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Supporting Information

A Facile 'Click' Approach to Functionalised Metallosupramolecular Architectures

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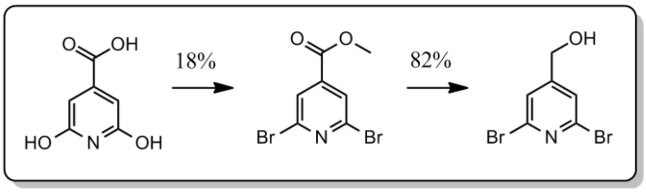
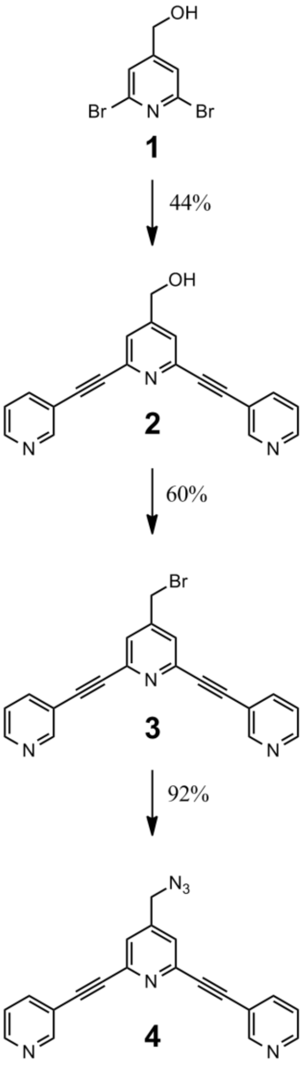
Contents

1 Experimental



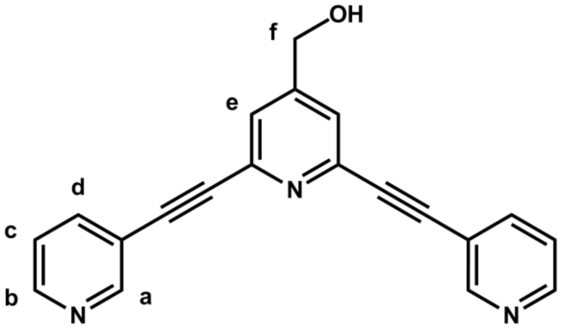


1.1 General

Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification except 3-iodopyridine[1], 2,5-dibromo-4-(hydroxymethyl)pyridine (**1**),[2] and *N*-propargyltheophylline[3] which were synthesised according to literature procedures. Solvents were laboratory reagent grade with the following exceptions: dry THF, toluene and DCM were obtained by passing the solvents through an activated alumina column on a PureSolv TM solvent purification system (Innovative Technologies, Inc., MA). Dry triethylamine was obtained by distillation over calcium hydride before use. Petrol refers to the fraction of petroleum ether boiling in the range 40-60 °C. ^{1}H and ^{13}C NMR spectra were recorded on either a 400 MHz Varian 400 MR or Varian 500 MHz VNMRS spectrometer. Chemical shifts are reported in parts per million and referenced to residual solvent peaks ($CDCl_3$: ^{1}H δ 7.26 ppm, ^{13}C δ 77.16 ppm; CD_3CN: ^{1}H δ 1.94, ^{13}C δ 1.32, 118.26 ppm, d_6-DMSO: ^{1}H δ 2.50 ppm; ^{13}C δ 39.52 ppm). Coupling constants (J) are reported in Hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, q = quartet, t = triplet, dt = double triplet, d = doublet, dd = double doublet, s = singlet. IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer with an attached ALPHA-P measurement module. Microanalyses were performed at the Campbell Microanalytical Laboratory at the University of Otago. Electrospray mass spectra (ESMS) were collected on a Bruker micro-TOF-Q spectrometer. UV-visible absorption spectra were acquired with a Perkin Elmer Lambda-950 spectrophotometer.

Safety Note: Whilst no problems were encountered during the course of this work, azide compounds are potentially explosive and appropriate precautions should be taken when working with them.

1.2 Synthesis of 2



A dry RBF was charged with (2,6-dibromopyridin-4-yl)methanol (1.00 g, 3.75 mmol, 1 eq.), $[Pd(PPh_3)_2Cl_2]$ (0.08 g, 0. 11 mmol, 0.03 eq.) and CuI (0.07 g, 0.38 mmol, 0.1 eq.) and purged with N_2. Toluene (dry, 18.7 mL) and triethylamine (dry, 6.3 mL) were added *via* syringe. Ethynyltrimethylsilane (1.3 mL, 9.37 mmol, 2.5 eq.) was added dropwise via syringe. The reaction was stirred at room temperature in the absence of light for 24 h. 3-iodopyridine (3.07 g, 14.99 mmol, 4 eq.), DBU (3.4 mL, 22.48 mmol, 6 eq.) and H_2O (0.054 mL, 3.00 mmol, 0.8 eq.) were added and the reaction stirred under N_2 at room temperature for a further 24 h. All solvents were removed *in vacuo* and the resulting dark solid taken up in DCM (100 mL). This organic phase was washed with 0.1 M EDTA/$NH_4OH_{(aq)}$ (100 mL) and H_2O (100 mL), dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude mixture was dry loaded onto silica gel and eluted with 2:3 acetone/DCM (R_f = 0.21) to give the product as an off-white solid, which was further purified by flash column chromatography on silica (EtOAc) to yield the pure product as a light yellow solid. Yield 0.52 g (1.65 mmol, 44%). M.p. ~160 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 8.83 (s, 2H, H_a), 8.60 (d, J = 4.8 Hz, 2H, H_b), 7.88 (d, J = 7.9 Hz, 2H, H_d), 7.56 (s, 2H, H_e), 7.32 (ddd, J = 7.8, 4.9, 0.6 Hz, 2H, H_c), 4.81 (s, 2H, H_f). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 152.8 (C_a), 151.3, 149.5 (C_b), 143.5, 139.2 (C_d), 124.2 (C_e), 123.3 (C_c), 119.4, 91.3, 86.3, 62.9 (C_f). IR (ATR): ν (cm^{-1}) 3199, 3035, 2907, 2829, 1596, 1547, 1415, 1077, 803, 698. HRESI-MS (DCM): m/z = 312.1129 $[MH]^+$ calc. 312.1131; 334.0935 $[MNa]^+$ calc. 334.0951. *Anal.* calc. for $C_{20}H_{13}N_3O$: C, 77.16; H, 4.21; N, 13.50%. Found: C, 76.99; H, 4.15; N, 13.23%.

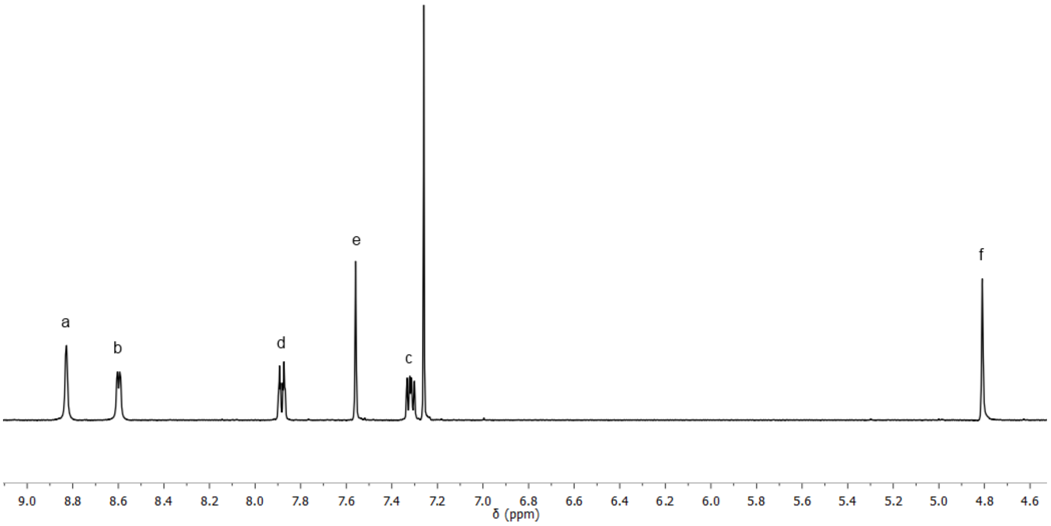


Figure 1 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **2**.

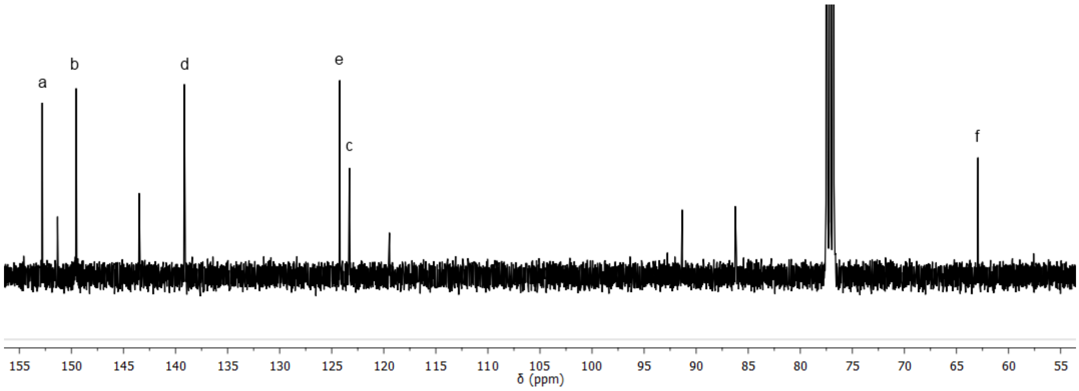
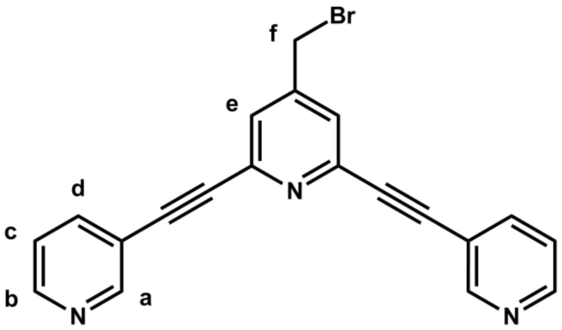


Figure 2 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **2**.

1.3 Synthesis of 3



A RBF was charged with **2** (0.20 g, 0.64 mmol, 1 eq.), PPh_3 (0.20 g, 0.77 mmol, 1.2 eq.) and CBr_4 (0.32 g, 0.96 mmol, 1.5 eq.) before purging with N_2. DCM (dry, 10 mL) was added via syringe and the reaction stirred in the absence of light for 4 h. The reaction mixture was loaded directly onto silica gel and the product obtained as a white solid by eluting with 1:4 acetone/DCM (R_f = 0.15). Yield 0.15

g (0.39 mmol, 60%). M.p. ~155 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 8.84 (s, 2H, H_a), 8.62 (d, J = 3.9 Hz, 2H, H_b), 7.90 (d, J = 7.7 Hz, 2H, H_d), 7.55 (s, 2H, H_e), 7.34 (dd, J = 6.9, 5.0 Hz, 2H, H_c), 4.40 (s, 2H, H_f). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 152.5 (C_a), 149.4 (C_b), 147.4, 143.8, 139.1 (C_d), 126.6 (C_e), 123.2 (C_c), 119.1, 90.8, 86.6, 29.2 (C_f). IR (ATR): ν (cm^{-1}) 3031, 2214, 1594, 1547, 1476, 1417, 1410, 1022, 803, 699, 670, 627, 558. HRESI-MS ($CHCl_3$): m/z = 374.0297 $[MH]^+$ calc. 374.0287. *Anal.* calc. for $C_{20}H_{12}N_3Br$: C, 64.19; H, 3.23; N, 11.23%. Found: C, 64.28; H, 3.13; N, 11.07%.

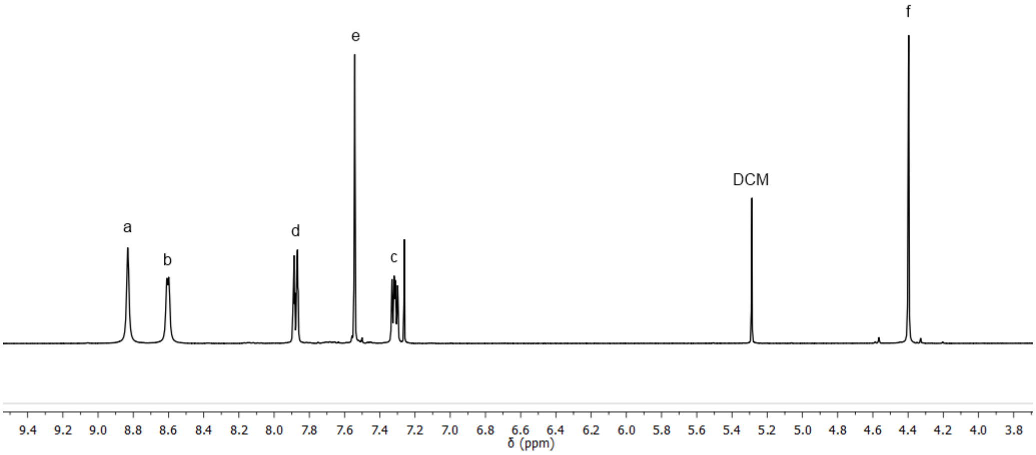


Figure 3 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **3**.

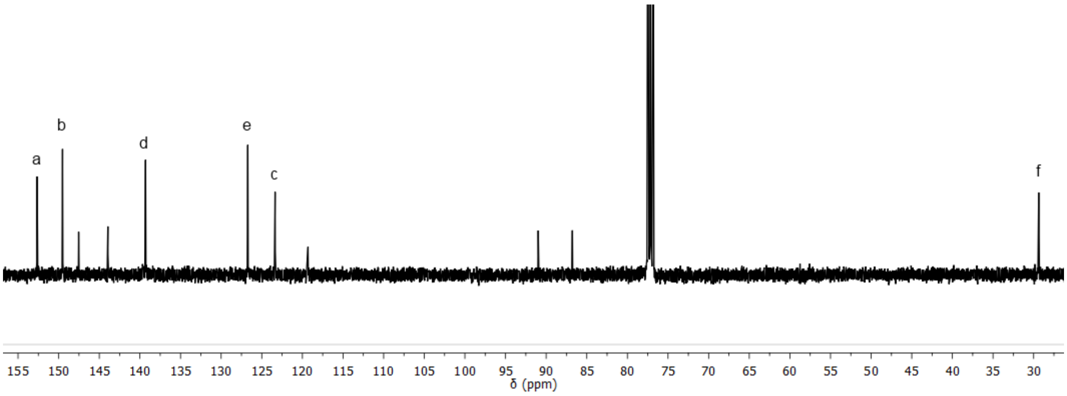
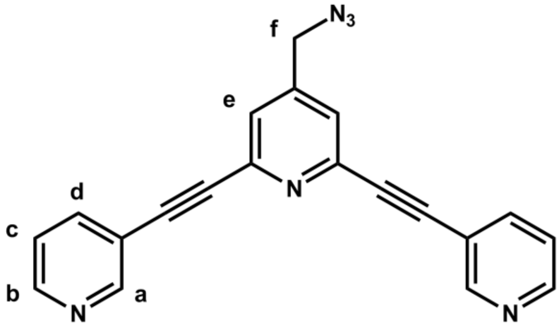


Figure 4 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **3**.

1.4 Synthesis of 4



3 (0.40 g, 1.07 mmol, 1 eq.) and sodium azide (0.08 g, 1.18 mmol, 1.1 eq.) were stirred in DMF (10 mL) for overnight. Water (140 mL) was added and stirred for 1 h. The resultant precipitate was isolated by filtration and washed with water (5 × 10 mL). The product was taken up in 1:3 isopropanol/DCM (80 mL), dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. After purification by column chromatography on silica (1:3 acetone/DCM, R_f = 0.15) the product was obtained as a light green solid. Yield 0.33 g (0.98 mmol, 92%). ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ: 8.83 (s, 2H, H_a), 8.61 (d, J = 4.8 Hz, 2H, H_b), 7.89 (ddd, J = 1.7, 2.0, 7.9 Hz, 2H, H_d), 7.49 (s, 2H, H_e), 7.32 (dd, J = 4.9, 7.9 Hz, 2H, H_c), 4.48 (s, 2H, H_f). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 152.8 (C_a), 149.7 (C_b), 146.0, 143.9, 139.2 (C_d), 125.3 (C_e), 123.3 (C_c), 119.3, 91.0, 86.9, 52.8 (C_f). IR (ATR): ν (cm^{-1}) 2110, 1595, 1581, 1543, 1478, 1425, 1215, 1372, 1321, 1287, 1187, 1173, 1022, 849, 820, 807, 702, 627, 542, 520. HRESI-MS ($CHCl_3$): *m/z* = 309.1141 $[(M-N_2)H]^+$ calc. 309.1135, 337.1200 $[MH]^+$ calc. 337.1196, 359.1013 $[MNa]^+$ calc. 359.1016, 375.0754 $[MK]^+$ calc. 375.0755, 695.2142 $[M_2Na]^+$ calc. 695.2139. *Anal.* calc. for $C_{20}H_{12}N_6$: C, 71.42; H, 3.60; N, 24.99%. Found: C, 71.50; H, 3.54; N, 24.91%.

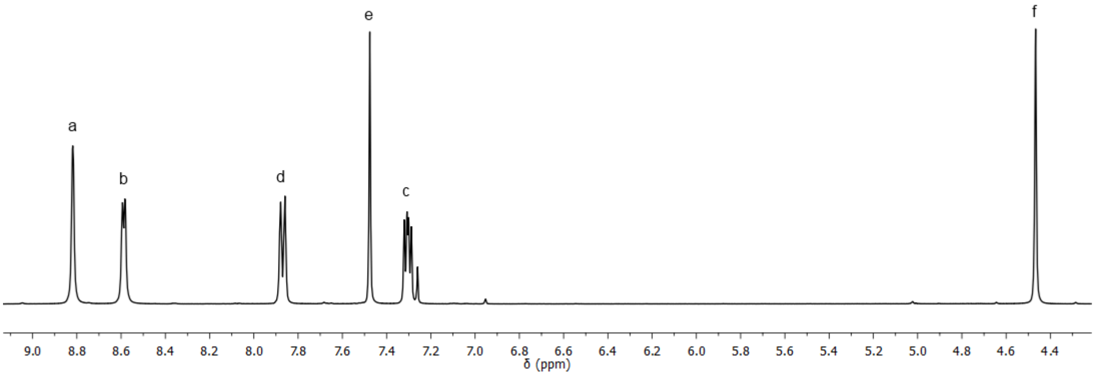


Figure 5 ^1H NMR (400 MHz, $CDCl_3$, 298 K) of **4**.

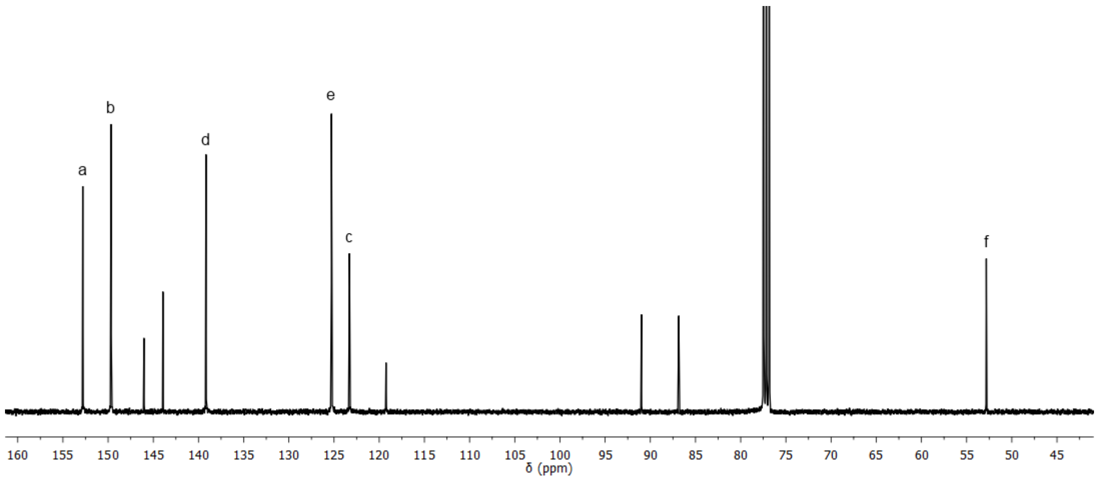
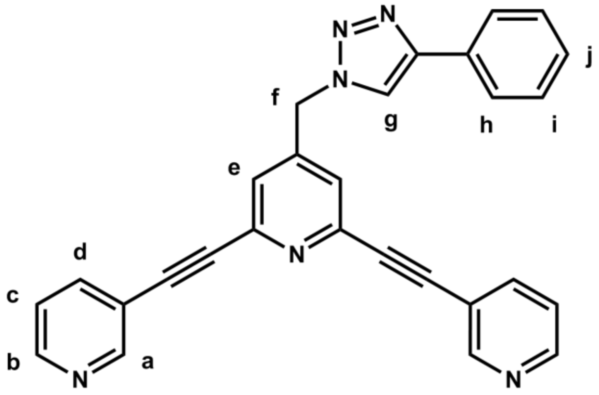


Figure 6 ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) of **4**.

1.5 Synthesis of 5a



4 (83 mg, 0.25 mmol, 1 eq.), $CuSO_4 \cdot 5H_2O$ (31 mg, 0.12 mmol, 0.5 eq.), sodium ascorbate (49 mg, 0.25 mmol, 1 eq.) and ethynylbenzene (54 µL, 0.25 mmol, 1 eq.) were stirred in 1:4 H_2O/DMF (5 mL) for 16 h. 0.1 M EDTA/$NH_4OH_{(aq)}$ (5 mL) was added and the reaction stirred for 1 h, resulting in a white precipitate which was isolated by filtration. The precipitate was taken up in DCM (20 mL), dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to yield the pure product. Yield 87 mg (0.20 mmol, 81 %). M.p. ~170 °C (decomp.). ^{1}H NMR (400 MHz, d_6-DMSO, 298 K) δ: 8.84 (s, 2H, H_a), 8.73 (s, 1H, H_g), 8.66 (s, 2H, H_b), 8.07 (d, J = 7.9 Hz, 2H, H_d), 7.88 (d, J = 7.2 Hz, 2H, H_h), 7.65 (s, 2H, H_e), 7.51 (dd, J = 5.0, 7.7 Hz, 2H, H_c), 7.46 (t, J = 7.6 Hz, 2H, H_i), 7.35 (t, J = 7.4 Hz, 1H, H_j), 5.81 (s, 2H, H_f). Diffusion coefficient (d_6-DMSO, 298 K) D: 2.00×10^{-10} m^2s^{-1}. ^{13}C NMR (125 MHz, d_6-DMSO, 298 K) δ: 150.0 (C_a), 149.9 (C_b), 146.8, 146.7, 142.7, 139.2 (C_d), 130.4, 128.9 (C_i), 128.0 (C_j), 126.0, 126.0 (C_e), 125.2, 123.8 (C_c), 122.3 (C_g), 90.5, 86.3, 51.1 (C_f). IR (ATR): ν (cm^{-1}) 3088, 3044, 2928, 2223, 1594, 1551, 1475, 1419, 1408, 1022. HRESI-MS ($CHCl_3$): *m/z* = 437.1509 $[M-H]^-$ calc. 437.1468; 473.1276 $[M+Cl]^-$ calc. 473.1240; 911.2869 $[M_2+Cl]^-$ calc. 911.2805. UV-Vis (DMSO, ε [$M^{-1}cm^{-1}$]): λ_{max} nm =321 (2.87×10^4). *Anal.* calc. for $C_{28}H_{18}N_6$: C, 76.70; H, 4.14; N, 19.17%. Found: C, 77.12; H, 4.18; N, 18.71%.

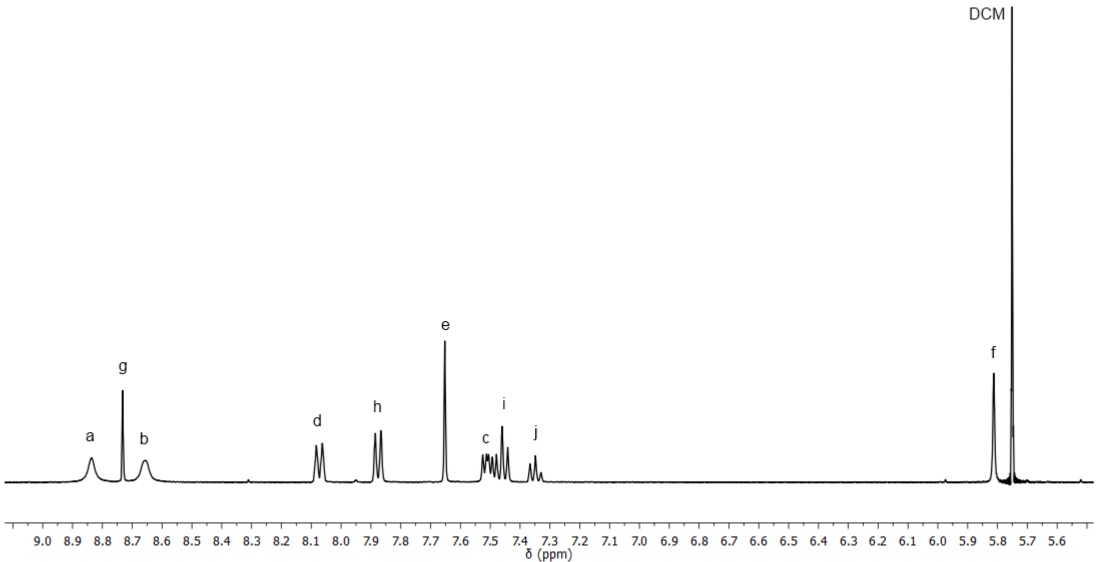


Figure 7 ^{1}H NMR spectrum (400 MHz, d_6-DMSO, 298 K) of **5a**.

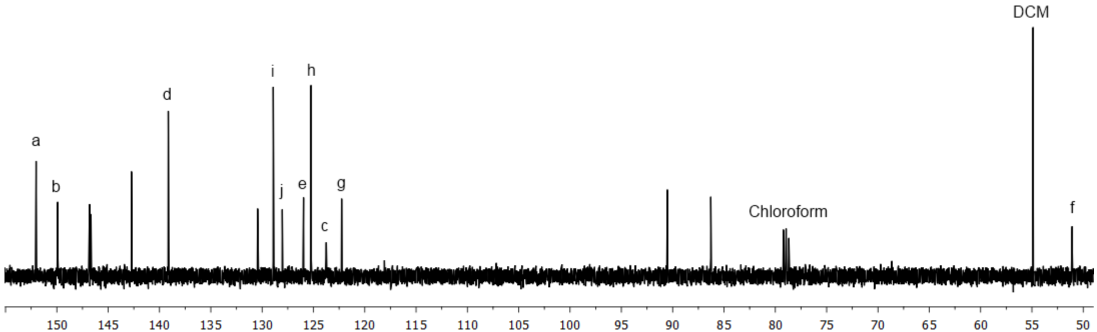
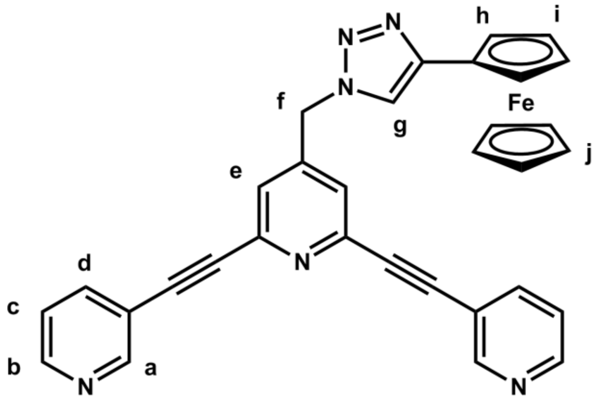


Figure 8 ^{13}C NMR spectrum (125 MHz, d_6-DMSO, 298 K) of **5a**.

1.6 Synthesis of 5b



4 (28 mg, 0.08 mmol, 1 eq.), $CuSO_4 \cdot 5H_2O$ (10 mg, 0.04 mmol, 0.5 eq.), sodium ascorbate (16 mg, 0.08 mmol, 1 eq.) and ethynylferrocene (17 mg, 0.08 mmol, 1 eq.) were stirred in 1:4 H_2O/DMF (5 mL) for 16 h. 0.1 M EDTA/$NH_4OH_{(aq)}$ (5 mL) was added and the reaction stirred for 1 h. H_2O (35 mL) was added, resulting in an orange precipitate which was isolated by filtration. The precipitate was taken up in DCM (20 mL), dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to yield the pure product. Yield 39 mg (0.07 mmol, 88%). (R_f = 0.19, 1:3 acetone/DCM). X-ray quality crystals were grown by vapour diffusion of petrol into a chloroform solution of the ligand. M.p. 183-185 °C. ^{1}H

NMR (400 MHz, $CDCl_3$, 298 K) δ: 8.78 (s, 2H, H_a), 8.56 (s, 2H, H_b), 7.82 (d, J = 7.9 Hz, 2H, H_d), 7.52 (s, 1H, H_g), 7.29 (s, 2H, H_e), 7.29 – 7.26 (m, 2H, H_c), 5.59 (s, 2H, H_f), 4.73 – 4.72 (m, 2H, H_h), 4.30 – 4.29 (m , 2H, H_i), 4.06 (s, 5H, H_j). Diffusion coefficient (d_6-DMSO, 298 K) D: 1.95 × 10^{-10} m^2s^{-1}. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 152.7 (C_a), 149.7 (C_b), 148.3, 145.5, 144.2, 139.1 (C_d), 124.7 (C_e), 123.3 (C_c), 119.1 (C_g), 119.0, 90.6, 87.3, 74.7, 69.7 (C_j), 69.0 (C_i), 66.8 (C_h), 52.0 (C_f). IR (ATR): ν (cm^{-1}) 3110, 3050, 2933, 2215, 1593, 1550, 1475, 1418, 1224, 1191, 1052, 1022. HRESI-MS ($CHCl_3$): *m/z* = 569.1157 $[MNa]^+$ calc. 569.1148. UV-Vis (DMSO, ε [$M^{-1}cm^{-1}$]): λ_{max} nm = 442 (3.05 × 10^2), 321 (3.40 × 10^4). *Anal.* calc. for $C_{32}H_{22}N_6Fe$: C, 70.34; H, 4.06; N, 15.38%. Found: C, 70.32; H, 4.35; N, 15.10%.

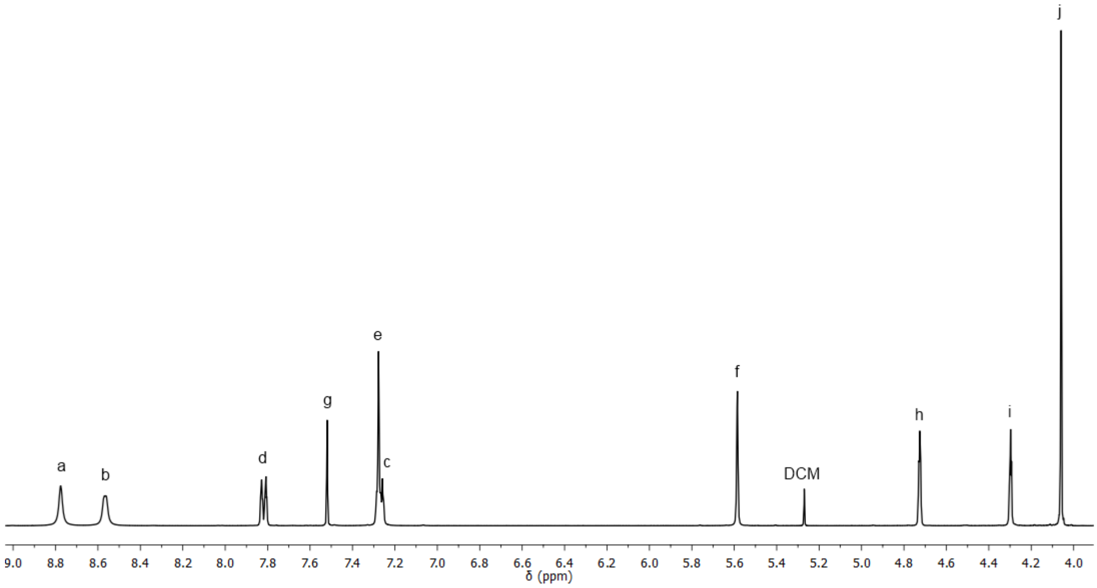


Figure 9 ^1H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **5b**.

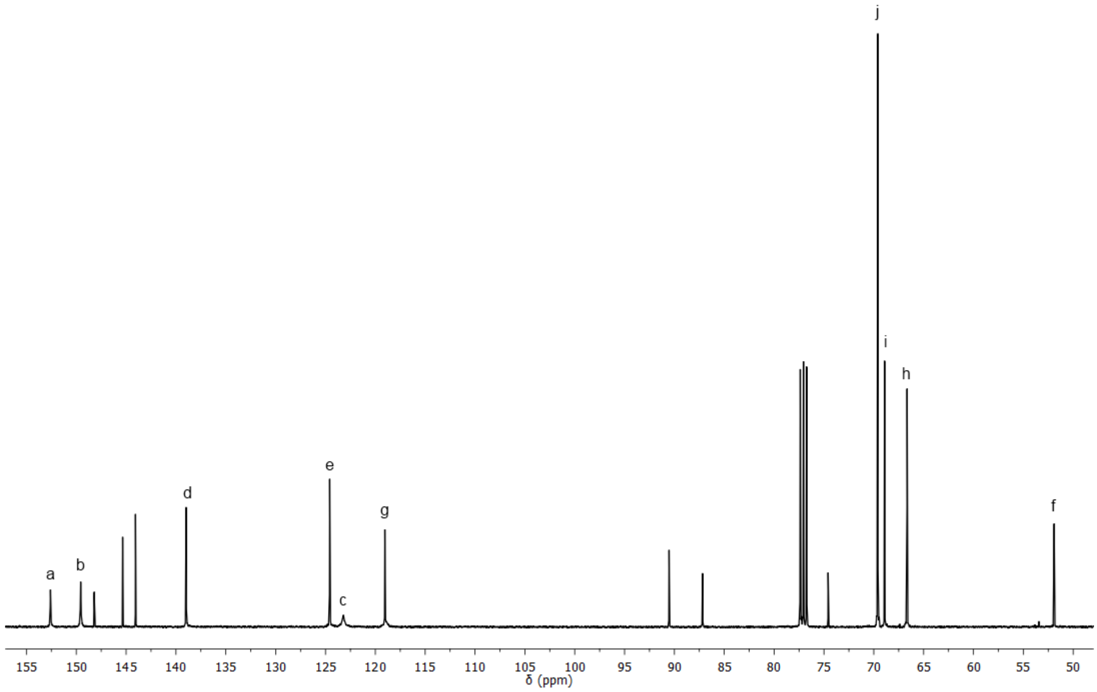
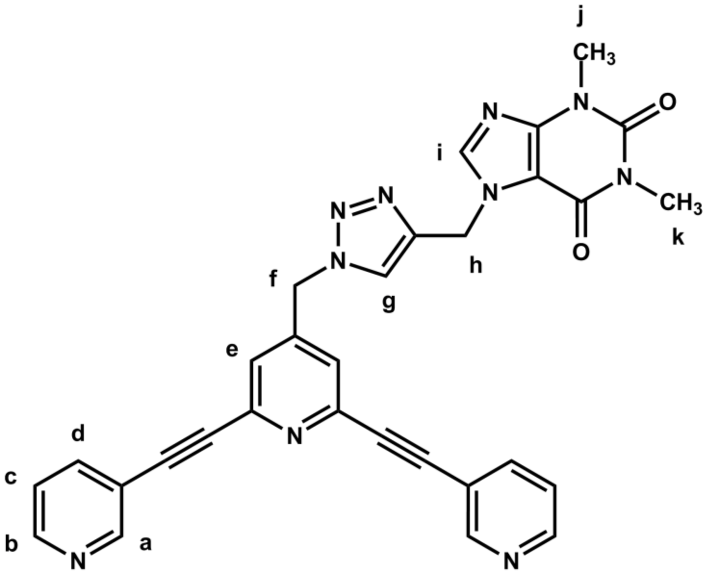


Figure 10 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **5b**.

1.7 Synthesis of 5c



To a stirring solution of **4** (100 mg, 0.30 mmol, 1 eq.), $CuSO_4 \cdot 5H_2O$ (37 mg, 0.15 mmol, 0.5 eq.) and sodium ascorbate (59 mg, 0.30 mmol, 1 eq.) in 1:4 H_2O/DMF (5 mL) was added *N*-propargyltheophylline (65 mg, 0.30 mmol, 1 eq). The reaction was stirred at room temperature overnight before adding to 0.1 M EDTA/$NH_4OH_{(aq)}$ (20 mL) and making up to a volume of 50 mL with H_2O. The resulting precipitate was isolated by filtration and washed with H_2O (2 × 5 mL). The precipitate was taken up in 1:3 isopropanol/chloroform (80 mL), dried ($MgSO_4$), filtered and the solvent removed in vacuo to yield the pure product as a light tan solid. Yield 106 mg (0.19 mmol, 64%). M.p. ~200 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 8.82 (s, 2H, H_a), 8.62 (s, 2H, H_b), 7.93 (s, 1H, H_g), 7.87 (d, J = 8.0 Hz, 2H H_d), 7.83 (s, 1H, H_i), 7.36 (s, 2H, H_e), 7.33 (dd, J = 5.1, 8.0 Hz, 2H, H_c), 5.61 (s, 2H, H_f), 5.54 (s, 2H, H_h), 3.55 (s, 3H, H_k), 3.38 (s, 3H, H_j). Diffusion coefficient (*d*$_6$-DMSO, 298 K) D: 2.54×10^{-10} m^2s^{-1}. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ: 155.6, 152.7 (C_a), 151.7, 149.8 (C_b), 149.3, 144.5, 144.3, 143.4, 141.5 (C_i), 139.2 (C_d), 125.2 (C_e), 124.3 (C_g), 123.4 (C_c), 119.0, 106.6, 90.6, 87.5, 52.4 (C_f), 41.6 (C_h), 30.0 (C_k), 28.2 (C_j). IR (ATR): ν (cm^{-1}) 2218, 1704, 1665, 1550, 1456, 1426, 1028. HRESI-MS ($CHCl_3$): *m/z* =577.1855 $[MNa]^+$ calc. 577.1819. UV-Vis (DMSO, ε [$M^{-1}cm^{-1}$]): λ_{max} nm = 320 (3.90×10^4). *Anal.* calc. for $C_{30}H_{22}N_{10}O_2 \cdot 0.1H_2O$: C, 63.13; H, 4.20; N, 24.54%. Found: C, 63.66; H, 4.25; N, 23.96%.

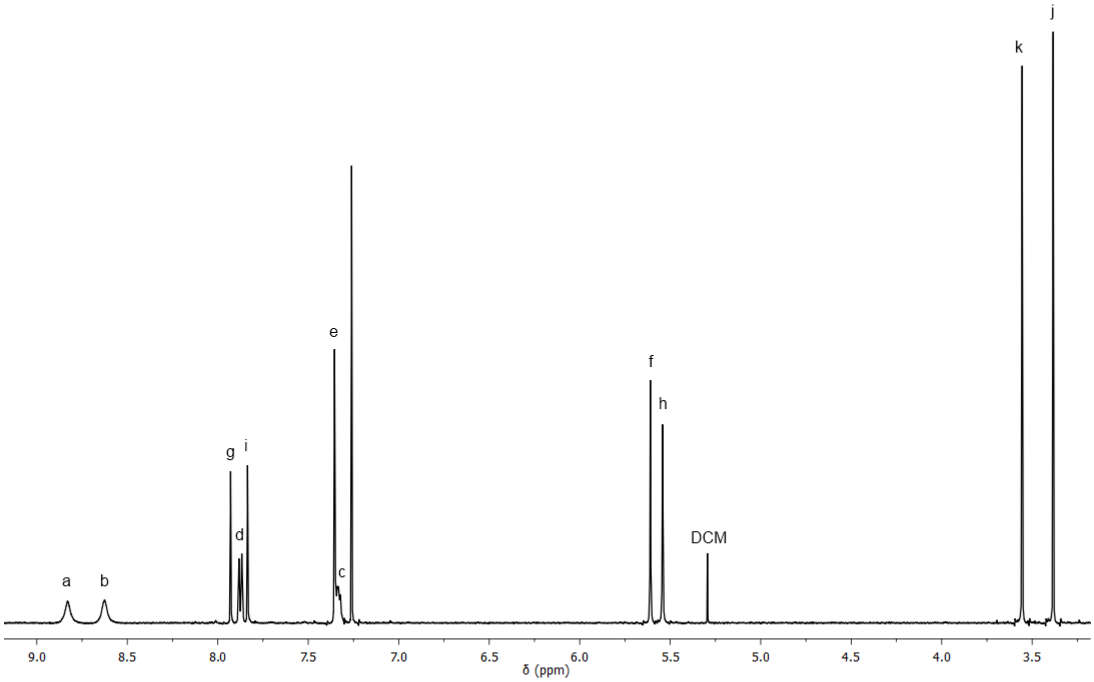


Figure 11 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **5c**.

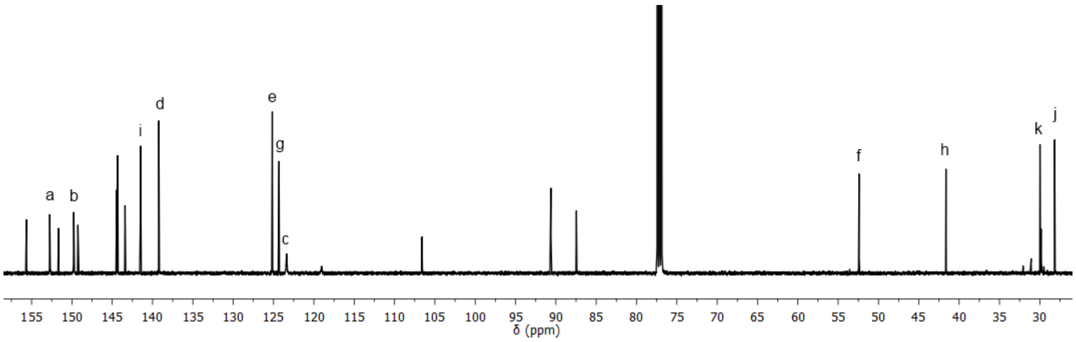
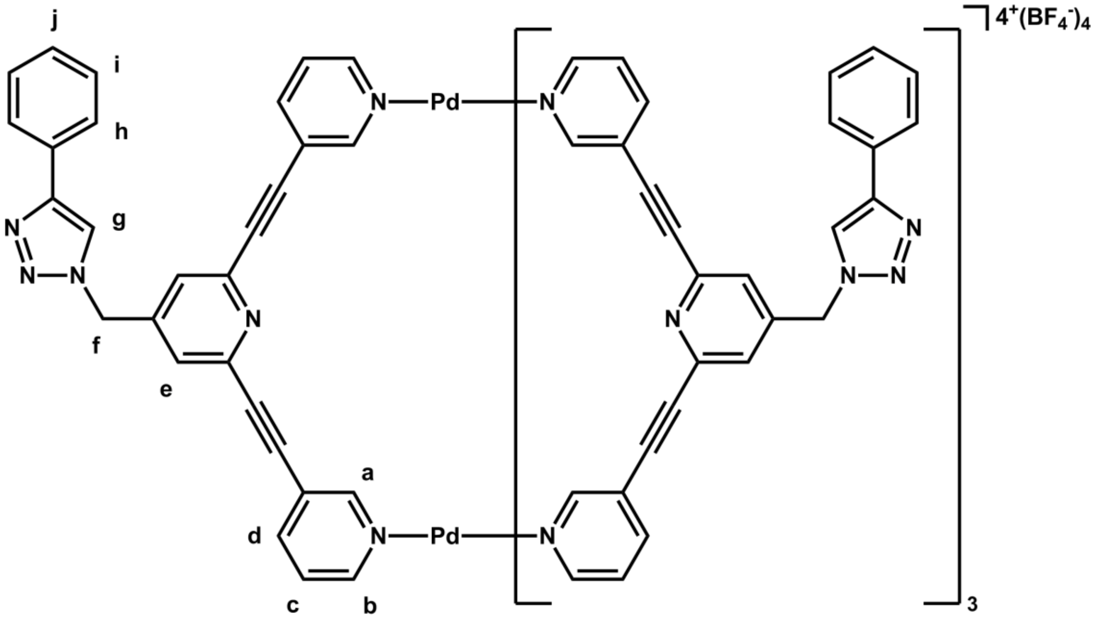


Figure 12 ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **5c**.

1.8 Synthesis of 6a



$[Pd(CH_3CN)_4](BF_4)_4$ (22 mg, 0.05 mmol, 1 eq.) was added as a solid to a stirring suspension of **5a** (44 mg, 0.1 mmol, 2 eq.) in acetone (10 mL). After stirring at room temperature for 2 h the product was filtered and washed with diethyl ether (5 mL) and DCM (5 mL) to give the product as a tan solid. Yield 44 mg (0.02 mmol, 76%). ^{1}H NMR (400 MHz, *d*$_6$-DMSO, 298 K) δ: 9.49 (s, 8H, H_a), 9.36 (d, J = 5.7 Hz, 8H, H_b), 8.65 (s, 4H, H_g), 8.32 (d, J = 8.0 Hz, 8H, H_d), 7.84-7.80 (m, 16H, H_c, H_h), 7.65 (s, 8H, H_e), 7.43 (t, J = 7.6 Hz, 8H, H_i), 7.33 (t, J = 7.4 Hz, 4H, H_j), 5.79 (s, 8H, H_f). Diffusion coefficient (*d*$_6$-DMSO, 298 K) D: 0.89 × 10^{-10} m^2s^{-1}. ^{13}C NMR (125 MHz, *d*$_6$-DMSO, 298 K) δ: 153.3 (C_a), 151.2 (C_b), 147.1, 146.7, 143.6 (C_d), 142.2, 130.3, 129.0 (C_i), 128.1 (C_j), 127.3 (C_c), 126.9 (C_e), 125.2 (C_h), 122.3 (C_g), 121.3, 92.8, 84.0, 51.0 (C_f). IR (ATR): ν (cm^{-1}) 3076, 1650, 1594, 1548, 1483, 1425, 1388, 1237, 1195, 1049. HRESI-MS (MeCN): *m/z* = 439.1656 $[LH]^+$ calc. 439.1666; 461.1480 $[LNa]^+$ calc. 461.1485; 798.1114 $[Pd_2L_3Cl_2]^{2+}$ calc. 798.1118; 1017.1907 $[Pd_2L_4Cl_2]^{2+}$ calc. 1017.1918. UV-Vis (DMSO, ε [$M^{-1}cm^{-1}$]): λ_{max} nm = 314 (8.97 × 10^4).

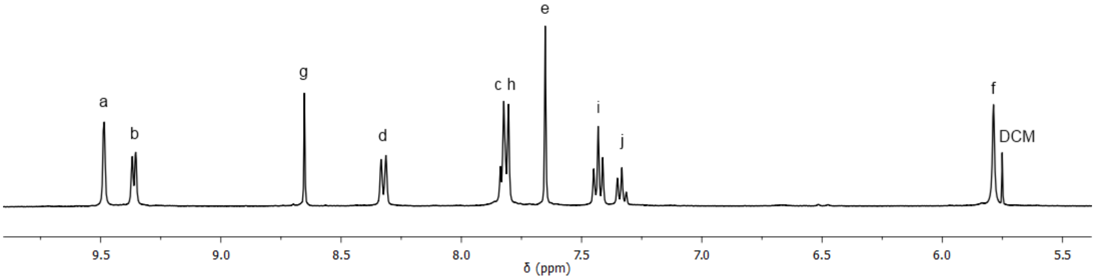


Figure 13 ^{1}H NMR spectrum (400 MHz, *d*$_6$-DMSO, 298 K) of **6a**.

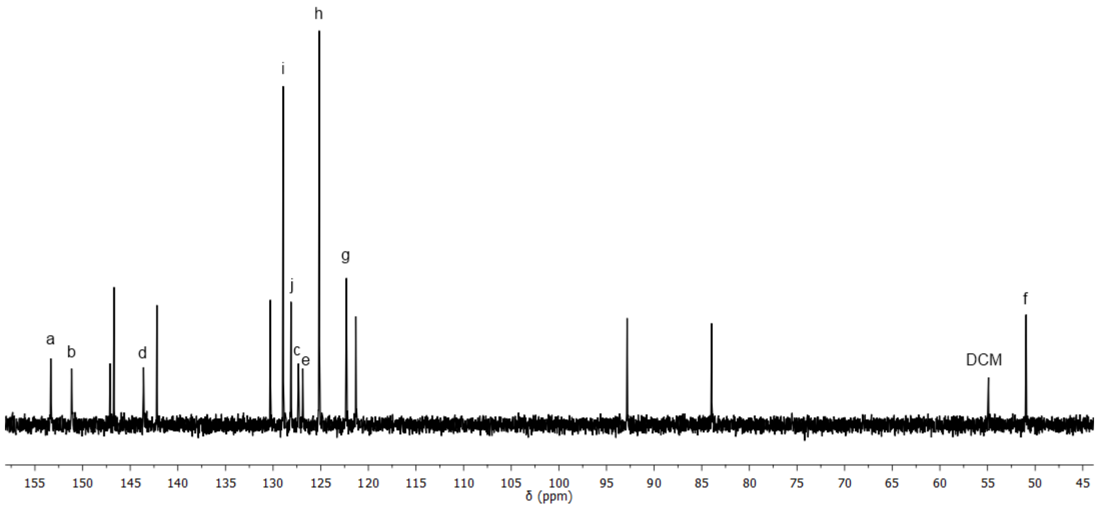
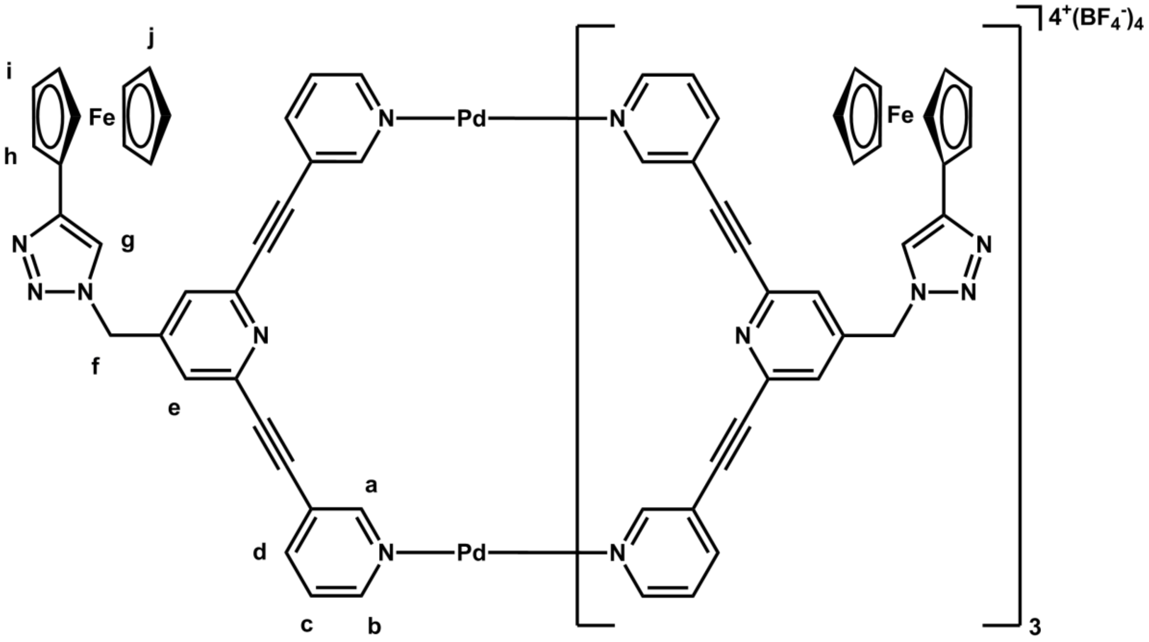


Figure 14 ^{13}C NMR spectrum (125 MHz, d_6-DMSO, 298 K) of **6a.**

1.9 Synthesis of 6b



5b (37 mg, 0.07 mmol, 2 eq.) and $[Pd(CH_3CN)_4](BF_4)_2$ (15 mg, 0.03 mmol, 1 eq.) were stirred in DMF (2 mL) for 90 minutes. The addition of diethyl ether resulted in a light orange precipitate. The product was isolated by filtration, washed with diethyl ether (2 × 5 mL) and dried *in vacuo*. Yield 29 mg (0.01 mmol, 63%). ^{1}H NMR (400 MHz, d_6-DMSO, 298 K) δ: 9.46 (s, 8H, H_a), 9.34 (d, J = 5.7 Hz, 8H, H_b), 8.27 (s, 4H, H_g), 8.25 (d, J = 8.2 Hz, 8H, H_d), 7.79 (dd, J = 6.0, 7.8 Hz, 8H, H_c), 7.52 (s, 8H, H_e), 5.76 (s, 8H, H_f), 4.72 (t, J = 1.8 Hz, 8H, H_h), 4.31 (t, J = 1.8 Hz, 8H, H_i), 4.00 (s, 20H, H_j). Diffusion coefficient (d_6-DMSO, 298 K) D: 0.85×10^{-10} m^2s^{-1}. ^{13}C NMR (125 MHz, d_6-DMSO, 298 K) δ: 153.4 (C_a), 151.1 (C_b), 147.7, 146.1, 143.4 (C_d), 142.2, 127.3 (C_c), 126.4 (C_e), 121.4, 121.2 (C_g), 92.8, 84.0, 75.4, 69.3 (C_j), 68.4 (C_i), 66.3 (C_h), 50.7 (C_f). IR (ATR): ν (cm^{-1}) 3076, 2929, 1650, 1592, 1482, 1427, 1387, 1332, 1254, 1222, 1194, 1048. HRESI-MS (MeCN): *m/z* = 546.1145 $[L]^+$ calc. 546.1250, 652.0199 $[Pd_2L_2]^{2+}$ calc. 652.0301, 925.0766 $[Pd_2L_3]^{2+}$ calc. 925.0935, 1254.6358 $[Pd_2L_4(CH_3CN)(H_2O)_4]^{2+}$ calc.

1254.6913, 1311.1659 $[Pd_2L_4(CH_3CO_2)_2(H_2O)_6]^{2+}$ calc. 1311.2019. UV-Vis (DMSO, ε $[M^{-1}cm^{-1}]$): λ_{max} nm = 426 (1.05×10^3), 314 (1.04×10^5).

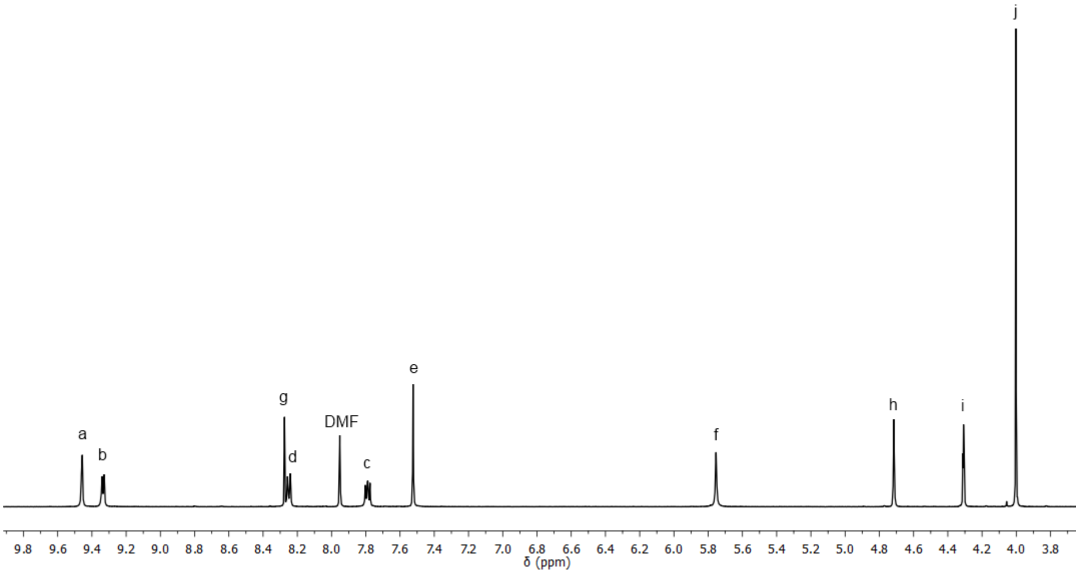


Figure 15 ^{1}H NMR spectrum (500 MHz, d_6-DMSO, 298 K) of **6b.**

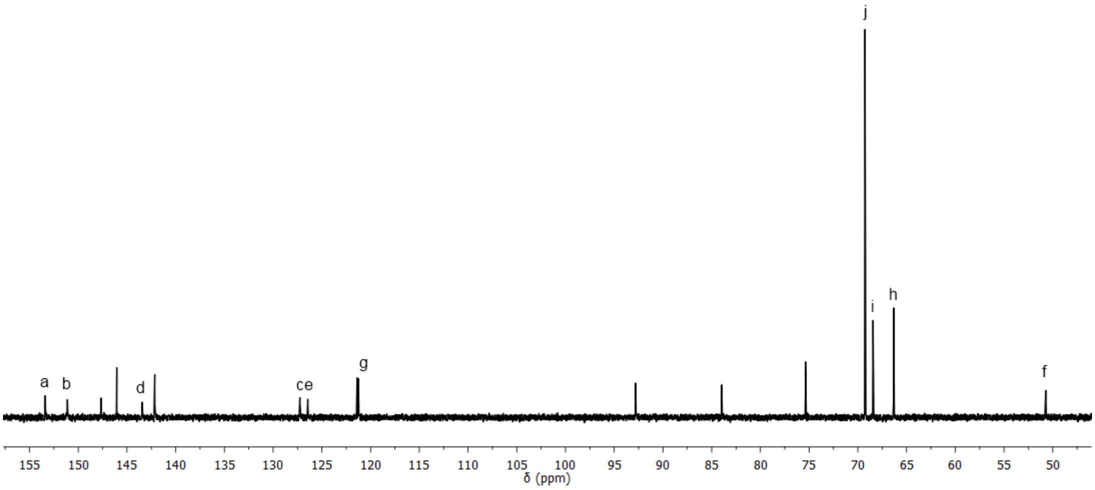
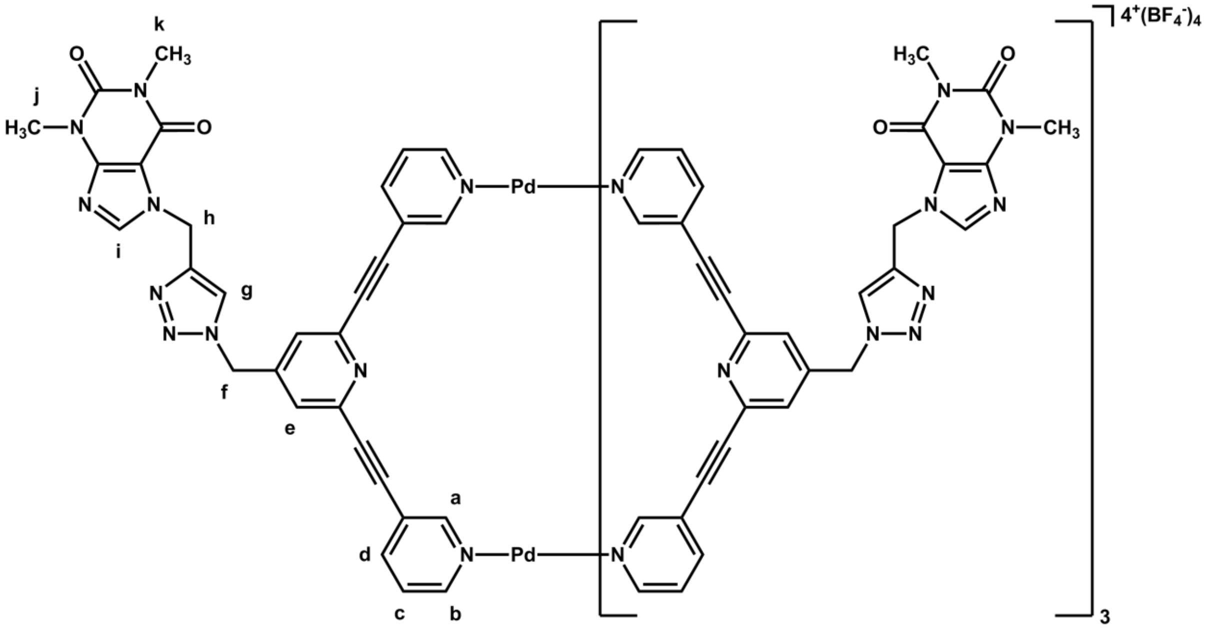


Figure 16 ^{13}C NMR spectrum (125 MHz, d_6-DMSO, 298 K) of **6b.**

1.10 Synthesis of 6c



A solution of $[Pd(CH_3CN)_4](BF_4)_4$ (22 mg, 0.05 mmol, 1 eq.) in MeCN (0.5 mL) was added to a solution of **5c** (55 mg, 0.1 mmol, 2 eq.) in MeCN (5 mL). After stirring at room temperature for 1 h the product was precipitated by vapour diffusion of diethyl ether. The precipitate was isolated by filtration and washed with diethyl ether (10 mL) and DCM (10 mL) before drying *in vacuo* to give the product as a tan solid. Yield 50 mg (0.02 mmol, 72%). ^{1}H NMR (400 MHz, *d*$_6$-DMSO, 298 K) δ: 9.55 (s, 8H, H_a), 9.38 (d, J = 5.5 Hz, 8H, H_b), 8.30 (d, J = 8.0, 8H, H_d), 8.17 (s, 4H, H_g), 8.15 (s, 4H, H_i), 7.85 (m, 8H, H_c), 5.70 (s, 8H, H_f), 5.53 (s, 8H, H_h), 3.27 (s, 12H, H_k), 3.06 (s, 12H, H_j). Diffusion coefficient (*d*$_6$-DMSO, 298 K) D: 0.80×10^{-10} m^2s^{-1}. ^{13}C NMR (125 MHz, *d*$_6$-DMSO, 298 K) δ: 154.2, 153.5 (C_a), 151.2 (C_b), 150.7, 148.4, 147.1, 143.4 (C_d), 142.9, 142.5 (C_i), 142.1, 127.3 (C_c), 126.9 (C_e), 124.8 (C_g), 121.3, 105.7, 92.7, 83.9, 50.8 (C_f), 41.2 (C_h), 29.3 (C_k), 27.4 (C_j). IR (ATR): ν (cm^{-1}) 1701, 1654, 1596, 1549, 1479, 1426, 1388, 1226, 1194, 1054. HRESI-MS (DMF/MeCN): *m/z* = 555.2061 $[LH]^+$ calc. 555.2000, 577.1874 $[LNa]^+$ calc. 577.1819, 607.1605 $[Pd_2L_4]^{4+}$ calc. 607.1449, 847.2100 $[Pd_2L_4(CH_3CO_2)(H_2O)_3]^{3+}$ calc. 847.2084, 1327.3030 $[Pd_2L_4(CH_3CO_2)_2(H_2O)_6]^{2+}$ calc. 1327.3354. UV-Vis (DMSO, ε $[M^{-1}cm^{-1}]$): λ_{max} nm = 316 (9.66×10^4).

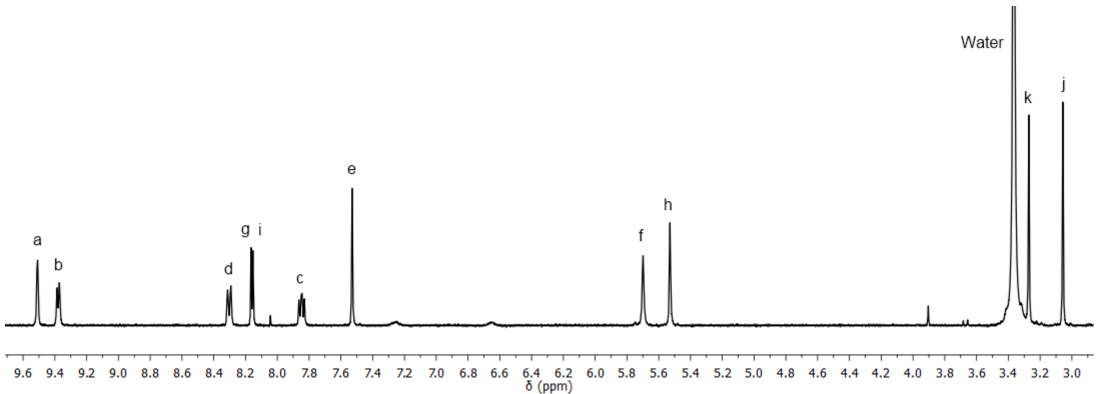


Figure 17 ^{1}H NMR spectrum (400 MHz, d_6-DMSO, 298 K) of **6c**.

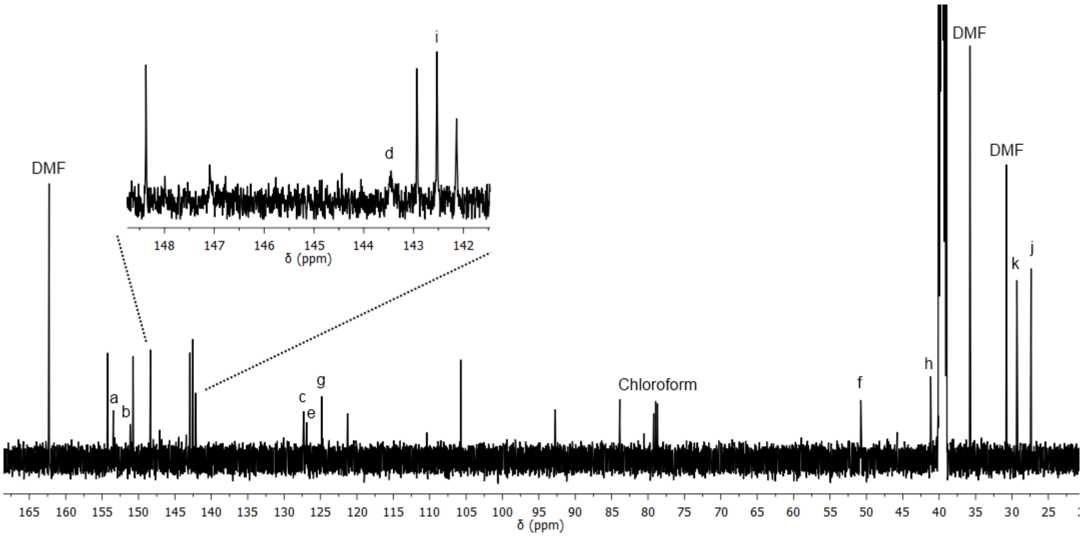


Figure 18 ^{13}C NMR spectrum (125 MHz, d_6-DMSO, 298 K) of **6c.**

1.11 Comparison of Diffusion Coefficients

Ligand	Ligand D (× 10^{-10} m^2 s^{-1})	Cage	Cage D (× 10^{-10} m^{2}s^{-1})	Ratio
5a	2.00	**6a**	0.89	2.25
5b	1.95	**6b**	0.85	2.29
5c	2.54	**6c**	0.80	3.18

2 ^{1}H NMR Cisplatin Binding Experiments

2.1 6a

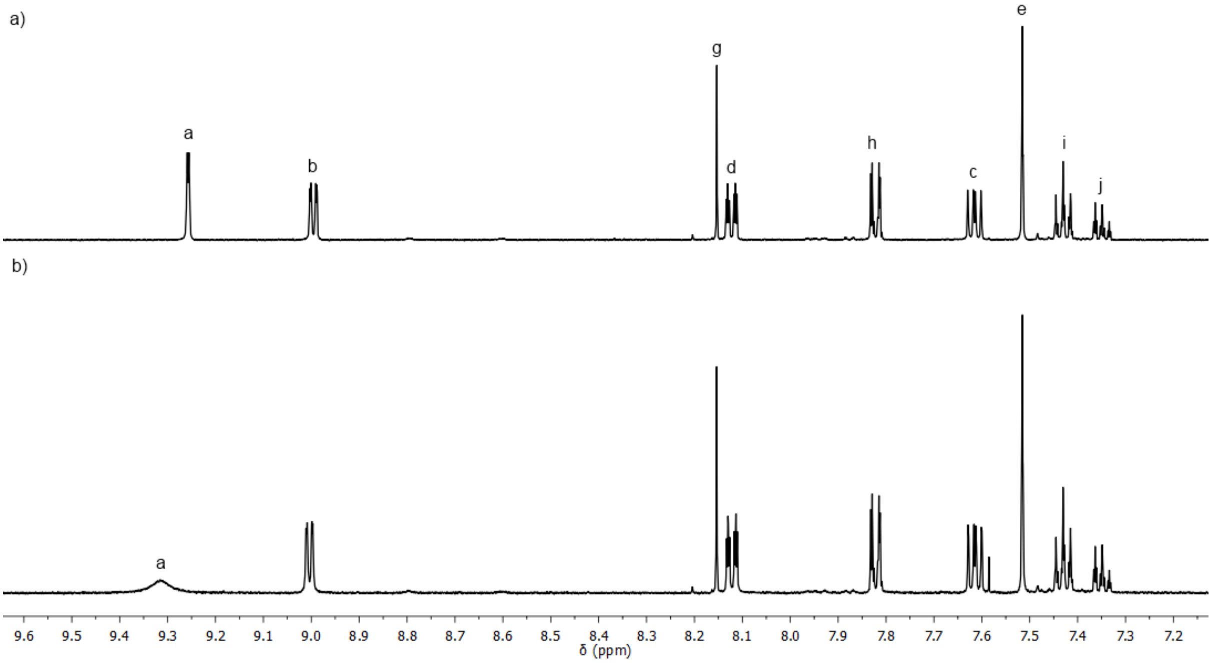


Figure 19 ^{1}H NMR spectra (500 MHz, CD_3CN, 298 K) of a) **6a** and b) **6a**⊃2[$Pt(NH_3)_2Cl_2$]

2.2 6b

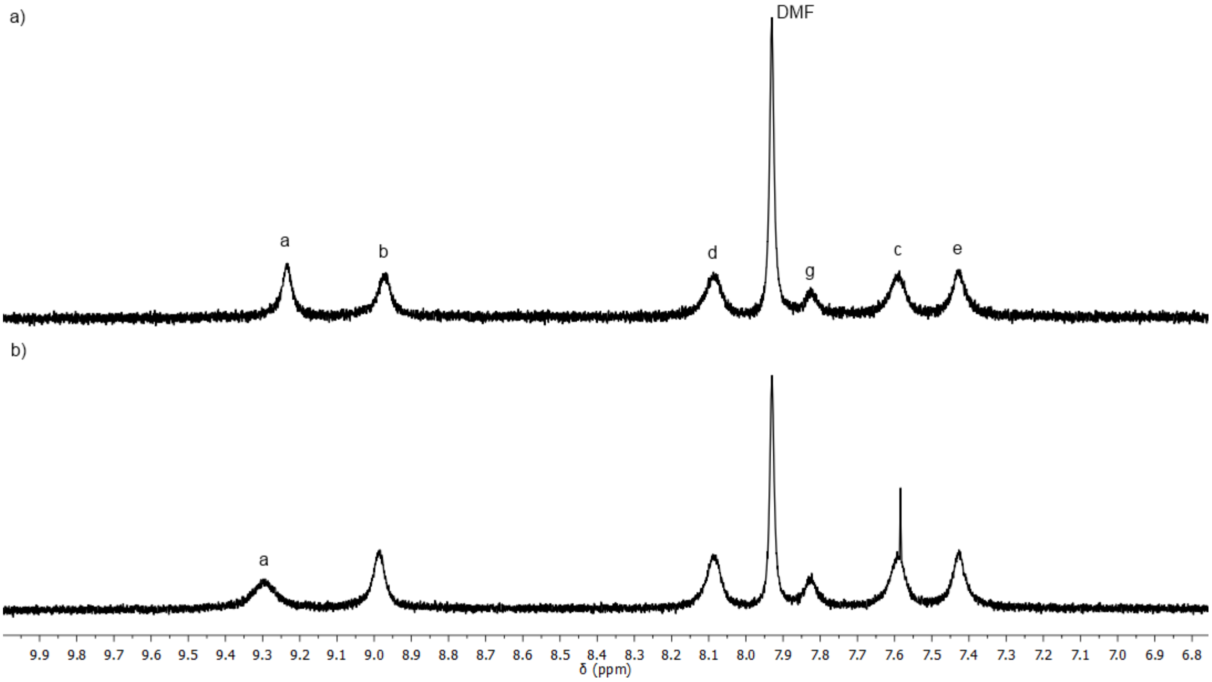


Figure 20 ^{1}H NMR spectra (500 MHz, CD_3CN, 298 K) of a) **6b** and b) **6b**⊃2[$Pt(NH_3)_2Cl_2$].

3 X-ray Data

Orange block crystals of [**6b**⊃(cisplatin)$_2$]·**6b** were grown by vapour diffusion of diethyl ether into a sonicated DMF solution of **6b** and cisplatin. X-ray data was collected at -173 °C on crystals mounted on a Hampton Scientific cryoloop at the MX2 beamline of the Australian Synchrotron.[4] The structure was solved by direct methods and refined against F2 using anisotropic thermal displacement parameters for all non-hydrogen atoms using SHELXTL 6.14 software. Hydrogen atoms were placed in calculated positions and refined using a riding model.

The structure was solved in the primitive triclinic space group P-1 and refined to an R_1 value of 9.34%. The tetrafluoroborate (BF_4^-) counterions and several solvent molecules were deemed too disordered to model, thus SQUEEZE was used to remove them (*vide infra*), resulting in a void electron count of 519. Eight BF_4^- anions total 328 electrons, with the remainder accounted for by five molecules of DMF (total 200 electrons).

The asymmetric unit contains of one palladium ion and two ligands for each of the [**6b**⊃(cisplatin)$_2$] and **6b** moieties. In addition there is one molecule of cisplatin within the cavity of the host-guest structure and a cluster of water molecules have been modelled inside the cavity of the non-cisplatin-containing **6b** structure.

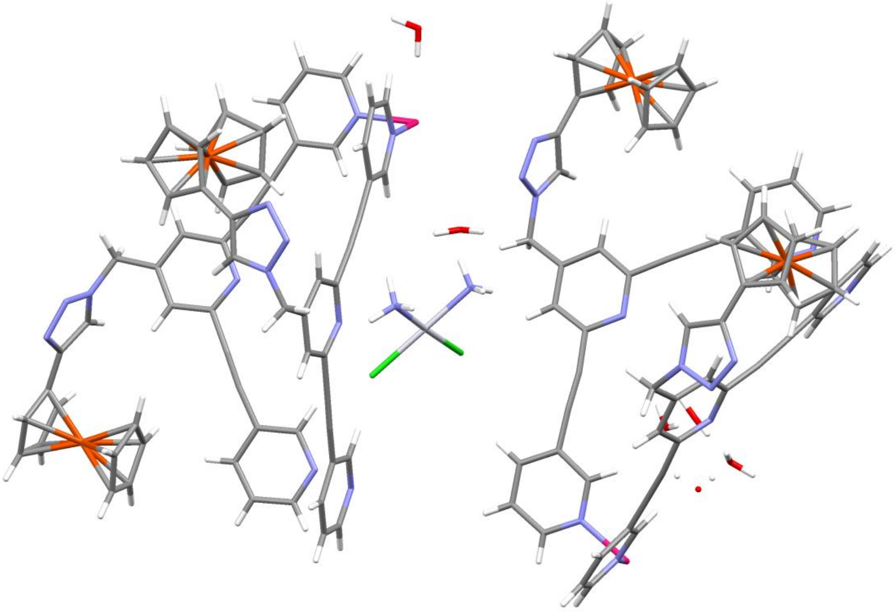


Figure 21 Mercury capped-stick model of the asymmetric unit of [**6b**⊃(cisplatin)$_2$]·**6b**.

Squeeze results for [**6b**⊃(cisplatin)$_2$]·**6b**.

Platon squeeze void nr	1
Platon squeeze void average x	-0.006
Platon squeeze void average y	0.000
Platon squeeze void average z	0.000
Platon squeeze void volume	2150
Platon squeeze void count electrons	519
Platon squeeze void content	Highly disordered tetrafluoroborate anions and solvent molecules. The number of electrons is consistent with eight tetrafluoroborate anions and five molecules of DMF.;

3.1 X-ray Structure Data for $[\mathbf{6b}\supset(\mathrm{cisplatin})_2]\cdot\mathbf{6b}$

Identification code	jl241hg	
Empirical formula	$C_{64}H_{52.50}ClFe_2N_{13}O_{2.75}PdPt_{0.50}$	
Formula weight	1398.79	
Temperature	100(2) K	
Wavelength	0.71080 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 14.809(3) Å	α= 105.56(3)°.
	b = 21.668(4) Å	β= 94.22(3)°.
	c = 24.158(5) Å	γ = 90.62(3)°.
Volume	7444(3) $Å^3$	
Z	4	
Density (calculated)	1.248 Mg/m^3	
Absorption coefficient	1.641 mm^{-1}	
F(000)	2814	
Crystal size	0.10 × 0.10 × 0.02 mm^3	
Theta range for data collection	1.12 to 31.08°.	
Index ranges	-21<=h<=21, -30<=k<=30, -33<=l<=33	
Reflections collected	158104	
Independent reflections	41676 [R(int) = 0.0724]	
Completeness to theta = 31.08°	87.2 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	41676 / 23 / 1485	
Goodness-of-fit on F^2	1.000	
Final R indices [I>2sigma(I)]	R1 = 0.0934, wR2 = 0.2786	
R indices (all data)	R1 = 0.1333, wR2 = 0.3050	
Largest diff. peak and hole	4.172 and -3.203 e.$Å^{-3}$	

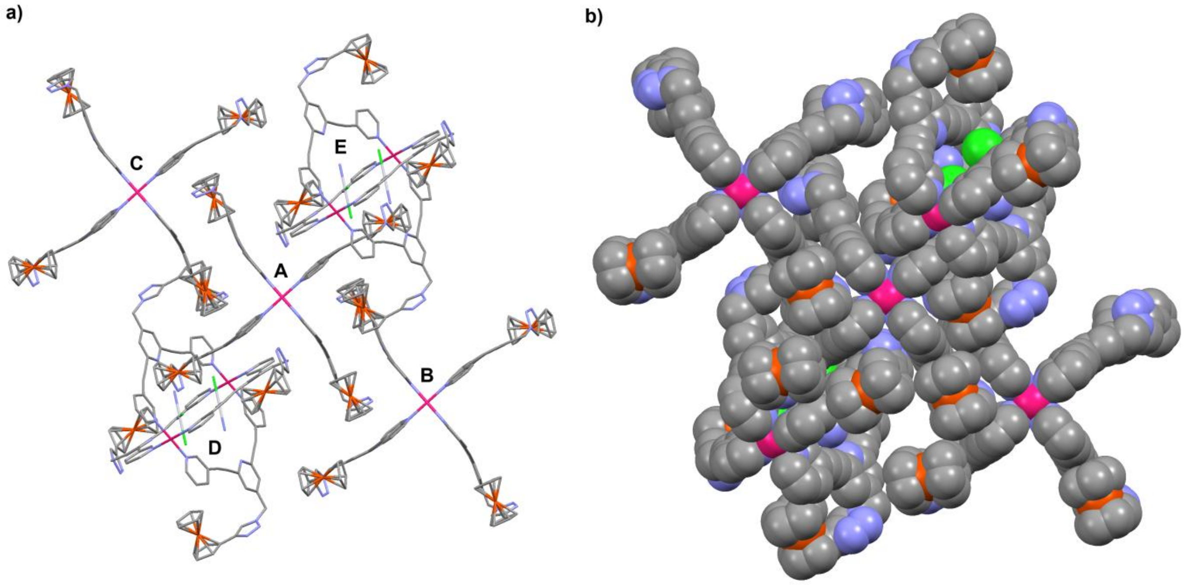


Figure 22 Mercury diagrams of a) capped-stick view and b) space-fill view showing intercalation of cages adjacent to **6b** (**A**), largely filling the internal cavity. The cage (**A**) is flanked by two **6b** moieties (**B** and **C**) and two [**6b**⊃(cisplatin)$_2$] moieties (**D** and **E**).

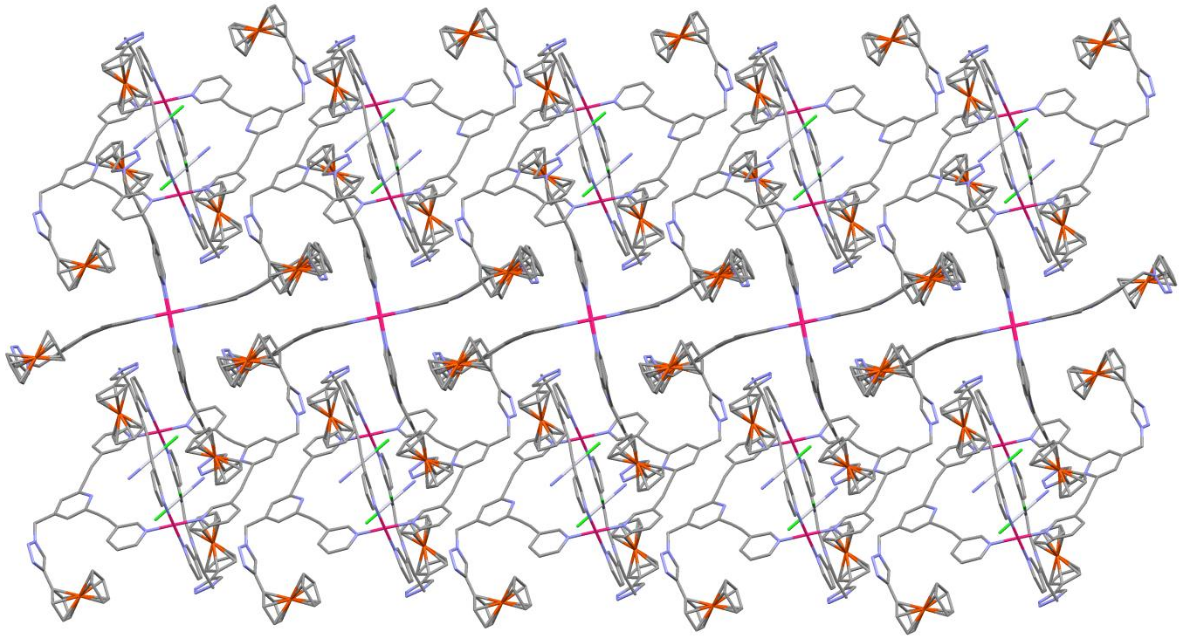


Figure 23 Capped-stick Mercury diagram showing the intercalating 1D chains of **6b** and [**6b** ⊃(cisplatin)$_2$] moieties which stack to form a 2D lattice structure.

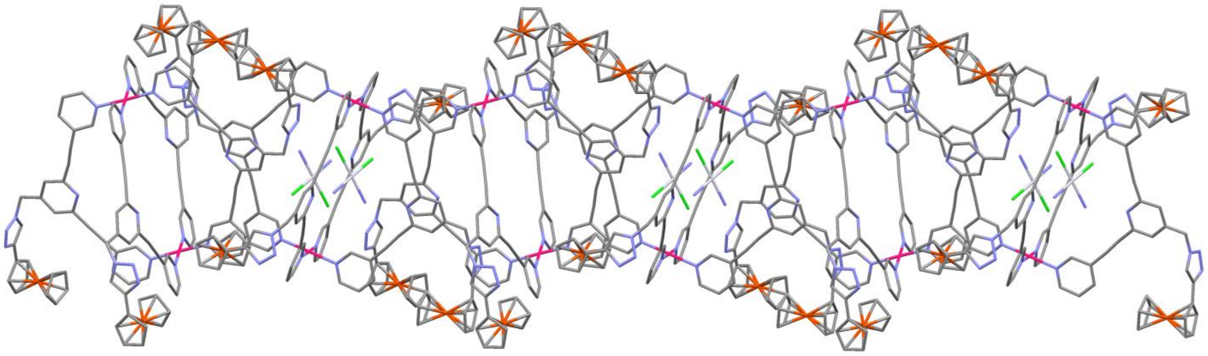


Figure 24 Capped-stick Mercury diagram (side view) showing 1D chains of alternating [**6b**⊃(cisplatin)$_2$] and **6b** moieties.

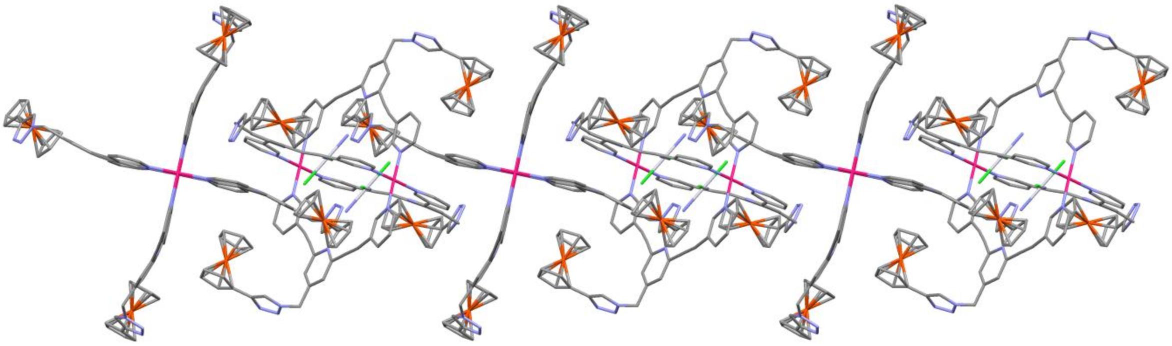


Figure 25 Capped-stick Mercury diagram (top view) showing 1D chains of alternating [**6b**⊃(cisplatin)$_2$] and **6b** moieties.

4 Electrochemistry

4.1 Results

The electrochemistry observed for the ligand and derived cage compounds appears as the sum of their components: the bis(ethynyl)pyridine framework, for which there is little literature precedent, and the various triazole attached substituents. The results of cyclic voltammetry in DMF solution of the ligands and cages are presented in Table 1 and representative voltammograms are illustrated in Figure 26 to Figure 29.

For the ligand species a cathodic sweep to -2.0 V shows two irreversible reductions at ca. -1.7 and -1.9 V. These we attribute to the 2,6-bis(ethynyl)pyridine structural element. It is unlikely the reductions involve the triazole unit as connection of this to the central pyridine is through a saturated methylene, and previous work with uncoordinated triazoles has their reduction appearing at highly negative potentials.[5] In the cage complexes, coordination of the pyridine termini to palladium has little effect on the position of the reduction processes. This is consistent with the *meta* attachment of these to the bis(ethynyl)pyridine that obviates resonance participation through the assembly.

The triazole provides a means of attachment of redox-active labels to the ligand and derived cages. Thus an anodic sweep on a DMF solution of the ferrocenyl labelled **5b** shows the predicted one-electron reversible oxidation at $E°$ 0.53 V (Figure 27). In dichloromethane solution $E°$ is 0.59 V, a value comparable with other reported 4-ferrocenyl triazoles.[6] As expected, complexation of the ligand with palladium does not affect the potential or reversibility of this process (within experimental error), but suggests such labelling offers scope for monitoring or detection in future practical applications of the cages. Predictably, the label groups do not affect the ligand/cage reduction potential.

Table 1 Electrochemical data for ligands and cages in DMF (0.1 M Bu_4NPF_6, 100 mVs^{-1}, referenced to $[Fc^*]^{+/0}$ = 0.00 V, $[FcH]^{+/0}$ = 0.51 V]).

	E_{pc}(ligand) / V	**$E°$(ferrocenyl) / V**
5a	-1.9, -1.7	
6a	-1.9, -1.7	
5b	-1.9, -1.7	0.53[a]
6b	-1.9, -1.8	0.54

[a] In CH_2Cl_2 $E°$ = 0.59 V (*vs.* $[Fc^*]^{+/0}$ = 0.00 V, $[FcH]^{+/0}$ = 0.55 V]).

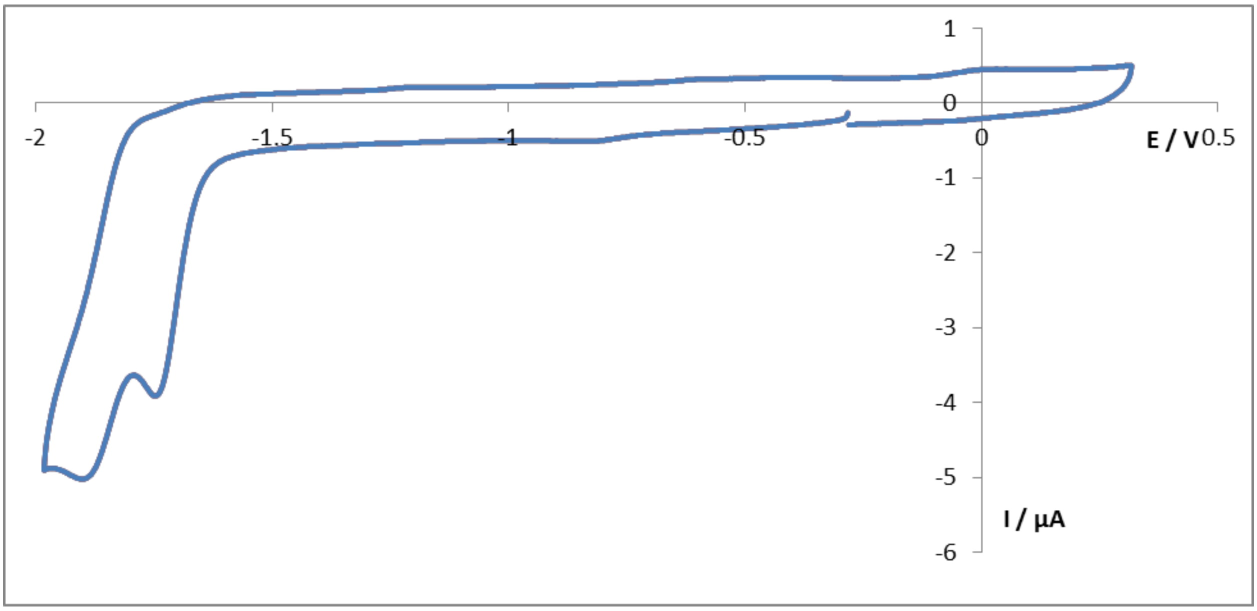


Figure 26 Cyclic voltammogram in DMF of **5a** (~1 × 10^{-3} M), 0.1 M Bu_4NPF_6, 100 mVs^{-1}, referenced to $[Fc^*]^{+/0}$ = 0.00 V.

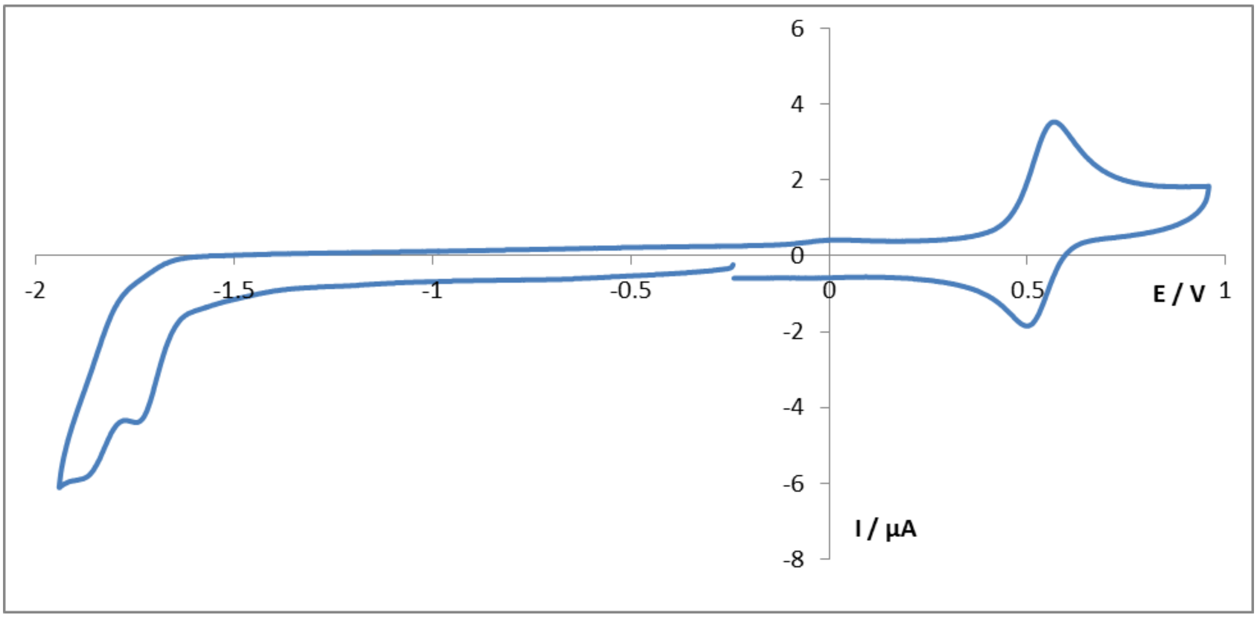


Figure 27 Cyclic voltammogram in DMF of **5b** (~1 × 10^{-3} M), 0.1 M Bu_4NPF_6, 100 mVs^{-1}, referenced to $[Fc^*]^{+/0}$ = 0.00 V.

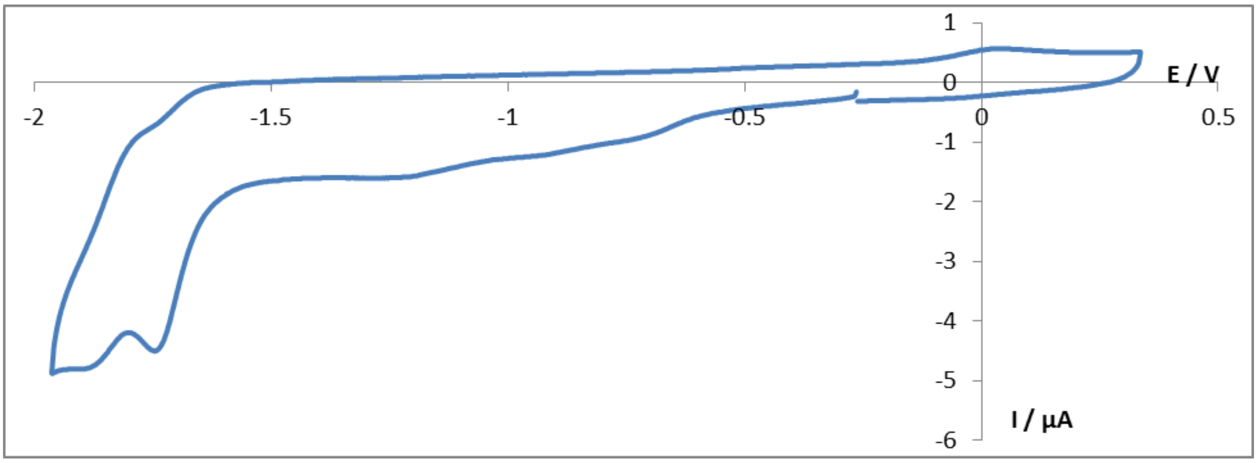


Figure 28 Cyclic voltammogram in DMF of **6a** (~0.25 × 10^{-3} M), 0.1 M Bu_4NPF_6, 100 mVs^{-1}, referenced to $[Fc^*]^{+/0}$ = 0.00 V.

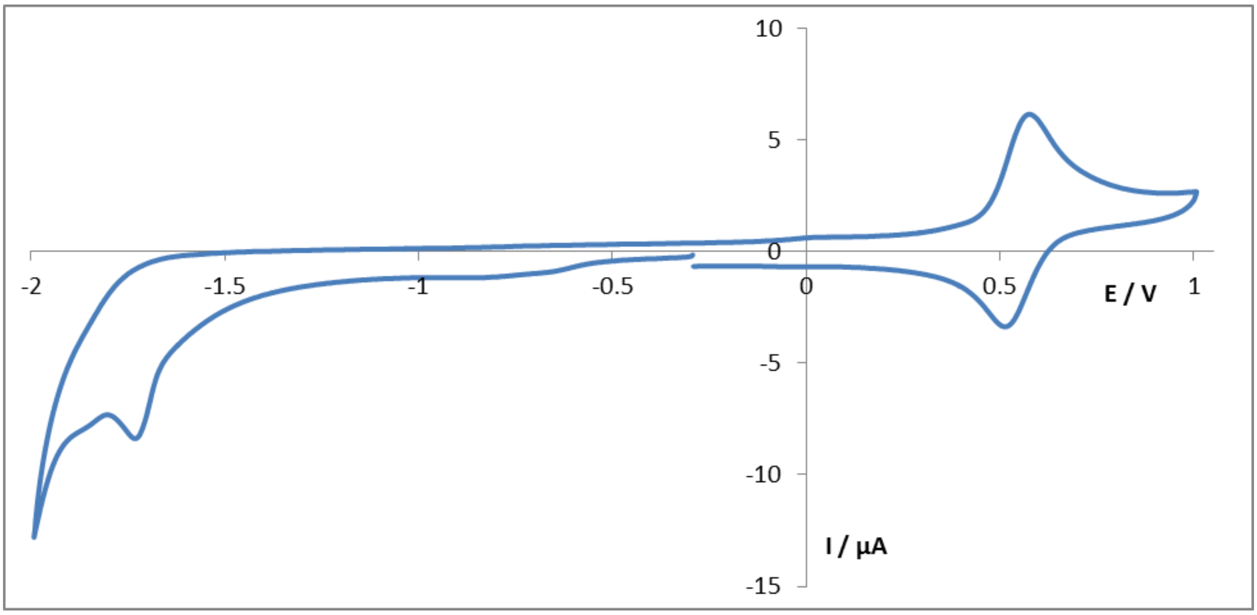


Figure 29 Cyclic voltammogram in DMF of **6b** (~0.25 × 10^{-3} M), 0.1 M Bu_4NPF_6, 100 mVs^{-1}, referenced to $[Fc^*]^{+/0}$ = 0.00 V.

4.2 Experimental

Cyclic voltammetric experiments in DMF were performed at 20°C on solutions degassed with argon. A three-electrode cell was used with Cypress Systems 1.4 mm diameter glassy carbon working, Ag/AgCl reference and platinum wire auxiliary electrodes. The solution was ~10^{-3} M in electroactive material and contained 0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte. Voltammograms were recorded with the aid of a Powerlab/4sp computer-controlled potentiostat. Potentials are referenced to the reversible formal potential (taken as *E*° = 0.00V) for the decamethylferricenium/decamethylferrocene ($[Fc^*]^{+/0}$) process,[7] where *E*° was calculated from the average of the oxidation and reduction peak potentials under conditions of cyclic voltammetry. Under the same conditions, *E*° measured for $[FcH]^{+/0}$ was 0.51 V.[8]

5 References

[1] E. A. Krasnokutskaya, N. I. Semenischeva, V. D. Filimonov, P. Knochel, *Synthesis* **2007**, 81.
[2] C. M. Amb, S. C. Rasmussen, *J. Org. Chem.* **2006**, *71*, 4696.
[3] J. W. Daly, W. L. Padgett, M. T. Shamim, *J. Med. Chem.* **1986**, *29*, 1305.
[4] T. M. McPhillips, S. E. McPhillips, H.-J. Chiu, A. E. Cohen, A. M. Deacon, P. J. Ellis, E. Garman, A. Gonzalez, N. K. Sauter, R. P. Phizackerley, S. M. Soltis, P. Kuhn, *Journal of Synchrotron Radiation* **2002**, *9*, 401.
[5] a)D. Schweinfurth, R. Pattacini, S. Strobel, B. Sarkar, *Dalton Trans.* **2009**, 9291; b)D. Schweinfurth, S. Strobel, B. Sarkar, *Inorg. Chim. Acta* **2011**, *374*, 253.
[6] a)K. J. Kilpin, E. L. Gavey, C. J. McAdam, C. B. Anderson, S. J. Lind, C. C. Keep, K. C. Gordon, J. D. Crowley, *Inorganic Chemistry* **2011**, *50*, 6334; b)C. Ornelas, J. Ruiz Aranzaes, E. Cloutet, S. Alves, D. Astruc, *Angewandte Chemie International Edition* **2007**, *46*, 872; c)M. Verschoor-Kirss, J. Kreisz, W. Feighery, W. M. Reiff, C. M. Frommen, R. U. Kirss, *Journal of Organometallic Chemistry* **2009**, *694*, 3262.
[7] I. Noviandri, K. N. Brown, D. S. Fleming, P. T. Gulyas, P. A. Lay, A. F. Masters, L. Phillips, *Journal of Physical Chemistry B* **1999**, *103*, 6713.
[8] F. Barriere, W. E. Geiger, *Journal of the American Chemical Society* **2006**, *128*, 3980.