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Electronic Supplementary Information

Cofacial Porphyrin Dimers Assembled From N-Heterocyclic Carbene-Metal Bonds

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1. Materials

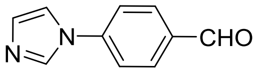
Reactions needing inert atmosphere were performed under argon using oven-dried glassware and Schlenk techniques. All solvents were obtained from commercial suppliers and used as received. Dry acetonitrile and DMSO were purchased from Alfa Aesar. DMF was purchased from Sigma-Aldrich. Dry THF was obtained by a PureSolve MD5 solvent purification system from Innovative Technology. Silver(I) oxide (Ag_2O) was purchased from Riedel-de Haën and gold(I) complex [AuCl(tht)] (tht = tetrahydrothiophene) was prepared according to the procedure described in the following reference: R. Usón and A. Laguna, *Inorg Synth.*, 1982, **21**, 71-74. Hydrogen tetrachloroaurate(III) trihydrate was used as starting material and purchased from Alfa Aesar. Pyrrole was purchased from TCI and distilled under reduced pressure before use. Imidazole, 4-fluorobenzaldehyde, iodomethane, potassium hexafluorophosphate and zinc(II) acetate dihydrate were purchased from Sigma-Aldrich. Preparative purifications were performed by silica gel flash column chromatography (Merck 40−60 μM). TLC were carried out on Merck DC Kieselgel 60 F-254 aluminium sheets and spots were visualized with UV-lamp (λ = 254/365 nm) if necessary.

2. Instruments and methods

NMR spectroscopy and MS spectrometry were performed at the Laboratoire de Mesures Physiques of the University of Montpellier. ^{1}H, COSY, ROESY, HSQC, HMBC, $^{13}C\{^{1}H\}$, ^{31}P, ^{19}F and DOSY spectra were recorded on Bruker 400 MHz Avance III HD, 500 MHz Avance III or 600 MHz Avance III spectrometers. DMSO-d_6 and $CDCl_3$ studies were used as received (purchased from Eurisotop, France). ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were calibrated to TMS on the basis of the relative chemical shift of the residual non-deuterated solvent as an internal standard. Chemical shifts (δ) are expressed in ppm from the residual non-deuterated solvent signal and coupling constants values (J) are expressed in Hz. Abbreviations used for ^{1}H NMR spectra are as follows: s, singlet; d, doublet; t, triplet; sept, septuplet; m, multiplet, br, broad. Mass spectra (HRMS) were recorded on ESI-TOF Q instruments in positive/negative modes. UV-visible absorption spectra were recorded in DMSO with a JASCO V-750 UV−visible spectrophotometer in 10 mm quartz cells (Hellma); molar extinction coefficients ε (L.mol^{-1}.cm^{-1}) are expressed as log ε. Abbreviation used: sh, shoulder.

3. Synthesis and characterization

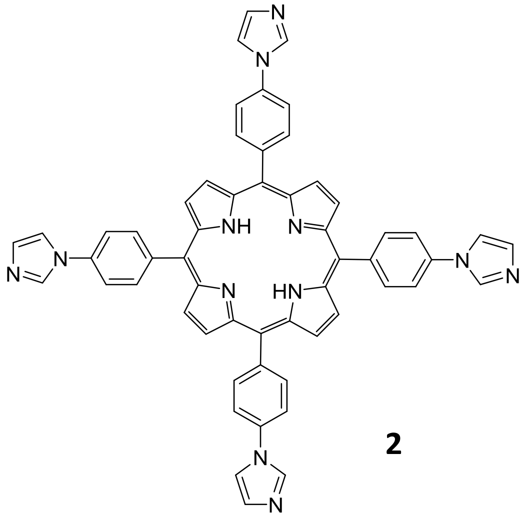
4-(1*H*-imidazol-1-yl)benzaldehyde



Synthesis of 4-(1*H*-imidazol-1-yl)benzaldehyde was performed according to the procedure reported in reference 15. In a 250 mL round-bottom-flask, 4-fluorobenzaldehyde (25.0 g, 0.20 mol, 1.0 eq), imidazole (20.4 g, 0.30 mol, 1.5 eq) and potassium carbonate (40 g, 0.29 mol, 1.45 eq) were mixed in DMF (300 mL), and Aliquat 336 (0.50 mL) was added. The reaction mixture was stirred under argon for 24 hours at 100°C. Then, half of the solvent was evaporated under reduced pressure and, after cooling at room temperature, the mixture was poured into an ice water bath and left overnight. The obtained light yellow solid was filtered, washed with cold Et_2O and dried. The 4-(1*H*-imidazol-1-yl)benzaldehyde was obtained as a yellow solid (18.6 g, 54%).

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K): δ = 10.05 (s, 1H, $H_{C\mathit{HO}}$), 8.03 (d, 2H, $^3J_{H,H}$ = 8.5Hz, H_{Ar}), 8.00 (d, 1H, $^3J_{H,H}$ = 1.2 Hz, $H_{imidazole}$), 7.59 (d, 2H, $^3J_{H,H}$ = 8.5Hz, H_{Ar}), 7.38 (t, 1H, $^3J_{H,H}$ = 1.2 Hz, $H_{imidazole}$), 7.27 (d, 1H, $^3J_{H,H}$ = 1.2 Hz, $H_{imidazole}$) ppm.

Free-base *meso* 5,10,15,20-tetrakis(4’-imidazolyl-phenyl)porphyrin 2



2

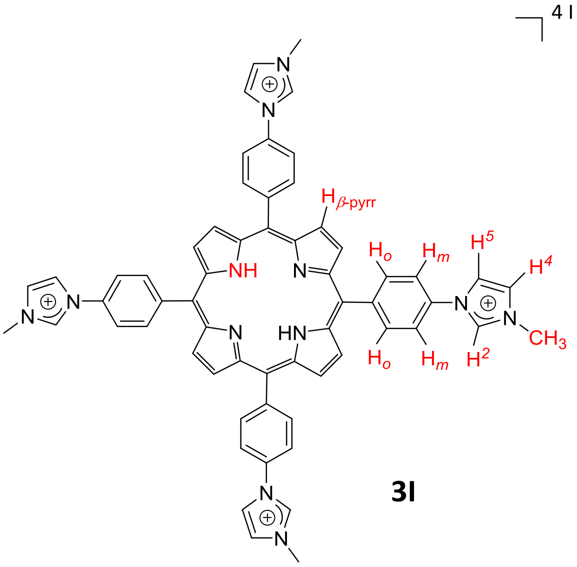
Synthesis of porphyrin **2** was performed according to the procedure reported in reference 16. 4-(*1*H-imidazol-1-yl) benzaldehyde (2.0 g, 11.6 mmol, 1.0 eq) and pyrrole (0.85 mL, 11.6 mmol, 1.0 eq) were added to propionic acid (200 mL). The reaction mixture was heated under reflux for 6 hours and the solvent was removed under reduced pressure. The crude solid was purified two times on silica gel column with $CHCl_3$/MeOH 92:8 as eluent. After evaporation of the solvent and recrystallization from $CHCl_3$/*n*-hexane, porphyrin **2** was obtained as a purple powder (0.8 g, 9%).

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K): δ = 8.96 (s, 8H, $H_{\beta\text{-pyrr}}$), 8.36 (d, 8H, $^3J_{H,H}$ = 8.1 Hz, H_o), 8.19 (s, 4H, H^2), 7.86 (d, 8H, $^3J_{H,H}$ = 8.1 Hz, H_m), 7.66 (s, 4H, H^5), 7.33 (s, 4H, H^4), -2.79 (s, 2H, N*H*) ppm.

UV/VIS (DMSO): λ_{max} (log ε) = 422 (5.37), 516 (4.26), 551 (4.09), 591 (3.96), 649 (3.95) nm.

ESI-MS (positive mode): *m/z* calcd for $C_{56}H_{39}N_{12}$, [**2**+H]$^+$: 879.34, found 879.40.

Free-base *meso* 5,10,15,20-tetrakis(4'-*N*-methylimidazolyl-phenyl)porphyrin iodide 3I



3I

Synthesis of porphyrin **2** was performed according to the procedure reported in reference 17. In a 250 mL round-bottom-flask, porphyrin **2** (350 mg, 1.0 eq, 0.40 mmol) was dissolved in dry THF (65 mL). Then, iodomethane (2.5 mL, 100 eq) was added and the reaction mixture was stirred under argon at 40°C overnight. The obtained precipitate was filtered, washed with THF and dried under reduced pressure to give porphyrin **3I** as a purple powder (0.455 g, 80%).

^{1}H NMR (400.1 MHz, DMSO-*d*$_6$, 298K): δ = 10.11 (s, 4H, H^{2}), 8.94 (s, 8H, H$_{\beta\text{-pyrr}}$), 8.63 (t, 4H, $^{3}J_{H,H}$ = 1.8 Hz, H^{5}), 8.55 (d, 8H, $^{3}J_{H,H}$ = 8.5 Hz, H$_{o}$), 8.28 (d, 8H, $^{3}J_{H,H}$ = 8.5 Hz, H$_{m}$), 8.15 (d, 4H, $^{3}J_{H,H}$ = 1.8 Hz, H^{4}), 4.10 (s, 12H, N-CH_3), -2.89 (s, 2H, N*H*) ppm.

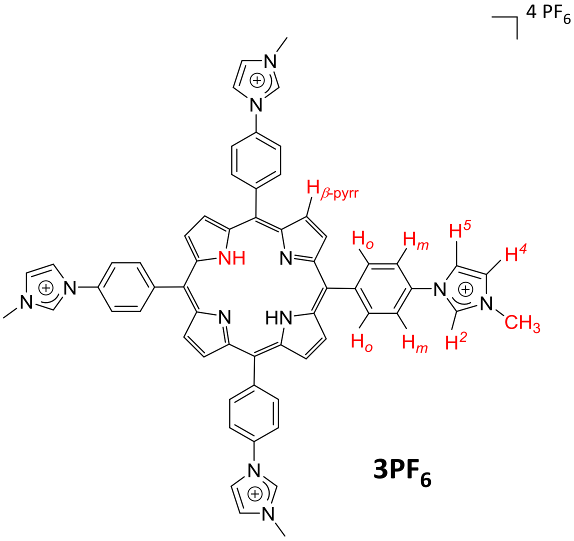
^{13}C{^{1}H} NMR (100.6 MHz, DMSO-*d*$_6$, 298K): δ = 142.3, 136.4, 135.5, 134.8, ~131.5 (br), 124.8, 121.2, 120.4, 118.8, 36.5 (N-CH_3) ppm.

UV/VIS (DMSO) : λ_{max} (log ε) = 420 (5.56), 515 (4.22), 550 (3.88), 590 (3.72), 645 (3.59) nm

ESI-MS (positive mode): *m/z* calcd for $C_{60}H_{50}N_{12}^{4+}$ [**3I** – 4I]$^{4+}$: 234.61, found: 234.74.

ESI-MS (negative mode): *m/z* calcd for I^{-}: 126.91, found: 126.94

Free-base *meso* 5,10,15,20-tetrakis(4’-*N*-methylimidazolyl-phenyl)porphyrin hexafluorophosphate 3PF₆



3PF₆

Porphyrin **3I** (615 mg, 0.425 mmol) was dissolved in water (60 mL) and added to a solution of potassium hexafluorophosphate (3.12 g, 40 eq, 17 mmol) in water (40 mL) was added. The mixture was stirred for 15 mn at room temperature and the obtained precipitate was filtered, washed with water and dried under reduced pressure to give porphyrin **3PF₆** as a purple powder (0.630 g, 98%).

^{1}H NMR (400.1 MHz, DMSO-*d*₆, 298K): δ = 10.08 (s, 4H, H^2), 8.93 (s, 8H, H$_{\beta\text{-pyrr}}$), 8.63 (t, 4H, $^3J_{H,H}$ = 1.8 Hz, H^5), 8.54 (d, 8H, $^3J_{H,H}$ = 8.6 Hz, H$_o$), 8.26 (d, 8H, $^3J_{H,H}$ = 8.6 Hz, H$_m$), 8.13 (d, 4H, $^3J_{H,H}$ = 1.8 Hz, H^4), 4.09 (s, 12H, N-CH_3), -2.89 (s, 2H, N*H*) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, DMSO-*d*₆, 298K): δ = 142.3, 136.4, 135.5, 134.8, 124.8, 121.2, 120.4, 118.8, 36.4 (N-CH_3) ppm.

^{31}P NMR (162.0 MHz, DMSO-*d*₆,, 298K): δ = -144.3 (sept, $^2J_{PF}$ = 711.3 Hz) ppm.

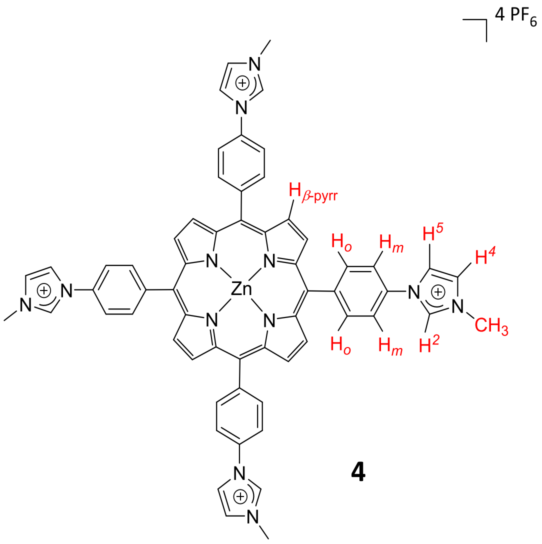
^{19}F NMR (376.5 MHz, DMSO-*d*₆,, 298K): δ = -71.1 (d, $^2J_{FP}$ = 711.3 Hz) ppm.

UV/VIS (DMSO): λ_{max} (log ε) = 420 (5.52), 515 (4.23), 549 (3.90), 589 (3.74), 646 (3.63) nm.

ESI-MS (positive mode): *m/z* calcd for $C_{60}H_{50}N_{12}^{4+}$ [**3PF₆** – 4PF₆]$^{4+}$: 234.61, found: 234.73.

ESI-MS (negative mode): *m/z* calcd for PF_6^- : 144.96, found: 145.06

Zinc(II) *meso* 5,10,15,20-tetrakis(4’-*N*-methylimidazolyl-phenyl)porphyrin hexafluorophosphate 4



4

In a 50 mL Schlenck tube, porphyrin **$3PF_6$** (150 mg, 1.0 eq, 0.10 mmol) was dissolved in a mixture of $CHCl_3/CH_3OH$ (12 mL/few drops). Then, a solution of $Zn(OAc)_2.2H_2O$ (28 mg, 1.2 eq, 0.12 mmol) dissolved in methanol (3 mL) was added. The mixture was stirred at 60°C under argon for two hours. The metalation reaction was monitored by UV-visible absorption spectroscopy. After cooling the reaction mixture at room temperature, solvents were evaporated. The obtained solid was recrystallized from acetone/*n*-hexane and obtained as a purple solid (0.142 g, 90%).

^{1}H NMR (600.3 MHz, DMSO-*d*$_6$, 298K): δ = 10.07 (t, 4H, $^4J_{H,H}$ = 1.9 Hz, H^2), 8.86 (s, 8H, H$_{\beta\text{-pyrr}}$), 8.62 (t, 4H, $^3J_{H,H}$ = 1.9 Hz, H^5), 8.47 (d, 8H, $^3J_{H,H}$ = 8.5 Hz, H$_o$), 8.21 (d, 8H, $^3J_{H,H}$ = 8.5 Hz, H$_m$), 8.13 (t, 4H, $^3J_{H,H}$ = 1.9 Hz, H^4), 4.09 (s, 12H, N-CH_3) ppm.

^{13}C{^{1}H} NMR (150.9 MHz, DMSO-*d*$_6$, 298K): δ = 149.3 (C$_{\alpha\text{-pyrr}}$), 143.9 (C$_p$), 136.3 (C^2), 135.4 (C$_o$), 134.4 (C$_i$), 131.9 (C$_{\beta\text{-pyrr}}$), 124.8 (C^4), 121.3 (C^5), 120.0 (C$_m$), 119.1 (C$_{meso}$), 36.4 (N-CH_3) ppm.

^{31}P NMR (162 MHz, DMSO-*d*$_6$, 298K): δ = -144.2 (sept, $^2J_{PF}$ = 711.5 Hz) ppm.

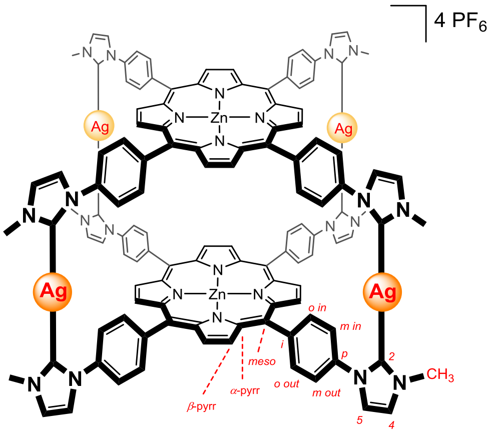
^{19}F NMR (376.5 MHz, DMSO-*d*$_6$, 298K): δ = -71.1 (d, $^2J_{FP}$ = 711.5 Hz) ppm.

UV/VIS (DMSO): λ_{max} (log ε) = 409 (sh 4.64), 430 (5.58), 561 (4.30), 600 (3.98) nm

High resolution ESI-MS (positive mode): *m/z* calcd for $C_{60}H_{48}N_{12}Zn^{4+}$ [**4** – $4PF_6$]$^{4+}$: 250.0848, found: 250.0864.

ESI-MS (negative mode): *m/z* calcd for PF_6^-: 144.96, found: 145.04

Cofacial porphyrin dimer [Ag_4(1)$_2$](PF_6)$_4$



[Ag_4(1)$_2$](PF_6)$_4$

In a 50 mL Schlenck tube, porphyrin **4** (80 mg, 0.051 mmol, 1.0 eq) was dissolved in dry acetonitrile (13 mL). The reaction mixture was degassed with argon for 20 minutes. Then, silver oxide (47 mg, 0.20 mmol, 4.0 eq) was added and the reaction mixture was vigorously stirred under argon at 70°C for 24 hours in the dark. After cooling at room temperature, the mixture was filtered through a pad of Celite and acetonitrile was evaporated under reduced pressure to give **[Ag_4(1)$_2$](PF_6)$_4$** as a purple powder (70 mg, 45%).

^{1}H NMR (600.3 MHz, DMSO-*d*$_6$, 298K): δ = 8.34 (br s, 16H, $H_{\beta\text{-pyrr}}$), 8.30 (br d, 8H, $^3J_{H,H}$ = 7.2 Hz, $H_{o\ \text{out}}$), 8.20 (br d, 8H, $^3J_{H,H}$ = 8.0 Hz, $H_{m\ \text{out}}$), 8.16 (br s, 8H, H^5), 7.92 (br s, 8H, H^4), 7.80 (br d, 8H, $^3J_{H,H}$ = 7.2 Hz, $H_{m\ \text{in}}$), 7.72 (br d, 8H, $^3J_{H,H}$ = 7.2 Hz, $H_{o\ \text{in}}$), 4.26 (s, 24H, N-*CH_3*).

^{13}C{^{1}H} NMR (150.9 MHz, DMSO-*d*$_6$, 298K): δ = 179.9 (br C^2_{NHC}), 147.3 ($C_{\alpha\text{-pyrr}}$), 142.7 (C_p), 138.9 (C_i), 135.2 ($C_{o\ out}$), 134.5 ($C_{o\ in}$), 130.2 ($C_{\beta\text{-pyrr}}$), 124.6 (C^4), 122.6 (C^5), 121.4 ($C_{m\ in}$), 121.0 ($C_{m\ out}$), 116.6 (C_{meso}), ~39.0 (N-*CH_3*) ppm.

^{19}F NMR (376.5 MHz, DMSO-d$_6$, 298K): δ = -71.1 (d, $^2J_{FP}$ = 711.5 Hz) ppm.

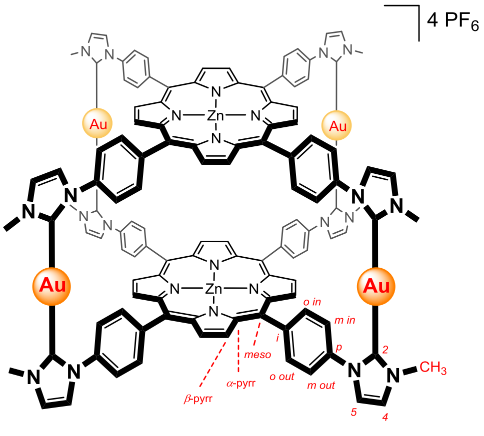
^{31}P NMR (162 MHz, DMSO-d$_6$, 298K): δ = -142.0 (sept, $^2J_{PF}$ = 711.5 Hz) ppm.

UV-Vis (DMSO): $\lambda_{\max}$ (log ε) = 413 (5.48), 561 (4.36), 602 (4.09) nm.

High resolution ESI-MS (positive mode): *m/z* calcd for $C_{120}H_{88}N_{24}Zn_2Ag_4^{4+}$ **[Ag_4(1)$_2$]$^{4+}$**: 607.0596, found: 607.0595.

ESI-MS (negative mode): *m/z* calcd for PF_6^-: 144.96, found: 144.96.

Cofacial porphyrin dimer **[Au$_4$(1)$_2$](PF$_6$)$_4$**



[Au$_4$(1)$_2$](PF$_6$)$_4$

In a 50 mL-Schlenck-tube, cofacial porphyrin dimer **[Ag$_4$(1)$_2$](PF$_6$)$_4$** (40 mg, 0.013 mmol, 1.0 eq) was dissolved in dry DMSO (0.5 mL), then dry CH_3CN (4 mL) was added. The reaction mixture was degassed with argon for 20 minutes. Then, [AuCl(tht)] (17 mg, 0.053 mmol, 4.0 eq) was added to the mixture which was vigorously stirred under argon at room temperature for 24 hours in the dark. Then, reaction mixture was filtered through a pad of celite, CH_3CN was removed under reduced pressure, and THF (~ 20 mL) was added. The obtained solid was filtered, washed with cold THF and dried under vacuum to give cofacial porphyrin dimer **[Au$_4$(1)$_2$](PF$_6$)$_4$** as a black powder (30 mg, 65%).

^{1}H NMR (600.3 MHz, DMSO-d_6, 298K): δ 8.36 (s br, 16H, $H_{\beta\text{-pyrr}}$), 8.24 (dd br, 8H, $^3J_{H,H}$ = 7.9 Hz and $^4J_{H,H}$ = 2.3 Hz, $H_{o\text{ out}}$), 8.17 (dd br, 8H, $^3J_{H,H}$ = 7.9 Hz and $^4J_{H,H}$ = 2.3 Hz, $H_{m\text{ out}}$), 8.17 (d br, $^3J_{H,H}$ = 1.7 Hz, 8H, H^5), 7.96 (d br, $^3J_{H,H}$ = 1.7 Hz, 8H, H^4), 7.83 (d br, 8H, $^3J_{H,H}$ = 7.6 Hz and $^4J_{H,H}$ = 2.3 Hz, $H_{m\text{ in}}$), 7.79 (d br, 8H, $^3J_{H,H}$ = 7.6 Hz and $^4J_{HH}$ = 2.3 Hz, $H_{o\text{ in}}$), 4.29 (s, 24H, N-CH_3) ppm.

^{13}C NMR (150.9 MHz, DMSO-d_6, 298K): δ 181.7 (C_{NHC}), 147.2, 142.9, 137.9, 135.5 ($C_{o\ out}$), 134.4 ($C_{o\ in}$), 130.2 ($C_{\beta\text{-pyrr}}$), 124.8 (C^4), 123.2 (C^5), 122.1 ($C_{m\ in}$), 122.0 ($C_{m\ out}$), 116.6, 38.4 (N-CH_3) ppm.

^{19}F NMR (376.5 MHz, DMSO-d_6, 298K): δ -71.1 (d, $^2J_{FP}$ = 711.4 Hz) ppm.

^{31}P NMR (162 MHz, DMSO-d_6, 298K): δ -144.20 (sept, $^2J_{PF}$ = 711.4 Hz) ppm

UV-Vis (DMSO): λ_{max} (log ε) = 413 (5.46), 562 (4.14), 604 (3.90) nm

High resolution ESI-MS (positive mode): *m/z* calcd for $C_{120}H_{88}N_{24}Zn_2Au_4^{4+}$ **[Au$_4$(1)$_2$]$^{4+}$**: 696.1199, found: 696.1213.

ESI-MS (negative mode): *m/z* calcd for PF_6^-: 144.96, found: 144.96.

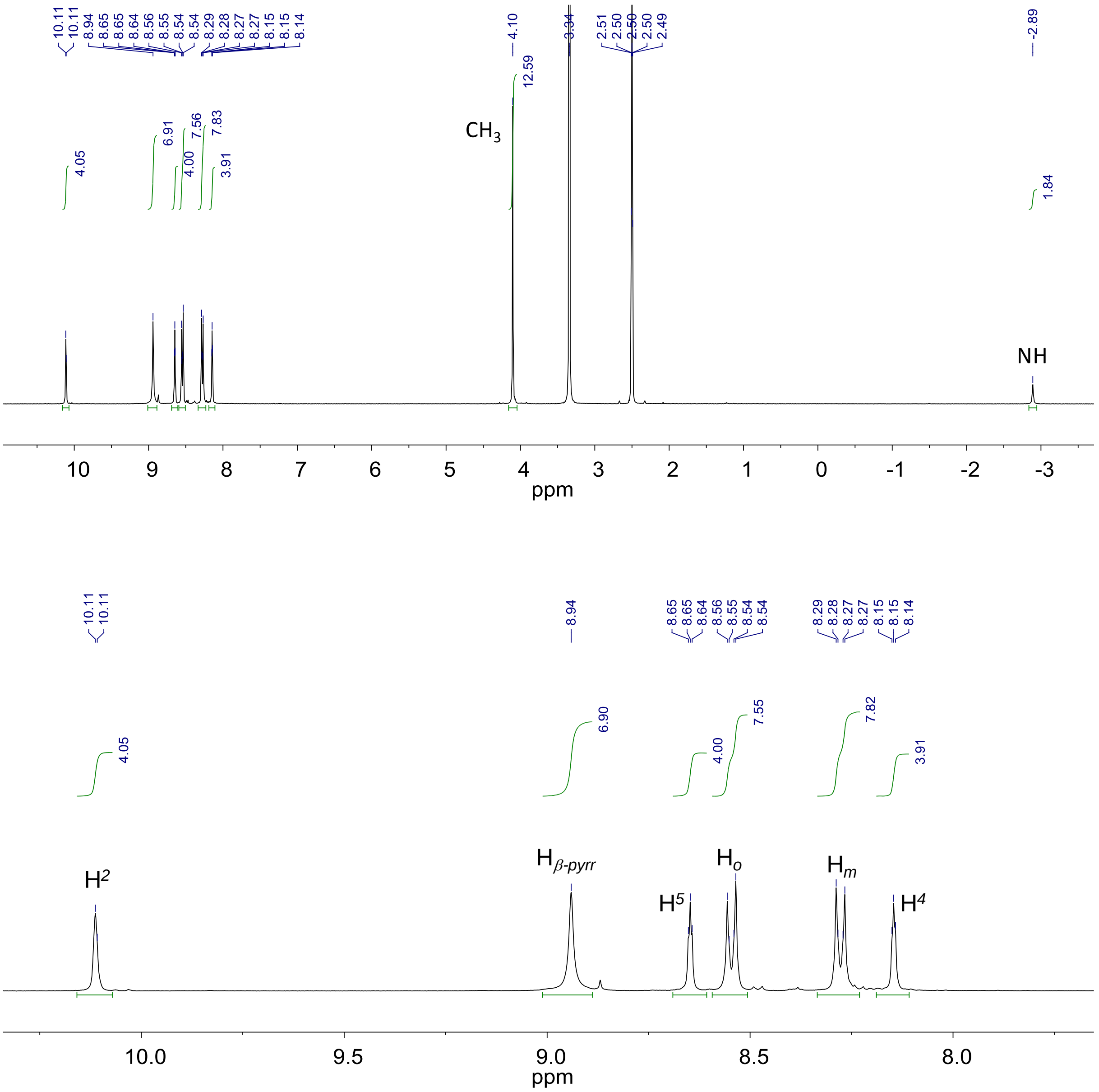


Figure S1. Full range (top) and partial (bottom) ^{1}H NMR spectra (400.1 MHz, DMSO-d_6, 298 K) of porphyrin **3I**.

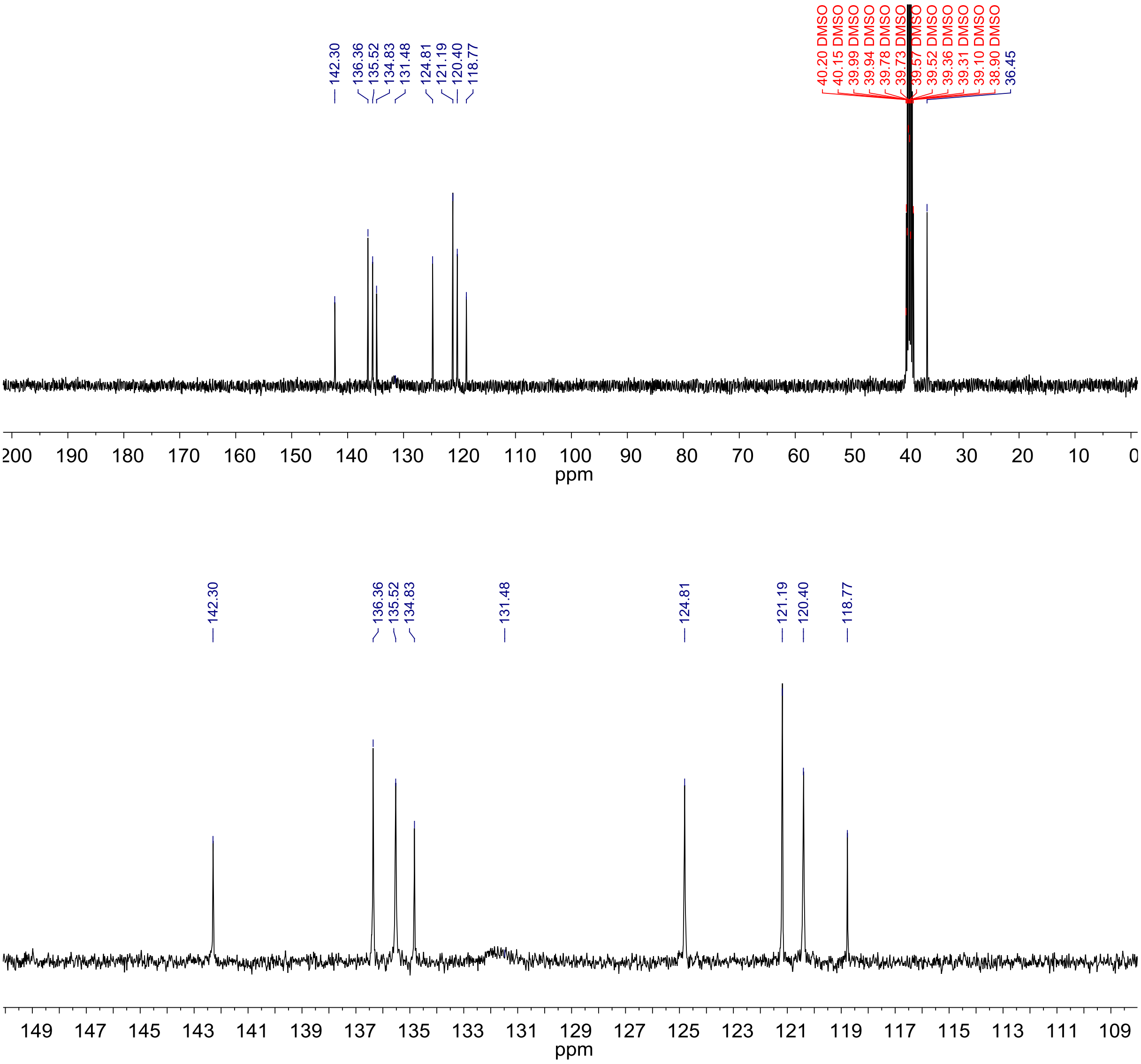


Figure S2. Full range (top) and partial (bottom) $^{13}C\{^{1}H\}$ NMR spectra (100.6 MHz, DMSO-d_6, 298 K) of porphyrin **3I**.

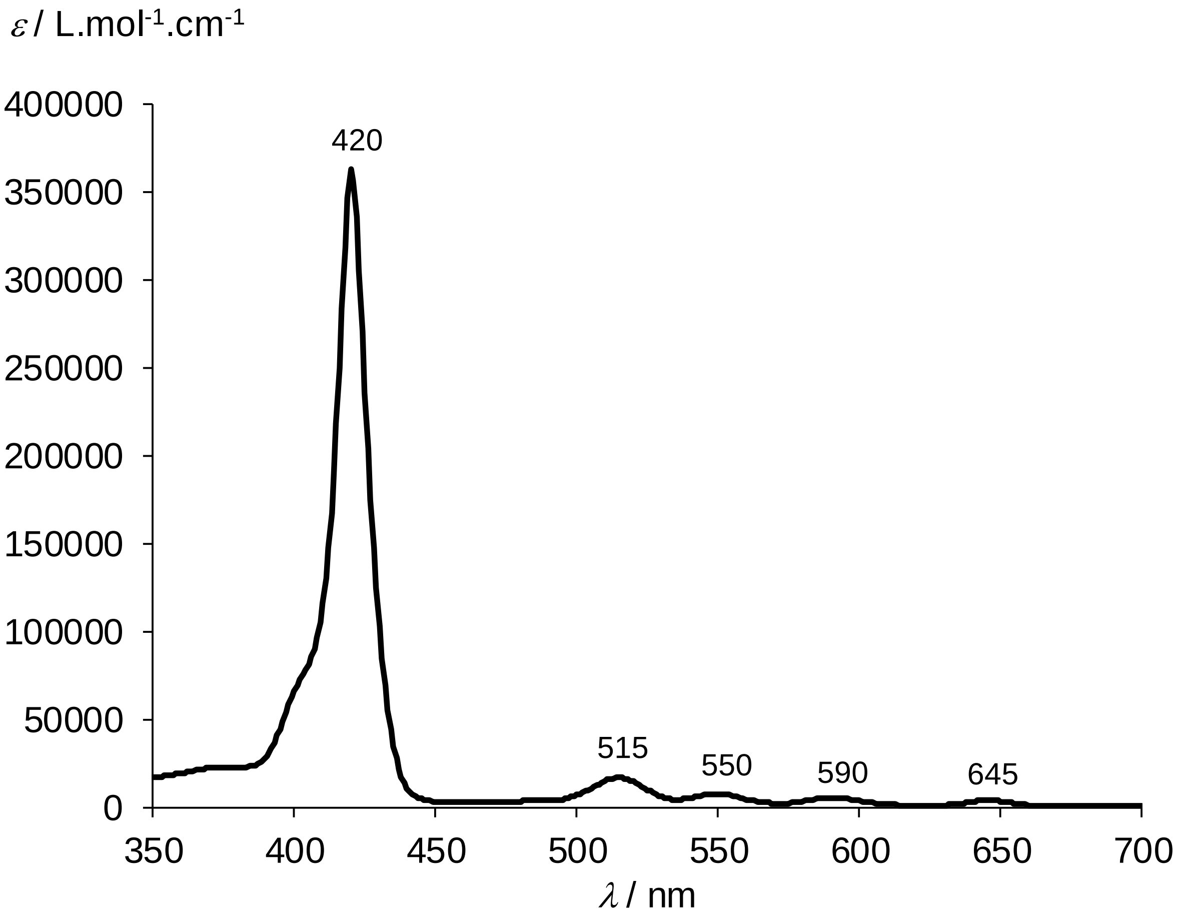


Figure S3. UV-vis spectrum (DMSO) of porphyrin **3I**.

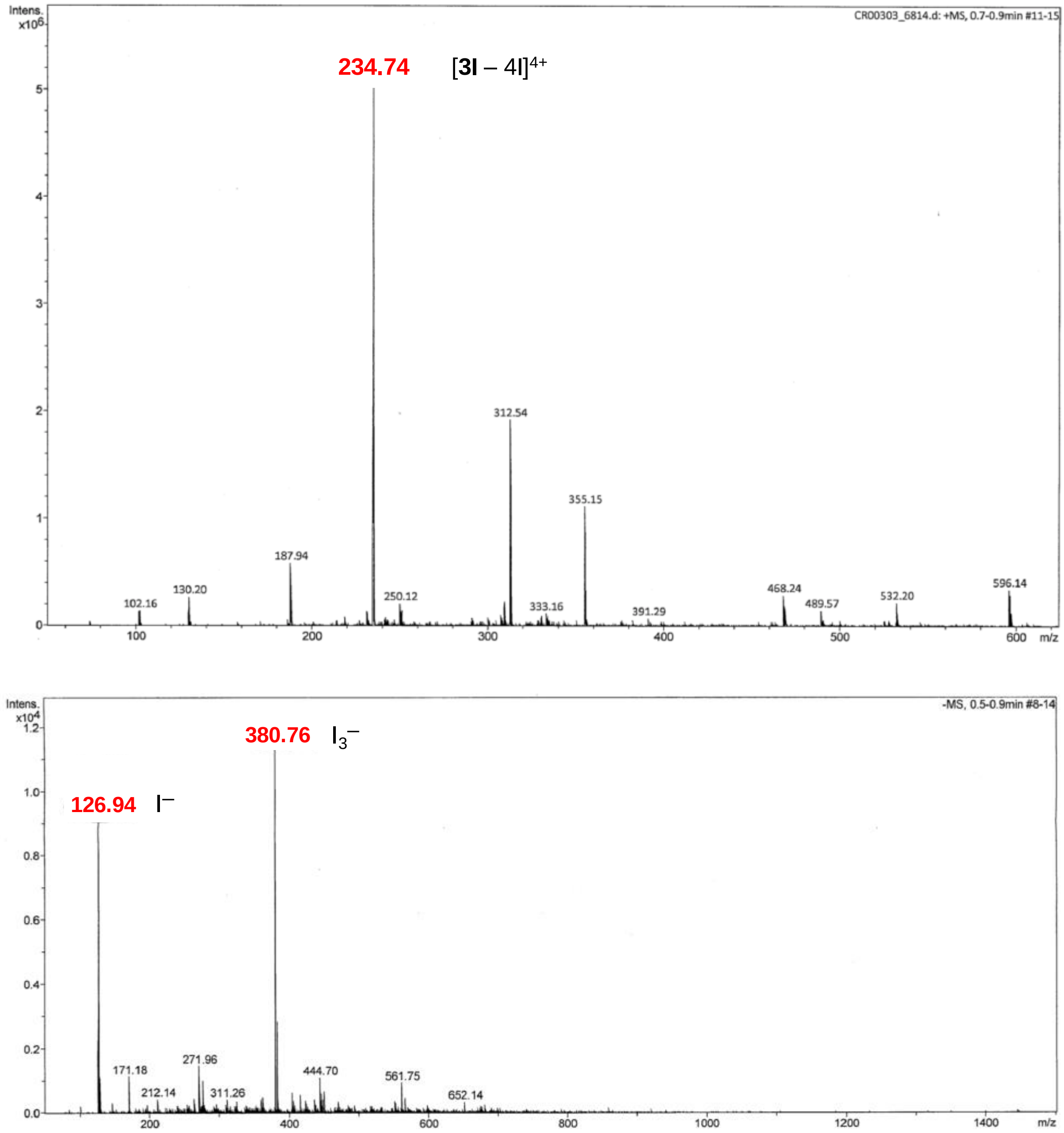


Figure S4. ESI-TOF positive mode (top) and negative mode (bottom) mass spectra of porphyrin **3I**.

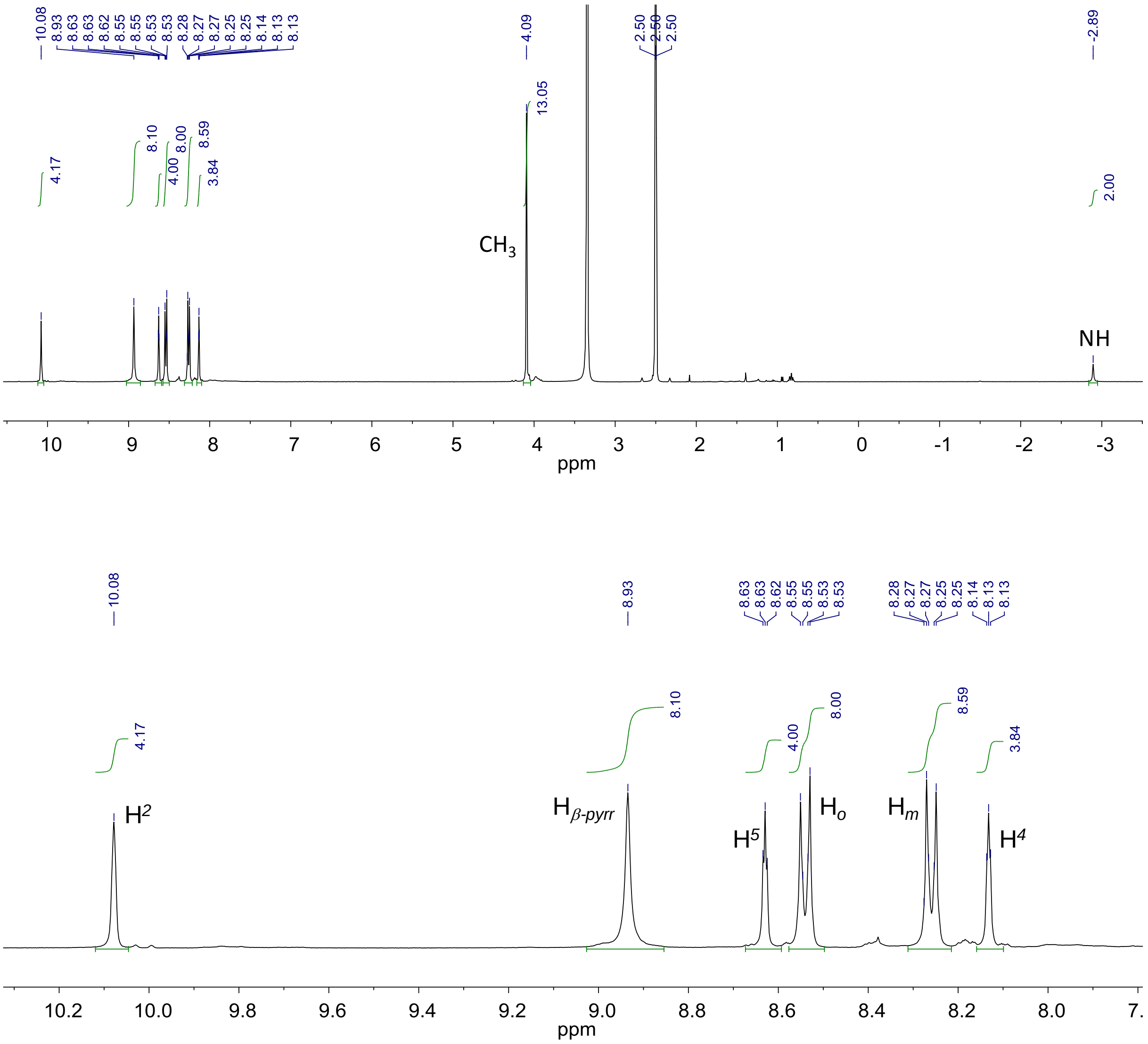


Figure S5. Full range (top) and partial (bottom) ^{1}H NMR spectra (400.1 MHz, DMSO-d_6, 298 K) of porphyrin **3PF$_6$**.

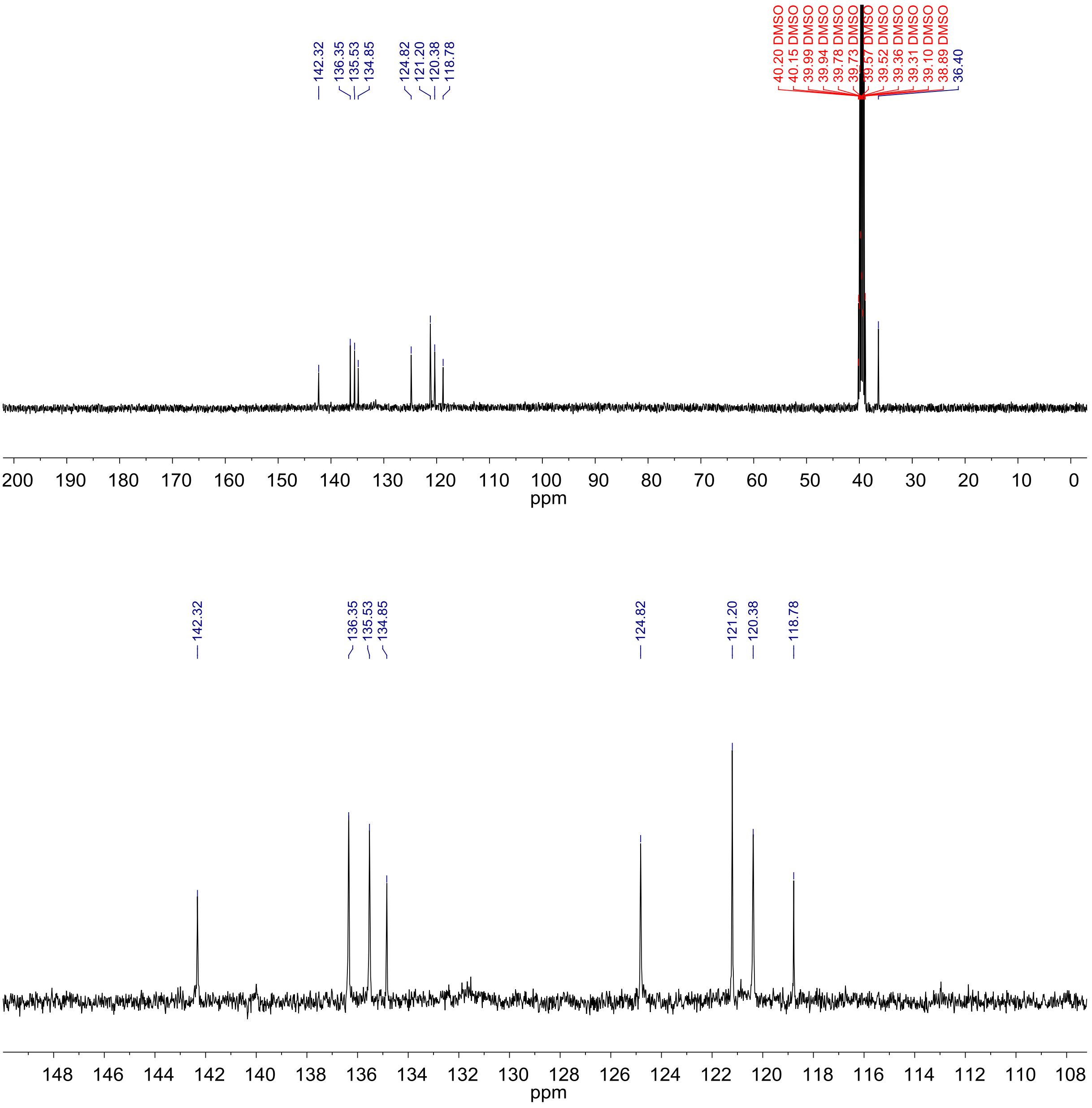


Figure S6. Full range (top) and partial (bottom) $^{13}C\{^{1}H\}$ NMR spectra (100.6 MHz, DMSO-*d*$_6$, 298 K) of porphyrin **3PF$_6$**.

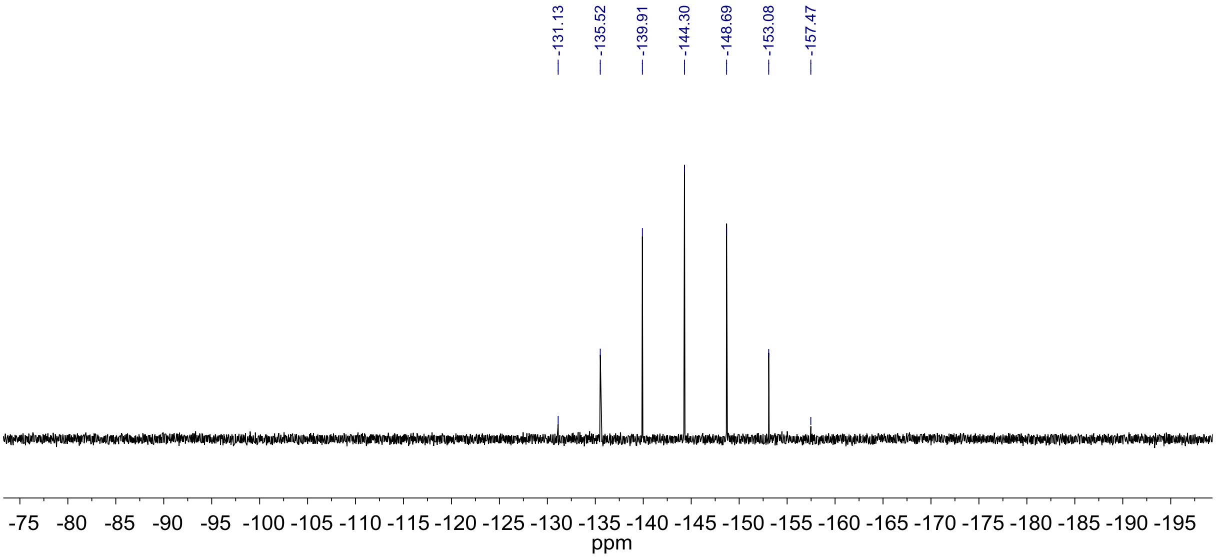


Figure S7. ^{31}P NMR spectra (162 MHz, DMSO-d_6, 298 K) of porphyrin **3PF$_6$**.

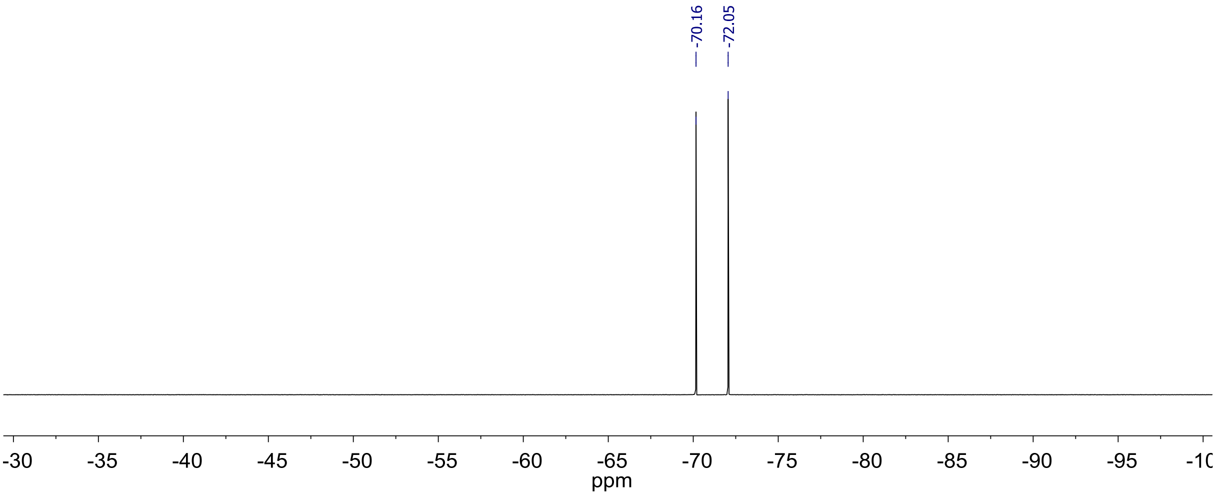


Figure S8. ^{19}F NMR spectra (376.5 MHz, DMSO-d_6, 298 K) of porphyrin **3PF$_6$**.

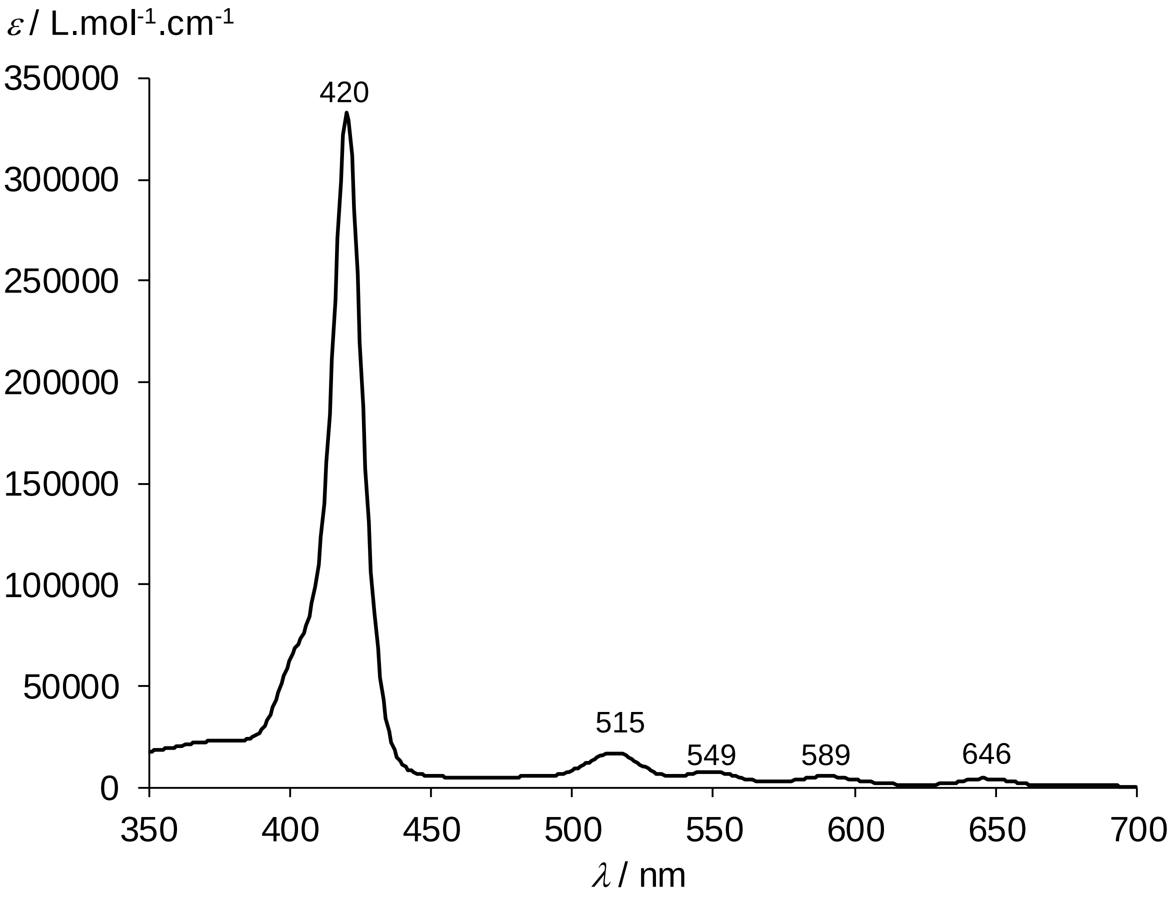


Figure S9. UV-vis spectrum (DMSO) of porphyrin **$3PF_6$**.

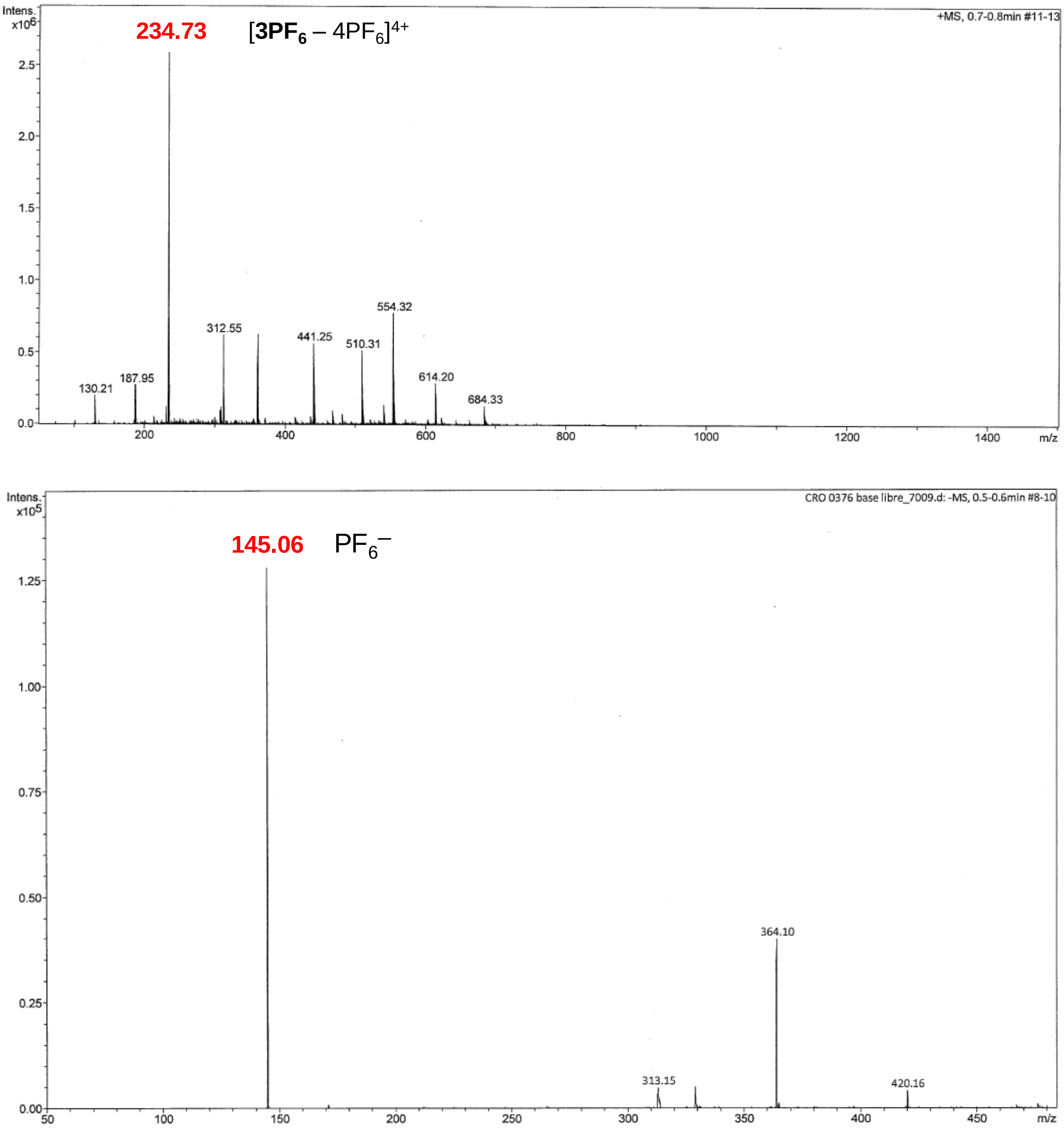


Figure S10. ESI-TOF positive mode (top) and negative mode (bottom) mass spectra of porphyrin **3PF$_6$**.

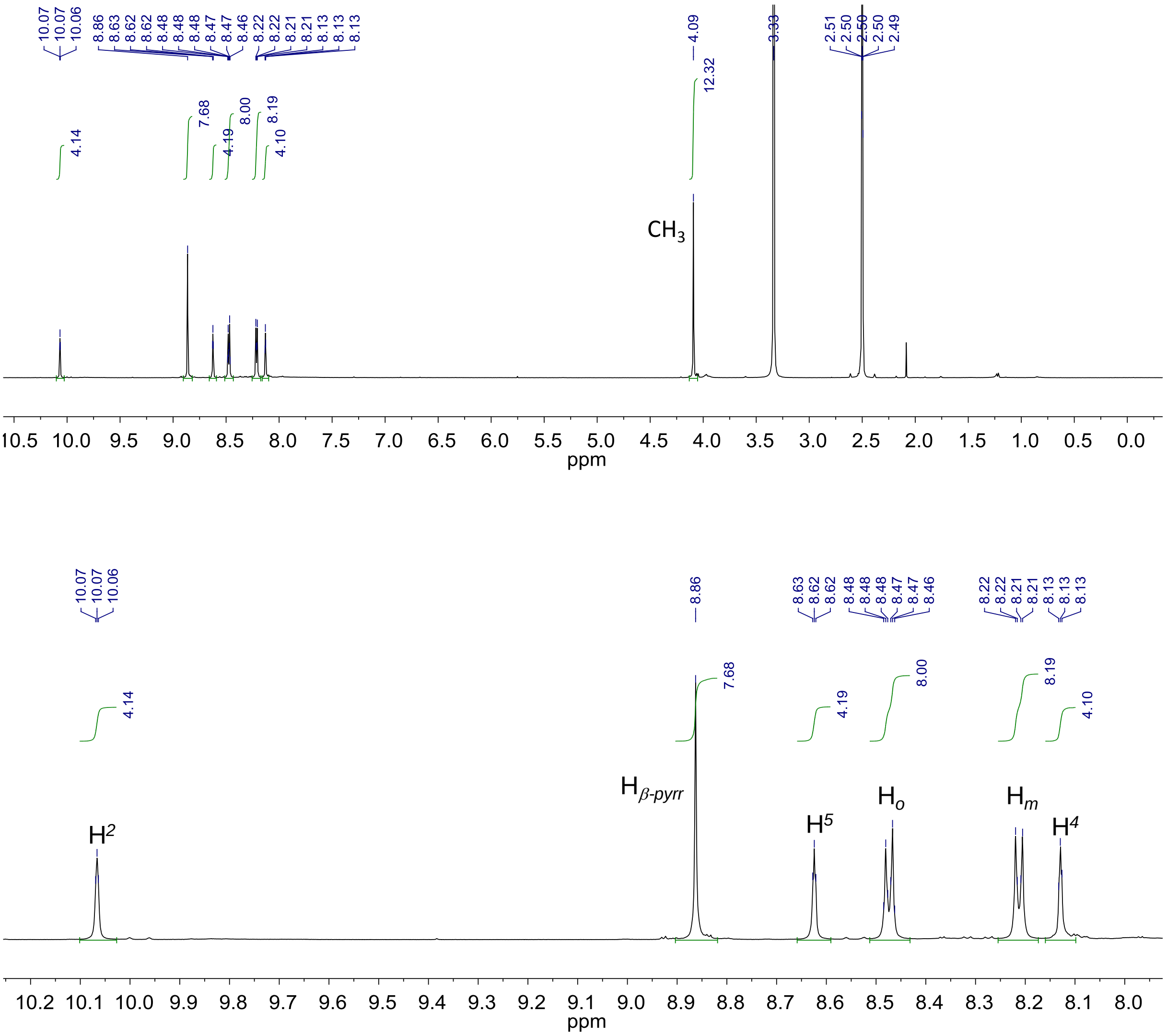


Figure S11. Full range (top) and partial (bottom) ^{1}H NMR spectra (600.3 MHz, DMSO-d_6, 298 K) of porphyrin **4**.

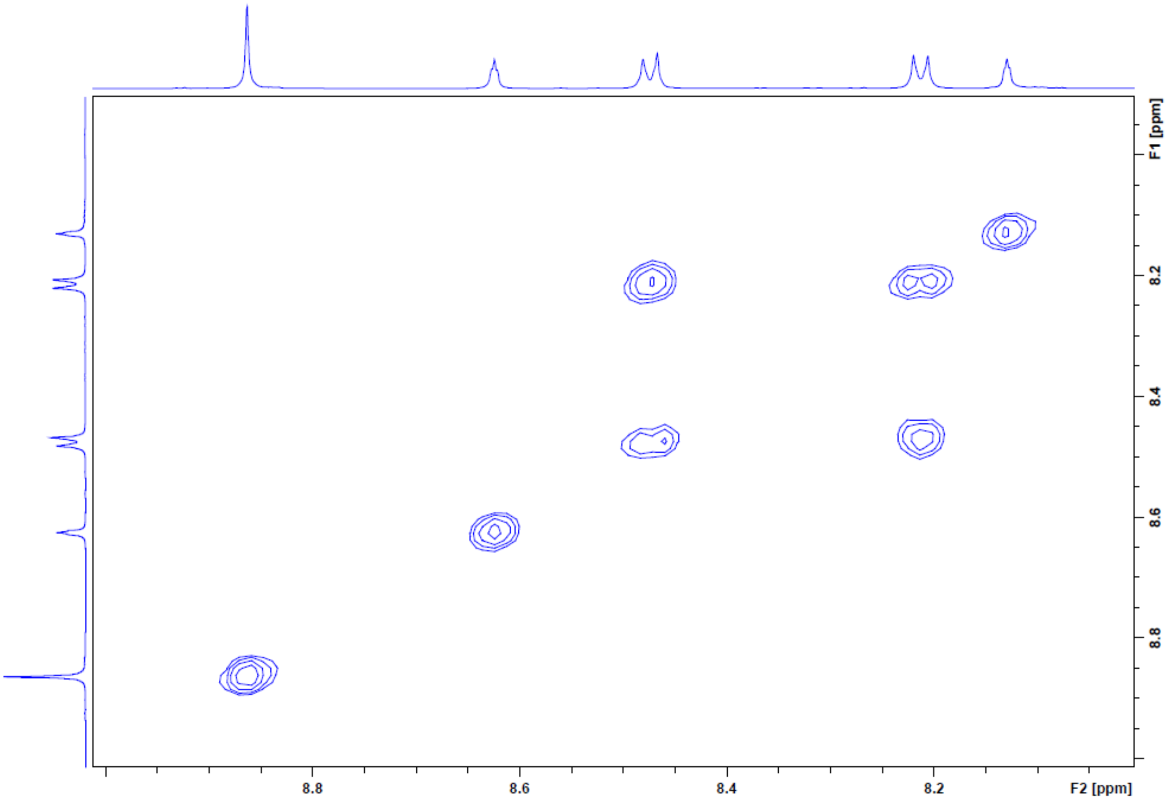


Figure S12. ^{1}H-^{1}H COSY NMR spectrum (600.3 MHz, DMSO-*d*$_6$, 298 K) of porphyrin **4**.

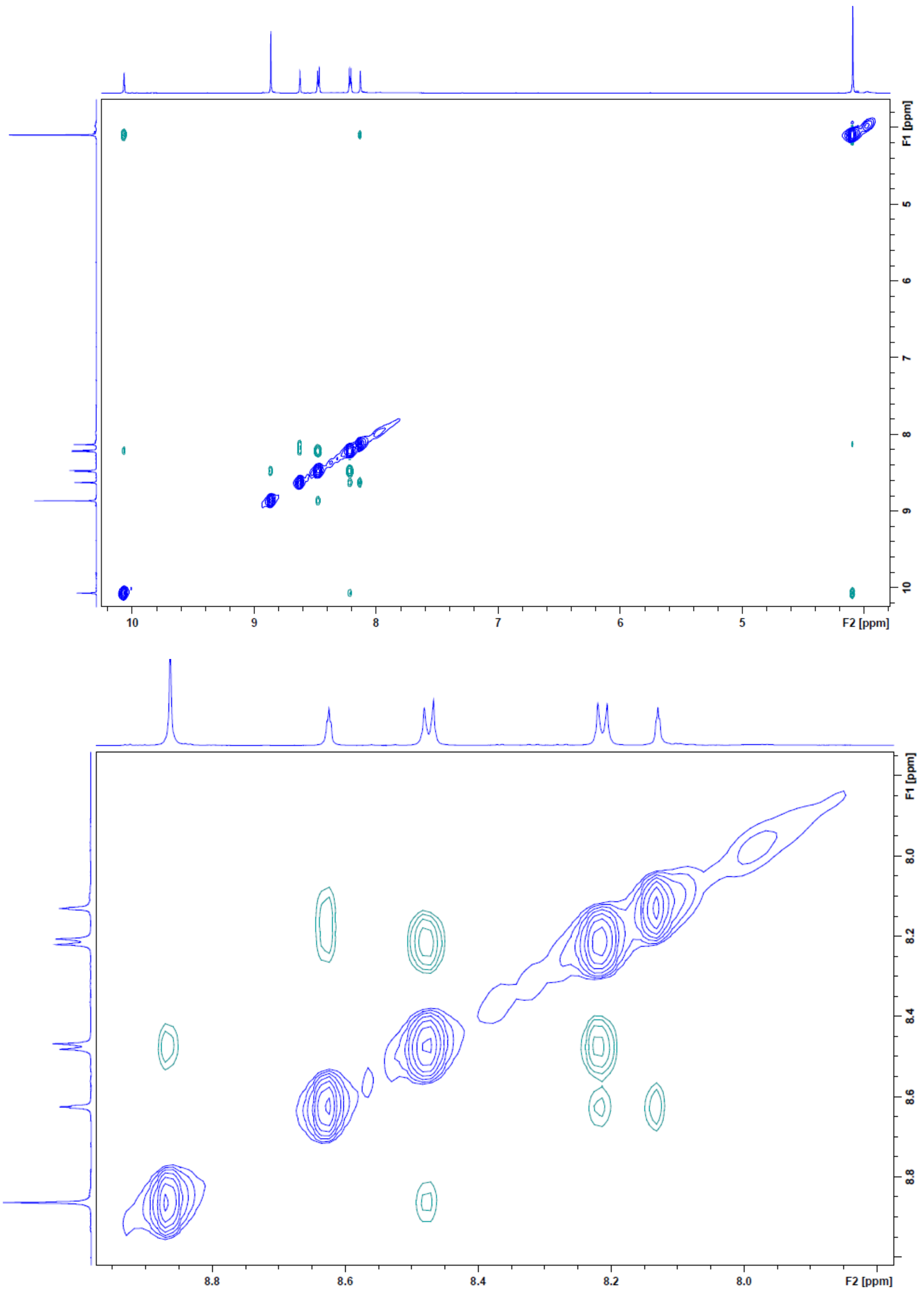


Figure S13. Full range (top) and partial (bottom) ^1H-^1H ROESY NMR spectra (600.3 MHz, DMSO-d_6, 298K) of porphyrin **4**.

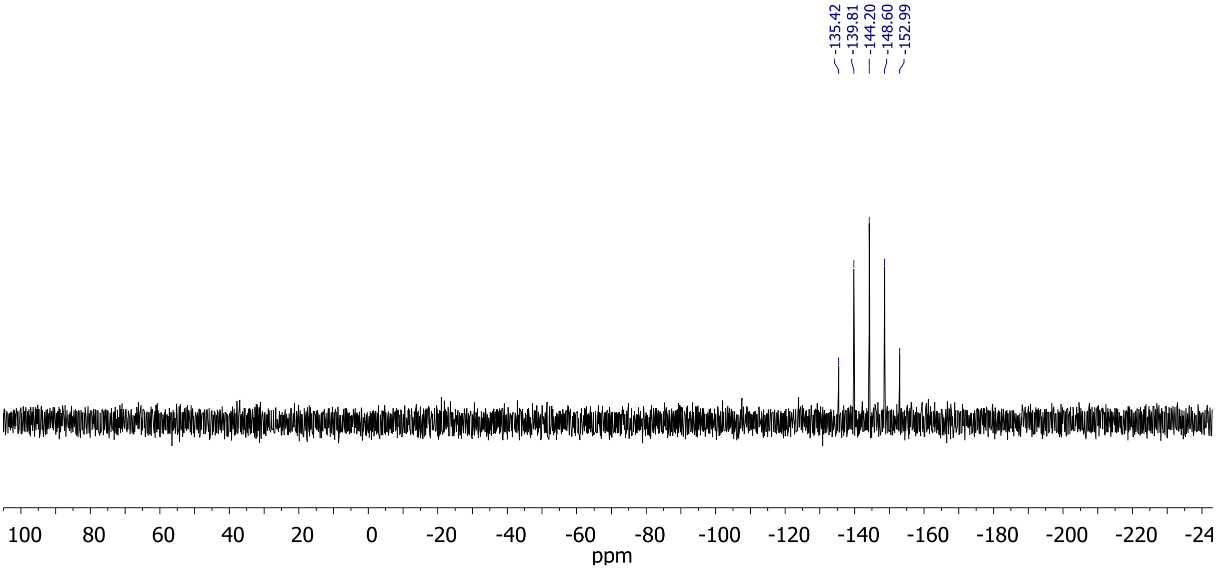


Figure S14. ^{31}P NMR spectrum (162 MHz, DMSO-d_6, 298 K) of porphyrin **4**.

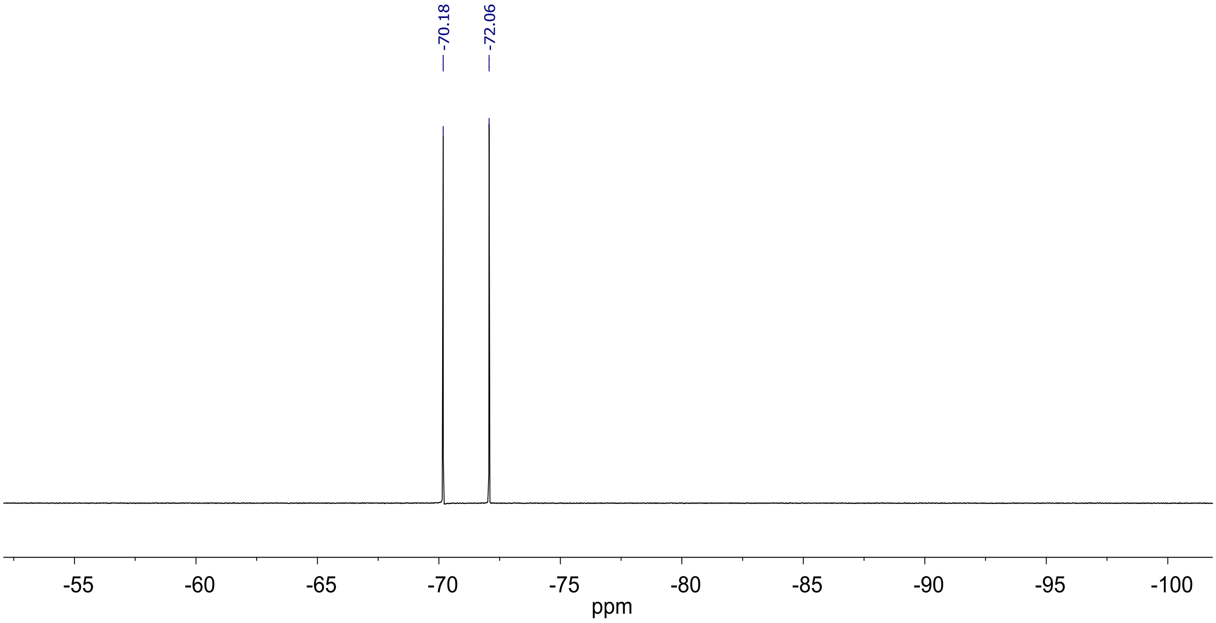


Figure S15. ^{19}F NMR spectrum (376.5 MHz, DMSO-d_6, 298 K) of porphyrin **4**.

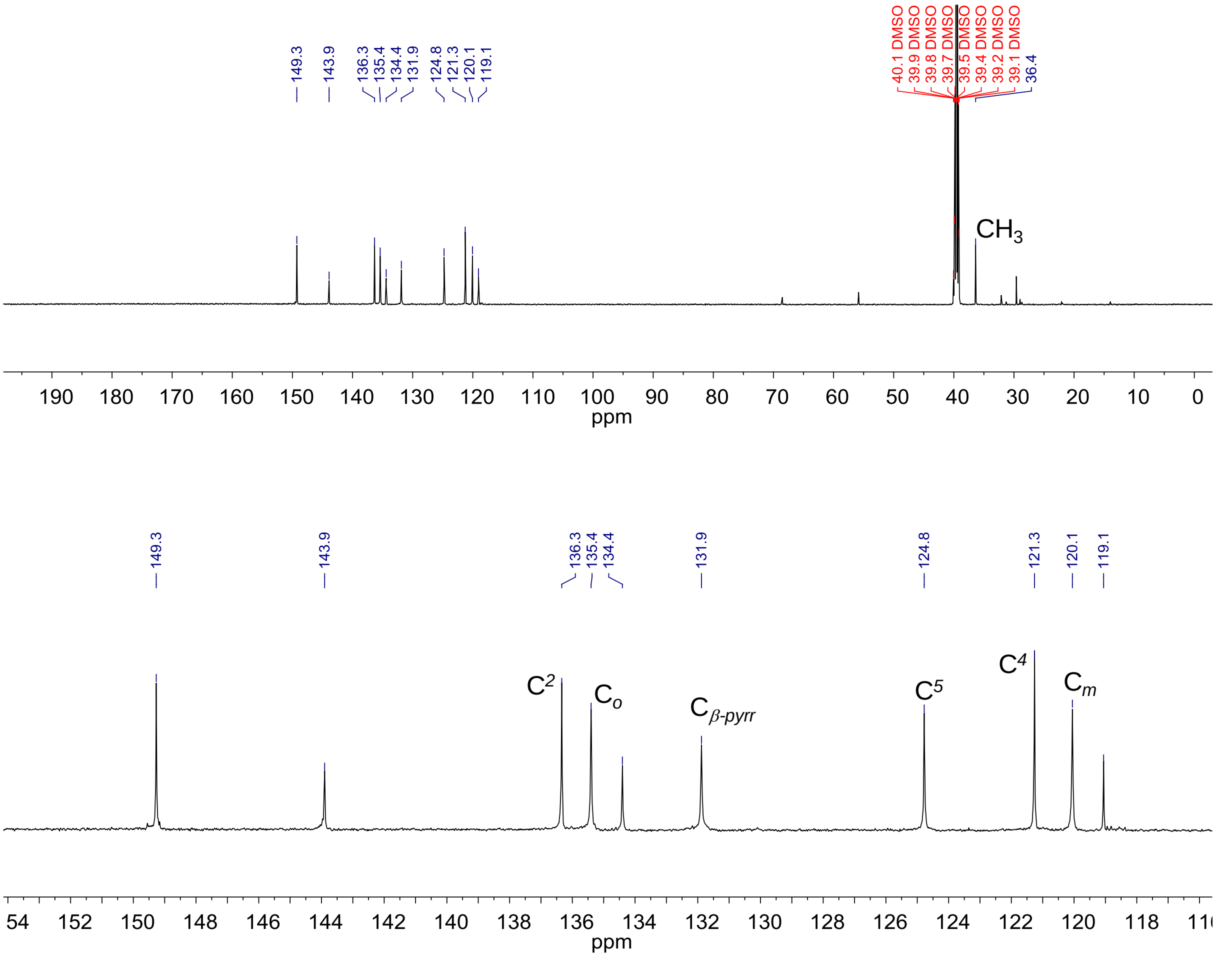
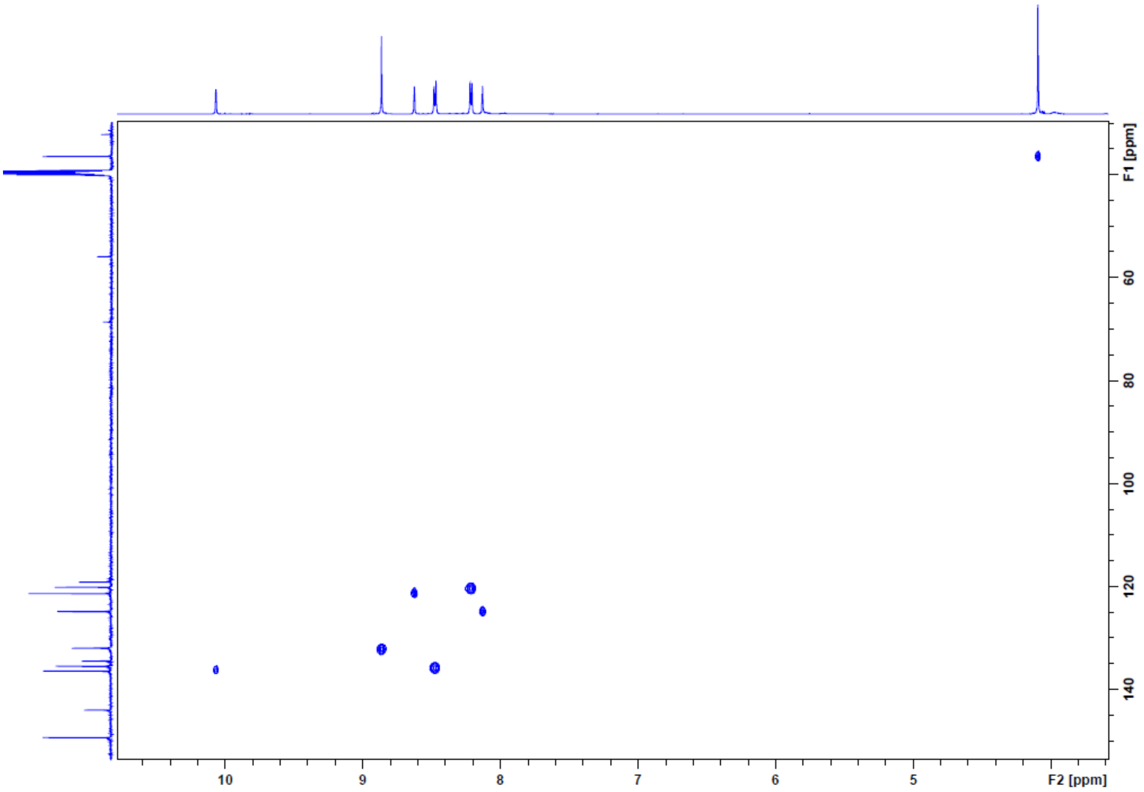


Figure S16. Full range (top) and partial (bottom) $^{13}C\{^1H\}$ NMR spectra (150.9 MHz, DMSO-d_6, 298 K) of porphyrin **4**.



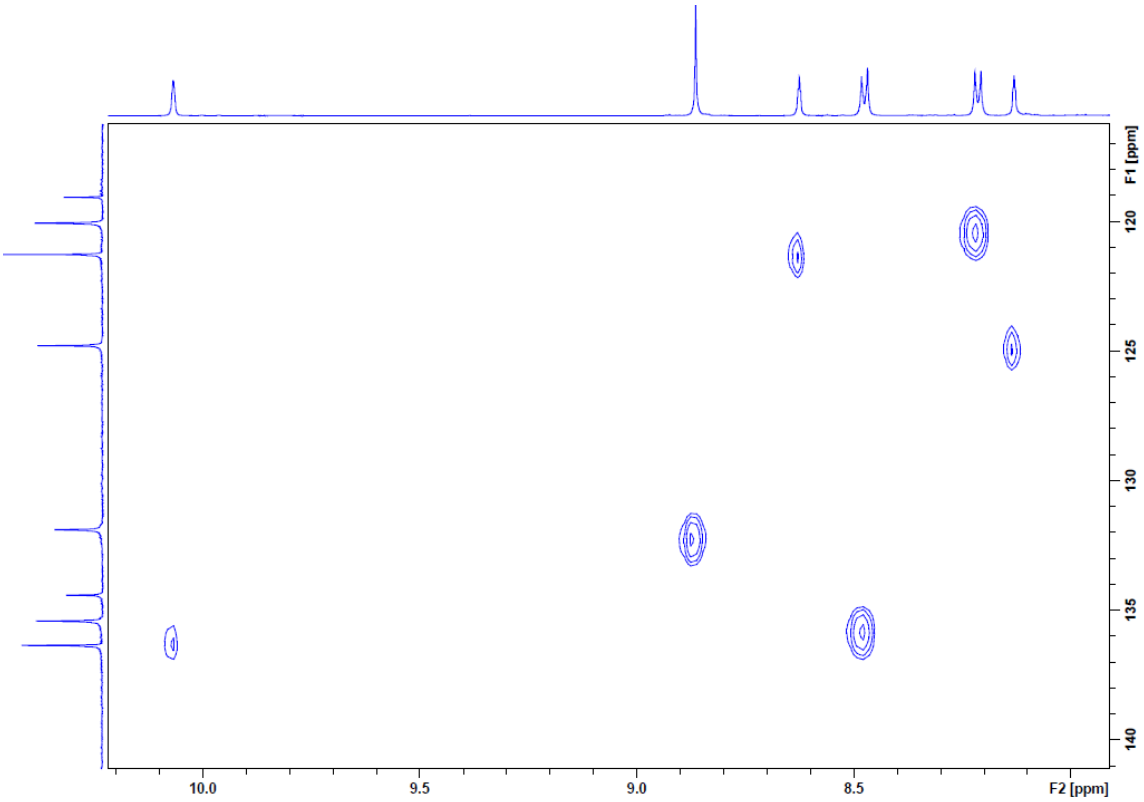


Figure S17. Full range (top) and partial (bottom) ^{1}H-^{13}C HSQC NMR spectra (600.3 MHz, DMSO-d_6, 298 K) of porphyrin **4**.

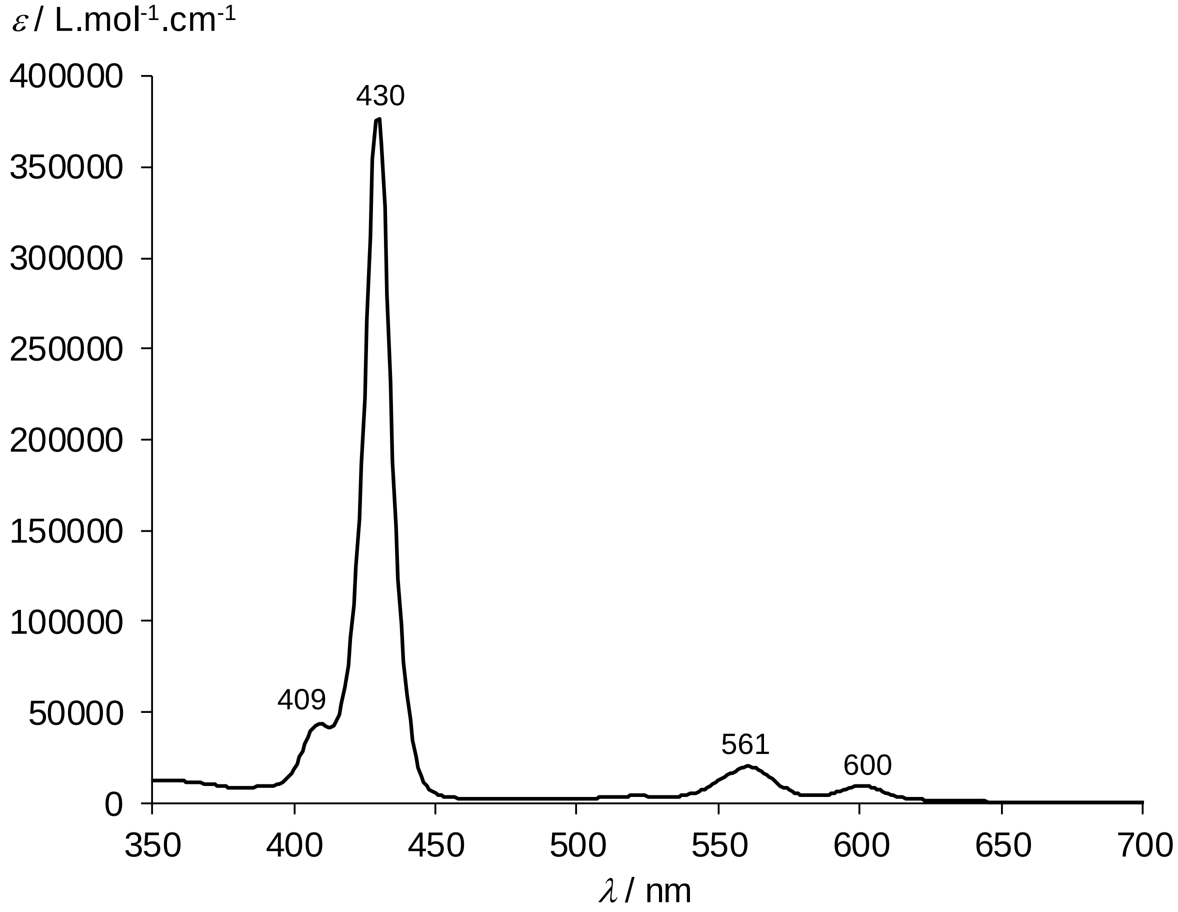


Figure S18. UV-vis spectrum (DMSO) of porphyrin **4**.

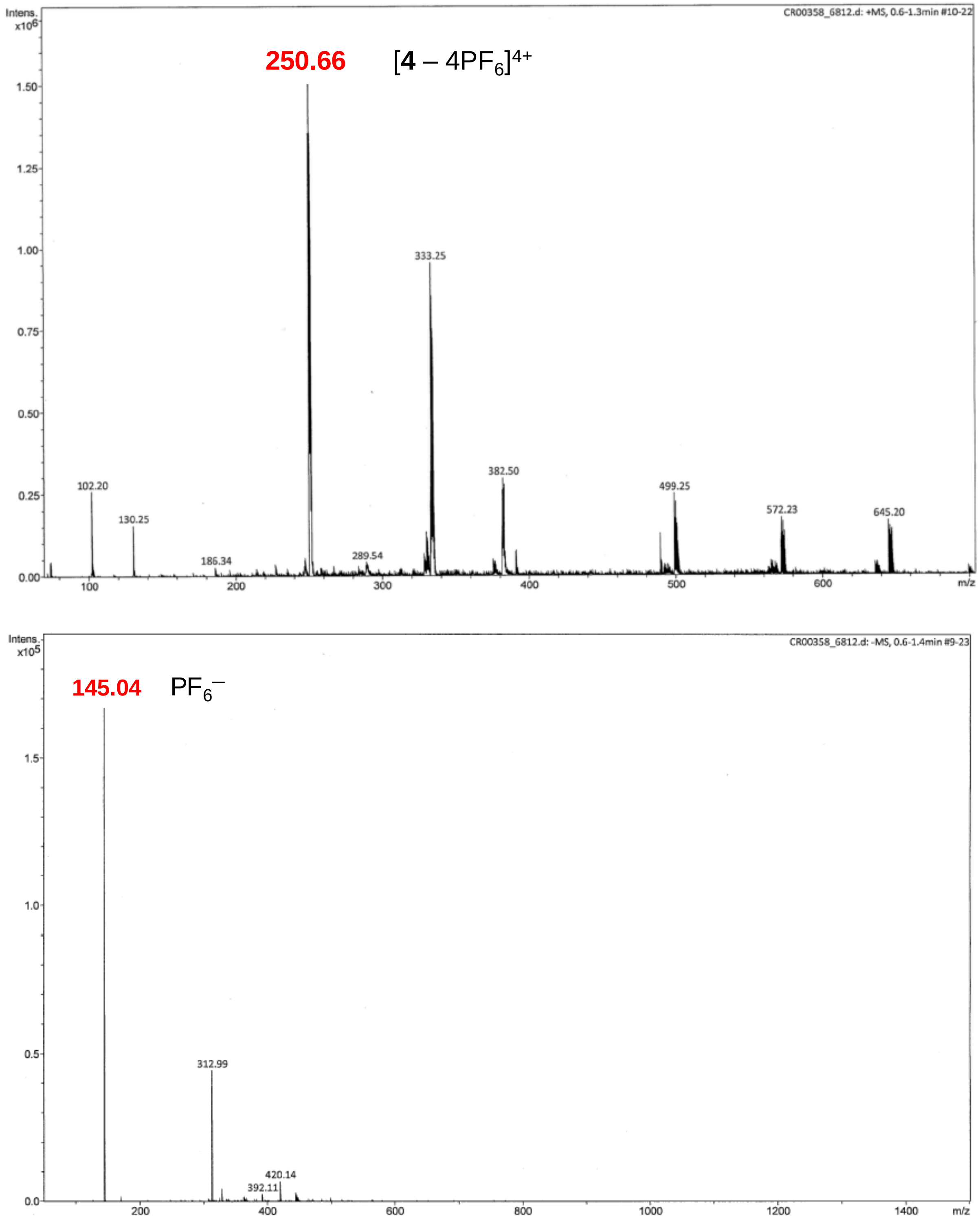


Figure S19. ESI-TOF positive mode (top) and negative mode (bottom) mass spectra of porphyrin **4**.

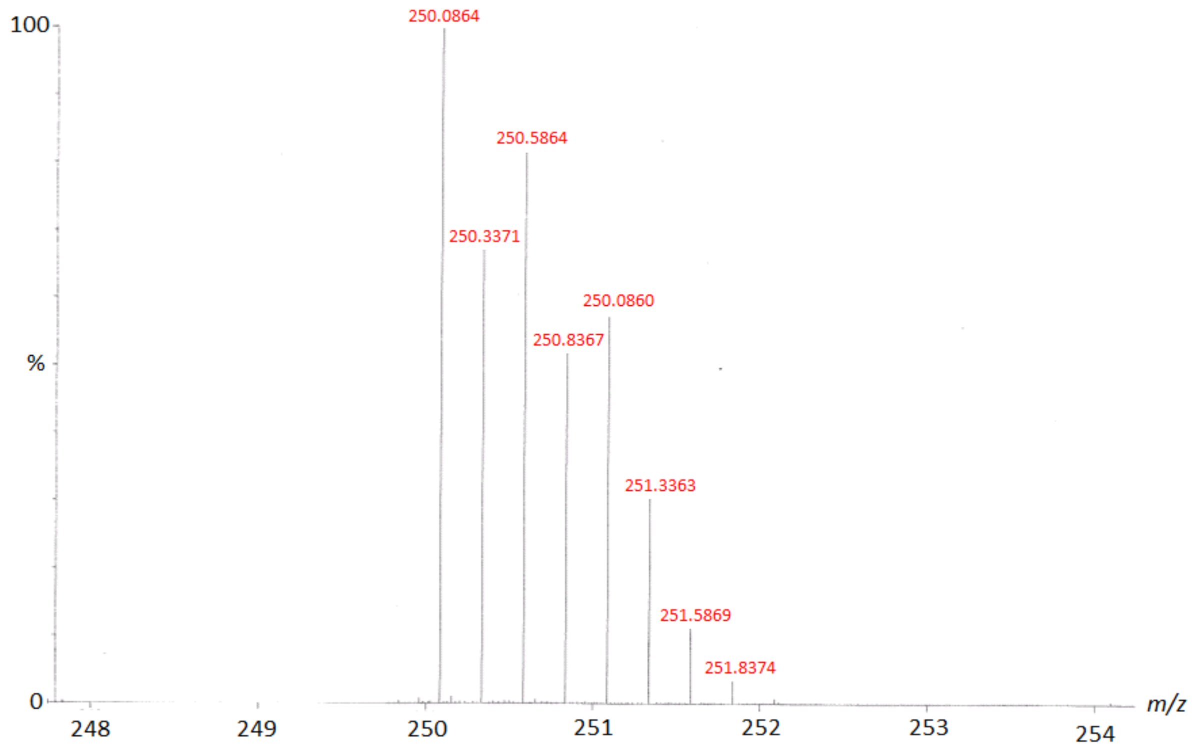
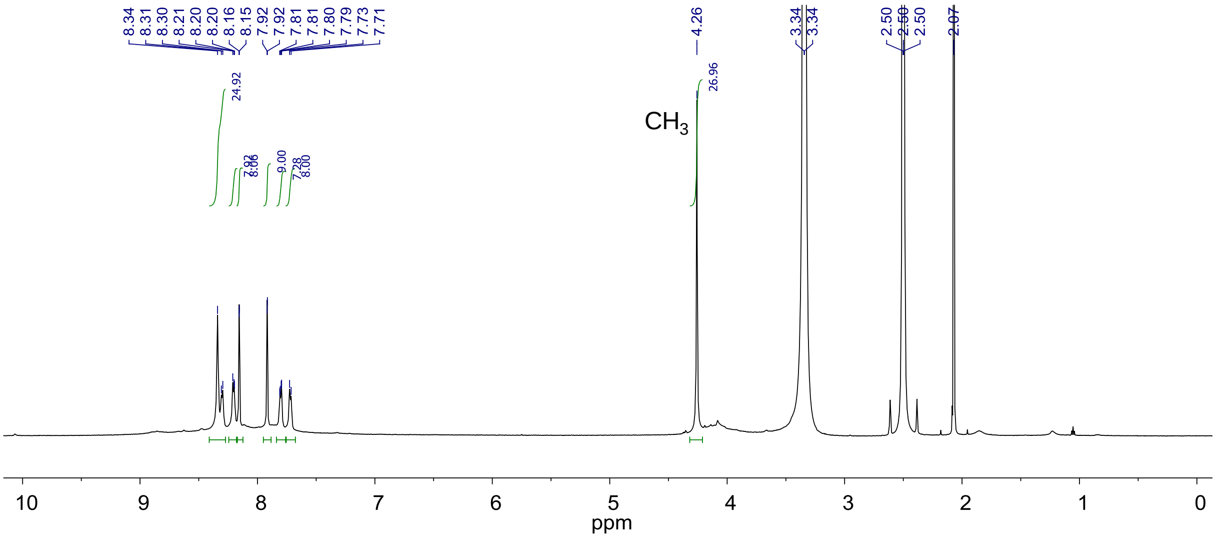


Figure S20. High-resolution ESI-TOF (positive mode) mass spectrum of porphyrin **4**.



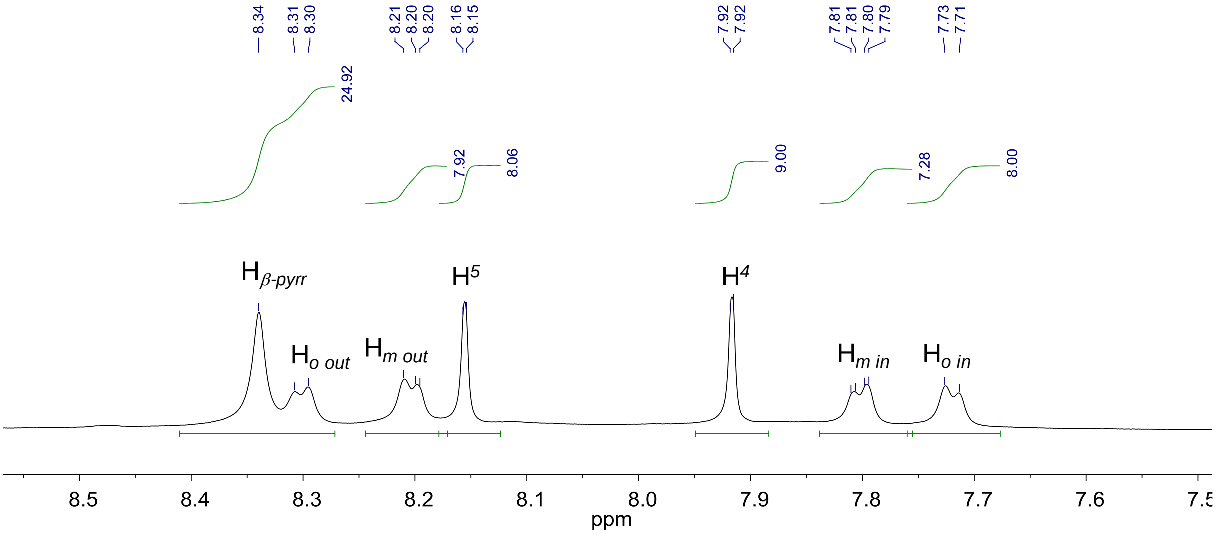


Figure S21. Full range (top) and partial (bottom) ^{1}H NMR spectra (600.3 MHz, DMSO-d_6, 298 K) of cofacial porphyrin dimer **[Ag$_4$(1)$_2$](PF$_6$)$_4$**.

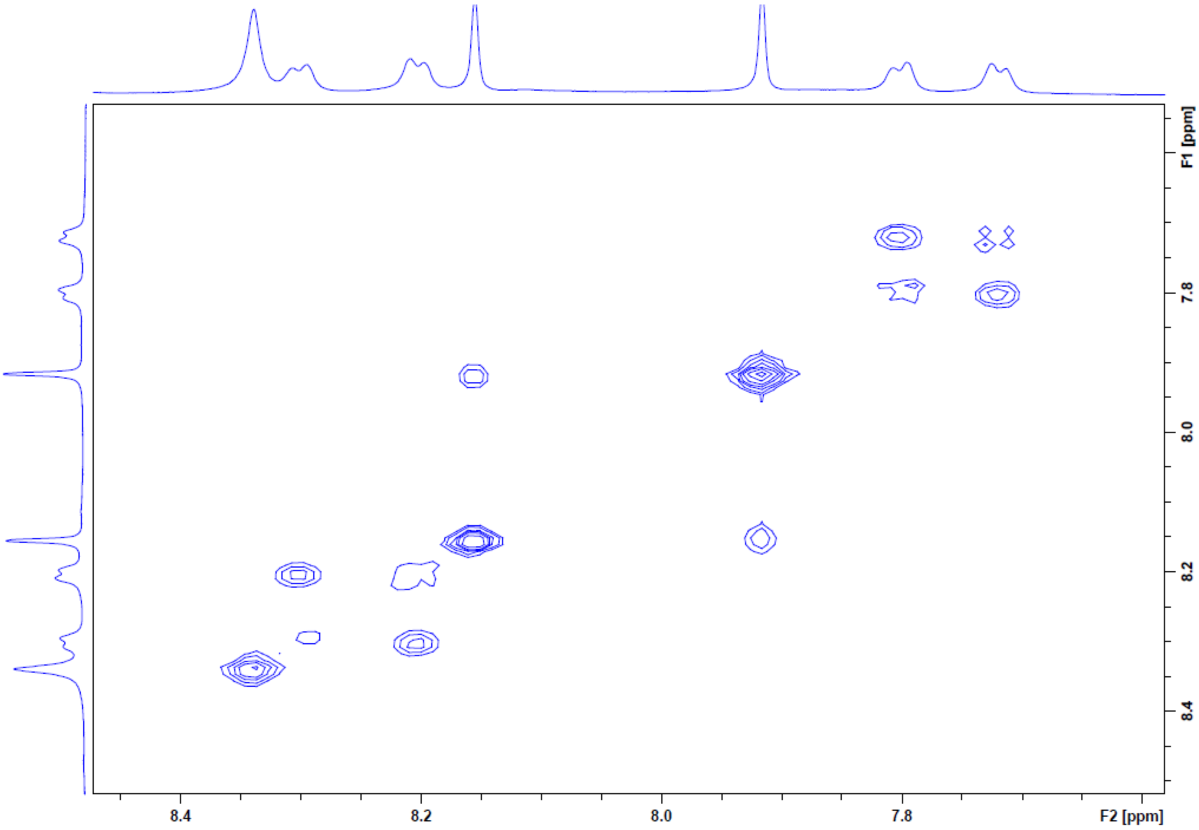


Figure S22. ^{1}H-^{1}H COSY NMR spectrum (600.3 MHz, DMSO-d_6, 298 K) of cofacial porphyrin dimer **[Ag$_4$(1)$_2$](PF$_6$)$_4$**.

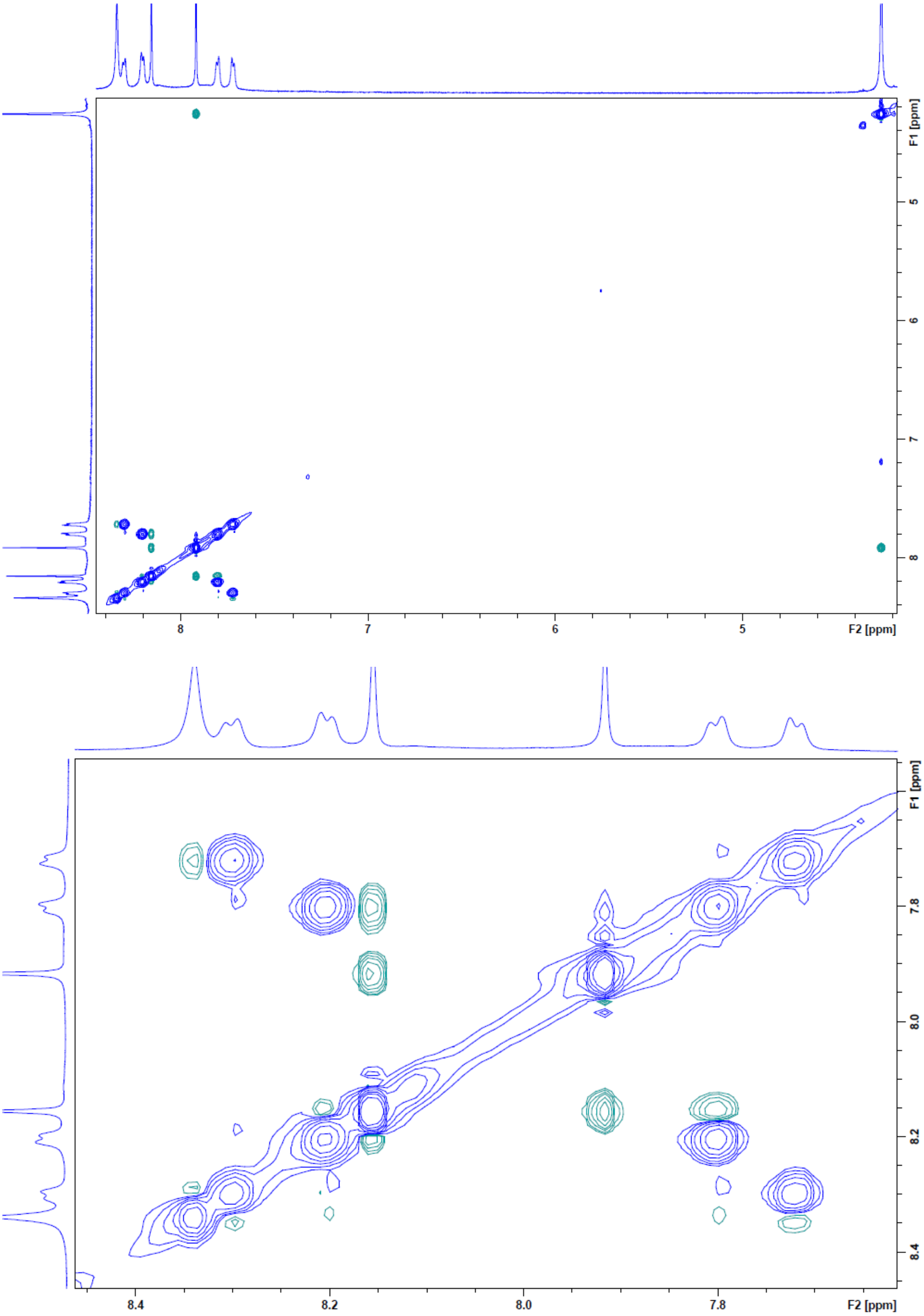


Figure S23. Full range (top) and partial (bottom) ^{1}H-^{1}H ROESY NMR spectra (600.3 MHz, DMSO-d_6, 298 K) of cofacial porphyrin dimer **[Ag$_4$(1)$_2$](PF$_6$)$_4$**. ROESY correlation spots are green.

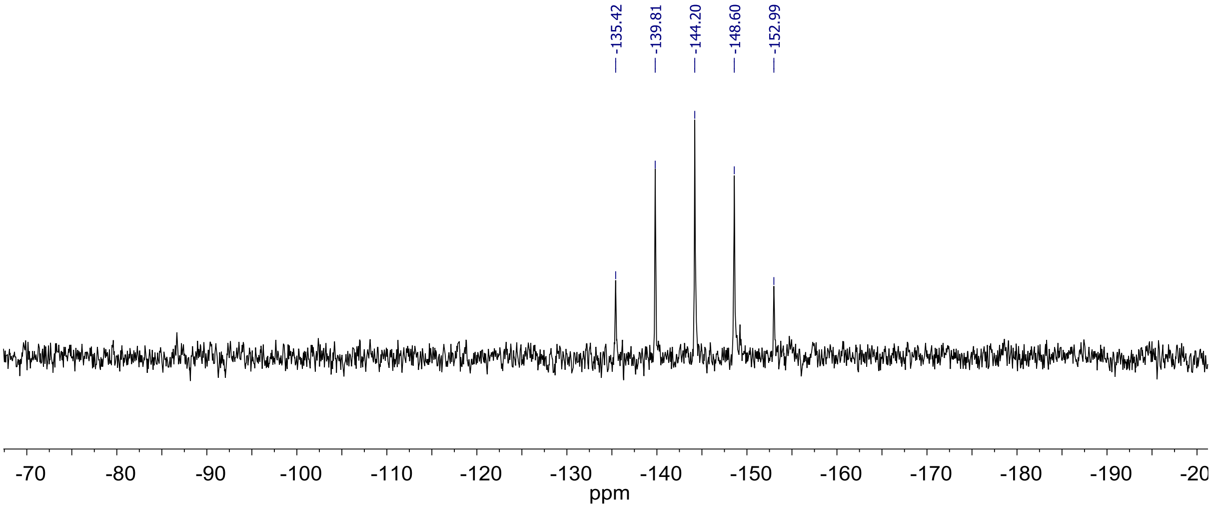


Figure S24. ^{31}P NMR spectra (162 MHz, DMSO-d_6, 298 K) cofacial porphyrin dimer **[Ag$_4$(1)$_2$](PF$_6$)$_4$**.

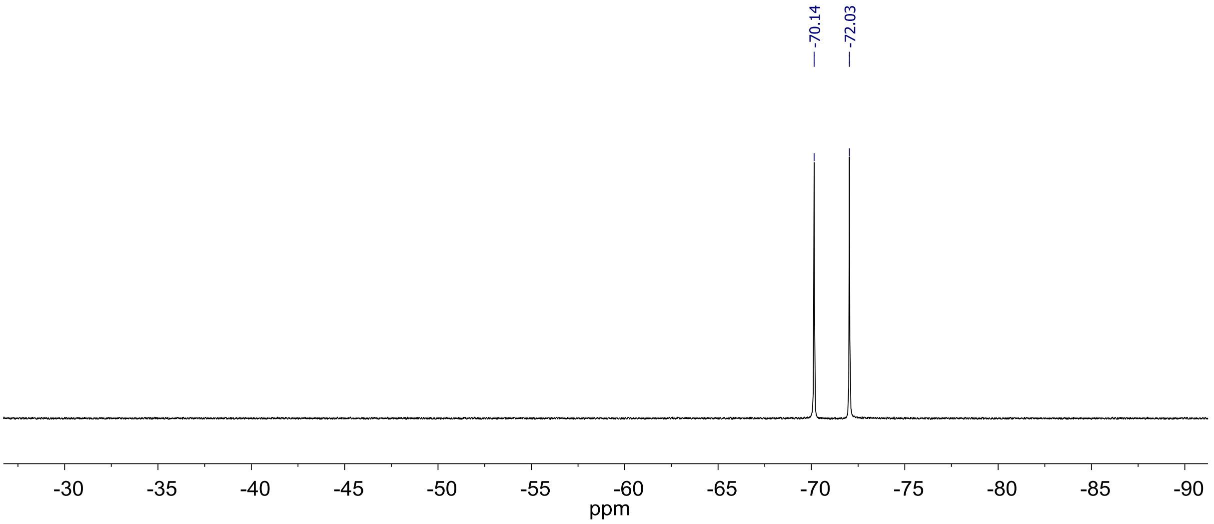


Figure S25. ^{19}F NMR spectra (376.5 MHz, DMSO-d_6, 298K) of cofacial porphyrin dimer **[Ag$_4$(1)$_2$](PF$_6$)$_4$**.

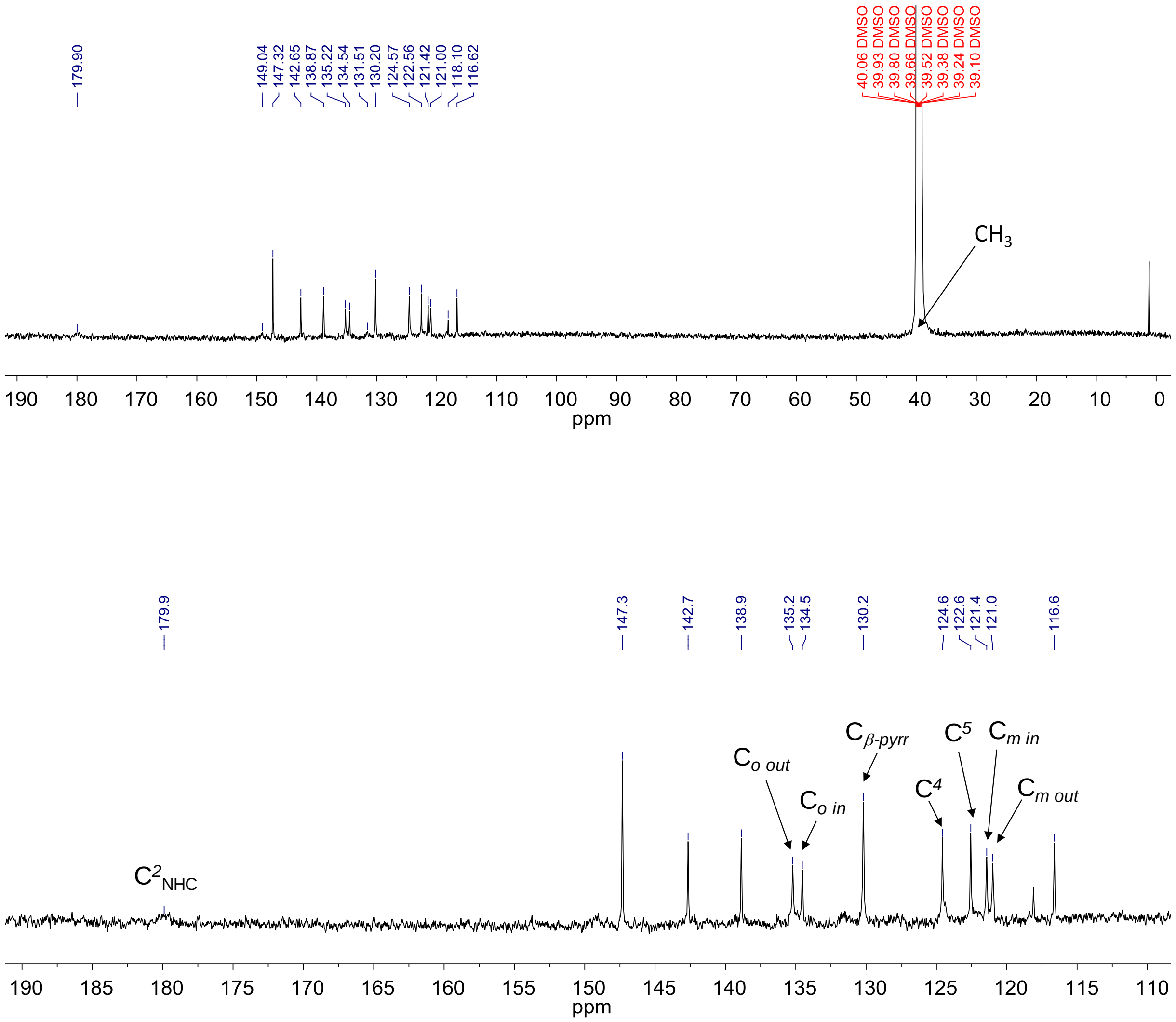


Figure S26. Full range (top) and partial (bottom) $^{13}C\{^1H\}$ NMR spectra (150.9 MHz, DMSO-*d*$_6$, 298 K) of cofacial porphyrin dimer **$[Ag_4(1)_2](PF_6)_4$**.

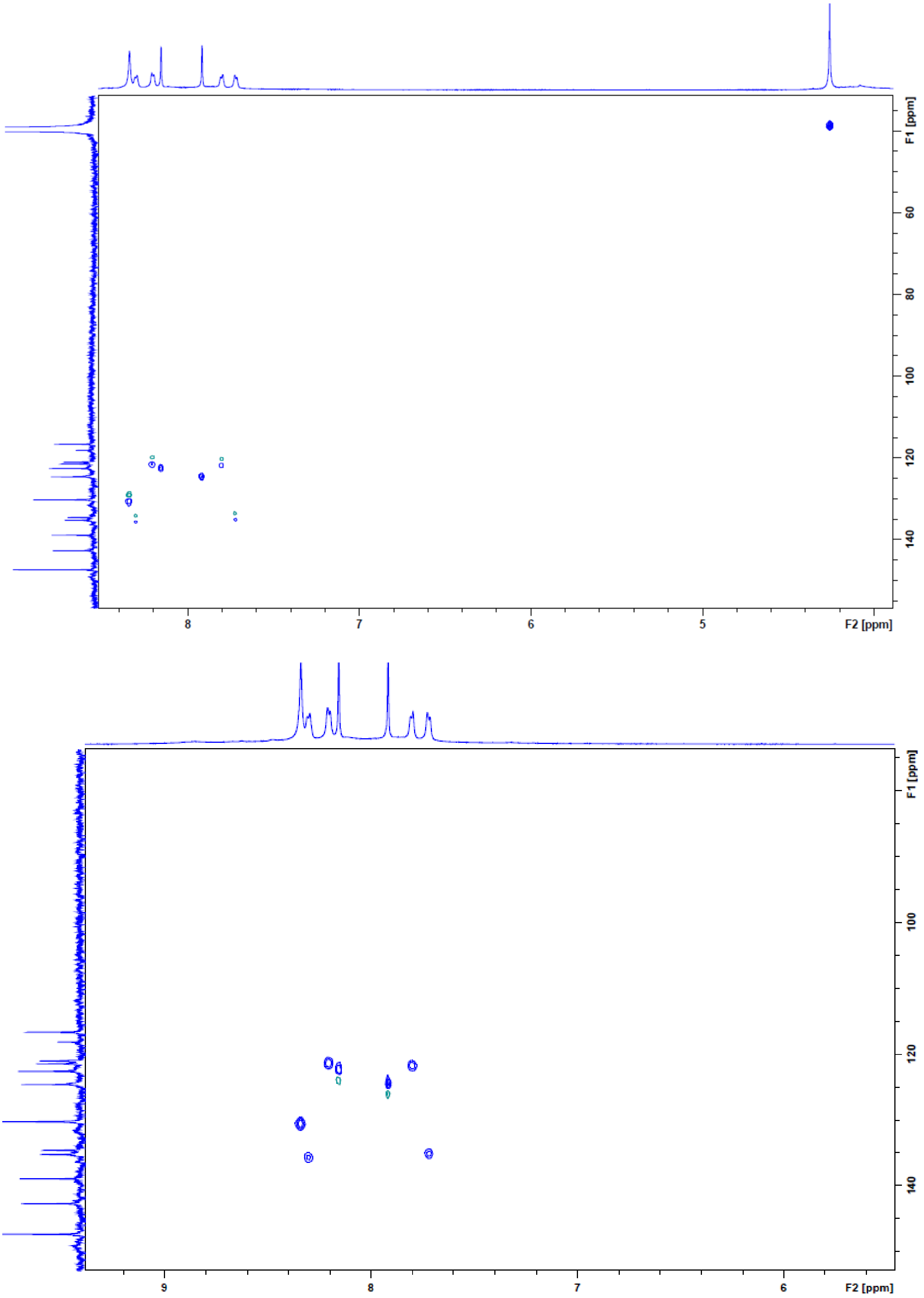
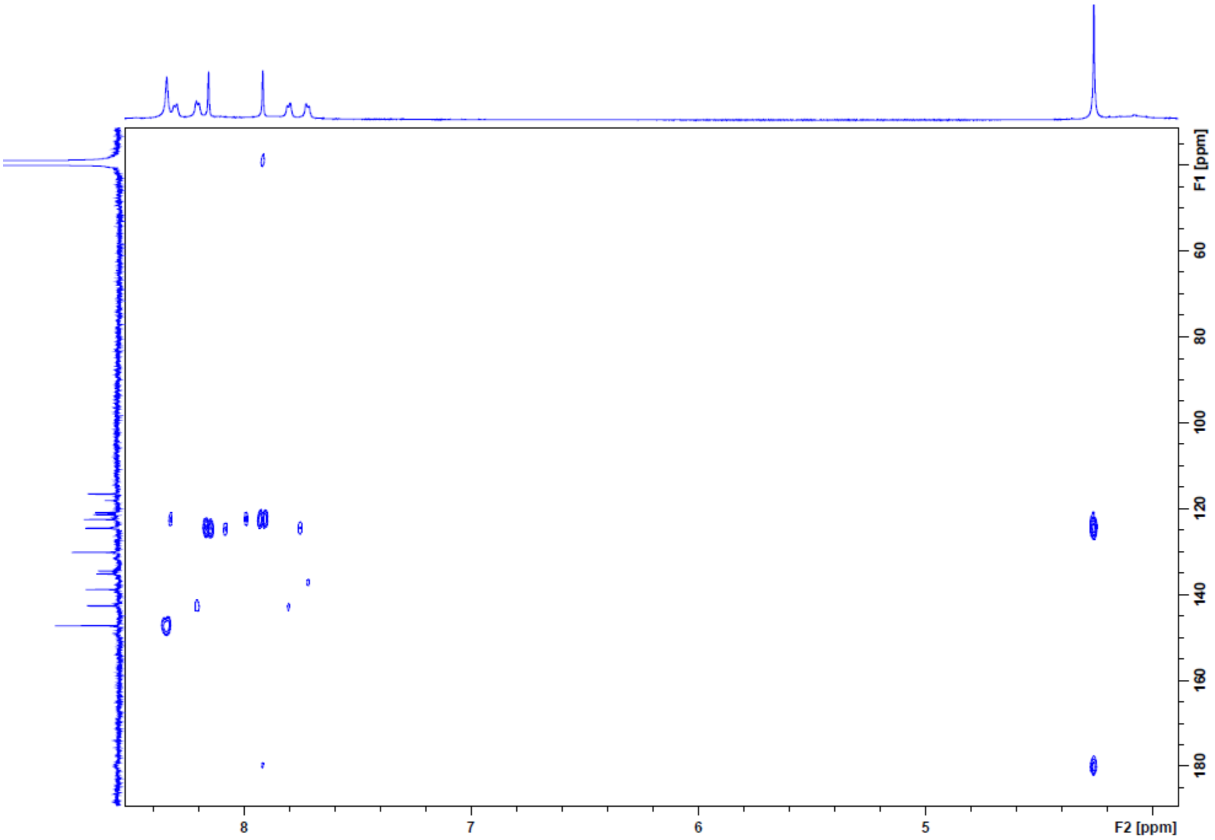


Figure S27. Full range (top) and partial (bottom) ^{1}H-^{13}C HSQC NMR spectra (600.3 MHz, DMSO-d_6, 298 K) of cofacial porphyrin dimer **[Ag_4(1)$_2$](PF_6)$_4$**.



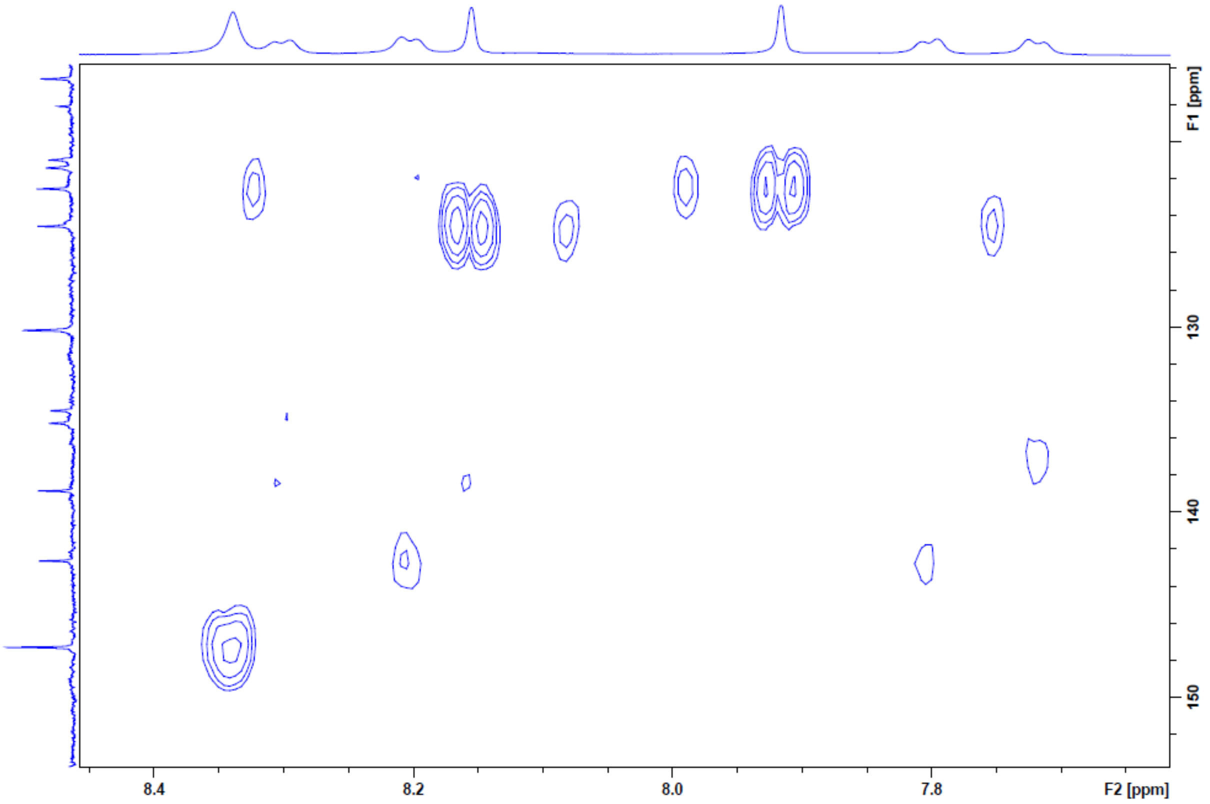


Figure S28. Full range (top) and partial (bottom) ^{1}H-^{13}C HMBC NMR spectra (600.3 MHz, DMSO-*d*$_6$, 298 K) of cofacial porphyrin dimer **[Ag$_4$(1)$_2$](PF$_6$)$_4$**.

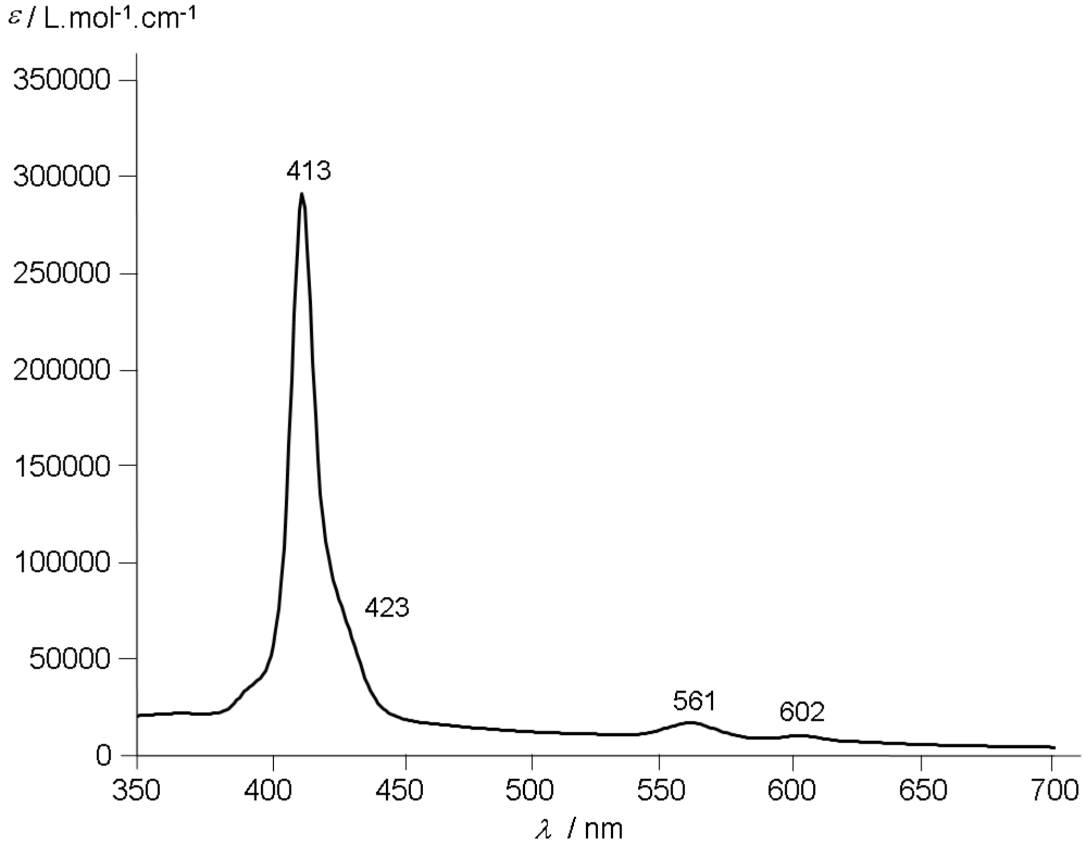


Figure S29. UV-vis spectrum (DMSO) of cofacial porphyrin dimer **[Ag$_4$(1)$_2$](PF$_6$)$_4$.**

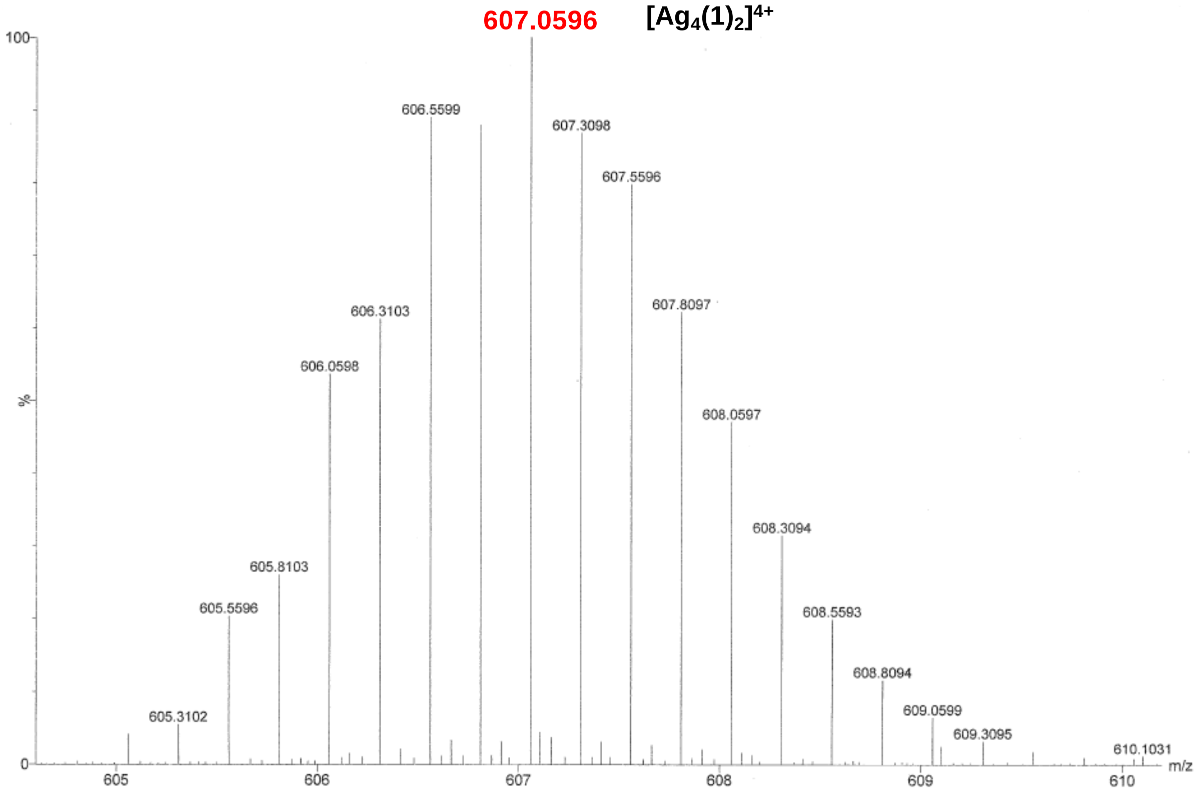


Figure S30. High resolution ESI-TOF (positive mode) mass spectrum of cofacial porphyrin dimer **$[Ag_4(1)_2](PF_6)_4$**.

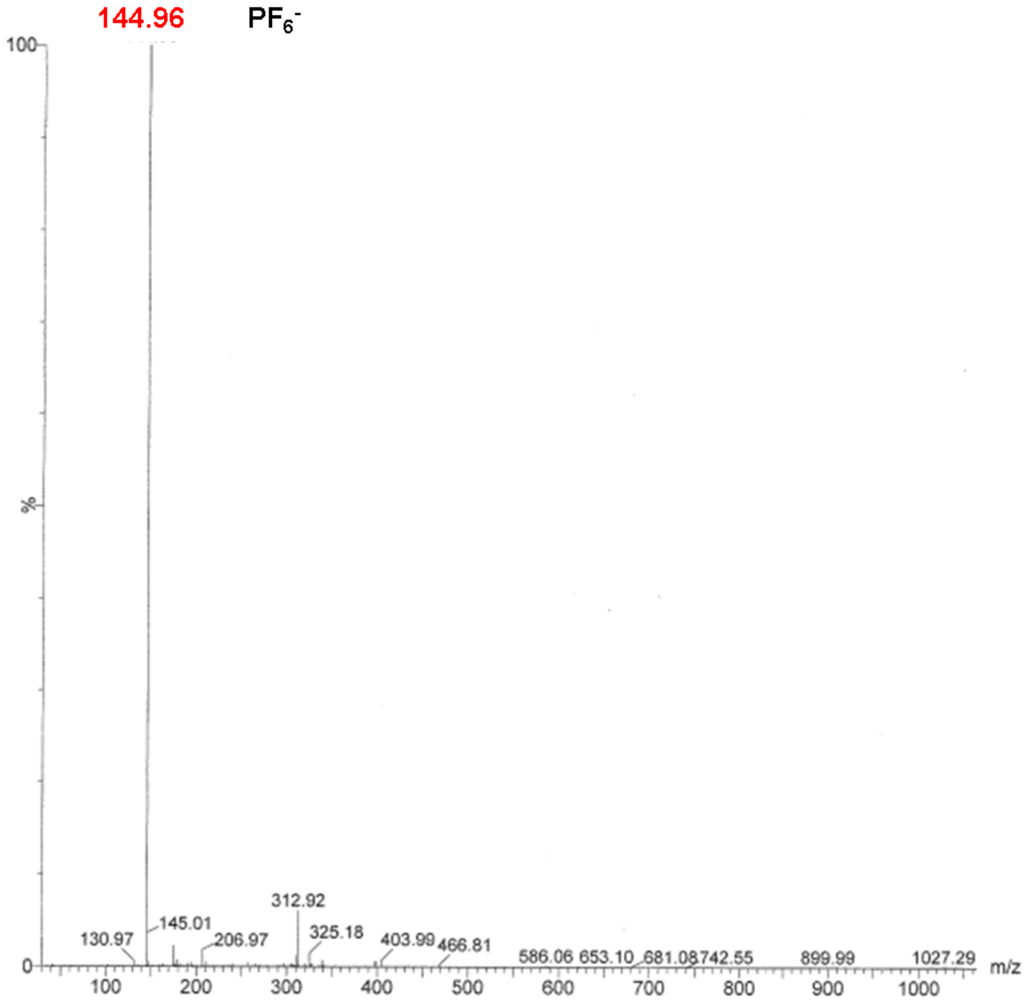


Figure S31. ESI-TOF (negative mode) mass spectrum of cofacial porphyrin dimer **$[Ag_4(1)_2](PF_6)_4$**.

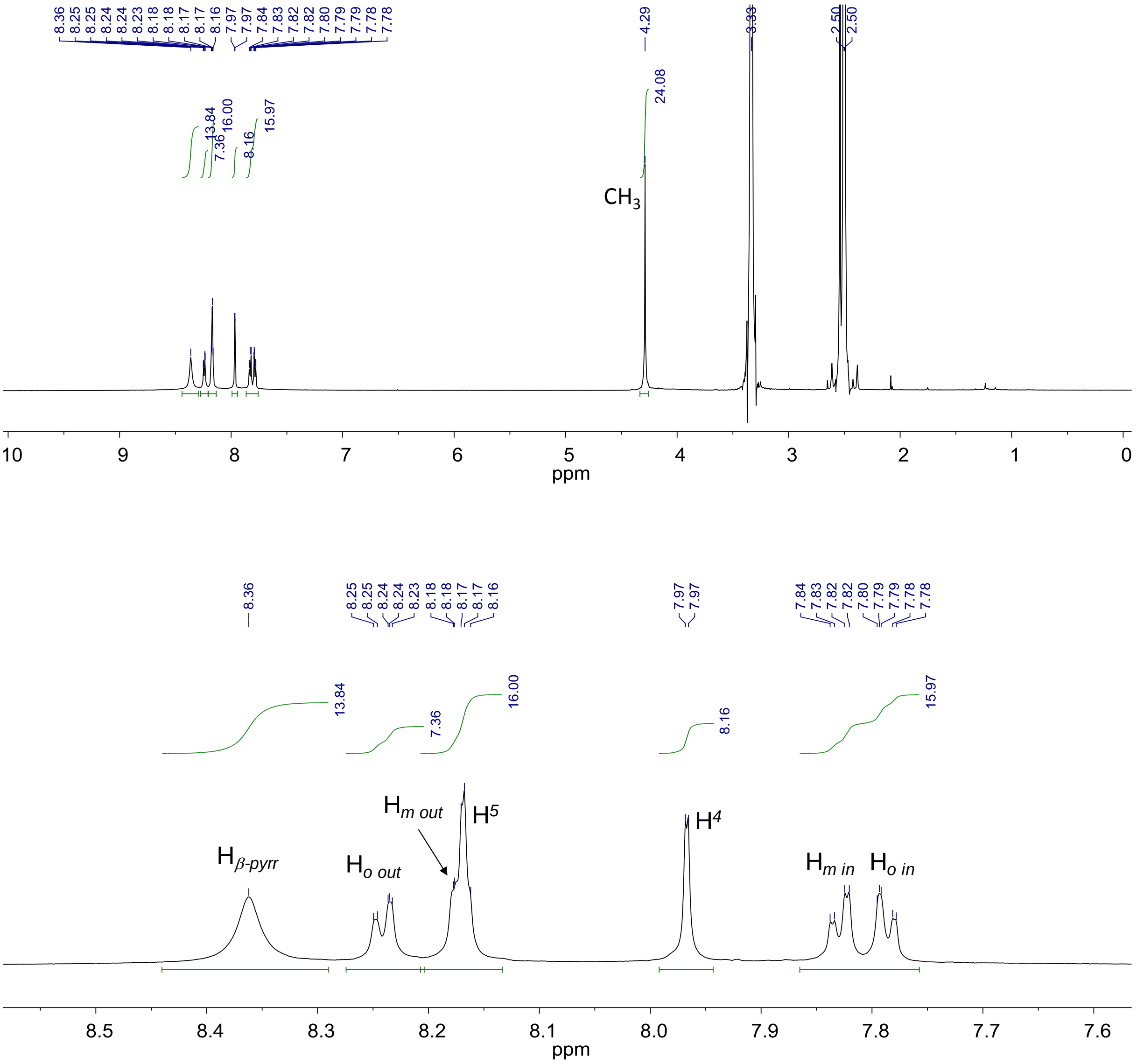


Figure S32. Full range (top) and partial (bottom) ^{1}H NMR spectra (600.3 MHz, DMSO-d_6, 298 K) of cofacial porphyrin dimer **$[Au_4(1)_2](PF_6)_4$**.

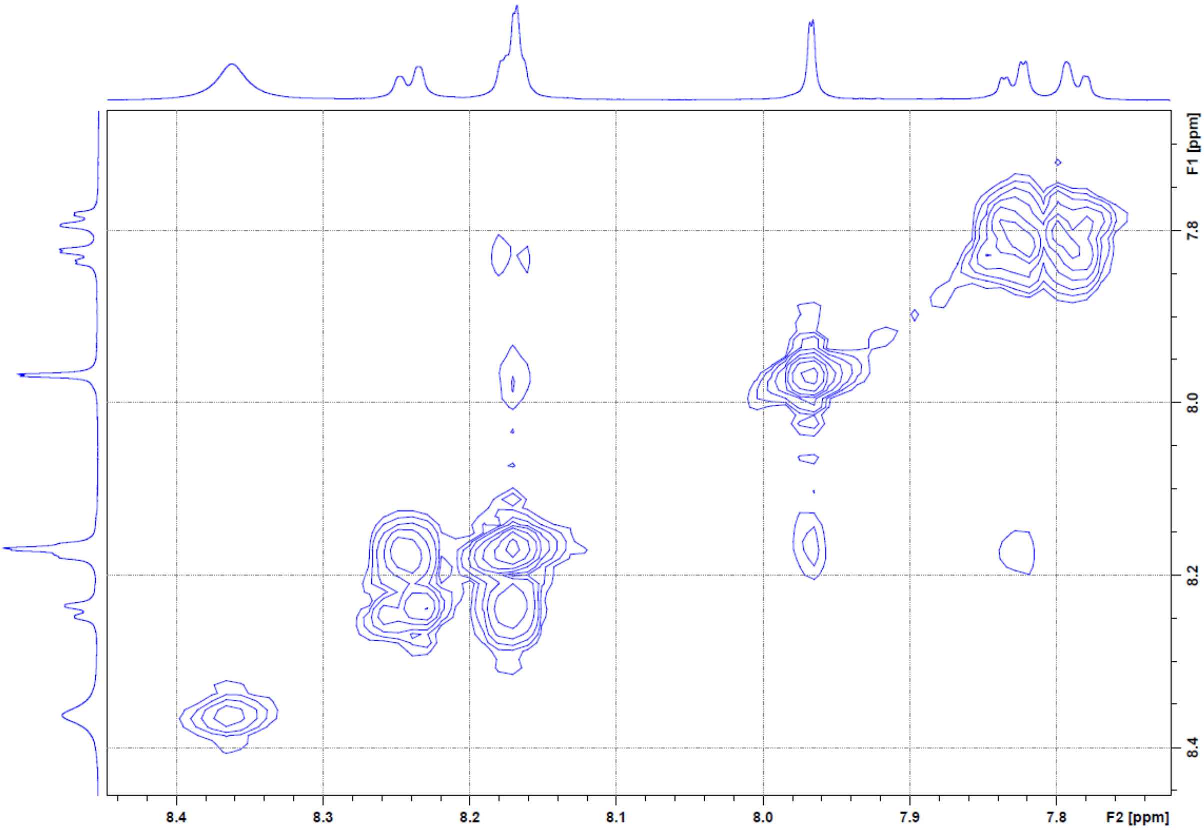


Figure S33. ^1H-^1H COSY NMR spectrum (600.3 MHz, DMSO-d_6, 298 K) of cofacial porphyrin dimer **[Au$_4$(1)$_2$](PF$_6$)$_4$.**

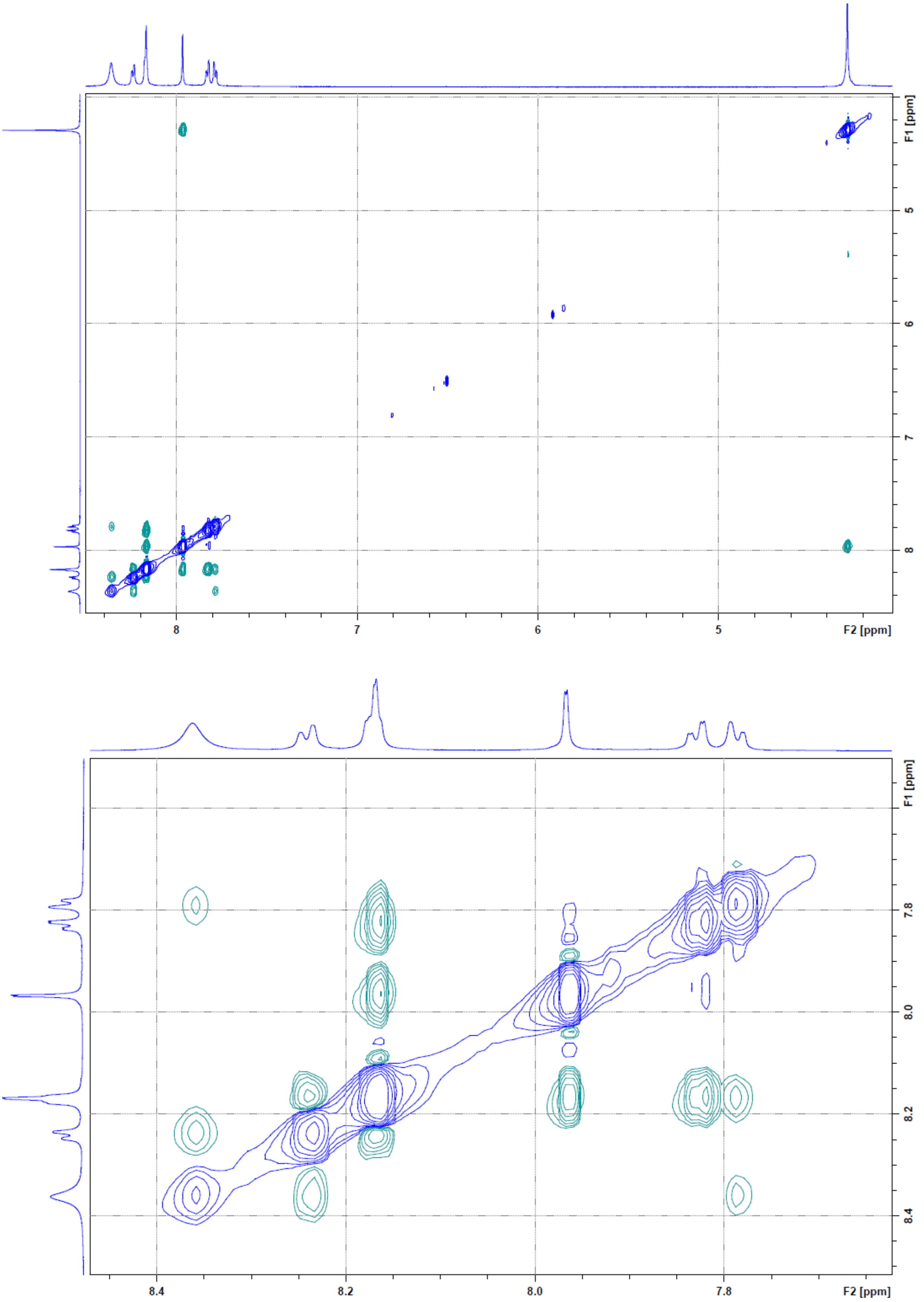


Figure S34. Full range (top) and partial (bottom) ^{1}H-^{1}H ROESY NMR spectra (600.3 MHz, DMSO-d_6, 298 K) of cofacial porphyrin dimer **[Au$_4$(1)$_2$](PF$_6$)$_4$**.

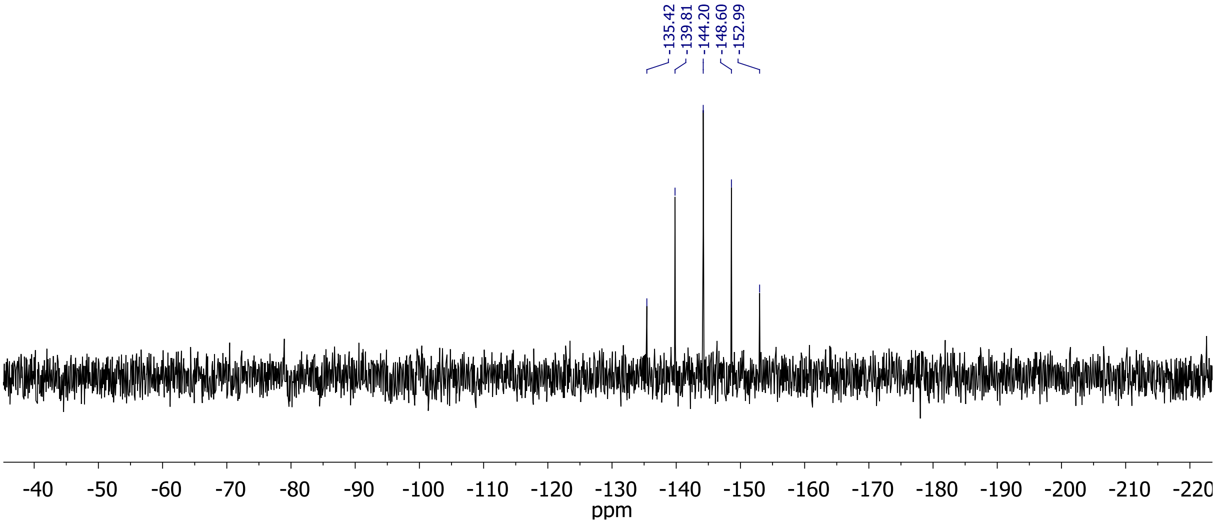


Figure S35. ^{31}P NMR spectra (162 MHz, DMSO-d_6, 298 K) cofacial porphyrin dimer **[Au$_4$(1)$_2$](PF$_6$)$_4$**.

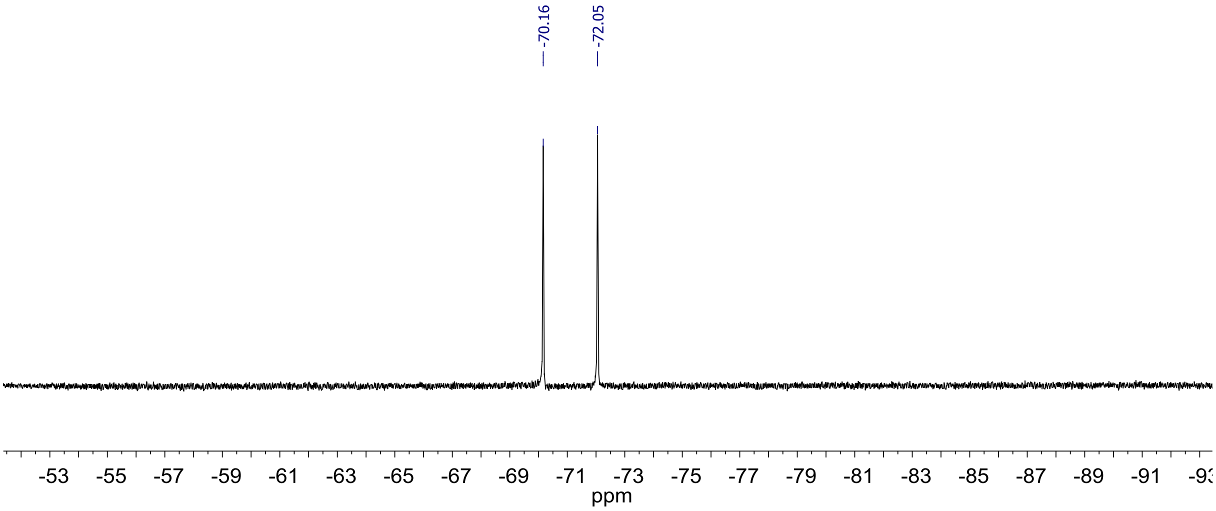


Figure S36. ^{19}F NMR spectra (376.5 MHz, DMSO-d_6, 298 K) of cofacial porphyrin dimer **[Au$_4$(1)$_2$](PF$_6$)$_4$**.

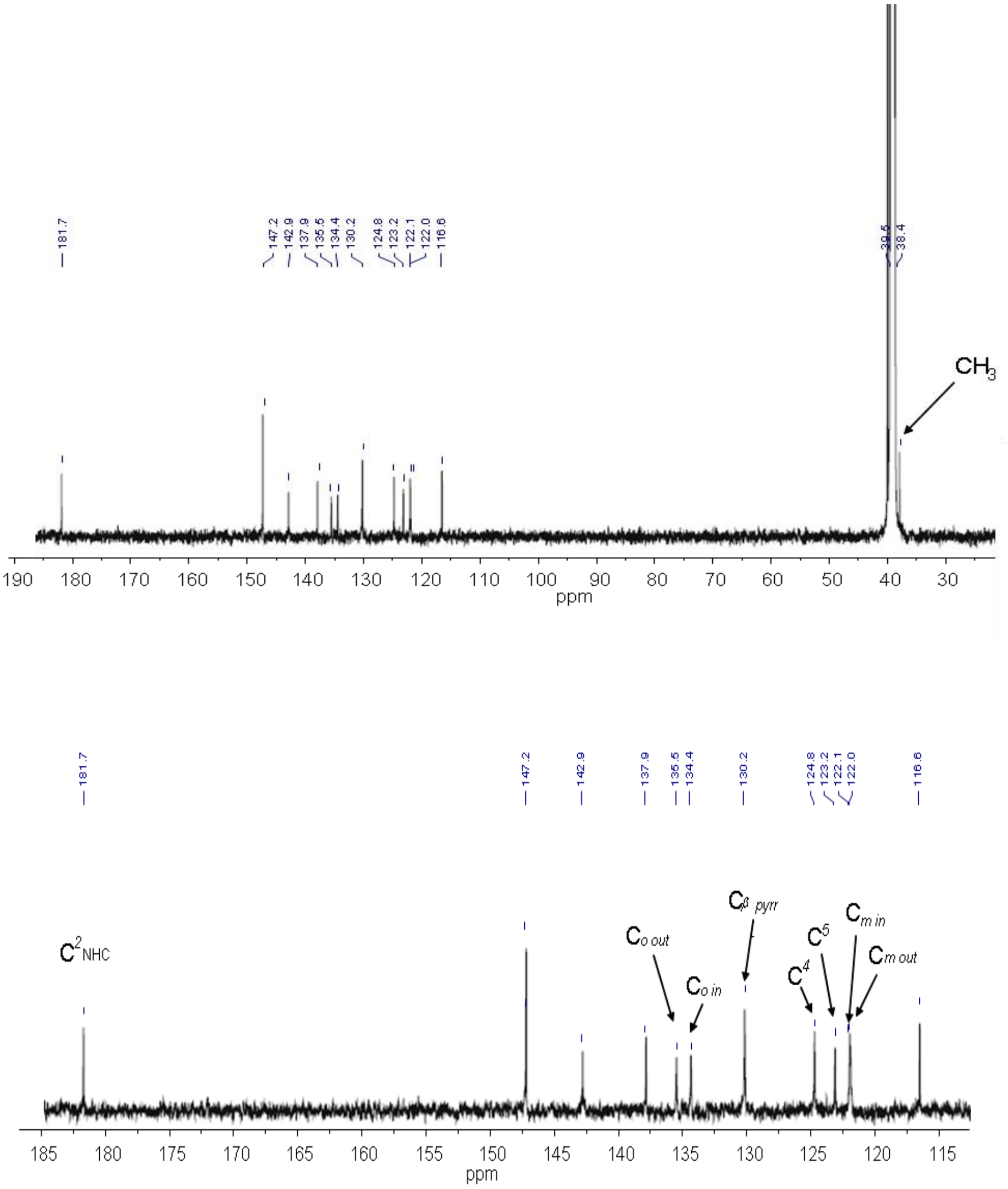


Figure S37. Full range (top) and partial (bottom) $^{13}C\{^1H\}$ NMR spectra (150.9 MHz, DMSO-d_6, 298 K) of cofacial porphyrin dimer **$[Au_4(1)_2](PF_6)_4$**.

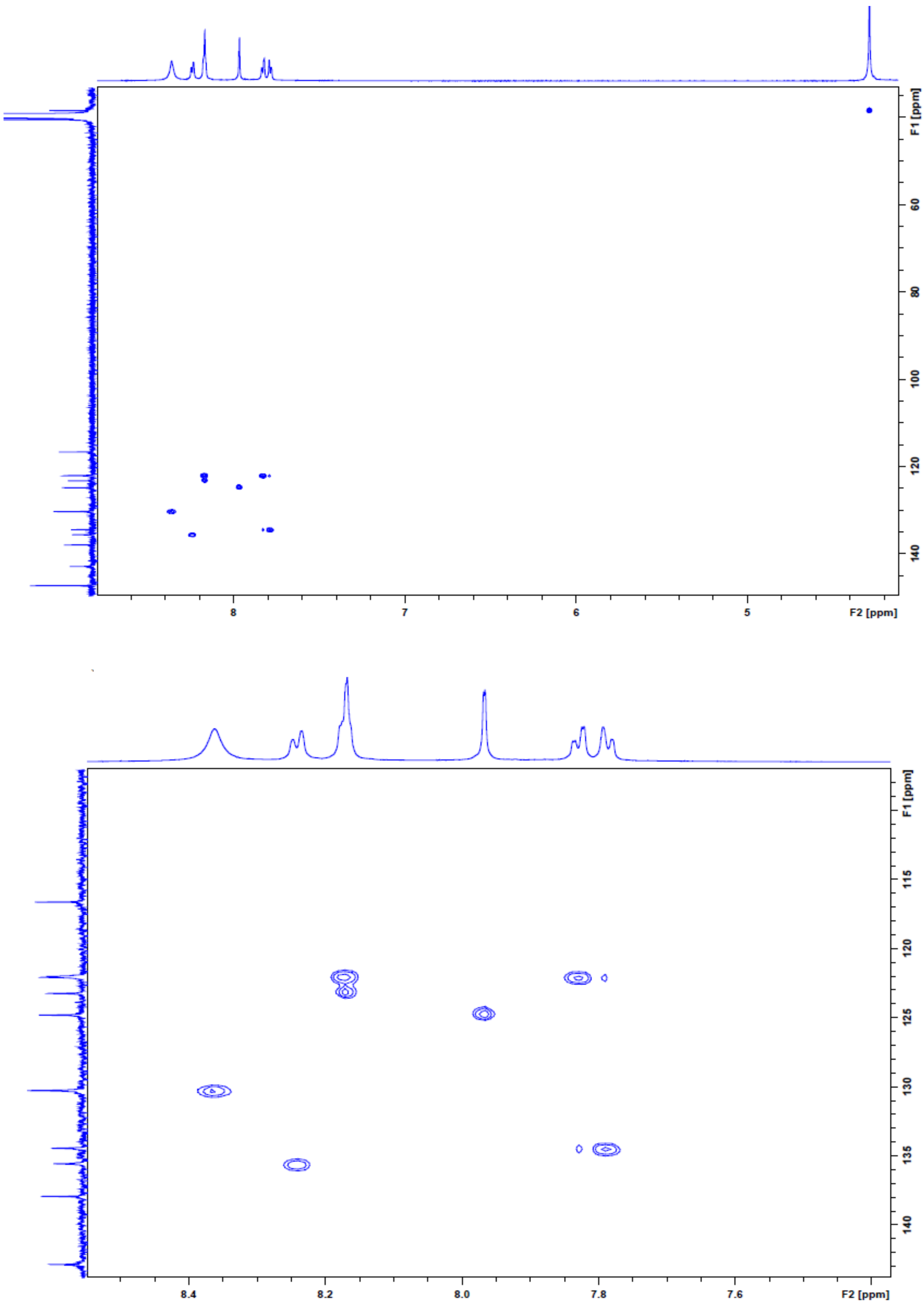


Figure S38. Full range (top) and partial (bottom) ^{1}H-^{13}C HSQC NMR spectra (600.3 MHz, DMSO-d_6, 298 K) of cofacial porphyrin dimer **[Au$_4$(1)$_2$](PF$_6$)$_4$**.

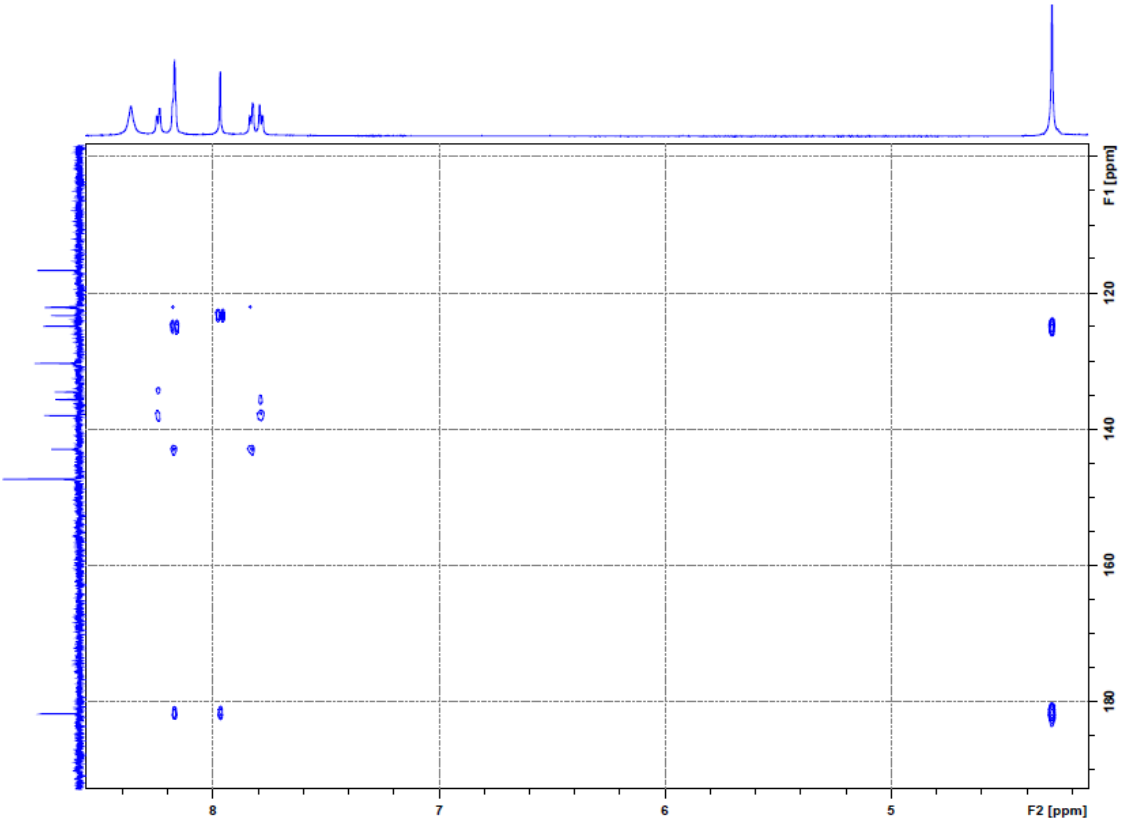


Figure S39. ^{1}H-^{13}C HMBC NMR spectrum (600.3 MHz, DMSO-d_6, 298 K) of cofacial porphyrin dimer **[Au$_4$(1)$_2$](PF$_6$)$_4$**.

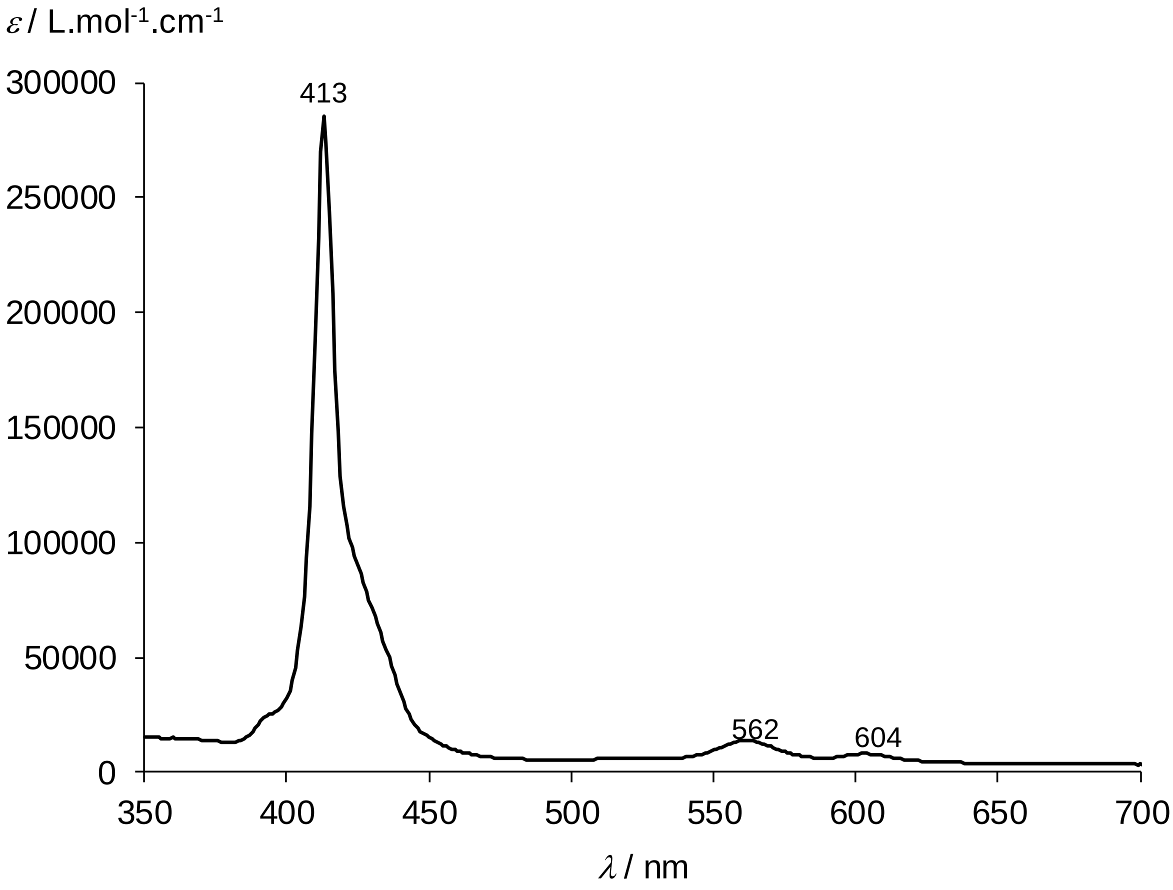


Figure S40. UV-vis spectrum (DMSO) of cofacial porphyrin dimer **[Au$_4$(1)$_2$](PF$_6$)$_4$**.

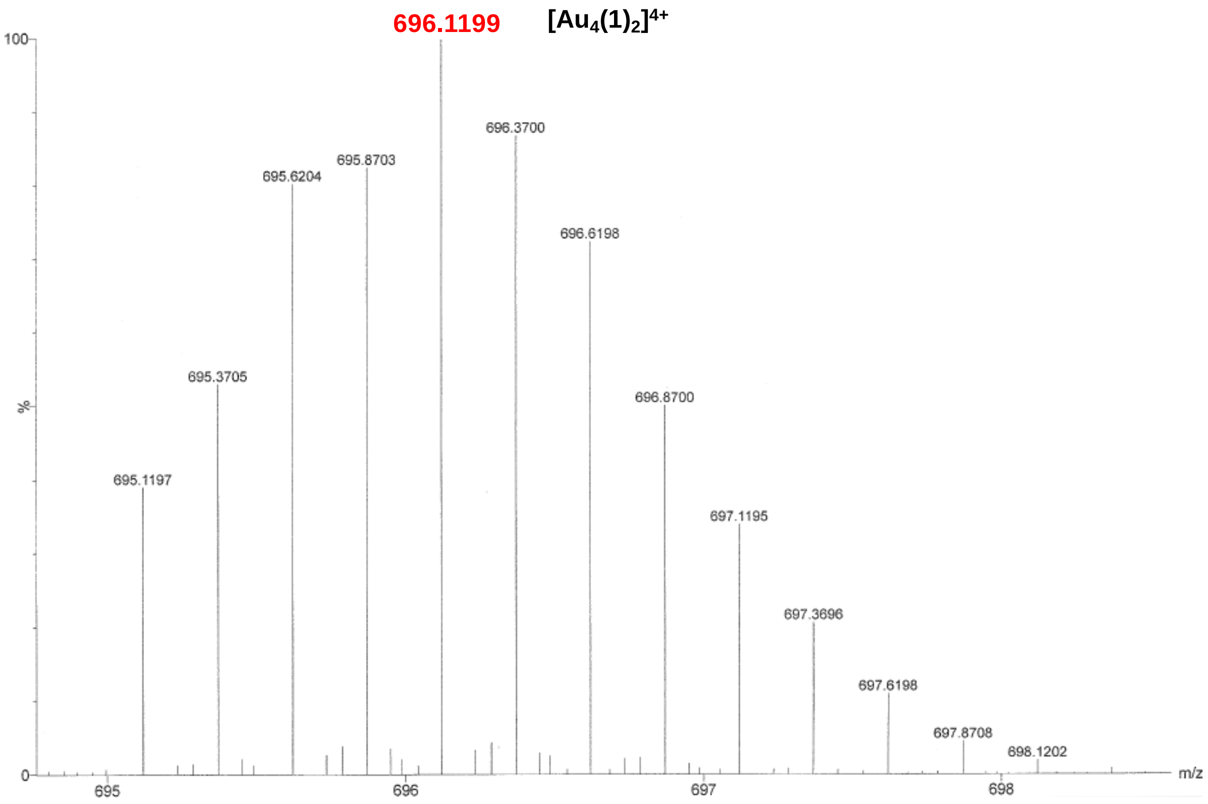


Figure S41. High resolution ESI-TOF (positive mode) mass spectrum of cofacial porphyrin dimer **[Au$_4$(1)$_2$](PF$_6$)$_4$**.

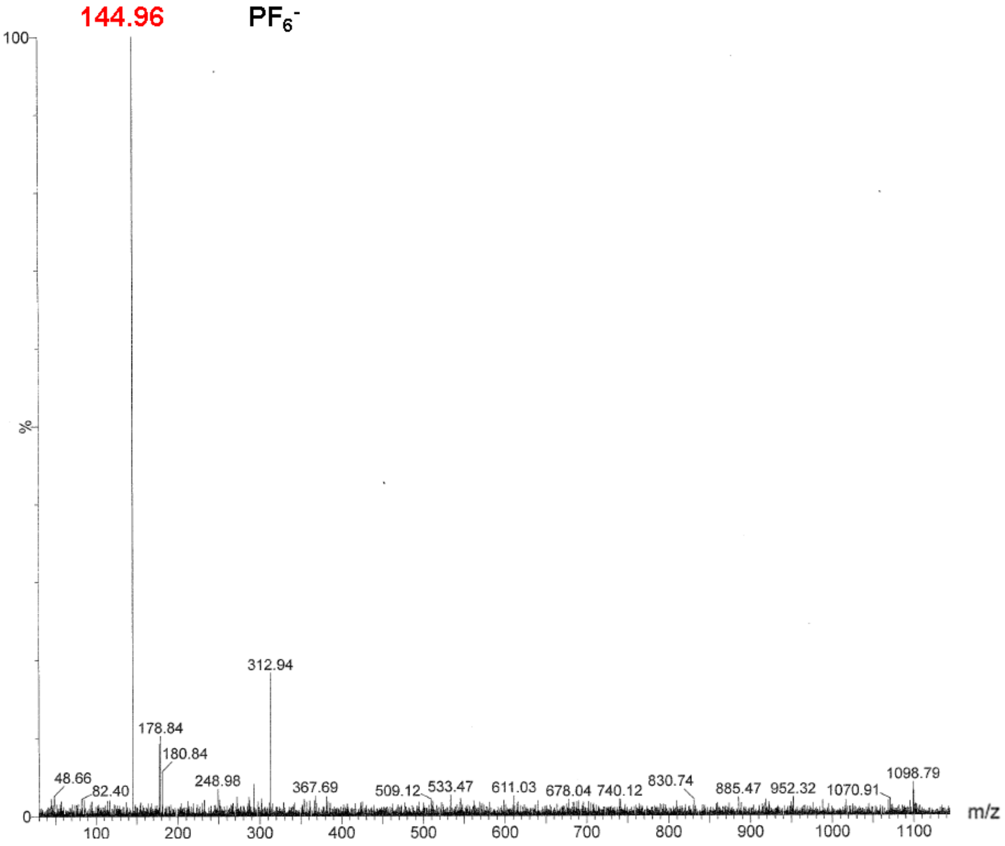


Figure S42. ESI-TOF (negative mode) mass spectrum of cofacial porphyrin dimer **$[Au_4(1)_2](PF_6)_4$**.

4. Determination of diffusion coefficients and hydrodynamic radii

^{1}H NMR spectra were recorded at 298 K on a Bruker Avance III 500 MHz NMR spectrometer, using Hélium BBO cryoprobe. 2D DOSY NMR were carried out using the Bruker pulse sequence *ledbpgp2s* (2D sequence for diffusion measurement using stimulated echo, Longitudinal Eddy Current Delay and bipolar gradient pulses for diffusion). For each sample, a rotation frequency of $\nu = 20$ Hz was applied to the NMR tube, avoiding convection current phenomenon to occur. Diffusion Time Δ was fixed to 0.1 s for each sample. The gradient strength δ ranged between 1.6 and 1.7 ms depending on the molecule size. Measurement of the autodiffusion coefficient was done thanks to Bruker "T1/T2 Relaxation" module. 2D DOSY spectra were visualized on the Bruker Topspin 3.5 pl5 software on 500 MHz spectrometers.

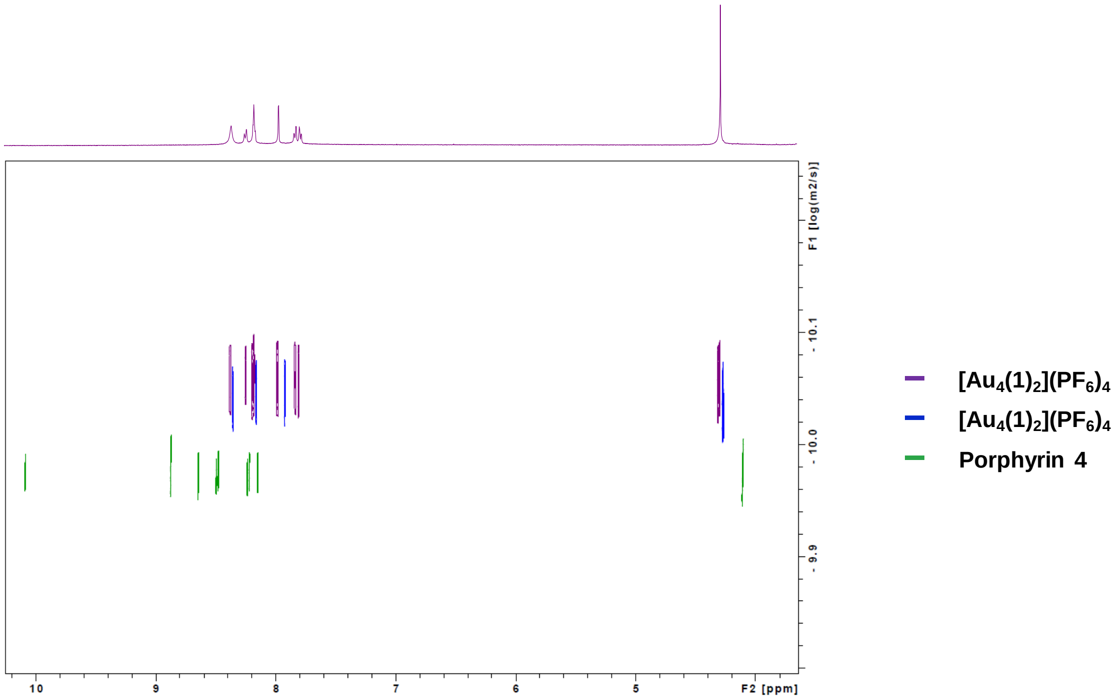


Figure S43. Superimposed ^{1}H 2D DOSY NMR (500 MHz, DMSO-d_6, 298 K) spectra of porphyrin **4** (green) and cofacial porphyrin dimers **[Ag$_4$(1)$_2$](PF$_6$)$_4$** (blue) and **[Au$_4$(1)$_2$](PF$_6$)$_4$** (purple).

Stokes-Einstein relationship :

$$D = \frac{kB\,.\,T}{6\,.\,\pi\,.\,n\,.\,r}$$

D	Diffusion coefficient (m^2.s)
kB	Boltzmann constant ($1.38064852 \times 10^{-23}$ m^2 kg s^{-2} K^{-1})
T	Temperature (298 K)
n	Dynamic viscosity of DMSO-d_6 (2.195 mPa.s)[a]
r	Hydrodynamic radius (m)

Table 1. Diffusion coefficients and hydrodynamic radii of porphyrin **4** and cofacial porphyrin dimers **[Ag$_4$(1)$_2$](PF$_6$)$_4$** and **[Au$_4$(1)$_2$](PF$_6$)$_4$**.

	D **(m^2.s)**	***r*** **(Å)**
Porphyrin **4**	10.80 x 10^{-11}	9.2
[Ag$_4$(1)$_2$](PF$_6$)$_4$	8.84 x 10^{-11}	11.2
[Au$_4$(1)$_2$](PF$_6$)$_4$	8.60 x 10^{-11}	11.6

[a] A. Sacco, E. Matteoli, *J. Sol. Chem.*, **1997**, *26*, 527.

5. Relative stabilities of cofacial porphyrin dimers toward lithium iodide.

The cofacial dimer **[Ag$_4$(1)$_2$](PF$_6$)$_4$** (0.9 mg, 3 x 10^{-7} mol) was dissolved in DMSO (150 mL, final concentration = 2 x 10^{-6} M, **solution A**). Lithium iodide (16 mg, 1.2 x 10^{-4} mol) was dissolved in DMSO (10 mL, final concentration = 1.2 x 10^{-2} M, **solution B**). Then, under stirring, successive additions of 4, 10, 20, 40 and 60 equivalents of LiI (respectively 100 µL, 250 µL, 500 µL, 1000 µL and 1500 µL of **solution B**) were poured into **solution A**. After each addition, a UV-visible absorption spectrum was recorded. The same procedure was used for cofacial dimer **[Au$_4$(1)$_2$](PF$_6$)$_4$** (1 mg, 3 x 10^{-7} mol).

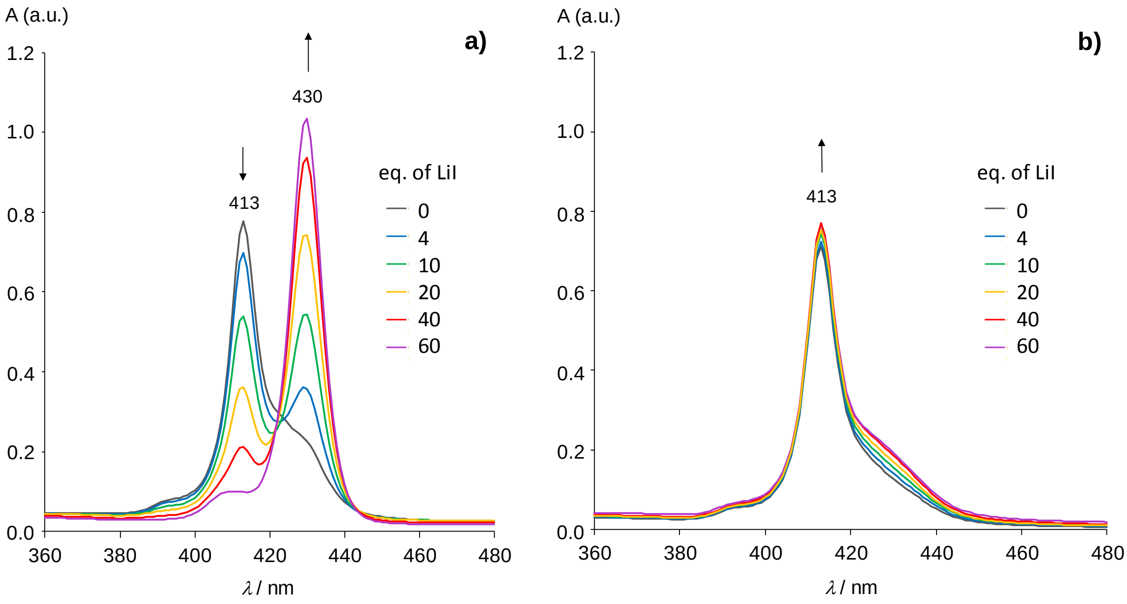


Figure S44. UV-visible absorption spectra of cofacial porphyrin dimers **[Ag$_4$(1)$_2$](PF$_6$)$_4$** (a) and **[Au$_4$(1)$_2$](PF$_6$)$_4$** (b) upon addition of lithium iodide.

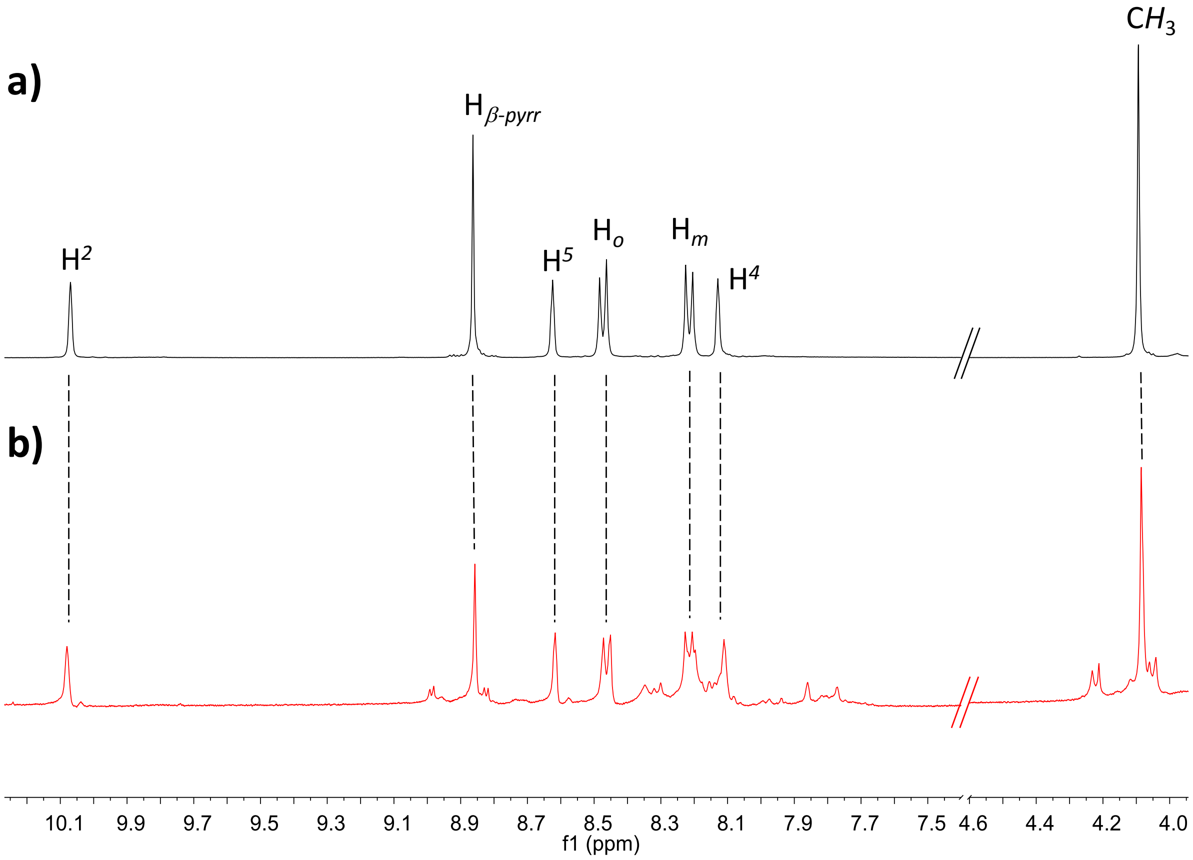


Figure S45. a) ^{1}H NMR spectrum (400.1 MHz, DMSO-d_6, 298K) of porphyr**in 4**; b) ^{1}H NMR spectrum (400.1 MHz, DMSO-d_6, 298K) of **[Ag$_4$(1)$_2$](PF$_6$)$_4$** after treatment with lithium iodide (LiI). In a 5 mL flask, **[Ag$_4$(1)$_2$](PF$_6$)$_4$** (0.9 mg, 3 x 10^{-4} mmol, 1.0 eq) was dissolved in DMSO-d_6 (1 mL). LiI (2.4 mg, 1.8 x 10^{-2} mmol, 60 eq) was added and the reaction mixture was stirred 15 minutes in the dark under argon atmosphere.