Supporting Information

Selective stepwise Suzuki cross-coupling reaction for the modeling of photosynthetic donor-acceptor systems

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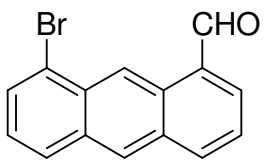
I. Synthesis

a. General procedures

All known compounds (5,15-bis-(3,5-di-*tert*-butyl)phenylporphyrin and its zinc(II) complex,[1] 5-bromo-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin and its zinc(II) complex,[2,3] 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10,20-(3,5-di-tert-butylphenyl)porphyrin zinc(II) and 5,15-di-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10,20-(3,5-di-tert-butylphenyl)porphyrin zinc(II),[4] 1,19-dideoxy-2,3,7,8,12,13,17,18-octamethyl-a,c-biladiene dihydrobromide,[5] 1,8-dibromoanthracene and 1,8-dibromo-10-anthrone[6] were synthesized as previously described.
The handling of all air/water sensitive materials was carried out using standard high vacuum techniques. Dried toluene was obtained by passing through alumina under N_2 in the solvent purification systems and then further dried over activated molecular sieves; extra dry DMF was purchased from Aldrich. Triethylamine and DCM were distilled from CaH_2; THF was distilled from sodium benzophenone ketyl. Unless specified otherwise all other solvents were used as commercially supplied. Where mixtures of solvents were used, ratios are reported by volume. Column chromatography was carried out on silica gel 60 at normal pressure. Size exclusion chromatography was carried out under gravity using cross-linked polystyrene Bio-Beads® SX-1 (200 – 400 mesh) in DCM.
UV-Vis spectra were recorded in solutions using Varian Cary 50 spectrophotometer (1 cm path length quartz cell). Emission, excitation spectra and fluorescence lifetimes were measured by using a double monochromator Fluorolog FL-1039 instrument from HORIBA Jobin Yvon, equipped with TCSPC module for time-resolved measurements (interchangeable NanoLED pulsed laser-diodes as sources and TBX-04 photomultiplier tube as a detector were used). Emission quantum yields of the compounds were measured relative to the fluorescence of free-base tetraphenylporphyrin (ϕ_f=0.11)[7] in deoxygenated toluene. Sample concentrations were chosen to obtain an absorbance of 0.03 - 0.07, at least three measurements were performed for each sample. All the measurements were performed using deoxygenated (by Ar bubbling) freshly distilled tetrahydrofurane. Fluorescence lifetimes were obtained by deconvolution and distribution lifetime analysis. NMR spectra were recorded at room temperature using Bruker Avance 300 and Bruker Avance II 600 instruments with the chemical shifts reported as δ in ppm and coupling constants expressed in Hz. Accurate mass measurements (HRMS) were carried out using a Bruker microTOF-Q™ ESI-TOF mass spectrometer. MALDI-TOF mass spectrometry was carried out with a Bruker Ultraflex II MALDI-TOF mass spectrometer using dithranol as the matrix.

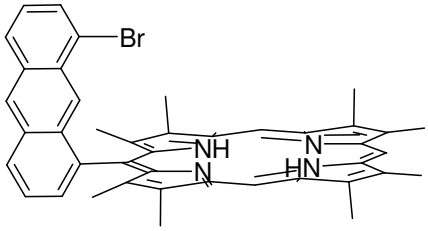
b. Experimental procedures

8-Bromo-anthracene-1-carbaldehyde (4)



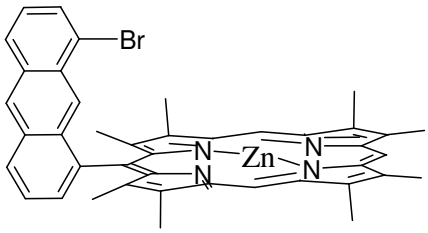
This compound was prepared by adapting a published procedure.[8] Phenyllithium (4.5 mL, 2.0 M solution in dibutylether) was added over a period of 10 min to a solution of 1,8-dibromoanthracene (3.00 g, 8.92 mmol) in dry THF (100 mL) cooled to -78 °C under an Ar atmosphere. After stirring at -78 °C under nitrogen for 1 h, dry DMF (5 mL) was added and the mixture was warmed to room temperature and stirred for an additional hour. The reaction was quenched with water (30 mL) and the organic solvent was removed by rotary evaporation. The resulting precipitate was filtered and washed with water. Purification by column chromatography (silica gel, 2:1 hexanes/dichloromethane) supplied **4** as a yellowish powder (3.12 g, 92% yield), m.p. 184-185 °C. **^{1}H NMR** (300 MHz, $CDCl_3$, 25°C): δ 10.48 (s, 1H), 10.32 (d, J = 0.75 Hz, 1H), 8.51 (s, 1H), 8.29 (d, J = 8.48 Hz, 1H), 8.06 (dd, J_1 = 6.78 Hz, J_2 = 1.32 Hz, 1H), 8.01 (d, J = 9.04 Hz, 1H), 7.90 (dd, J_1 = 7.25 Hz, J_2 = 1.04 Hz, 1H), 7.67 (dd, J_1 = 8.48 Hz, J_2 = 6.78 Hz, 1H), 7.38 (dd, J_1 = 8.38 Hz, J_2 = 7.25 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$, 25°C): δ 193.18, 138.77, 135.50, 132.52, 131.92, 130.38, 128.12, 127.82, 126.38, 124.84, 124.79. Anal, calcd. for $C_{15}H_9BrO$: C, 63.18; H, 3.18; found C, 62.24; H, 3.09.

5-(8-Bromo-anthracen-1-yl)-2,3,7,8,12,13,17,18-octamethylporphyrin (6a)



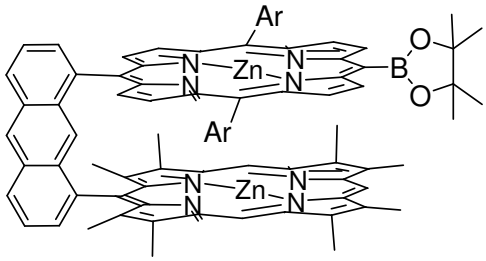
A mixture of 1,19-dideoxy-2,3,7,8,12,13,17,18-octamethyl-a,c-biladiene dihydrobromide **5** (1.59 g, 2.77 mmol), 8-bromo-anthracene-1-carbaldehyde **4** (0.79 g, 2.77 mmol) and p-toluenesulfonic acid (3.75 g, 1.94 mmol) in 300 ml of absolute ethanol was deoxygenated by bubbling Ar for 10 min and heated at reflux for 48 h under Ar. Allowed to cool, the mixture was evaporated to dryness in vacuum. Solid residue was taken up in CH_2Cl_2 (200 ml), washed with water (2 × 100 ml), brine (1 × 100 ml), dried over Na_2SO_4 and evaporated in vacuum. Crude material was purified by treating with TFA (0.05 mL), dissolution in CH_2Cl_2 and precipitation as free bases upon addition of methanol. The precipitate was collected, washed with methanol and dried in vacuum. Dark-brown microcrystalline solid (0.65 g, 35%), m.p. > 300°C. **UV/vis** (THF) λmax (log ε) 403 (5.13), 501 (4.13), 533 (3.83), 573 (3.75), 627 (3.54). **^{1}H NMR** (300 MHz, $CDCl_3$/TFA, 25°C): δ 10.32 (s, 2H), 10.20 (s, 1H), 9.11 (s, 1H), 8.82 (s, 1H), 8.59 (d, *J* = 8.48 Hz, 1H), 8.15 (m, 2H), 8.00 (t, *J* = 8.10 Hz, 1H), 7.70 (d, *J* = 4.71 Hz, 1H), 7.37 (m, 1H), 3.55 (s, 12H), 3.20 (s, 6H), 1.96 (s, 6H), -0.54 (br. s, 2H), -1.45 (br. s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$/TFA, 25°C): δ 143.91, 143.45, 142.09, 141.99, 141.72, 138.22, 137.90, 137.88, 137.43, 137.19, 136.17, 134.56, 134.36, 132.73, 131.80, 131.48, 131.34, 130.16, 128.09, 127.98, 126.42, 126.35, 125.16, 123.36, 118.04, 98.24, 96.45, 13.08, 12.01, 11.95, 11.83. **ESI HRMS** *m/z* 677.22414; calcd for $C_{42}H_{37}BrN_4$ (MH^+) 677.22744.

Zinc(II) 5-(8-bromo-anthracen-1-yl)-2,3,7,8,12,13,17,18-octamethylporphyrin (6b)



A suspension of porphyrin **6b** (0.6 g, 0.886 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (0.39 g, 1.772 mmol) in DMF (50 ml) was refluxed for 1h. Water was added and the precipitate filtered, washed with water, MeOH and acetone. The residue was dissolved in boiling $CDCl_3$ (200 ml), MeOH was added and the volume was reduced to precipitate the product. Filtration gave the title compound (0.62 g, 95%) as a purple red solid, m.p. > 300°C. **UV/vis** (THF) λmax (log ε) 335 (4.36), 411 (5.45), 541 (4.22), 577 (4.12). **^{1}H NMR** (300 MHz, d^6-DMSO, 25°C): δ 10.09 (s, 2H), 10.04 (s, 1H), 9.04 (s, 1H), 8.65 (d, *J* = 9.04 Hz, 1H), 8.24 (d, *J* = 8.67 Hz, 1H), 8.04 (m, 3H), 7.55 (d, *J* = 7.72 Hz, 1H), 7.33 (m, 1H), 3.61 (s, 6H), 3.60 (s, 6H), 3.40 (s, 6H), 1.95 (s, 6H). ^{13}C NMR not obtained because of very poor solubility. **ESI HRMS** *m/z* 761.12334; calcd for $C_{42}H_{35}BrN_4Zn$ ($M+Na^+$) 761.12288.

Zinc(II) 5-{8-[zinc(II)-10,20-Bis-(3,5-di-tert-butyl-phenyl)-15-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-porphyrin-5-yl]-anthracen-1-yl}-2,3,7,8,12,13,17,18-octamethyl-porphyrin (9)



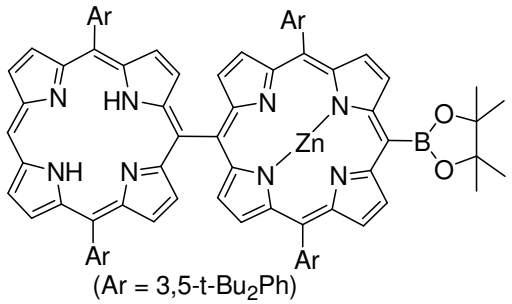
(Ar = 3,5-t-Bu$_2$Ph)

Porphyrin **6b** (0.25 g, 0.337 mmol), 5,15-di-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-20,25-(3,5-di-tert-butylphenyl)porphyrin **7** (0.405 g, 0.404 mmol), Cs_2CO_3 (0.033 g, 0.677 mmol), and $Pd(PPh_3)_4$ (0.039 g, 0.0337 mmol) were dissolved in a mixture of dry DMF (12.5 mL) and dry toluene (25 mL). The solution was deoxygenated via bubbling Ar for 10 min and the resulting mixture was heated at 90 °C for 5 h under Ar. Allowed to cool, the

mixture was quenched with water and extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4 and evaporated. Purification by column chromatography on silica gel, using hexanes-dichloromethane (content of CH_2Cl_2 was gradually increased from 30 to 50 vol%), supplied **8** as a purple crystalline solid (0.304 g, 58% yield), m.p. > 300°C. **UV/vis** (THF) λmax (log ε) 407 (5.53), 431 (5.22), 545 (4.29), 577 (4.06). **^{1}H NMR** (300 MHz, CD_2Cl_2, 25°C): δ 9.50 (d, *J* = 4.71 Hz, 2H), 9.12 (s, 2H), 9.07 (s, 1H), 8.93 (s, 1H), 8.65 (d, *J* = 4.71 Hz, 2H), 8.60 (d, *J* = 8.67 Hz, 1H), 8.51 (d, *J* = 8.67 Hz, 1H), 8.40 (d, *J* = 4.71 Hz, 2H), 8.22 (d, *J* = 4.71 Hz, 2H), 8.10 (t, *J* = 1.66 Hz, 2H), 7.87-7.82 (m, 1H), 7.78 (t, *J* = 1.88 Hz, 2H), 7.73-7.70 (m, 2H), 7.66-7.63 (m, 1H), 7.44 (t, *J* = 1.70 Hz, 2H), 7.26 (s, 1H), 3.13 (s, 6H), 3.11 (s, 12H), 1.92 (s, 6H), 1.83 (s, 12H), 1.74 (s, 18H), 1.36 (s, 18H). **^{13}C NMR** (75 MHz, CD_2Cl_2, 25°C): δ 153.42, 149.80, 149.70, 149.18, 148.93, 148.89, 147.91, 147.30, 147.12, 146.26, 142.25, 142.23, 141.03, 137.99, 137.19, 136.74, 136.60, 136.02, 135.91, 133.76, 132.53, 132.32, 131.97, 131.86, 131.38, 131.24, 131.20, 129.52, 129.33, 129.09, 128.74, 126.63, 125.98, 124.85, 121.33, 121.20, 118.55, 116.35, 96.30, 95.94, 85.48, 35.65, 35.30, 32.34, 31.84, 25.73, 15.30, 12.45, 11.74, 11.58. **ESI HRMS** *m/z* 1532.63227; calcd for $C_{96}H_{97}BN_8O_2Zn_2$ (M^+) 1532.64195.

Zinc(II) 5-[10,20-Bis-(3,5-di-tert-butyl-phenyl)-porphyrin-5-yl]-10,20-bis-(3,5-di-tert-butyl-phenyl)-15-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-porphyrin (10a)

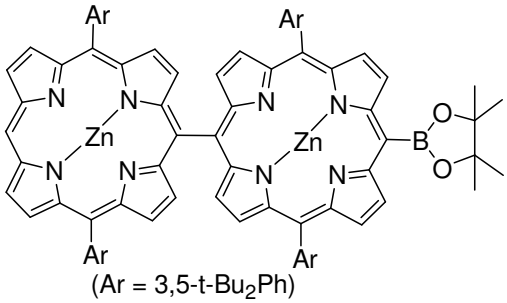
5-Bromo-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin (0.12 g, 0.1566 mmol), 5,15-di-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-20,25-(3,5-di-tert-butylphenyl)-porphyrin (0.187 g, 0.1866 mmol), Cs_2CO_3 (0.076 g, 0.235 mmol), and $Pd(PPh_3)_4$ (0.018 g, 0.0157 mmol) were dissolved in a mixture of dry DMF (6 mL) and dry toluene (12 mL). The mixture was reacted according to the conditions described above for preparation of **8** for 5 h. Purple crystalline solid (0.098 g, 52% yield), m.p. > 300°C. **UV/vis** (THF) λmax (log ε) 316 (4.34), 417 (5.28), 447 (5.13), 514 (4.44), 560 (4.45), 592 (4.06). **^{1}H NMR** (300 MHz, $CDCl_3$, 25°C): δ 10.37 (s, 1H), 10.02 (d, *J* = 4.71 Hz, 2H), 9.46 (d, *J* = 4.71 Hz, 2H), 9.19 (d, *J* = 4.71 Hz, 2H), 9.14 (d, *J* = 4.71 Hz, 2H), 8.75 (d, *J* = 4.71 Hz, 2H), 8.67 (d, *J* = 4.90 Hz, 2H), 8.18 (d, *J* = 4.71 Hz, 2H), 8.13 (d, *J* = 1.88 Hz, 4H), 8.11 (d, *J* = 1.88 Hz, 4H), 8.09 (d, *J* = 4.71 Hz, 2H), 7.74 (m, 4H), 1.94 (s, 12H), 1.48 (s, 72H), - 2.29 (br s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$, 25°C): δ 154.26, 154.11, 150.84, 150.20, 148.89, 148.49, 141.73, 140.64, 134.13, 133.22, 132.72, 132.01, 129.95, 129.61, 123.12, 121.85, 121.03, 120.83, 120.58, 118.82, 85.36, 35.04, 35.02, 31.74, 31.72, 25.47. **ESI HRMS** *m/z* 1559.85262; calcd for $C_{102}H_{116}BN_8O_2Zn$ (MH^+) 1559.86155.



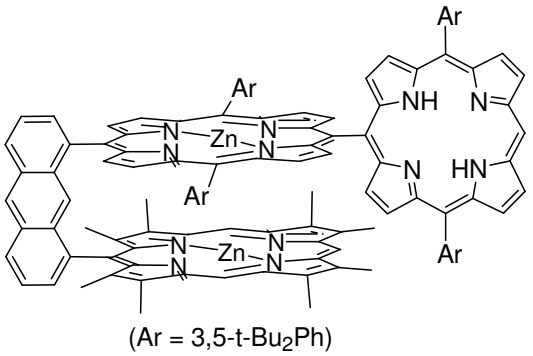
Zinc(II) 5-[10,20-Bis-(3,5-di-tert-butyl-phenyl)-porphyrin-5-yl]-10,20-bis-(3,5-di-tert-butyl-phenyl)-15-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-porphyrin (10b)

Prepared according to the procedure outlined for **10a**.

Purple crystalline solid (86% yield), m.p. > 300°C. **UV/vis** (THF) λmax (log ε) 418 (5.24), 453 (5.20), 562 (4.59). **^{1}H NMR** (300 MHz, d^8-THF, 25°C): δ 10.30 (s, 1H), 9.95 (d, *J* = 4.71 Hz, 2H), 9.42 (d, *J* = 4.33 Hz, 2H), 9.01 (d, *J* = 4.52 Hz, 2H), 8.93 (d, *J* = 4.52 Hz, 2H), 8.58 (d, *J* = 4.52 Hz, 2H), 8.53 (d, *J* = 4.71 Hz, 2H), 8.11 (dd, J_1 = 5.52 Hz, J_2 = 1.79 Hz, 8H), 8.03 (d, *J* = 4.52 Hz, 2H), 8.00 (d, *J* = 4.71 Hz, 2H), 7.78 (t, *J* = 1.51 Hz, 4H), 1.89 (s, 12H), 1.47 (s, 72H). **^{13}C NMR** (75 MHz, CD_2Cl_2, 25°C): δ 154.90, 154.63, 151.57, 151.27, 150.78, 150.60, 150.41, 149.32, 149.24, 142.31 142.15, 134.32, 134.14, 133.42, 133.34, 132.58, 132.28, 130.21, 123.64, 123.44, 121.57, 85.95, 35.48, 32.00, 25.81. **ESI HRMS** *m/z* 810.37814; calcd for $C_{102}H_{113}BN_8O_2Zn_2$ (M^{2+}) 810.37814.



Zinc(II) 5-{8-[zinc(II)-10,20-bis-(3,5-di-tert-butyl-phenyl)-15-(10,20-bis-(3,5-di-tert-butyl-phenyl)-porphyrin-5-yl)-porphyrin-5-yl]-anthracen-1-yl}-2,3,7,8,12,13,17,18-octamethyl-porphyrin (11)



(Ar = 3,5-t-Bu_2Ph)

Porphyrin **8** (0.064 g, 0.0417 mmol), 5-bromo-10,20-bis(3,5-di-*tert*-butylphenyl)-porphyrin (0.064 g, 0.0836 mmol), Cs_2CO_3 (0.02 g, 0.0625 mmol), and $Pd(PPh_3)_4$ (0.005 g, 0.0043 mmol) were dissolved in a mixture of dry DMF (2 mL) and dry toluene (4 mL). The mixture was reacted according to the conditions described above for the preparation of **9** over 24 h. The separation of target product from the starting materials and by-products was performed by column chromatography on silica gel, using hexanes-dichloromethane (content of CH_2Cl_2 was gradually increased from 30 to 50 vol%), followed by preparative size exclusion chromatography (BioRad Bio-Beads SX-1 packed in CH_2Cl_2 in a 4 × 50 cm gravity-flow column; flow rate 4 mL min^{-1}). Dark-brown crystalline solid (0.025 g, 29% yield), m.p. > 300°C. **UV/vis** (THF) λmax (log ε) 411 (5.34), 457 (4.93), 513 (4.28), 565 (4.30). **^{1}H NMR** (300 MHz, CD_2Cl_2, 25°C): δ 10.37 (s, 1H), 9.60 (s, 1H), 9.49 (d, *J* = 4.52 Hz, 1H), 9.47 (s, 2H), 9.45 (d, *J* = 4.14 Hz, 1H), 9.19 (s, 1H), 9.13 (d, *J* = 4.89 Hz, 1H), 9.05 (d, *J* = 4.14 Hz, 1H), 8.89 (d, *J* = 4.14 Hz, 1H), 8.89 (d, *J* = 4.14 Hz, 1H), 8.66 (d, *J* = 9.03 Hz, 1H), 8.89 (d, *J* = 4.14 Hz, 1H), 8.63 (d, *J* = 7.53 Hz, 1H), 8.61 (d, *J* = 4.52 Hz, 2H), 8.48 (d, *J* = 4.52 Hz, 2H), 8.40 (d, *J* = 4.89 Hz, 1H), 8.37 (d, *J* = 4.89 Hz, 2H), 8.35 (d, *J* = 1.88 Hz, 2H), 8.15 (s, 2H), 8.13 (s, 1H), 8.01 (d, *J* = 1.88 Hz, 2H), 8.00 (s, 1H), 7.88-7.83 (m, 3H), 7.69 (s, 1H), 7.66 (s, 1H), 7.65 (s, 3H), 7.61 (d, *J* = 6.02 Hz, 1H), 7.54 (s, 2H), 7.47 (d, *J* = 4.89 Hz, 1H), 6.96 (d, *J* = 4.52 Hz, 1H), 3.27 (s, 6H), 3.20 (s, 6H), 3.15 (s, 6H), 2.00 (s, 6H), 1.76 (s, 18H), 1.51 (s, 18H), 1.39 (s, 18H), 1.29 (s, 18H), -2.49 (br. s, 2H). **ESI HRMS** *m/z* 2091.98056; calcd for $C_{138}H_{139}N_{12}Zn_2$ (MH^+) 2091.98232.

II. NMR and mass spectra

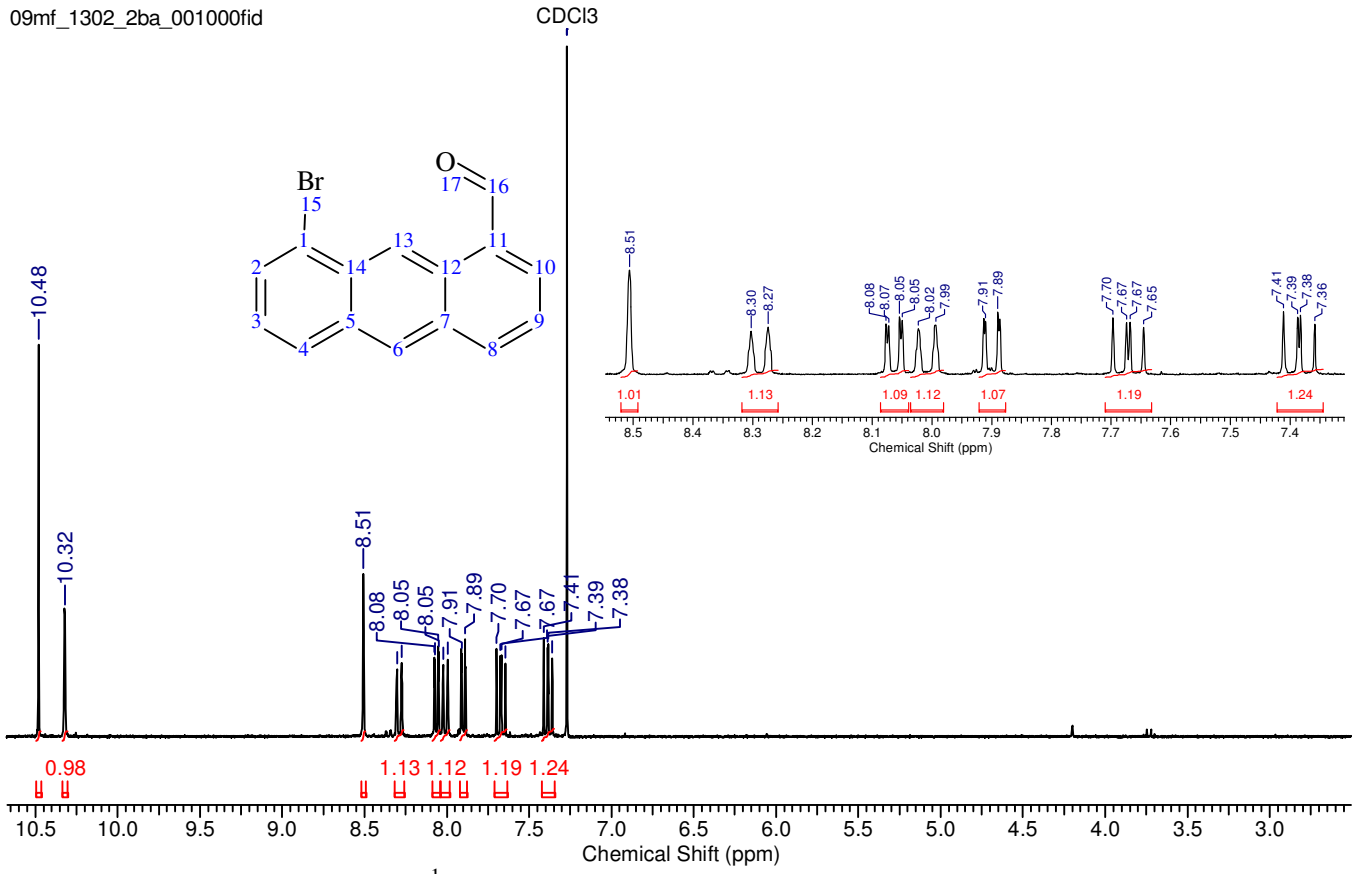


Figure S1. ^{1}H NMR specrum of **4** (300 MHz, $CDCl_3$, 298 K).

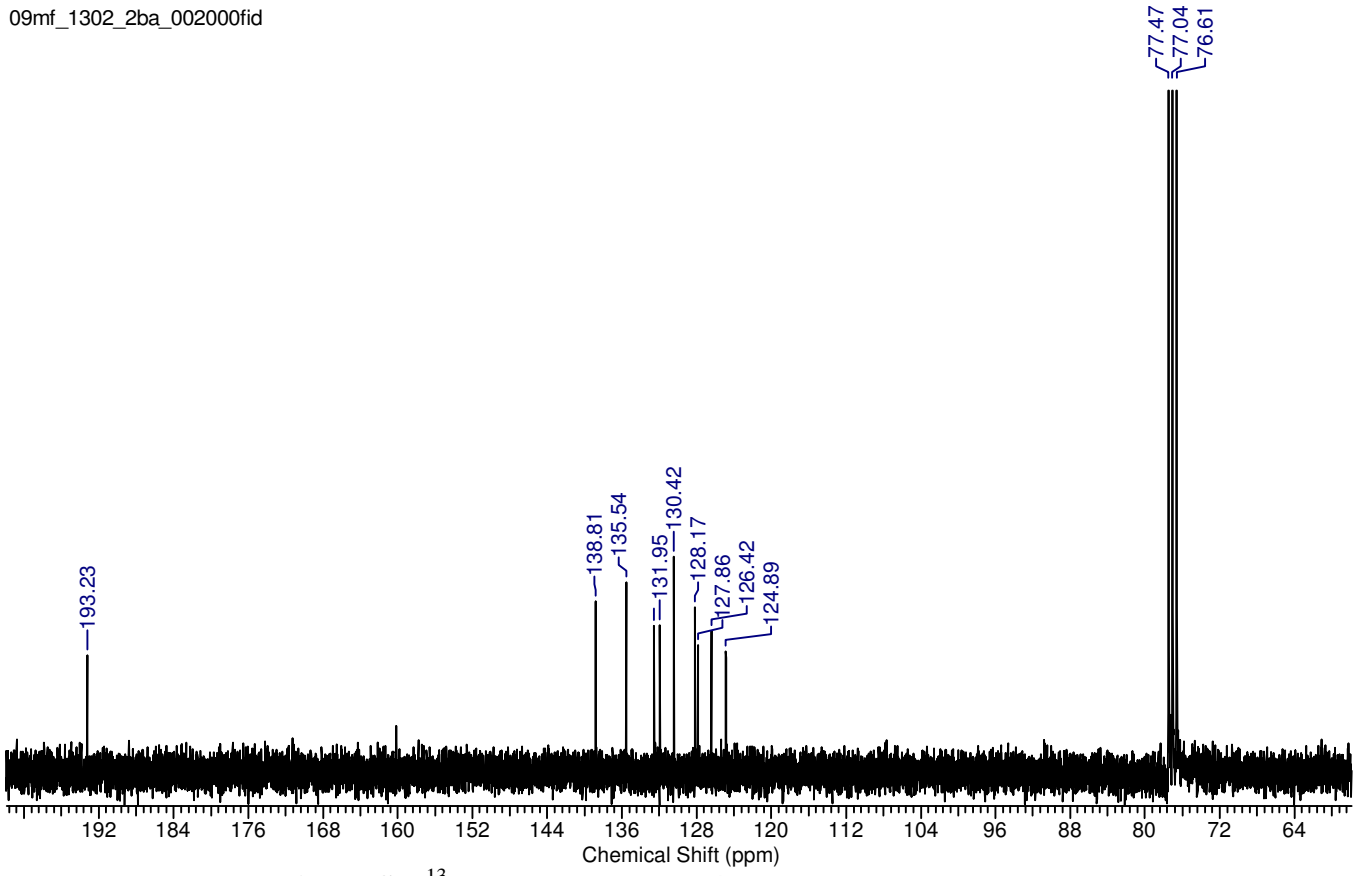


Figure S2. ^{13}C NMR specrum of **4** (300 MHz, $CDCl_3$, 298 K).

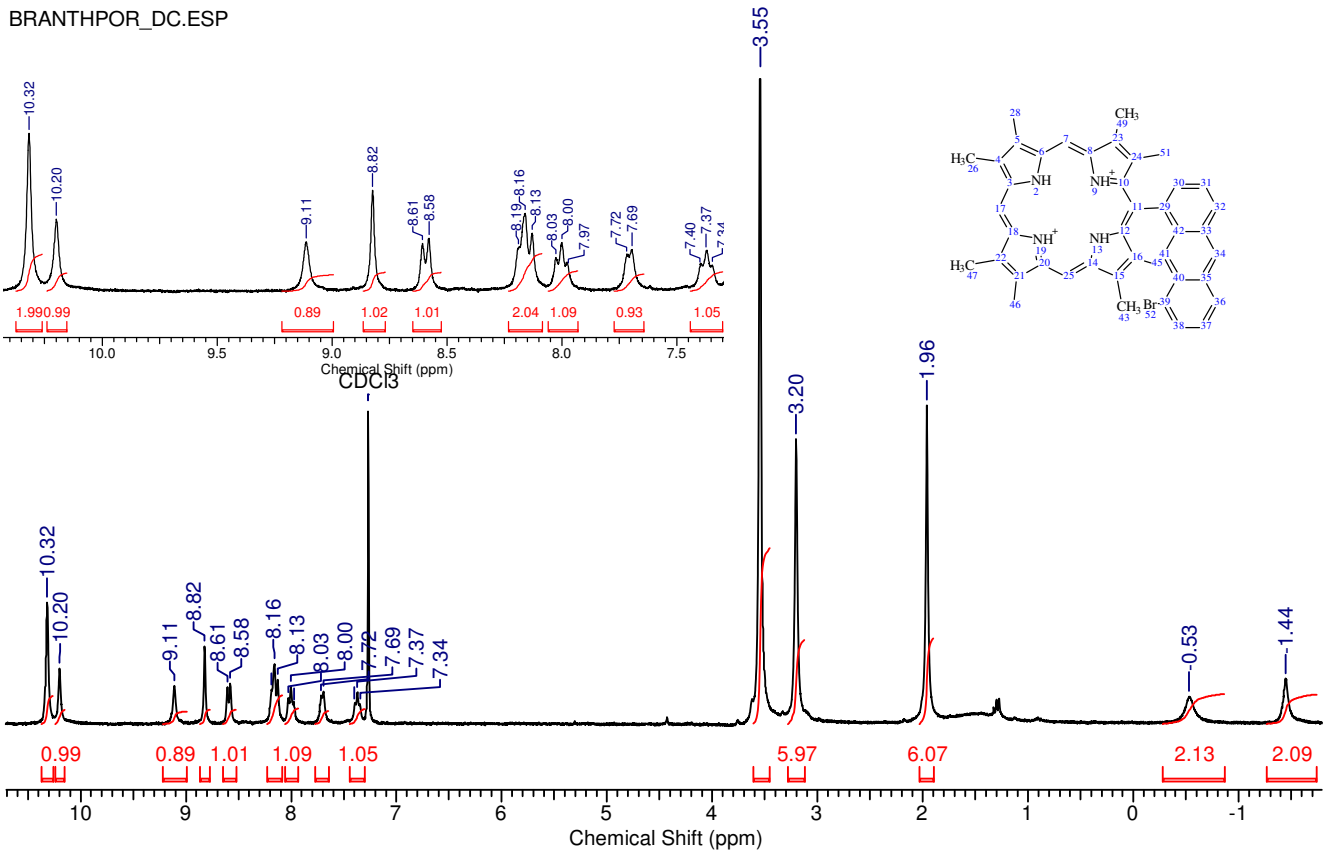


Figure S3. ^{1}H NMR specrum of **6a** (300 MHz, $CDCl_3$/TFA, 298 K).

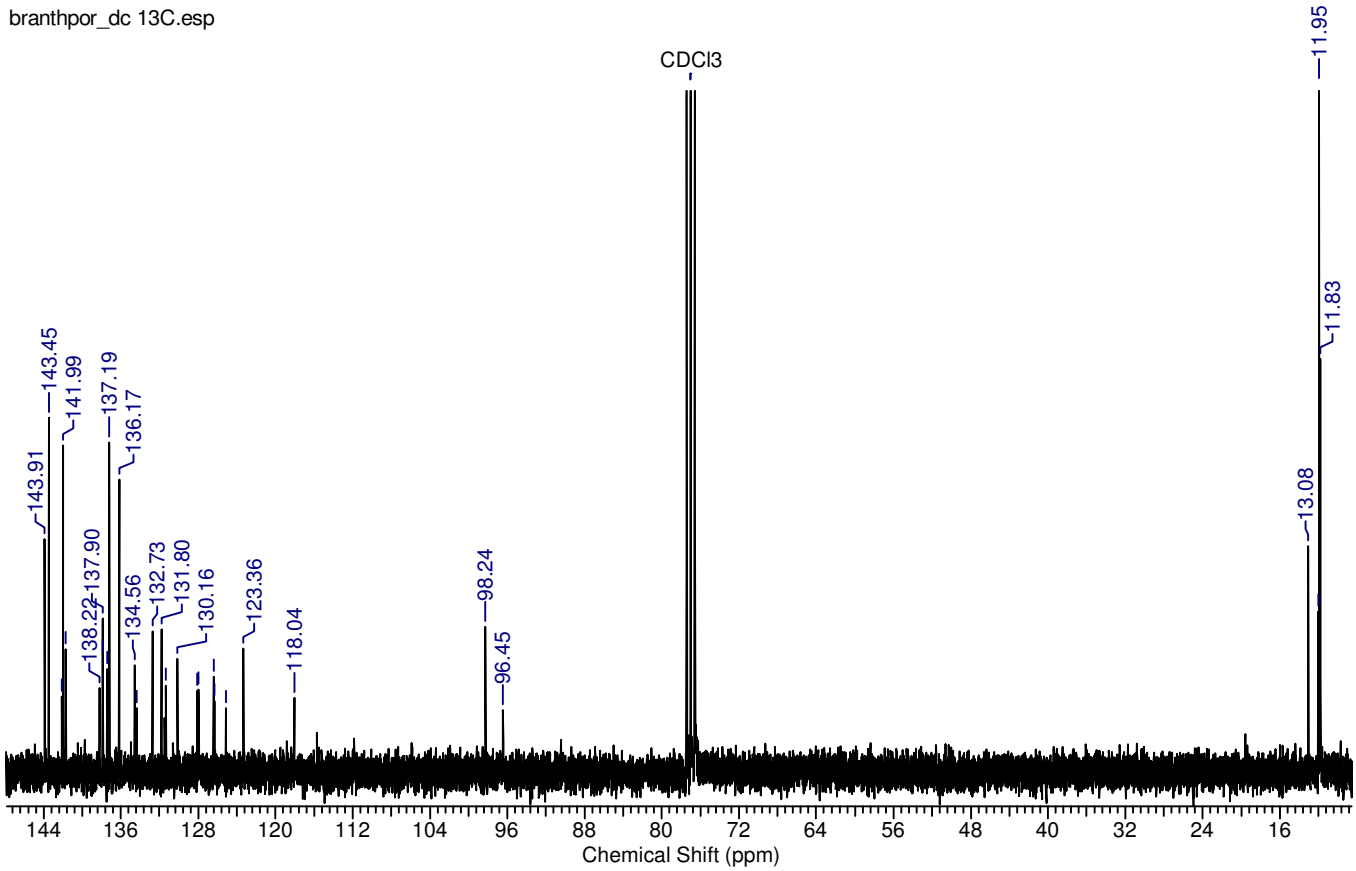
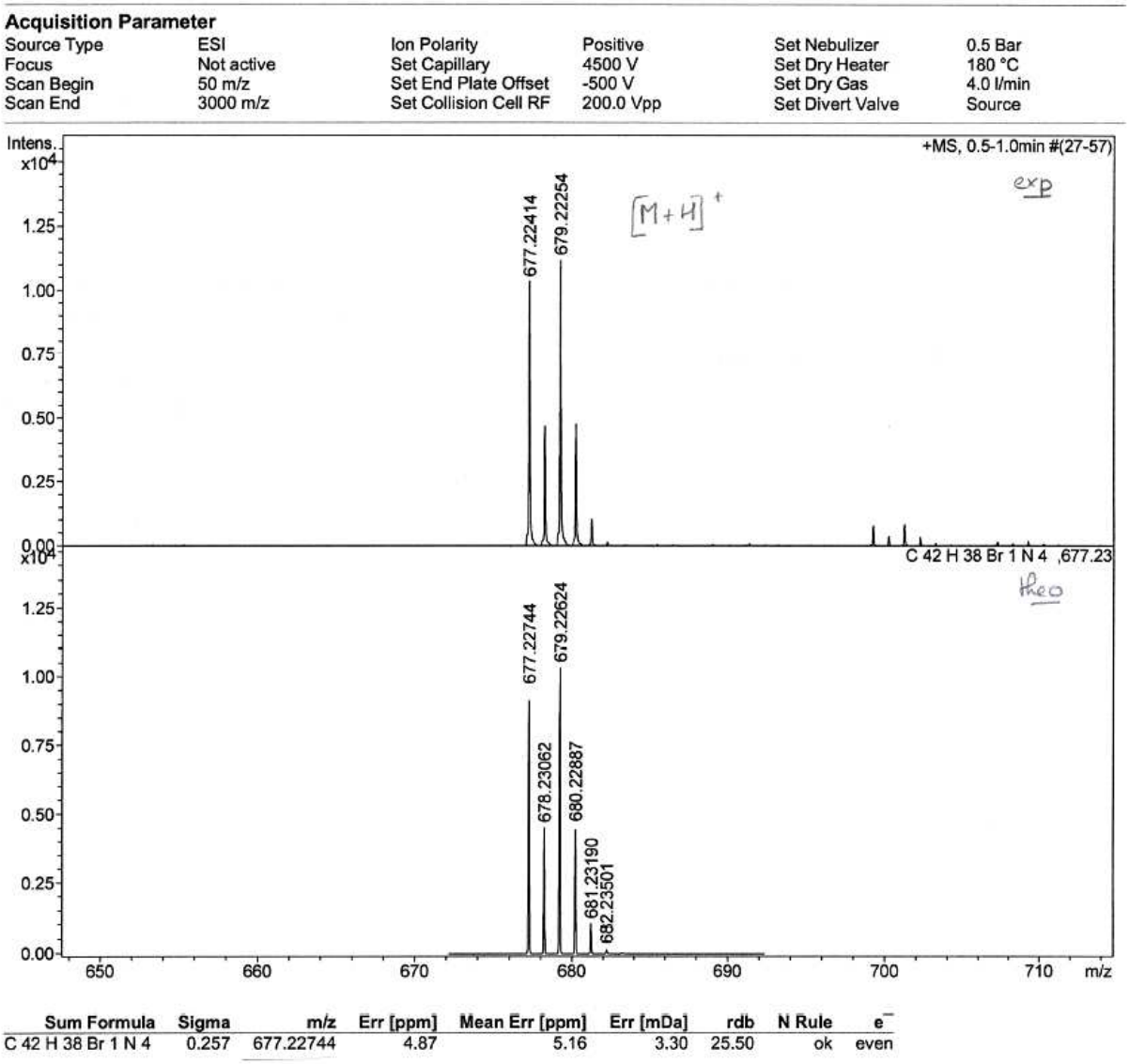


Figure S4. ^{13}C NMR specrum of **6a** (75 MHz, $CDCl_3$/TFA, 298 K).



Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 42 H 38 Br 1 N 4	0.257	677.22744	4.87	5.16	3.30	25.50	ok	even

Figure S5. ESI HRMS specrum of **6a** (positive mode).

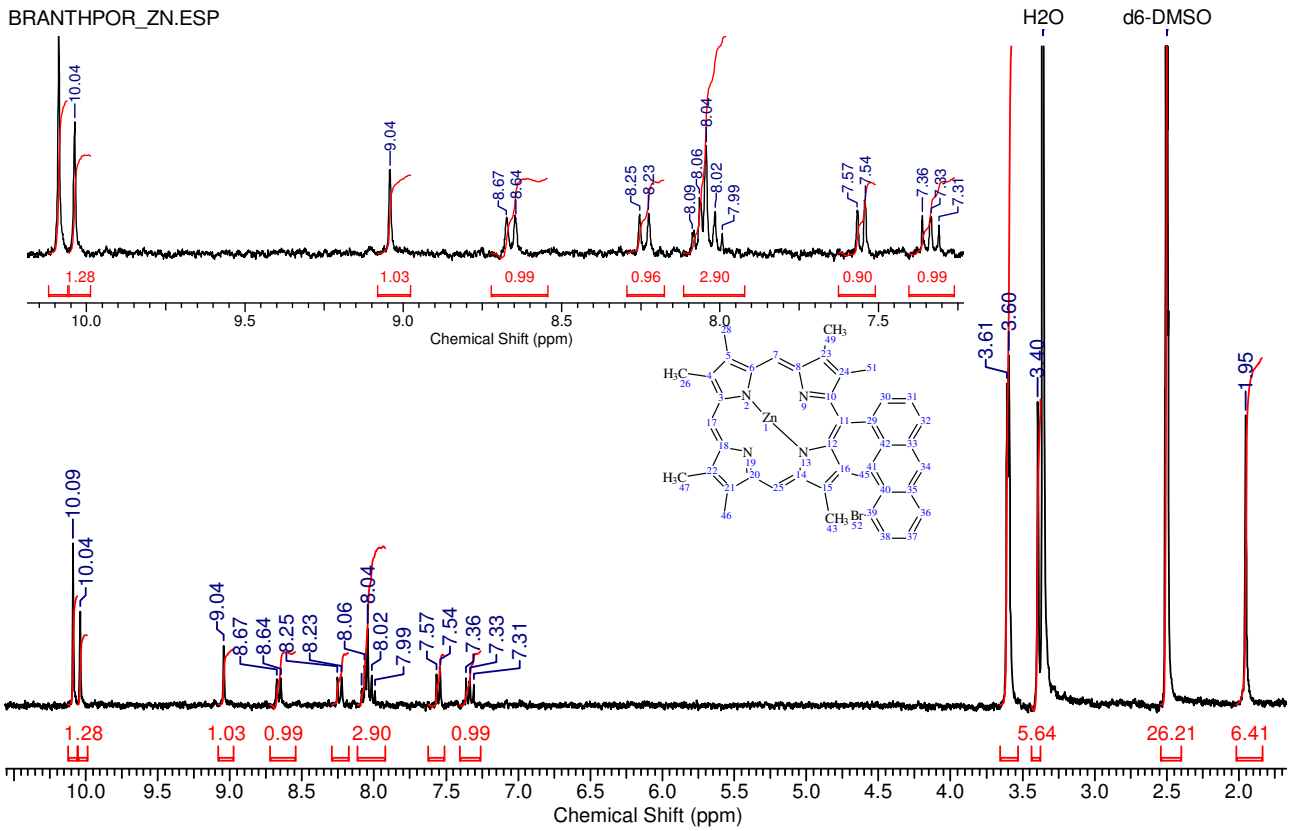
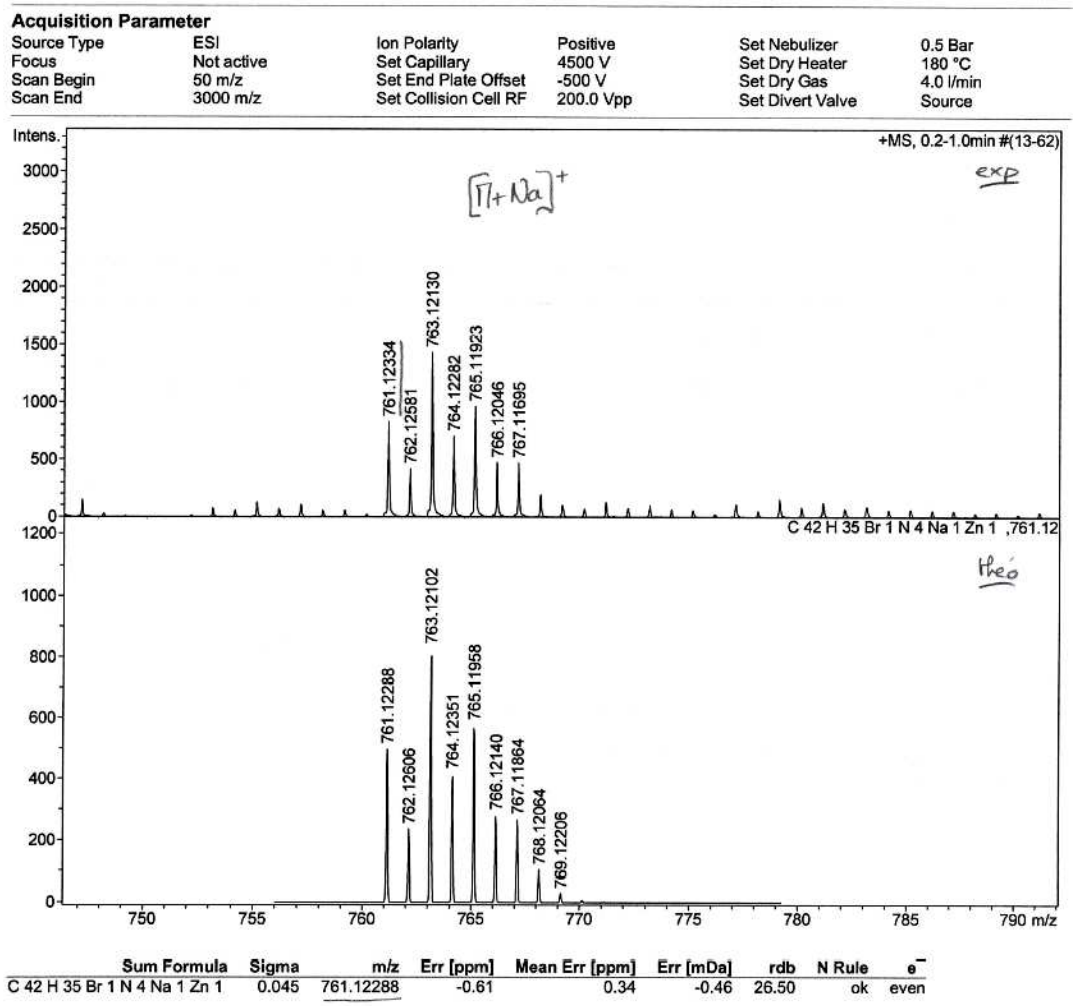


Figure S6. ^{1}H NMR specrum of **6b** (300 MHz, d^{6}-DMSO, 298 K).



Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 42 H 35 Br 1 N 4 Na 1 Zn 1	0.045	761.12288	-0.61	0.34	-0.46	26.50	ok	even

Figure S7. ESI HRMS specrum of **6b** (positive mode).

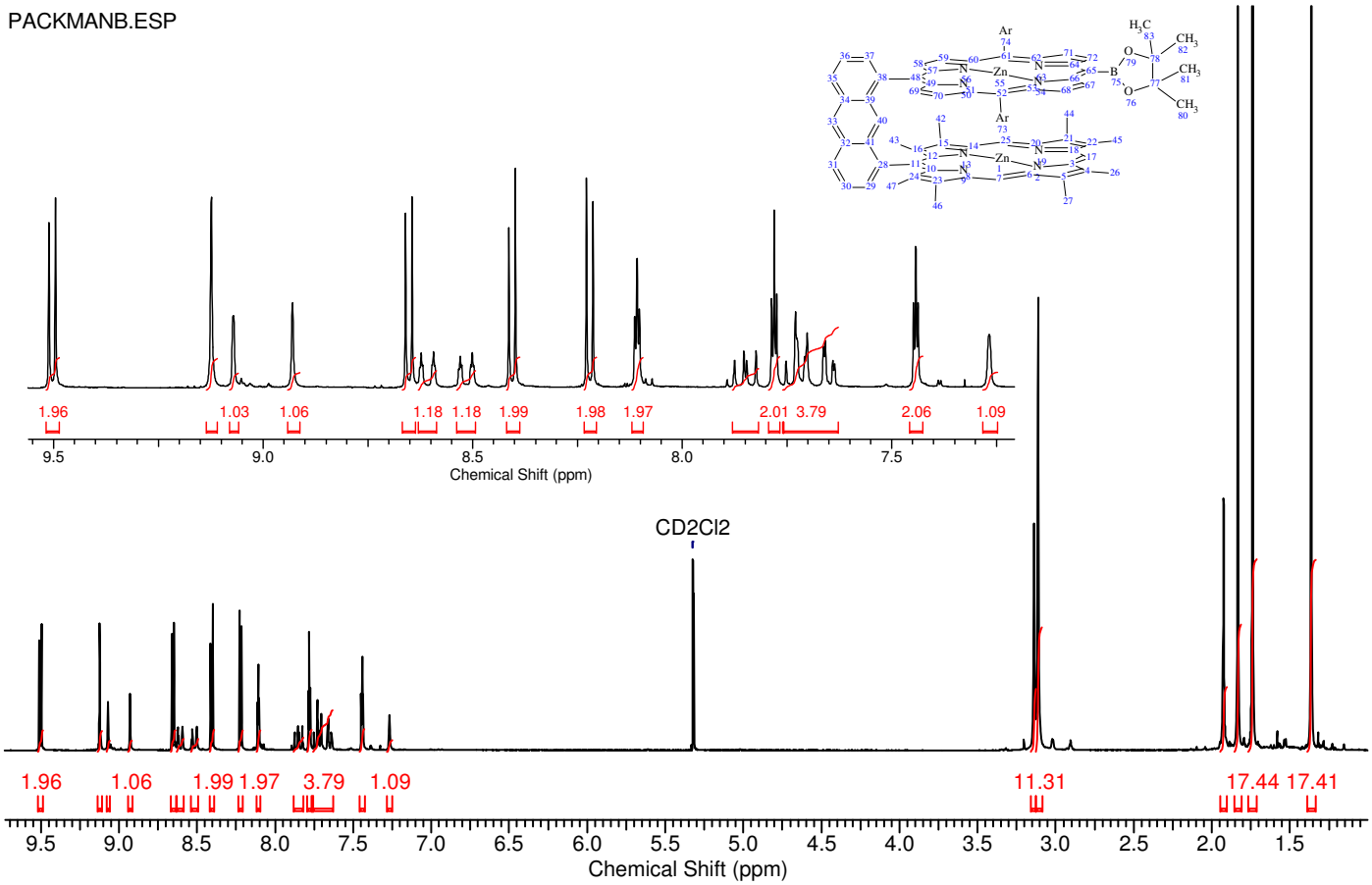


Figure S8. ^{1}H NMR specrum of **9** (300 MHz, CD_2Cl_2, 298 K).

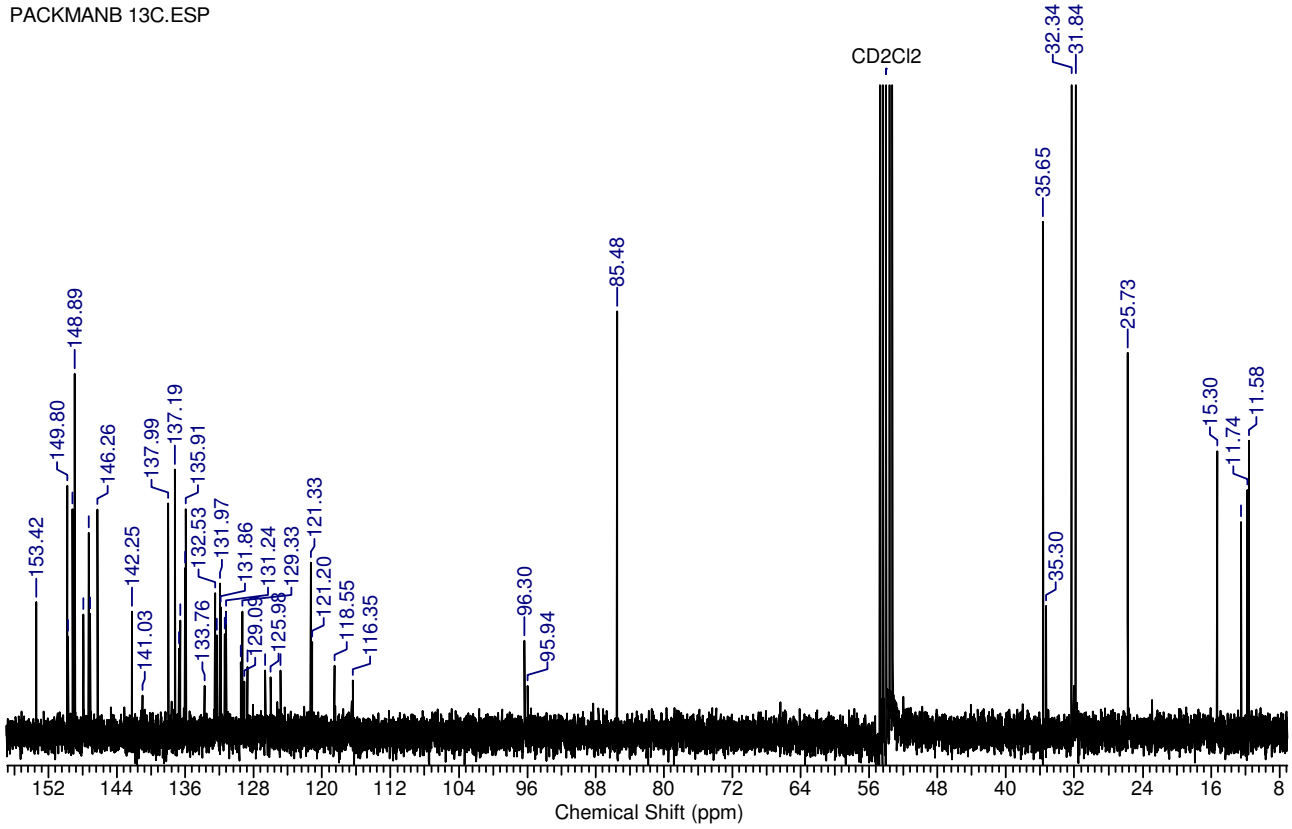


Figure S9. ^{13}C NMR specrum of **9** (75 MHz, CD_2Cl_2, 298 K).

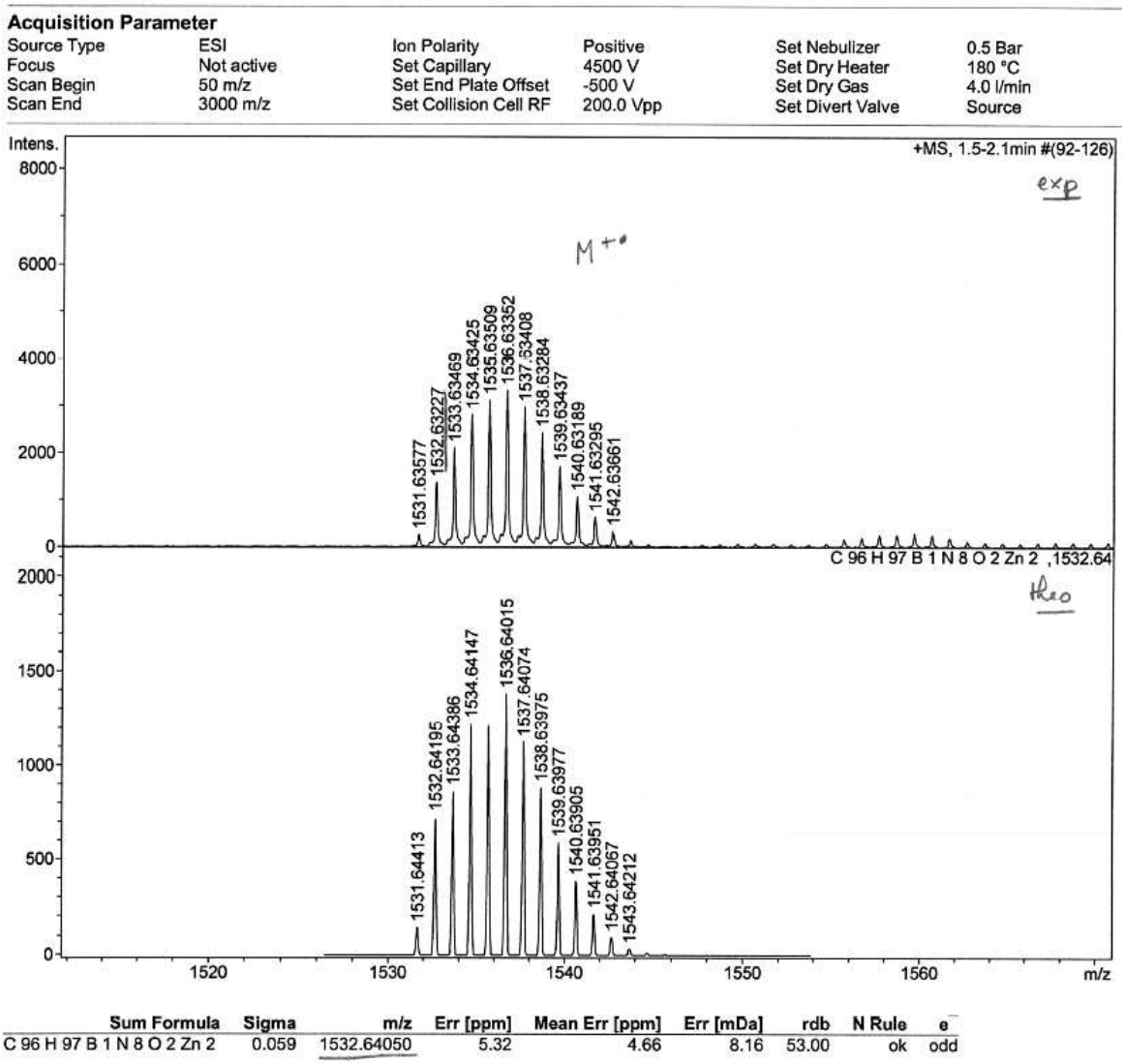


Figure S10. ESI HRMS specrum of **9** (positive mode).

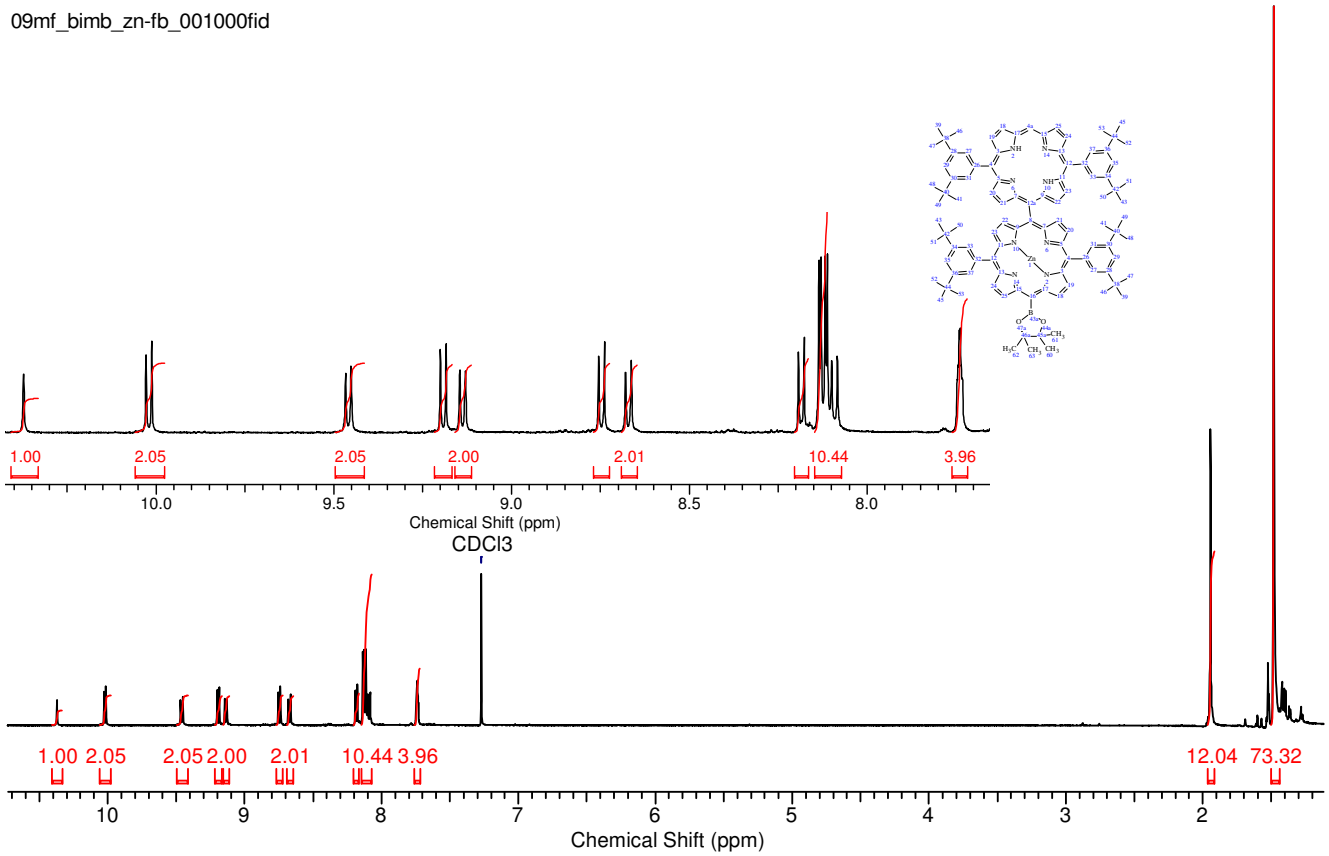


Figure S11. ^{1}H NMR specrum of **10a** (300 MHz, $CDCl_3$, 298 K).

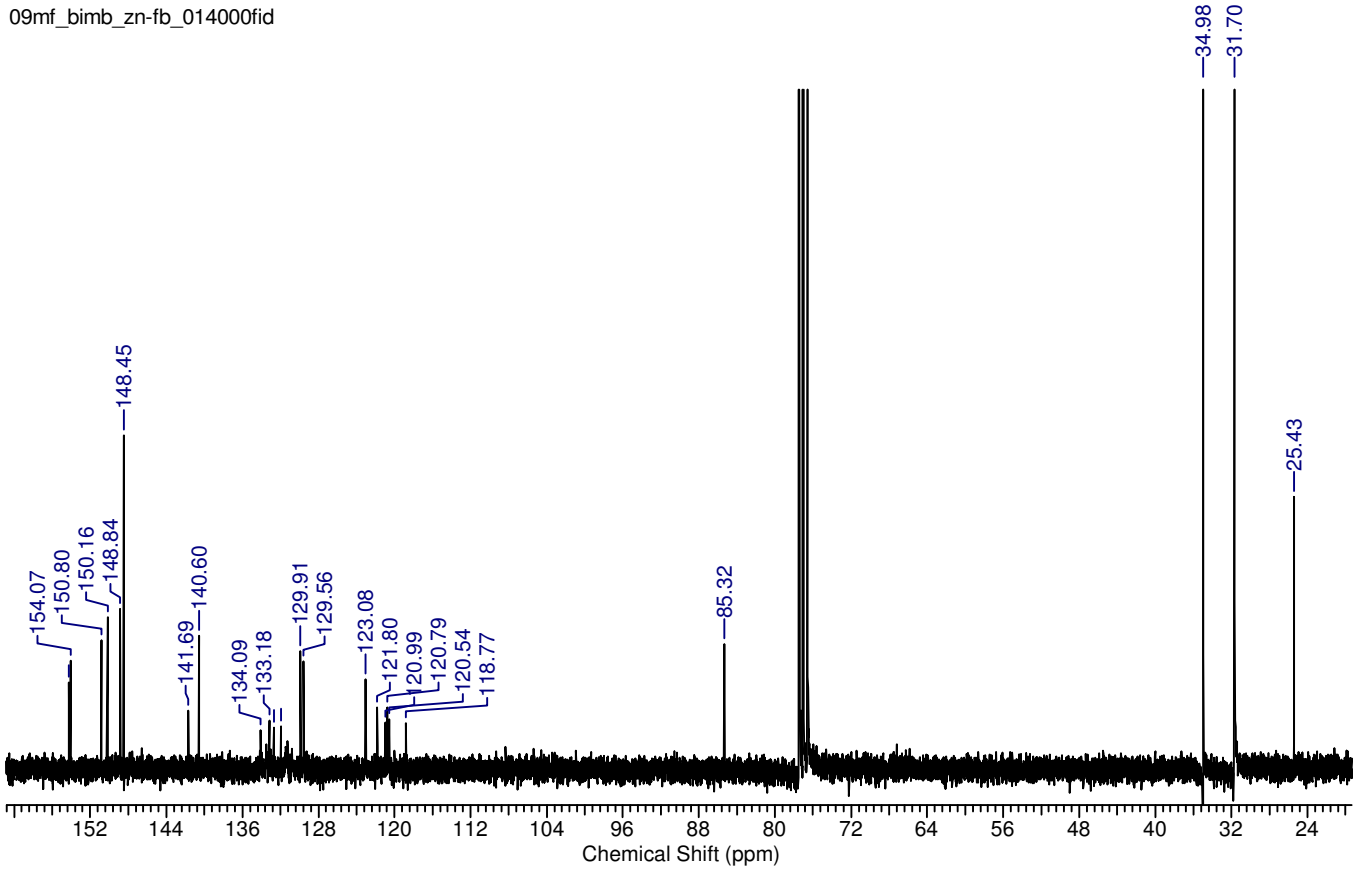


Figure S12. ^{13}C NMR specrum of **10a** (300 MHz, $CDCl_3$, 298 K).

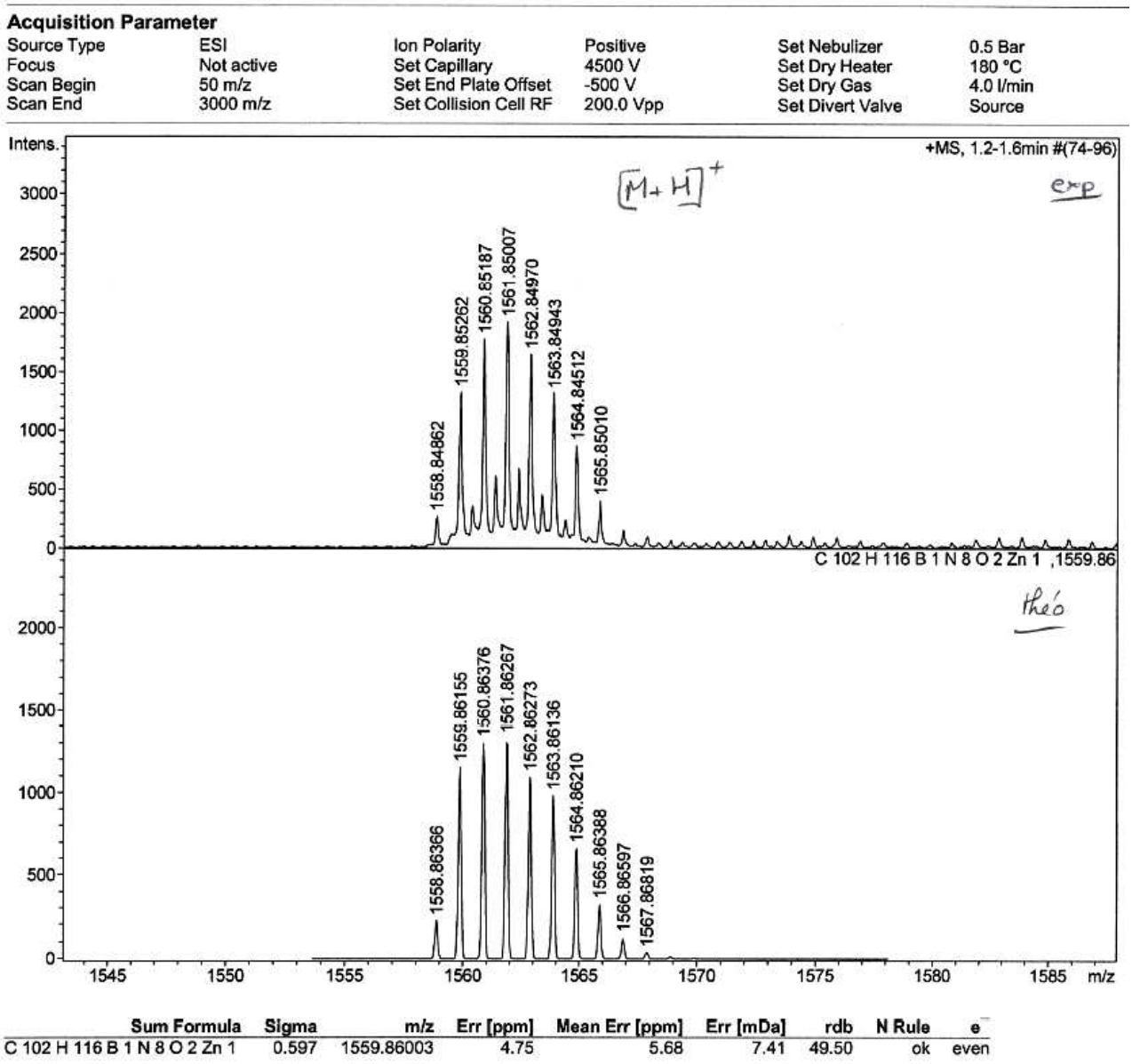


Figure S13. ESI HRMS specrum of **10a** (positive mode). Experimentally seen cluster of ions is a combination of $[M+H]^+$ and $[M+H]_2^{2+}$ clusters.

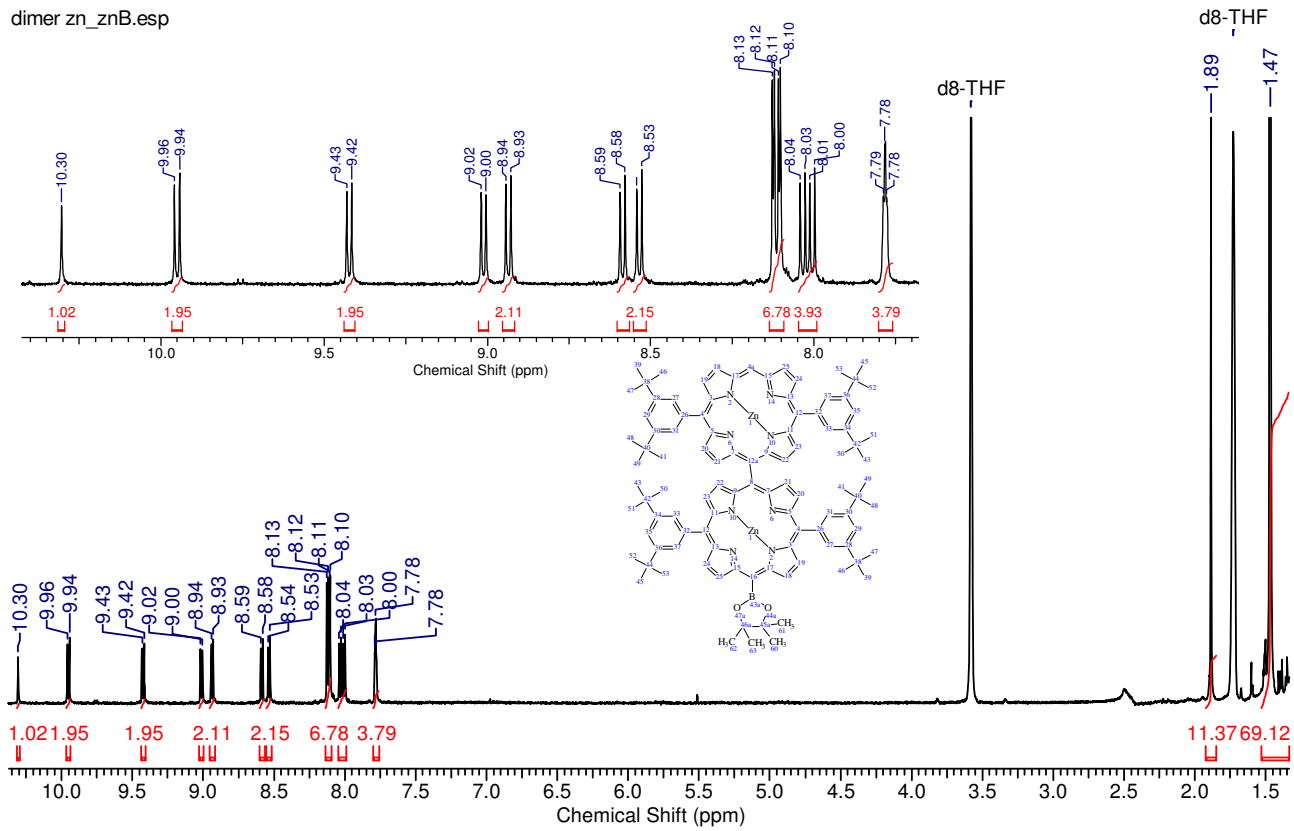


Figure S14. ^{1}H NMR specrum of **10b** (300 MHz, d^{8}-THF, 298 K).

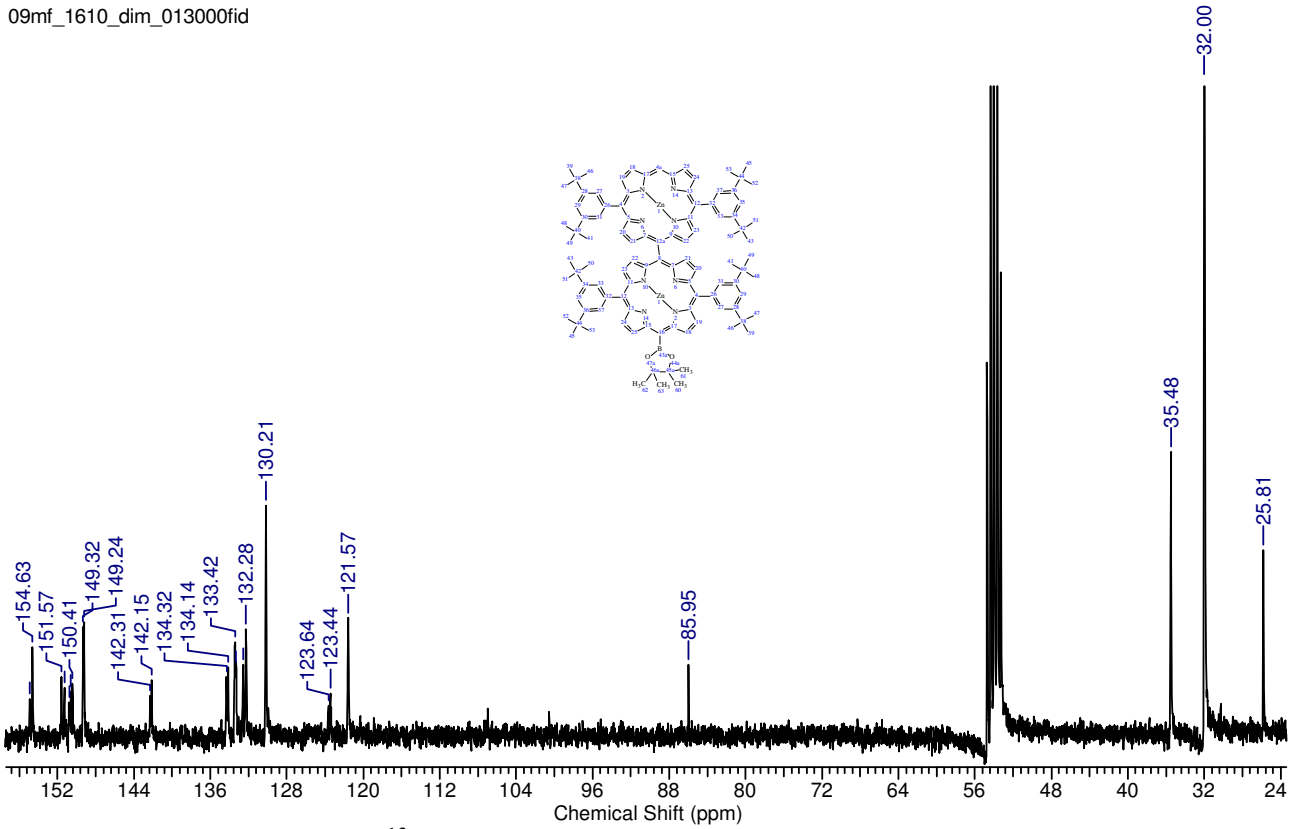


Figure S15. ^{13}C NMR specrum of **10b** (75 MHz, CD_2Cl_2, 298 K).

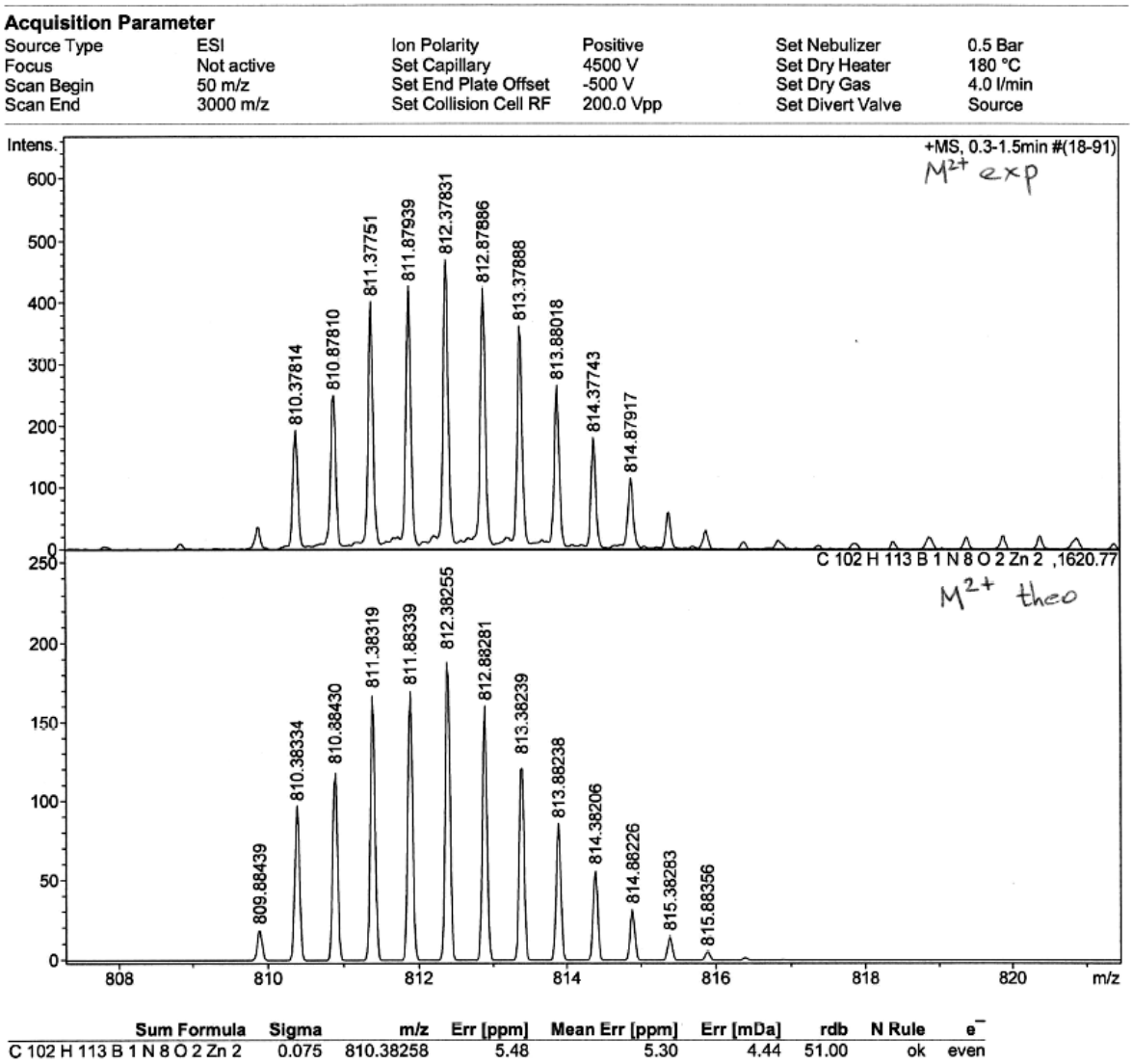


Figure S16. ESI HRMS specrum of **10b** (positive mode).

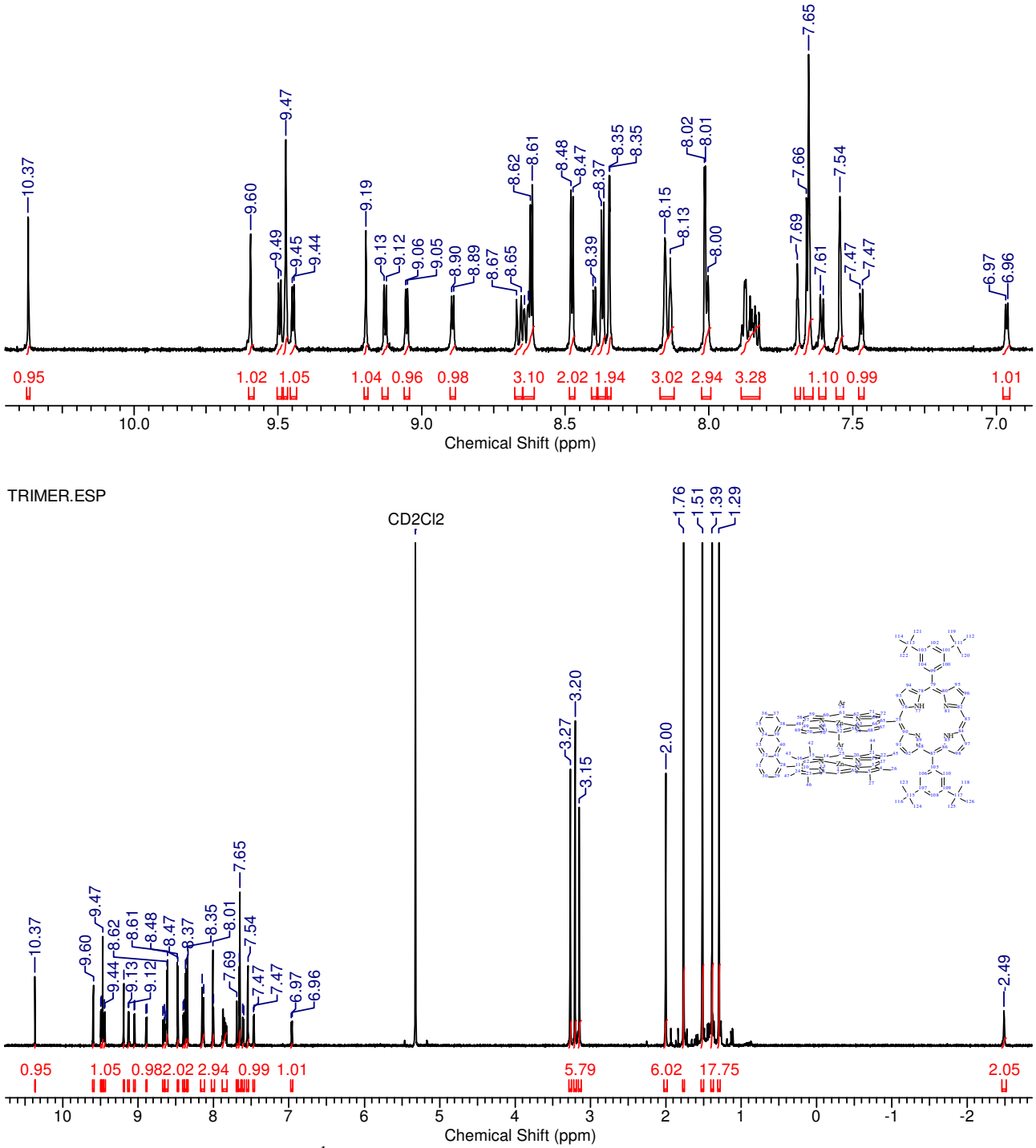


Figure S17. ^{1}H NMR specrum of **11** (600 MHz, CD_2Cl_2, 298 K).

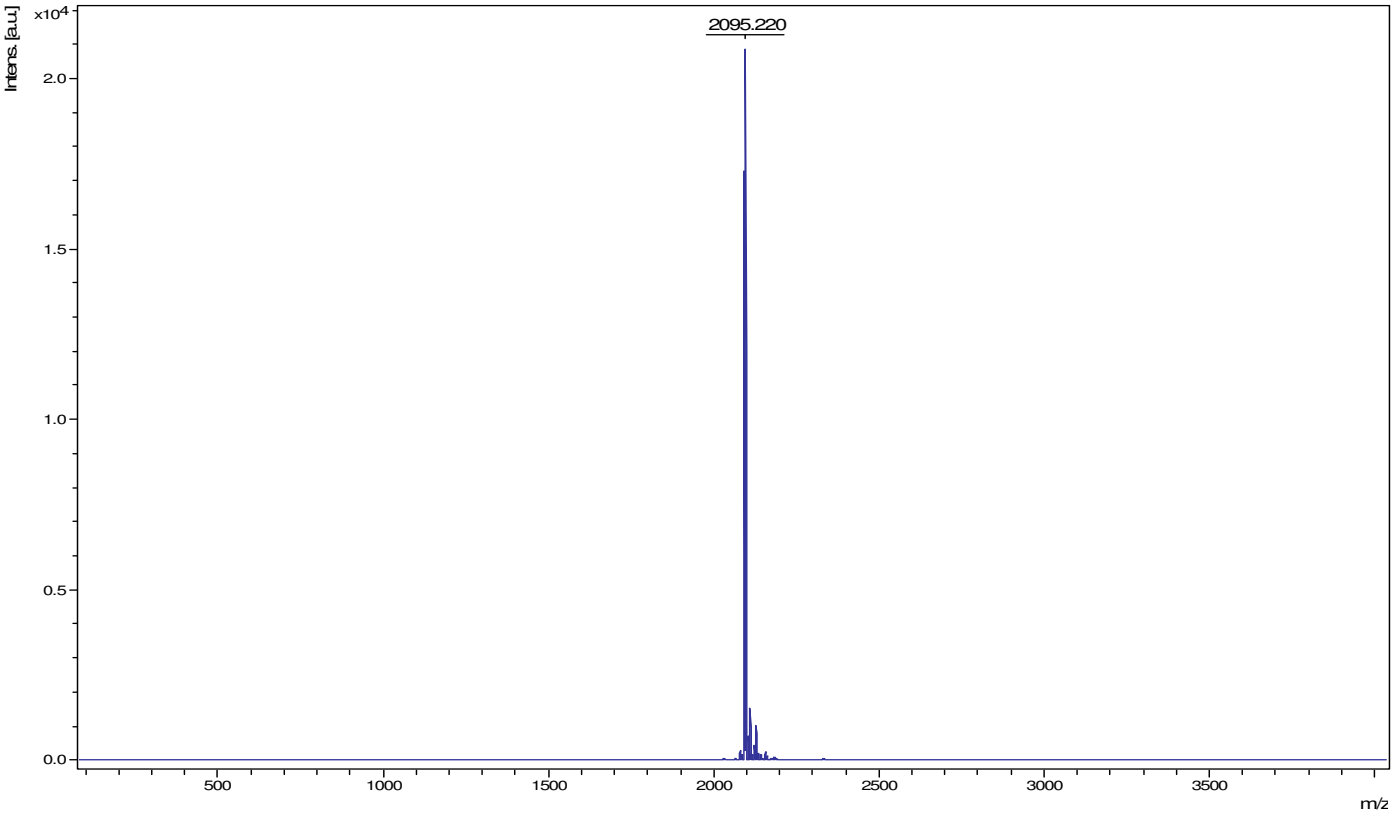


Figure S18. MALDI-TOF specrum of **11** (positive mode).

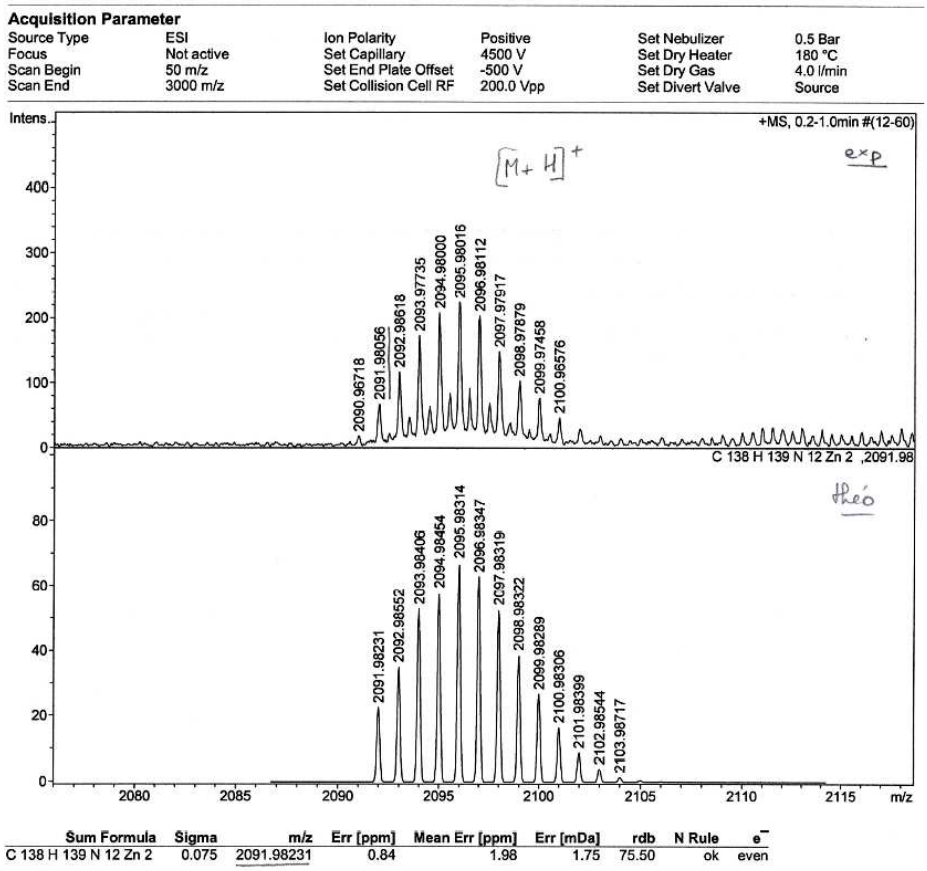
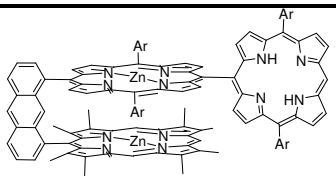
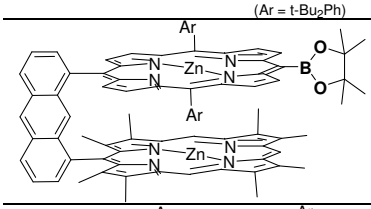
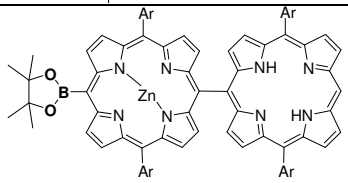
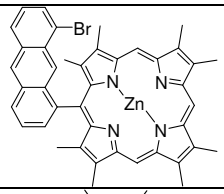
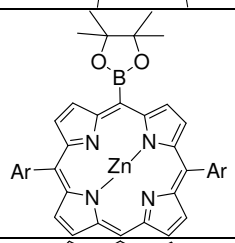
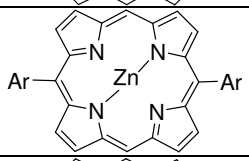
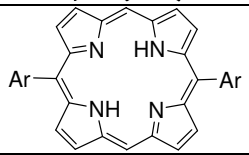


Figure S19. ESI HRMS specrum of **11** (positive mode). Experimentally seen cluster of ions is a combination of $[M+H]^+$ and $[M+H]_2^{2+}$ clusters.

III. Absorption, emission and excitation spectra

Porphyrin[a,b]	Absorption $\lambda_{max}(\varepsilon)$, nm	Fluorescence λ_{max} (λ_{ex}), nm	Φ_F[c]	τ_F, ns
 (Ar = t-Bu$_2$Ph)	411 (5.34) 457 (4.93) 513 (4.28) 565 (4.30)	655, 717 (560)	0.062	6.1
	407 (5.53) 431 (5.22) 545 (4.29) 577 (4.06)	608, 657 (550)	0.036	2.5
	316 (4.34) 417 (5.28) 447 (5.13) 514 (4.44) 560 (4.45) 592 (4.06)	650, 716 (560)	0.07	7.1
	335 (4.36) 411 (5.45) 541 (4.22) 577 (4.12)	580, 634 (540)	0.028	1.6
	417 548	595, 645 (550)	0.035	2.6
	413 (5.6) 506 (3.29) 543 (4.15) 580 (3.42)	587, 638 (540)	0.038	4.2
	407 (5.7) 502 (4.32) 535 (3.94) 576 (3.79)	635, 700 (535)	0.075	10.1

[a] In all cases Ar corresponds to 3,5-di-*tert*-butylphenyl group.
[b] All measurements were performed in deoxygenated THF at 298 K.
[c] Measured relative to the fluorescence of free-base tetraphenylporphyrin (ϕ_f=0.11).

Table 1. Photophysical parameters of the prepared porphyrins and corresponding semiproducts.

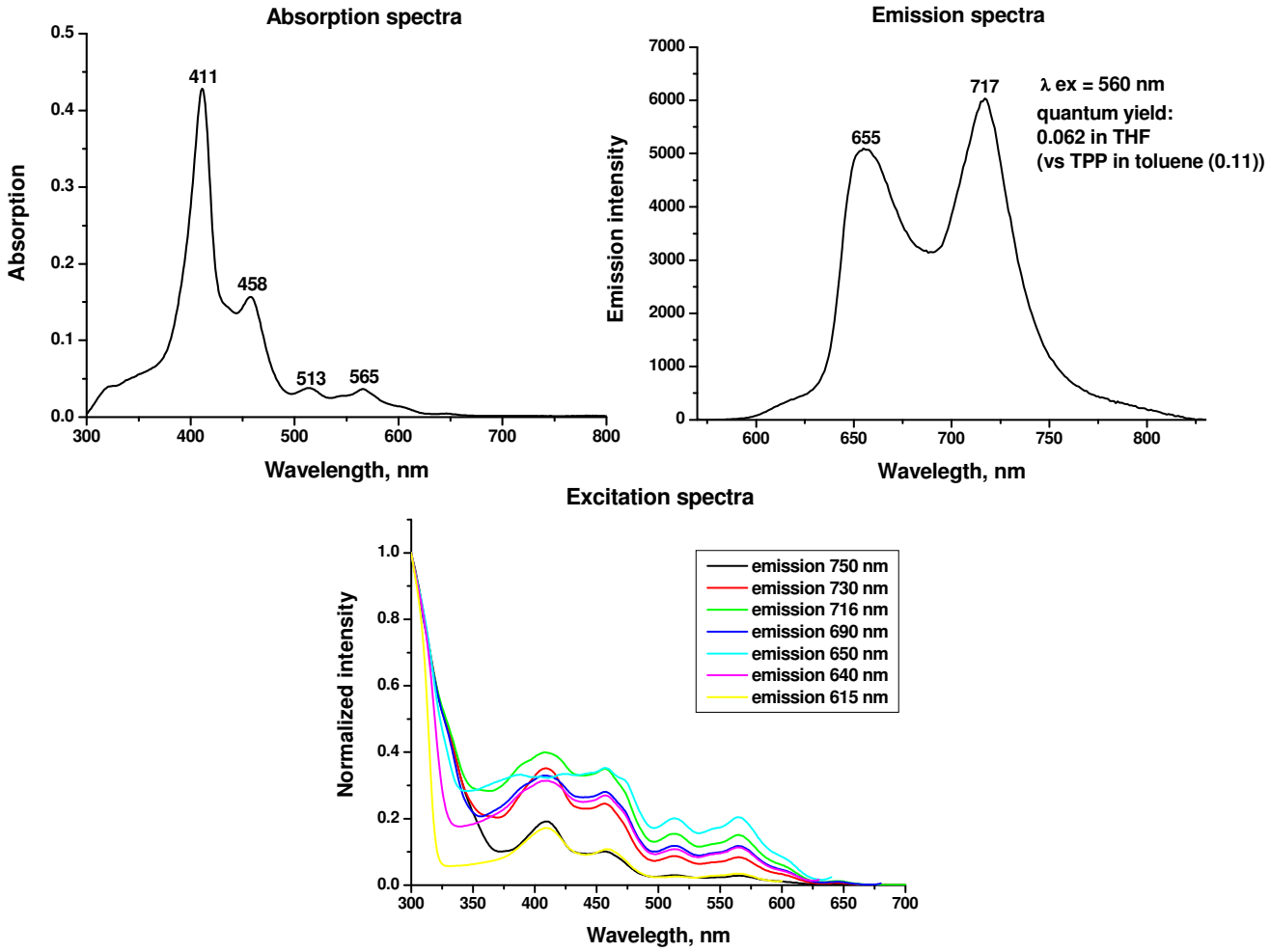


Figure S20. Optical spectra of trimer **11**.

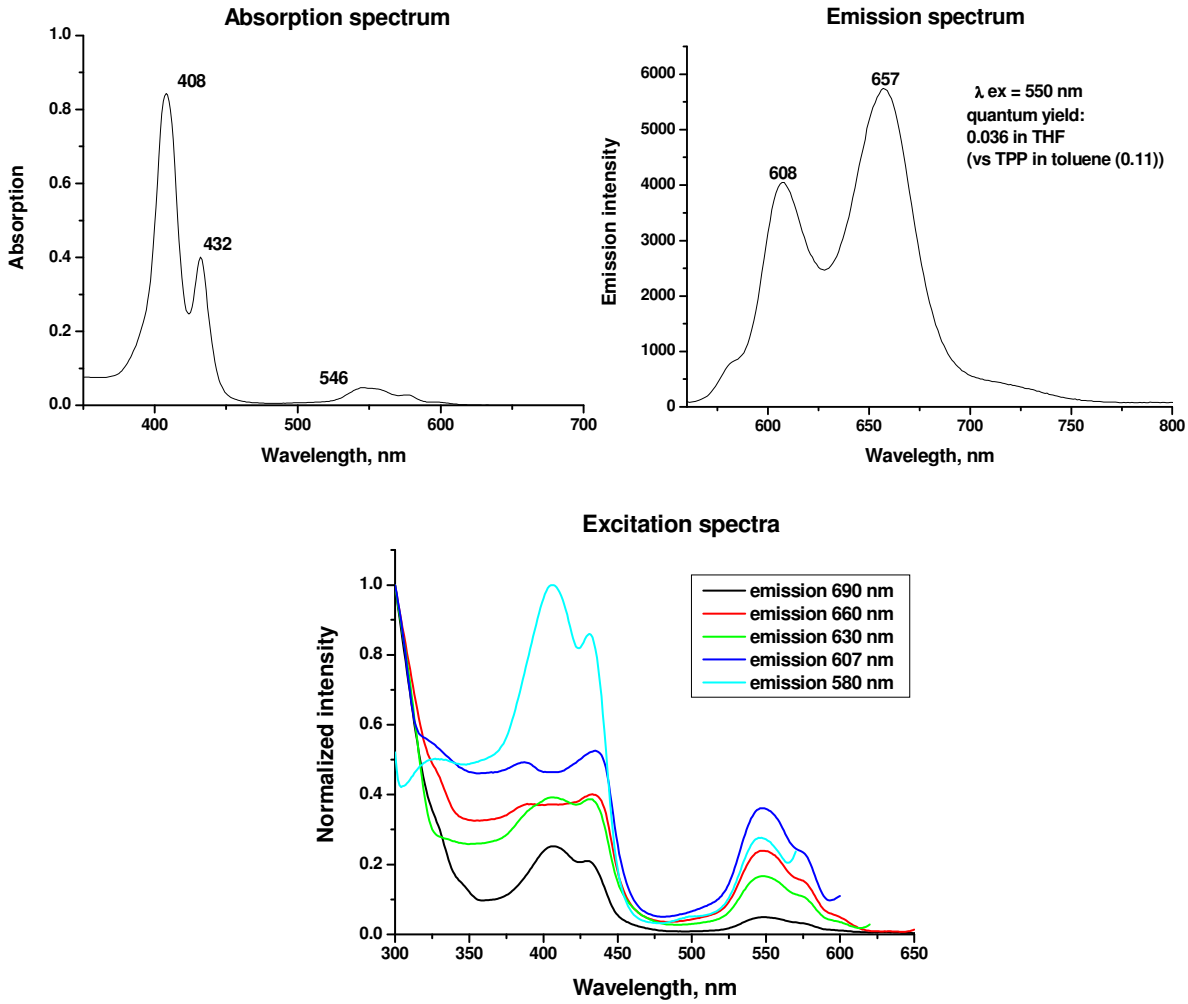


Figure S21. Optical spectra of face-to-face dimer **9**.

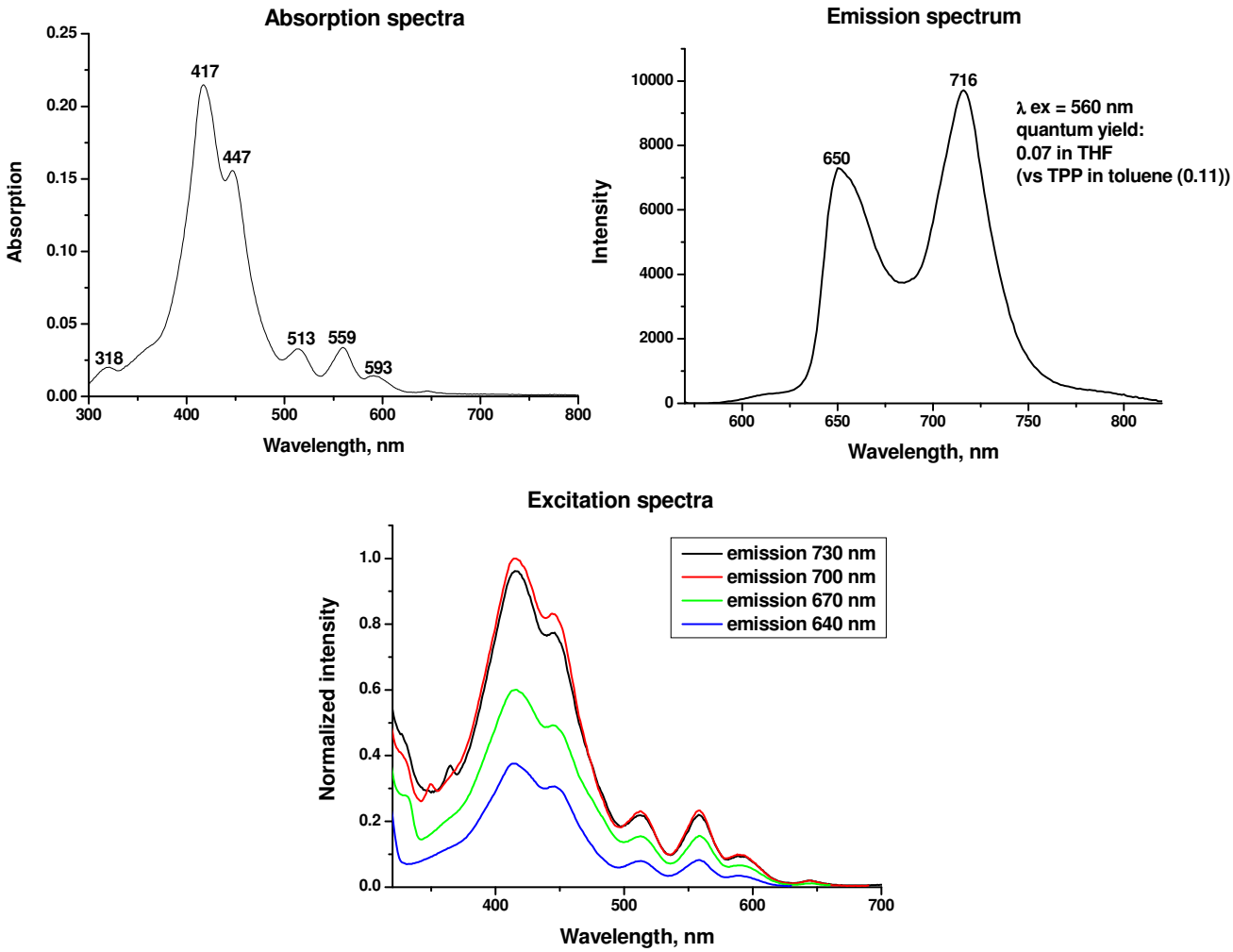


Figure S22. Optical spectra of *meso-meso* linked dimer **10a**.

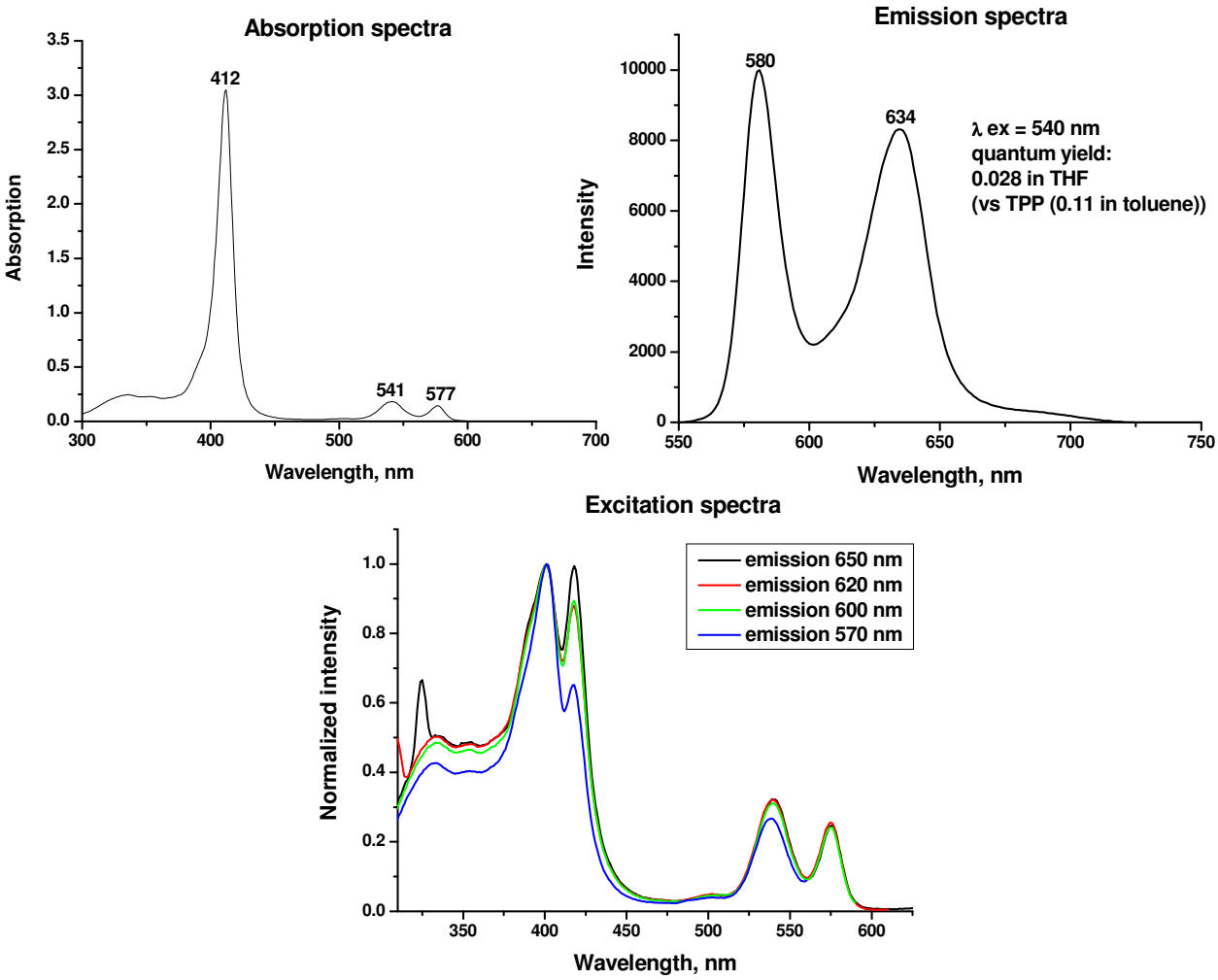


Figure S23. Optical spectra of porphyrin **6b**.

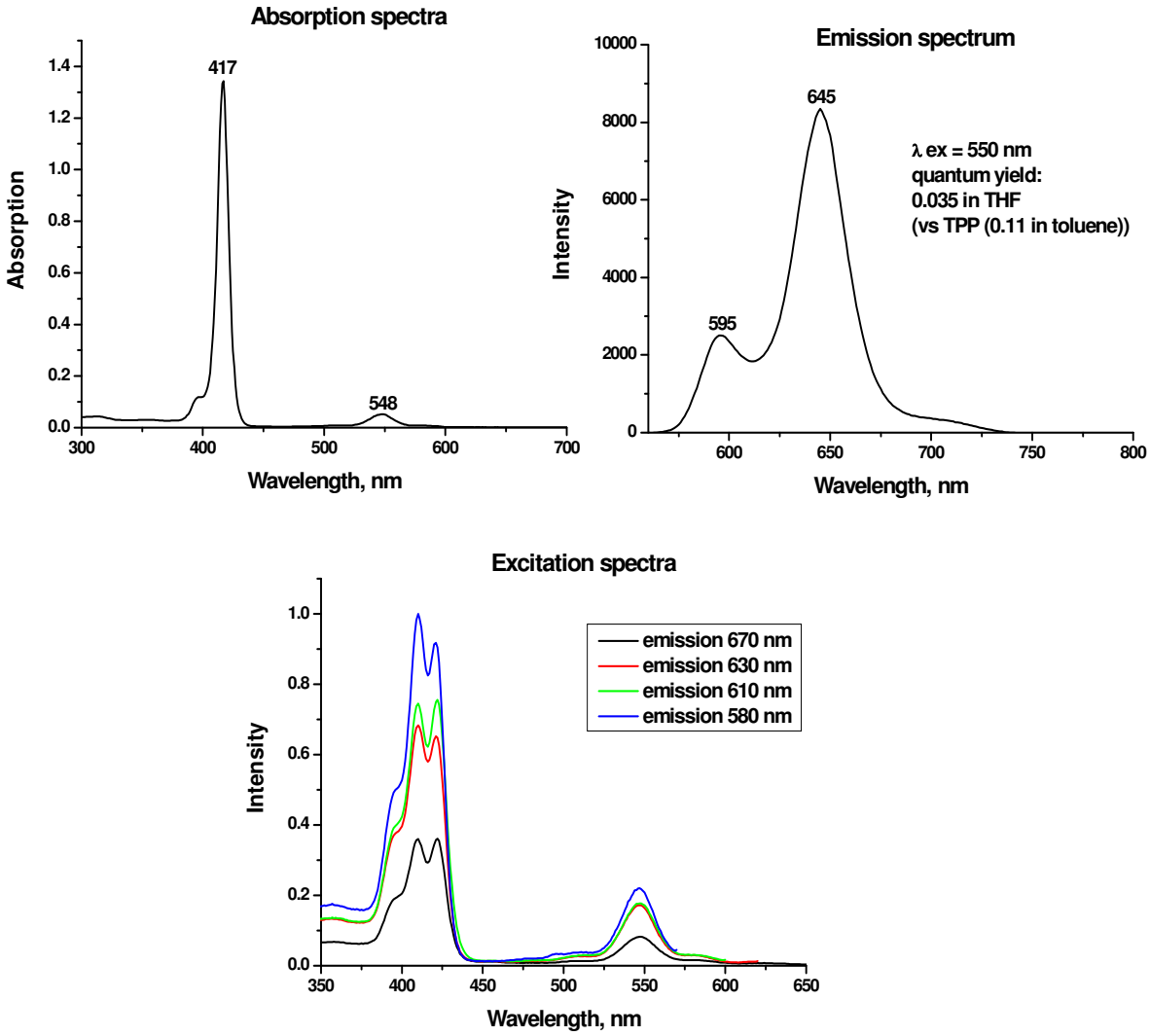


Figure S24. 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10,20-(3,5-di-tert-butylphenyl)porphyrin zinc(II).

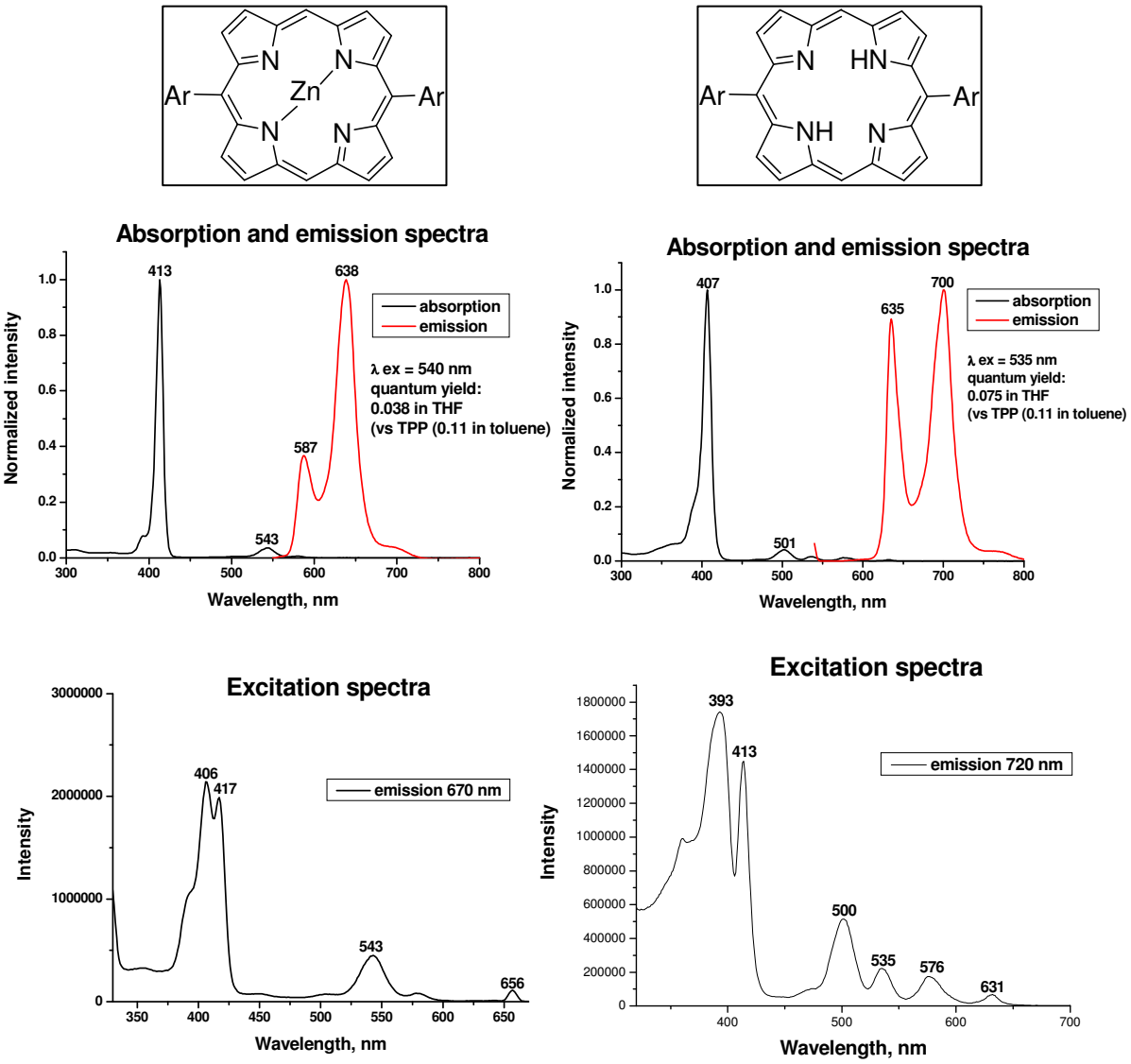


Figure S25. 5,15-bis-(3,5-di-tert-butyl)phenylporphyrin and its zinc(II) complex.

IV. References

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