

Experimental part

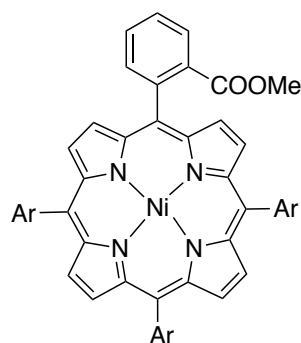
The effect of the linking unit on the electronic and magnetic interactions in copper(II) porphyrin dimers linked by metal ions

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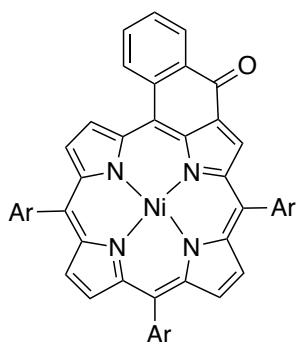
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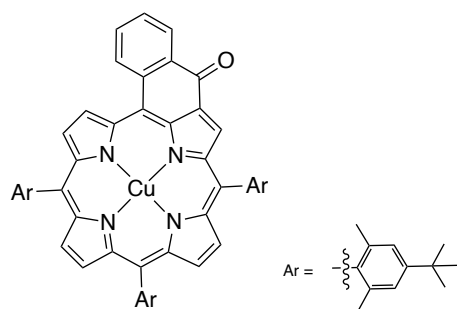
Synthesis



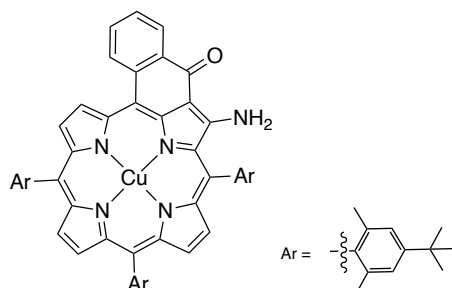
3 - To a degassed solution of pyrrole (1.4 mL, 20.8 mmol), 2,6-dimethyl-4-tertbutylbenzaldehyde (2.97g, 15.6 mmol), methyl-2-formylbenzoate (854 mg, 5.2 mmol) in chloroform (780 mL), borontrifluoride etherate (5.7 mM) was added. The resulting orange-red solution was shielded from light and stirred for 2h under argon and at rt. Chloranil (3.7g, 15 mmol) was added and the resulting solution was refluxed for half an hour. On cooling, the solution was filtered through a pad of alumina (~20 cm). Solvent was then evaporated and the desired A₃B porphyrin was obtained *via* column chromatography (SiO₂; cyclohexane:dichloromethane, 80:20, 60:40, 50:50) to obtain the free-base purple porphyrin. This porphyrin was then dissolved in toluene (150 mL) with Ni(acac)₂ (1.4g, 5.5 mmol) and heated to reflux for 16 h. Solvent was then evaporated and excess nickel salts were removed *via* filtration of the porphyrin through an alumina column (dichloromethane) to obtain the titled product (1.17 g 1.1 mmol, 21%). ¹H NMR (500 MHz, CDCl₃) : δ 8.51-8.45 (m, 6H, H_{pyrr}), 8.43 (d, *J* = 4.8 Hz, 2H, H_{pyrr}), 8.25-8.15 (m, 1H, H_{Ph-ester}), 8.06-7.95 (m, 1H, H_{Ph-ester}), 7.73-7.66 (m, 2H, H_{Ph-ester}), 7.35-7.28 (m, 6H, H_{Ar}), 2.78 (s, 3H, COOCH₃), 1.83 (s, 6H, H_{Me}), 1.81 (s, 3H, H_{Me}), 1.81 (s, 3H, H_{Me}), 1.75 (s, 6H, H_{Me}), 1.47 ppm (s, 27H, H_{tBu}). ¹³C NMR (125 MHz, CDCl₃) : δ 167.9, 150.8, 142.7, 142.62, 142.59, 142.5, 141.7, 138.63, 138.60, 138.59, 138.58, 137.42, 137.38, 135.5 (CH), 134.3, 134.0, 131.4 (CH), 131.3 (CH), 131.2 (CH), 131.0 (CH), 129.9 (CH), 129.7 (CH), 129.6 (CH), 128.6 (CH), 128.2 (CH), 126.5 (CH), 123.92 (CH), 123.90 (CH), 123.88 (CH), 117.5, 117.3, 117.1, 51.6 (CH₃), 34.68, 31.7 (CH₃), 22.0 (CH₃), 21.9 (CH₃), 21.8 ppm (CH₃). ESI-TOF: Calcd for C₆₄H₆₆N₄NiO₂ (M⁺) 980.45; obsd 980.45



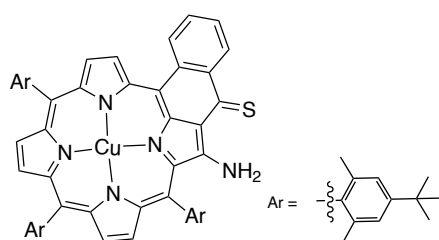
4 - A suspension of **3** (558 mg, 0.576 mmol) and lithium hydroxide (1g, excess) in a dioxane:water (8:2) solution was refluxed for 16 h. On cooling, dichloromethane (60 mL) was added and the organic phase was extracted (3 x dichloromethane), washed (3 x water) and dried over sodium sulphate. The solvent was then evaporated and the porphyrin was redissolved in dry toluene and heated at 50 °C under argon with oxalyl chloride (3 mL, excess). A dean-stark was used to remove excess oxalyl chloride. On cooling, tin(IV) chloride (1 mL, excess) was added and the solution turned instantly green. After half an hour of stirring at r.t. the solution was poured onto ice cold concentrated NaOH (150 mL). The organic phase was extracted (3 x dichloromethane), washed (3 x water) and dried over sodium sulphate. The solvent was evaporated and the titled product was purified *via* column chromatography (SiO₂; 1:1 dichloromethane:cyclohexane) to afford the titled product (443 mg, 0.47 mmol, 81%). ¹H NMR (500 MHz, CDCl₃): δ 9.21 (d, *J* = 5.1 Hz, 1H, H_{pyrr}), 8.97 (s, 1H, H_{pyrr}), 8.47- 8.45 (m, 2H, H_{pyrr} + H_{cyclPh}), 8.28 (d, *J* = 4.9 Hz, 1H, H_{pyrr}), 8.27 (d, *J* = 4.7 Hz, 1H, H_{pyrr}), 8.22 (d, *J* = 4.9 Hz, 1H, H_{pyrr}), 8.18 (d, *J* = 4.9 Hz, 1H, H_{pyrr}), 8.06-7.95 (br dd, 1H, H_{cyclPh}), 7.71-7.65 (br ddd, 1H, H_{cyclPh}), 7.47-7.41 (br ddd, 1H, H_{cyclPh}), 7.35 (s, 2H, H_{Ar}), 7.32 (2s, 4H, H_{Ar}), 1.94 (s, 6H, H_{Me}), 1.91 (s, 6H, H_{Me}), 1.90 (s, 6H, H_{Me}), 1.51 (2s, 18H, H_{tBu}), 1.43 ppm (s, 9H, H_{tBu}). ¹³C NMR (125 MHz, CDCl₃): δ 183.0, 151.3, 151.2, 145.1, 144.8, 143.9, 143.4, 142.8, 141.2, 141.0, 140.0, 138.9, 138.4, 138.18, 138.17, 135.9, 135.7, 135.34 (CH), 135.29, 135.26, 133.71 (CH), 133.70, 133.5 (CH), 133.1 (CH), 132.9 (CH), 132.84 (CH), 132.75 (CH), 132.1 (CH), 166, 131.3 (CH), 129.3 (CH), 127.4 (CH), 124.4, 124.12, 124.09, 119.8, 117.1, 108.3, 31.63 (CH₃), 34.65, 34.64, 34.63, 31.59 (CH₃), 21.9 (CH₃), 21.79 (CH₃), 21.78 (CH₃). ESI-TOF: Calcd for C₆₃H₆₂N₄NiO (M⁺) 948.43; obsd 948.43



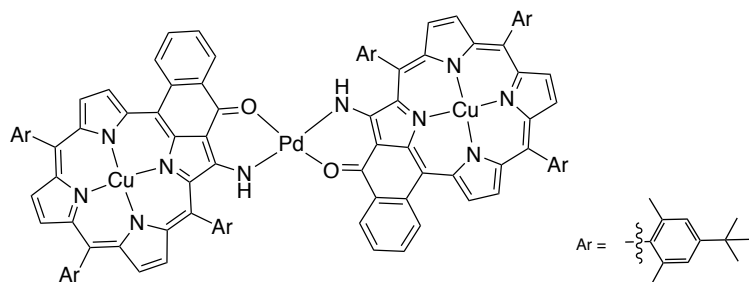
5 - The free-base porphyrin (140 mg, 0.18 mmol) and an excess of $\text{Cu}(\text{OAc})_2$ (85 mg, 0.47 mmol) were refluxed in toluene (50 mL) for 16 h. The solvent was evaporated and the product was purified *via* column chromatography (SiO_2 ; dichloromethane:cyclohexane 1:1) followed by precipitation to afford the titled product (141 mg, 0.17 mmol, 94%). MALDI-TOF: Calcd for $\text{C}_{63}\text{H}_{62}\text{N}_4\text{OCu}$ (M^+) 954.43; obsd 954.391.



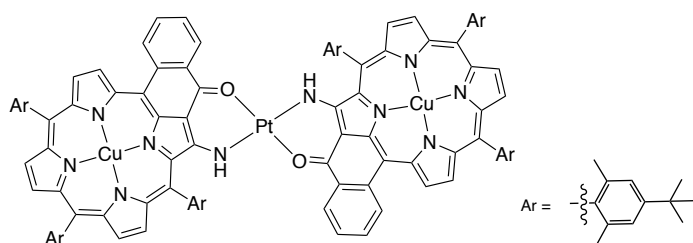
6 – **5** (173 mg, 0.181 mmol), 4-amino-4H-1,2,4-triazole (304 mg, 3.62 mmol) and NaOH (724 mg, 18.1 mmol) were refluxed for 2 h in toluene:ethanol (8:2) under argon. Water (50 mL) was then added and the organic phase was washed with water and dried over sodium sulphate. The solvent was evaporated and the porphyrin was purified by column chromatography (SiO_2 ; dichloromethane:cyclohexane 2:1) to afford the titled product (161 mg, 0.167 mmol, 92%). HR-ESI: Calcd for $\text{C}_{63}\text{H}_{63}\text{N}_5\text{OCu}$ (M^+) 968.4312; obsd 968.4323. Elemental analysis: calcd %N 7.22 %C 78.03 %H 6.55. obsd %N 7.15 %C 77.68 %H 6.60.



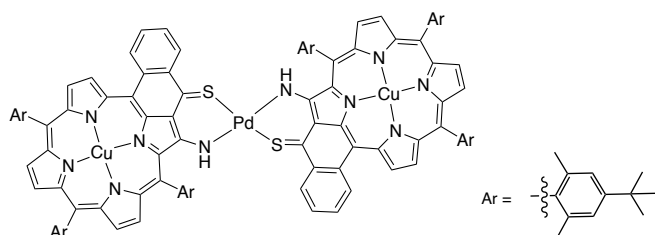
7 - **6** (65 mg, 0.067 mmol) and Lawesson's reagent (162 mg, 0.402 mmol) were heated to reflux in toluene for 2h under argon. On cooling, the solvent was evaporated and the product was purified by column chromatography (SiO_2 ; cyclohexane:dichloromethane 1:1) to afford the titled product (57 mg, 0.058 mmol, 86%). MALDI-TOF: Calcd for $\text{C}_{63}\text{H}_{63}\text{N}_5\text{OCu}$ ($\text{M} + \text{H}^+$) 985.42; obsd 985.447



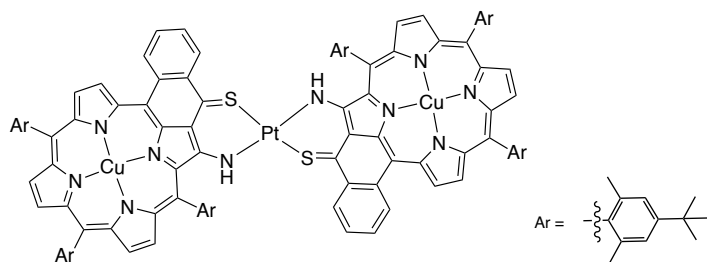
8 - 6 (35 mg, 0.036 mmol) and $\text{Pd}(\text{OAc})_2$ (4 mg, 0.018 mmol) were heated to reflux in toluene (20 mL) for 16 h under argon. On cooling, the solvent was evaporated and the product was purified by column chromatography (SiO_2 ; cyclohexane:dichloromethane 60:40) to afford the titled product as a brown solid (13 mg, 6.4 μmol , 36%). MALDI-TOF: Calcd for $\text{C}_{126}\text{H}_{124}\text{N}_{10}\text{O}_2\text{PdCu}_2$ (M^+) 2040.75; obsd 2040.924.



10 - 6 (10 mg, 0.01 mmol) and $\text{Pt}(\text{acac})_2$ (2 mg, 5.6 μmol) were heated to reflux in 1,2-dichlorobenzene for 4 days under argon. On cooling, the solvent was evaporated by trap to trap distillation and the product was purified by column chromatography (SiO_2 ; cyclohexane:dichloromethane 60:40) to afford the titled product as a brown solid (2 mg, 0.94 μmol , 18%). MALDI-TOF: Calcd for $\text{C}_{126}\text{H}_{124}\text{N}_{10}\text{O}_2\text{PdCu}_2$ (M^+) 2132.62; obsd 2132.901



9 - 7 (15 mg, 0.016 mmol) and $\text{Pd}(\text{OAc})_2$ (2 mg, 8.6 μmol) were heated to reflux in toluene for 1 h under argon. On cooling, the solvent was evaporated and the product was purified by column chromatography (SiO_2 ; cyclohexane:dichloromethane 1:1) to afford the titled product (5 mg, 2.4 μmol , 57%). MALDI-TOF: Calcd for $\text{C}_{126}\text{H}_{124}\text{N}_{10}\text{S}_2\text{PdCu}_2$ (M^+) 2072.71; obsd 2072.117.



11 - 7 (8 mg, 8.4 μmol) and $\text{Pt}(\text{acac})_2$ (1.8 mg, 4.6 μmol) were heated to reflux in 1,2-dichlorobenzene for 4 h under argon. On cooling, the solvent was evaporated by trap to trap distillation and the product was purified by column chromatography (SiO_2 ; cyclohexane:dichloromethane 1:1) to afford the titled product as a deep red solid (4 mg, 1.89 μmol , 45%). MALDI-TOF: Calcd for $\text{C}_{126}\text{H}_{124}\text{N}_{10}\text{S}_2\text{PtCu}_2$ (M^+) 2161.77; obsd 2161.712.

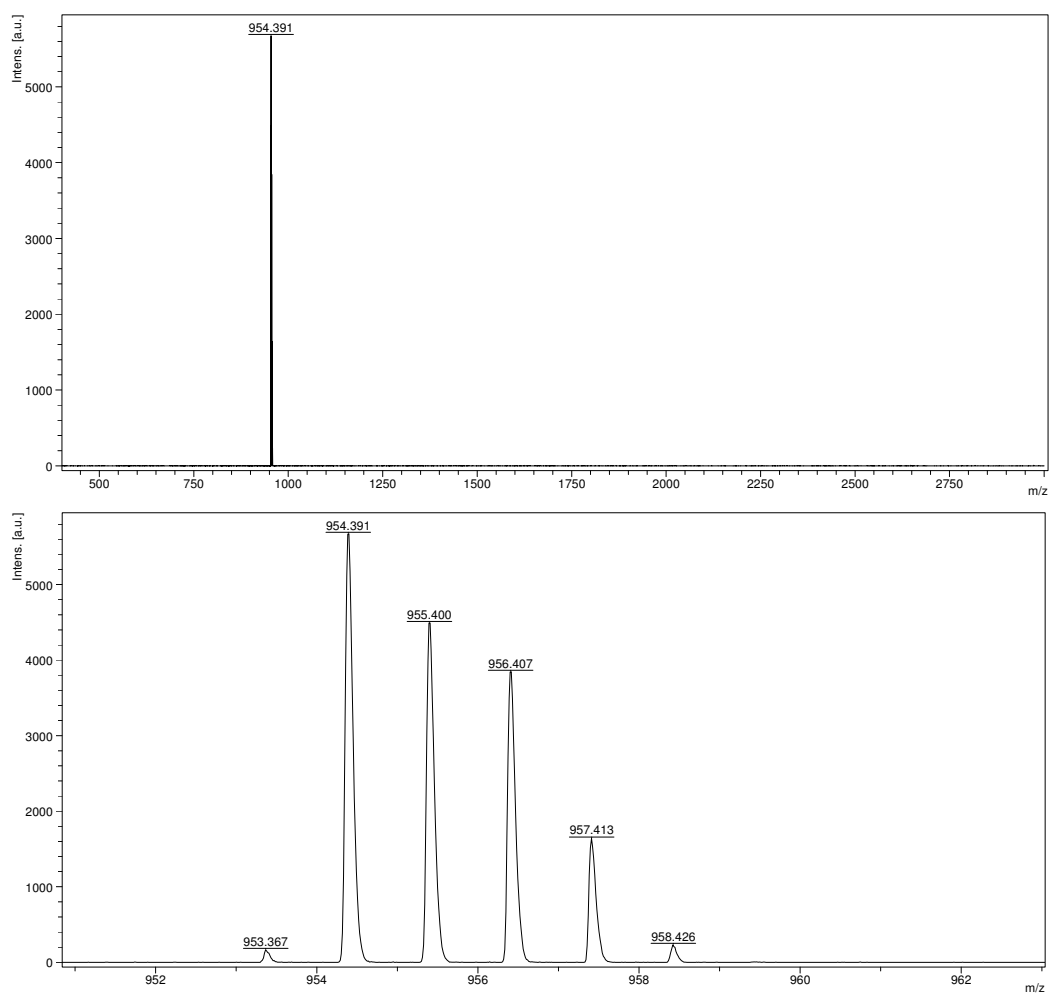


Figure S1: MALDI Mass spectroscopy of **5** (top) and a zoom of the spectrum (bottom).

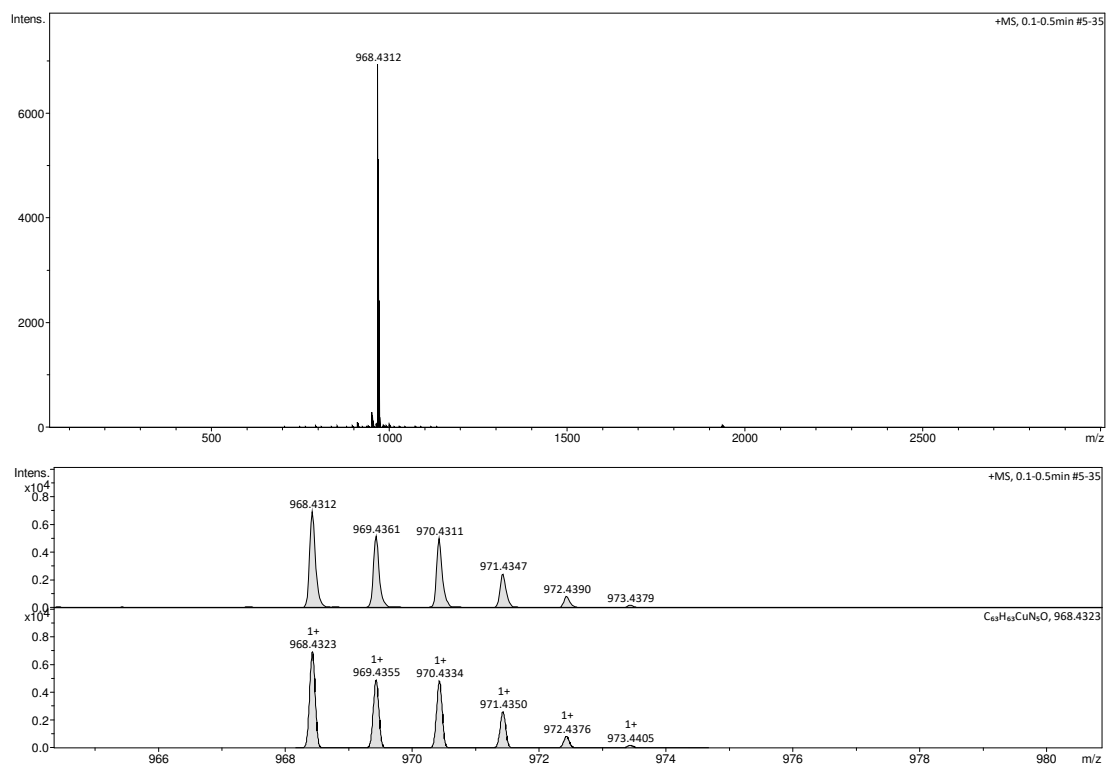
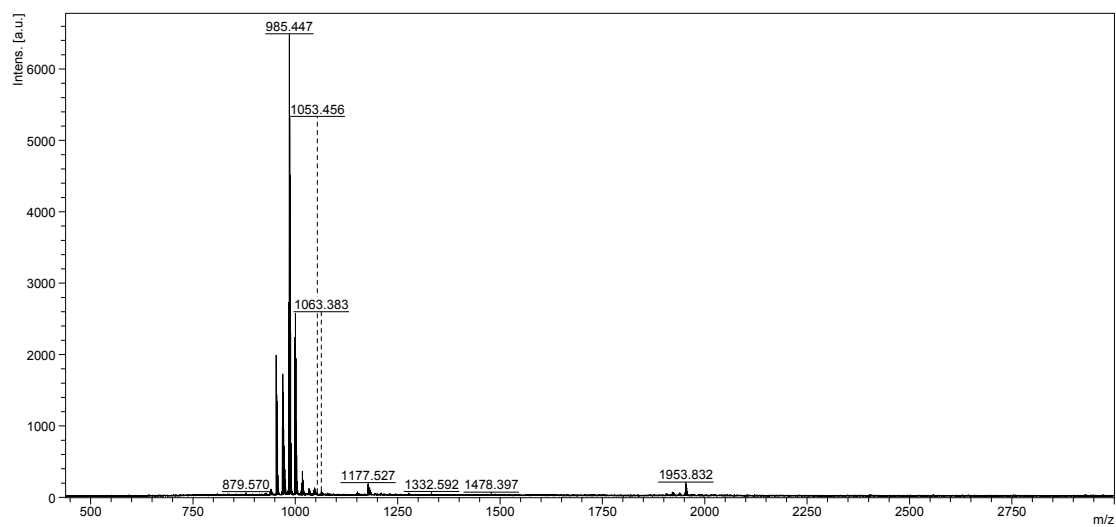


Figure S2: MALDI Mass spectroscopy of **6** (top) and a zoom of the spectrum (bottom).



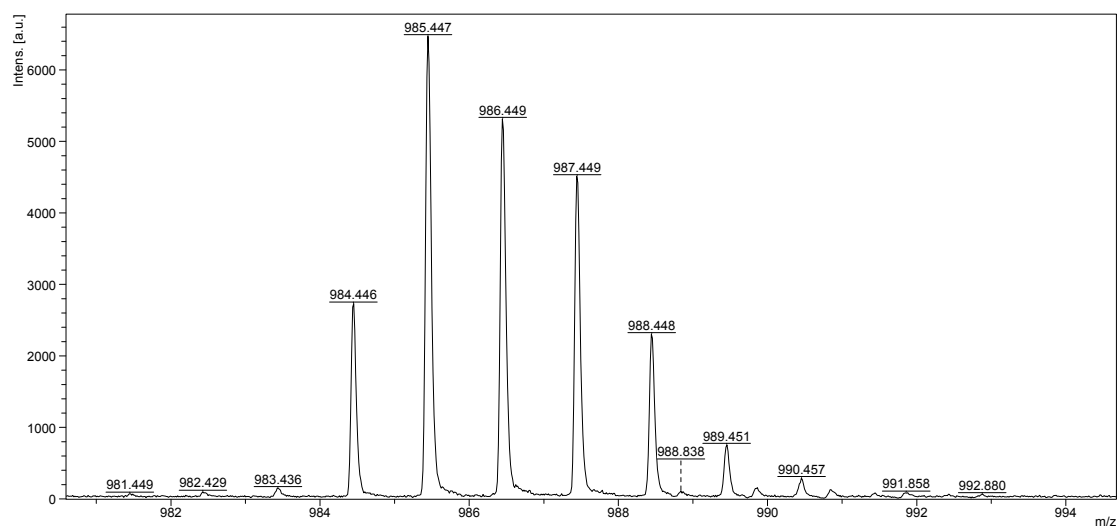


Figure S3: MALDI Mass spectroscopy of **7** (top) and a zoom of the spectrum (bottom).

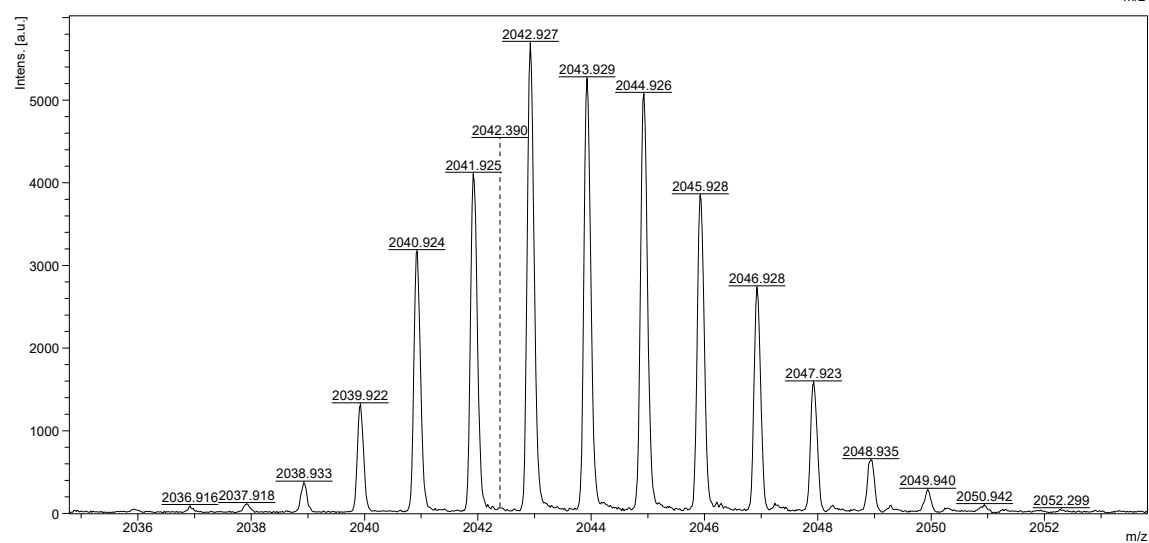
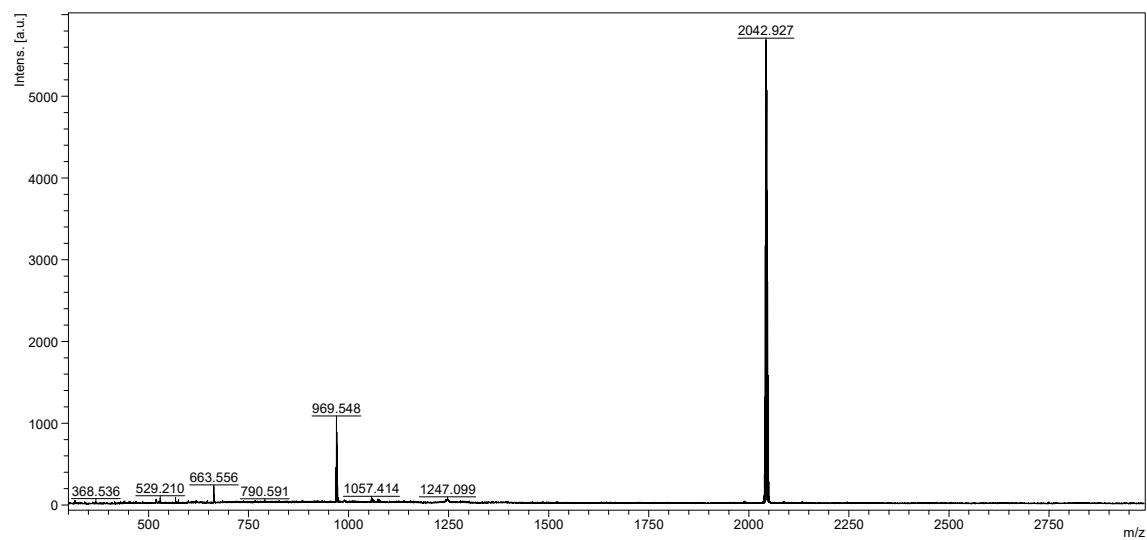


Figure S4: MALDI Mass spectroscopy of **8** (top) and a zoom of the spectrum (bottom).

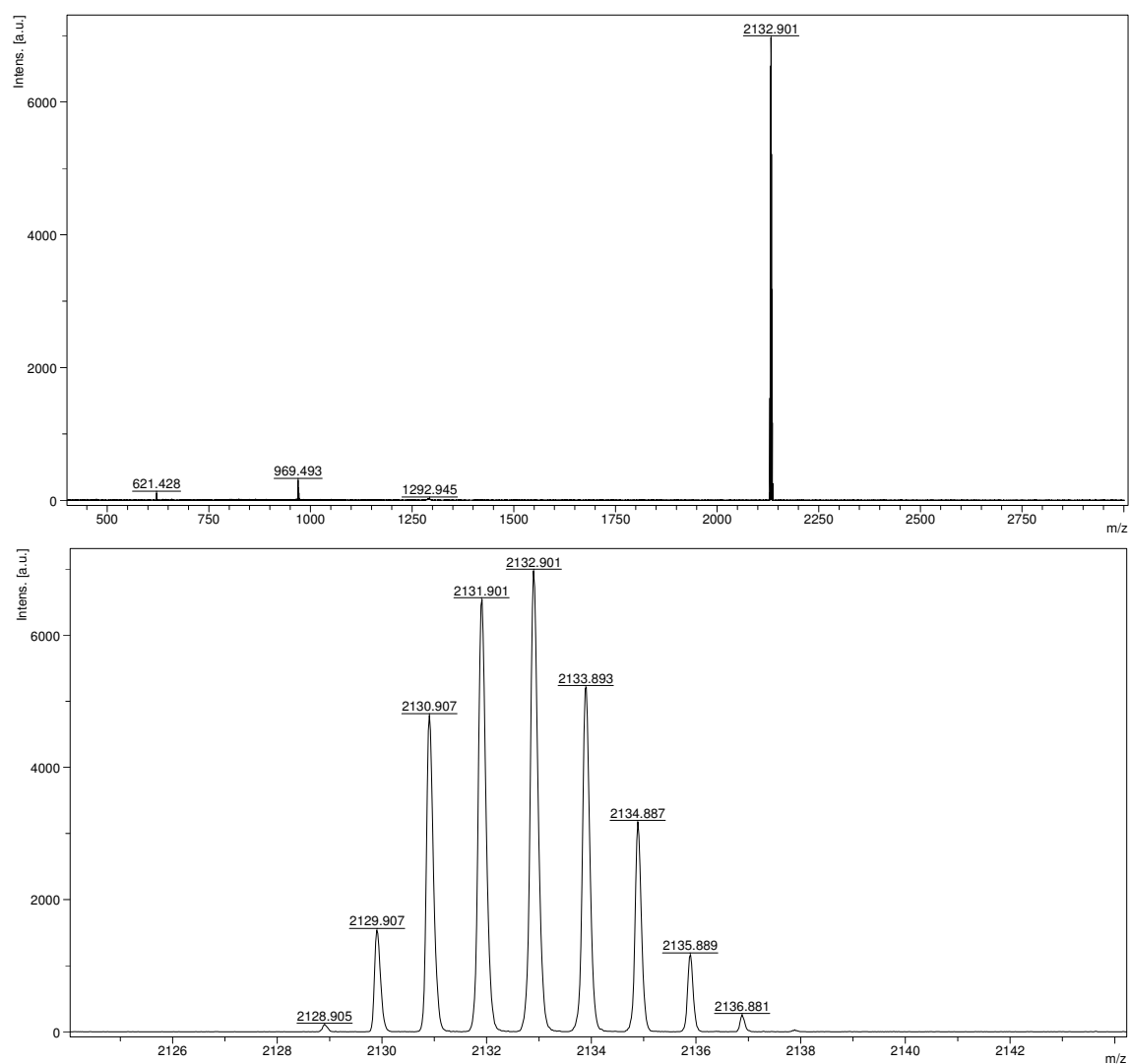
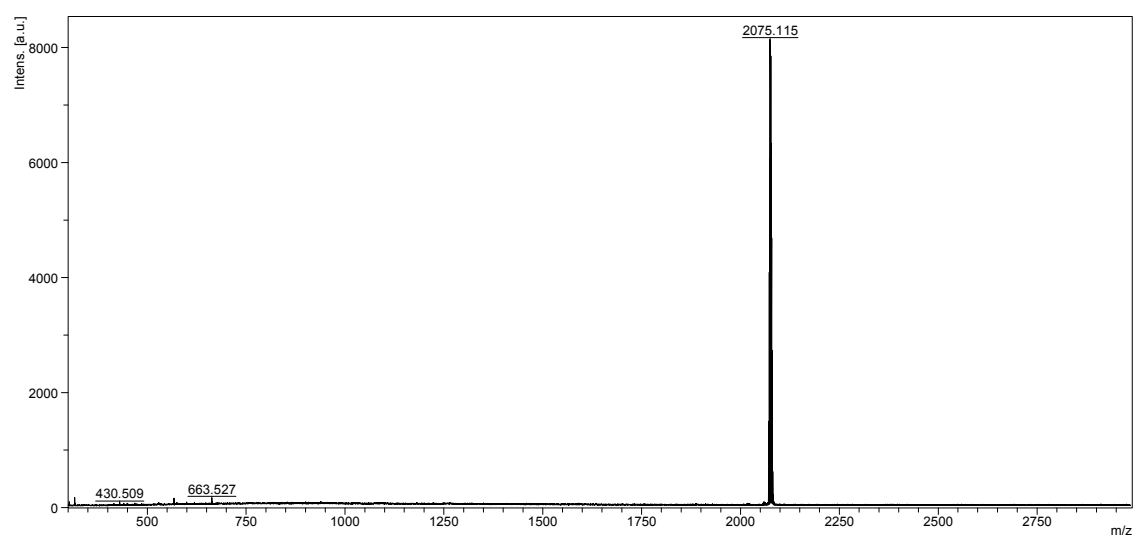


Figure S5: MALDI Mass spectroscopy of **10** (top) and a zoom of the spectrum (bottom).



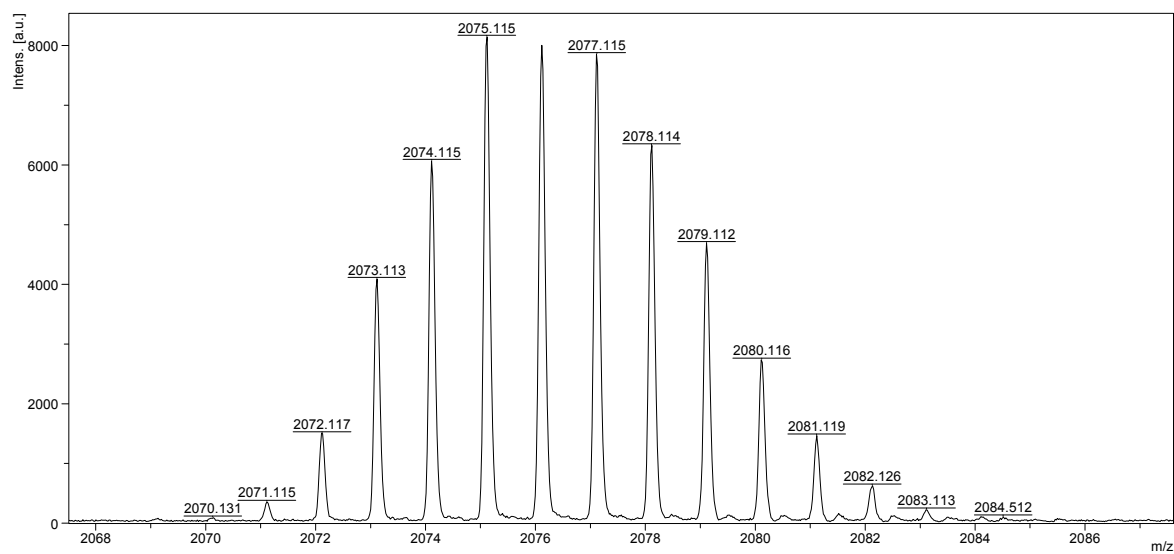


Figure S6: MALDI Mass spectroscopy of **9** (top) and a zoom of the spectrum (bottom).

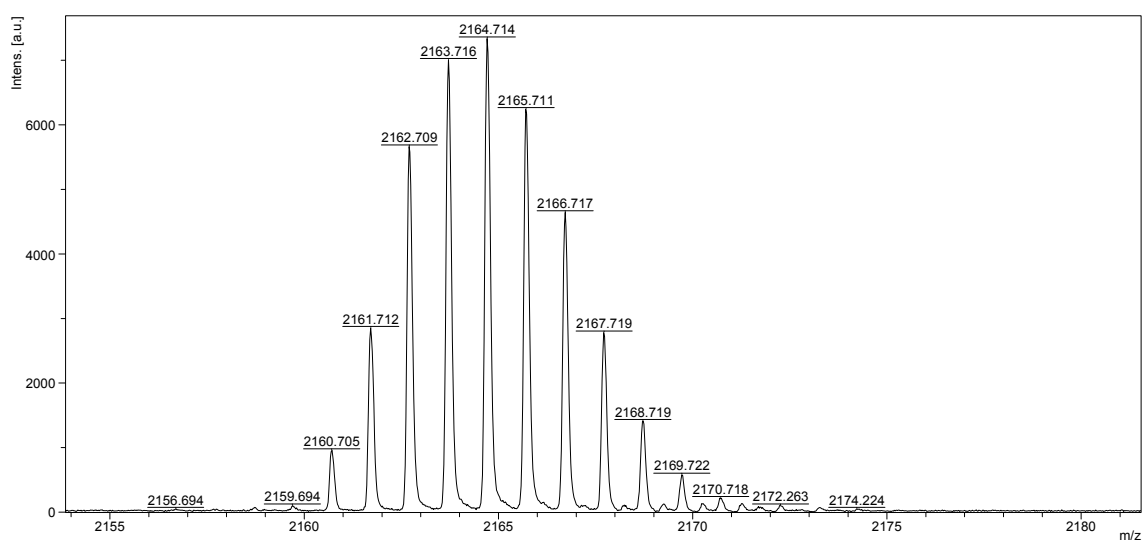
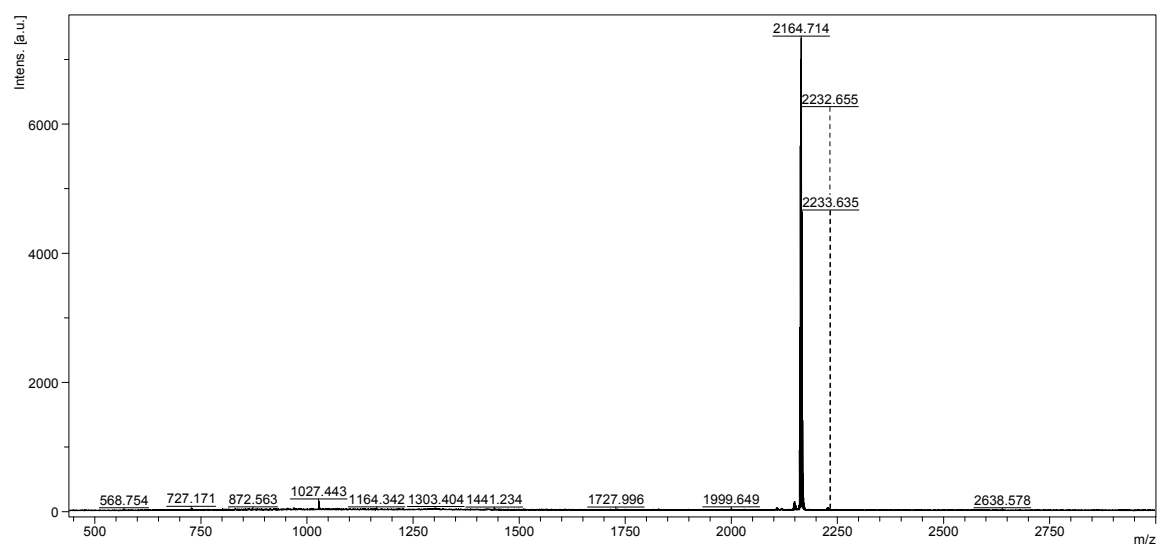


Figure S7: MALDI Mass spectroscopy of **11** (top) and a zoom of the spectrum (bottom).

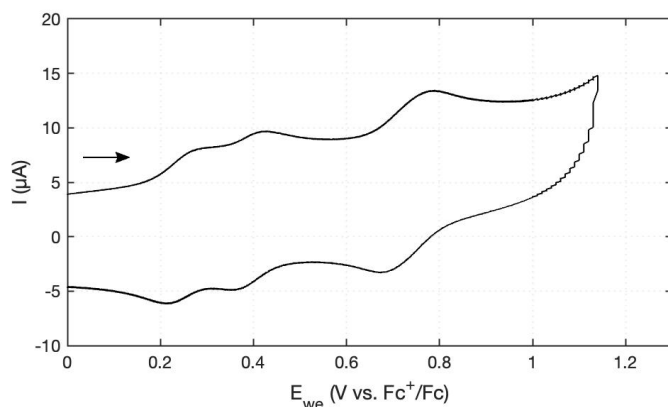


Figure S8: Cyclic voltammetry of **8** in dichloromethane with tetrabutylammonium hexafluorophosphate (0.1 M) at a scan rate of 100 mV/s. Arrow shows direction of the measurement; only the oxidation is shown to emphasise the splitting.

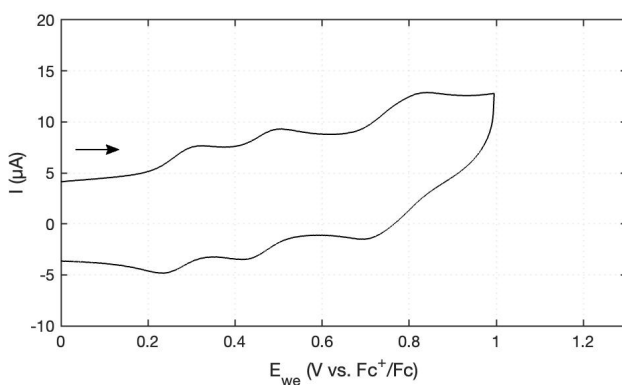


Figure S9: Cyclic voltammetry of **9** in dichloromethane with tetrabutylammonium hexafluorophosphate (0.1 M) at a scan rate of 100 mV/s. Arrow shows direction of the measurement; only the oxidation is shown to emphasise the splitting.

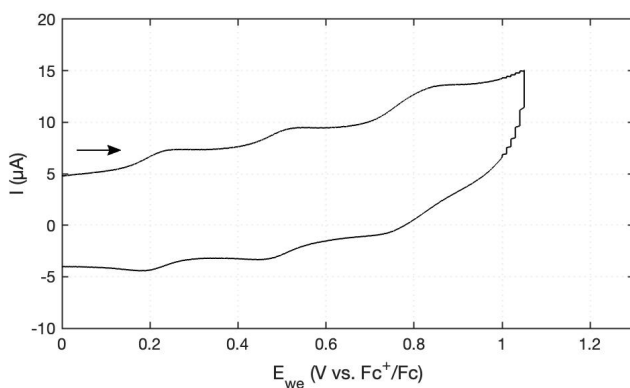


Figure S10: Cyclic voltammetry of **11** in dichloromethane with tetrabutylammonium hexafluorophosphate (0.1 M) at a scan rate of 100 mV/s. Arrow shows direction of the measurement; only the oxidation is shown to emphasise the splitting.

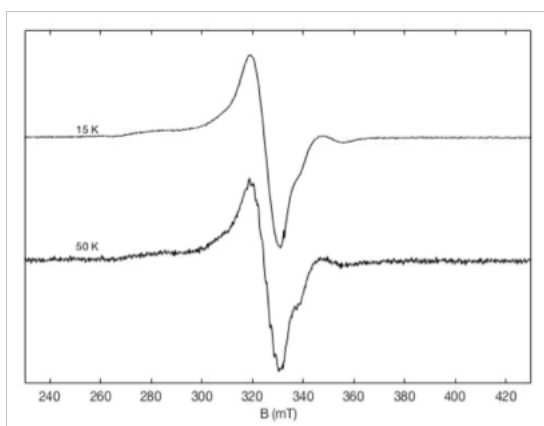


Figure S11: X-band experimental EPR spectrum of porphyrin dimer **8** (10^{-4} M; $\text{CH}_2\text{Cl}_2\text{:CHCl}_3$; 80:20) at 15 K and 50 K, recorded with a microwave power of 0.1 mW and a modulation amplitude of 0.4 mT.

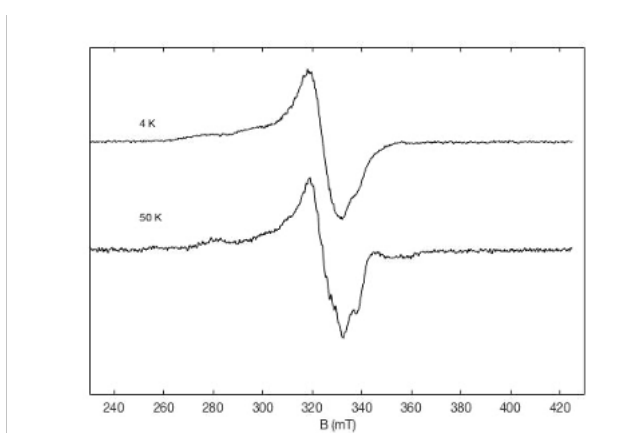


Figure S12: X-band experimental EPR spectra of **10** (10^{-4} M; 80:20; $\text{CH}_2\text{Cl}_2\text{:CHCl}_3$) at 4 K and 50 K recorded with a microwave power of 0.1 mW and a modulation amplitude of 0.4 mT.

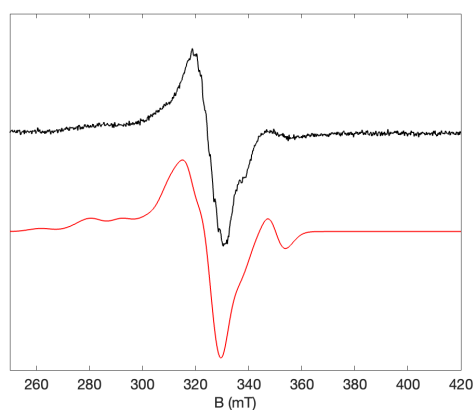


Figure S13: X-band experimental EPR spectrum of porphyrin dimer **9** (10^{-4} M; $\text{CH}_2\text{Cl}_2\text{:CHCl}_3$; 80:20) at 50 K, recorded with a microwave power of 0.1 mW and a modulation amplitude of 0.4 mT and the corresponding simulation (red). Simulation parameters are given in Table 2.

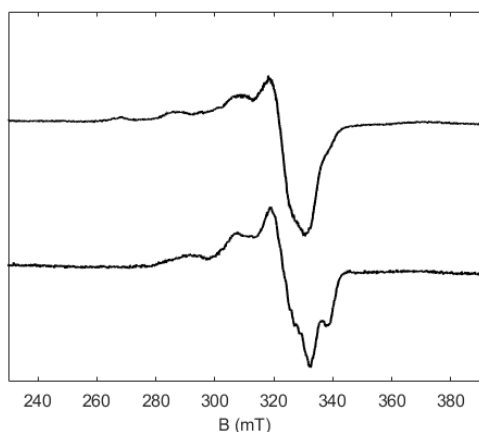


Figure S14: X-band experimental EPR spectra of **9** (10^{-4} M; 80:20; $\text{CH}_2\text{Cl}_2:\text{CHCl}_3$) at 5 K and 50 K recorded with a microwave power of 0.1 mW and a modulation amplitude of 0.4 mT.

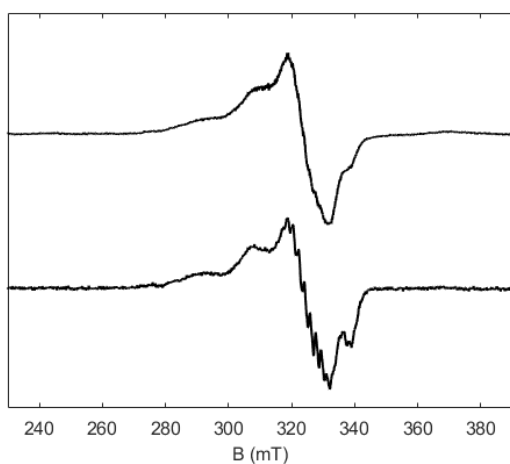


Figure S15: X-band experimental EPR spectra of **11** (10^{-4} M; 80:20; $\text{CH}_2\text{Cl}_2:\text{CHCl}_3$) at 5 K and 50 K recorded with a microwave power of 0.1 mW and a modulation amplitude of 0.4 mT.

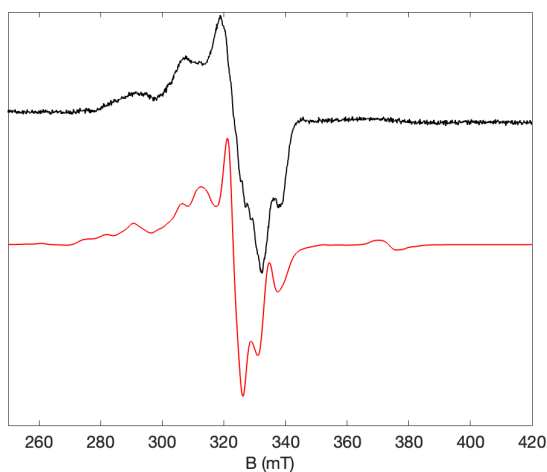


Figure S16: X-band experimental EPR spectrum of porphyrin dimer **10** (10^{-4} M; $\text{CH}_2\text{Cl}_2:\text{CHCl}_3$; 80:20) at 50 K, recorded with a microwave power of 0.1 mW and a modulation amplitude of 0.4 mT and the corresponding simulation (red). Simulation parameters are given in Table 2.