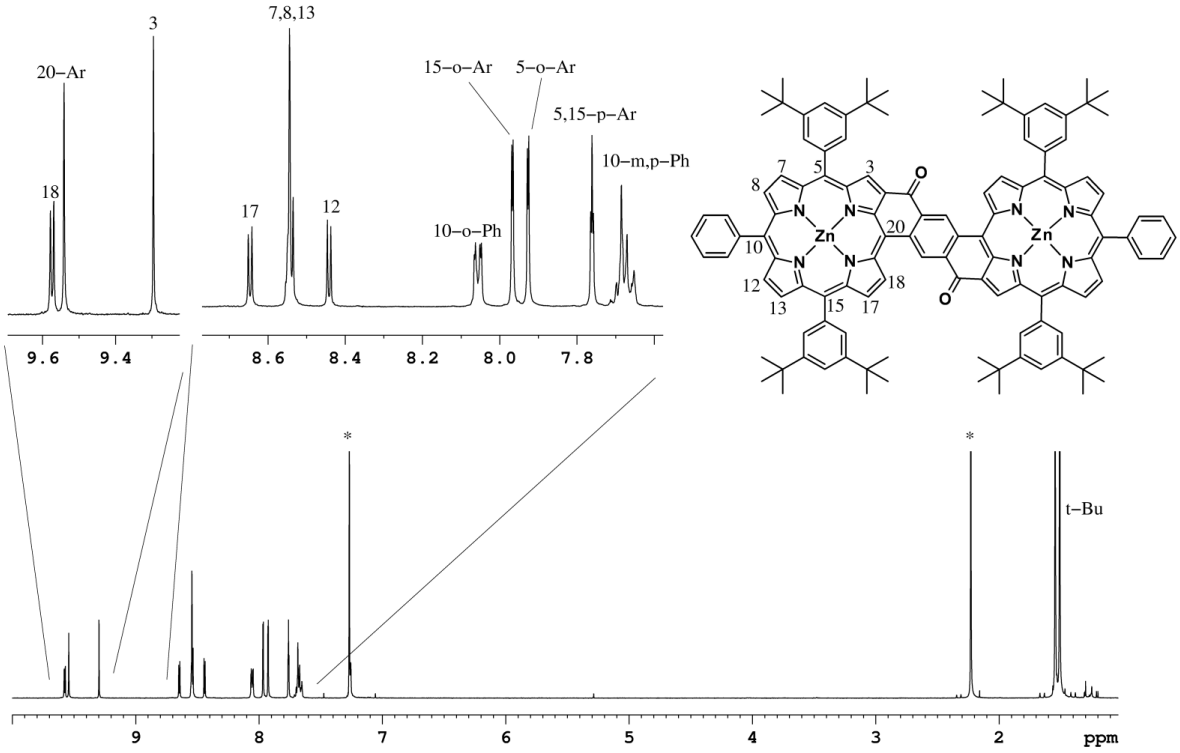

Figure S11. ^{1}H NMR spectrum of dimer **5** ($CDCl_3$ with 1% pyridine-d_5, 298 K, 500 MHz). Asterisk indicates residual solvent and water.

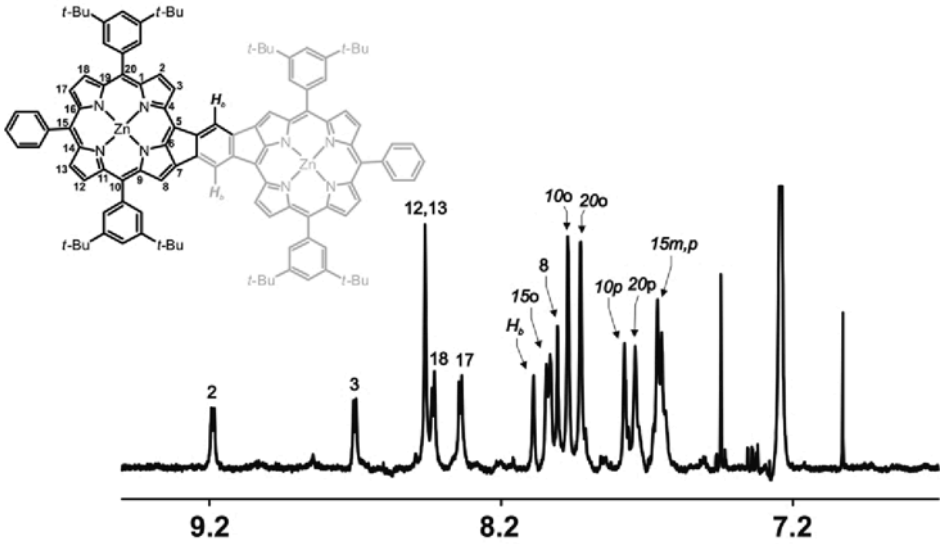

Figure S12. ^{1}H NMR spectrum of **4** ($CDCl_3$, 298 K, 500 MHz).

4.7. ^{13}C NMR Spectrum of Porphyrin Dimer 5

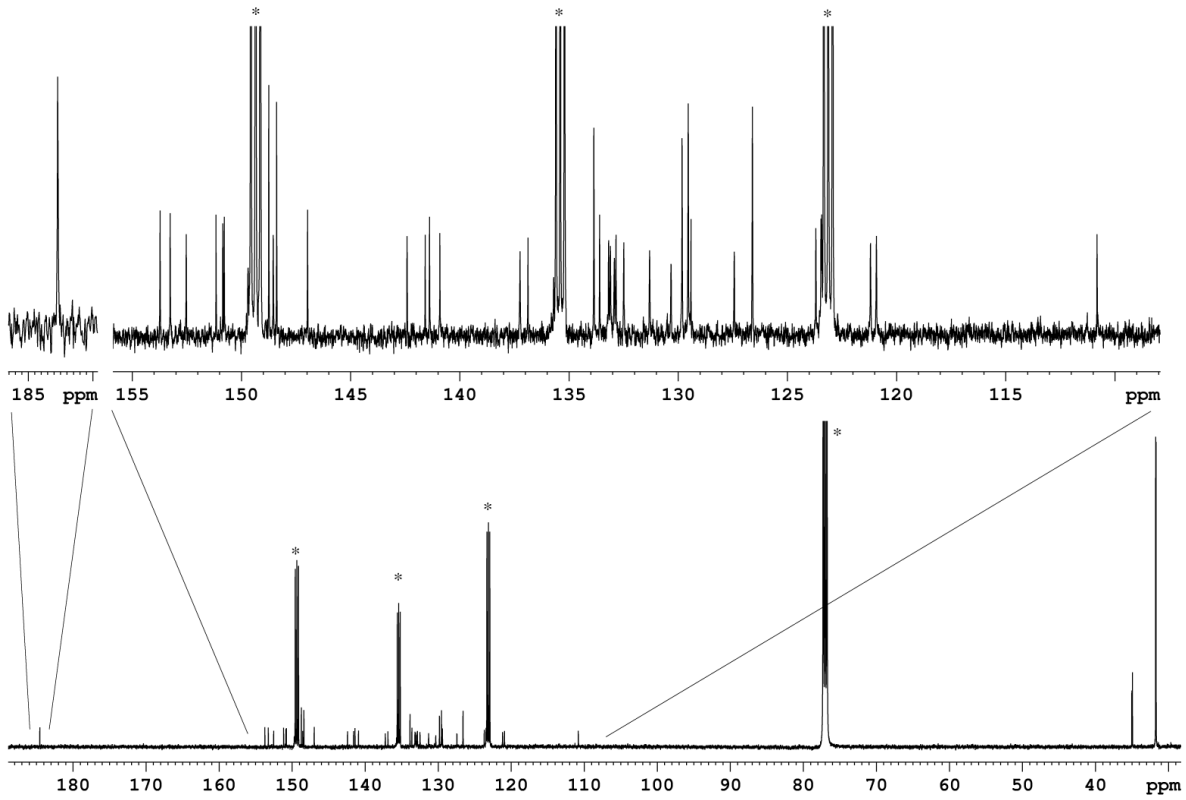

Figure S13. ^{13}C NMR spectrum of **5** ($CDCl_3$ with 1% pyridine-d_5, 298 K, 125 MHz). Asterisk indicates solvent.

4.8. *^{1}H–^{1}H COSY NMR Spectrum of Porphyrin Dimer 5*

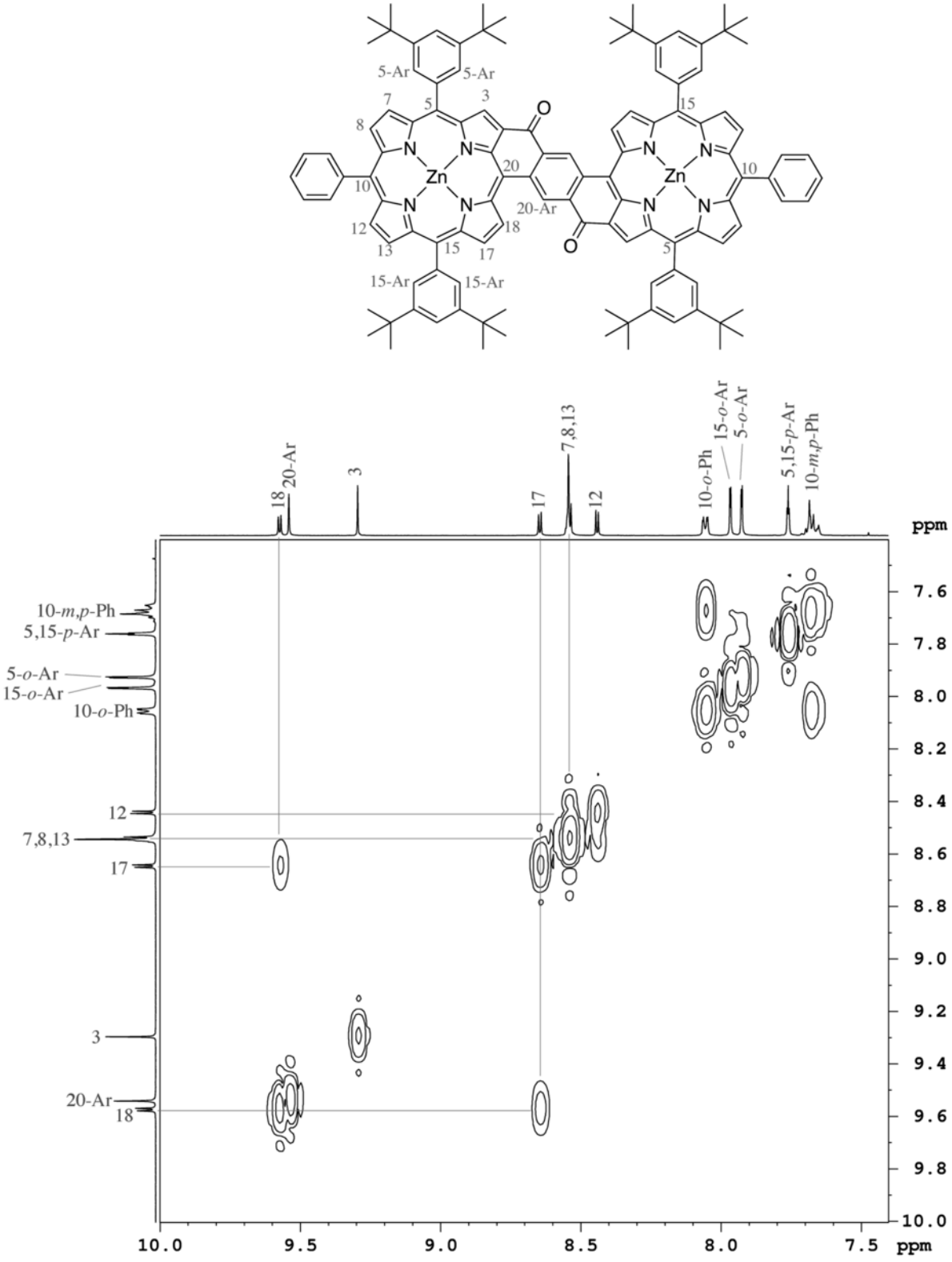

Figure S14. ^{1}H–^{1}H COSY NMR spectrum of **5** ($CDCl_3$ with 1% pyridine-d_5, 298 K).

4.9 ^{1}H–^{1}H ROESY NMR Spectrum of Porphyrin Dimer 5

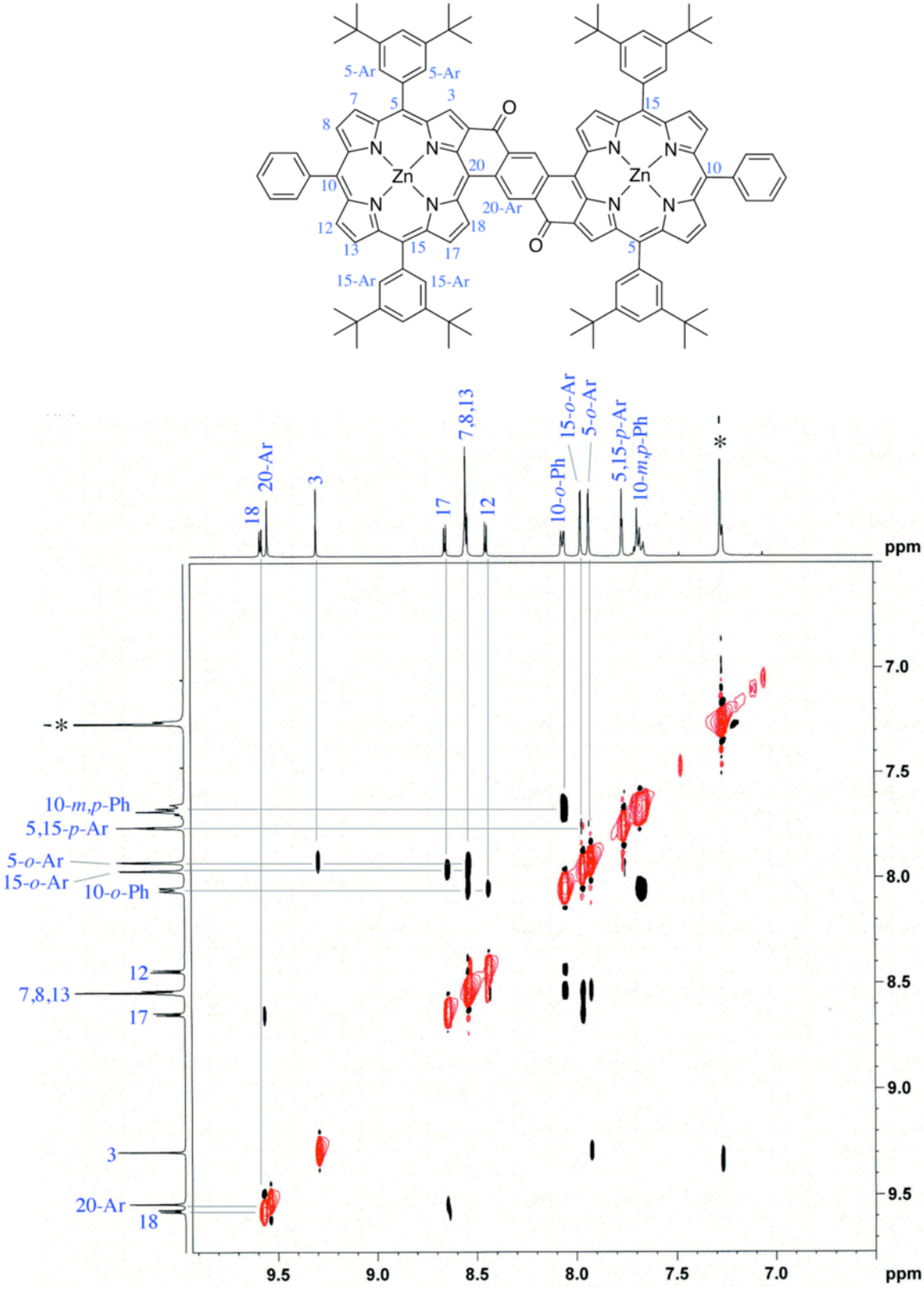

Figure S15. ^{1}H–^{1}H ROESY NMR spectrum of **5** ($CDCl_3$ with 1% pyridine-d_5, 298 K). Asterisk indicates residual solvent.

4.10. *^{1}H–^{13}C HSQC NMR Spectrum of Porphyrin Dimer 5*

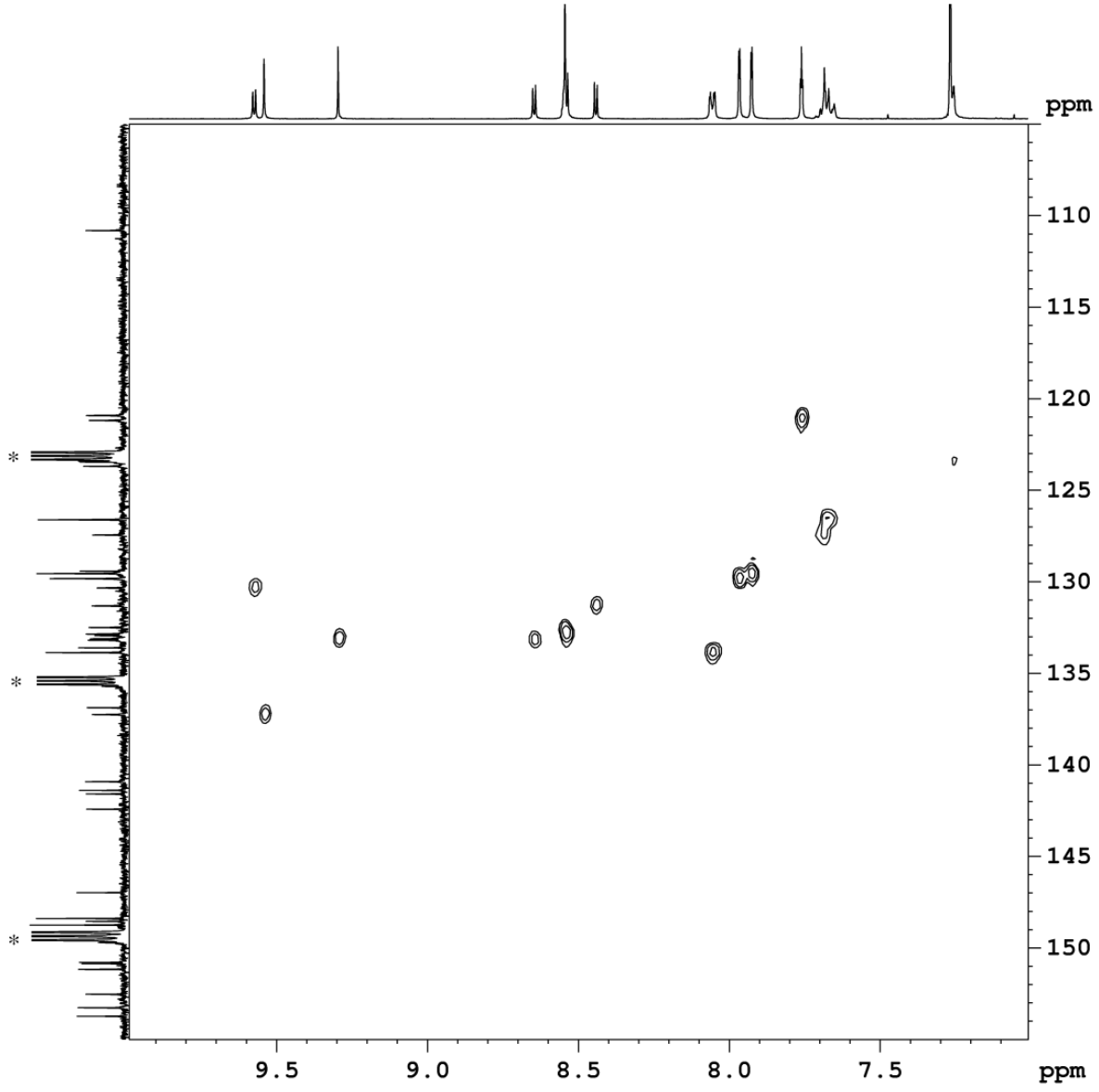

Figure S16. ^{1}H–^{13}C HSQC NMR spectrum of **5** ($CDCl_3$ with 1% pyridine-d_5, 298 K). Asterisk indicates solvent.

4.11. *FT-IR Spectra of Porphyrin Dimers 3b and 5*

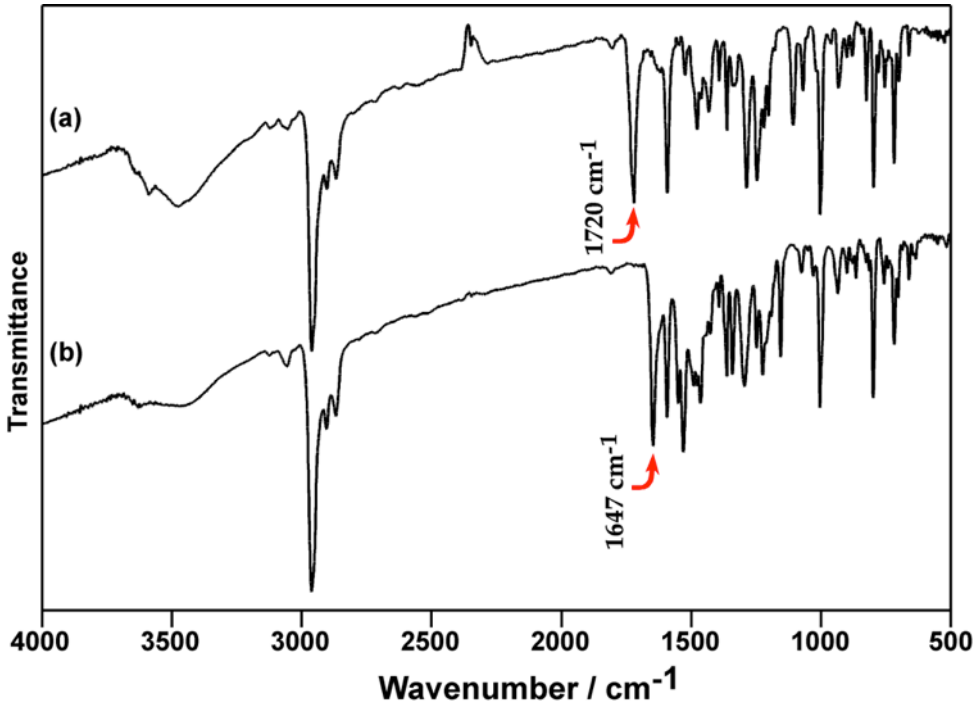

Figure S17. FT-IR spectra of porphyrin dimers **3b** (a) and **5** (b) in KBr disks. The signals due to the C=O stretch of the ester and ketone groups are indicated by red arrows.

4.12. *^{1}H and ^{13}C NMR Spectra of Porphyrin Dimer 11*

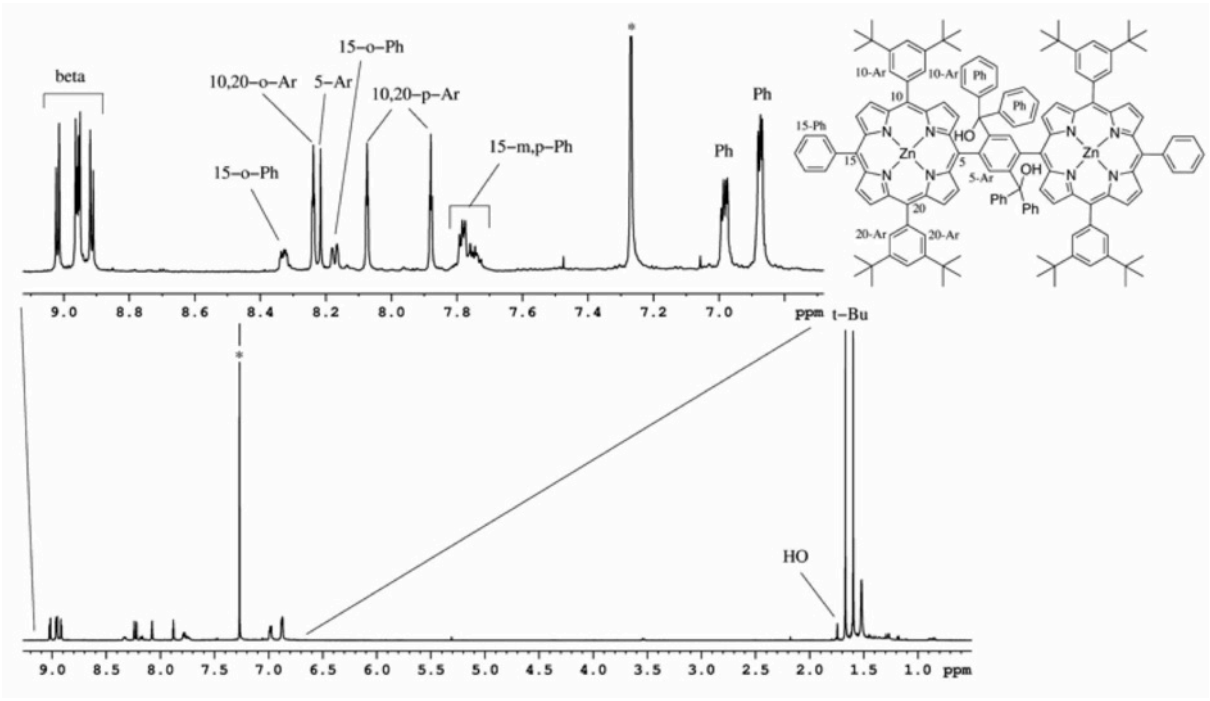

Figure S18. ^{1}H NMR spectrum of **11** (500 MHz, 298 K, $CDCl_3$). Asterisk indicates residual solvent.

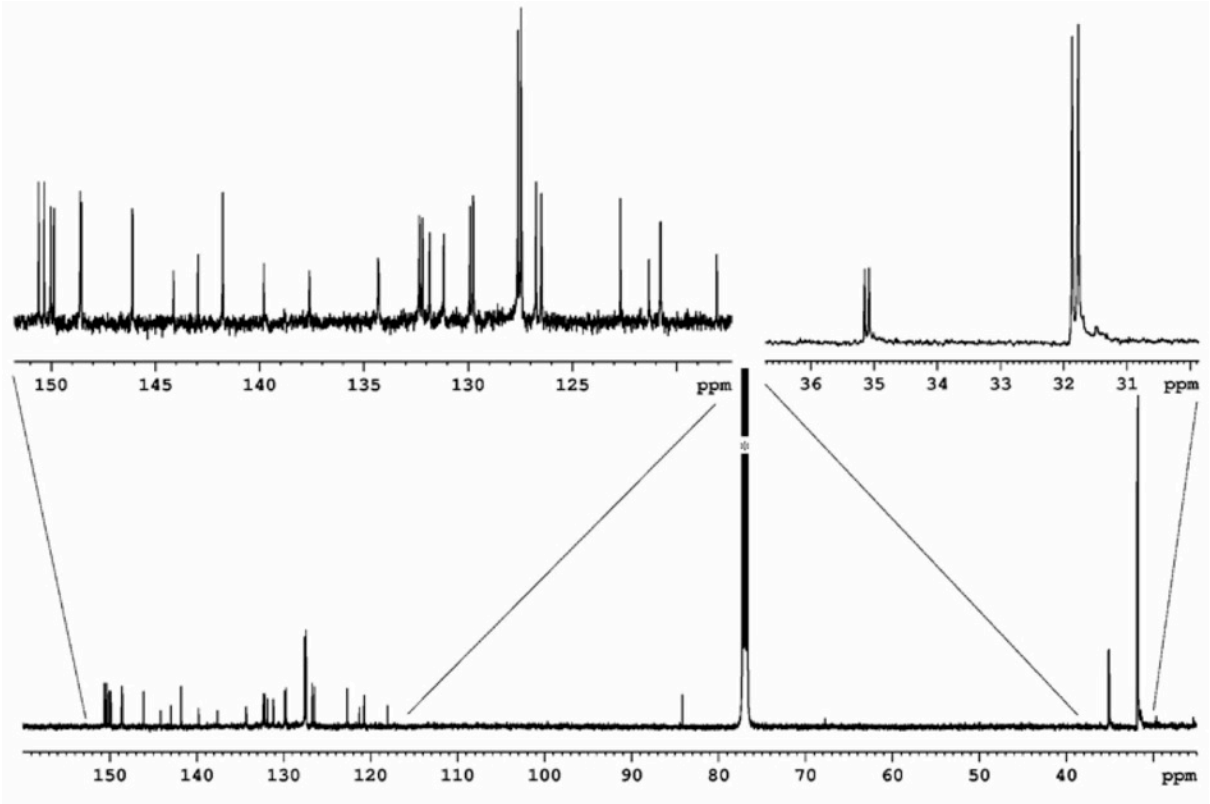

Figure S19. ^{13}C NMR spectrum of **11** (125 MHz, 298 K, $CDCl_3$). Asterisk indicates solvent.

4.13. *^{1}H and ^{13}C NMR Spectra of Porphyrin Dimer 6*

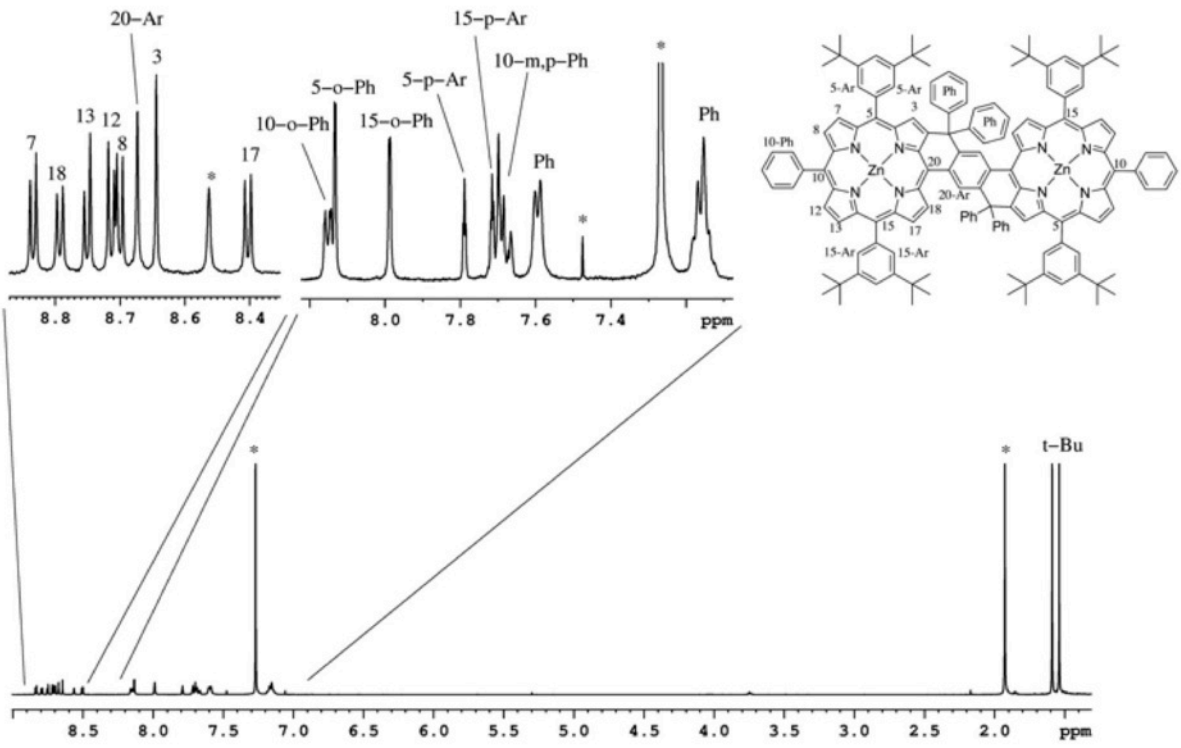

Figure S20. ^{1}H NMR spectrum of **6** (500 MHz, 298 K, $CDCl_3$ with 1% pyridine-d_5). Asterisk indicates residual solvent and water.

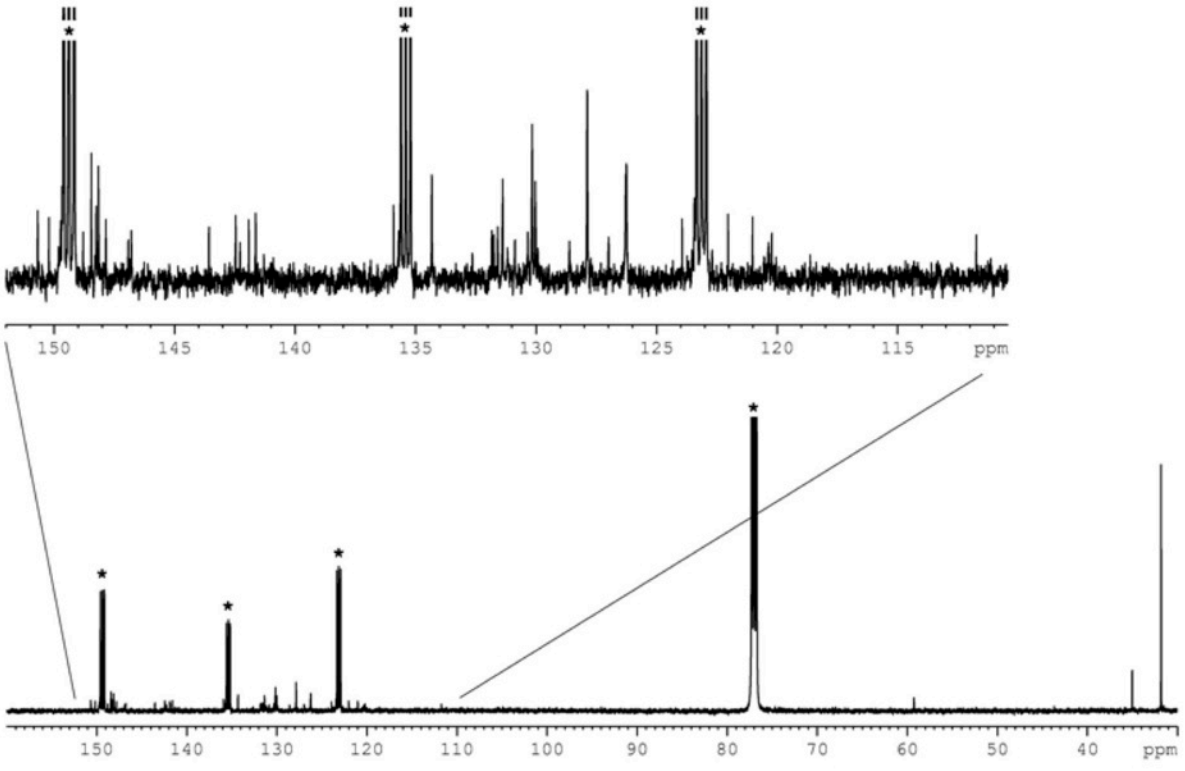

Figure S21. ^{13}C NMR spectrum of **6** (125 MHz, 298 K, $CDCl_3$ with 1% pyridine-d_5). Asterisk indicates solvent.

4.14. *^{1}H–^{1}H COSY NMR Spectrum of Porphyrin Dimer 6*

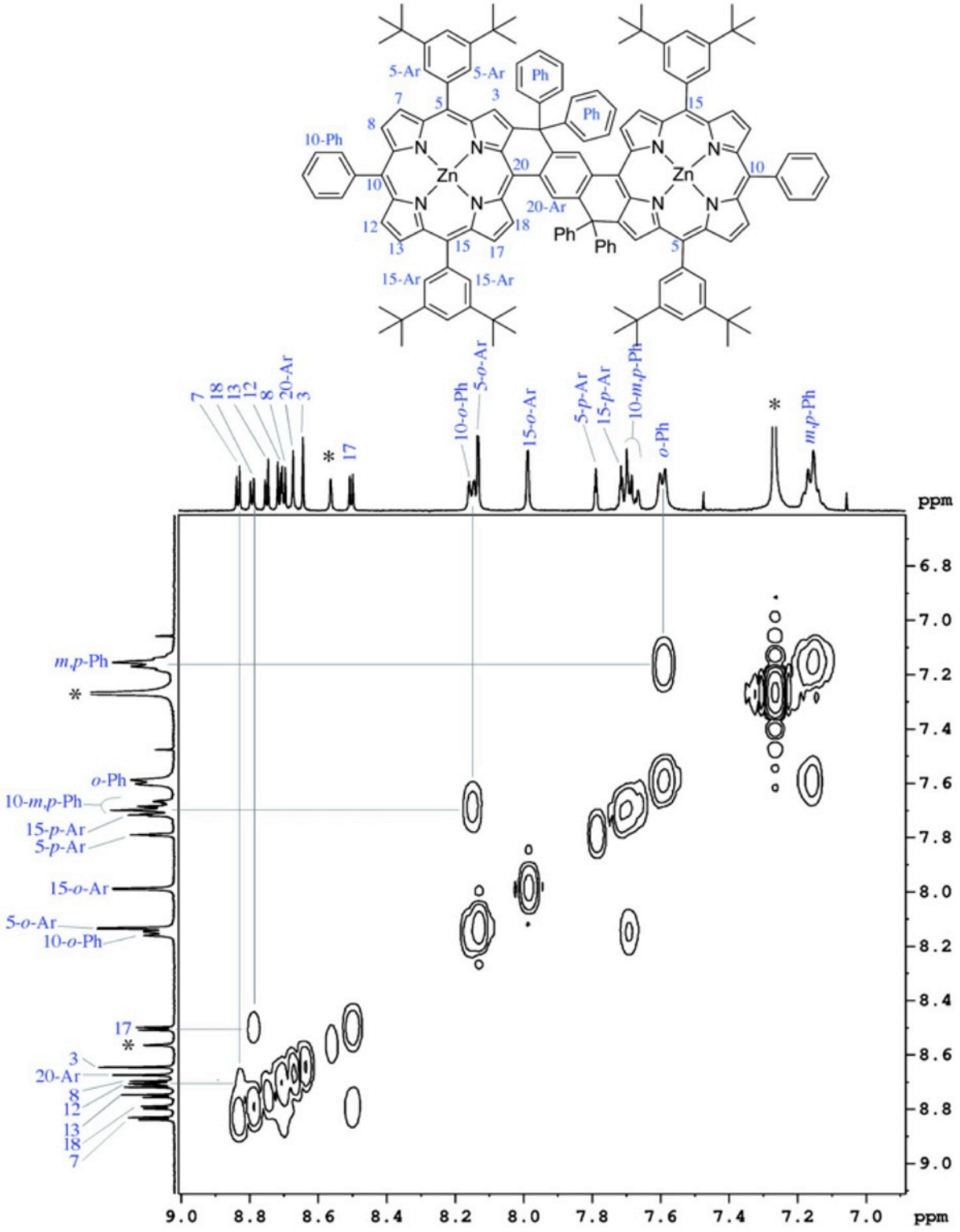

Figure S22. ^{1}H–^{1}H COSY NMR spectrum of **6** (298 K, $CDCl_3$ with 1% pyridine-d_5). Asterisk indicates residual solvent and water.

4.15. *^{1}H–^{1}H ROESY NMR Spectrum of Porphyrin Dimer 6*

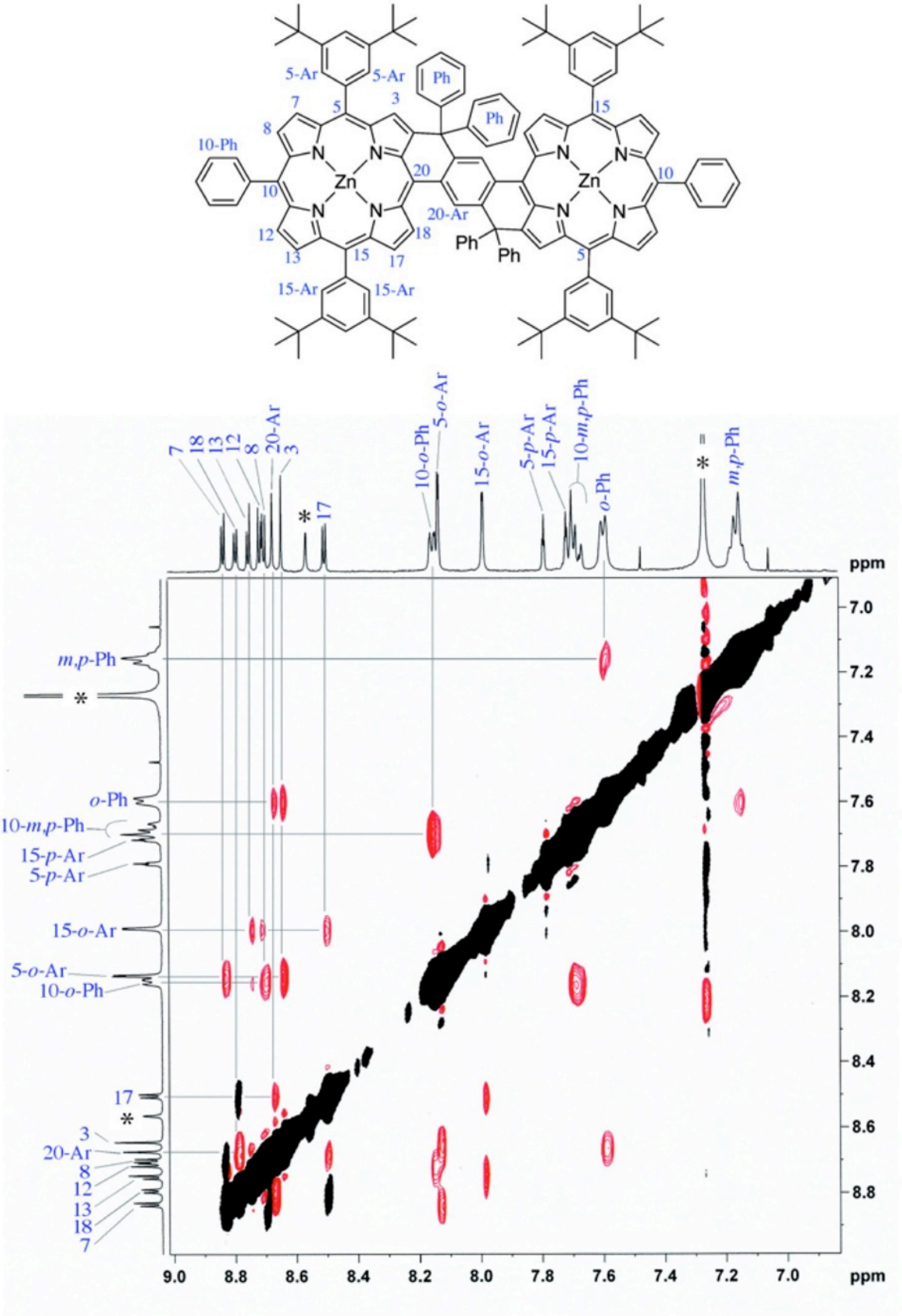

Figure S23. ^{1}H–^{1}H ROESY NMR spectrum of **6** (298 K, $CDCl_3$ with 1% pyridine-d_5). Asterisk indicates residual solvent and water.

4.16. *^{1}H–^{13}C HSQC NMR Spectrum of Porphyrin Dimer 6*

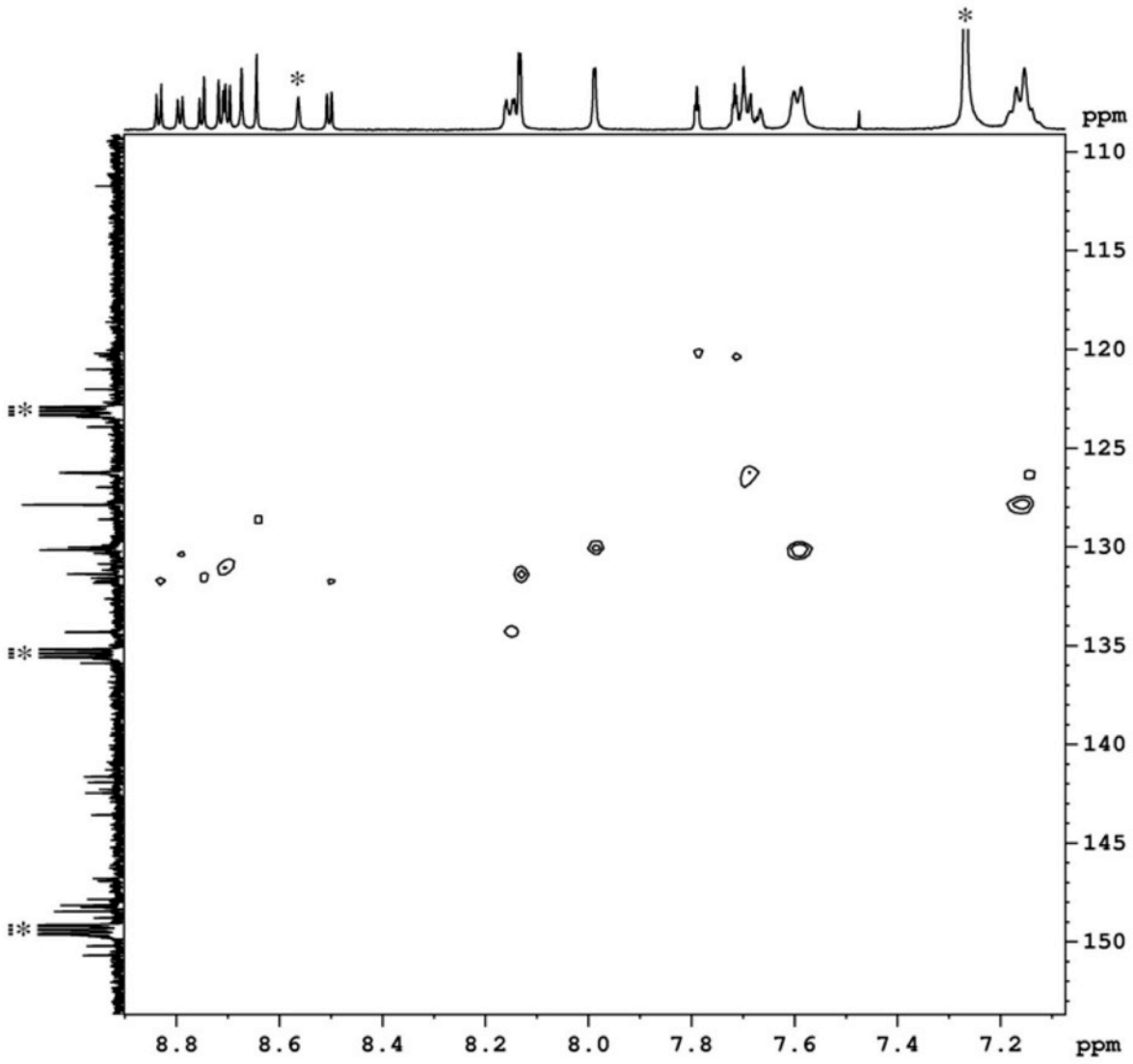

Figure S24. ^{1}H–^{13}C HSQY NMR spectrum of **6** (298 K, $CDCl_3$ with 1% pyridine-d_5). Asterisk indicates residual solvent and water.

5. Mass Spectra

5.1. *Mass Spectrum of 9b*

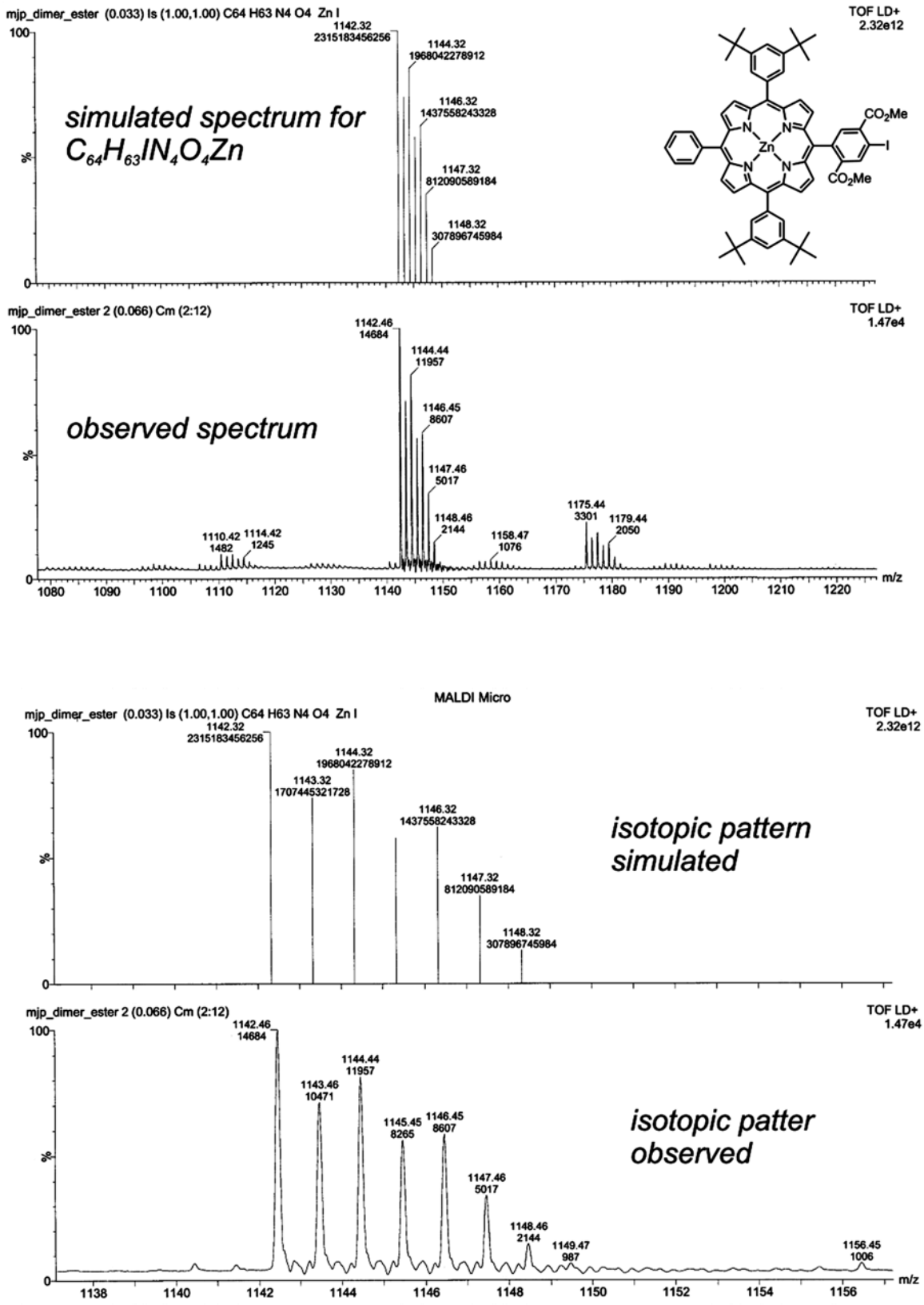

Figure S25. MALDI-TOF spectrum recorded for **9b**.

5.2. *Mass Spectrum for 3b*

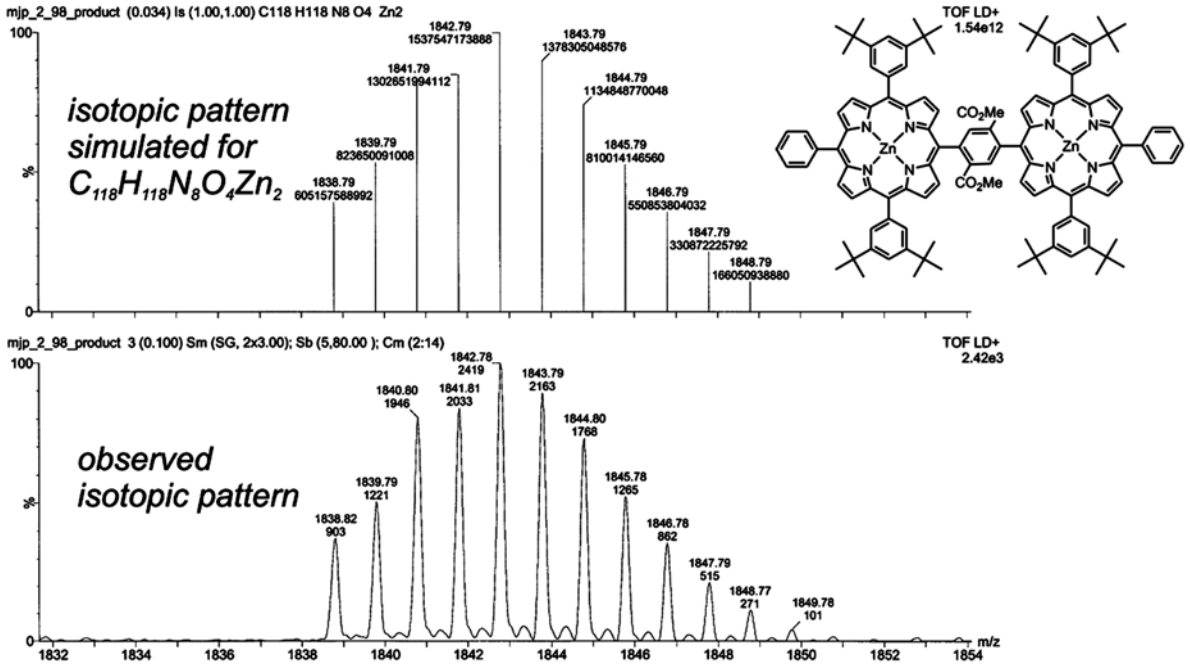

Figure S26. MALDI-TOF spectrum recorded for **3b**.

5.3. *Mass Spectrum for 5*

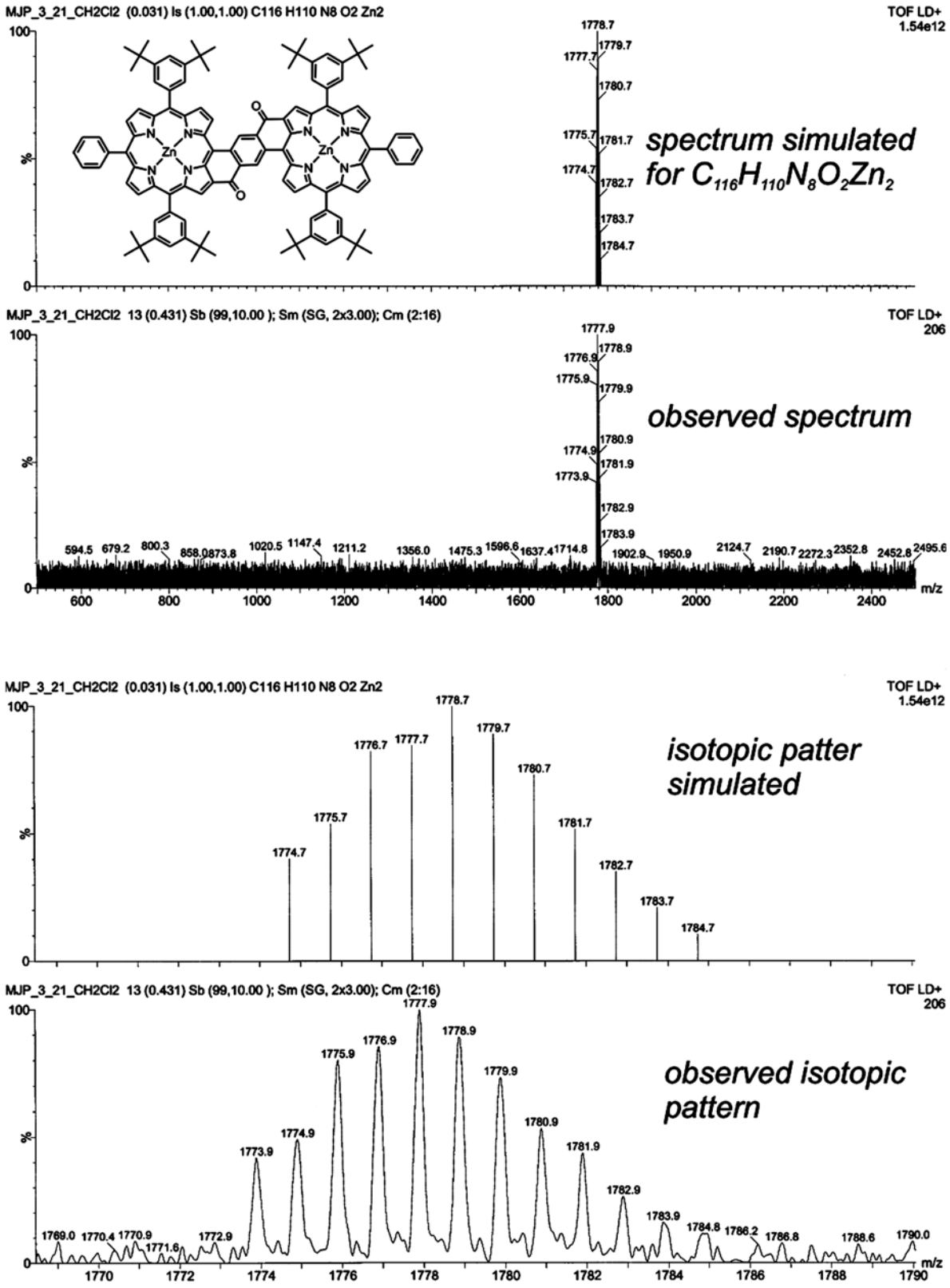

Figure S27. MALDI-TOF spectrum recorded for **5**.

5.4. *Mass Spectrum for 9a*

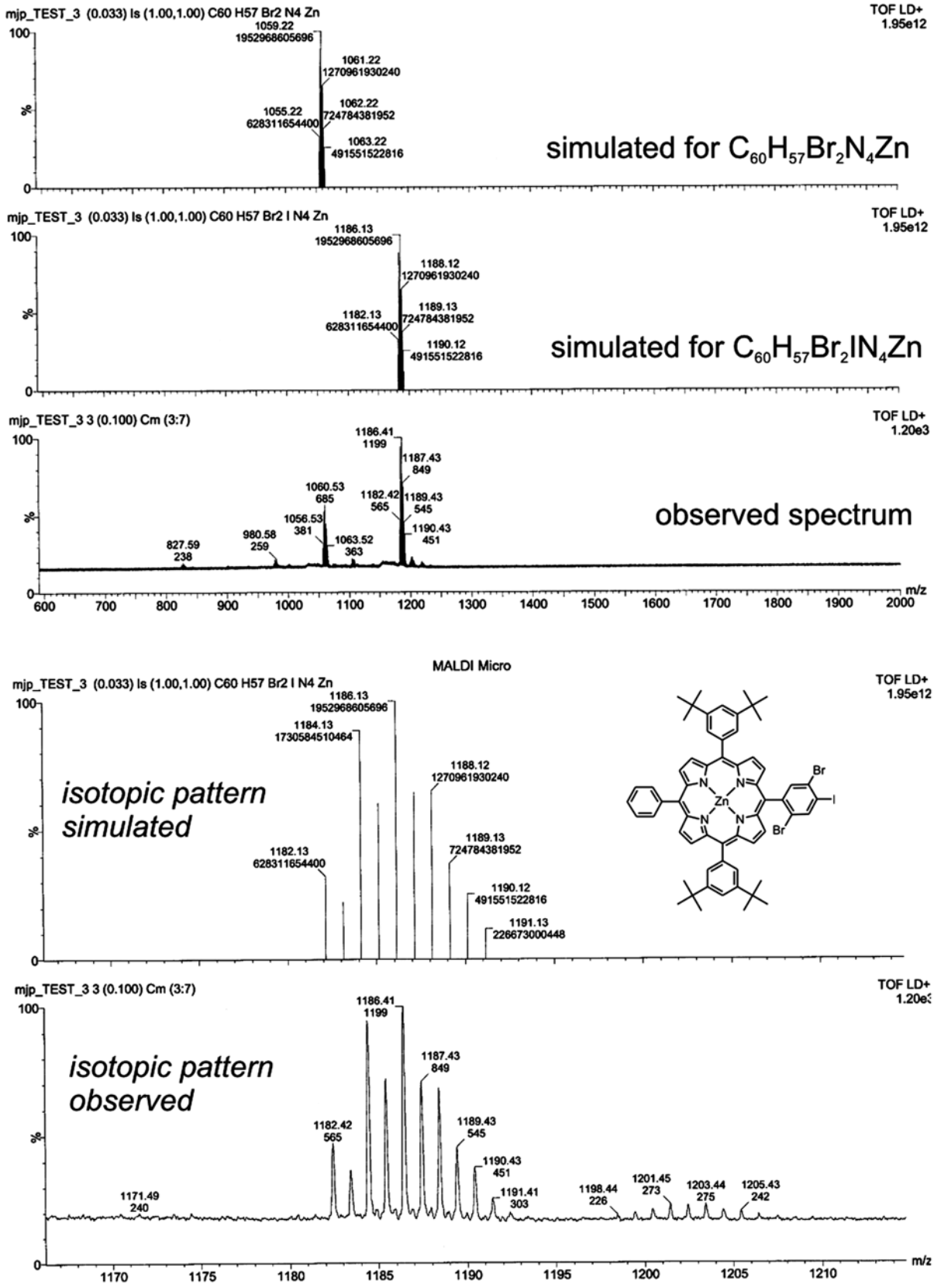

Figure S28. MALDI-TOF spectrum recorded for **9a**.

5.5. *Mass Spectrum for 3a*

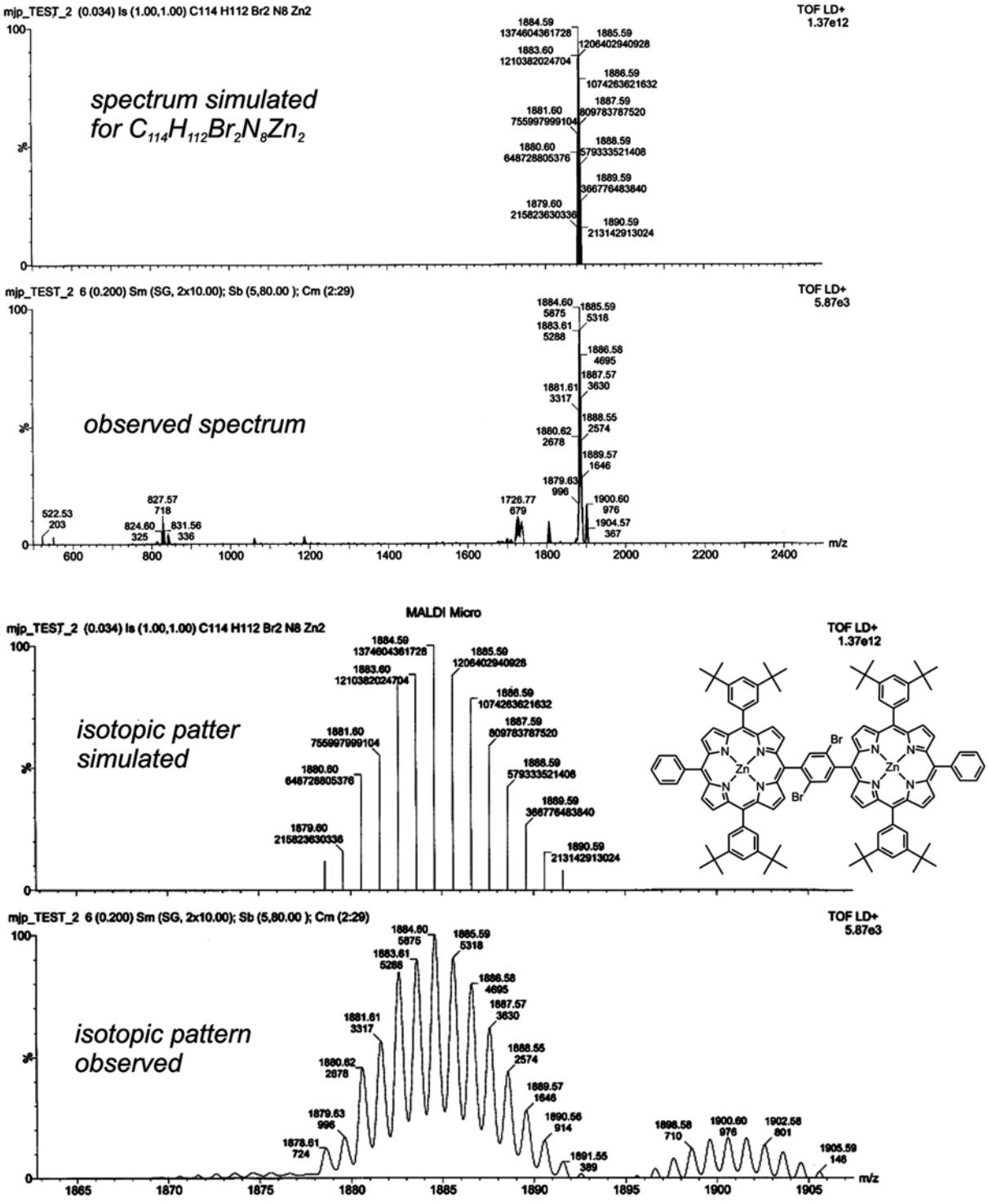

Figure S29. MALDI-TOF spectrum recorded for **3a**.

5.6. Mass Spectrum for 4

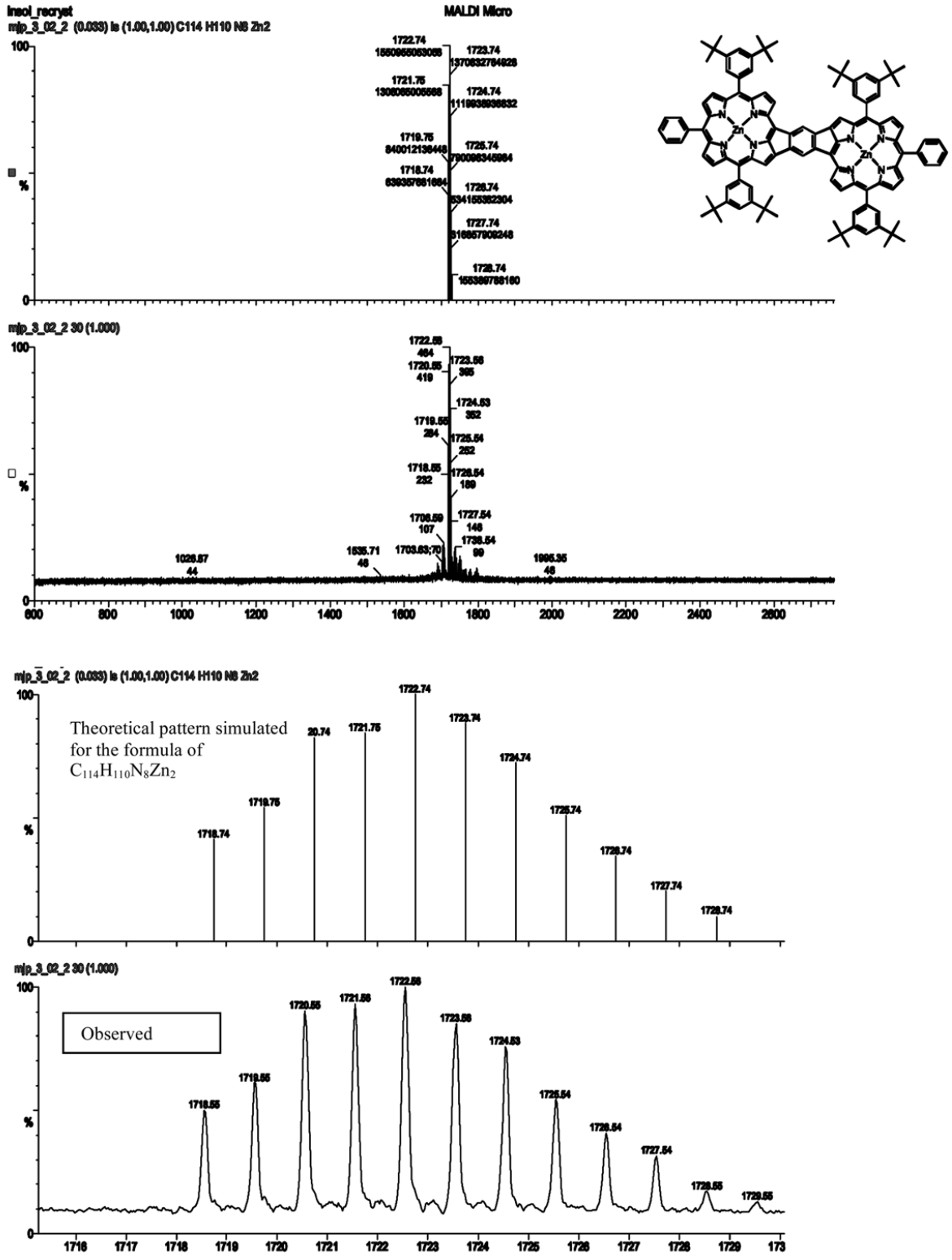

Figure S30. MALDI-TOF mass spectrum recorded for **4**.

5.7. Mass Spectrum for 11

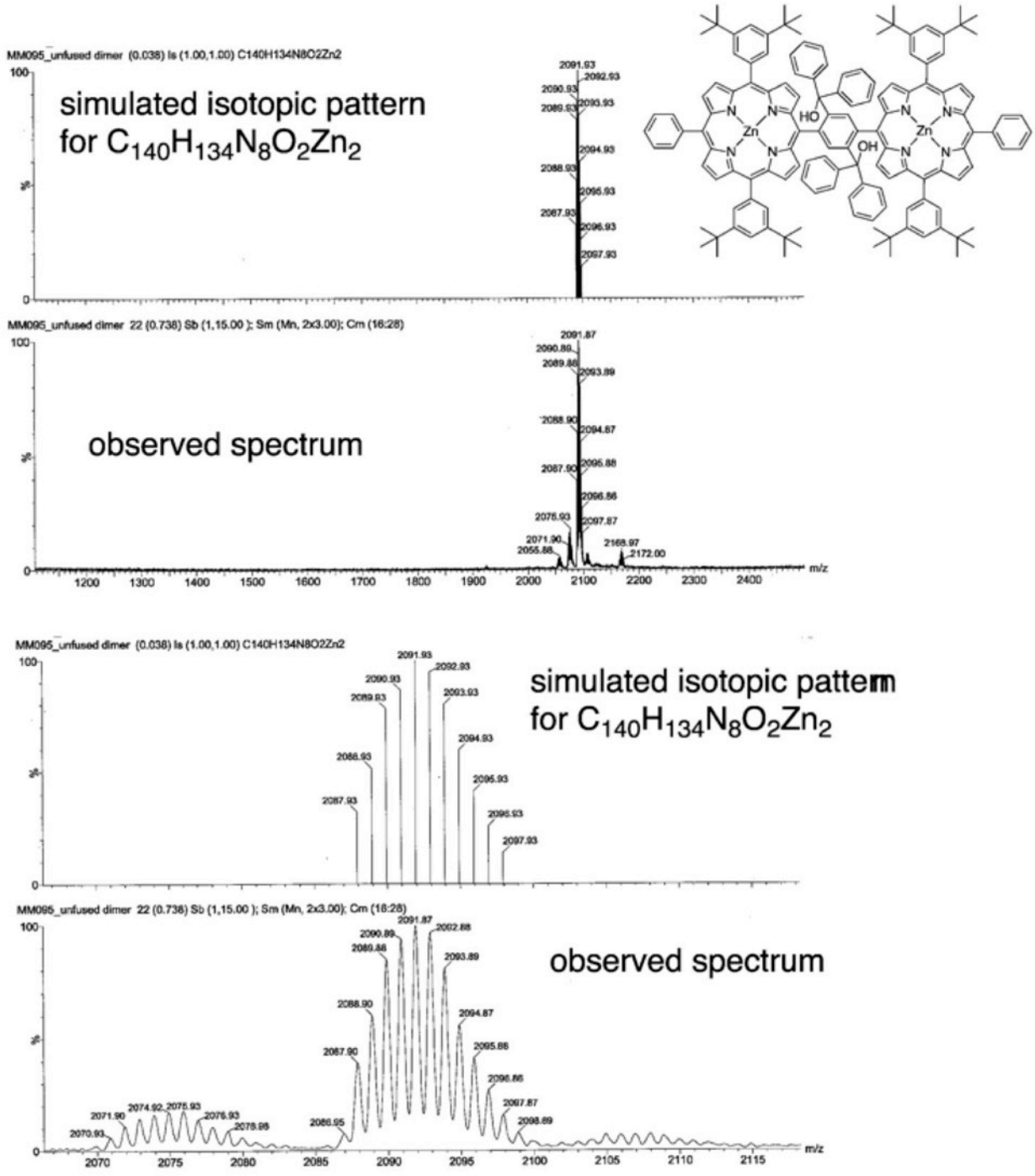

Figure S31. MALDI-TOF MS spectrum and simulated pattern for **11**.

5.8. Mass Spectrum for Porphyrin Dimer 6.

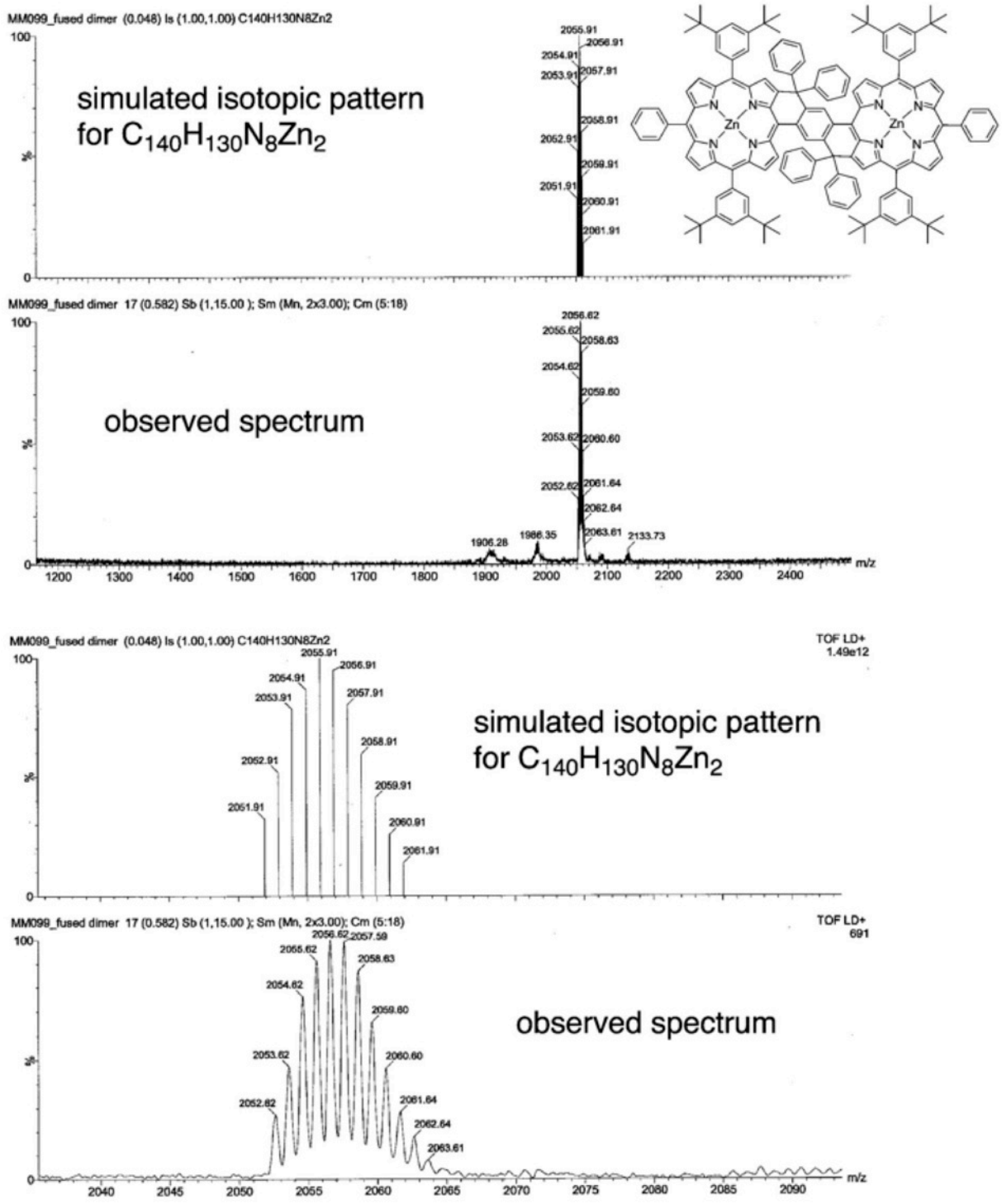

Figure S32. MALDI-TOF MS spectrum and simulated pattern for **6**.

5.9. Mass Spectrum for Porphyrin Dimer 12.

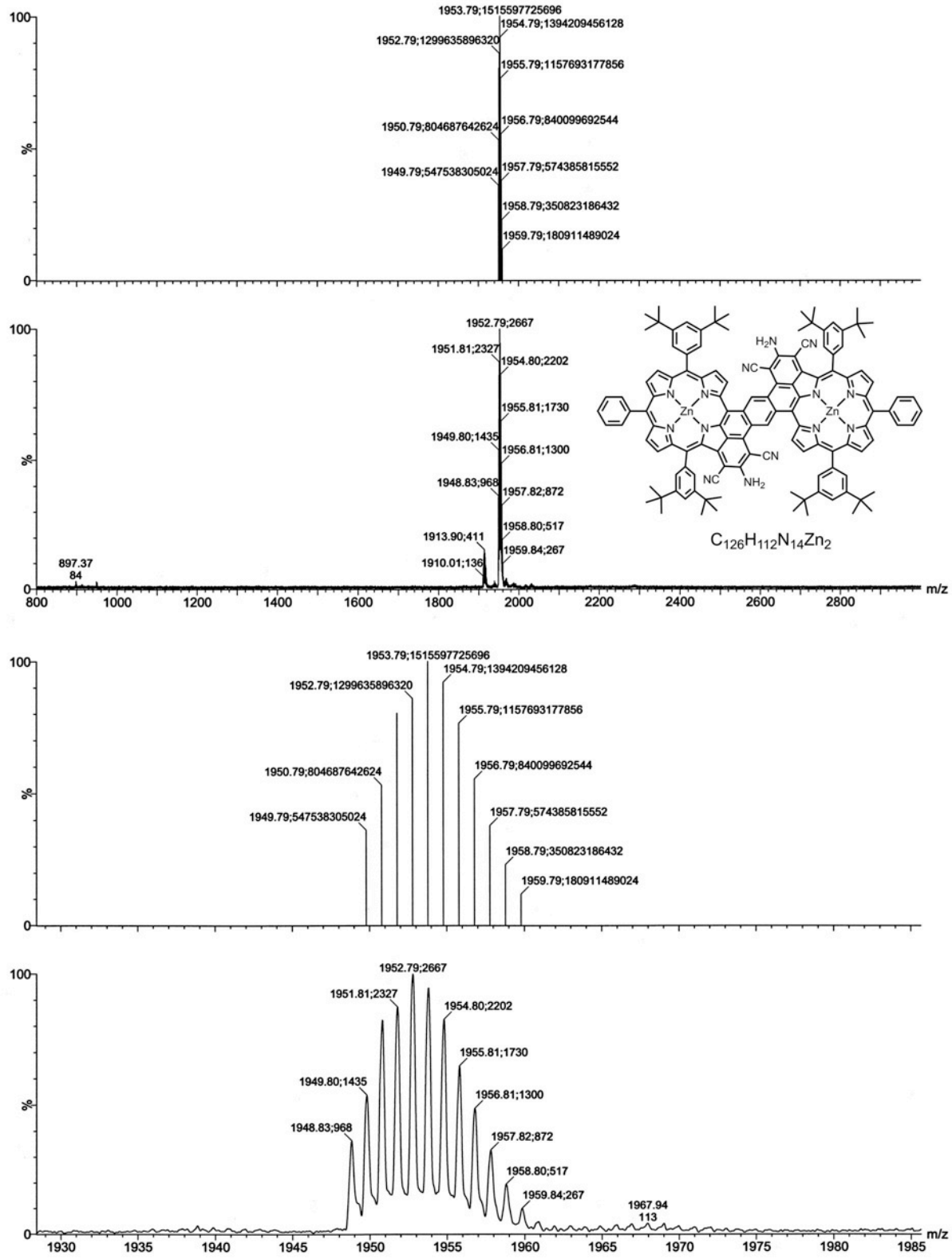

Figure S33. MALDI-TOF MS spectrum and simulated pattern for **12**.

6. Near-IR Fluorescence Measurements

For luminescence experiments, the samples were placed in fluorimetric 1-cm path cuvettes. The steady-state NIR luminescence spectra were obtained with an Edinburgh FLS920 spectrometer equipped with Hamamatsu R5509-72 cooled photomultiplier tube (400–1700 nm) at 193 K and a TM300 emission monochromator with NIR grating blazed at 1000 nm. An Edinburgh Xe900 450 W Xenon arc lamp was used as exciting light source. Corrected spectra were obtained *via* a calibration curve supplied with the instrument. Luminescence quantum yields (Φ_{em}) in solution obtained from spectra on a wavelength scale (nm) were measured according to the approach described by Demas and Crosby [J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991–1024] using air-equilibrated [$Ru(bpy)_3Cl_2$ in water solution Φ_{em} = 0.028; K. Nakamaru, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697] as standard. Experimental uncertainties are estimated to be ± 20% for emission quantum yields, ± 2 nm and ± 5 nm for absorption and emission peaks respectively.

7. Time-Resolved Photophysical Measurements

Ultrafast pump-probe transient absorption measurements were performed using a commercially available femtosecond pump-probe UV-vis spectrometer (HELIOS) purchased from Ultrafast Systems LLC. Briefly, 1-mJ, 150 fs pulses at 800 nm at a 1 KHz repetition rate were obtained from a Ti:sapphire laser (Spectra Physics Hurricane). The output laser beam was split into pump and probe by a beam splitter. The pump beam was directed into a frequency doubler (400 nm) and then focused into the sample. The probe beam was delayed in a computer-controlled optical delay (Newport) and then focused into a sapphire plate to generate white light continuum. The white light was then overlapped with the pump beam in a 2 mm quartz cuvette and then coupled into a CCD detector (Ocean Optics). Data acquisition was controlled by software (Surface Explorer Pro) developed by Ultrafast Systems LLC. The chirp effects were within experimental error, so no chirp corrections were made.

Nanosecond transient absorption measurements were carried out using the third harmonic (355 nm) of a Q-switched Nd:YAG laser (Quantel Brilliant, pulse width ca. 5 ns). Pulse fluences of up to 4 mJ cm^{-2} at the excitation wavelength were typically used. Laser-induced transmittance changes are monitored using white light from a 75 W Xenon source (Photon Technology International) focused through the sample, and re-imaged on the entrance slit of a Digikrom 240 monochromator. The resolved or dispersed light is detected with a Hamamatsu R-928 photomultiplier tube and the current is routed through a back-off circuit that measures and compensates for I_0, the background transmitted intensity. The real time current is recorded across 50 ohms on a Tektronix TDS 3054 digital oscilloscope. Data were collected and analyzed using routines written in National Instruments Lab View 5.1. All samples were deoxygenated using a freeze-pump-thaw method.

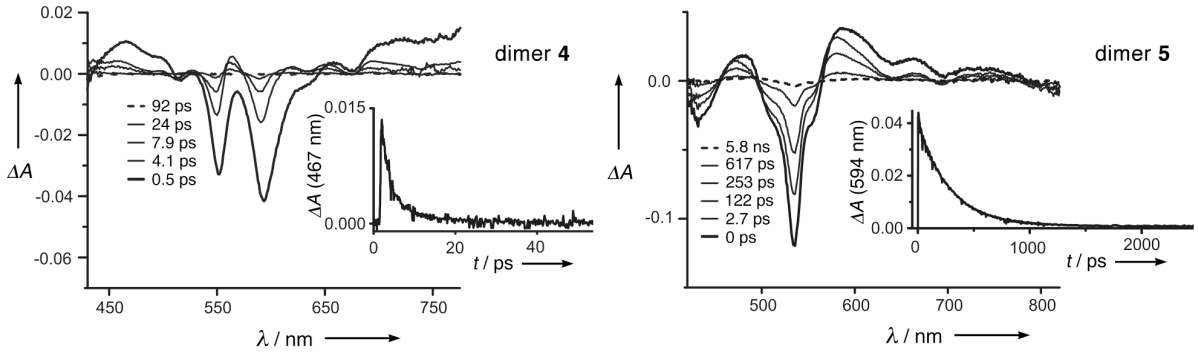

Figure S34. Transient absorption spectra for porphyrin dimers **4** (left) and **5** (right), recorded in benzene with 1% pyridine; excitation at 400 nm. Insets show decay observed for each dimer at selected wavelengths.

The singlet and triplet molar absorption coefficient and the triplet quantum yield of compound **5** were determined using singlet depletion and a relative actinometry experiment, respectively [J. E. Rogers, T. M. Cooper, P. A. Fleitz, D. J. Glass, D. G. McLean, *J. Phys. Chem. A* **2002**, *106*, 10108]. Figure S35 shows the

quantified singlet and triplet excited state spectra overlaid with the quantified ground state absorption spectrum. The peak maximum for the singlet excited state is at 578 nm with a value of 42,200 M^{-1} cm^{-1} and the triplet excited state is at 460 nm with a value of 89,000 M^{-1} cm^{-1}. The triplet quantum yield was measured using benzophenone in benzene as an actinometer. In benzene, the triplet excited state of benzophenone has a known molar absorption coefficient of 7220 M^{-1} cm^{-1} at 530 nm [J. K. Hurley, N. Sinai, H. Linschitz, *Photochem. Photobiol*. **1983**, *38*, 241]. Using this value to compute the overall concentration of excited states we then applied this to the data collected for dimer **5**. Based on measurements taken at two different benzophenone concentrations the overall $\Phi_T = 0.049 \pm 0.001$.

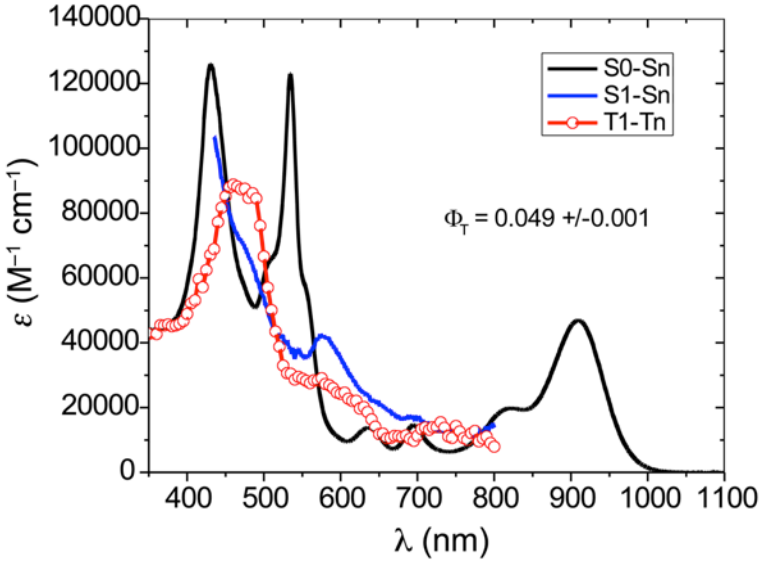

Figure S35. Linear absorption spectrum (S_0-S_n, black), singlet excited state absorption spectrum (S_1-S_n, blue) and triplet excited state absorption spectrum (T_1-T_n, red) of porphyrin dimer tape **5** in benzene with 1% pyridine.

Table S1. Selected photophysical parameters for keto-linked porphyrin dimer **5** in benzene with 1% pyridine.

parameter	value
S_0-S_n max	430 nm; 533 nm
S_1-S_n max	578 nm
$\varepsilon_{S1\text{-}Sn}$ max	42200 ± 4000 M^{-1} cm^{-1}
T_1-T_n max	460 nm
$\varepsilon_{T1\text{-}Tn}$	88900 ± 9000 M^{-1} cm^{-1}
Φ_T (triplet yield)	0.049 ± 0.001
τ_1 (intramolecular vibrational relaxation of S_1)	7.7 ± 5.6 ps
τ_2 (S_1 lifetime)	252 ± 64 ps
τ_3 (T_1 lifetime)	344 ± 9 ns (aerated solution) 27 ± 2 μs (O_2-free solution)

Table S2. Selected photophysical parameters for indene-fused porphyrin dimer **4** in benzene with 1% pyridine.

parameter	value
S_0-S_n max	417 nm
S_1-S_n max	467 nm
τ_1 (intramolecular vibrational relaxation of S_1)	1.7 ± 0.8 ps
τ_2 (S_1 lifetime)	12.9 ± 4.9 ps

8. Two-Photon Absorption Measurements

The 2PA measurements were performed using fluorescence excitation technique described in detail earlier [N. S. Makarov, M. Drobizhev, A. Rebane, *Optics Express* **2008**, *16*, 4029–4047]. A Ti:Sapphire femtosecond oscillator seeded a 1-kHz repetition rate Ti:Sapphire femtosecond regenerative amplifier (Legend HP, Coherent). The pulses from the amplifier were frequency down-converted with a TOPAS-C femtosecond optical parametric amplifier (Light Conversion). The OPA output wavelength was continuously tunable for the signal from λ_{ex} = 1100 to 1600 nm; and for the idler from λ_{ex} = 1600 to 2200 nm. There was a small wavelength tuning gap ~10 nm around the degeneracy point, λ_{ex} =1590 nm. The OPA output pulse energy was 100–200 μJ.

The sample solution in a 1-cm spectroscopic cuvette was placed ~15 cm behind a f = 25 cm focusing lens. A small fraction of the excitation beam was split off by a glass plate and was directed to a pyroelectric detector (J3-02, Molectron) used for reference. The fluorescence was collected at right angle with respect to the excitation beam with a spherical mirror (f = 50 cm, diameter d = 10 cm) and focused with unity magnification ratio on the entrance slit of an imaging diffraction grating spectrometer (Triax 550, Jobin Yvon). The raw 2PA spectrum (in relative units) was obtained by measuring the intensity of the two-photon excited fluorescence as a function of the OPA wavelength, where the fluorescence intensity was normalized to the square of the reference channel intensity. The raw spectra in the λ_{ex} = 1100 to 1600 nm range were then corrected with respect to the previously characterized 2PA standard Stryryl 9M [N. S. Makarov, M. Drobizhev, A. Rebane, *Optics Express* **2008**, *16*, 4029–4047]. The absolute 2PA cross sections were determined by the relative fluorescence technique using the same reference standard. Because in the 1600–2100 nm range there are currently no suitable reference standards, only the raw 2PA spectra were measured in this wavelength range.

We checked and confirmed the quadratic dependence on the laser power in both wavelength ranges, thus excluding possible artifacts e.g. due to linear absorption. The resulting 2PA spectrum is plotted in Figure S36a.

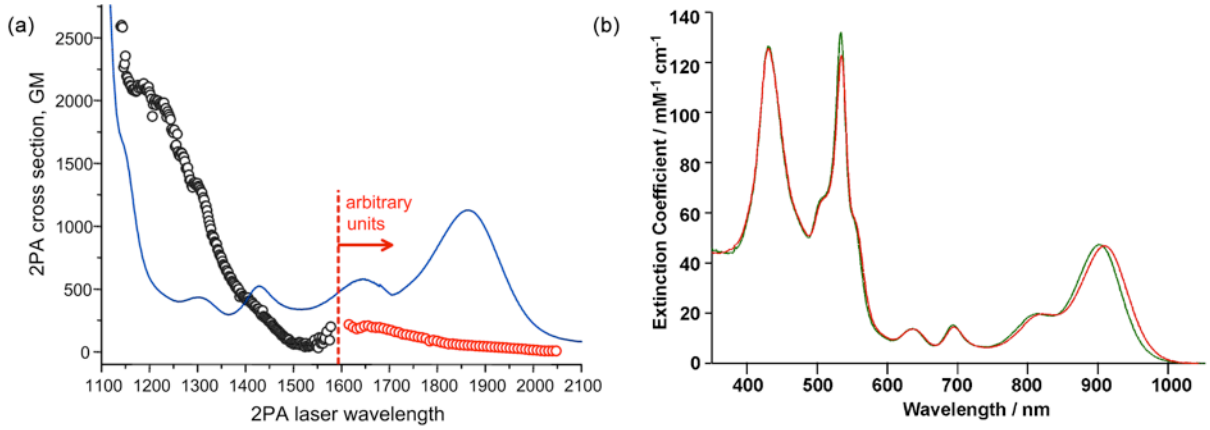

Figure S36. (a) Two-photon absorption spectrum of porphyrin dimer tape **5** in CCl_4 with 1% pyridine, compared with the one-photon absorption spectrum (S_0-S_n, blue line) at the same transition energy. (b) Linear absorption spectra of **5** in benzene with 1% pyridine (red line) and in carbon tetrachloride with 1% pyridine (green line).

The shape of the 2PA spectrum of **5** resembles that of other *meso*-substituted porphyrin dimers [M. Drobizhev, Y. Stepanenko, Y. Dzenis, A. Karotki, A. Rebane, P. N. Taylor, H. L. Anderson, *J. Am. Chem. Soc.* **2004**, *126*, 15352–15353]. At 1100–1300 nm, there is a very strong 2PA band which we can tentatively attribute to two factors: First, there appears to be a two-photon allowed transition at around 1200–1300 nm; Second, there is a resonance enhancement of the 2PA as the laser wavelength approaches the Q-band. Even though we did not measure the actual two-photon cross-section at 1600–2100 nm, based on this analysis we would not expect the value to exceed, $\sigma_2 < 250$ GM in that region.

The 2PA spectrum of **5** was recorded in carbon tetrachloride containing 1% pyridine, to avoid NIR absorption of the solvent . The linear absorption spectra of **5** in carbon tetrachloride / pyridine and benzene / pyridine are almost identical, as shown in Figure S36b.

9. Electrochemistry Experiments

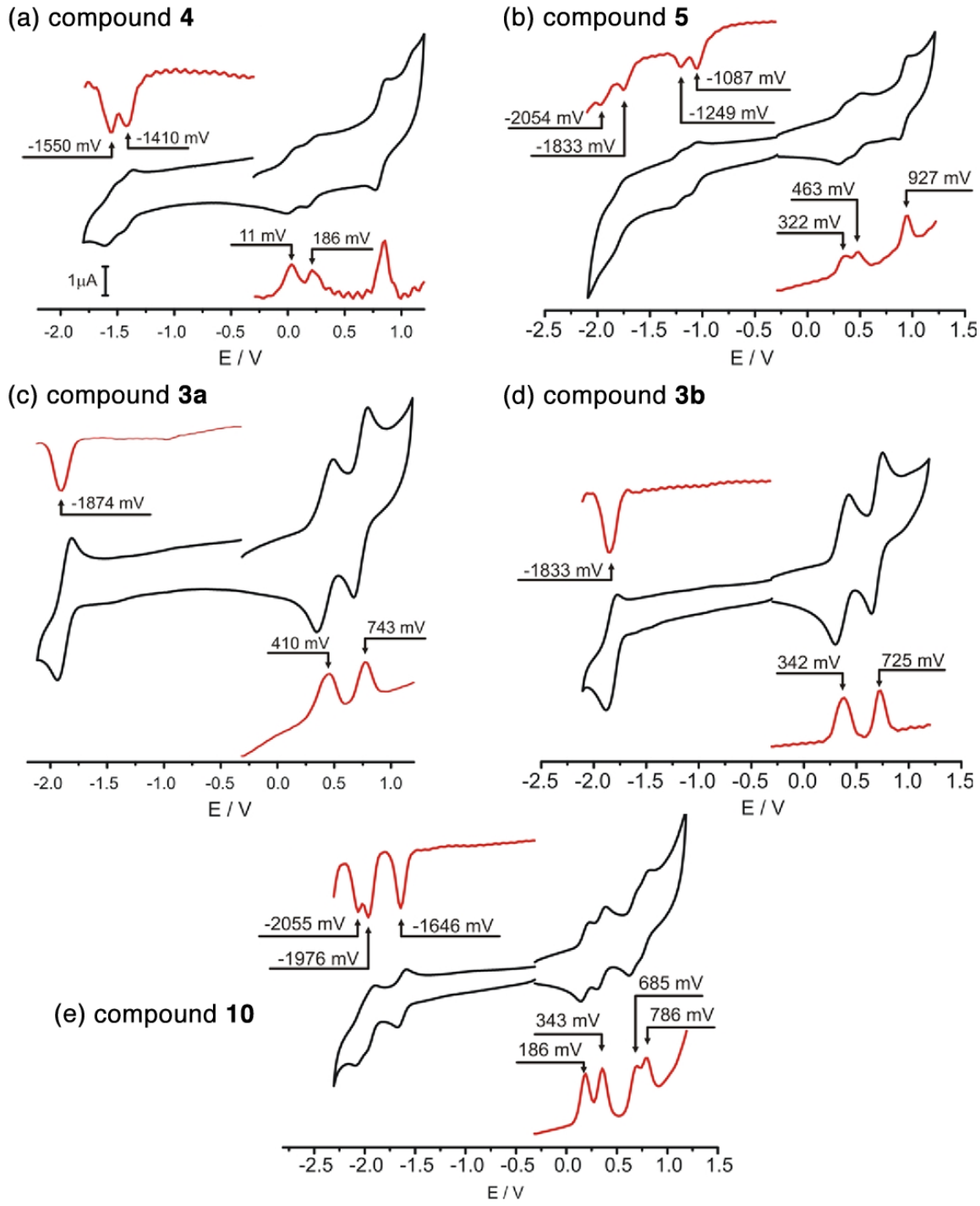

Figure S37. Electrochemical experiments for porphyrin dimers (a) **4**, (b) **5**, (c) **3a**, (d) **3b** and (e) **10** (CH_2Cl_2 with 0.1 M Bu_4NPF_6 as a supporting electrolyte, scan rate 100 mV s^{-1}; glassy carbon working electrode, Pt counter electrode, $Ag/AgNO_3$ reference electrode). The red lines present the square-wave experiments recorded for the same samples (CH_2Cl_2 with 0.1 M Bu_4NPF_6 square wave frequency 8 Hz; glassy carbon working electrode, Pt counter electrode, $Ag/AgNO_3$ reference electrode). All potentials are relative to internal ferrocene (Fc/Fc^+ at $E = 0$).

10. X-ray Structures Determinations

10.1. *Crystal Data for Dibromo Porphyrin Dimer 3a*
(CCDC deposit number: CCDC 860947)

X-ray quality crystals were obtained by slow diffusion of methanol into a solution of **3a** in chloroform. Data were collected using a Nonius Kappa CCD detector with a molybdenum source (λ = 0.71073) at the X-ray facilities in the Chemistry Research Laboratory, Oxford University. Data were solved by direct methods using the SHELXS software [G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112–122], followed by the CRYSTALS package to complete the modeled disorder [P. W. Betteridge, J. R. Carruthers, R. I. Cooper, C. K. Prout, D. J. Watkin, *J. Appl. Crystallogr.* **2003**, *36*, 1487–1487]. The asymmetric unit contains a half of a molecule, placed at the inversion center, with a methanol molecule coordinated to the zinc. The low quality of the data required isotropic refinement of peripheral *t*-butyl groups with restraints used for these groups. Beside the two disordered molecules of chloroform, an additional disordered methanol molecule was found and refined with appropriate restraints.

3a [CCDC 860947]: $C_{122}H_{120}Br_2N_8Zn_2 \cdot 4(CHCl_3) \cdot 2(MeOH)$, M = 2482.27, Z = 1, triclinic, space group P-1, a = 10.337(2) Å, b = 15.431(3) Å, c = 19.611(4) Å, α = 82.82(3) °, β = 84.35(3) °, γ = 82.95(3) °, V = 3069.3(11) Å^3, T = 100(2) K, μ = 1.356 mm^{-1}. Of 18383 reflections measured, 11702 were independent (R_{int} = 0.035). Final refinement (on F) gave R = 0.114 (5843 reflections with $I > 3\sigma(I)$) and wR = 0.1167. $\Delta\rho_{min/max}$ = –1.64 / 4.01.

10.2. *Crystal Data for Keto-Linked Porphyrin Dimer Tape 5*
(CCDC deposit numbers: CCDC 860948 and 860949)

X-Ray quality crystals of **5** were grown by a vapor diffusion of *n*-heptane into a solution of **5** in toluene/pyridine (80:20) at room temperature. By varying the rate of the vapor diffusion, two different solvates of **5** were crystallized, in some cases concomitantly. The crystal structures of both polymorphs were determined by X-ray analysis (see Figure S38). Data were collected using beamline I19 (EH1) at Diamond Light Source. Raw frame data were processed (including unit cell refinement, multiscan absorption correction and inter-frame scaling) using CrystalClear [Rigaku Americas and Rigaku Corporation (2009). CrystalClear (Version 2.0). Rigaku Americas, 9009 TX, USA 77381–5209] and the structures were solved by direct methods with SIR92 [A. Altomare, G. Carascano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343–350] within the CRYSTALS suite [P. W. Betteridge, J. R. Carruthers, R. I. Cooper, C. K. Prout, D. J. Watkin, *J. Appl. Crystallogr.* **2003**, *36*, 1487–1487]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Both structures featured disordered *t*-butyl groups and solvent. Some distance, thermal and vibrational restraints were employed in order to maintain sensible geometries and displacement ellipsoids. Hydrogen atoms were generally visible in the difference map, but were positioned geometrically and refined separately (with restraints) prior to inclusion in the final refinements with a riding model [R. I. Cooper, A. L. Thompson & D. J. Watkin, *J. Appl. Cryst.* **2010**, *43*, 1100–1107].

In both cases, the porphyrin dimer occupies a special position such that the two halves are related by inversion through the center of the phenylene bridge. Pyridine is coordinated to both zinc sites. The molecular structures of the two solvates are identical, except for slight rotation of the pyridine and distortion of the tape.

5-$(C_5H_5N)_2 \cdot 2(C_7H_{16}) \cdot 2(C_5H_5N)$ **[CCDC 860948]**: $C_{126}H_{120}N_{10}O_2Zn_2 \cdot 2(C_7H_{16}) \cdot 2(C_5H_5N)$: M =2295.77, Z = 1, triclinic, space group P-1, a = 11.998(2) Å, b = 14.379(3) Å, c = 19.482(4) Å, α = 82.891(6) °, β = 87.456(5) °, γ = 76.474(5) °, V = 3242.4(11) Å^3, T = 150 K, μ = 0.427 mm^{-1}. Of 71371 reflections measured, 21647 were independent (R_{int} = 0.109). Final refinement (on F^2) gave R = 0.0704 (9221 reflections with $I > 2\sigma(I)$) and wR = 0.1272. $\Delta\rho_{min/max}$ = –0.60 / 0.57.

5-$(C_5H_5N)_2 \cdot 1.426(C_7H_{16}) \cdot 1.518(C_5H_5N)$ **[CCDC 860949]**: $C_{126}H_{120}N_{10}O_2\ Zn_2 \cdot 1.426\ (C_7H_{16}) \cdot 1.518(C_5H_5N)$: M =2338.09, Z = 1, triclinic, space group P-1, a = 10.038(11) Å, b = 18.807(18) Å, c = 19.38(2) Å, α = 78.31(4) °, β = 84.46(4) °, γ = 82.55(4) °, V = 3544(6) Å^3, T = 150 K, μ = 0.392 mm^{-1}. Of 33468 reflections measured,

15005 were independent (R_{int} = 0.049). Final refinement (on F^2) gave R = 0.1106 (8978 reflections with $I > 2\sigma(I)$) and wR = 0.2531. $\Delta\rho_{min/max}$ = –1.14 / 0.62.

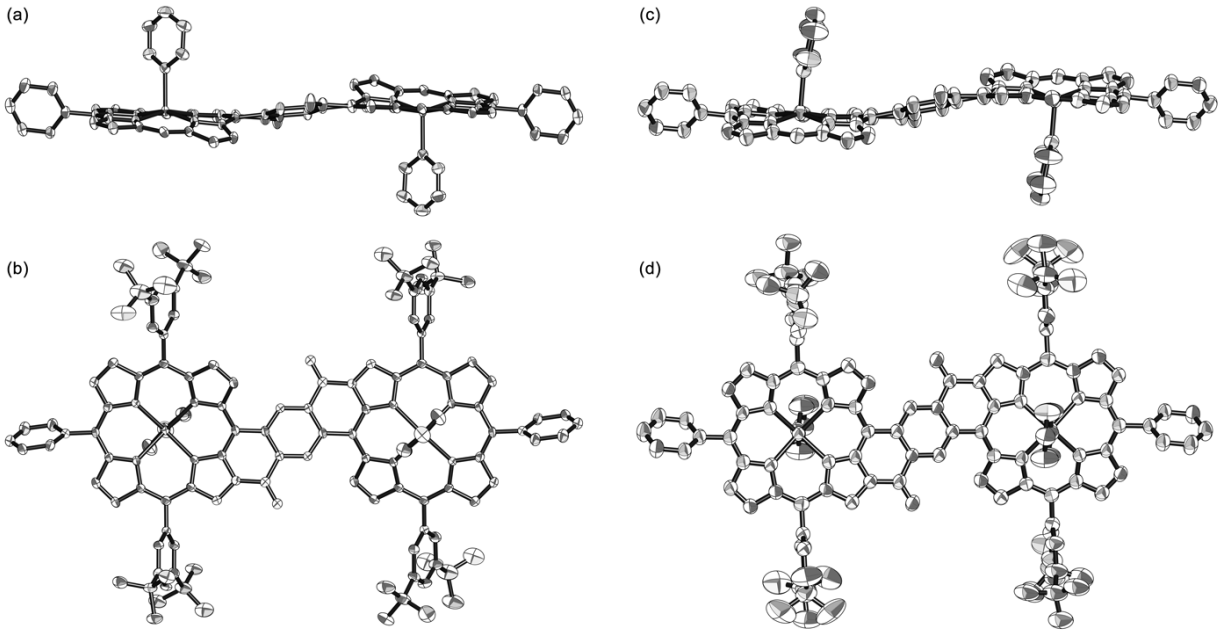

Figure S38. Comparison of the two crystal structures of porphyrin dimer **5**. (a, b) Two orthogonal views of the structure in **5**-$(C_5H_5N)_2$·2(C_7H_{16})·2(C_5H_5N); (b, c) Two orthogonal views of the structure in **5**-$(C_5H_5N)_2$·1.426(C_7H_{16})·1.518(C_5H_5N); (50% thermal ellipsoids; H atoms, *t*-Bu groups and coordinated methanol omitted for clarity).

10.3. *Crystal Data for CPh_2-Linked Porphyrin Dimer 6*

(CCDC deposit numbers: CCDC 860950)

X-Ray quality crystals of **6** were grown by a vapor diffusion of *n*-propanol into a solution of **6** in toluene/pyridine (80:20) at room temperature. Data were collected using beamline I19 (EH1) at Diamond Light Source. Raw frame data were processed (including unit cell refinement, multiscan absorption correction and inter-frame scaling) using CrystalClear [Rigaku Americas and Rigaku Corporation (2009). CrystalClear (Version 2.0). Rigaku Americas, 9009 TX, USA 77381–5209] and the structures were solved by direct methods with SIR92 [A. Altomare, G. Carascano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343–350] within the CRYSTALS suite [P. W. Betteridge, J. R. Carruthers, R. I. Cooper, C. K. Prout, D. J. Watkin, *J. Appl. Crystallogr.* **2003**, *36*, 1487–1487]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Disorder was observed in one *t*-butyl group, the terminal phenyl group and in the toluene solvent. Distance, thermal and vibrational restraints were employed in order to maintain sensible geometries and displacement ellipsoids. Hydrogen atoms were generally visible in the difference map, but were positioned geometrically and refined separately (with restraints) prior to inclusion in the final refinements with a riding model [R. I. Cooper, A. L. Thompson & D. J. Watkin, *J. Appl. Cryst.* **2010**, *43*, 1100–1107].

6 [CCDC 860950]: $C_{150}H_{140}N_{10}Zn_2$, 4(C_7H_8), C_6H_6: M = 2660.26, Z = 1, triclinic, spacegroup P-1, a = 11.254(3) Å, b = 16.718(4) Å, c = 19.850(4) Å, α = 83.634(6)°, β = 79.865(4)°, γ = 87.849(7)°, V = 3653.1(14) Å^3, T = 100(2) K, μ = 0.387 mm^{-1}. Of 79373 reflections collected, 24243 were independent (R_{int} = 0.047). Final refinement (on F^2) gave R = 0.0769 (19889 Reflections $I > 2\sigma$(I)) and wR = 0.1594. $\Delta\rho_{min/max}$ = -0.93 / 2.12.

10.4. *Crystal Data for Singly Indene-Fused Porphyrin Dimer 10*
(CCDC deposit number: CCDC 860951)

The crystal was obtained by slow diffusion of methanol into a solution of **10** in chloroform. Crystallographic data for a small crystal of fused porphyrin dimer **10** were collected using the synchrotron radiation source at Station 9.8, Daresbury SRS, UK, on a Bruker SMART CCD diffractometer. The structure was solved by direct methods using the program SIR92 [A. Altomare, G. Carascano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343–350]. The refinement and graphical calculations were performed using the CRYSTALS program suite [P. W. Betteridge, J. R. Carruthers, R. I. Cooper, C. K. Prout, D. J. Watkin, *J. Appl. Crystallogr.* **2003**, *36*, 1487–1487]. The asymmetric unit contains two porphyrin units (one dimer), each with a Zn-coordinated CH_3OH molecule, as well as half of a free, disordered $CHCl_3$ molecule, three free (disordered) methanol molecules and a molecule of H_2O (disordered). In view of the severe shortage of data, the atoms in the solvent molecules and disordered, peripheral, *t*-Bu groups were refined with isotropic displacement parameters.

10 [CCDC 860951]: $C_{116}H_{117}BrN_8O_2Zn_2,\cdot CHCl_3,\cdot 3(CH_3OH)\cdot H_2O$: M =3951.13, Z = 1, triclinic, space group P-1, a = 15.4354(8) Å, b = 16.6155(9) Å, c = 21.9618(12) Å, α = 98.915(1) °, β = 98.974(1) °, γ = 93.126(1) °, V = 5478.4(5) Å^3, T = 120(2) K, μ = 0.893 mm^{-1}. Of 62260 reflections measured, 32269 were independent (R_{int} = 0.023). Final refinement (on F) gave R = 0.0915 (17394 reflections with $I > 3\sigma(I)$) and wR = 0.1069. $\Delta\rho_{min/max}$ = –1.34 / 2.11.

10.5. *Crystal Data for Porphyrin Dimer 12*
(CCDC deposit numbers: CCDC 860952)

X-Ray quality crystals of **12** were grown by a vapor diffusion of *n*-propanol into a solution of **12** in toluene/pyridine (80:20) at room temperature. Data were collected using beamline I19 (EH1) at Diamond Light Source. Raw frame data were processed (including unit cell refinement, multiscan absorption correction and inter-frame scaling) using CrystalClear [Rigaku Americas and Rigaku Corporation (2009). CrystalClear (Version 2.0). Rigaku Americas, 9009 TX, USA 77381–5209] and the structures were solved by direct methods with SIR92 [A. Altomare, G. Carascano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343–350] within the CRYSTALS suite [P. W. Betteridge, J. R. Carruthers, R. I. Cooper, C. K. Prout, D. J. Watkin, *J. Appl. Crystallogr.* **2003**, *36*, 1487–1487]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Disorder was observed in one *t*-butyl group and in the cycloheane solvent. Distance, thermal and vibrational restraints were employed in order to maintain sensible geometries and displacement ellipsoids. Hydrogen atoms were generally visible in the difference map, but were positioned geometrically and refined separately (with restraints) prior to inclusion in the final refinements with a riding model [R. I. Cooper, A. L. Thompson & D. J. Watkin, *J. Appl. Cryst.* **2010**, *43*, 1100–1107].

12 [CCDC 860952]: $C_{136}H_{122}N_{16}Zn_2$, $4(C_6H_{12})$, $2(C_6H_6)$, M = 2660.26, Z = 1, triclinic, space group P-1, a = 12.428(4) Å, b = 14.323(5) Å, c = 21.854(8) Å, α = 80.953(8)°, β = 87.360(11)°, γ = 69.226(11)°, V = 3592(2) Å^3, T = 100(2) K, μ = 0.393 mm^{-1}. Of 58776 reflections measured, 22887 were independent (R_{int} = 0.037). Final refinement (on F^2), R = 0.0796 (18736 reflections with $I > 2\sigma$(I)), wR = 0.1880. $\Delta\rho_{min/max}$ = –1.88 / 0.75.