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Supporting Information

‘Click’ to Functionalise: Synthesis, Characterisation and Enhancement of the Physical Properties of a Series of *Exo*- and *Endo*-Functionalised Pd_2L_4 Nanocages

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Contents

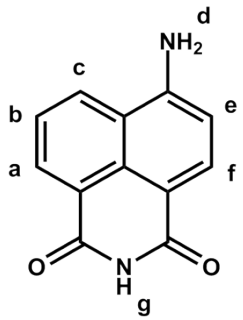
1 Synthesis

1.1 General

Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. 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. For organic samples sufficiently acceptable data were obtained through injection of room temperature samples with nebuliser gas temperature set to 180 °C. Due to the instability of the palladium complexes under these conditions it was necessary to reduce the nebuliser gas temperature to 100 °C and employ a pseudo-cold stream injection method by cooling the sample in an ice bath. UV-visible absorption spectra were acquired with a Jasco V550 UV/VIS 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 4-amino-1,8-naphthalimide



4-Amino-1,8-naphthalic anhydride (0.32 g, 1.52 mmol) was stirred in 35% ammonium hydroxide solution (25 mL) at 70 °C for 2.5 h. The product was filtered off as a brown precipitate and washed with H_2O (5 mL), acetone (2 mL) and diethyl ether (2 mL) before drying *in vacuo*. Yield 0.29 g (1.37

mmol, 90%). M.p. >230 °C. ^{1}H NMR (400 MHz, d_6-DMSO, 298 K) δ: 11.19 (s, 1H, H_g), 8.60 (d, J = 8.4 Hz, 1H, H_a), 8.37 (d, J = 8.2 Hz, 1H, H_c), 8.13 (d, J = 8.3 Hz, 1H, H_f), 7.63 (t, J = 7.9 Hz, 1H, H_b), 7.38 (s, 2H, H_d), 6.83 (d, J = 8.4 Hz, 1H, H_e). ^{13}C NMR (100 MHz, d_6-DMSO, 298 K) δ: 164.5, 163.7, 152.6, 133.1 (C_f), 131.0 (C_c), 130.2, 129.3 (C_a), 123.9 (C_b), 122.4 (C_d), 119.7, 108.1 (C_e), 107.9. IR (ATR): ν (cm^{-1}) 3438, 3329, 3207, 3139, 3011, 2820, 1664, 1628, 1562, 1525, 1479, 1372, 1267, 1219, 1136, 841, 769, 751, 701, 505, 442. HRESI-MS (DMF/MeOH): m/z = 235.0488 $[MNa]^+$ calc. 235.0478, 447.1081 $[M_2Na]^+$ calc. 447.1069, 463.0829 $[M_2K]^+$ calc. 463.0803.

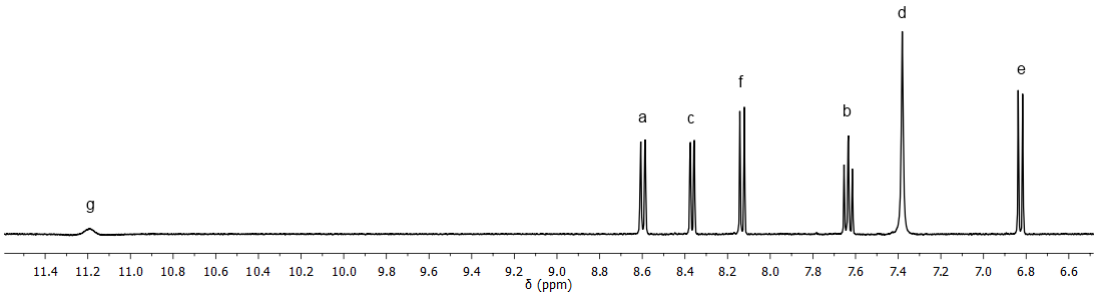


Figure 1 ^{1}H NMR spectrum (400 MHz, d_6-DMSO, 298 K) of 4-amino-1,8-naphthalimide.

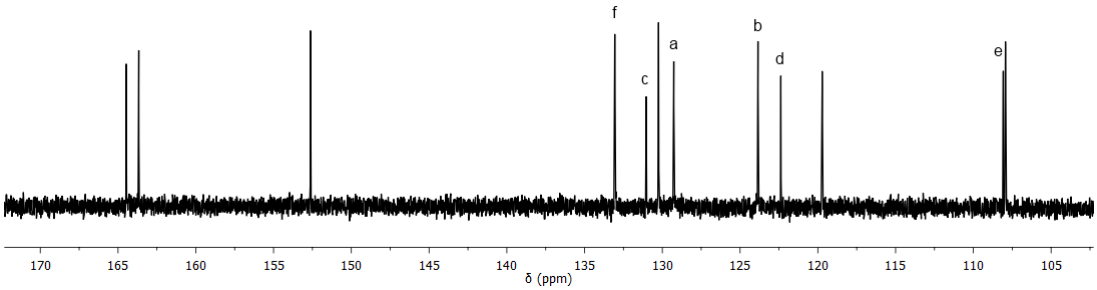
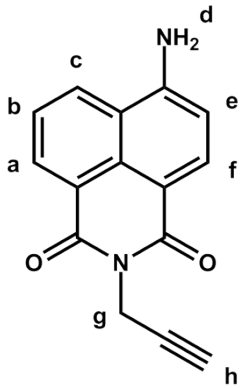


Figure 2 ^{13}C NMR spectrum (100 MHz, d_6-DMSO, 298 K) of 4-amino-1,8-naphthalimide.

1.3 Synthesis of *N*-propargyl-4-amino-1,8-naphthalimide



A RBF was charged with 4-amino-1,8-naphthalimide (0.29 g, 1.37 mmol, 1 eq.) and potassium tert-butoxide (0.15 g, 1.37 mmol, 1 eq.) and purged with N_2. DMF (5 mL) was added via syringe and the reaction stirred at room temperature for 10 minutes. Propargyl bromide (0.23 mL of 80% solution in toluene, 2.05 mmol, 1.5 eq.) was subsequently added via syringe and the reaction stirred for a further 30 minutes before adding to ice water (200 mL), precipitating the product as a yellow solid. Once all the ice had melted the product was isolated by filtration, washed with H_2O (3 × 10 mL), acetone (5 mL) and diethyl ether (2 × 5 mL) and dried *in vacuo*. Yield 0.29 g (1.15 mmol, 84%). M.p. >230 °C. ^{1}H NMR (400 MHz, d_6-DMSO, 298 K) δ: 8.64 (d, J = 8.3 Hz, 1H, H_a), 8.45 (d, J = 7.2 Hz, 1H, H_c), 8.21 (d, J = 8.4 Hz, 1H, H_f), 7.66 (t, J = 7.8 Hz, 1H, H_b), 7.53 (s, 2H, H_d), 6.86 (d, J = 8.4 Hz, 1H, H_e), 4.74 (d, J = 2.2 Hz, 2H, H_g), 3.07 (t, J = 2.2 Hz, 1H, H_h). ^{13}C NMR (100 MHz, d_6-DMSO, 298 K) δ: 163.1, 162.0, 153.1, 134.2 (C_f), 131.3 (C_c), 129.7, 129.7 (C_a), 124.0 (C_b), 121.4 (C_d), 119.4, 108.3 (C_e), 107.0, 80.0, 72.4, 28.6 (C_g). IR (ATR): ν (cm^{-1}) 3503, 3415, 3350, 3238, 1673, 1564, 1530, 1477, 1397, 1369, 1336, 1306, 1247, 1106, 937, 772, 756, 702, 678, 646. HRESI-MS (DMF/MeOH): m/z = 273.0624 $[MNa]^+$ calc. 273.0634.

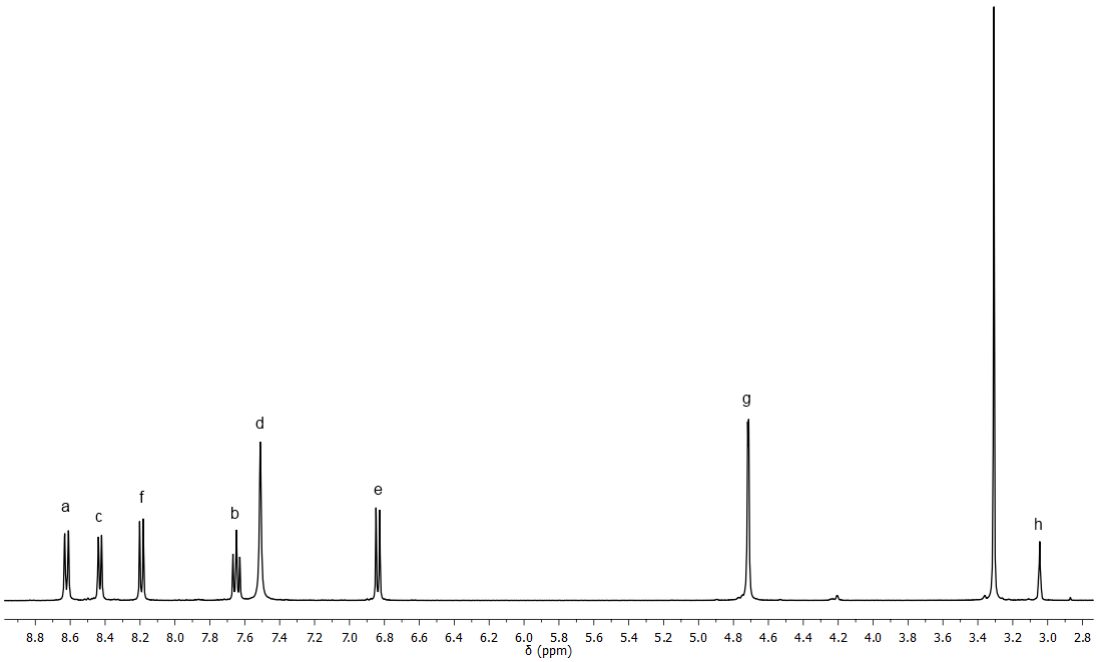


Figure 3 ^{1}H NMR spectrum (400 MHz, d_6-DMSO, 298 K) of N-propargyl-4-amino-1,8-naphthalimide.

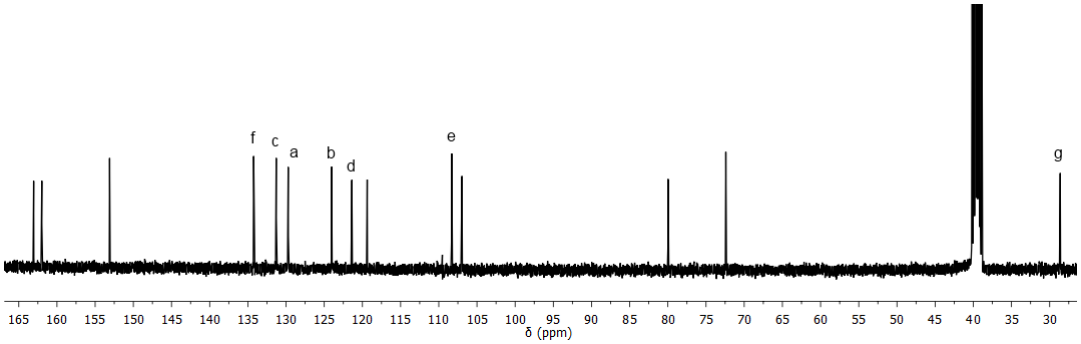
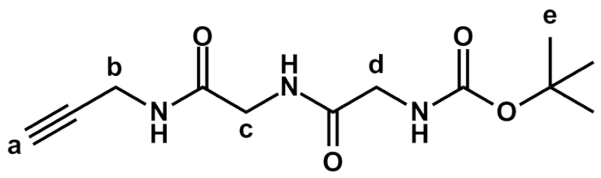


Figure 4 ^{13}C NMR spectrum (100 MHz, d_6-DMSO, 298 K) of N-propargyl-4-amino-1,8-naphthalimide.

1.4 Synthesis of *tert*-butyl(2-oxo-2-((2-oxo-2-(prop-2-yn-1-ylamino)ethyl)amino)ethyl)carbamate



A RBF was charged with *N*-Boc-GlyGly (0.20 g, 0.86 mmol, 1 eq.), DMAP (0.01 g, 0.09 mmol, 0.1 eq.) and DCC (0.19 g, 0.90 mmol, 1.05 eq.) and purged with N_2. DCM (4 mL) and propargyl amide (0.12 mL, 1.72 mmol, 2 eq.) were added via syringe. After stirring at RT for 20 h, the reaction mixture was filtered through a sintered funnel. The filtrate was taken to dryness *in vacuo* to give a yellow solid. After purification by column chromatography on silica deactivated with triethylamine (1:19 MeOH/$CHCl_3$) the pure product was obtained as an off-white solid. Yield 0.11 g (0.42 mmol, 48%). M.P. 117-119 °C. ^{1}H NMR (400 MHz, d_6-DMSO, 298 K) δ: 8.22 (t, J = 5.4 Hz, 1H, H_{NH}), 8.05 (t, J = 5.6 Hz, 1H, H_{NH}), 7.00 (t, J = 5.8 Hz, 1H, H_{NH}), 3.86 (dd, J = 2.5, 5.6 Hz, 2H, H_b), 3.69 (d, J = 5.9 Hz, 2H), 3.57 (d, J = 6.1 Hz, 2H), 3.10 (t, J = 2.5 Hz, 1H, H_a), 1.39 (s, 9H, H_e). ^{13}C NMR (100 MHz, d_6-DMSO, 298 K) δ: 169.7, 168.6, 155.8, 80.9, 78.2, 73.0, 43.3, 41.8, 28.2 (C_e), 27.8 (C_b). IR (ATR): ν (cm^{-1}) 3307, 3292, 3069, 2981, 2932, 2921, 2853, 1704, 1678, 1650, 1555, 1526, 1416, 1365, 1279, 1243, 1178, 1030, 948. HRESI-MS (DCM): m/z = 170.0895 $[M\text{-}CO_2C(CH_3)_3+H_2]^+$ calc. 170.0924, 214.0788 $[M\text{-}C(CH_3)_3+H_2]^+$ calc. 214.0822, 270.1397 $[MH]^+$ calc. 270.1448, 292.1221 $[MNa]^+$ calc. 292.1268, 561.2581 $[M_2Na]^+$ calc. 561.2643, 830.3949 $[M_3Na]^+$ calc. 830.4019.

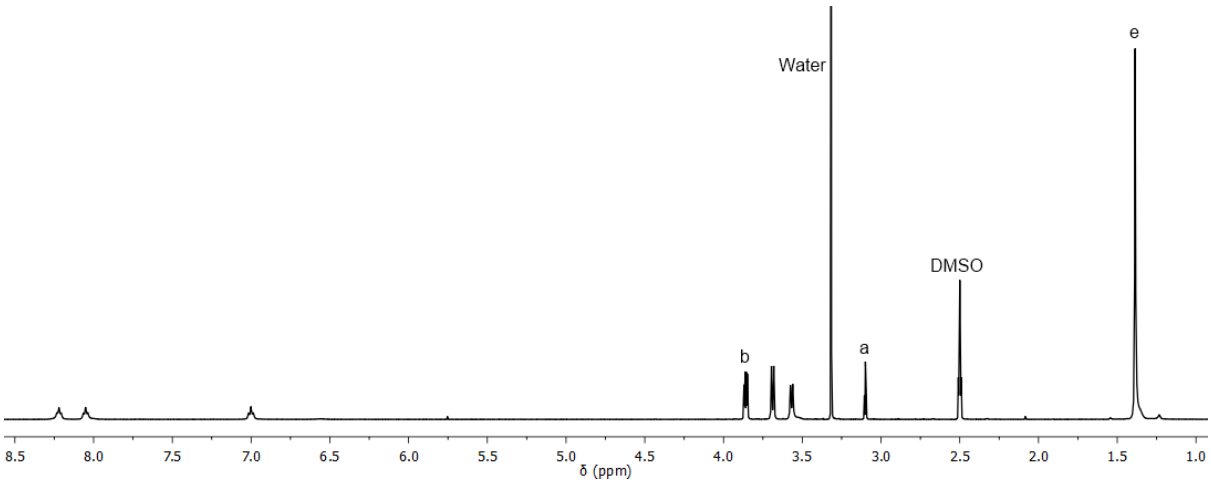


Figure 5 ^{1}H NMR spectrum (400 MHz, d_6-DMSO, 298 K) of *tert*-butyl(2-oxo-2-((2-oxo-2-(prop-2-yn-1-ylamino)ethyl)amino)ethyl)carbamate.

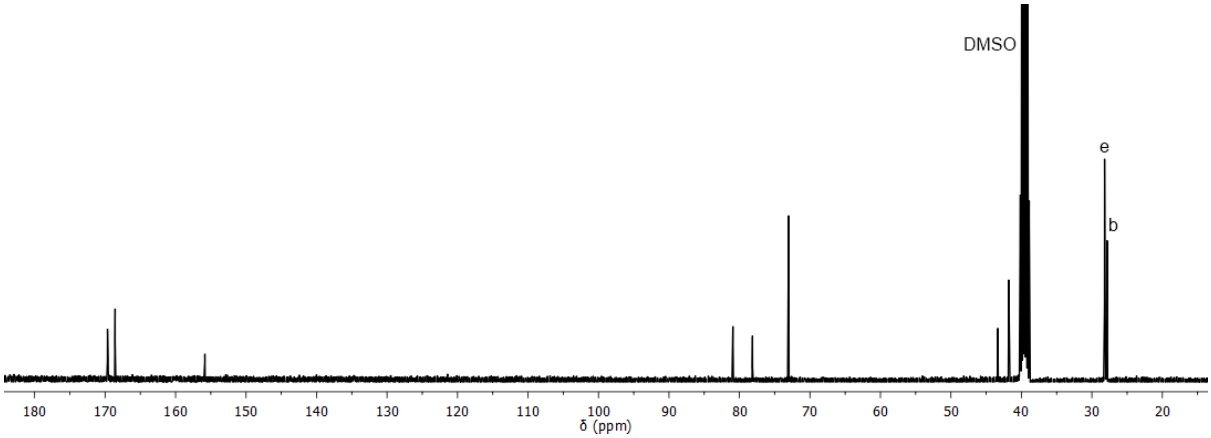
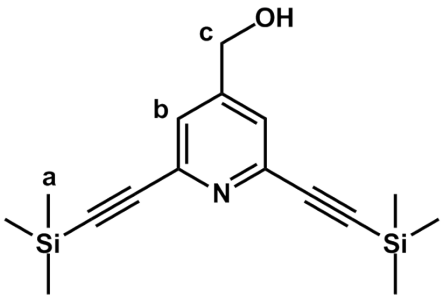


Figure 6 ^{13}C NMR spectrum (100 MHz, d_6-DMSO, 298 K) of *tert*-butyl(2-oxo-2-((2-oxo-2-(prop-2-yn-1-ylamino)ethyl)amino)ethyl)carbamate.

1.5 Synthesis of 2,6-bis((trimethylsiliyl)ethynyl)pyridin-4-yl-methanol



A dry RBF was charged with (2,6-dibromopyridin-4-yl)methanol (3.00 g, 11.24 mmol, 1 eq.), $[Pd(PPh_3)_2Cl_2]$ (0.16 g, 0.23 mmol, 0.02 eq.) and CuI (0.21 g, 1.12 mmol, 0.1 eq.) and purged with N_2. THF (dry, 20 mL) and triethylamine (dry, 20 mL) were added via syringe. TMS-acetylene (4.8 mL, 33.70 mmol, 3 eq.) was subsequently added dropwise via syringe. The reaction was stirred at room temperature in the absence of light for 48 h. 0.1 M EDTA/$NH_4OH_{(aq)}$ (40 mL) was added. After stirring for 30 minutes H_2O (50 mL) was added and the reaction extracted with DCM (3 × 100 mL). The organic layer was washed with brine (50 mL) and H_2O (50 mL), dried ($MgSO_4$), filtered, and the solvent removed in vacuo. The product was purified by column chromatography on silica, eluting with 1:1 petroleum ether/DCM, and obtained as an off-white solid. Yield 2.54 g (8.43 mmol, 75%). M.P. 108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.34 (s, 2H, H_b), 4.68 (d, J = 3.7 Hz, 2H, H_c), 3.84 (s, 1H, H_{OH}), 0.22 (s, 18H, H_a). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 151.8, 143.0, 124.2 (C_b), 103.1, 95.6, 62.5 (C_c), -0.2 (C_a). IR (ATR): ν (cm^{-1}) 3286, 2956, 2898, 2159, 1595, 1550, 1453, 1404, 1247, 1199, 1143, 1079, 991, 953, 836, 759. HRESI-MS (DCM): *m/z* = 302.1415 $[MH]^+$ calc. 302.1391, 324.1234 $[MNa]^+$ calc. 324.1210, 340.0941 $[MK]^+$ calc. 340.0950, 625.2523 $[M_2Na]^+$ calc. 625.2529.

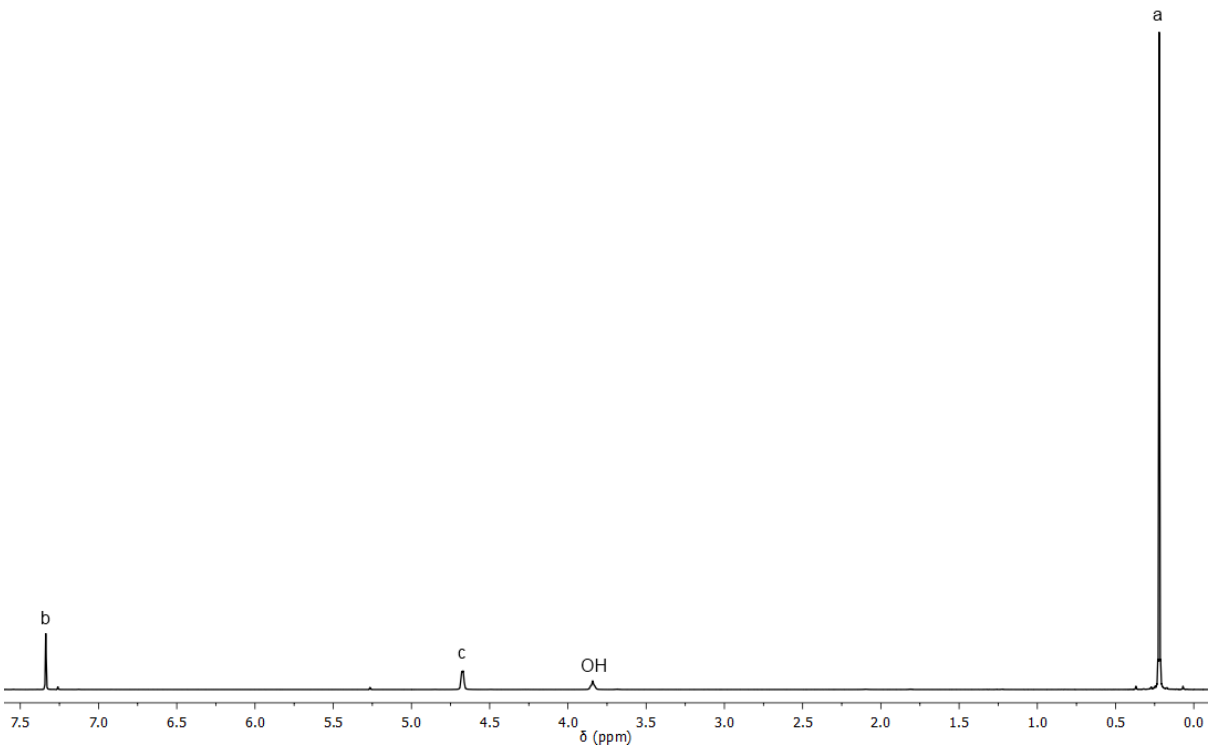


Figure 7 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of 2,6-bis((trimethylsiliyl)ethynyl)pyridin-4-yl-methanol.

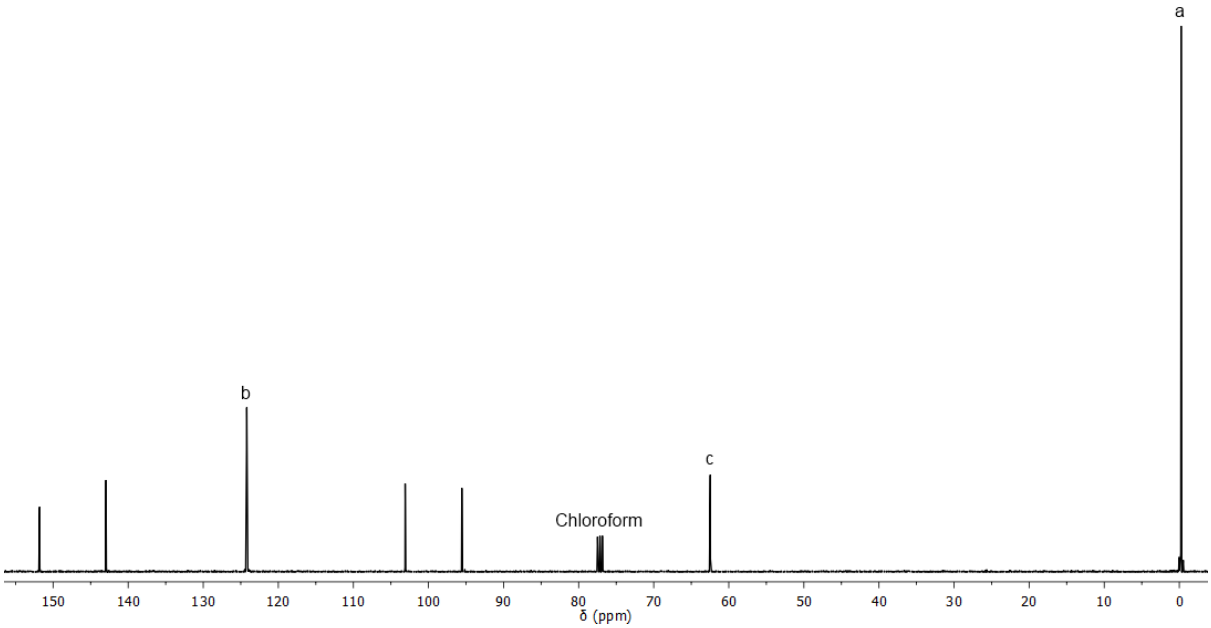
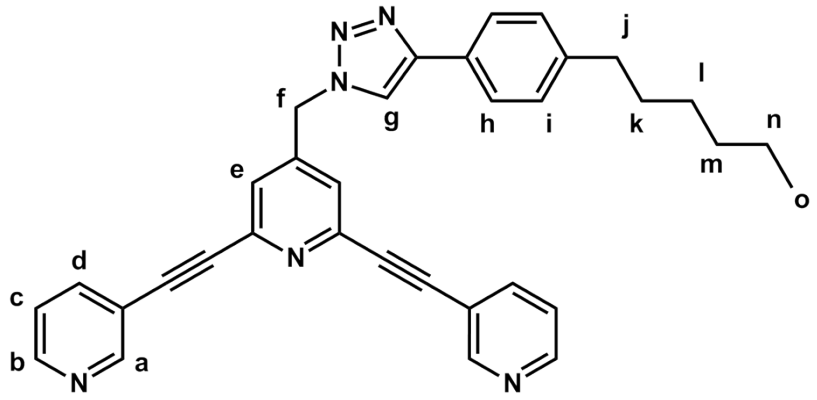


Figure 8 ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) spectrum of 2,6-bis((trimethylsiliyl)ethynyl)pyridin-4-yl-methanol.

1.6 Synthesis of 2 from 2,6-bis((trimethylsiliyl)ethynyl)pyridin-4-yl-methanol

A dry RBF was charged with 2,6-bis((trimethylsilyl)ethynyl)pyridin-4-yl)methanol (0.90 g, 2.98 mmol, 1 eq.), 3-iodopyridine (2.25 g, 10.98 mmol, 3.7 eq.), $[Pd(PPh_3)_2Cl_2]$ (0.06 g, 0.09 mmol, 0.03 eq.) and CuI (0.06 g, 0.30 mmol, 0.1 eq.) and purged with N_2. Toluene (dry, 15 mL), triethylamine (dry, 5 mL) and DBU (2.7 mL, 17.93 mmol, 6.0 eq) were added via syringe. Under a flow of N_2, H_2O (0.04 mL, 2.39 mmol, 0.8 eq.) was added. The reaction mixture was stirred in the absence of light under N_2 for 24 h. 0.1 M EDTA/$NH_4OH_{(aq)}$ (20 mL) was added and the reaction stirred for 30 minutes before filtering through filter paper and flushing through with DCM (100 mL). The organic layer was isolated and washed with brine (50 mL) and H_2O (50 mL), dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The pure product was obtained as a light yellow solid following column chromatography on silica, eluting with 2:3 acetone/DCM (R_f = 0.21). Yield 0.70 g (2.25 mmol, 75%).

1.7 Synthesis of 5d



To a stirring solution of **4** (50 mg, 0.15 mmol, 1 eq.), $CuSO_4 \cdot 5H_2O$ (19 mg, 0.07 mmol, 0.5 eq.) and sodium ascorbate (29 mg, 0.15 mmol, 1 eq.) in DMF (5 mL) was added 1-ethynyl-4-hexylbenzene (40 µL, 0.19 mmol, 1.3 eq.). After stirring at room temperature for 16 h the reaction mixture was added to 0.1 M EDTA/$NH_4OH_{(aq)}$ (5 mL) and stirred for 3 h, resulting in a white precipitate. The volume was made up to 100 mL with water and the precipitate isolated by filtration. The solid was subsequently taken up in 1:3 ^{i}PrOH/DCM (100 mL) and the solvent removed *in vacuo* to give the crude product. Purification by column chromatography on silica (2:3 acetone/DCM) gave the pure product as a white solid. Yield 74 mg (0.14 mmol, 95%). M.P. 140-142 °C. ^{1}H NMR (500 MHz, d_6-DMSO, 298 K) δ: 8.83 (dd, J = 0.9, 2.2 Hz, 2H, H_a), 8.67 (s, 1H, H_g), 8.66 (dd, J = 2.0, 4.9 Hz, 2H, H_b), 8.07 (ddd, J = 1.7, 2.1, 7.9 Hz, 2H, H_d), 7.77 (d, J = 8.3 Hz, 2H, H_h), 7.64 (s, 2H, H_e), 7.51 (ddd, J = 0.9, 4.9, 7.9 Hz, 2H, H_c), 7.27 (d, J = 8.4 Hz, 2H, H_i), 5.80 (s, 2H, H_f), 2.59 (t, J = 7.6 Hz, 2H, H_j), 1.60-1.54 (m, 2H, H_k), 1.31-1.22 (m, 6H, H_l, H_m, H_n), 0.85 (t, J = 7.0 Hz, 3H, H_o). Diffusion coefficient (d_6-DMSO, 298 K) D: 1.78×10^{-10} m^2s^{-1}. ^{13}C NMR (125 MHz, d_6-DMSO, 298 K) δ: 152.0 (C_a), 149.9 (C_b), 146.9, 146.7, 142.7, 142.3, 139.1 (C_d), 128.8 (C_i), 127.9, 125.9 (C_e), 125.2 (C_h), 123.7 (C_c), 121.8 (C_g), 118.1, 90.5, 86.3, 51.0 (C_f), 34.9 (C_j), 31.1, 30.8 (C_k), 28.2, 22.0, 13.9 (C_o). IR (ATR): ν (cm^{-1}) 3081, 3044, 2954, 2921, 2851, 2215, 1593, 1549, 1476, 1457, 1418, 1225, 1208, 1189, 1048, 1022, 807, 702. HRESI-MS (DCM): *m/z* = 523.2561 $[LH]^+$ calc. 523.2605; 545.2412 $[LNa]^+$ calc. 545.2424. UV-Vis (DMSO, ε [$M^{-1}cm^{-1}$]): λ_{max} nm = 320 (2.80×10^4).

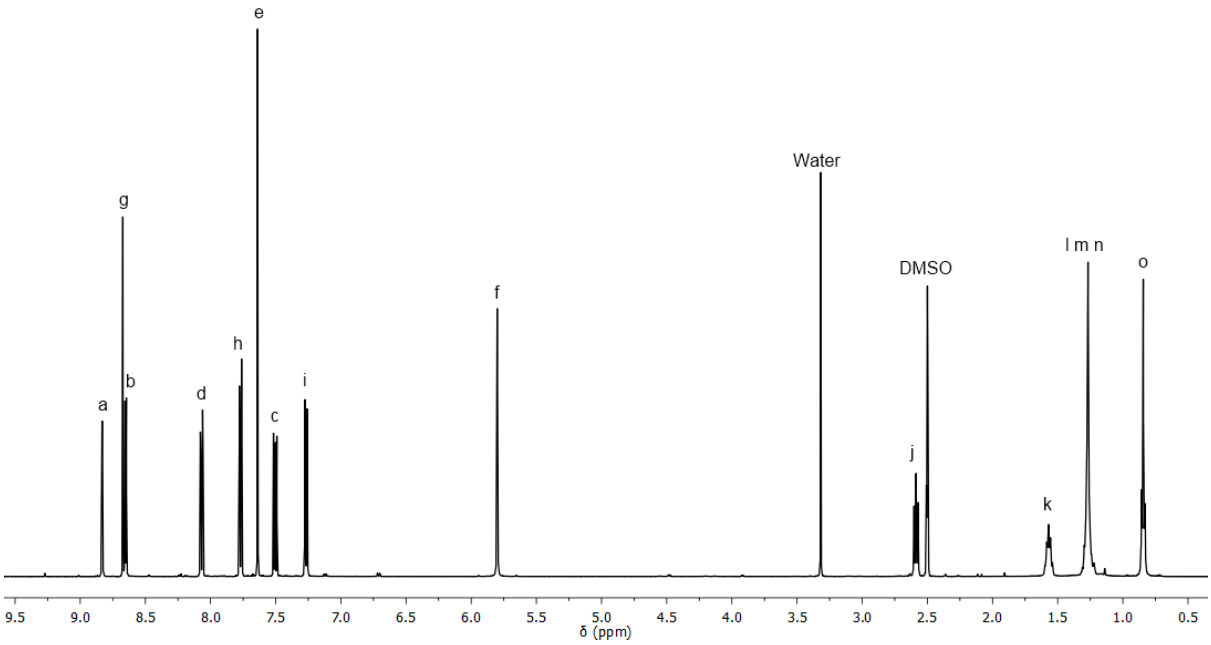


Figure 9 ^{1}H NMR spectrum (500 MHz, d_6-DMSO, 298 K) of **5d**.

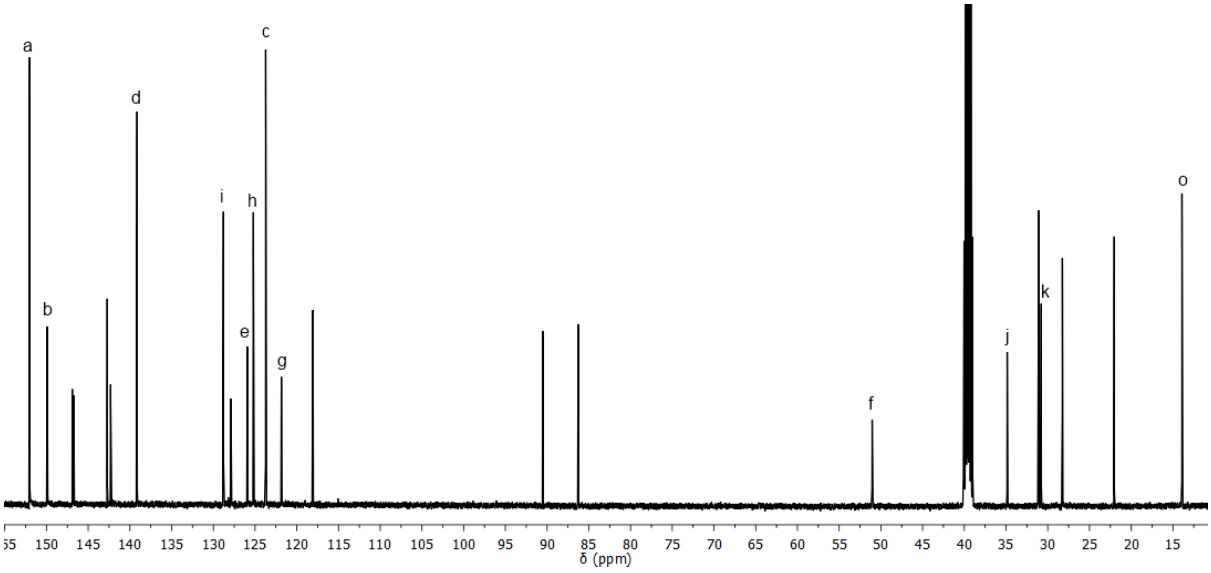
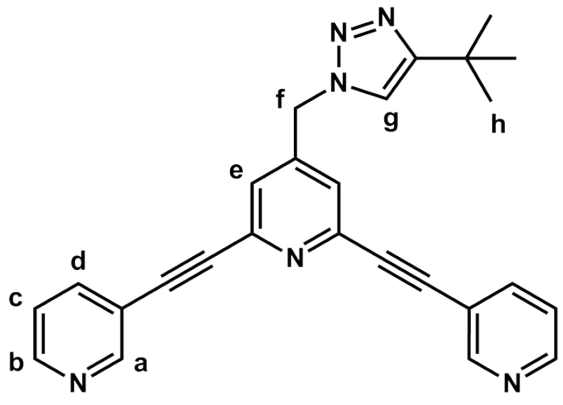


Figure 10 ^{13}C NMR spectrum (125 MHz, d_6-DMSO, 298 K) of **5d**.

1.8 Synthesis of 5e



To a stirring solution of **4** (95 mg, 0.28 mmol, 1 eq.), $CuSO_4 \cdot 5H_2O$ (35 mg, 0.14 mmol, 0.5 eq.) and sodium ascorbate (56 mg, 0.28 mmol, 1 eq.) in DMF (10 mL) was added 3,3'-dimethyl-1-butyne (174 µL, 1.41 mmol, 5 eq.). After stirring at room temperature for 36 h the reaction mixture was added to 0.1 M EDTA/$NH_4OH_{(aq)}$ (25 mL) and stirred for 1 h. After making up to 100 mL with water, the resulting precipitate was isolated by filtration, taken up in 1:3 ^{i}PrOH/DCM (100 mL), dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to give the crude product as a white solid. Purified by column chromatography on silica (2:3 acetone/DCM). Yield 114 mg (0.27 mmol, 97%). M.P. 170-172 °C. ^{1}H NMR (400 MHz, d_6-DMSO, 298 K) δ: 8.84 (s, 2H, H_a), 8.67 (s, 2H, H_b), 8.07 (d, J = 7.9 Hz, 2H, H_d), 8.03 (s, 1H, H_g), 7.60 (s, 2H, H_e), 7.52 (dd, J = 4.9, 7.9 Hz, 2H, H_c), 5.67 (s, 2H, H_f), 1.29 (s, 9H, H_h). Diffusion coefficient (d_6-DMSO, 298 K) D: 2.08 × 10^{-10} m^2s^{-1}. ^{13}C NMR (100 MHz, d_6-DMSO, 298 K) δ: 156.8, 152.0 (C_a), 149.9 (C_b), 146.9, 142.7, 139.1 (C_d), 126.1 (C_e), 123.8 (C_c), 120.6 (C_g), 118.1, 90.5, 86.3, 50.7 (C_f), 30.5, 30.2 (C_h). IR (ATR): ν (cm^{-1}) 3128, 3036, 2961, 2868, 2220, 1600, 1548, 1476, 1460, 1425, 1413, 1218, 1189, 1110, 1045, 1021, 805, 699. HRESI-MS (DCM): *m/z* = 419.1986 $[LH]^+$ calc. 419.1979; 441.1816 $[LNa]^+$ calc. 441.1798; 859.3729 $[L_2Na]^+$ calc. 859.3704. UV-Vis (DMSO, ε [$M^{-1}cm^{-1}$]): λ_{max} nm = 319 (2.53 × 10^4).

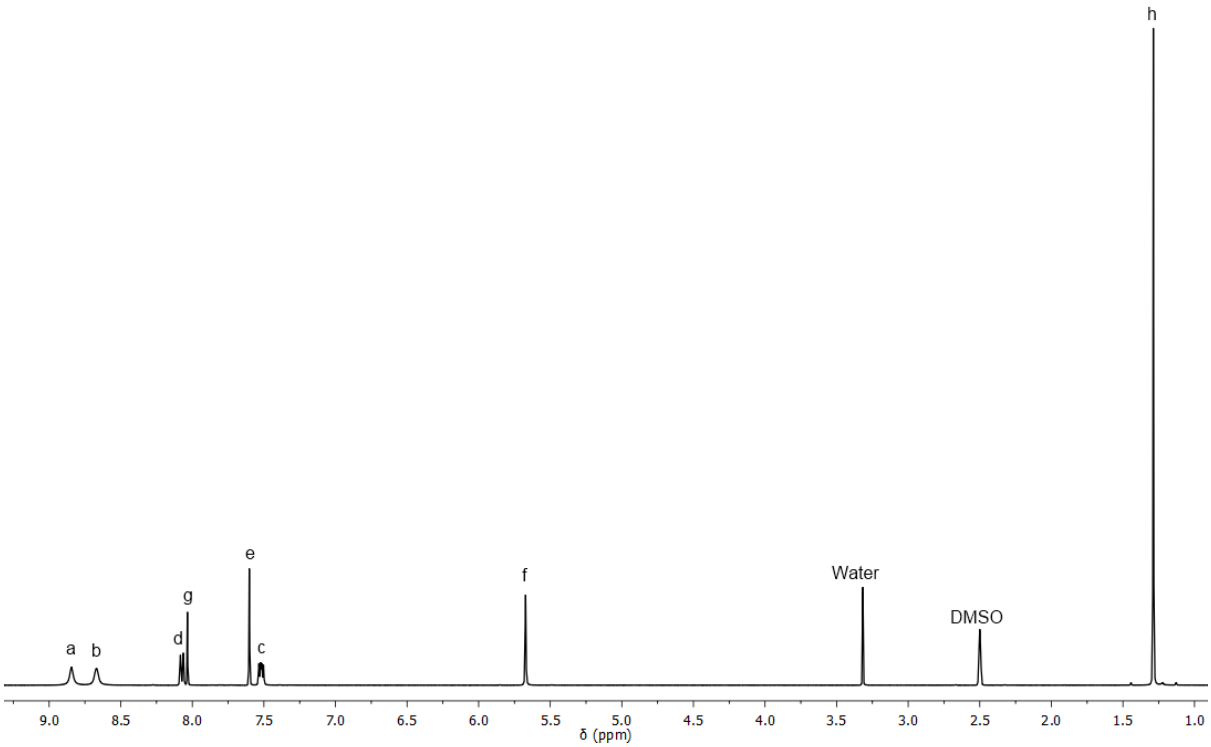


Figure 11 ^{1}H NMR spectrum (400 MHz, d_6-DMSO, 298 K) of **5e**.

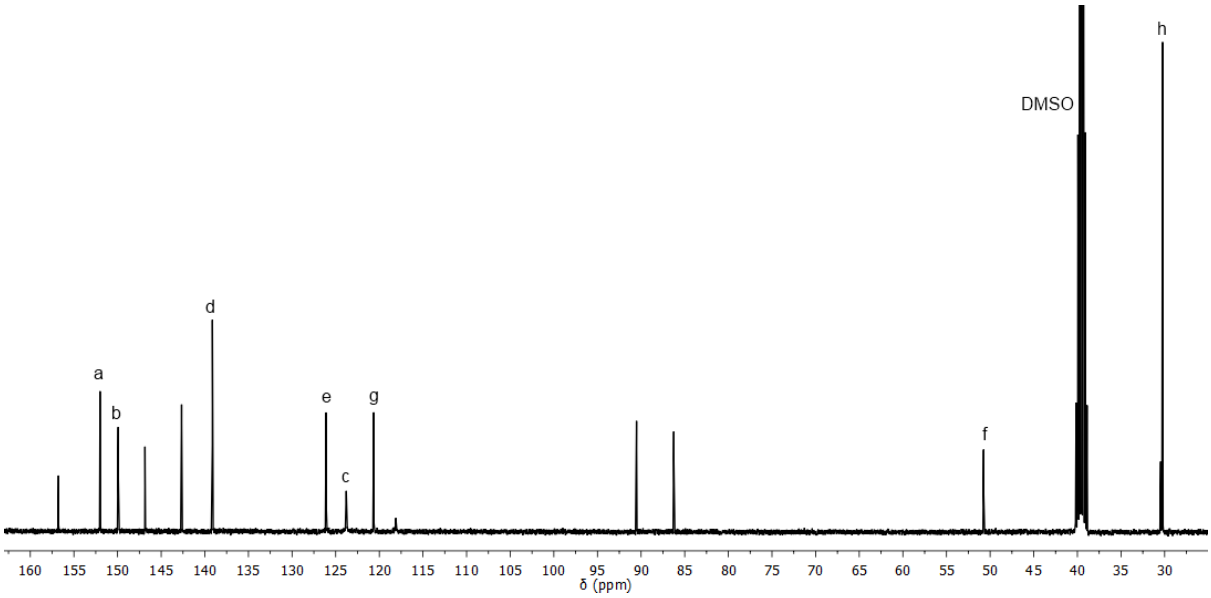
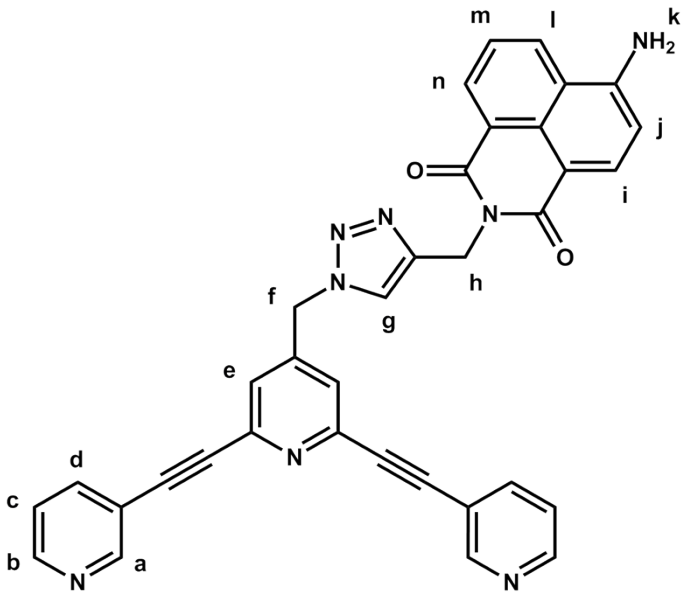


Figure 12 ^{13}C NMR spectrum (100 MHz, d_6-DMSO, 298 K) of **5e**.

1.9 Synthesis of 5f



To a stirring solution of **4** (121 mg, 0.36 mmol, 1 eq.), $CuSO_4 \cdot 5H_2O$ (45 mg, 0.18 mmol, 0.5 eq.) and sodium ascorbate (72 mg, 0.36 mmol, 1 eq.) in 1:4 H_2O/DMF (5 mL) was added *N*-propargyl-4-amino-1,8-naphthalimide (109 mg, 0.44 mmol, 1.2 eq). The reaction was stirred at room temperature for 16 h before adding to 0.1 M EDTA/$NH_4OH_{(aq)}$ (20 mL) and making up to a volume of 100 mL with H_2O. After stirring for 2 h a yellow precipitate was filtered off and washed with H_2O (3 × 20 mL), acetone (5 mL) and diethyl ether (2 × 5 mL). This precipitate was then dry loaded onto a silica column. After eluting with 1:9 acetone/DCM to remove impurities, the product was eluted with 1:9 MeOH/DCM (R_f = 0.35). After removing solvent *in vacuo* the pure product was obtained as a bright yellow powder. Yield 144 mg (0.25 mmol, 68%). M.p. >230 °C. ^{1}H NMR (400 MHz, d_6-DMSO, 298 K) δ: 8.82 (d, J = 1.3 Hz, 2H, H_a), 8.66 (dd, J = 1.3, 4.8 Hz, 2H, H_b), 8.62 (d, J = 8.5 Hz, 1H, H_n), 8.43 (d, J = 7.2 Hz, 1H, H_l), 8.21-8.18 (m, 2H, H_g, H_i), 8.05 (dt, J = 1.8, 8.0 Hz, 2H, H_d), 7.63 (t, J = 7.9 Hz, 1H, H_m), 7.53-7.48(m, 6H, H_c, H_e, H_k), 6.83 (d, J = 8.4 Hz, 1H, H_j), 5.67 (s, 2H, H_f), 5.30 (s, 2H, H_h). Diffusion coefficient (d_6-DMSO, 298 K) D: 1.53 × 10^{-10} m^2s^{-1}. ^{13}C NMR (125 MHz, d_6-DMSO, 298 K) δ: 163.6, 162.6, 152.9, 152.0 (C_a), 149.9 (C_b), 146.8, 144.1, 142.6, 139.1 (C_d), 134.1, 131.2 (C_l), 129.8, 129.5 (C_n), 125.9 (C_e), 124.2, 124.0 (C_m), 123.7 (C_c), 121.7, 119.4, 118.1, 108.2 (C_j), 107.3, 90.5, 86.2, 50.8 (C_f), 34.8 (C_h). IR (ATR): ν (cm^{-1}) 3343, 3195, 2220, 1661, 1635, 1575, 1547, 1417, 1375, 1363, 1306, 1293, 1239, 1119, 1047, 1022, 793, 774, 761, 700, 628. HRESI-MS (DMF/$CHCl_3$): *m/z* = 609.1731 $[MNa]^+$ calc. 609.1758. UV-Vis (DMSO, ε [$M^{-1}cm^{-1}$]): λ_{max} nm = 439 (1.37 × 10^4), 320 (2.87 × 10^4).

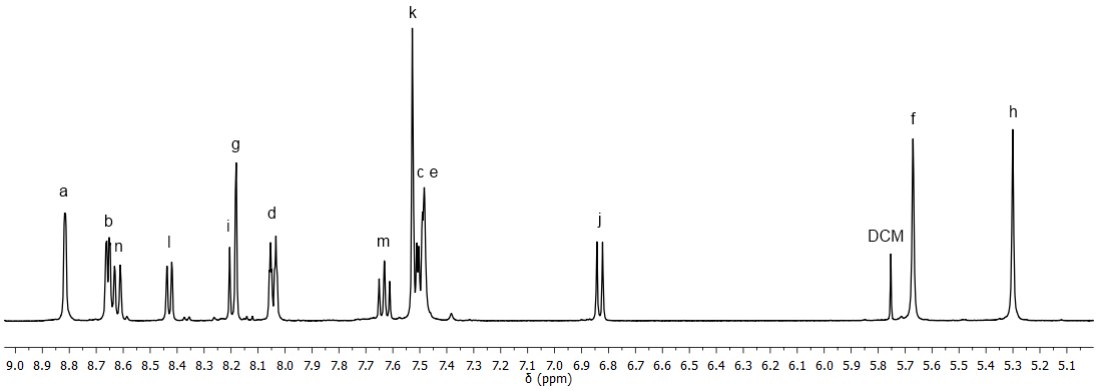


Figure 13 ^{1}H NMR spectrum (400 MHz, d_6-DMSO, 298 K) of **5f**.

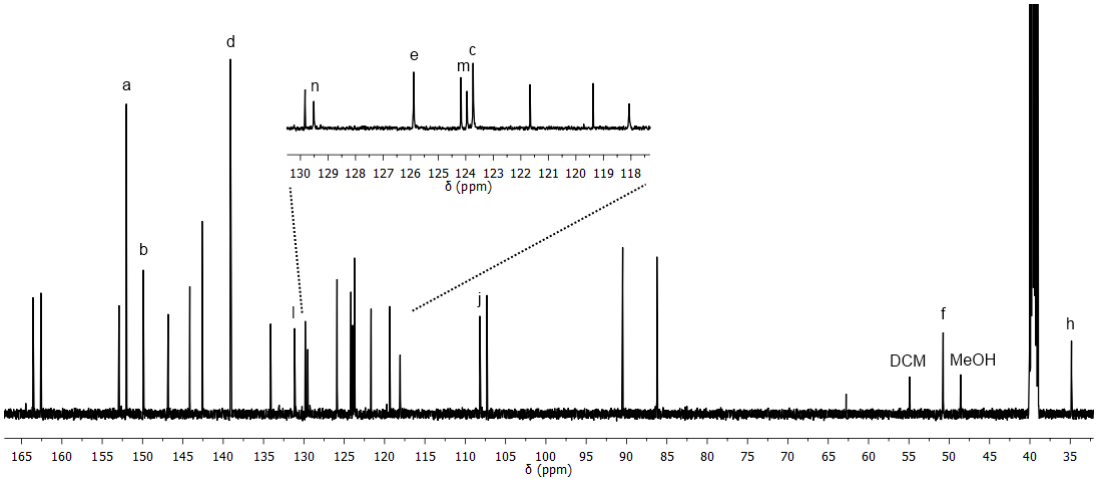
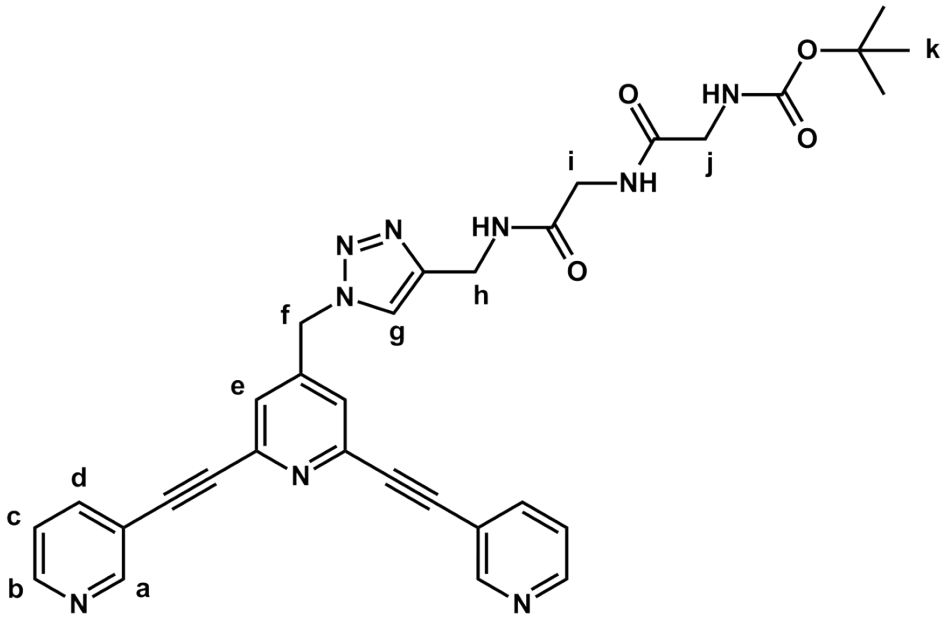


Figure 14 ^{13}C NMR spectrum (125 MHz, d_6-DMSO, 298 K) of **5f**.

1.10 Synthesis of 5g



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.) were stirred in DMF (5 mL). *tert*-Butyl(2-oxo-2-((2-oxo-2-(prop-2-yn-1-ylamino)ethyl)amino)ethyl)carbamate (80 mg, 0.30 mmol, 1 eq.) was added as a solid and the reaction mixture stirred at room temperature for 120 h. 0.1 M EDTA/$NH_4OH_{(aq)}$ (25 mL) was added and the mixture made up to a volume of 75 mL with H_2O. After stirring for 3 h the reaction mixture was extracted with ethyl acetate (4 × 50 mL). The combined organic layers were washed with water (6 × 50 mL), dried ($MgSO_4$), filtered and the solvent removed in vacuo to give the pure product as an off-white solid. Yield 139 mg (0.23 mmol, 77%). M.P. 178-180 °C. ^{1}H NMR (500 MHz, d_6-DMSO, 298 K) δ: 8.84 (d, J = 2.3 Hz, 2H, H_a), 8.67 (dd, J = 1.7, 4.9 Hz, 2H, H_b), 8.31 (t, J = 5.4, 1H, H_{NH}), 8.09-8.07 (m, 3H, H_g, H_d), 8.04 (t, J = 5.9, 1H, H_{NH}), 7.58 (s, 2H, H_e), 7.52 (ddd, J = 1.0, 4.9, 7.8 Hz, 2H, H_c), 7.00 (t, J = 6.0 Hz, 1H, H_{NH}), 5.73 (s, 2H, H_f), 4.35 (d, J = 5.8 Hz, 2H, H_h), 3.72 (d, J = 5.8 Hz, 2H), 3.57 (d, J = 6.0 Hz, 2H), 1.35 (s, 9H, H_k). Diffusion coefficient (d_6-DMSO, 298 K) D: 1.63 × 10^{-10} m^2s^{-1}. ^{13}C NMR (100 MHz, d_6-DMSO, 298 K) δ: 169.7, 168.8, 155.8, 152.0 (C_a), 149.9 (C_b), 146.8, 145.3, 142.7, 139.1 (C_d), 125.9 (C_e), 123.8 (C_g), 123.8 (C_c), 118.1, 90.5, 86.3, 78.1, 50.8 (C_f), 43.4, 42.0, 34.2 (C_h), 28.1 (C_k). IR (ATR): ν (cm^{-1}) 3346, 3247, 3133, 3055, 1681, 1662, 1545, 1513, 1420, 1406, 1279, 1248, 1162, 1061, 1025. HRESI-MS (DCM): *m/z* = 392.1616 $[MH_2\text{-}C_9H_{15}N_2O_4]^+$ calc. 392.1618; 506.2058 $[MH_2\text{-}C_5H_9O_2]^+$ calc. 506.2047; 606.2588 $[MH]^+$ calc. 606.2572; 628.2406 $[MNa]^+$ calc. 628.2391; 644.2157 $[MK]^+$ calc. 644.2131. UV-Vis (DMSO, ε [$M^{-1}cm^{-1}$]): λ_{max} nm = 319 (2.59 × 10^4).

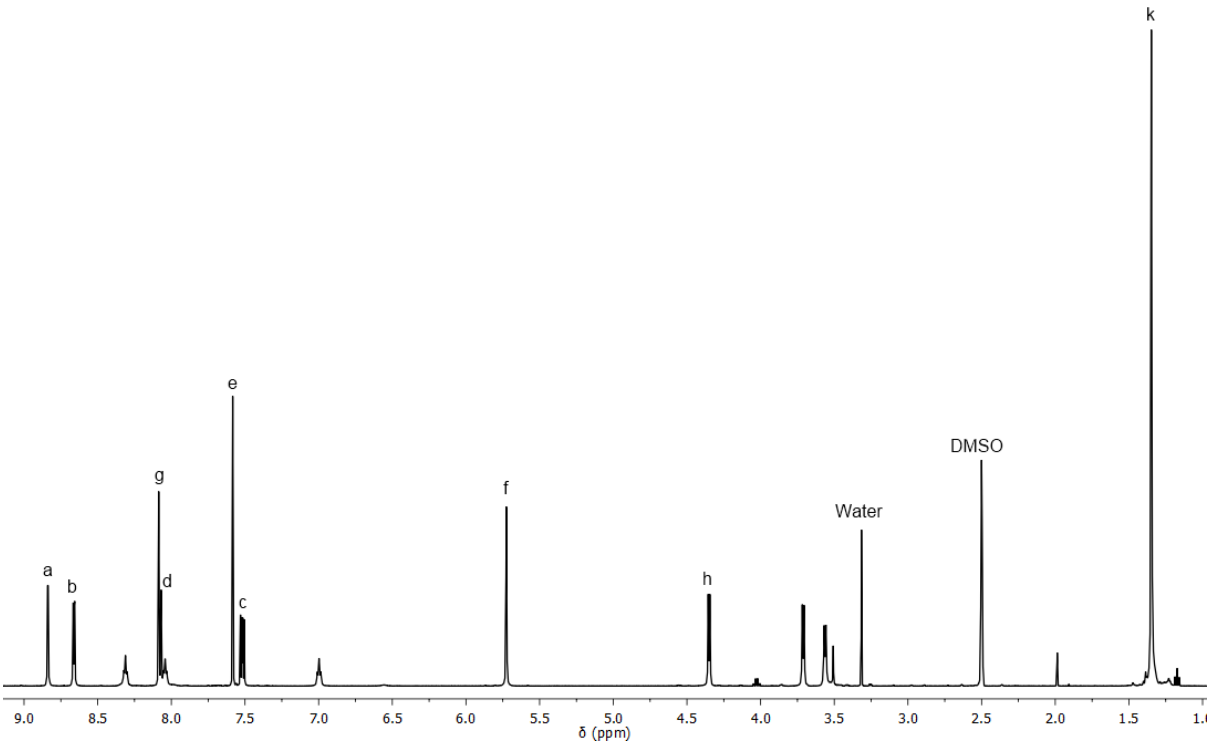


Figure 15 ^{1}H NMR spectrum (500 MHz, d_6-DMSO, 298 K) of **5g**.

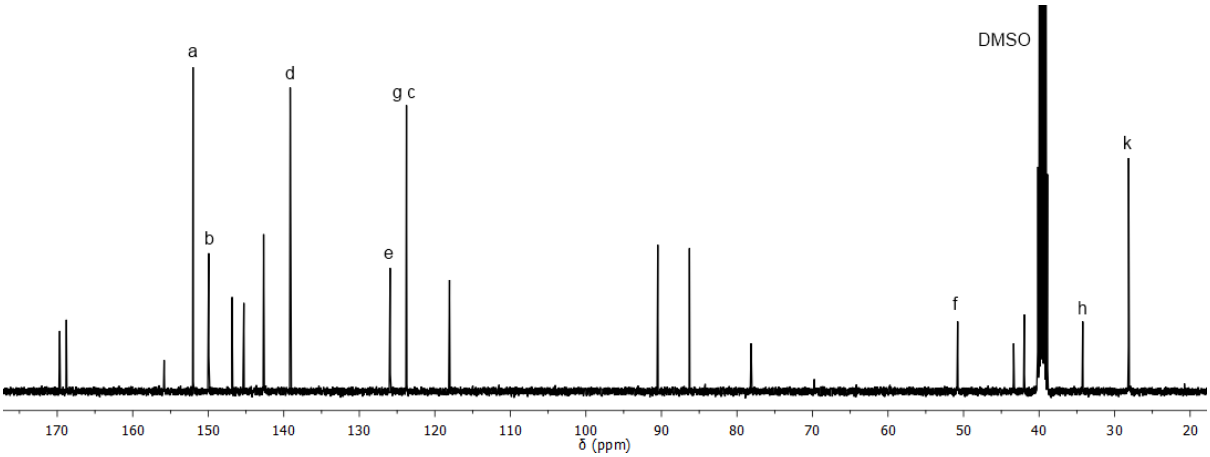
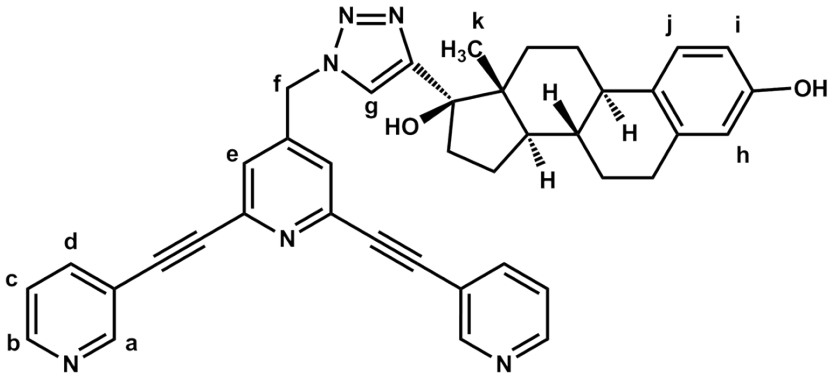


Figure 16 ^{13}C NMR spectrum (100 MHz, d_6-DMSO, 298 K) of **5g**.

1.11 Synthesis of 5h



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 DMF (5 mL) was added 17α-ethynylestradiol (132 mg, 0.45 mmol, 1.5 eq). The reaction was stirred at room temperature for 16 h before adding to 0.1 M $EDTA/NH_4OH_{(aq)}$ (20 mL) and making up to a volume of 50 mL with H_2O. After stirring for 2 h a white precipitate was filtered off and washed with H_2O (3 × 20 mL). The precipitate was taken up in 1:3 isopropanol/DCM (200 mL), dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The product was purified by column chromatography on silica (1:1 acetone/DCM) to give the product as an off white solid. Yield 164 mg (0.26 mmol, 87%). ^{1}H NMR (500 MHz, d_6-DMSO, 298 K) δ: 8.93 (s, 1H, H_{OH}), 8.81 (dd, J = 1.8, 2.1 Hz, 2H, H_a), 8.65 (dd, J = 1.7, 4.9 Hz, 2H, H_b), 8.06 (s, 1H, H_g), 8.02 (ddd, J = 1.7, 2.2, 7.9 Hz, 2H H_d), 7.49 (s, 2H, H_e), 7.47 (ddd, J = 0.9, 4.9, 7.9 Hzm 2H, H_c), 6.74 (d, J = 8.3 Hz, 1H, H_i), 6.38 – 6.35 (m, 2H, H_j, H_h), 5.76 (s, 2H, H_f), 5.18 (s, 1H, H_{OH}), 2.75 – 2.61 (m, 2H), 2.44 – 2.36 (m, 1H), 2.07 – 1.92 (m, 2H), 1.87 – 1.73 (m, 3H), 1.65 – 1.15 (m, 6H), 0.92 (s, 3H, Hk), 0.65 – 0.56 (m, 1H). Diffusion coefficient (d_6-DMSO, 298 K) D: 1.57 × 10^{-10} m^2s^{-1}. ^{13}C NMR (125 MHz, d_6-DMSO, 298 K) δ: 154.8, 154.7, 152.0 (C_a), 149.9 (C_b), 147.5, 142.6, 139.0 (C_d), 137.0, 130.3, 125.8 (C_e), 125.5 (C_i), 123.7 (C_g), 123.7 (C_c), 118.0, 114.9 (C_h), 112.6 (C_j), 90.4, 86.2, 81.0, 50.7 (C_f), 47.6, 46.8, 43.2, 39.2, 37.1, 32.8, 29.2, 27.2, 26.1, 23.6, 14.3 (C_k). IR (ATR): ν (cm^{-1}) 3288, 2923, 2217, 1600, 1548, 1499, 1445, 1424, 1350, 1215, 1190, 1142, 1057, 910, 805, 732, 700. HRESI-MS (MeOH): *m/z* = 633.2981 $[MH]^+$ calc. 633.2973, 655.2814 $[MNa]^+$ calc. 655.2792, 671.2562 $[LK]^+$ calc. 671.2531. UV-Vis (DMSO, ε [$M^{-1}cm^{-1}$]): λ_{max} nm = 319 (2.63 × 10^4).

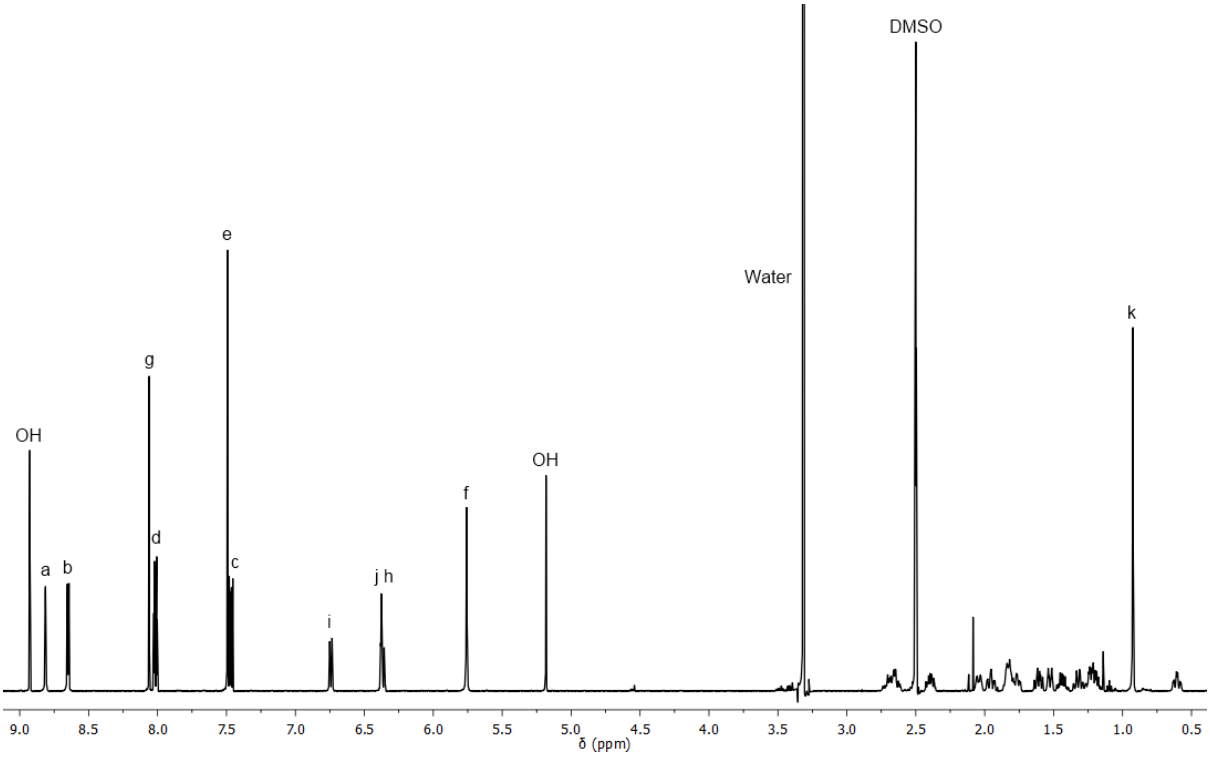


Figure 17 ^{1}H NMR spectrum (500 MHz, d_6-DMSO, 298 K) of **5h**.

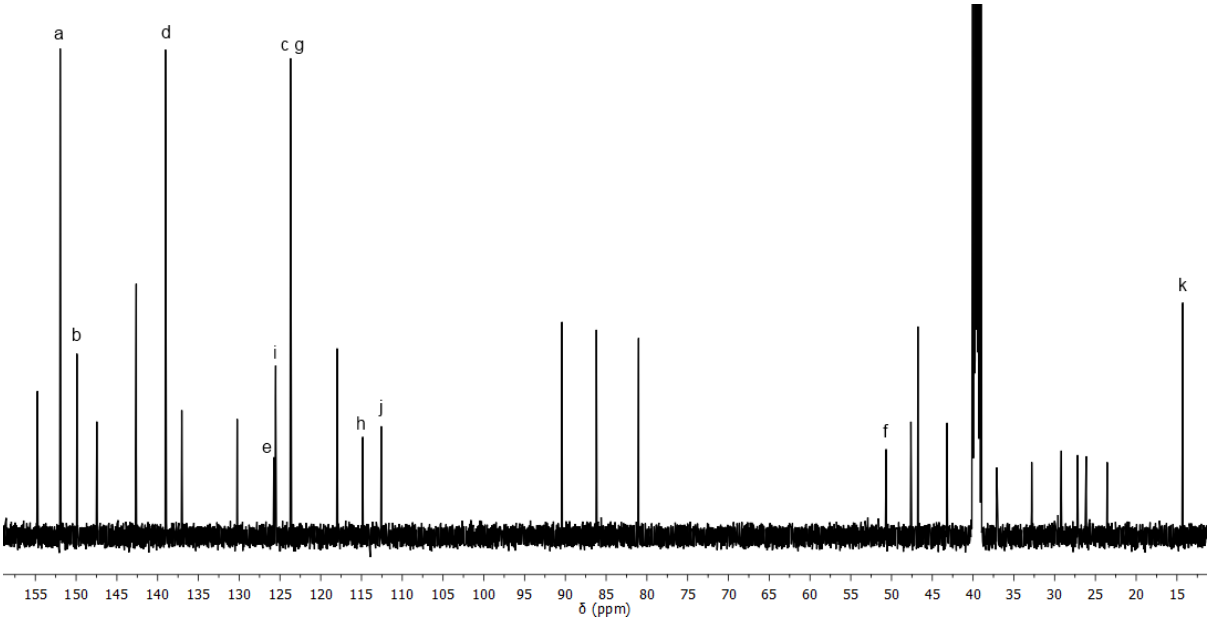
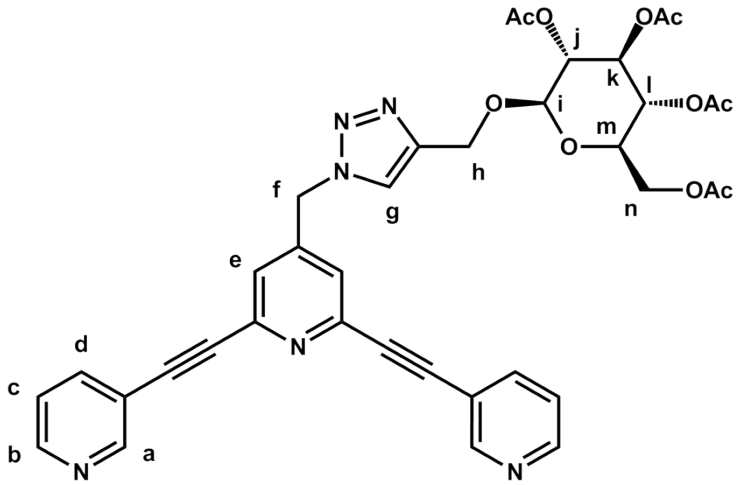


Figure 18 ^{13}C NMR spectrum (125 MHz, d_6-DMSO, 298 K) of **5h**.

1.12 Synthesis of 5i



4 (50 mg, 0.15 mmol, 1 eq.), $CuSO_4 \cdot 5H_2O$ (19 mg, 0.07 mmol, 0.5 eq.) and sodium ascorbate (29 mg, 0.15 mmol, 1 eq.) were stirred in DMF (5 mL). 2-Propynyl-tetra-*O*-acetyl-β-D-glucopyranoside (57 mg, 0.15 mmol, 1 eq.) was added as a solid and the reaction mixture stirred at room temperature for 14 h. 0.1 M EDTA/$NH_4OH_{(aq)}$ (10 mL) was added and the mixture made up to a volume of 50 mL with H_2O. After stirring for 1 h the green solution was extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with water (8 × 50 mL), dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to give the product as a light yellow/green oil. Yield 98 mg (0.14 mmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 8.80 (s, 2H, H_a), 8.60 (d, J = 4.2 Hz, 2H, H_b), 7.86 (dt, J = 1.8, 7.8 Hz, 2H, H_d), 7.61 (s, 1H, H_g), 7.35 (s, 2H, H_e), 7.31 (dd, J = 4.9, 2H, 7.8 H_c), 5.57 (s, 2H, H_f), 5.20 (t, J = 9.5 Hz, 1H, H_k), 5.07 (t, J = 9.7 Hz, 1H, H_l), 5.02-4.95 (m, 2H, H_j, H_h), 4.86 (d, J = 12.7 Hz, 1H, $H_{h'}$), 4.69 (d, J = 7.9 Hz, 1H, H_i), 4.23 (dd, J = 4.6, 12.4 Hz, 1H, H_n), 4.16 (dd, J = 2.3, 12.3 Hz, 1H, $H_{n'}$), 3.72 (ddd, J = 2.4, 4.5, 10.0 Hz, 1H, H_m), 2.05 (s, 3H, H_{OAc}), 2.00 (s, 3H, H_{OAc}), 1.97 (s, 3H, H_{OAc}), 1.95 (s, 3H, H_{OAc}). Diffusion coefficient (d_6-DMSO, 298 K) D: 1.51 × 10^{-10} m^2s^{-1}. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 170.7, 170.3, 169.5, 169.5, 152.8 (C_a), 149.8 (C_b), 145.6, 144.9, 144.3, 139.1 (C_d), 125.1 (C_e), 123.3 (C_g), 123.3 (C_c), 119.0, 100.5 (C_i), 90.6, 87.3, 72.8 (C_k), 72.1 (C_m), 71.3 (C_j), 68.4 (C_l), 63.5 (C_h), 61.8 (C_n), 52.2 (C_f), 20.9, 20.8, 20.7. IR (ATR): ν (cm^{-1}) 2962, 2217, 1750, 1550, 1421, 1367, 1217, 1038, 753, 704. HRESI-MS ($CHCl_3$): *m/z* = 745.2215 $[MNa]^+$ calc. 745.2229. UV-Vis (DMSO, ε [$M^{-1}cm^{-1}$]): λ_{max} nm = 319 (2.21 × 10^4).

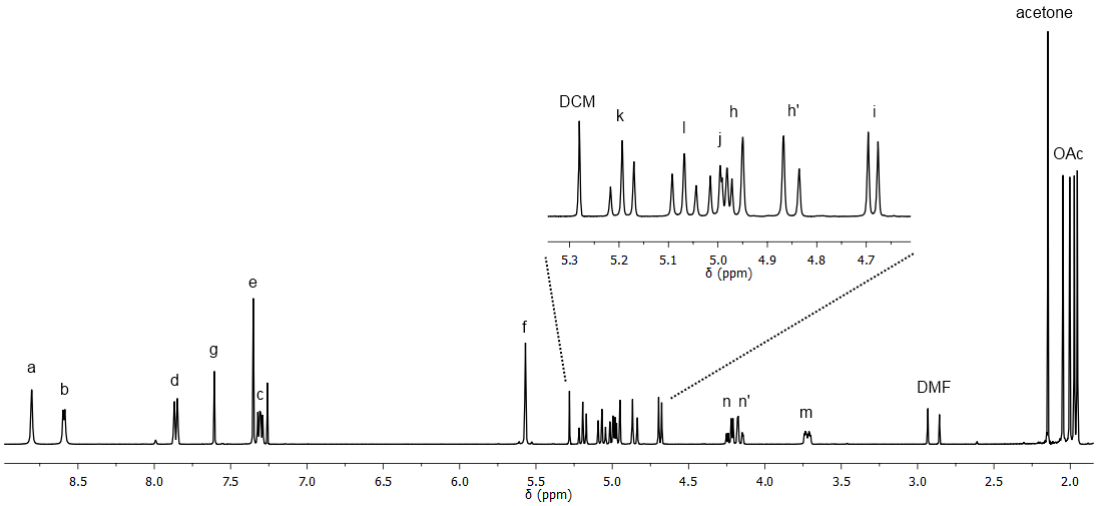


Figure 19 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **5i**.

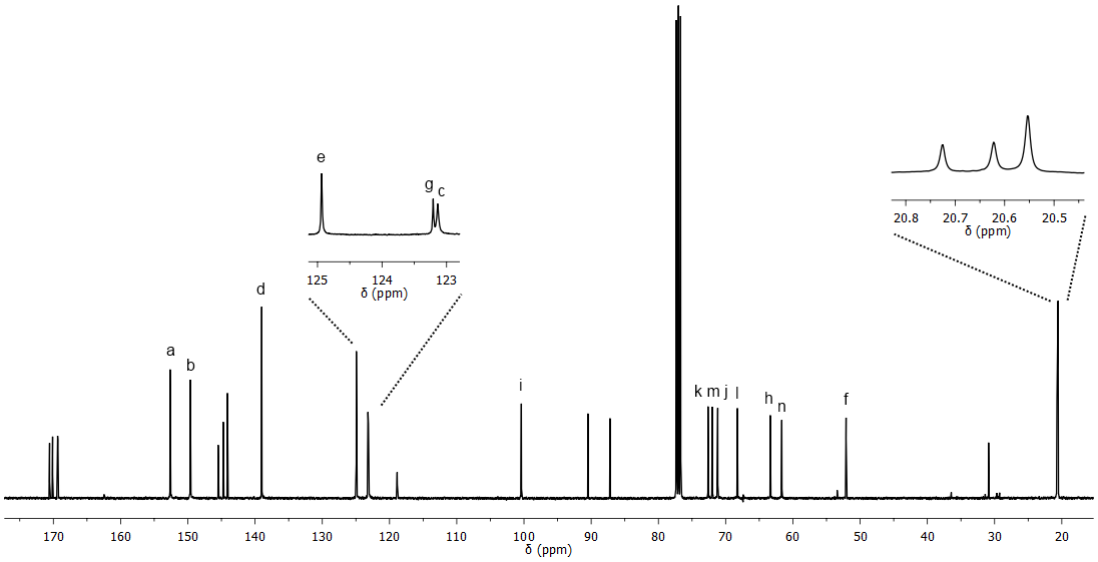
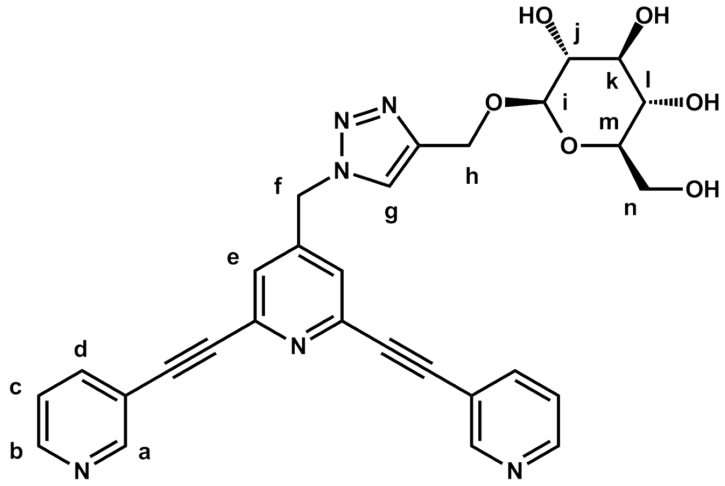


Figure 20 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **5i**.

1.13 Synthesis of 5j



5i (98 mg, 0.14 mmol) and Amberlite IRA-400 (OH-) (200 mg) were gently stirred in MeOH (15 mL) for 24 h. The Amberlite beads were removed by filtration and the solvent removed *in vacuo* to give the crude product as an off-white solid. This was purified by column chromatography on silica, eluting with 1:9 MeOH/chloroform (R_f < 0.05) to yield the product as a white solid. Yield 58 mg (0.10 mmol, 77%). M.p. 114-116 °C. ^{1}H NMR (400 MHz, d_6-DMSO, 298 K) δ: 8.84 (s, 2H, H_a), 8.66 (d, J = 4.4 Hz, 2H, H_b), 8.30 (s, 1H, H_g), 8.08 (d, J = 7.9 Hz, 2H, H_d), 7.59 (s, 2H, H_e), 7.52 (dd, J = 5.0, 7.8 Hz, 2H, H_c), 5.75 (s, 2H, H_f), 5.04 (d, J = 4.8 Hz, 1H, H_{OH}), 4.94-4.87 (m, 3H, H_h, 2 × H_{OH}), 4.68 (d, J = 12.3 Hz, 1H, $H_{h'}$), 4.55 (t, J = 5.8 Hz, 1H, H_{OH}), 4.28 (d, J = 7.8 Hz, 1H, H_i), 3.73-3.68 (m, 1H, H_n), 3.48-3.43 (m, 1H, $H_{n'}$), 3.17-3.12 (m, 2H, H_m, H_k), 3.07-2.96 (m, 2H, H_l, H_j). Diffusion coefficient (d_6-DMSO, 298 K) D: 1.54 × 10^{-10} m^2s^{-1}. ^{13}C NMR (100 MHz, d_6-DMSO, 298 K) δ: 152.0 (C_a), 149.9 (C_b), 146.8, 144.5, 142.7, 139.2 (C_d), 125.9 (C_e), 125.1 (C_g), 123.8 (C_c), 118.1, 102.2 (C_i), 90.5, 86.3, 77.0 (C_k), 76.7 (C_m), 73.4 (C_j), 70.1 (C_l), 61.5 (C_h), 61.2 (C_n), 50.9 (C_f). IR (ATR): ν (cm^{-1}) 3346, 2923, 2217, 1600, 1555, 1480, 1422, 1376, 1192, 1159, 1081, 1039, 998, 803, 700. HRESI-MS (MeOH): *m/z* = 553.1843 $[M-H]^-$ calc. 553.1841, 589.1600 $[MCl]^-$ calc. 589.1597. UV-Vis (DMSO, ε [$M^{-1}cm^{-1}$]): λ_{max} nm = 320 (2.13 × 10^4).

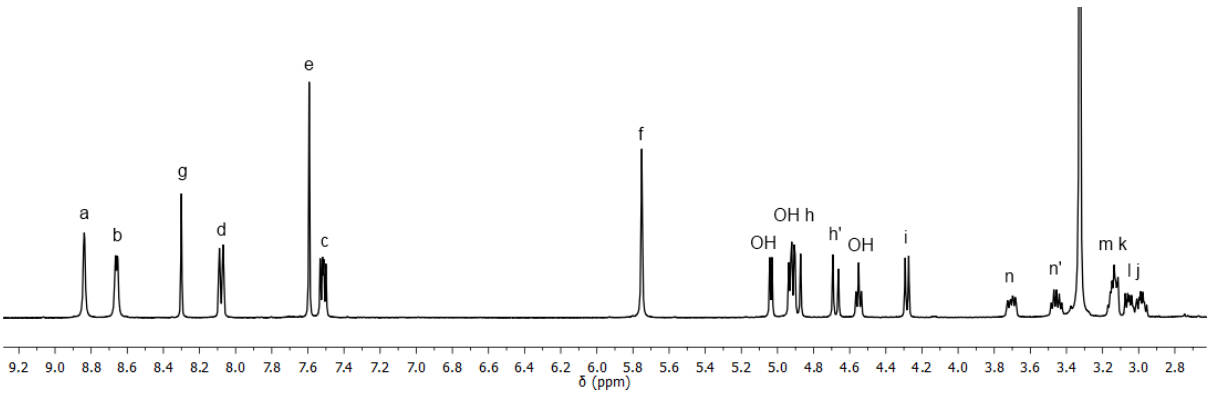


Figure 21 ^{1}H NMR spectrum (400 MHz, d_6-DMSO, 298 K) of **5j**.

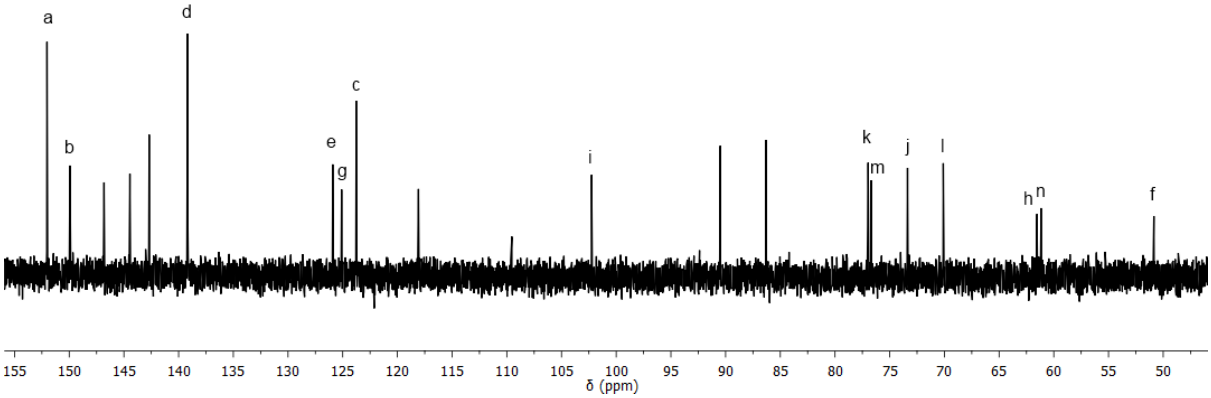


Figure 22 ^{13}C NMR spectrum (100 MHz, d_6-DMSO, 298 K) of **5j**.

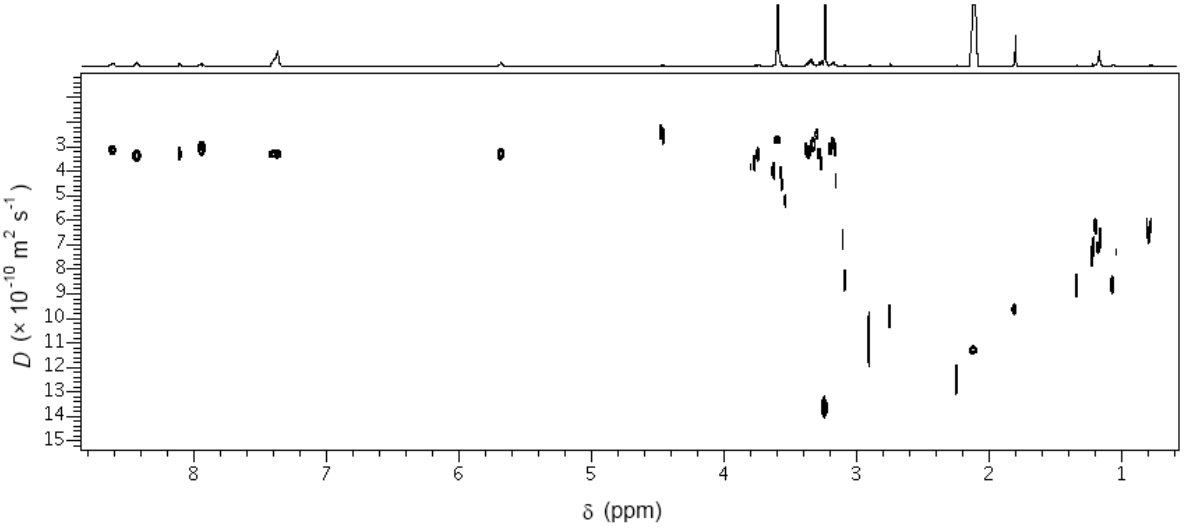
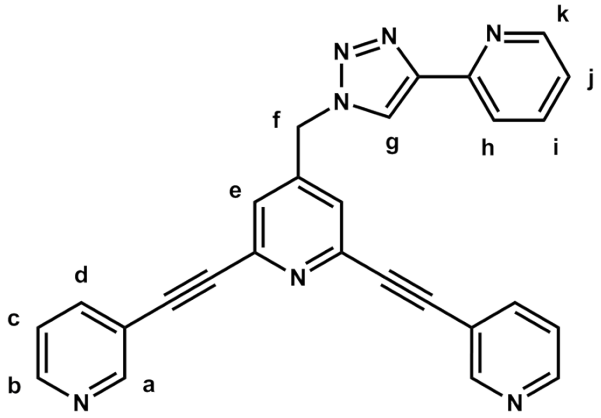


Figure 23 ^{1}H DOSY NMR spectrum (500 MHz, D_2O, 298 K) of **5j**.

1.14 Synthesis of 5k



To a stirring solution of **4** (50 mg, 0.15 mmol, 1 eq.), $CuSO_4 \cdot 5H_2O$ (19 mg, 0.07 mmol, 0.5 eq.) and sodium ascorbate (29 mg, 0.15 mmol, 1 eq.) in DMF (5 mL) was added 2-ethynylpyridine (15 µL, 0.15 mmol, 1 eq.). After stirring at room temperature for 48 h, 0.1 M EDTA/$NH_4OH_{(aq)}$ (5 mL) was added and stirred for an additional 2 h. The resulting off-white precipitate was collected by filtration, washed with H_2O (5 × 2 mL) and dried *in vacuo*. Yield 60 mg (0.14 mmol, 92%). M.p. 184-186 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 8.81 (s, 2H, H_a), 8.60-8.57 (m, 3H, H_b, H_k), 8.26 (s, 1H, H_g), 8.22 (d, J = 7.9 Hz, 1H, H_h), 7.87-7.80 (m, 3H, H_d, H_i), 7.39 (s, 2H, H_e), 7.32-7.25 (m, 3H, H_c, H_j), 5.65 (s, 2H, H_f). Diffusion coefficient (d_6-DMSO, 298 K) D: 1.91 × 10^{-10} m^2s^{-1}. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 152.8 (C_a), 149.7 (C_b), 149.7, 149.4 (C_k), 149.3, 144.8, 144.3, 139.2 (C_d), 137.4 (C_i), 125.1 (C_e), 123.4 (C_c), 123.3 (C_j), 122.7 (C_g), 120.6 (C_h), 119.1, 90.7, 87.4, 52.4 (C_f). IR (ATR): ν (cm^{-1}) 3144, 3037, 2997, 2921, 2851, 2208, 1597, 1561, 1547, 1475, 1462, 1414, 1197, 1041, 1022, 802, 784, 772, 698, 626, 517. HRESI-MS ($CHCl_3$): *m/z* = 440.1581 $[MH]^+$ calc. 440.1618, 462.1403 $[MNa]^+$ calc. 462.1438, 901.2942 $[M_2Na]^+$ calc. 901.2983. UV-Vis (DMSO, ε [$M^{-1}cm^{-1}$]): λ_{max} nm = 319 (3.55 × 10^4).

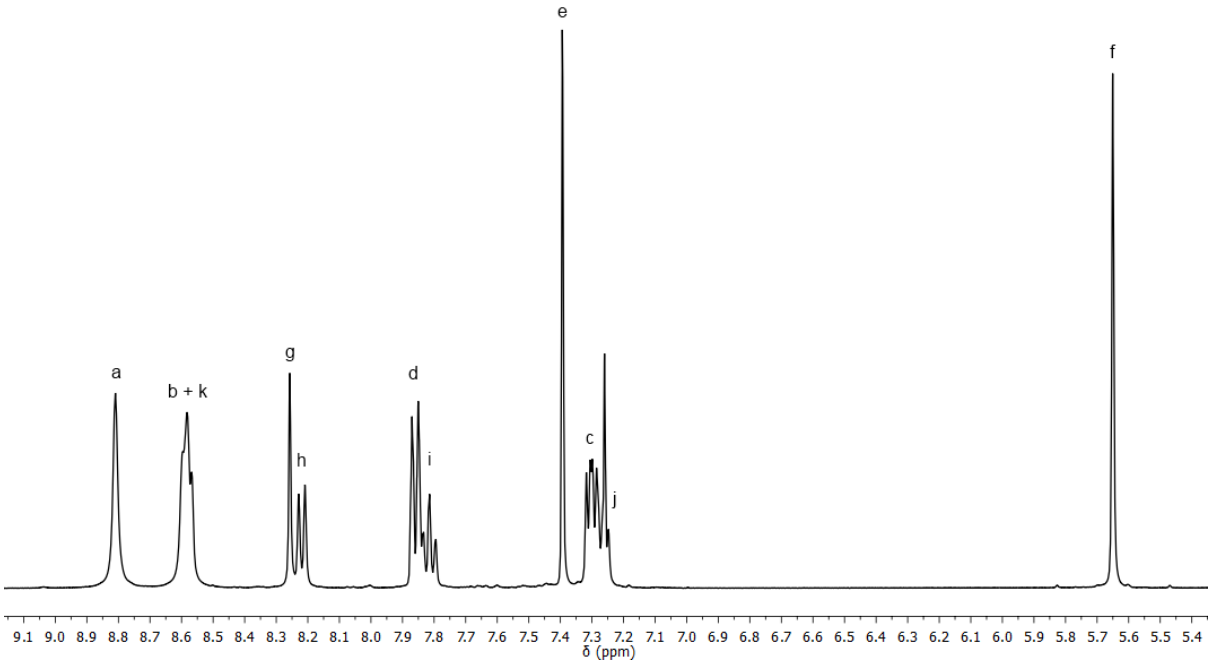


Figure 24 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **5k**.

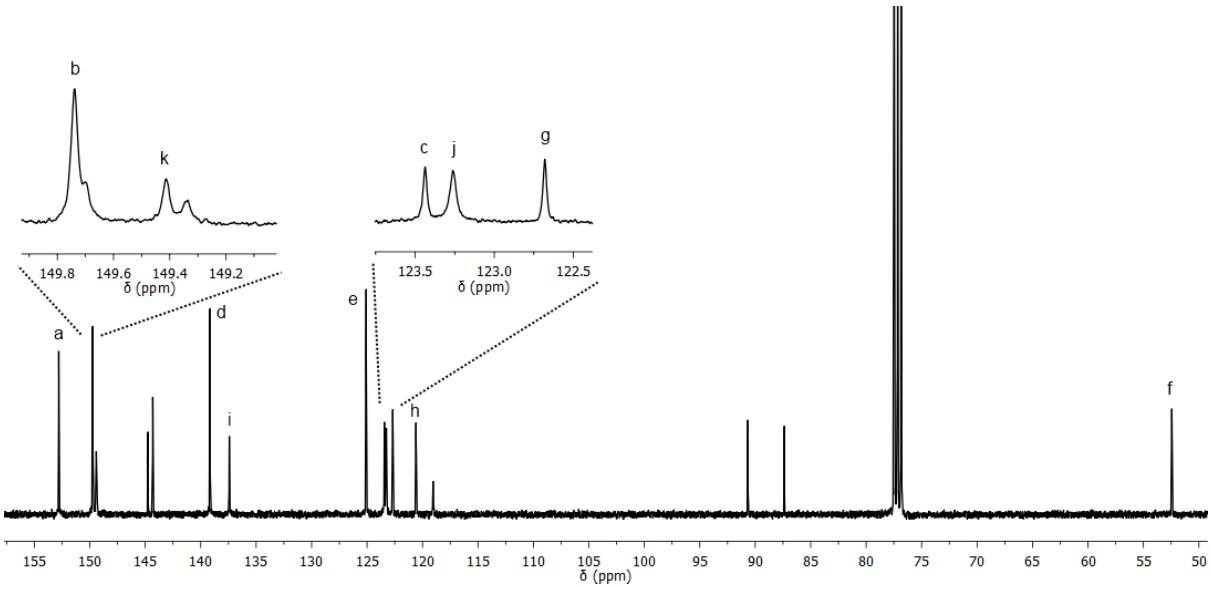
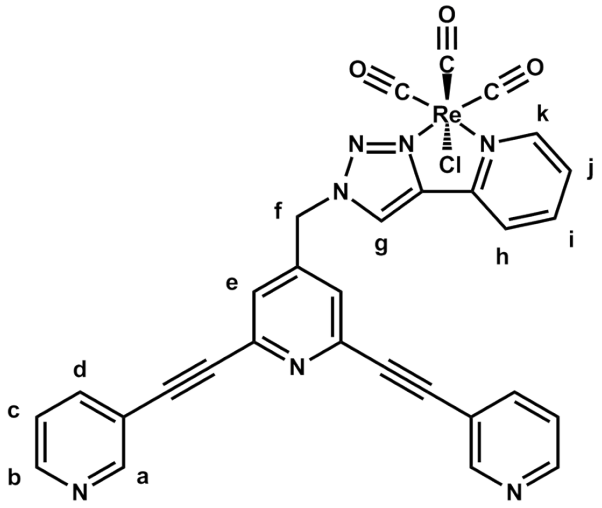


Figure 25 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **5k**.

1.15 Synthesis of 5k^{Re}



A RBF was charged with **5k** (50 mg, 0.11 mmol, 1 eq.) and $Re(CO)_5Cl$ (41 mg, 0.11 mmol, 1 eq.) and purged with N_2. MeOH (25 mL) was added *via* syringe and the reaction heated at reflux for 7 h before stirring at 60 °C for 12 h. The solvent volume was reduced *in vacuo* to ~5 mL. Diethyl ether was added to precipitate the product as an off-white solid. Yield 53 mg (0.07 mmol, 62%). ^{1}H NMR (500 MHz, d_6-acetone, 298 K) δ: 9.24 (s, 1H, H_g), 9.09 (dt, J = 1.2, 5.6 Hz, 1H, H_k), 8.82 (s, 2H, H_a), 8.65 (dd, J = 1.2, 4.8 Hz, 2H, H_b), 8.28-8.27 (m, 2H, H_h, H_i), 8.03 (dt, J = 1.9, 7.9 Hz, 2H, H_d), 7.71 (s, 2H, H_e), 7.70-7.68 (m, 1H, H_j), 7.49 (ddd, J = 0.8, 4.9, 7.9 Hz, 2H, H_c), 6.16 (s, 2H, H_f). Diffusion coefficient (d_6-DMSO, 298 K) D: 1.73 × 10^{-10} m^2s^{-1}. ^{13}C NMR (125 MHz, d_6-acetone, 298 K) δ: 154.0 (C_k), 153.2 (C_a), 150.7 (C_b), 150.3, 150.1, 145.7, 144.7, 141.1 (C_i), 139.8 (C_d), 127.2 (C_j), 126.9 (C_e), 126.7 (C_g), 124.4 (C_c), 123.6 (C_h), 119.6, 91.4, 87.2, 54.2 (C_f). IR (ATR): ν (cm^{-1}) 3068, 2218, 2021, 1927, 1896, 1594, 1549, 1476, 1457, 1419, 804, 781, 701, 642, 630, 533, 484. HRESI-MS (acetone): *m/z* = 708.0906 $[M-Cl]^+$ calc. 708.0917, 744.0665 $[MH]^+$ calc. 744.0684, 766.0480 $[MNa]^+$ calc. 766.0503, 782.0256 $[MK]^+$ calc. 782.0243, 1451.1445 $[M_2-Cl]^+$ calc. 1451.1528, 1487.1315 $[M_2H]^+$ calc. 1487.1295. UV-Vis (DMSO, ε [$M^{-1}cm^{-1}$]): λ_{max} nm = 350 (shoulder, 2.80 × 10^3), 320 (2.26 × 10^4).

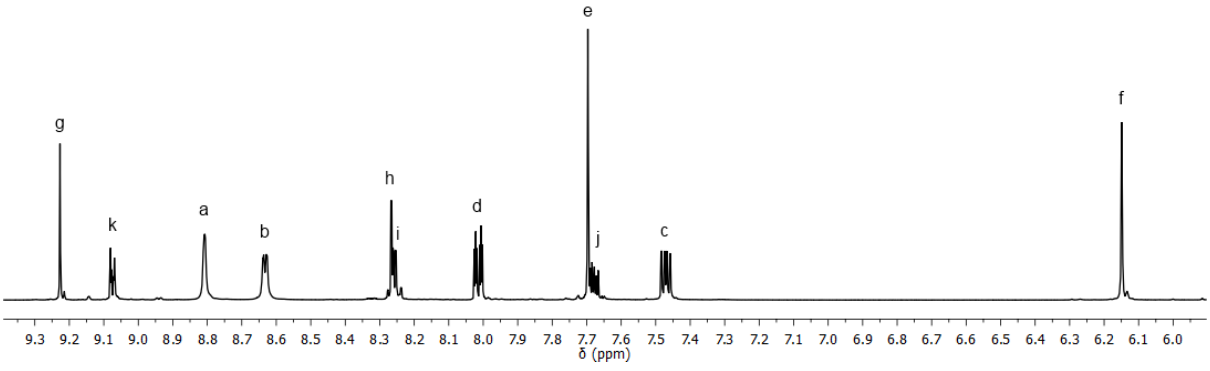


Figure 26 ^{1}H NMR spectrum (500 MHz, d_6-acetone, 298 K) of **5k^{Re}**.

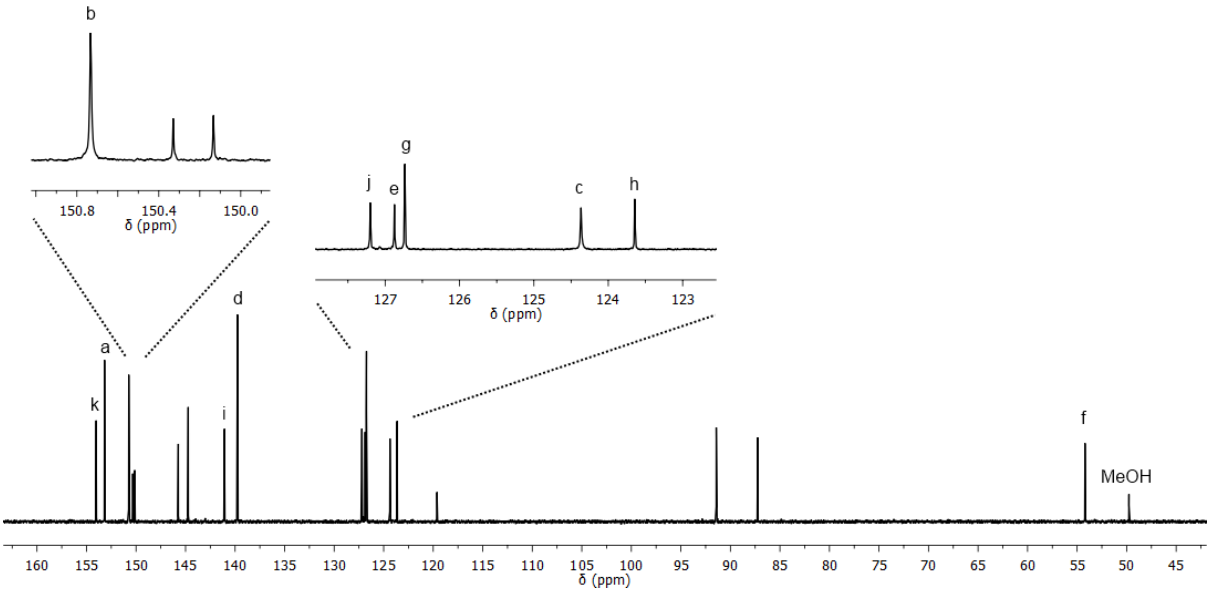
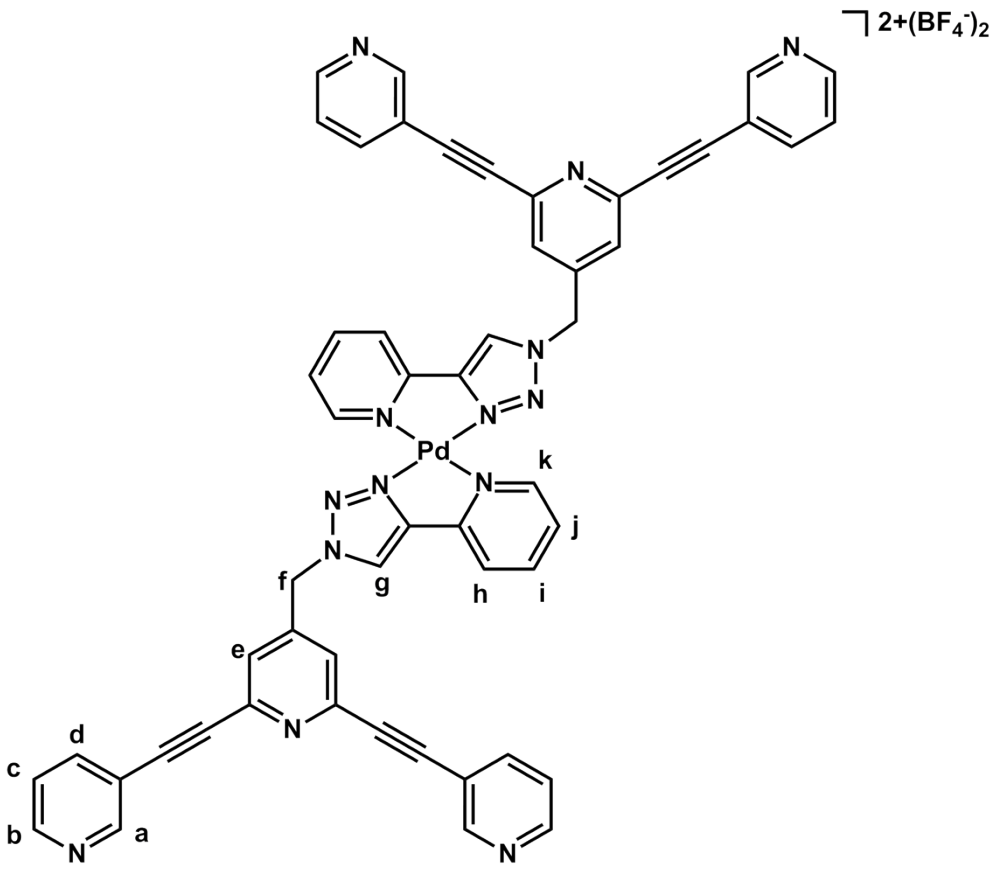


Figure 27 ^{13}C NMR spectrum (125 MHz, d_6-acetone, 298 K) of **5k^{Re}**.

1.16 Synthesis of $5k^{Pd}$



To a stirring suspension of **5k** (48 mg, 0.11 mmol, 2 eq.) in MeCN (3 mL) was added dropwise a solution of $[Pd(CH_3CN)_4](BF_4)_2$ (24 mg, 0.06 mmol, 1 eq.) in MeCN (2 mL). After stirring at room temperature for 1 h, EtOAc (15 mL) was added to precipitate the product as a white solid, which was isolated by filtration, washed with Et_2O and dried *in vacuo*. Yield 51 mg (0.04 mmol, 81%). ^{1}H NMR (400 MHz, d_6-DMSO, 298 K) δ: 9.56 (s, 2H, H_g), 9.47 (d, J = 5.8 Hz, 2H, H_k), 8.83 (d, J = 2.1 Hz, 4H, H_a), 8.67 (dd, J = 1.6, 4.9 Hz, 4H, H_b), 8.56 (td, J = 1.0, 7.8 Hz, 2H, H_i), 8.50-4.48 (m, 2H, H_h), 8.06 (dt, J = 2.1, 7.9 Hz, 4H, H_d), 7.96-7.93 (d, 2H, H_j), 7.90 (s, 4H, H_e), 7.53 (dd, J = 4.9, 7.9 Hz, 4H, H_c), 6.20 (s, 4H, H_f). Diffusion coefficient (d_6-DMSO, 298 K) D: 1.39×10^{-10} m^2s^{-1}. ^{13}C NMR (125 MHz, d_6-DMSO, 298 K) δ: 151.9 (C_a), 151.4 (C_k), 150.1 (C_b), 148.5, 147.5, 144.4, 143.4 (C_i), 142.9, 139.1 (C_d), 128.0 (C_g), 127.0 (C_j), 126.5 (C_e), 123.8 (C_c), 123.5 (C_h), 118.0, 90.4, 86.6, 53.9 (C_f). IR (ATR): ν (cm^{-1}) 3114, 2219, 1626, 1596, 1552, 1478, 1462, 1422, 1286, 1193, 1051, 812, 780. HRESI-MS (DMSO/MeCN): *m/z* = 440.1682 $[LH]^+$ calc. 440.1618, 492.1119 $[PdL_2]^{2+}$ calc. 492.1066. UV-Vis (DMSO, ε [$M^{-1}cm^{-1}$]): λ_{max} nm = 315 (6.25×10^4).

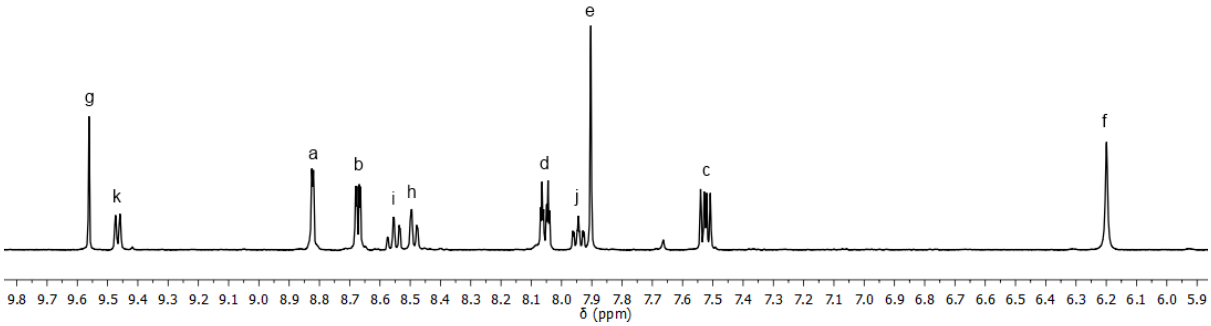


Figure 28 ^{1}H NMR (400 MHz, d_6-DMSO, 298K) spectrum of **5k^{Pd}**.

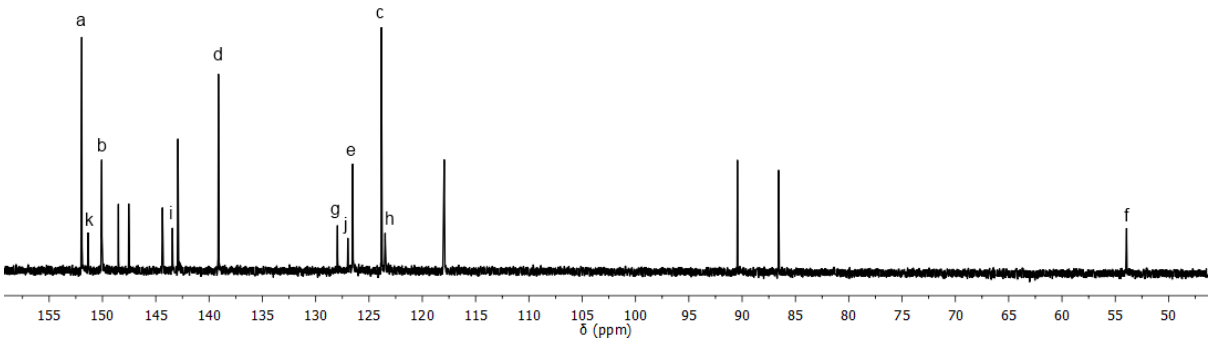


Figure 29 ^{13}C NMR (125 MHz, d_6-DMSO, 298 K) spectrum of **5k^{Pd}**.

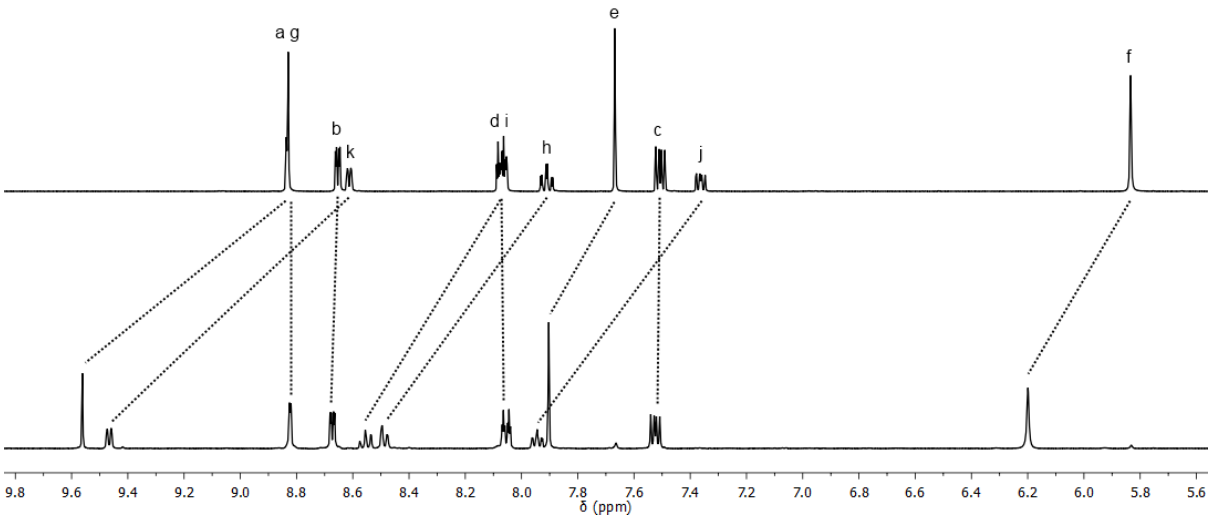
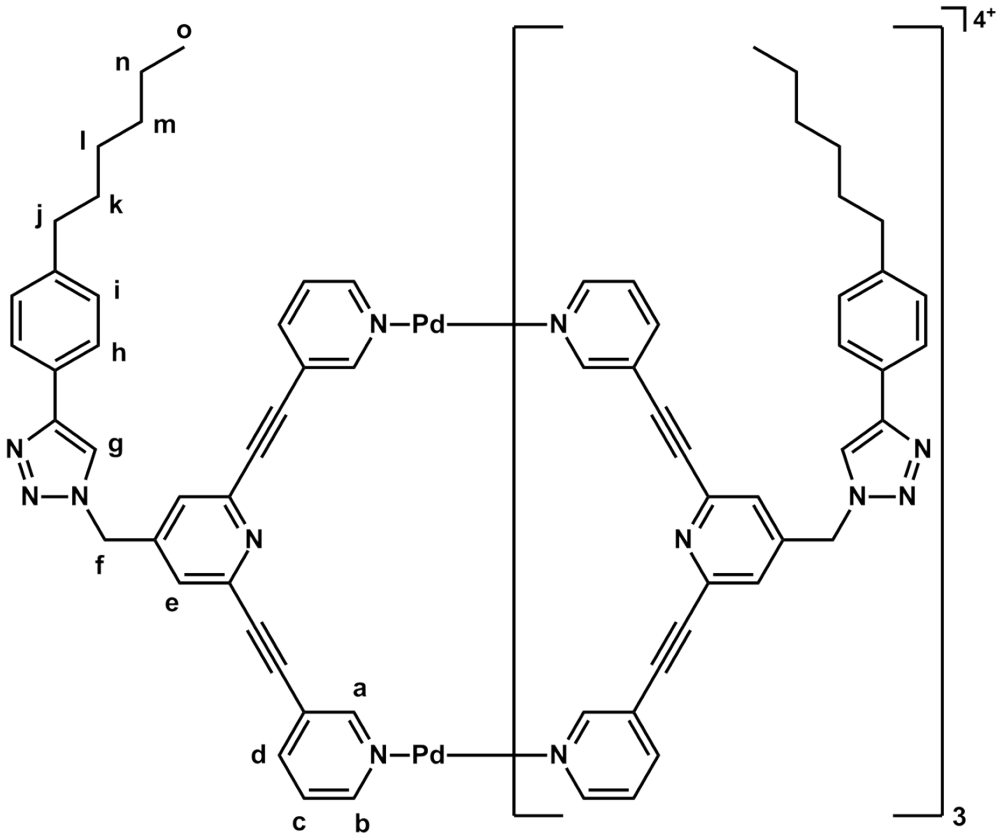


Figure 30 Stacked ^{1}H NMR (400 MHz, d_6-DMSO, 298 k) spectra of **5k** (top) and **5k^{Pd}** (bottom).

1.17 Synthesis of $[Pd_2(5d)_4](BF_4)_4$ (6d)



5d (105 mg, 0.20 mmol, 2 eq.) and $[Pd(CH_3CN)_4](BF_4)_2$ (44 mg, 0.10 mmol, 1 eq.) were stirred in DMF (3 mL) for 1 h. Vapour diffusion of diethyl ether resulted in a tan precipitate that was isolated by filtration, washed with diethyl ether and dried *in vacuo*. Yield 124 mg (0.05 mmol, 93%). ^{1}H NMR (500 MHz, d_6-DMSO, 298 K) δ: 9.48 (d, J = 1.7 Hz, 8H, H_a), 9.36 (d, J = 6.0 Hz, 8H, H_b), 8.59 (s, 4H, H_g), 8.32 (dd, J = 1.5, 8.1 Hz, 8H, H_d), 7.82 (dd, J = 6.0, 7.9 Hz, 8H, H_c), 7.71 (d, J = 8.2 Hz, 8H, H_h), 7.64 (s, 8H, H_e), 7.24 (d, J = 8.3 Hz, 8H, H_i), 5.77 (s, 8H, H_f), 2.57 (t, J = 7.6 Hz, 8H, H_j), 1.58-1.52 (m, 8H, H_k), 1.28-1.23 (m, 24H, H_l, H_m, H_n), 0.84 (t, J = 7.1 Hz, 12H, H_o). Diffusion coefficient (d_6-DMSO, 298 K) D: 0.83×10^{-10} m^2s^{-1}. ^{13}C NMR (125 MHz, d_6-DMSO, 298 K) δ: 153.4 (C_a), 151.1 (C_b), 147.2, 146.8, 143.6 (C_d), 142.4, 142.2, 128.8 (C_i), 127.8, 127.3 (C_c), 126.9 (C_e), 125.1 (C_h), 121.9 (C_g), 121.3, 92.8, 84.0, 50.9 (C_f), 34.8 (C_j), 31.1, 30.8 (C_k), 28.2, 22.0, 13.9 (C_o). IR (ATR): ν (cm^{-1}) 3075, 2927, 2855, 1647, 1593, 1550, 1484, 1427, 1387, 1253, 1194, 1049, 974, 814. HRESI-MS (DMSO/MeCN): *m/z* = 523.2615 $[LH]^+$ calc. 523.2605, 575.2095 $[Pd_2L_4]^{4+}$ calc. 575.2055, 778.6034 $[Pd_2L_4Cl]^{3+}$ calc. 778.5970, 795.9374 $[Pd_2L_4(BF_4)]^{3+}$ calc. 795.9421. UV-Vis (DMSO, ε [$M^{-1}cm^{-1}$]): λ_{max} nm = 314 (1.25×10^5).

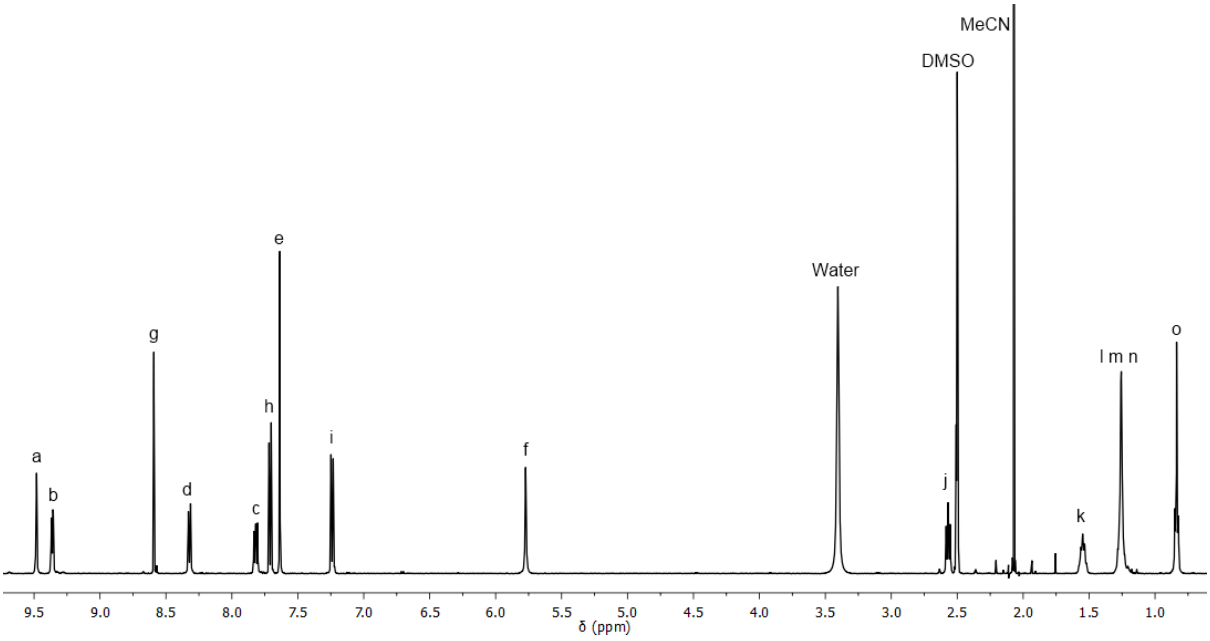


Figure 31 ^{1}H NMR spectrum (500 MHz, d_6-DMSO, 298 K) of **6d**.

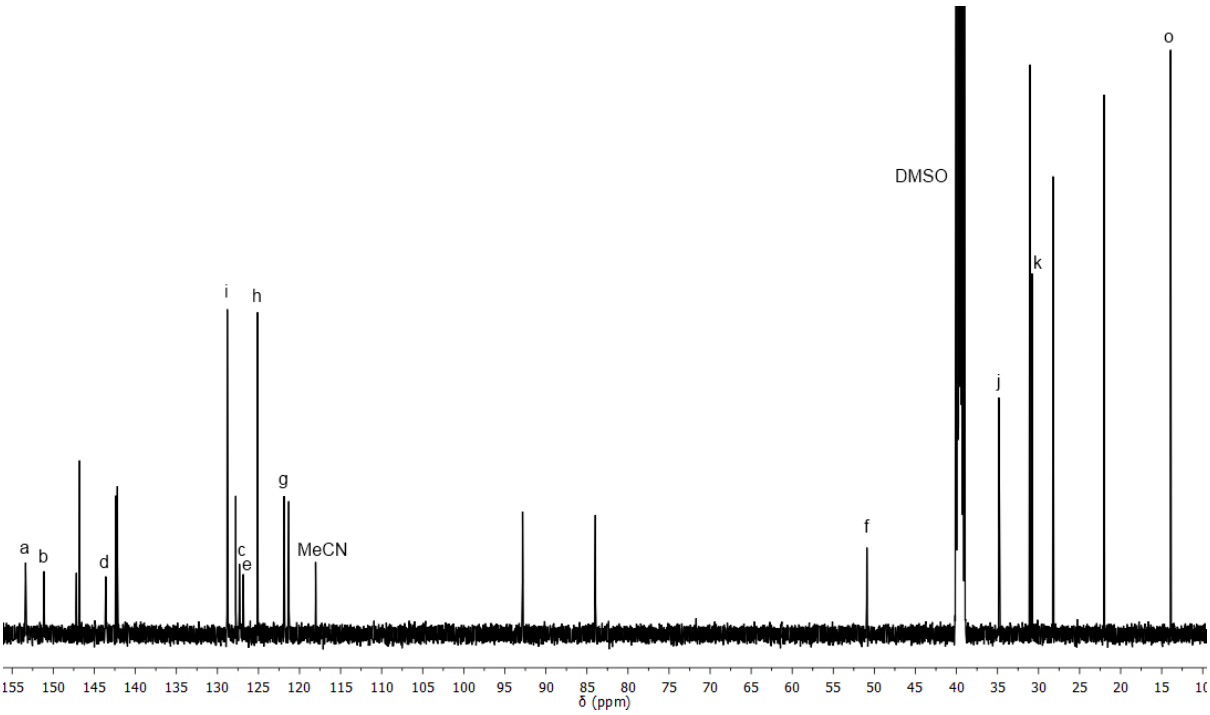
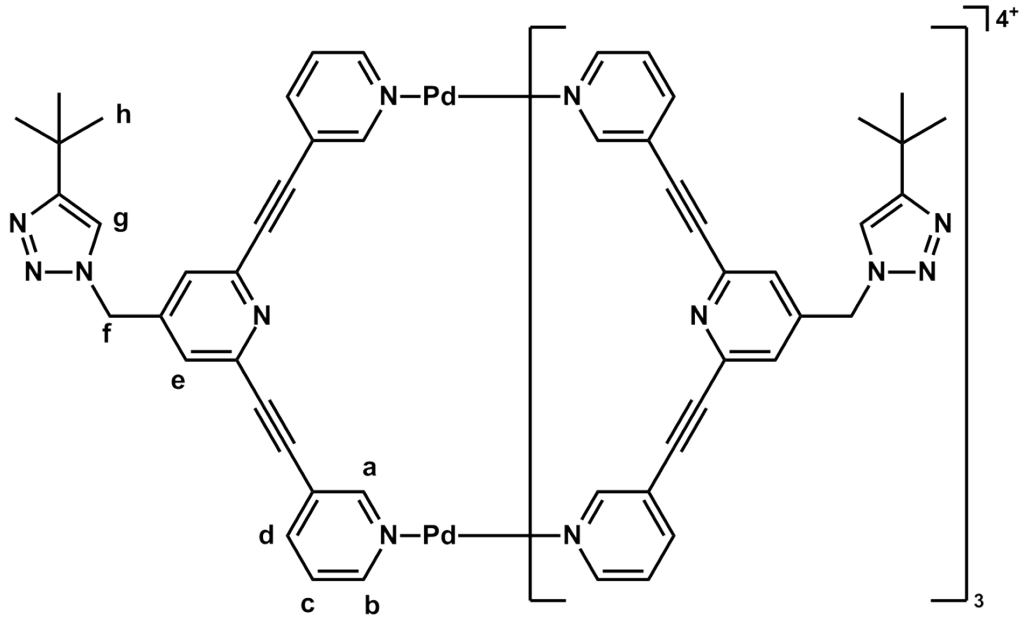


Figure 32 ^{13}C NMR spectrum (125 MHz, d_6-DMSO, 298 K) of **6d**.

1.18 Synthesis of $[Pd_2(5e)_4](BF_4)_4$ (6e)



5e (42 mg, 0.2 mmol, 2 eq.) and $[Pd(CH_3CN)_4](BF_4)_2$ (22 mg, 0.1 mmol, 1 eq.) were stirred in DMF (3 mL) for 1 h. Following precipitation by vapour diffusion of diethyl ether, the product was isolated by filtration, washed with diethyl ether and dried *in vacuo* to give the product as a tan solid. Yield 58 mg (0.03 mmol, 88%). ^{1}H NMR (500 MHz, d_6-DMSO, 298 K) δ: 9.50 (d, J = 1.8 Hz, 8H, H_a), 9.37 (dd, J = 1.1, 5.9 Hz, 8H, H_b), 8.34 (dt, J = 1.5, 8.1 Hz, 8H, H_d), 7.94 (s, 4H, H_g), 7.85 (dd, J = 6.1, 7.9 Hz, 8H, H_c), 7.64 (s, 8H, H_e), 5.63 (s, 8H, H_f), 1.23 (s, 36H, H_h). Diffusion coefficient (d_6-DMSO, 298 K) D: 0.93 × 10^{-10} m^2s^{-1}. ^{13}C NMR (125 MHz, d_6-DMSO, 298 K) δ: 156.7, 153.3 (C_a), 151.2 (C_b), 147.2, 143.6 (C_d), 142.1, 127.4 (C_c), 127.2 (C_e), 121.3, 120.6 (C_g), 92.9, 84.0, 50.6 (C_f), 30.4, 30.2 (C_h). IR (ATR): ν (cm^{-1}) 3078, 2963, 2865, 1667, 1650, 1596, 1554, 1484, 1461, 1427, 1385, 1195, 1045, 1024, 817. HRESI-MS (DMSO/MeCN): *m/z* = 419.2105 $[LH]^+$ calc. 419.1430, 471.1535 $[Pd_2L_4]^{4+}$ calc. 471.1430, 639.8497 $[Pd_2L_4Cl]^{3+}$ calc. 639.8466, 657.1946 $[Pd_2L_4(BF_4)]^{3+}$ calc. 657.1917, 750.1708 $[Pd_2L_3Cl\text{-}H]^{2+}$ calc. 750.1705, 768.1588 $[Pd_2L_3Cl_2]^{2+}$ calc. 768.1587, 977.2530 $[Pd_2L_4Cl_2]^{2+}$ calc. 977.2543, 1003.2730 $[Pd_2L_4(BF_4)Cl]^{2+}$ calc. 1003.2720. UV-Vis (DMSO, ε [$M^{-1}cm^{-1}$]): λ_{max} nm = 314 (1.08 × 10^5).

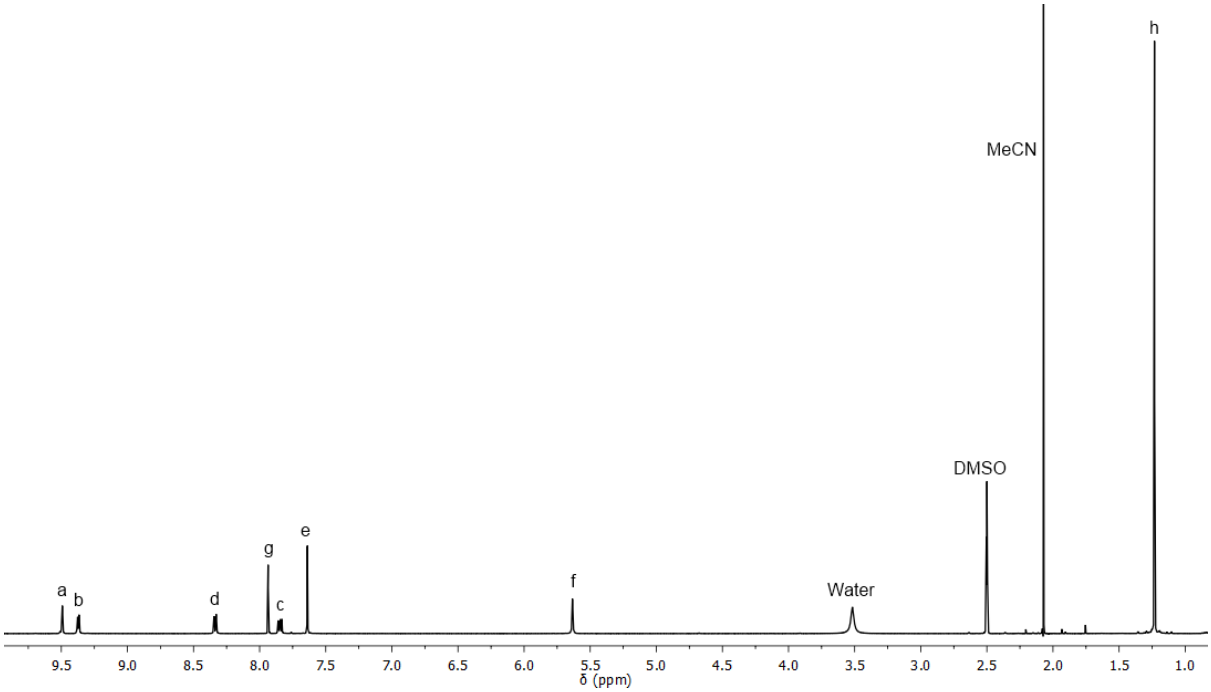


Figure 33 ^{1}H NMR spectrum (500 MHz, d_6-DMSO, 298 K) of **6e**.

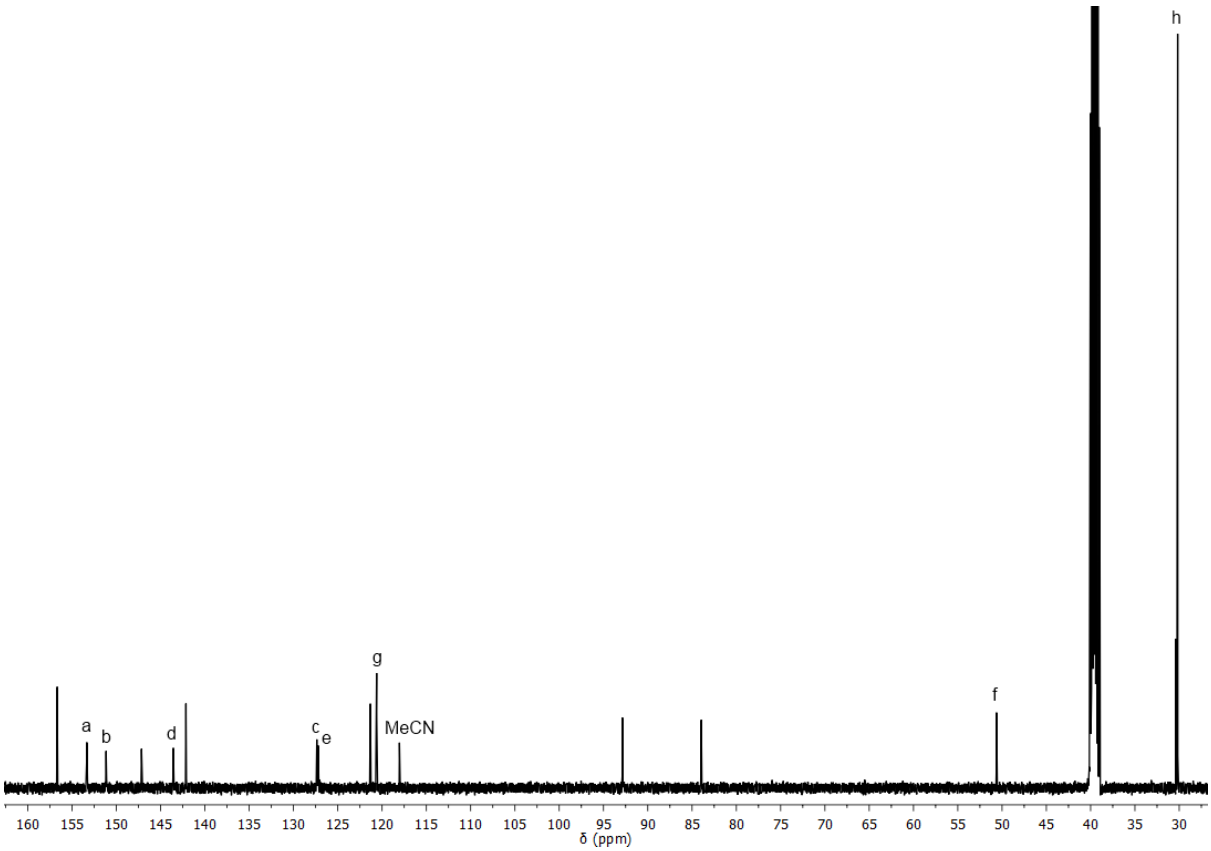
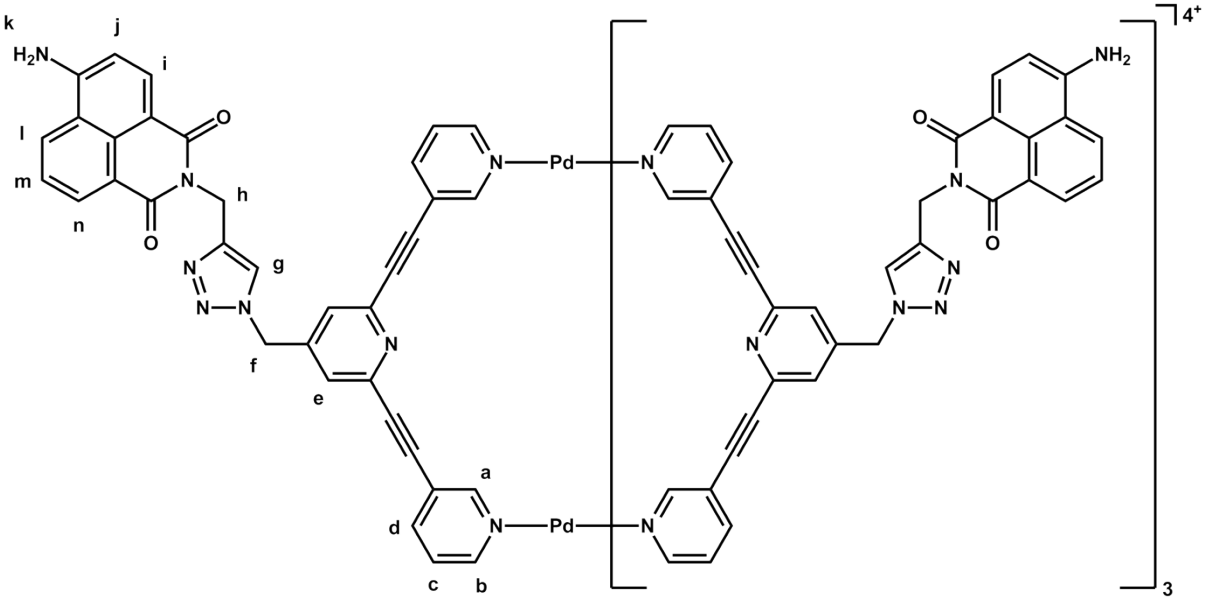


Figure 34 ^{13}C NMR spectrum (125 MHz, d_6-DMSO, 298 K) of **6e**.

1.19 Synthesis of $[Pd_2(5f)_4](BF_4)_4$ (6f)



5f (59 mg, 0.1 mmol, 2 eq.) and $[Pd(CH_3CN)_4](BF_4)_2$ (22 mg, 0.05 mmol, 1 eq.) were stirred in DMF (3 mL) for 2 h. The product was precipitated as a yellow/orange solid by vapour diffusion of diethyl ether over a few days. Yield 72 mg (0.02 mmol, 99%). ^{1}H NMR (500 MHz, d_6-DMSO, 298 K) δ: 9.50 (s, 8H, H_a), 9.37 (d, J = 5.7 Hz, 8H, H_b), 8.57 (d, J = 8.4 Hz, 4H, H_n), 8.35-8.31 (m, 12H, H_d, H_l), 8.13 (d, J = 8.4 Hz, 4H, H_i), 8.10 (s, 4H, H_g), 7.84-7.82 (m, 8H, H_c), 7.60 (s, 8H, H_e), 7.58-7.54 (m, 4H, H_m), 7.47 (s, 8H, H_k), 6.79 (d, J = 8.4 Hz, 4H, H_j), 5.64 (s, 8H, H_f), 5.24 (s, 8H, H_h). Diffusion coefficient (d_6-DMSO, 298 K) D: 0.71 × 10^{-10} m^2s^{-1}. ^{13}C NMR (125 MHz, d_6-DMSO, 298 K) δ: 163.5, 162.5, 153.5 (C_a), 152.9, 151.1 (C_b), 144.0, 143.5 (C_d), 142.2, 134.1 (C_i), 131.1 (C_l), 129.8, 129.5 (C_n), 127.3 (C_c), 127.1 (C_e), 124.2 (C_g), 123.9, 123.9 (C_m), 121.5, 121.3, 119.3, 108.2 (C_j), 107.2, 92.8, 84.0, 50.7 (C_f), 34.8 (C_h). IR (ATR): ν (cm^{-1}) 3369, 3241, 3076, 2931, 1648, 1577, 1528, 1481, 1425, 1369, 1246, 1051, 778, 692, 660, 479. HRESI-MS (DMF/MeCN): *m/z* = 857.1939 $[LH]^+$ calc. 587.1938, 609.1735 $[LNa]^+$ calc. 609.1758, 625.1489 $[LK]^+$ calc. 625.1497, 1369.8731 $[Pd_2L_4Cl_2(CH_3CN)(H_2O)_4]^{2+}$ calc. 1369.7810. UV-Vis (DMSO, ε [$M^{-1}cm^{-1}$]): λ_{max} nm = 439 (3.96 × 10^4), 313 (8.81 × 10^4).

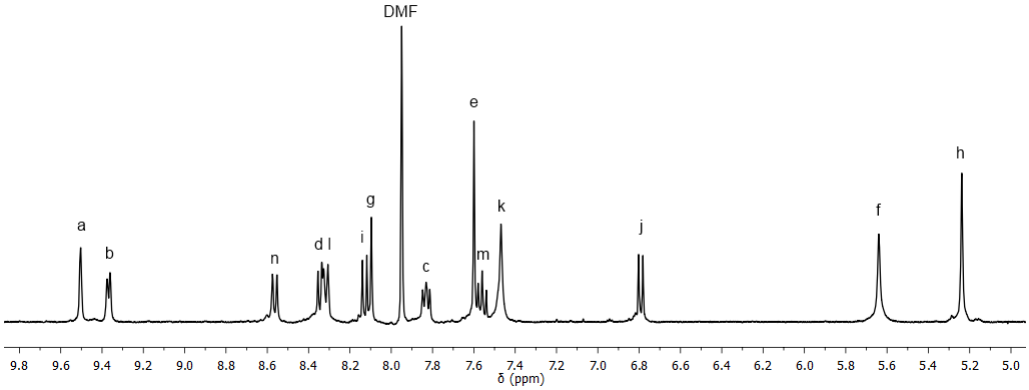


Figure 35 ^{1}H NMR spectrum (500 MHz, d_6-DMSO, 298 K) of **6f**.

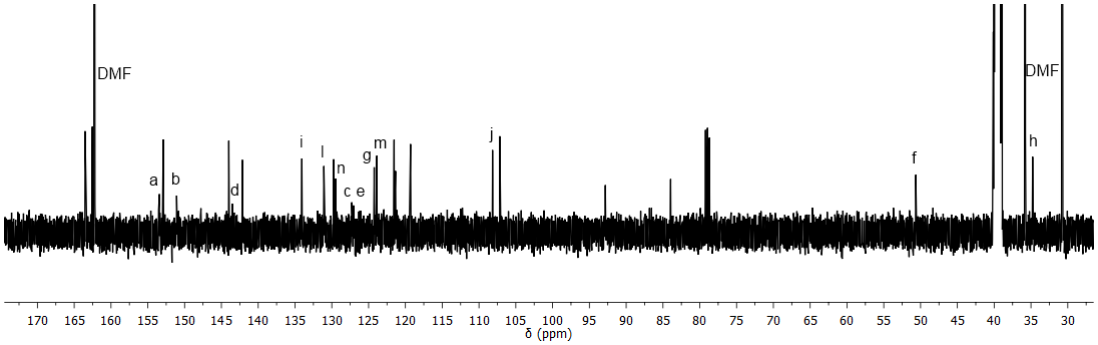


Figure 36 ^{13}C NMR spectrum (125 MHz, d_6-DMSO, 298 K) of **6f**.

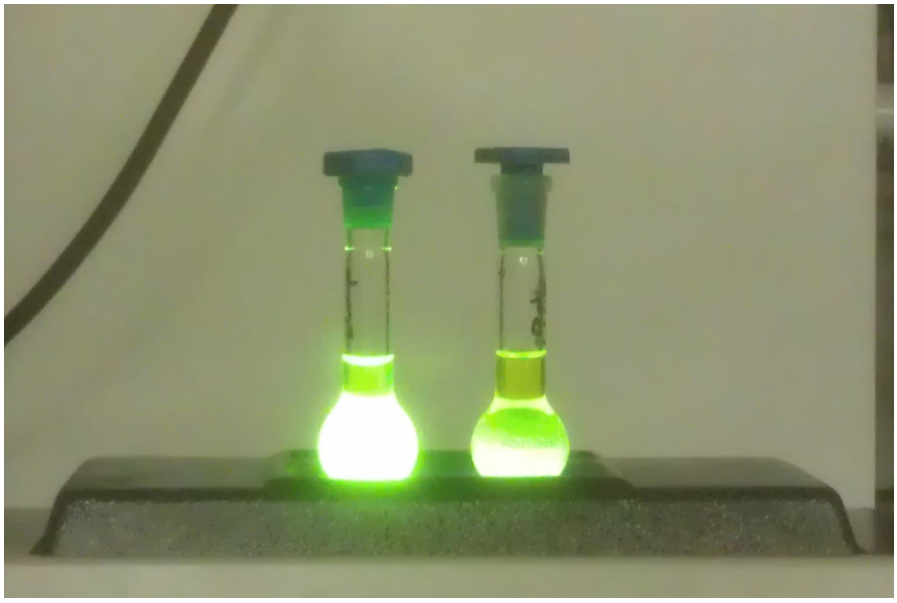
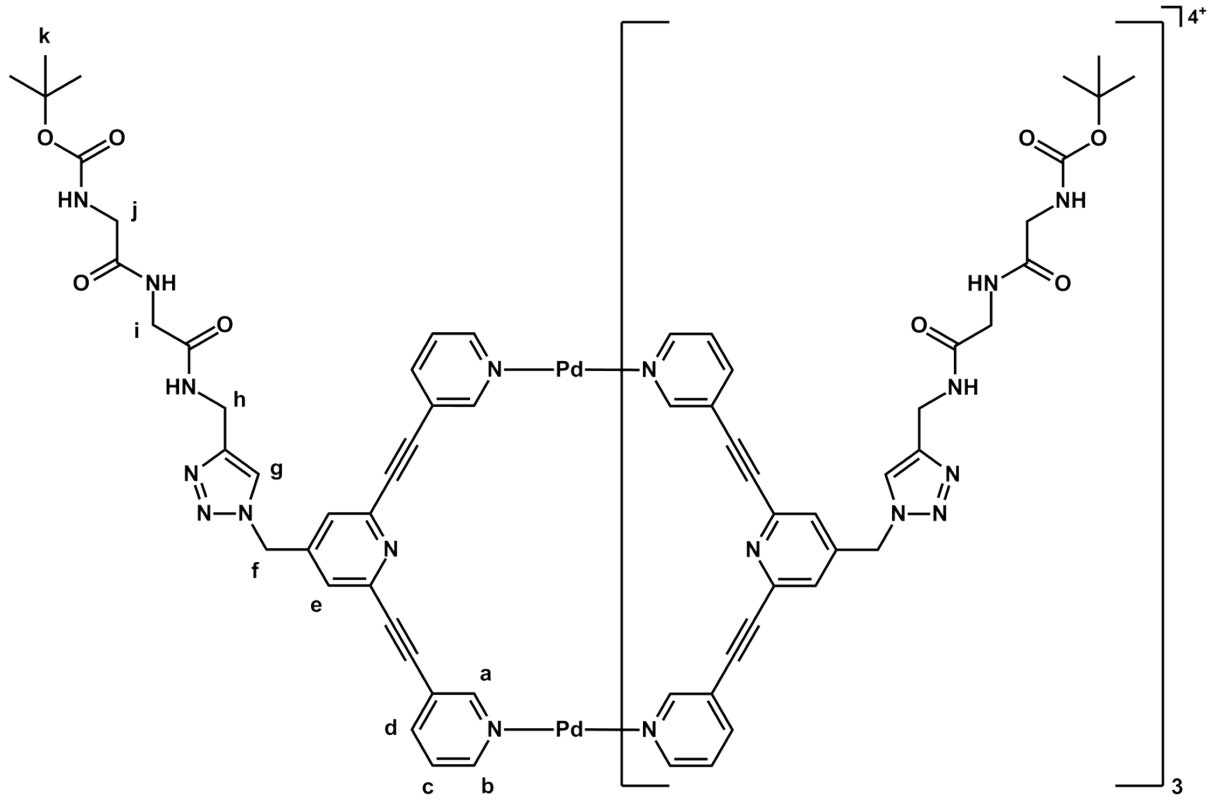


Figure 37 Photograph of fluorescing DMSO solutions of **5f** (left) and **6f** (right) upon excitation with UV light (λ_{ex} = 345 nm).

1.20 Synthesis of $[Pd_2(5g)_4](BF_4)_4$ (6g)



5g (61 mg, 0.10 mmol, 2 eq.) and $[Pd(CH_3CN)_4](BF_4)_2$ (22 mg, 0.05 mmol, 1 eq.) were stirred in DMF (3 mL) at room temperature for 1 h. After filtering through celite the solution was left for vapour diffusion of diethyl ether. The resulting precipitate was isolated by filtration, washed with diethyl ether, and dried *in vacuo* to give the product as a light brown solid. Yield 69 mg (0.02 mmol, 92%). ^{1}H NMR (400 MHz, d_6-DMSO, 298 K) δ: 9.49 (s, 8H, H_a), 9.38 (d, J = 5.5 Hz, 8H, H_b), 8.34 (d, J = 8.1 Hz, 8H, H_d), 8.27 (t, J = 5.7 Hz, 4H, H_{NH}), 8.04-8.01 (m, 4H, H_{NH}), 8.01 (s, 4H, H_g), 7.85 (dd, J = 5.6, 8.2 Hz, 8H, H_d), 6.98 (t, J = 5.9 Hz, 4H, H_{NH}), 5.70 (s, 8H, H_f), 4.29 (d, J = 5.7 Hz, 8H, H_h), 3.66 (d, J = 5.8 Hz, 8H, H_{CH2}), 3.54 (d, J = 5.8 Hz, 8H, H_{CH2}), 1.31 (s, 36H, H_k). Diffusion coefficient (d_6-DMSO, 298 K) D: 0.74 × 10^{-10} m^2s^{-1}. ^{13}C NMR (100 MHz, d_6-DMSO, 298 K) δ: 169.7, 168.8, 155.8, 153.4 (C_a), 151.2 (C_b), 147.2, 145.2, 143.6 (C_d), 142.2, 127.4 (C_c), 126.9 (C_e), 123.9 (C_g), 121.3, 92.8, 84.0, 78.1, 50.6 (C_f), 43.3, 41.9, 34.2 (C_h), 28.1 (C_k). IR (ATR): ν (cm^{-1}) 3066, 2978, 2930, 1653, 1594, 1523, 1484, 1387, 1366, 1247, 1164, 1048, 1023, 944, 815. HRESI-MS (DMSO/MeCN): *m/z* = 606.2565 $[LH]^+$ calc. 606.2572, 889.2607 $[Pd_2L_4Cl]^{3+}$ calc. 889.2592, 906.6048 $[Pd_2L_4(BF_4)]^{3+}$ calc. 906.6043, 1030.7626 $[Pd_2L_3Cl\text{-}H]^{2+}$ calc. 1030.7598, 1333.3892 $[Pd_2L_4Cl\text{-}H]^{2+}$ calc. 1333.3851. UV-Vis (DMSO, ε [$M^{-1}cm^{-1}$]): λ_{max} nm = 319 (8.54×10^4).

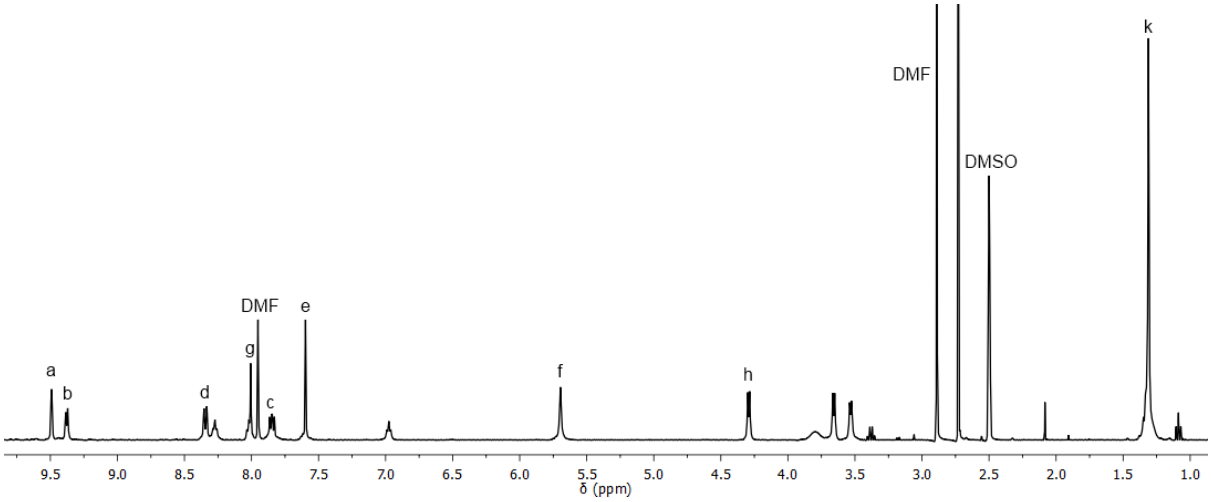


Figure 38 ^{1}H NMR spectrum (400 MHz, d_6-DMSO, 298 K) of **6g**.

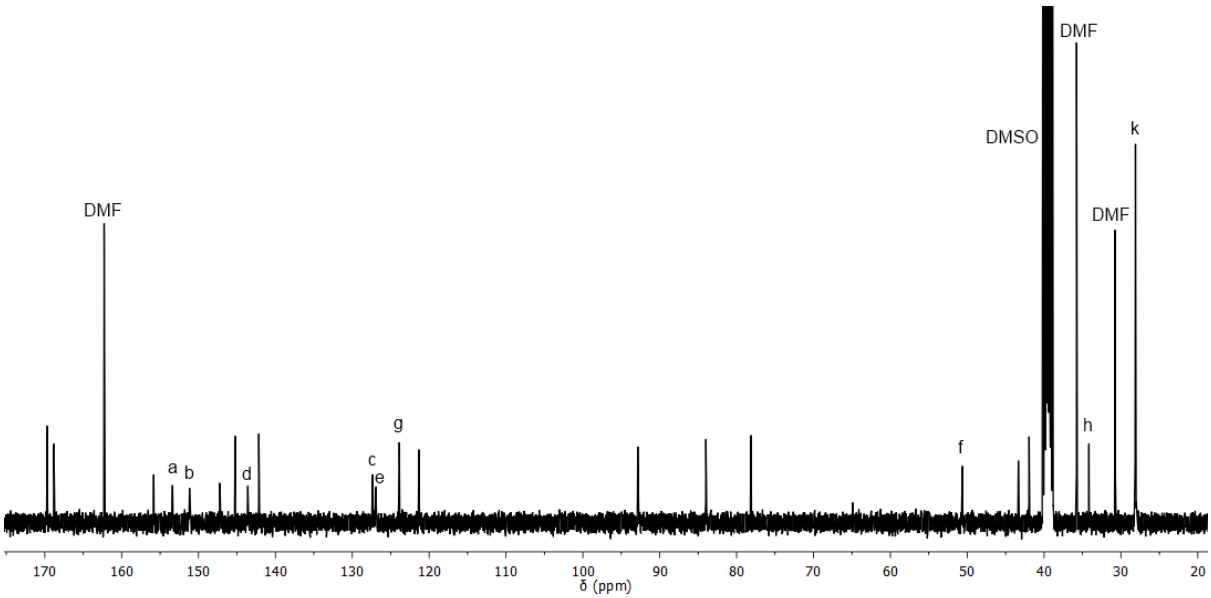
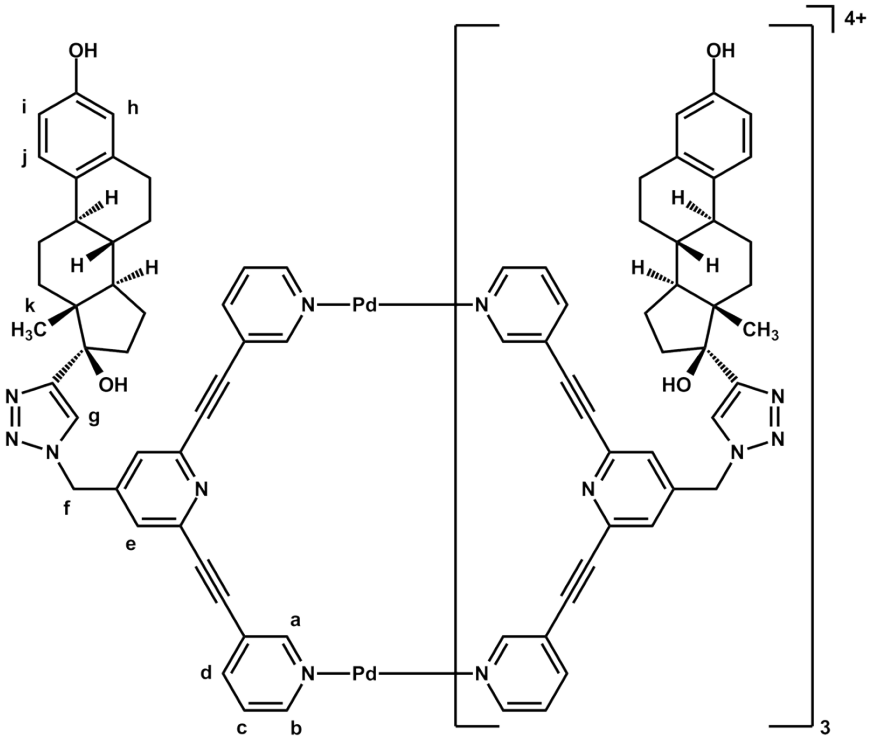


Figure 39 ^{13}C NMR spectrum (100 MHz, d_6-DMSO, 298 K) of **6g**.

1.21 Synthesis of $[Pd_2(5h)_4](BF_4)_4$ (6h)



5h (63 mg, 0.1 mmol, 2 eq.) and $[Pd(CH_3CN)_4](BF_4)_2$ (22 mg, 0.05 mmol, 1 eq.) were stirred in DMF (5 mL) for 1 h. The product was precipitated by vapour diffusion of diethyl ether, washed with further diethyl ether and dried *in vacuo* to give the product as a tan solid. Yield 62 mg (0.02 mmol, 81 %). ^{1}H NMR (400 MHz, d_6-DMSO, 298 K) δ: 9.45 (s, 8H, H_a), 9.35 (d, J = 5.5 Hz, 8H, H_b), 8.96 (br, 4H, H_{OH}), 8.23 (d, J = 8.1 Hz, 8H, H_d), 7.95 (s, 4H, H_g), 7.72 (dd, J = 6.5, 7.4 Hz, 8H, H_c), 7.51 (s, 8H, H_e), 6.69 (d, J = 8.6 Hz, 8H, H_i), 6.38 (d, J = 2.1 Hz, 4H, H_h), 6.15 (dd, J = 1.9, 8.3 Hz, 4H, H_j), 5.73 (s, 8H, H_f), 5.10 (br, 4H, H_{OH}), 2.72 – 2.59 (m, 8H), 2.38 – 2.31 (m, 4H), 2.01 – 1.88 (m, 8H), 1.83 – 1.70 (m, 12H), 1.59 – 1.14 (m, 24H), 0.89 (s, 12H, H_k), 0.58 – 0.51 (m, 4H). Diffusion coefficient (d_6-DMSO, 298 K) D: 0.68 × 10^{-10} m^2s^{-1}. ^{13}C NMR (125 MHz, d_6-DMSO, 298 K) δ: 154.8, 154.5, 153.3 (C_a), 151.1 (C_b), 147.8, 143.4 (C_d), 142.1, 137.1, 130.2, 127.2 (C_c), 126.6 (C_e), 125.7 (C_i), 123.7 (C_g), 121.2, 114.9 (C_h), 112.4 (C_j), 92.8, 83.9, 81.0, 50.6 (C_f), 47.5, 46.7, 43.2, 39.2, 36.9, 32.7, 29.1, 27.1, 26.1, 23.5, 14.2 (C_k). IR (ATR): ν (cm^{-1}) 3074, 2927, 2864, 1651, 1594, 1551, 1484, 1427, 1386, 1287, 1251, 1196, 1053, 816. HRESI-MS (DMSO/MeCN): *m/z* = 369.1173 $[PdL]^{2+}$ calc. 369.0969, 633.2915 $[LH]^+$ calc. 633.2973, 685.2400 $[Pd_2L_4]^{4+}$ calc. 685.2424, 913.3186 $[Pd_2L_4\text{-}H]^{3+}$ calc. 913.3208. UV-Vis (DMSO, ε [$M^{-1}cm^{-1}$]): λ_{max} nm = 315 (9.78×10^4).

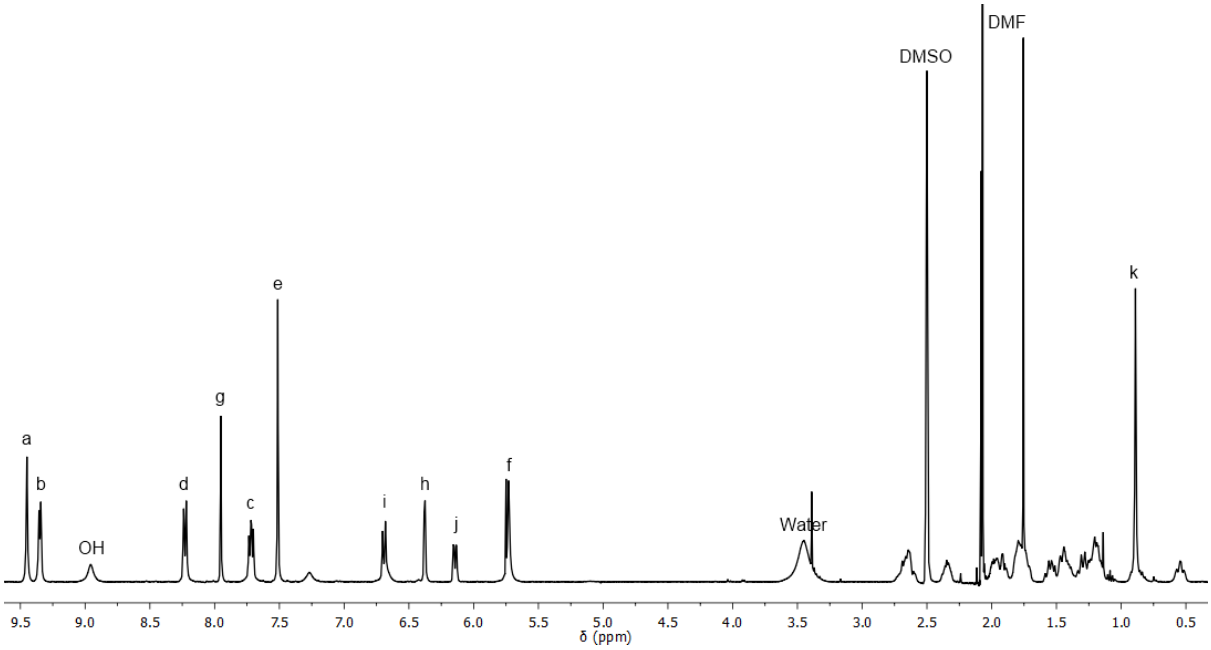


Figure 40 ^{1}H NMR spectrum (400 MHz, d_6-DMSO, 298 K) of **6h**.

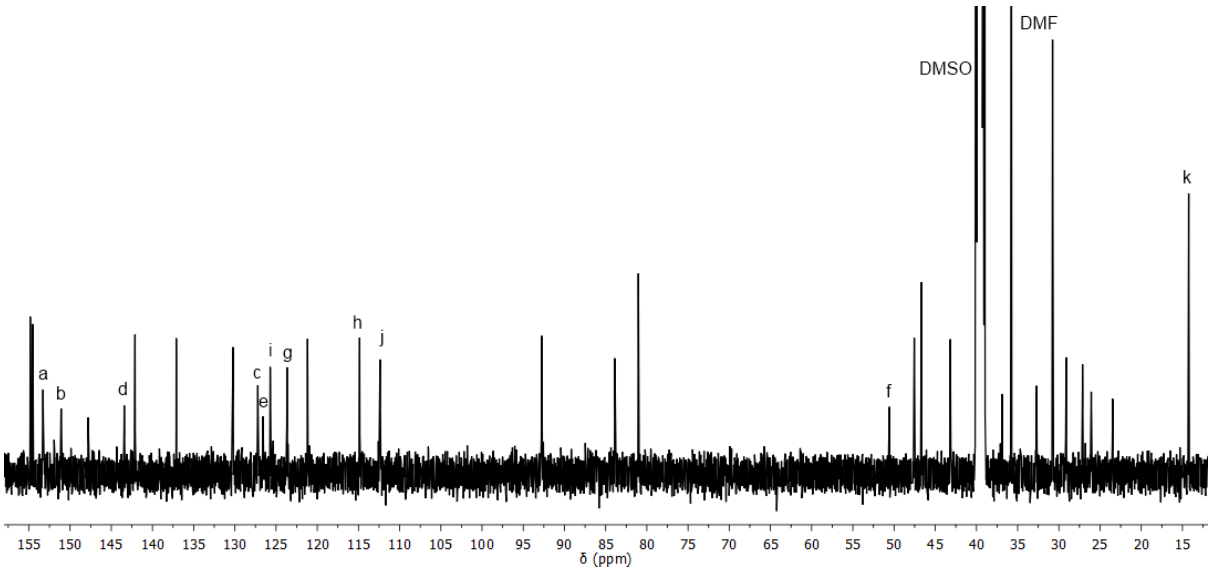
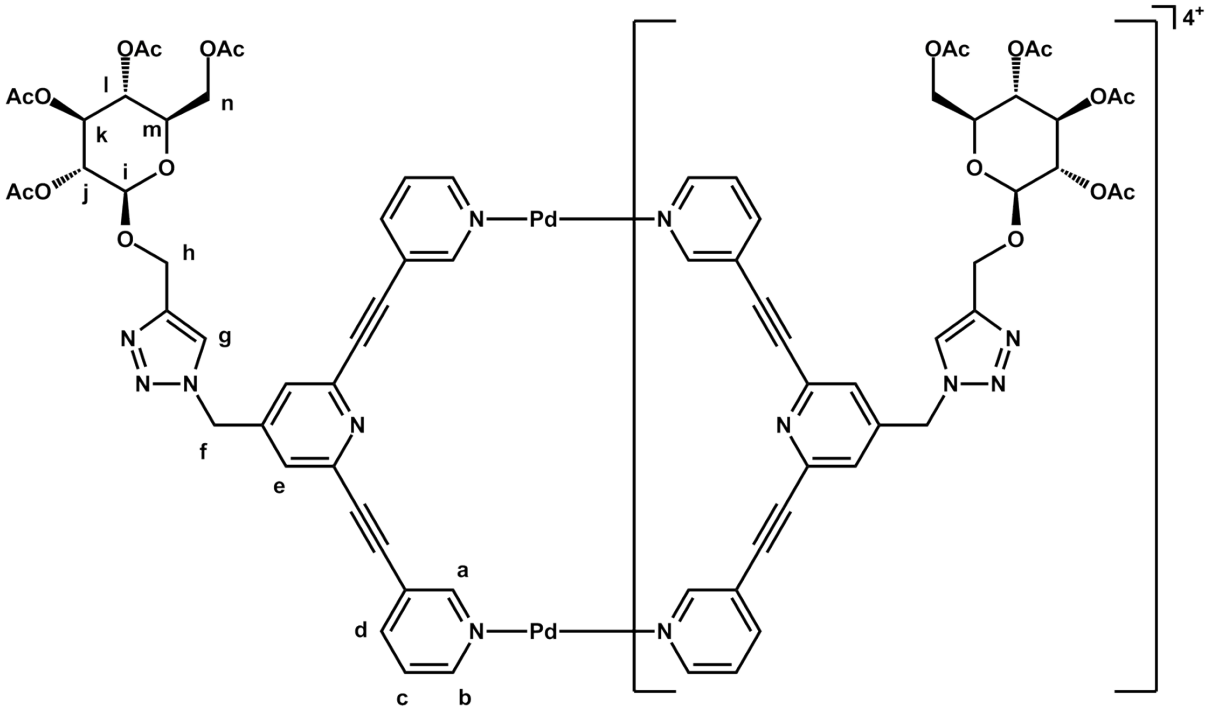


Figure 41 ^{13}C NMR spectrum (125 MHz, d_6-DMSO, 298 K) of **6h**.

1.22 Synthesis of $[Pd_2(5i)_4](BF_4)_4$ (6i)



A solution of $[Pd(CH_3CN)_4](BF_4)_2$ (19 mg, 0.04 mmol, 1 eq.) in DMF (1 mL) was added dropwise to a solution of **5i** (61 mg, 0.08 mmol, 2 eq.) in DMF (4 mL). The reaction was stirred at room temperature for 1 h, followed by vapour diffusion of diethyl ether to precipitate the product as a tan solid which was isolated by filtration and washed with diethyl ether. Yield 41 mg (0.01 mmol, 56%). ^{1}H NMR (400 MHz, d_6-DMSO, 298 K) δ: 9.49 (s, 8H, H_a), 9.39 (d, J = 5.7 Hz, 8H, H_b), 8.33 (d, J = 8.1 Hz, 8H, H_d), 8.17 (s, 4H, H_g), 7.86-7.83 (m, 8H, H_c), 7.60 (s, 8H, H_e), 5.74 (s, 8H, H_f), 5.23 (t, J = 6.9 Hz, 4H, H_k), 4.90-4.67 (m, 20H, H_h, H_i, H_j, H_l), 4.15 (dd, J = 4.9, 12.1 Hz, 4H, H_n), 4.01-3.95 (m, 8H, H_m, $H_{n'}$), 1.96 (s, 12H, H_{OAc}), 1.89 (s, 12H, H_{OAc}), 1.88 (s, 12H, H_{OAc}), 1.87 (s, 12H, H_{OAc}). Diffusion coefficient (d_6-DMSO, 298 K) D: 1.00 × 10^{-10} m^2s^{-1}. ^{13}C NMR (125 MHz, d_6-DMSO, 298 K) δ: 170.0, 169.5, 169.2, 168.9, 153.4 (C_a), 151.1 (C_b), 147.2, 145.2, 143.6 (C_d), 142.2, 127.3 (C_c), 126.8 (C_e), 125.2 (C_g), 121.4, 98.7 (C_i), 92.8, 83.9, 71.9 (C_k), 70.8 (C_j), 70.6 (C_m), 68.1 (C_l), 62.0 (C_h), 61.6 (C_n), 50.7 (C_f), 20.4, 20.3, 20.3, 20.2. IR (ATR): ν (cm^{-1}) 3077, 2939, 1747, 1656, 1595, 1552, 1484, 1427, 1376, 1220, 1165, 1033, 905, 815, 694, 659. HRESI-MS (DMF/MeCN): *m/z* = 775.2087 $[Pd_2L_4]^{4+}$ calc. 775.1861. UV-Vis (DMSO, ε [$M^{-1}cm^{-1}$]): λ_{max} nm = 314 (9.32 × 10^4).

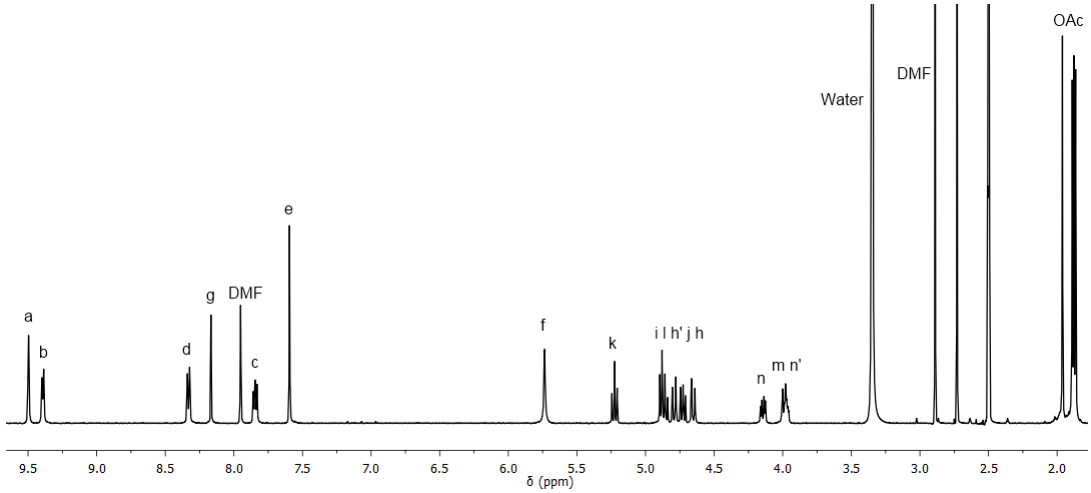


Figure 42 ^{1}H NMR spectrum (500 MHz, d_6-DMSO, 298 K) of **6i**.

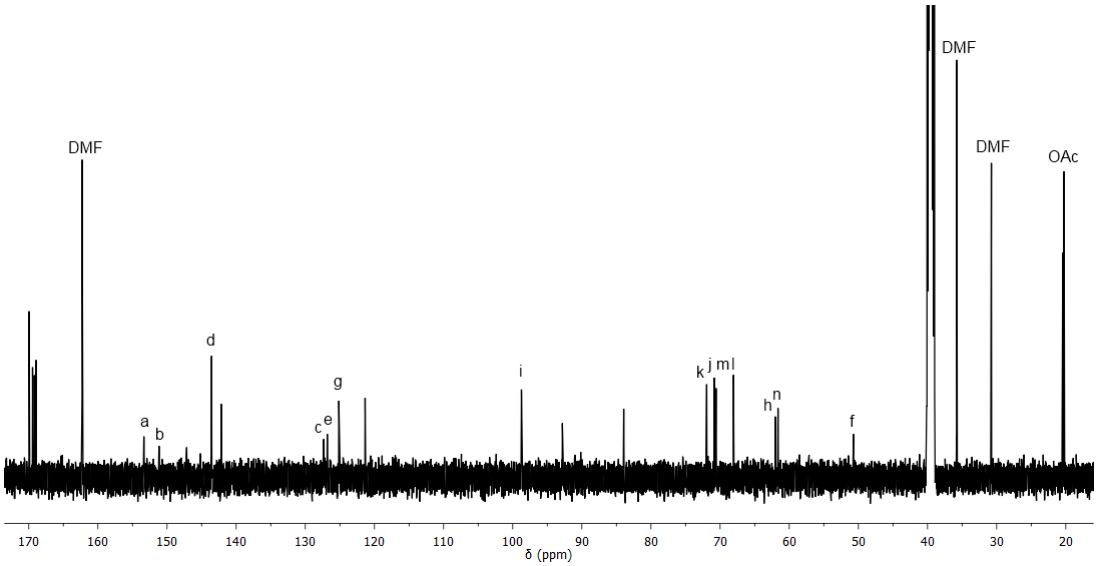
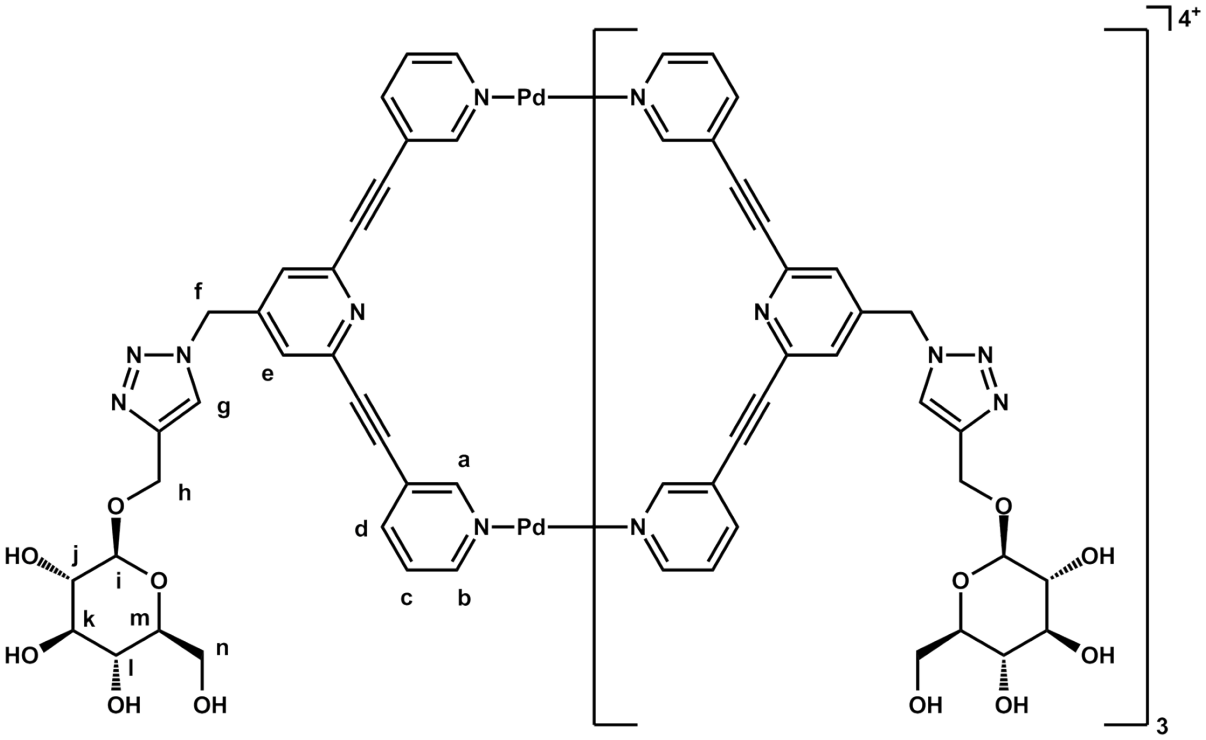


Figure 43 ^{13}C NMR spectrum (125 MHz, d_6-DMSO, 298 K) of **6i**.

1.23 Synthesis of $[Pd_2(5j)_4](X)_4$ (6j)



a) X = NO_3^-

5j (83 mg, 0.15 mmol, 2 eq.) and $[Pd(NO_3)_2(H_2O)_2]$ (20 mg, 0.08 mmol, 1 eq.) were stirred in DMF (5 mL) for 1 h. The product was precipitated as a white solid by vapour diffusion of diethyl ether. After filtration and washing with further diethyl ether, the product was dried *in vacuo*. Yield 93 mg (0.04 mmol, 93%). ^{1}H NMR (500 MHz, d_6-DMSO, 298 K) δ: 9.83 (s, 8H, H_a), 9.40 (d, J = 5.6 Hz, 8H, H_b), 8.33 (d, J = 8.0 Hz, 8H, H_d), 8.23 (s, 4H, H_g), 7.83-7.81 (m, 8H, H_c), 7.56 (s, 8H, H_e), 5.73 (s, 8H, H_f), 4.99 (d, J = 4.7 Hz, 4H, H_{OH}), 4.92-4.90 (m, 8H, H_{OH}), 4.84 (d, J = 12.3 Hz, 4H, H_h), 4.64 (d, J = 12.1 Hz, 4H, $H_{h'}$), 4.53-4.51 (m, 4H, H_{OH}), 4.24 (d, J = 7.6 Hz, 4H, H_i), 3.69-3.66 (m, 4H, H_n), 3.44-3.41 (m, 4H, $H_{n'}$), 3.13-3.09 (m, 8H, H_m, H_k), 3.04-2.90 (m, 4H, H_l), 2.96-2.92 (m, 4H, H_j). Diffusion coefficient (d_6-DMSO, 298 K) D: 0.75 × 10^{-10} m^2s^{-1}. ^{13}C NMR (125 MHz, d_6-DMSO, 298 K) δ: 153.6 (C_a), 151.1 (C_b), 146.9, 144.3, 143.5 (C_d), 142.3, 127.3 (C_c), 126.8 (C_e), 125.2 (C_g), 121.4, 102.1 (C_i), 92.9, 83.7, 76.9 (C_k/C_m), 76.7 (C_k/C_m), 73.3 (C_j), 70.1 (C_l), 61.4 (C_h), 61.1 (C_n), 50.7 (C_f). IR (ATR): ν (cm^{-1}) 3354, 2921, 2852, 1596, 1551, 1481, 1459, 1424, 1324, 1192, 1041, 806, 691, 453. HRESI-MS (DMSO/MeCN): *m/z* = 555.2073 $[LH]^+$ calc. 555.1987; 607.1603 $[Pd_2L_4]^{4+}$ calc. 607.1436; 809.2089 $[Pd_2L_4\text{-}H]^{3+}$ calc. 809.1890; 821.2033 $[Pd_2L_4Cl]^{3+}$ calc. 821.1811; 830.2078 $[Pd_2L_4NO_3]^{3+}$ calc. 830.1876. UV-Vis (DMSO, ε [$M^{-1}cm^{-1}$]): λ_{max} nm = 319 (1.08 × 10^5).

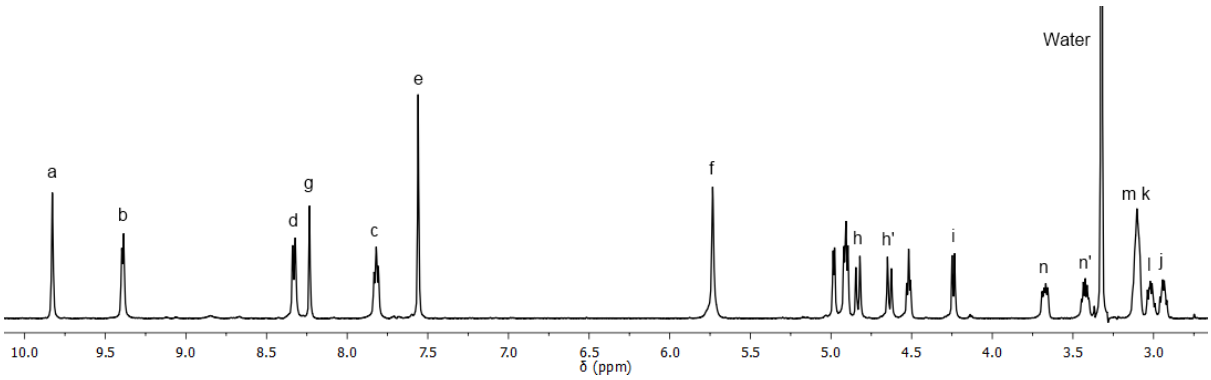


Figure 44 ^{1}H NMR spectrum (500 MHz, d_6-DMSO, 298 K) of **6j** (X = NO_3^-).

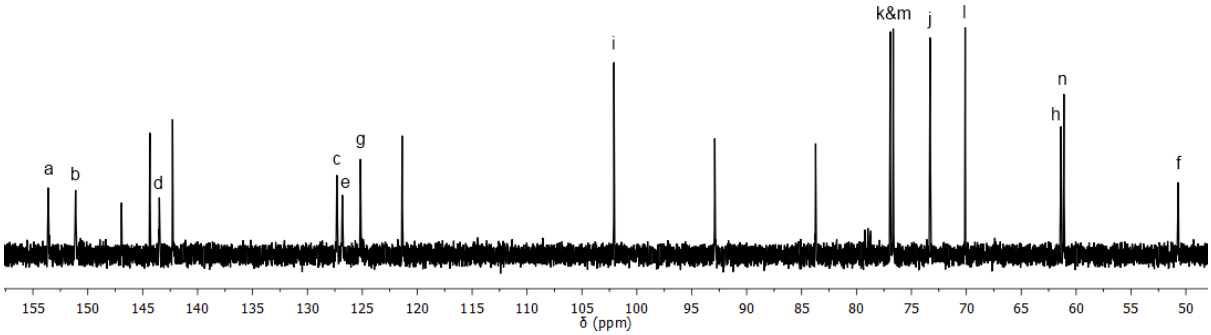


Figure 45 ^{13}C NMR spectrum (125 MHz, d_6-DMSO, 298 K) of **6j** (X = NO_3^-).

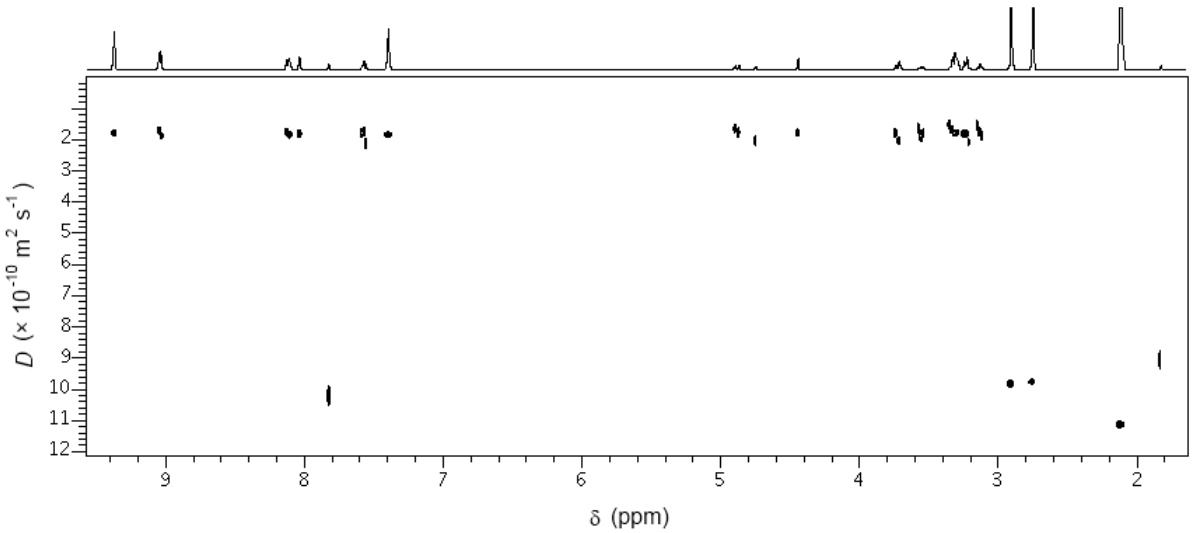


Figure 46 ^{1}H DOSY NMR spectrum (500 MHz, D_2O, 298 K) of **6j**.

b) X = BF_4^-

5j (25 mg, 0.05 mmol, 2 eq.) and $[Pd(CH_3CN)_4](BF_4)_2$ (10 mg, 0.02 mmol, 1 eq.) were stirred in DMF (3 mL) for 2 h. The product was precipitated as a white solid by vapour diffusion of diethyl ether. After filtration and washing with further diethyl ether, the product was dried *in vacuo*. Yield 23 mg (0.01 mmol, 74%). ^{1}H NMR (500 MHz, d_6-DMSO, 298 K) δ: 9.50 (s, 8H, H_a), 9.38 (d, J = 5.5 Hz, 8H, H_b), 8.35 (d, J = 7.7 Hz, 8H, H_d), 8.23 (s, 4H, H_g), 7.84 (dd, J = 5.5, 7.8 Hz, 8H, H_c), 7.60 (s, 8H, H_e), 5.73 (s, 8H, H_f), 4.83 (d, J = 12.4 Hz, 4H, H_h), 4.64 (d, J = 12.0 Hz, 4H, $H_{h'}$), 4.24 (d, J = 7.8 Hz, 4H, H_i), 3.68 (d, J

= 11.4 Hz, 4H, H_n), 3.44-3.41 (m, 4H, $H_{n'}$), 3.11-3.09 (m, 8H, H_k, H_m), 3.03-3.00 (m, 4H, H_l), 2.95-2.92 (m, 4H, H_j). Diffusion coefficient (d_6-DMSO, 298 K) D: 0.84 × 10^{-10} m^2s^{-1}. ^{13}C NMR (125 MHz, d_6-DMSO, 298 K) δ: 153.4 (C_a), 151.1 (C_b), 147.2, 144.3, 143.6 (C_d), 142.2, 127.4 (C_c), 126.8 (C_e), 125.2 (C_g), 121.3, 102.1, 92.8, 84.0, 76.9, 76.7, 73.3 (C_j), 70.1 (C_l), 61.4 (C_h), 61.1 (C_n), 50.7 (C_f).

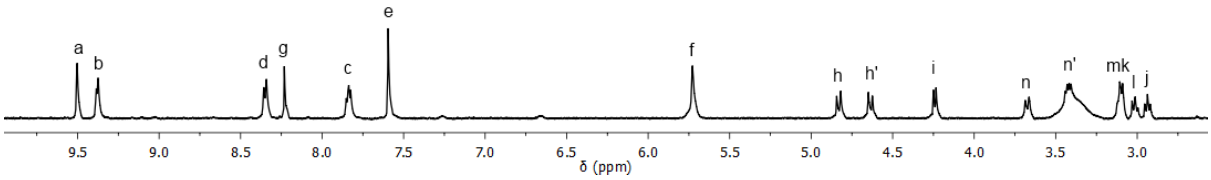


Figure 47 ^{1}H NMR spectrum (500 MHz, d_6-DMSO, 298 K) of **6j** (X = BF_4^-).

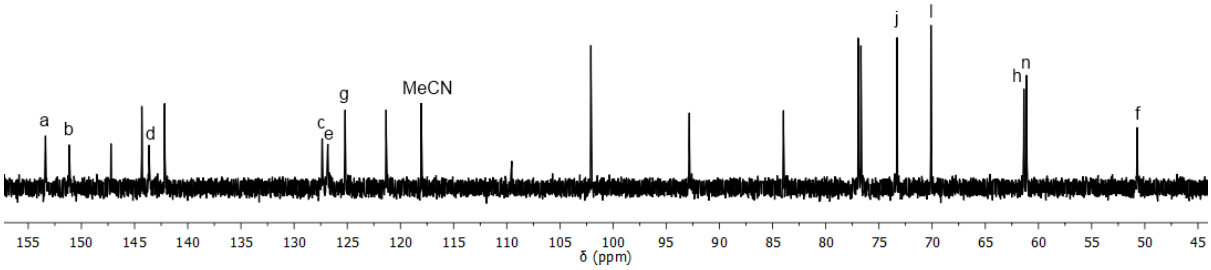
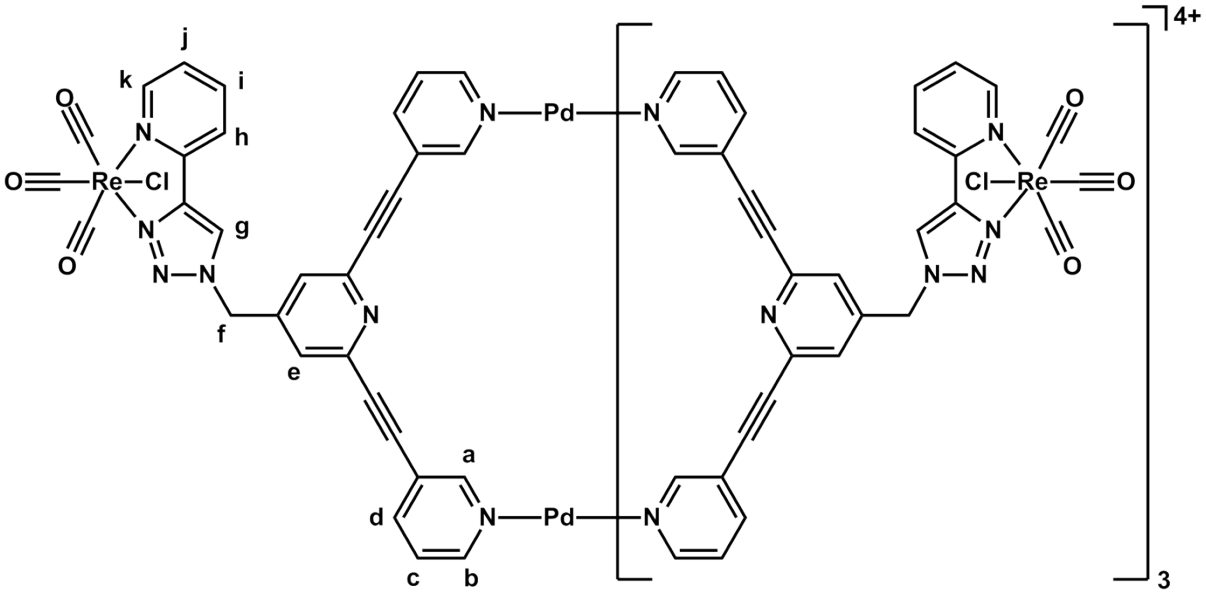


Figure 48 ^{13}C NMR spectrum (125 MHz, d_6-DMSO, 298 K) of **6j** (X = BF_4^-).

1.24 Synthesis of $[Pd_2(5k^{Re})_4](BF_4)_4$ ($6k^{Re}$)



To a solution of **$5k^{Re}$** (40 mg, 0.05 mmol, 2 eq.) in d_7-DMF (600 µL) was added a 368 mM solution of $[Pd(CH_3CN)_4](BF_4)_2$ in d_7-DMF (75 µL, 0.03 mmol, 1 eq.). Quantitative conversion to **$6k^{Re}$** was observed by ^{1}H NMR spectroscopy. Addition of diethyl ether precipitated the product as a tan solid which was washed with further diethyl ether (4 × 5 mL) and dried *in vacuo*. Yield 38 mg (0.01 mmol, 79%). ^{1}H NMR (500 MHz, d_6-DMSO, 298 K) δ: 9.51 (s, 8H, H_a), 9.35 (d, J = 5.7 Hz, 8H, H_b), 9.28 (s, 4H, H_g), 8.98 (d, J = 5.5 Hz, 4H, H_k), 8.27-8.25 (m, 16H, H_d, H_h, H_i), 7.84-7.81 (m, 8H, H_c), 7.67-7.64 (m, 12H, H_e, H_j), 6.04 (s, 8H, H_f). Diffusion coefficient (d_6-DMSO, 298 K) D: 0.84 × 10^{-10} m^2s^{-1}. ^{13}C NMR (125 MHz, d_6-DMSO, 298 K) δ: 197.5, 196.5, 189.4, 171.4, 153.4 (C_a), 153.1 (C_k), 151.2 (C_b), 148.6, 148.4, 145.7, 143.4, 142.4, 140.7, 127.3 (C_c), 126.9 (C_g), 126.7, 122.9, 121.2, 92.8, 84.3, 52.6 (C_f). IR (ATR): ν (cm^{-1}) 3080, 2929, 2020, 1880, 1656, 1593, 1553, 1484, 1457, 1427, 1388, 1330, 1286, 1243, 1196, 1052. HRESI-MS (DMSO/MeCN): *m/z* = 710.0938 $[L\text{-}Cl]^+$ calc. 710.0946, 827.3254 $[Pd_2L_3Cl]^{3+}$ calc. 827.3212, 1075.6852 $[Pd_2L_4Cl]^{3+}$ calc. 1075.6756, 1170.5560 $[PdL_3]^{2+}$ calc. 1170.5460, 1258.4788 $[Pd_2L_3Cl_2]^{2+}$ calc. 1258.4662, 1455.1638 $[L_2\text{-}Cl]^+$ calc. 1455.1582, 1491.1392 $[L_2H]^+$ calc. 1491.1347, 1631.0087 $[Pd_2L_4Cl_2]^{2+}$ calc. 1630.9978, 1657.0360 $[Pd_2L_4(BF_4)Cl]^{2+}$ calc. 1657.0156. UV-Vis (DMSO, ε [$M^{-1}cm^{-1}$]): λ_{max} nm = 350 (shoulder, 1.96 × 10^4), 319 (1.30 × 10^5).

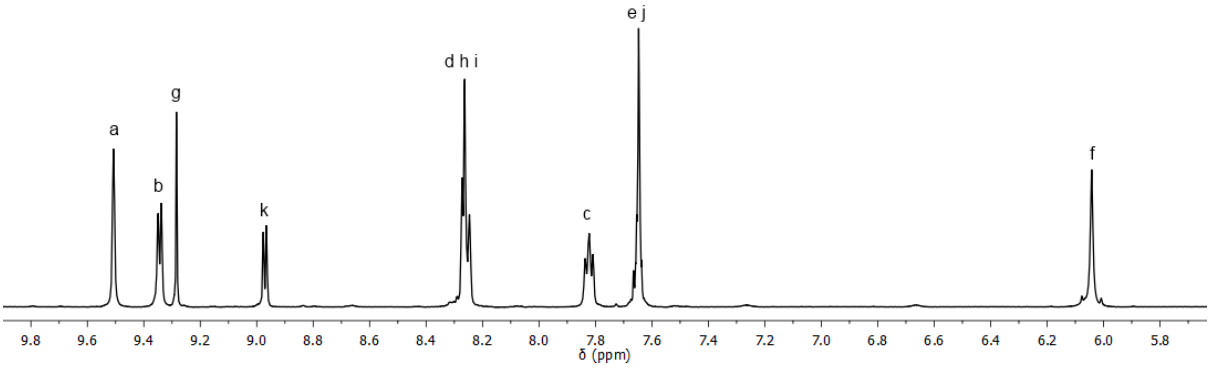


Figure 49 ^{1}H NMR (500 MHz, d_6-DMSO, 298 K) spectrum of **$6b^{Re}$**.

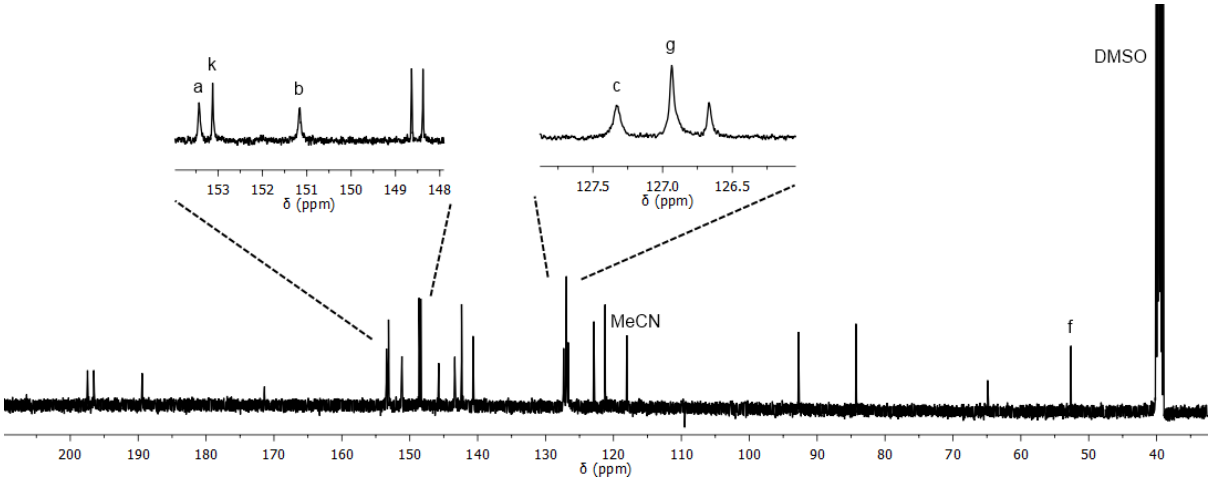


Figure 50 ^{13}C NMR (125 MHz, d_6-DMSO, 298 K) spectrum of **6k^{Re}**.

2 ^{1}H NMR data and proposed structure of 5k^{Pd} palladium(II) coordination polymer

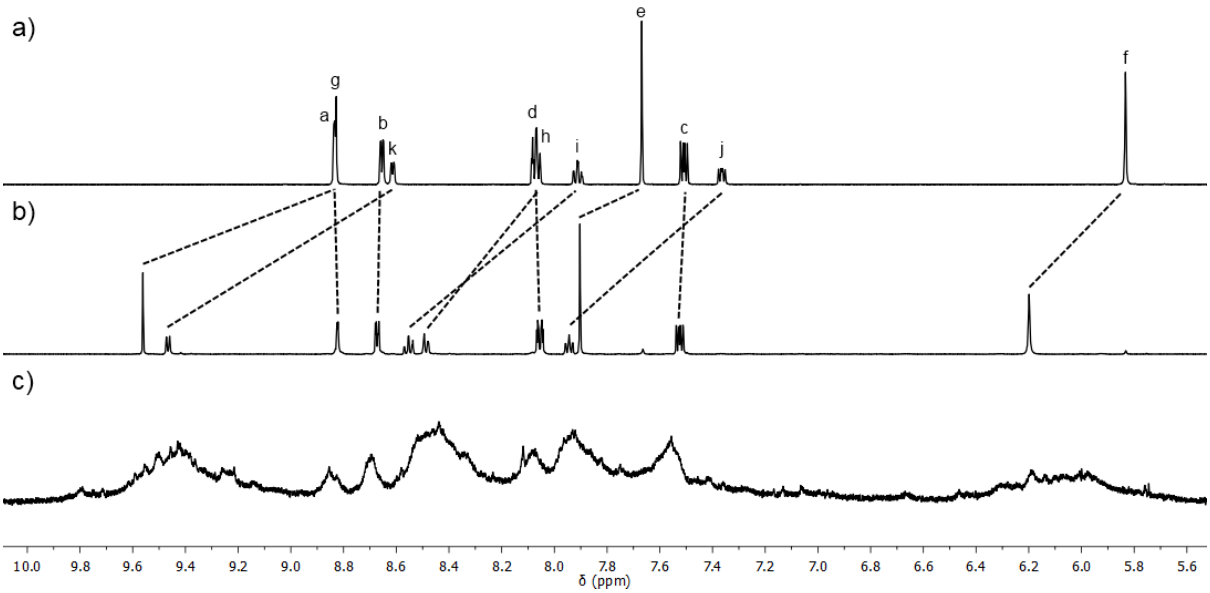


Figure 51 ^{1}H NMR (500 MHz, d_6-DMSO, 298 K) spectra of a) **5k**, b) **5k^{Pd}**, and c) **5k^{Pd}** upon addition of one equivalent of $[Pd(CH_3CN)_4](BF_4)_2$.

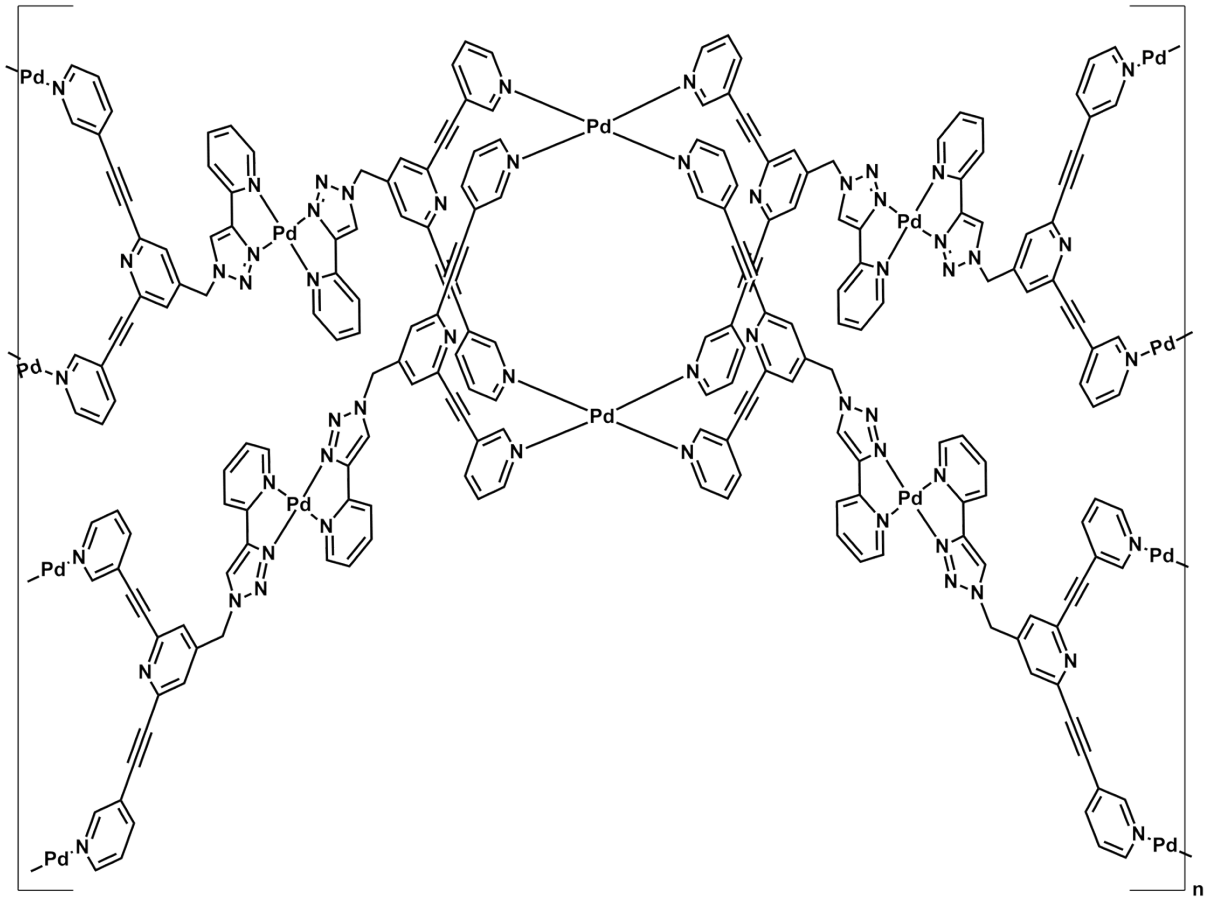


Figure 52 Proposed structure of the coordination polymer formed upon addition of one equivalent of $[Pd(CH_3CN)_4](BF_4)_2$ to **5k^{Pd}**.

3 Cisplatin Host-Guest NMR Spectra

3.1 6a⊃(cisplatin)$_2$

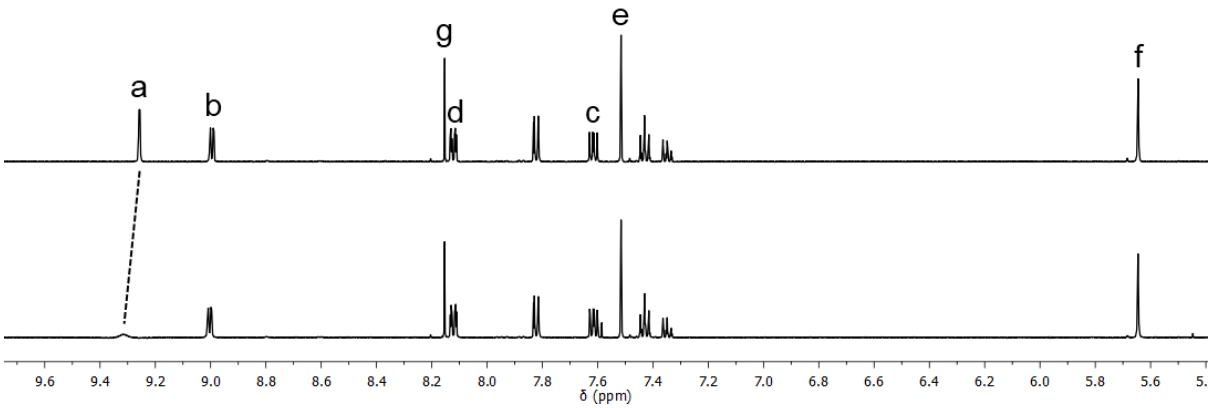


Figure 53 ^{1}H NMR spectra (400 MHz, CD_3CN) of **6a** (top) and **6a**⊃(cisplatin)$_2$ (bottom).

3.2 6b⊃(cisplatin)$_2$

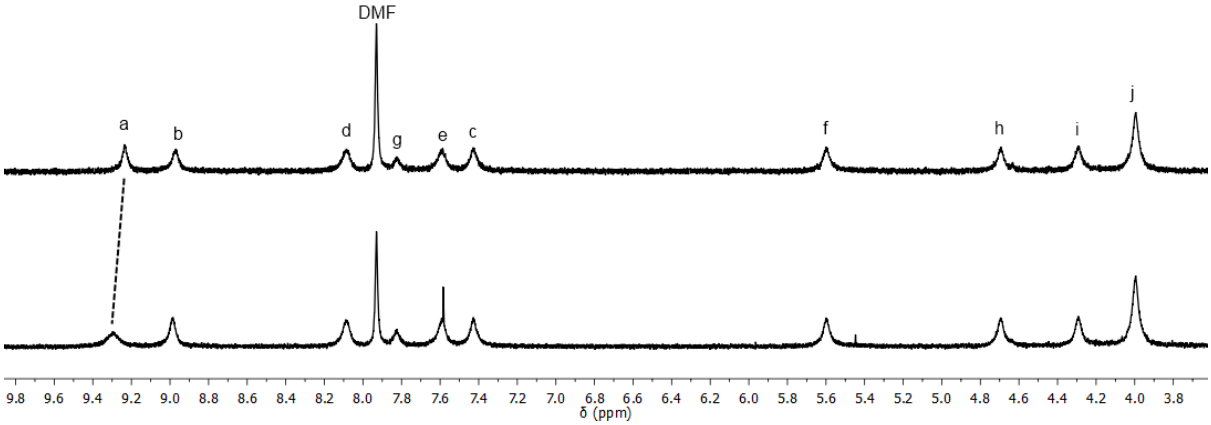


Figure 54 ^{1}H NMR spectra (400 MHz, CD_3CN) of **6b** (top) and **6b**⊃(cisplatin)$_2$ (bottom).

3.3 6d⊃(cisplatin)$_2$

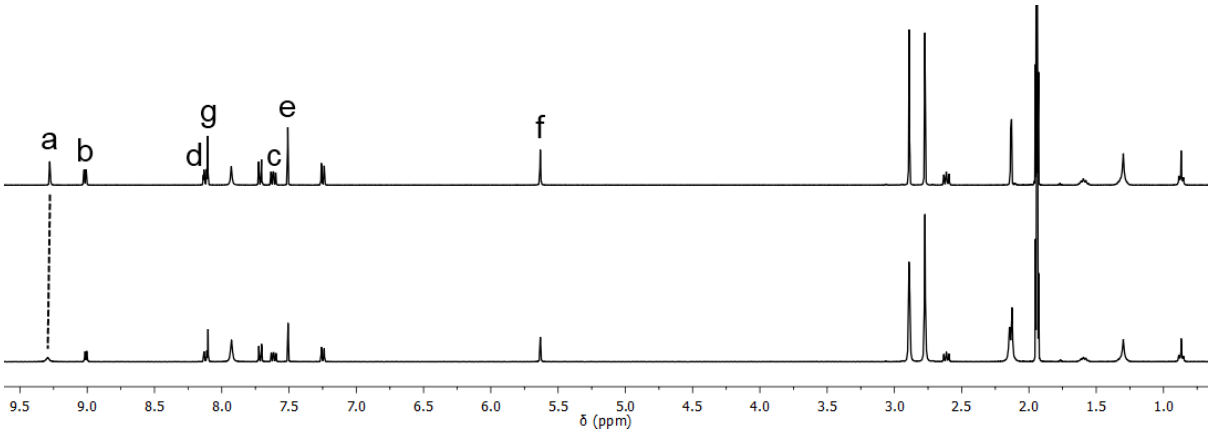


Figure 55 ^{1}H NMR spectra (400 MHz, CD_3CN) of **6d** (top) and **6d**⊃(cisplatin)$_2$ (bottom).

3.4 6e⊃(cisplatin)$_2$

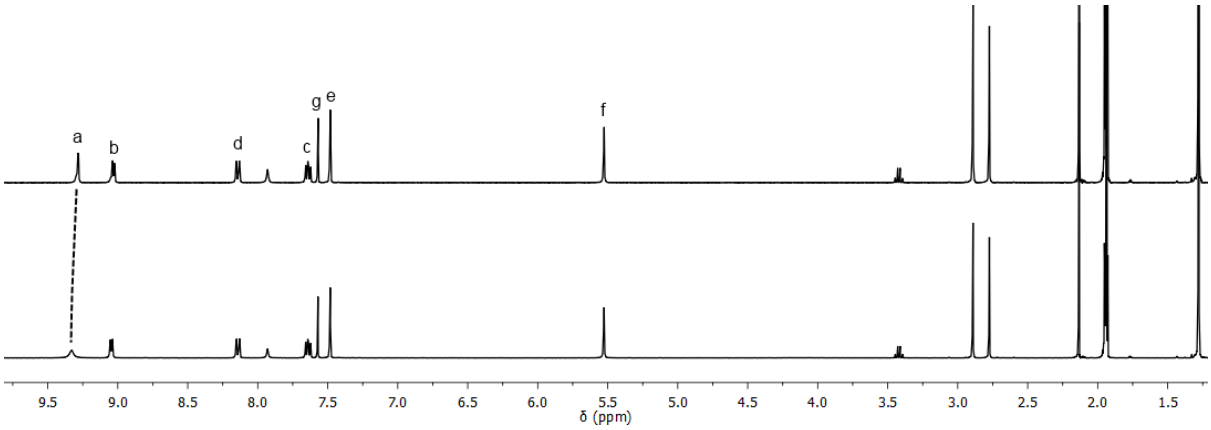


Figure 56 ^{1}H NMR spectra (400 MHz, CD_3CN) of **6e** (top) and **6e**⊃(cisplatin)$_2$ (bottom).

3.5 6i⊃(cisplatin)$_2$

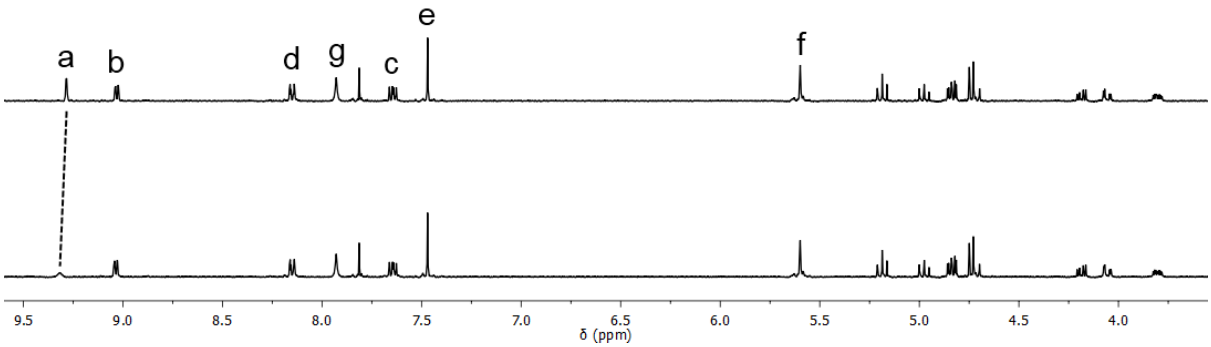


Figure 57 ^{1}H NMR spectra (400 MHz, CD_3CN) of **6i** (top) and **6i**⊃(cisplatin)$_2$ (bottom).

4 UV-Vis Data

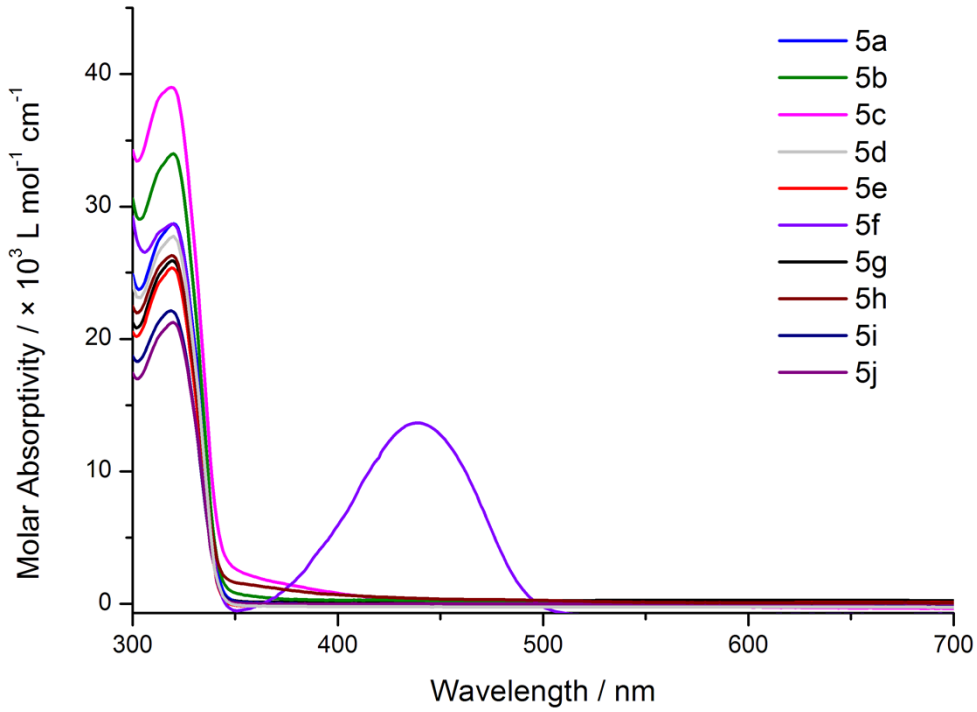


Figure 58 UV-Vis spectra (DMSO, 10^{-5} M, 298 K) of ligands **5a**-**5j**.

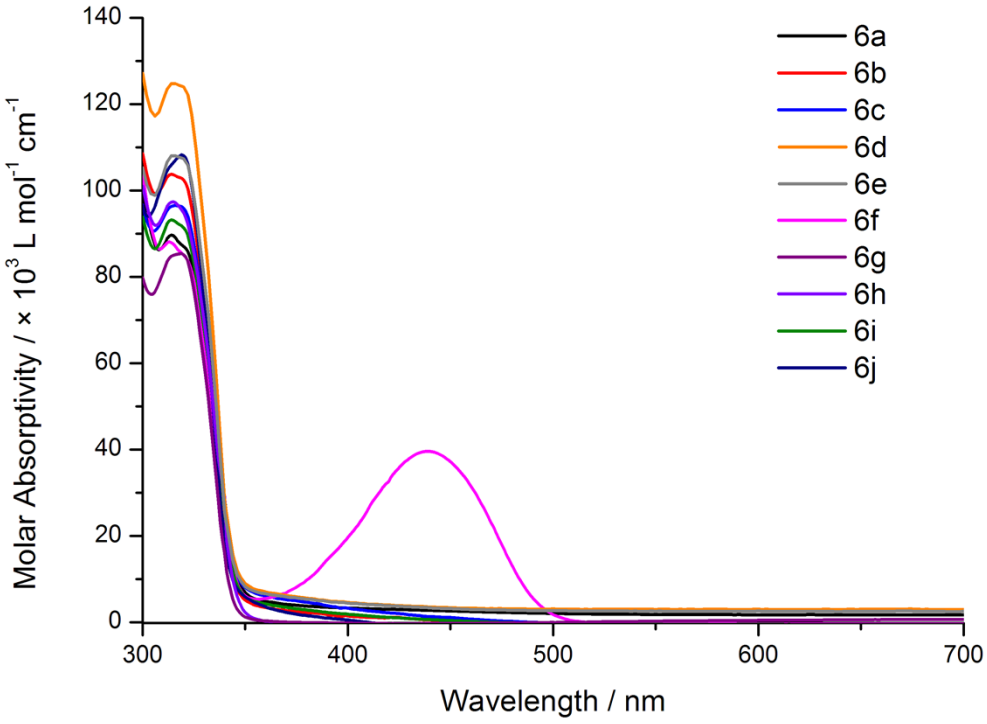


Figure 59 UV-Vis spectra (DMSO, 10^{-6} M, 298 K) of cages **6a**-**6j**.

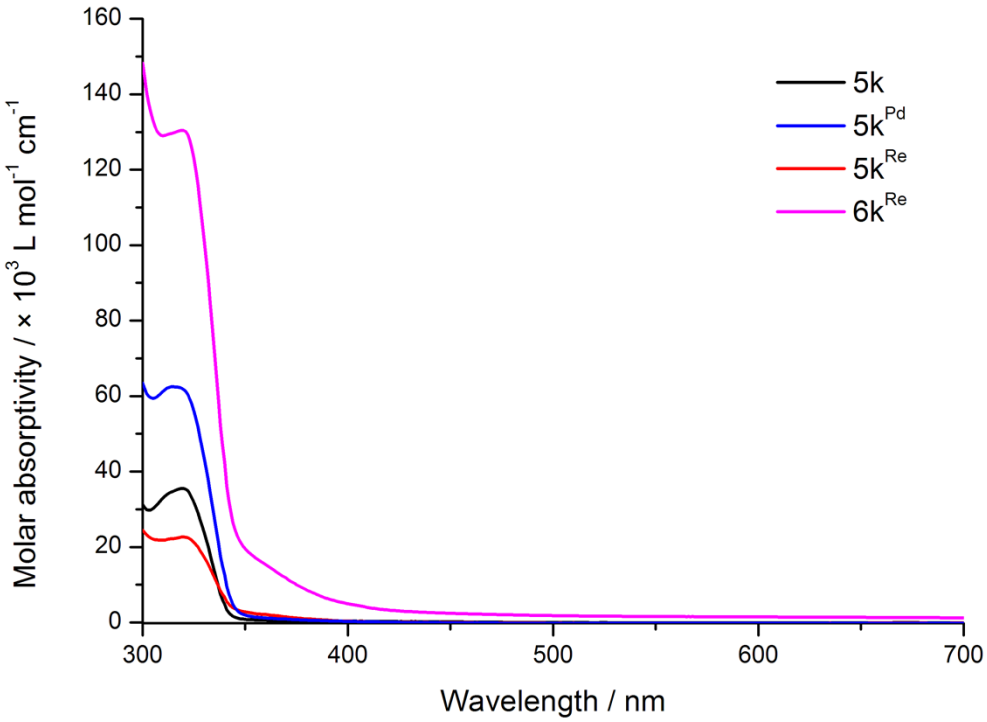


Figure 60 UV-Vis spectra (DMSO, 10^{-6} M, 298 K) of **5k**, **5k^{Pd}**, **5k^{Re}** and **6k^{Re}**.

Table 1 Absorption maxima and extinction coefficients for mononuclear complexes of **5k**.

Compound	λ_{max} / nm (ε / L mol^{-1} cm^{-1})
5k	319 (3.55×10^4)
5k^{Re}	320 (2.26×10^4)
5k^{Pd}	315 (6.25×10^4)
6k^{Re}	319 (1.30×10^5)

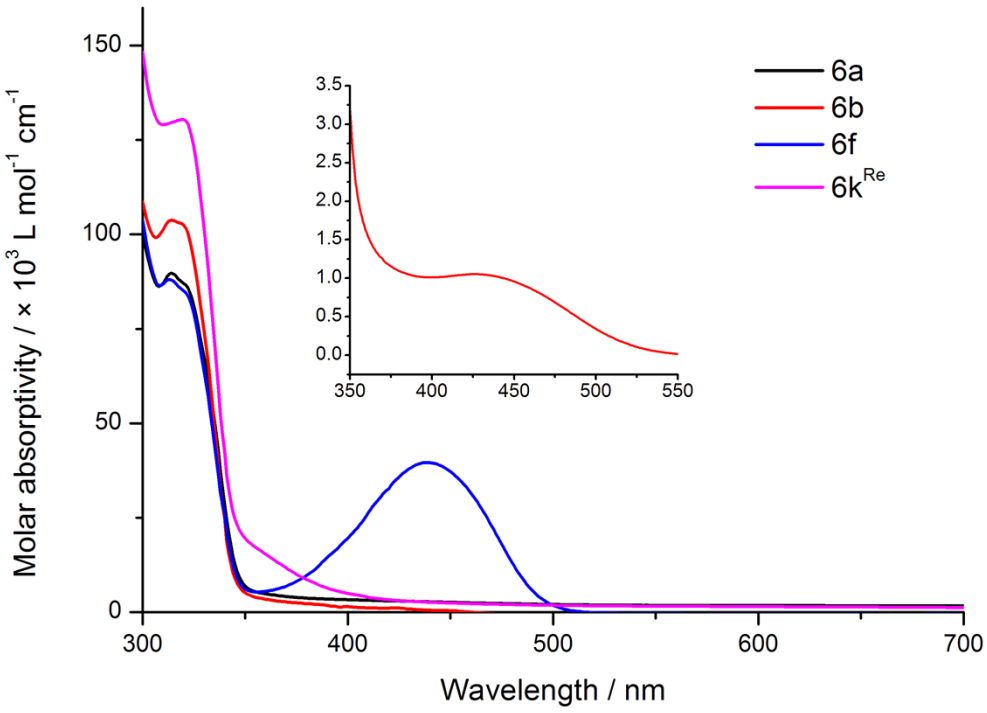


Figure 61 UV-Vis spectra (DMSO, 10^{-5} M, 298 K) of cages **6a**, **6b**, **6f**, and **6k^{Re}**.

5 Electrochemistry

5.1 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 electrode, Ag/AgCl reference and platinum wire auxiliary electrodes. The solution was ~10^{-3} M in electroactive material and contained 0.1 M Bu_4NPF_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 decamethylferrocene $[Fc^*]^{+/0}$ process.[4] Under the same conditions, E° calculated for $[FcH]^{+/0}$ was 0.48 V.[5]

5.2 Cyclic Voltammograms

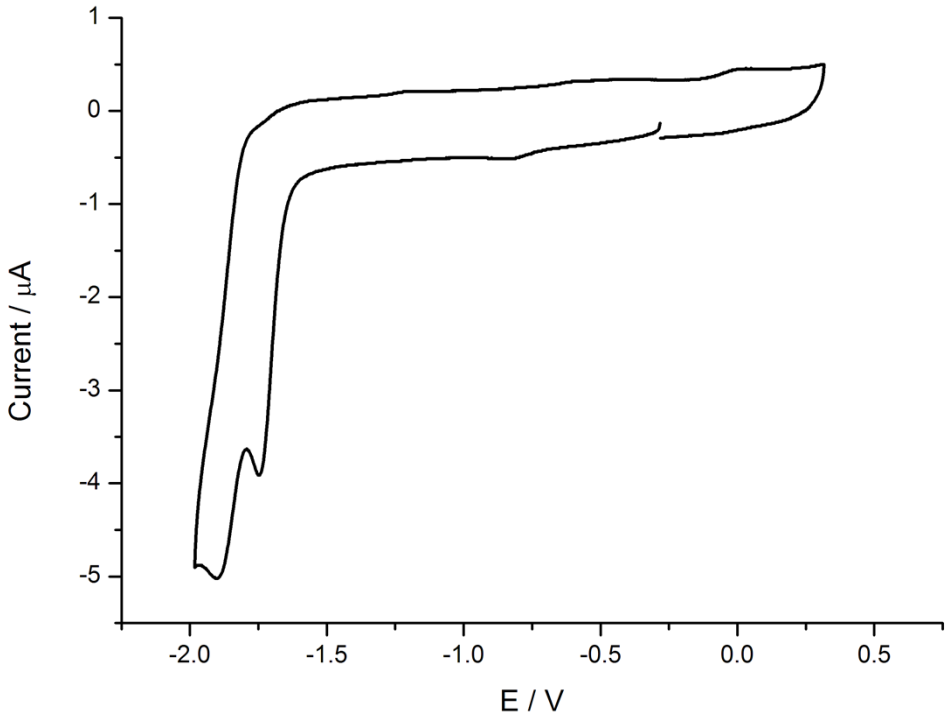


Figure 62 Cyclic voltammogram of **5a**.

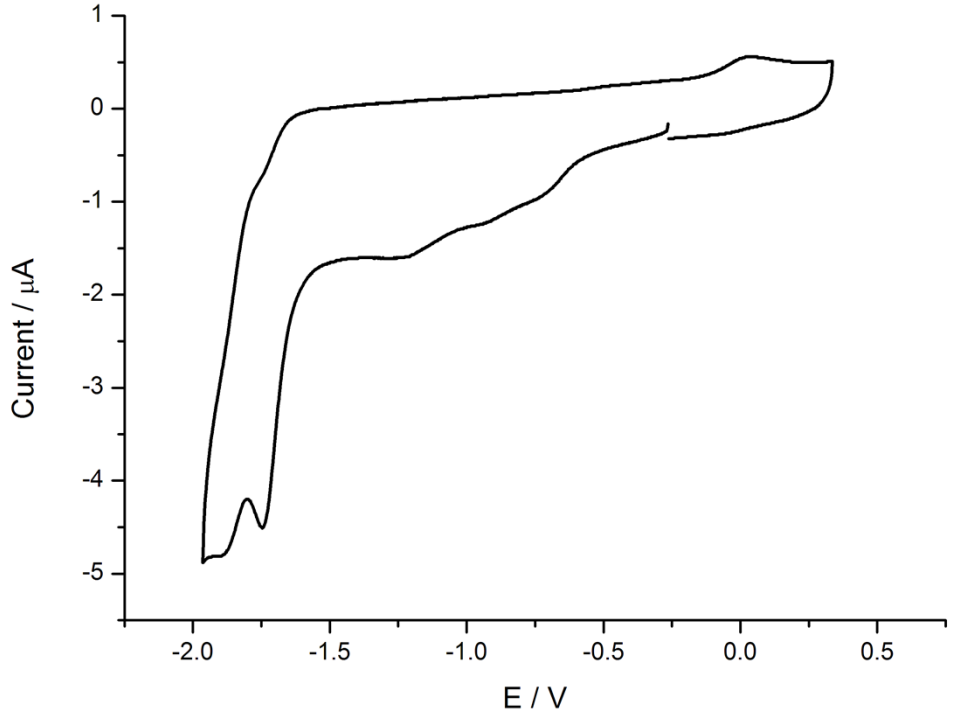


Figure 63 Cyclic voltammogram of **6a**.

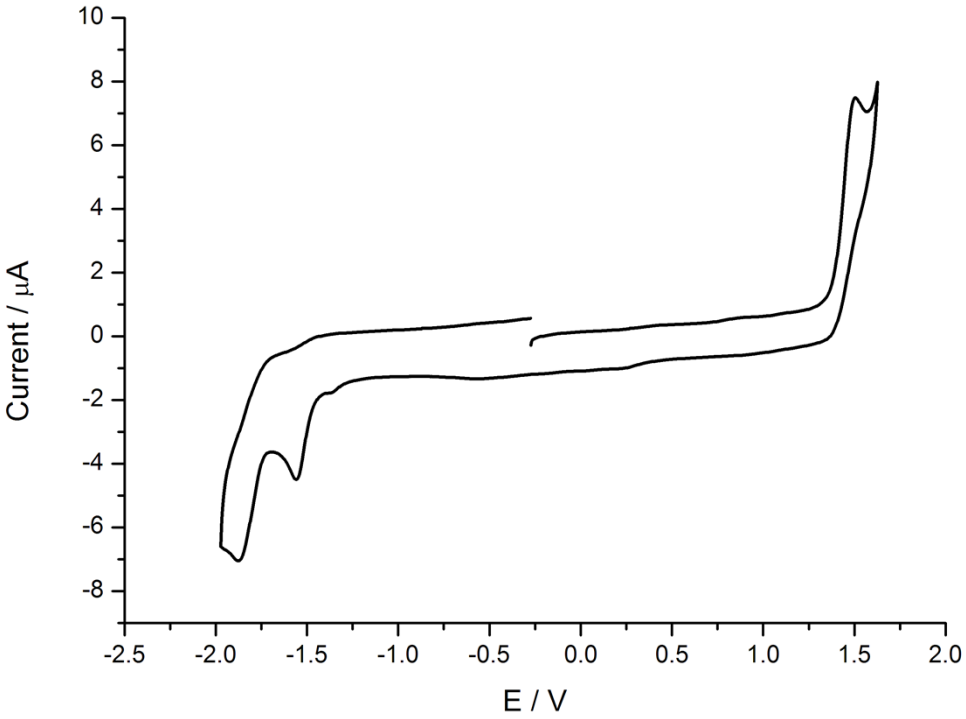


Figure 64 Cyclic voltammogram of **5k**^{Re}.

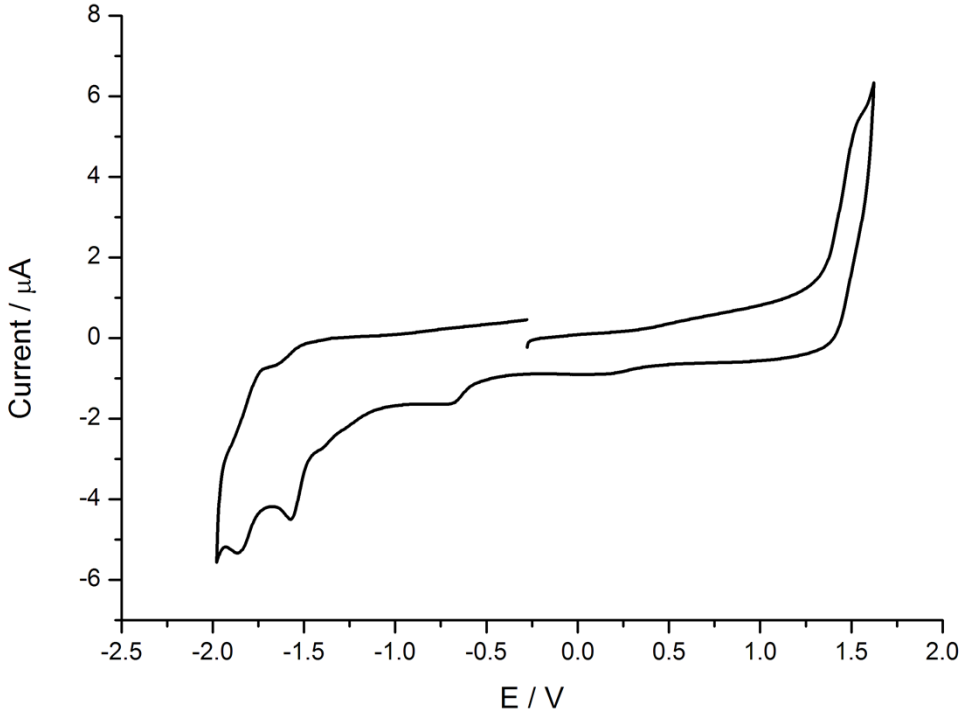


Figure 65 Cyclic voltammogram of **6k**^{Re}.

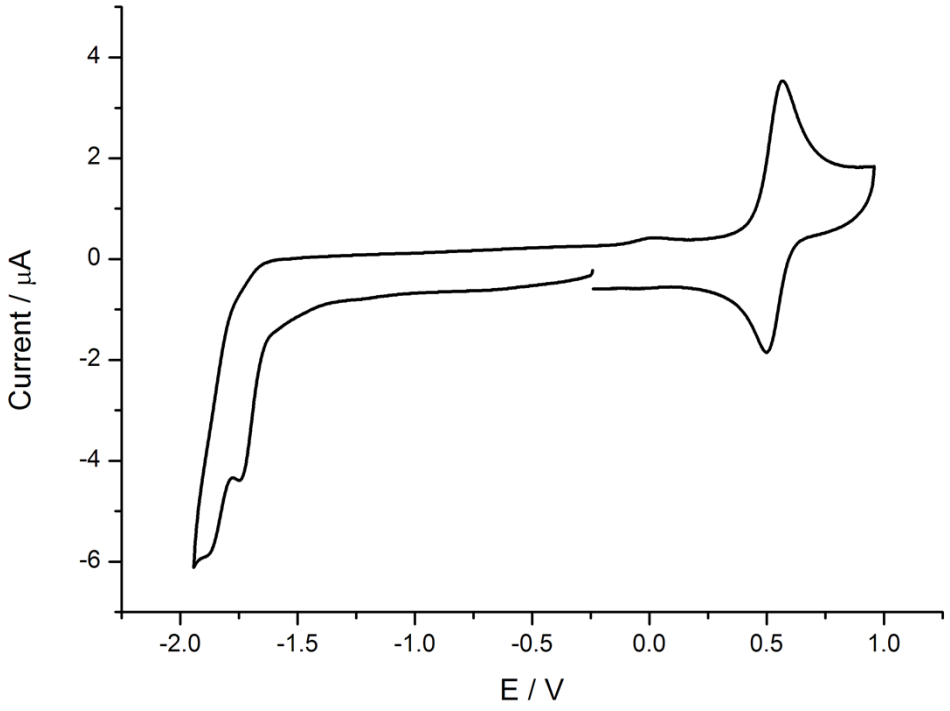


Figure 66 Cyclic voltammogram of **5b**.

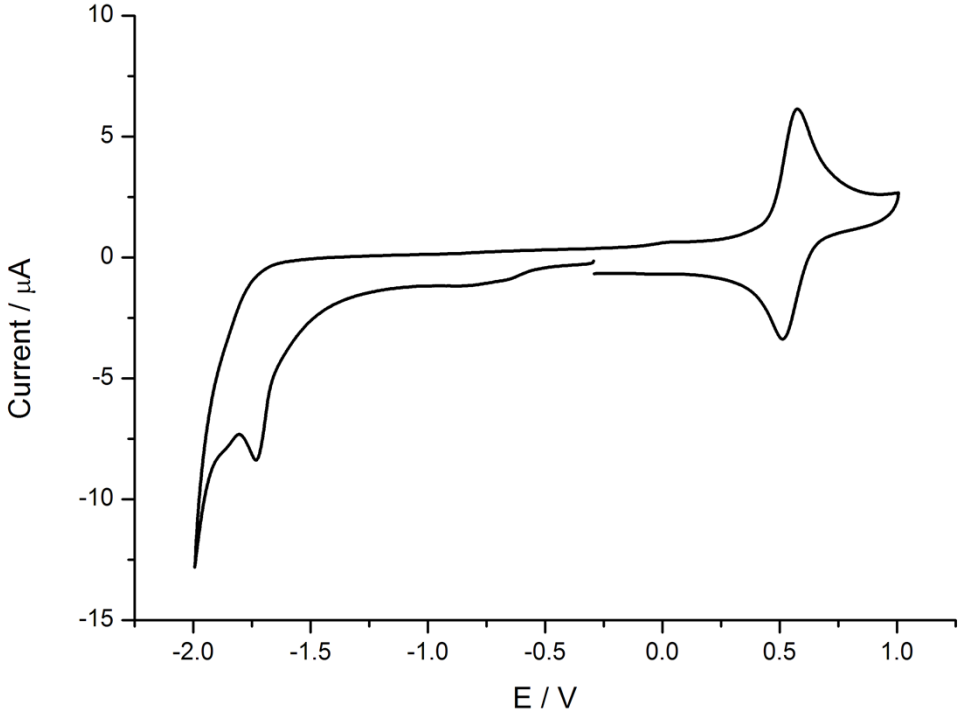


Figure 67 Cyclic voltammogram of **6b**.

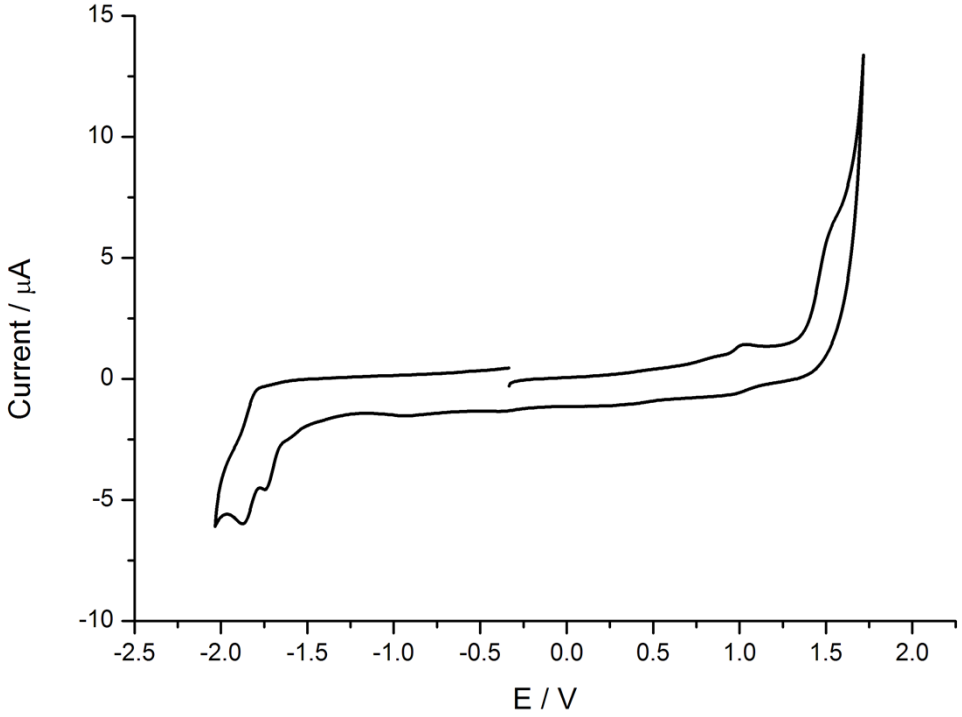


Figure 68 Cyclic voltammogram of **5c**.

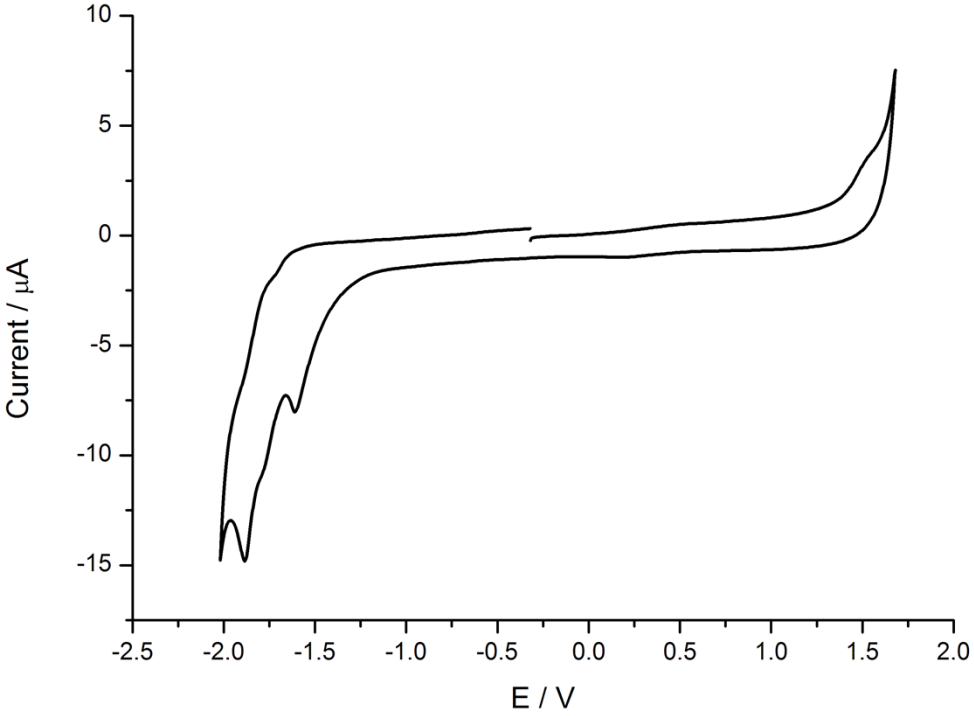


Figure 69 Cyclic voltammogram of **6c**.

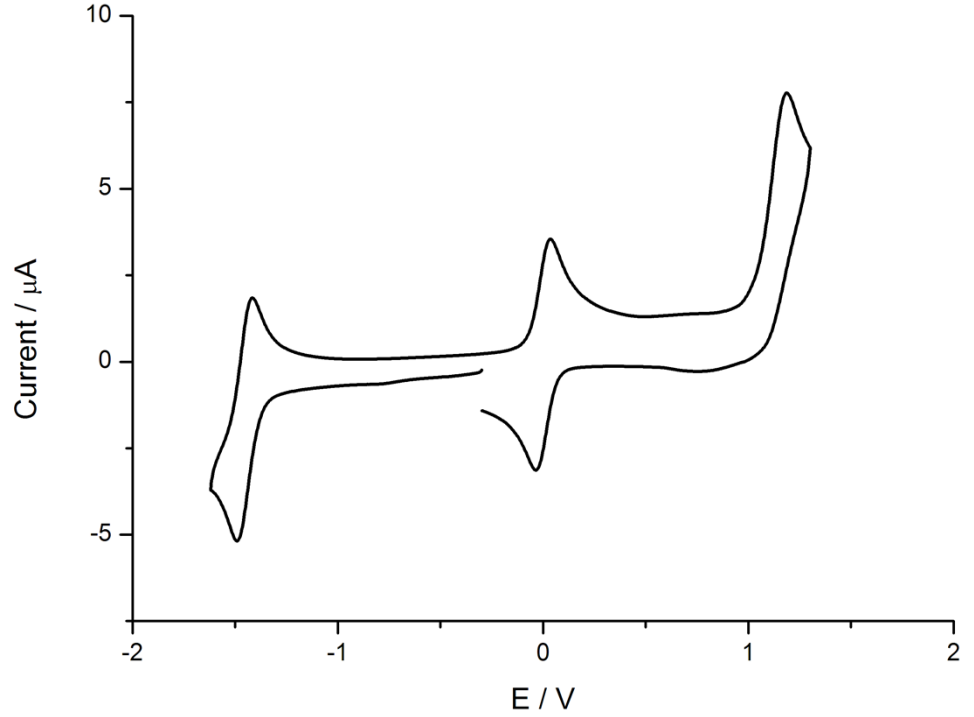


Figure 70 Cyclic voltammogram of **5f**.

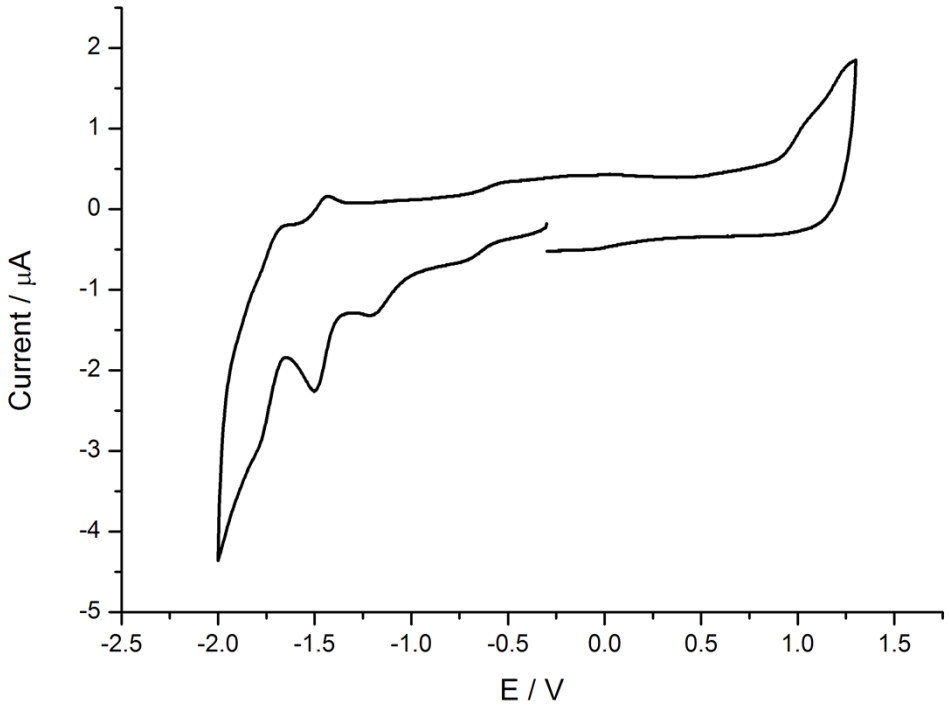


Figure 71 Cyclic voltammogram of **6f**.

6 Emission Spectroscopy

The experimental setup utilised to obtain emission spectra is similar to that described in detail elsewhere for collection of resonance Raman spectra .[6, 7] Briefly, a 135° back-scattering configuration was used for the incident beam and collection lens to reduce self-absorption. The exciting laser wavelengths were provided by a Krypton ion laser, 337.0 nm (Innova I-302, Coherent, inc.) and solid state diode laser, 448.0 nm (Crystal Laser). Spectra were obtained at room temperature in DMF solutions of 10^{-5} M concentration. The spectrograph used was a Pixis 110 B CCD with a 300 groove mm^{-1} grating and an Acton 2150 spectrograph (Princeton Instruments). Winspec/32 (Roper Scientific, New Jersey) software was used to collect the spectra traces.

Fluorescence quantum yields were calculated relative to a known standard, $ReCl(CO)_3$bipy, using the method described by Fery-Forgues *et al.* [8]

Excited state lifetimes were obtained from transient emission spectra acquired using 354.7 nm pulsed laser excitation from a Brilliant (Quantel) Nd:YAG operating at 10 Hz. Samples were dissolved in DMF at concentrations around 10^{-5} M and degassed (under argon) for 15 minutes directly before undertaking spectral measurements.

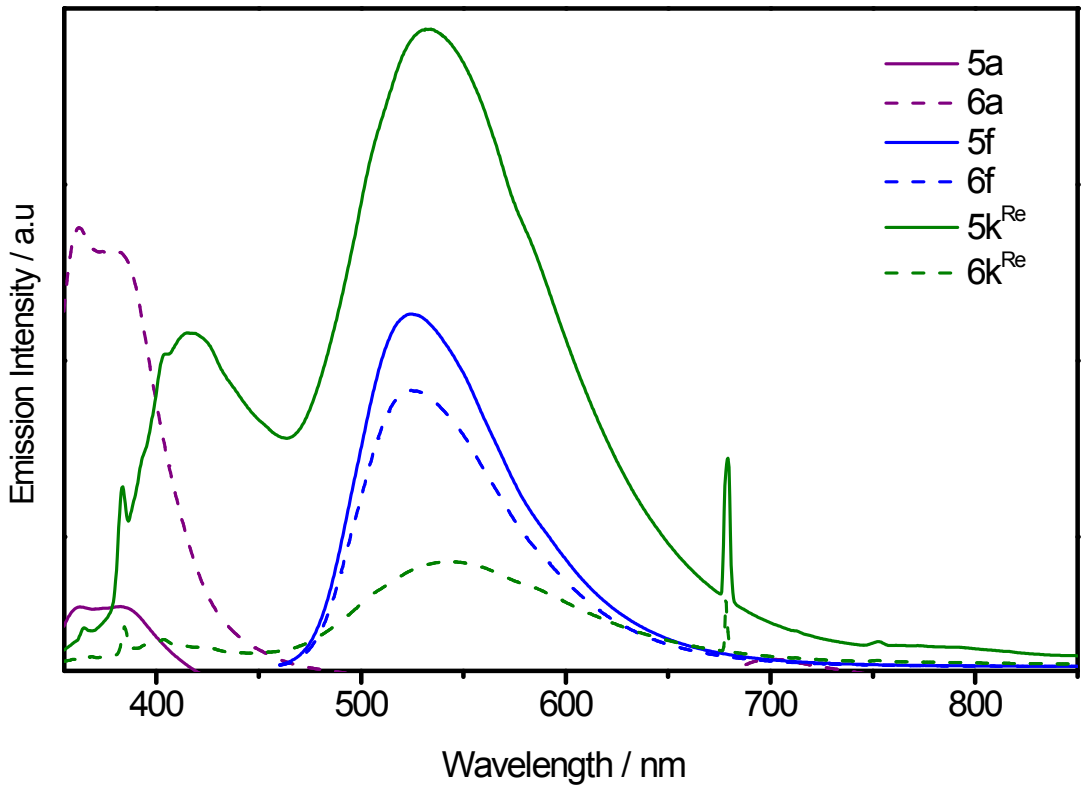


Figure 72 Emission spectra of ligands **5a**, **5f**, **5k^{Re}**, and cages **6a**, **6f**, and **6k^{Re}**.

7 X-ray Crystallography

7.1 General

X-ray data for **5b**, **5k^{Re}** and **5a^{Ag}** were collected at 89 K on a Bruker Kappa Apex II area detector diffractometer using monochromated Mo Kα radiation. The structures were all solved by direct methods and refined against F2 using anisotropic thermal displacement parameters for all non-hydrogen atoms using APEX II software. Hydrogen atoms were placed in calculated positions and refined using a riding model.

X-ray data for **5c** was collected at 100 K on an Agilent Technologies SuperNova diffractometer with Atlas detector using Cu Kα radiation. The structure was solved by SUPERFLIP[9] and refined against F_2 using anisotropic thermal displacement parameters for all non-hydrogen atoms, except where noted below, using SHELXTL 6.14 software. Hydrogen atoms were placed in calculated positions and refined using a riding model.

X-ray data for [**6b**⊃(cisplatin)$_2$]·**6b** was collected at -173 °C on crystals mounted on a Hampton Scientific cryoloop at the MX2 beamline of the Australian Synchrotron.[10] The structure was solved by direct methods and refined against F_2 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.

7.2 Crystal data and structure refinement for $5a^{Ag}$

Empirical formula	$C_{28}H_{18}AgF_6N_6Sb$	
Formula weight	782.10	
Temperature	89(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.1876(13) Å	α= 112.398(3)°.
	b = 12.2069(18) Å	β= 100.820(5)°.
	c = 12.521(2) Å	γ = 90.607(7)°.
Volume	1546.5(4) $Å^3$	
Z	2	
Density (calculated)	1.680 Mg/m^3	
Absorption coefficient	1.570 mm^{-1}	
F(000)	760	
Crystal size	0.34 × 0.30 × 0.11 mm^3	
Theta range for data collection	1.99 to 26.45°.	
Index ranges	-14<=h<=14, -15<=k<=15, -15<=l<=15	
Reflections collected	46689	
Independent reflections	6310 [R(int) = 0.0440]	
Completeness to theta = 26.45°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8463 and 0.6174	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6310 / 0 / 379	
Goodness-of-fit on F^2	1.082	
Final R indices [I>2sigma(I)]	R1 = 0.0292, wR2 = 0.0870	
R indices (all data)	R1 = 0.0340, wR2 = 0.0900	
Largest diff. peak and hole	1.772 and -1.174 $e.Å^{-3}$	

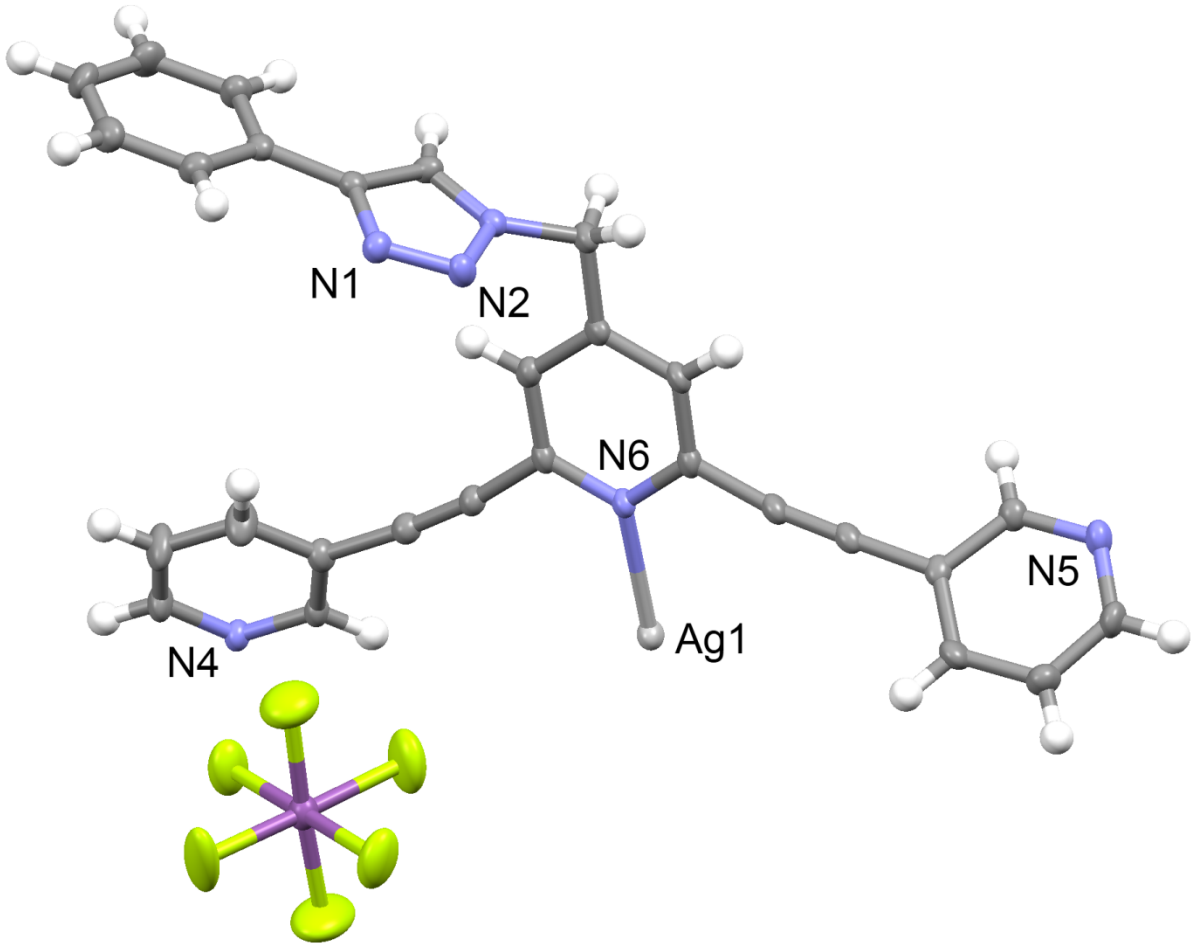


Figure 73 Ellipsoid plot of the asymmetric unit of **5a**^{Ag}. Ellipsoids are shown at the 50% probability level.

The crystal lattice for this coordination polymer contained a small amount of diffuse electron density that could not be appropriately modelled. The SQUEEZE routine within PLATON was employed to resolve this, giving a void electron count of 31 that was assigned to a disordered molecule of acetone (32 electrons).

SQUEEZE Results

Platon squeeze void average x	-0.041
Platon squeeze void average y	0.500
Platon squeeze void average z	1.000
Platon squeeze void volume	240.8
Platon squeeze void count electrons	31.2
Platon squeeze details	Disordered molecule of acetone that could not be effectively modelled.

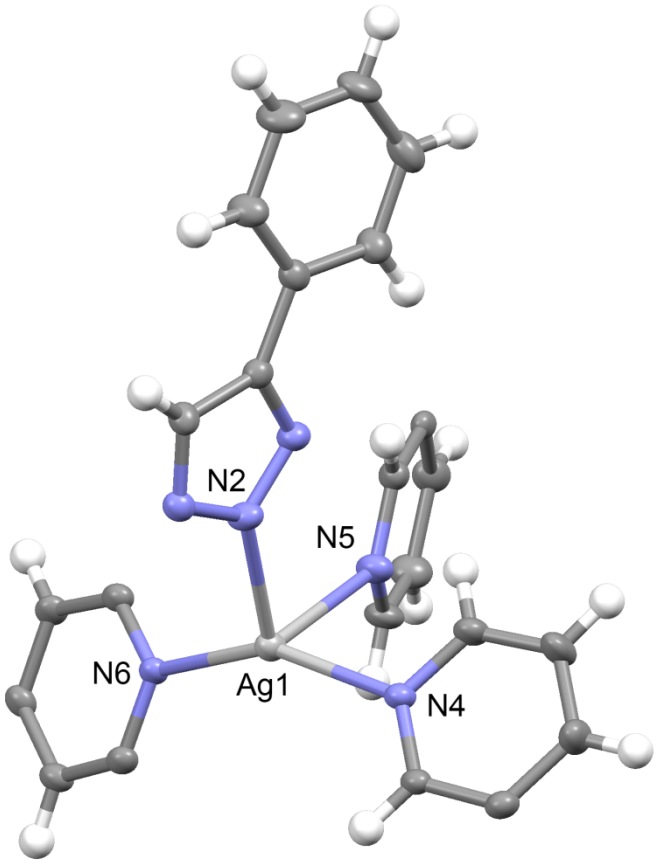


Figure 74 Ellipsoid plot showing the coordination environment of the silver(I) ions in the crystal structure of **5a^{Ag}**. Ellipsoids are shown at the 50% probability level. Bond lengths (Å): Ag1-N2 2.403(2), Ag1-N4 2.277(3), Ag1-N5 2.468(3), Ag1-N6 2.255(3).

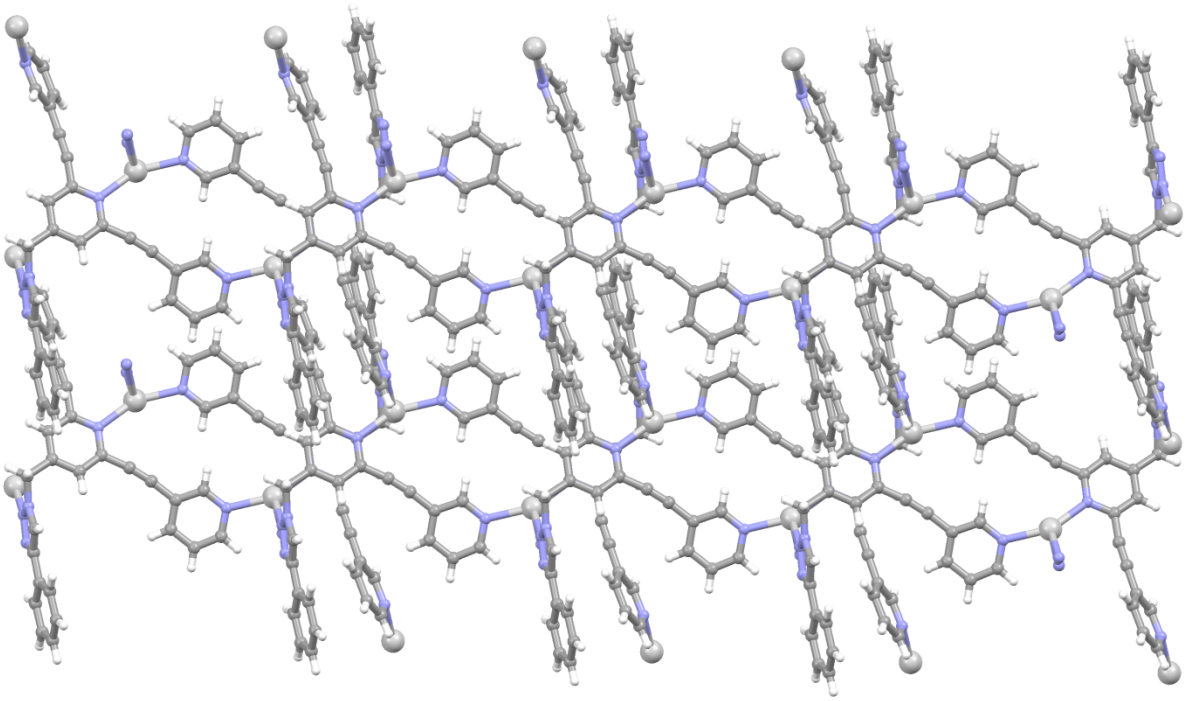


Figure 75 Ball-and-stick model showing the extended crystal lattice in the structure of **5a^{Ag}**.

7.3 Crystal data and structure refinement for 5b

Empirical formula	$C_{33}H_{23}Cl_3FeN_6$	
Formula weight	665.77	
Temperature	89(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.4645(5) Å	α= 105.696(2)°.
	b = 16.4498(5) Å	β= 102.138(2)°.
	c = 16.6038(6) Å	γ = 95.838(2)°.
Volume	2904.99(19) $Å^3$	
Z	4	
Density (calculated)	1.522 Mg/m^3	
Absorption coefficient	0.831 mm^{-1}	
F(000)	1360	
Crystal size	0.67 × 0.11 × 0.09 mm^3	
Theta range for data collection	1.32 to 26.44°.	
Index ranges	-14<=h<=14, -20<=k<=20, -20<=l<=20	
Reflections collected	45392	
Independent reflections	11804 [R(int) = 0.0645]	
Completeness to theta = 26.44°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9290 and 0.6059	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11804 / 0 / 775	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0420, wR2 = 0.0926	
R indices (all data)	R1 = 0.0692, wR2 = 0.1077	
Largest diff. peak and hole	0.721 and -0.649 $e.Å^{-3}$	

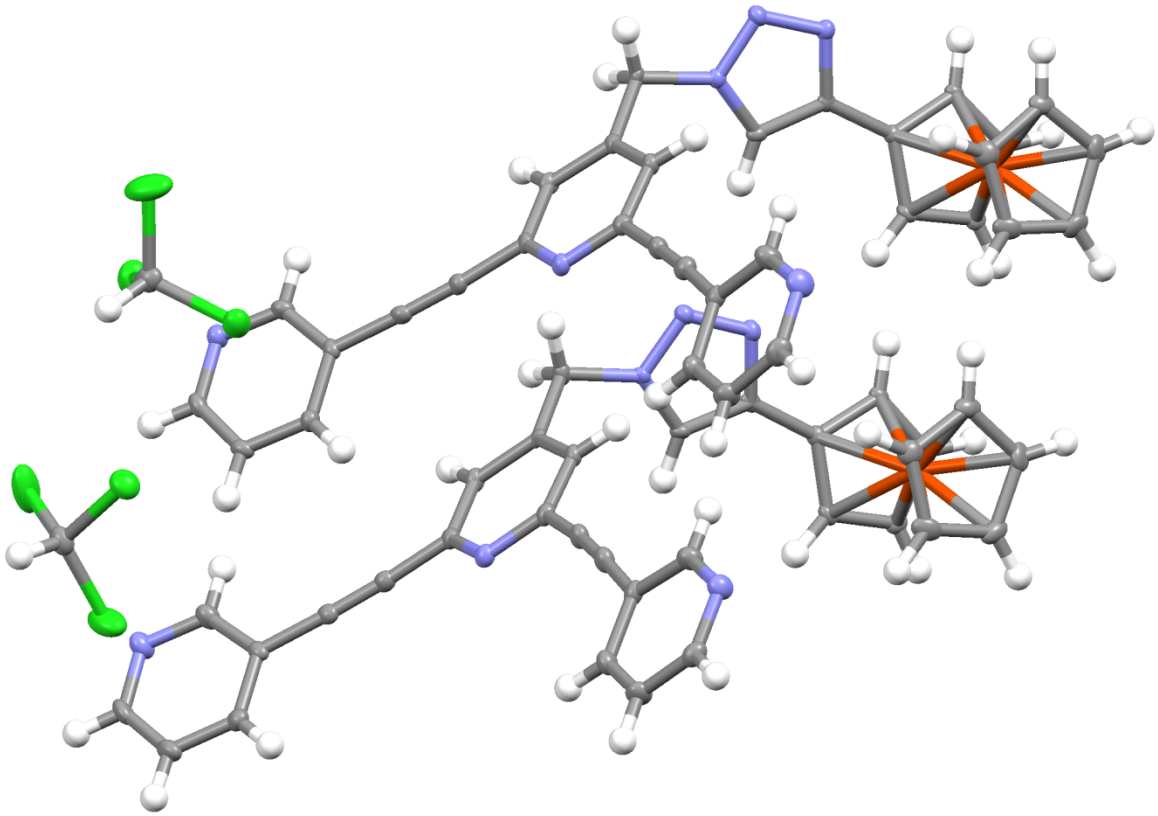


Figure 76 Ellipsoid plot of the asymmetric unit of **5b**. Ellipsoids are shown at the 50% probability level.

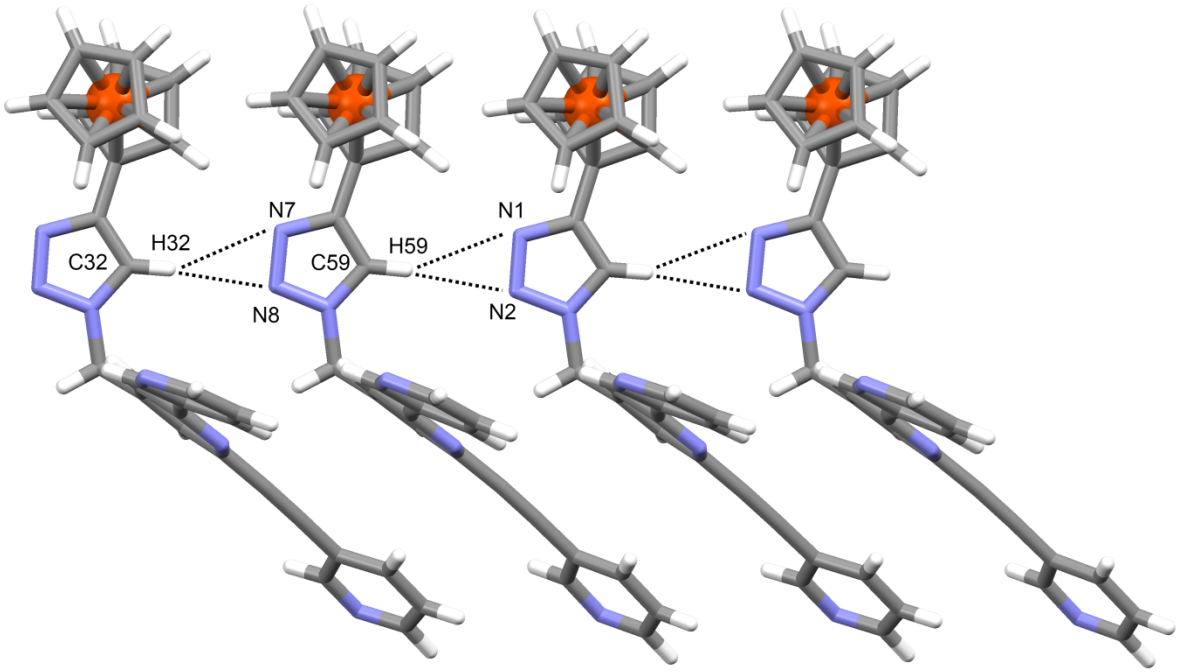


Figure 77 Capped-sticks models showing bifurcated hydrogen-bonding between the triazolyl units in the crystal lattice of **5b**. Interaction lengths (Å): H32···N7 2.855(2), H32···N8 2.619(2), H59···N1 2.867(2), H59···N2 2.702(2).

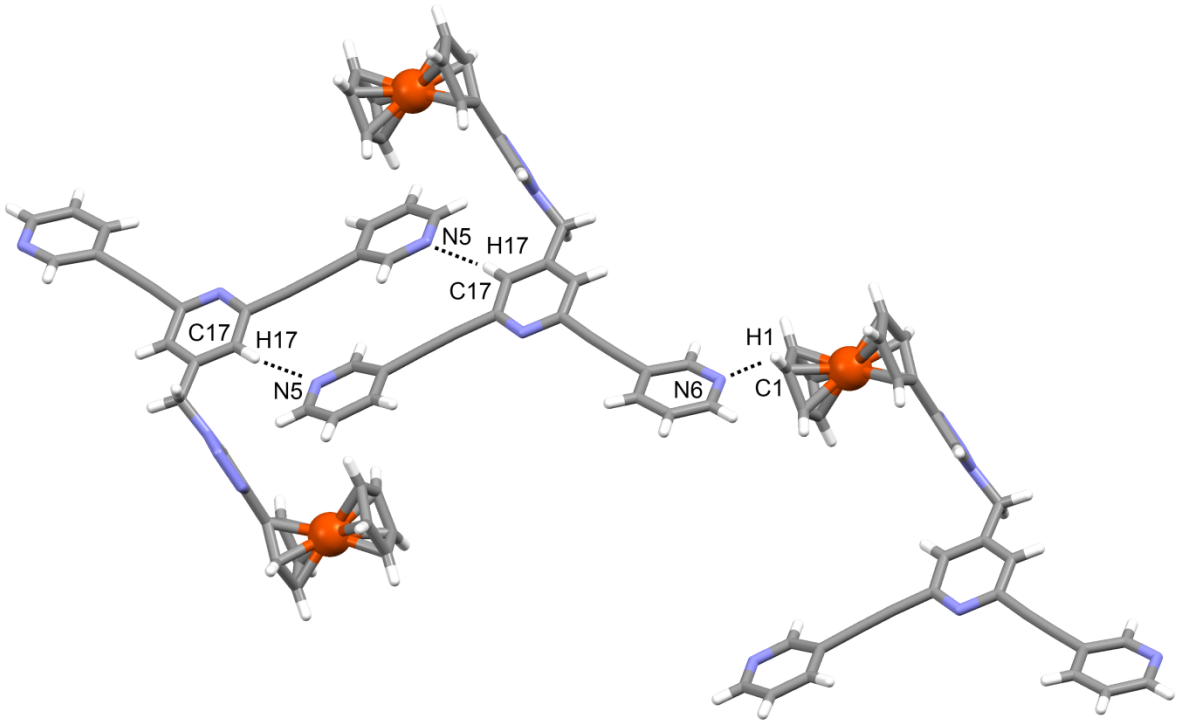


Figure 78 Capped-sticks model showing hydrogen bonding in the crystal lattice of **5b**. Interaction lengths (Å): H17···N5 2.540(3), H1···N6 2.550(2).

7.4 Crystal data and structure refinement for $5k^{Re}$

Empirical formula	$C_{62}H_{37}Cl_2N_{15}O_6Re_2$	
Formula weight	1531.37	
Temperature	89(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 40.00(2) Å	α= 90°.
	b = 7.730(3) Å	β= 97.713(14)°.
	c = 19.823(10) Å	γ = 90°.
Volume	6073(5) $Å^3$	
Z	4	
Density (calculated)	1.675 Mg/m^3	
Absorption coefficient	4.135 mm^{-1}	
F(000)	2984	
Crystal size	0.89 × 0.12 × 0.07 mm^3	
Theta range for data collection	1.03 to 26.74°.	
Index ranges	-50<=h<=50, -8<=k<=9, -25<=l<=24	
Reflections collected	23068	
Independent reflections	6224 [R(int) = 0.0616]	
Completeness to theta = 26.74°	96.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7606 and 0.1200	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6224 / 0 / 392	
Goodness-of-fit on F^2	1.096	
Final R indices [I>2sigma(I)]	R1 = 0.0619, wR2 = 0.1535	
R indices (all data)	R1 = 0.0992, wR2 = 0.1846	
Largest diff. peak and hole	2.889 and -1.591 $e.Å^{-3}$	

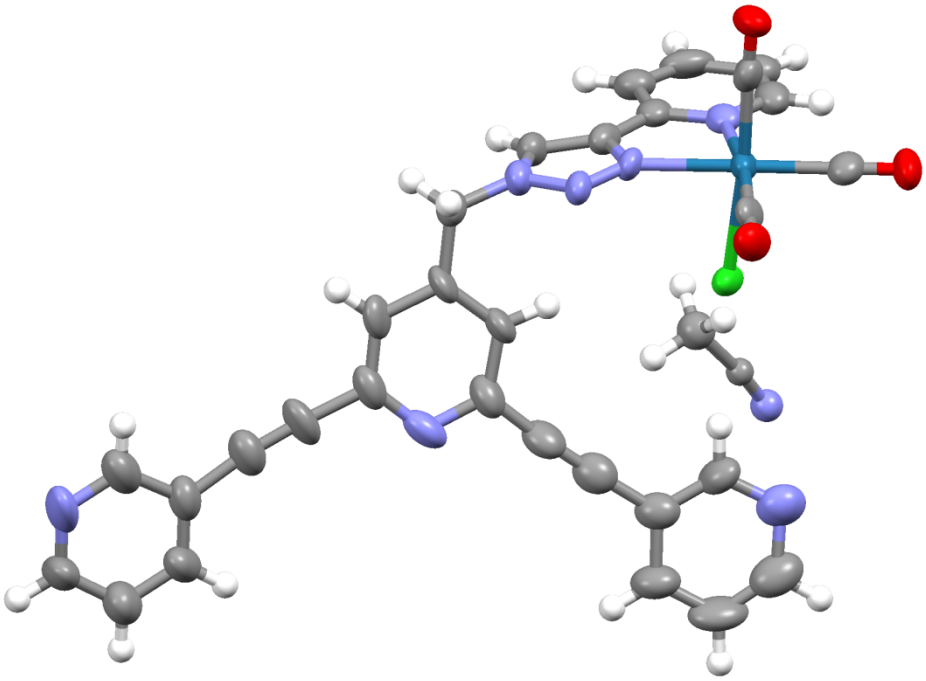


Figure 79 Ellipsoid plot of the asymmetric unit of **5k^{Re}**. Ellipsoids are shown at the 50% probability level.

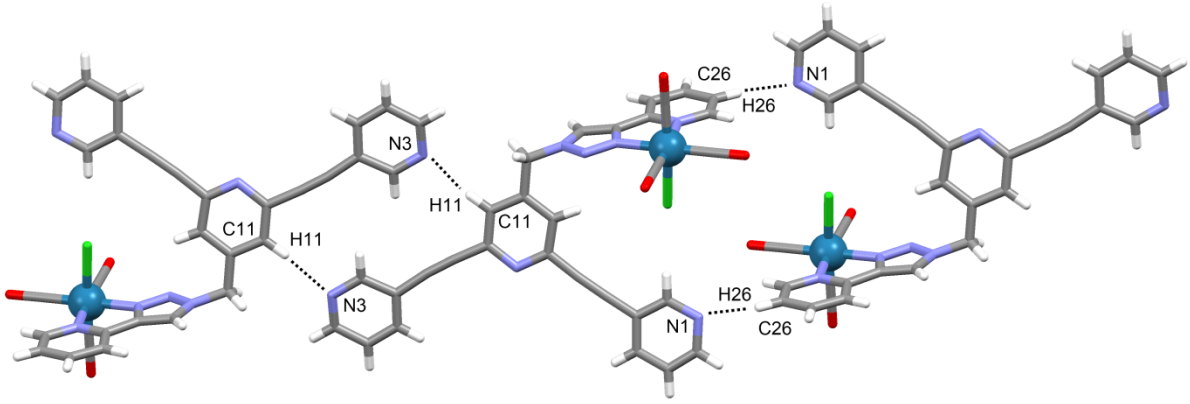


Figure 80 Capped-sticks model showing hydrogen bonding in the crystal lattice of **5k^{Re}**. Interaction lengths (Å): H11···N3 2.33(1), H26···N1 2.30(1).

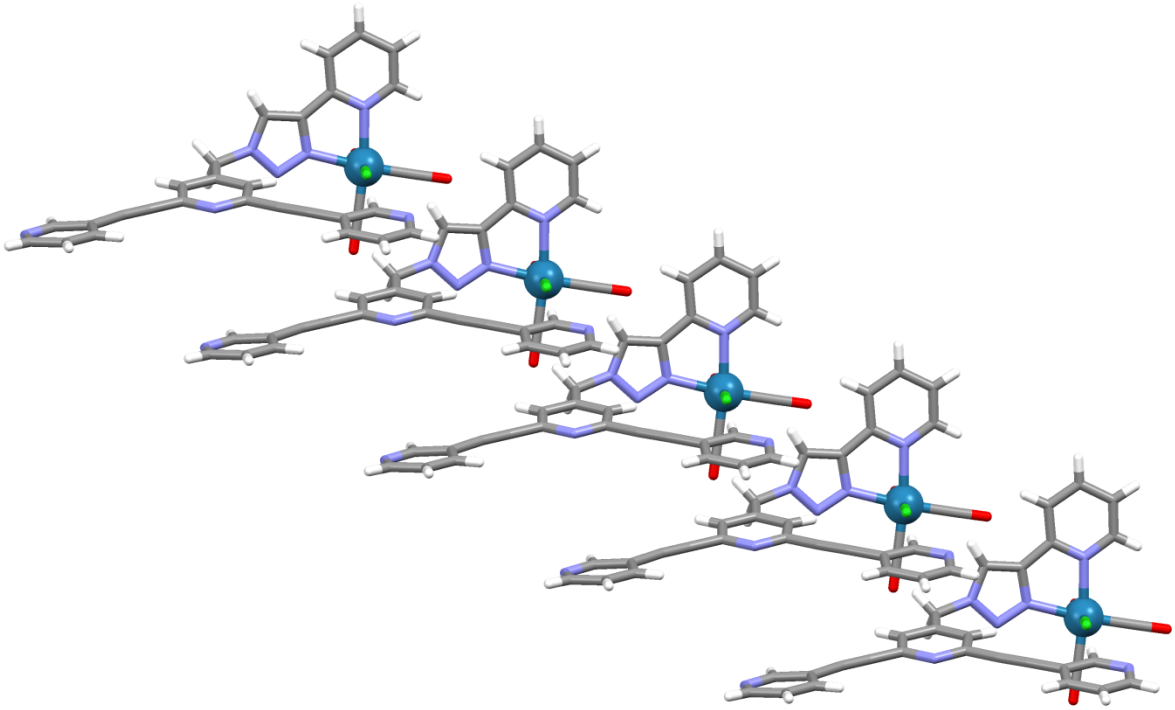


Figure 81 Capped-sticks model showing π-stacked one dimensional tapes throughout the crystal lattice of **5k^{Re}**.

7.5 Crystal data and structure refinement for 5c

Empirical formula	$C_{30}H_{22}N_{10}O_{2.88}$	
Formula weight	568.58	
Temperature	100(2) K	
Wavelength	1.54180 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 4.188(5) Å	α= 90.000(5)°.
	b = 21.206(5) Å	β= 91.247(5)°.
	c = 30.008(5) Å	γ = 90.000(5)°.
Volume	2664(3) $Å^3$	
Z	4	
Density (calculated)	1.417 Mg/m^3	
Absorption coefficient	0.798 mm^{-1}	
F(000)	1180	
Crystal size	0.42 × 0.05 × 0.04 mm^3	
Theta range for data collection	3.61 to 58.93°.	
Index ranges	-4<=h<=4, -23<=k<=19, -33<=l<=33	
Reflections collected	16775	
Independent reflections	3836 [R(int) = 0.1983]	
Completeness to theta = 58.93°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9688 and 0.7304	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3836 / 0 / 386	
Goodness-of-fit on F^2	0.991	
Final R indices [I>2sigma(I)]	R1 = 0.0828, wR2 = 0.2076	
R indices (all data)	R1 = 0.1065, wR2 = 0.2368	
Largest diff. peak and hole	0.542 and -0.420 $e.Å^{-3}$	

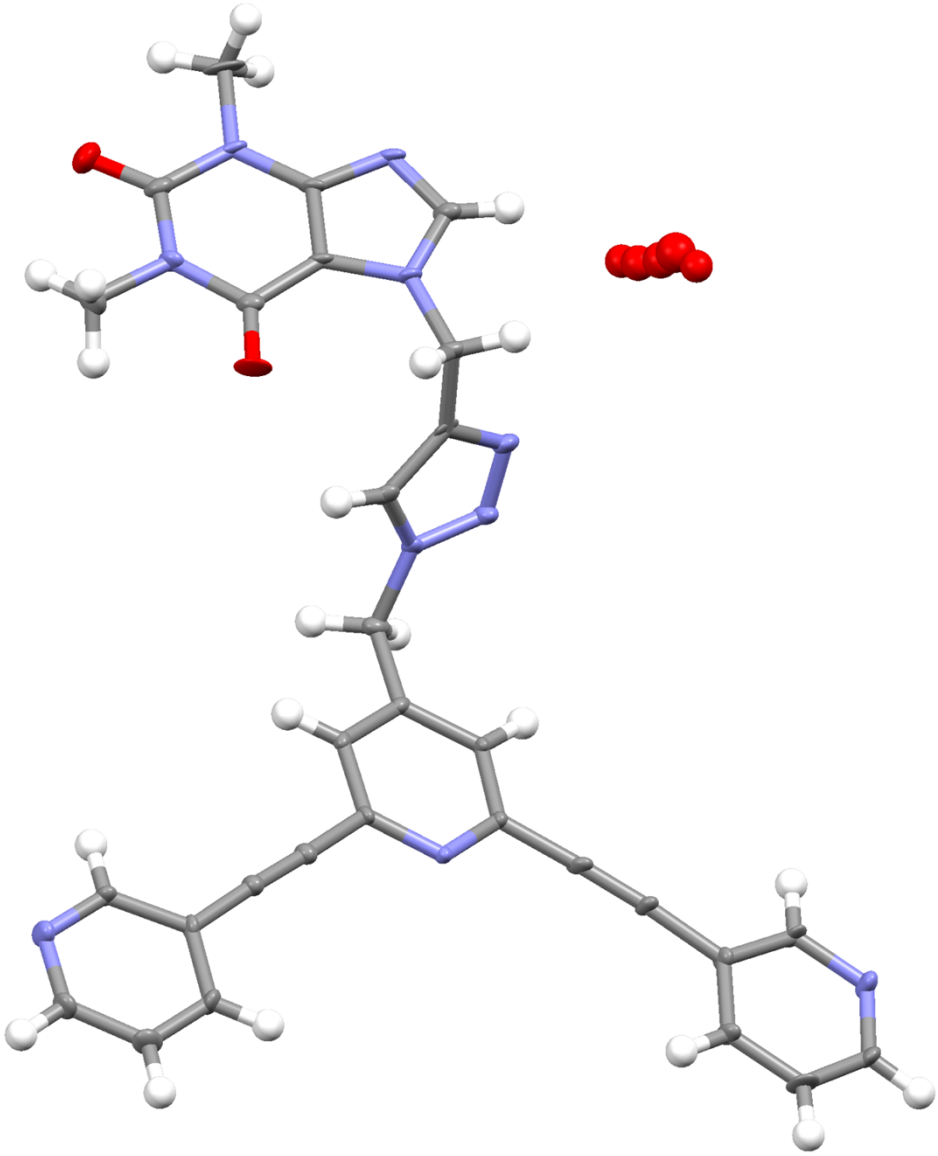


Figure 82 Ellipsoid plot of the asymmetric unit of **5c**. Ellipsoids are shown at the 50% probability level.

The crystals of this compound diffracted poorly, thus the SHEL command was used to omit reflections below 0.9 Å. Oxygen atoms of disordered water molecules could not be refined anisotropically thus were left isotropic.

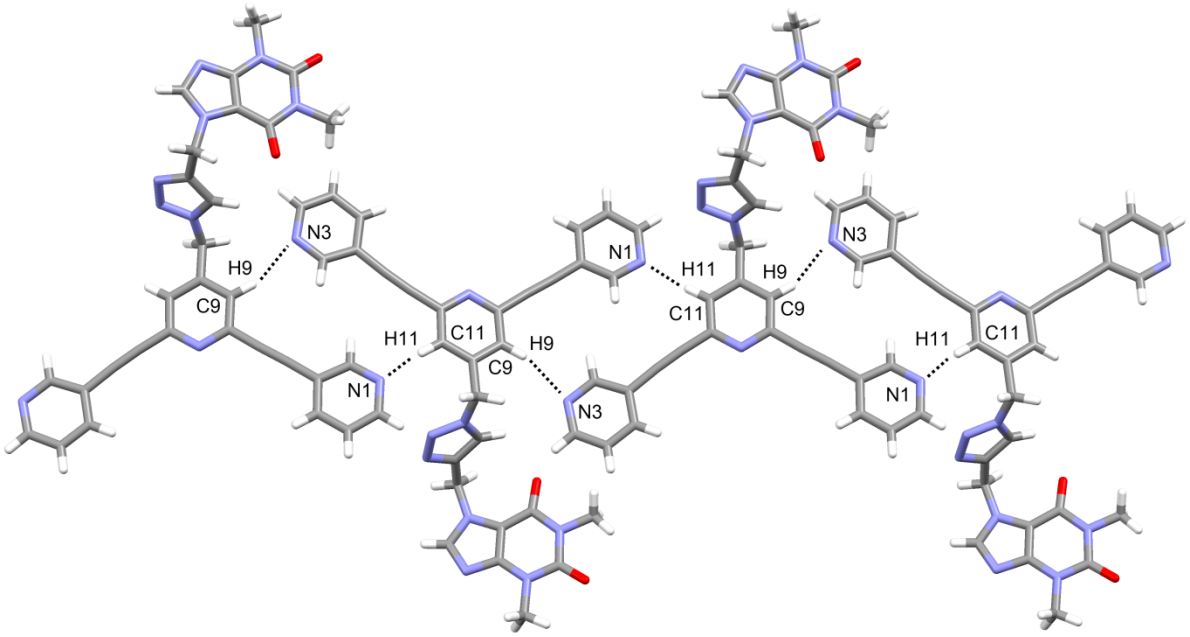


Figure 83 Capped-sticks model showing hydrogen-bonding interactions forming one dimensional tapes throughout the crystal lattice of **5c**. Interaction lengths (Å): H9···N3 2.555(8), H11···N1 2.420(8).

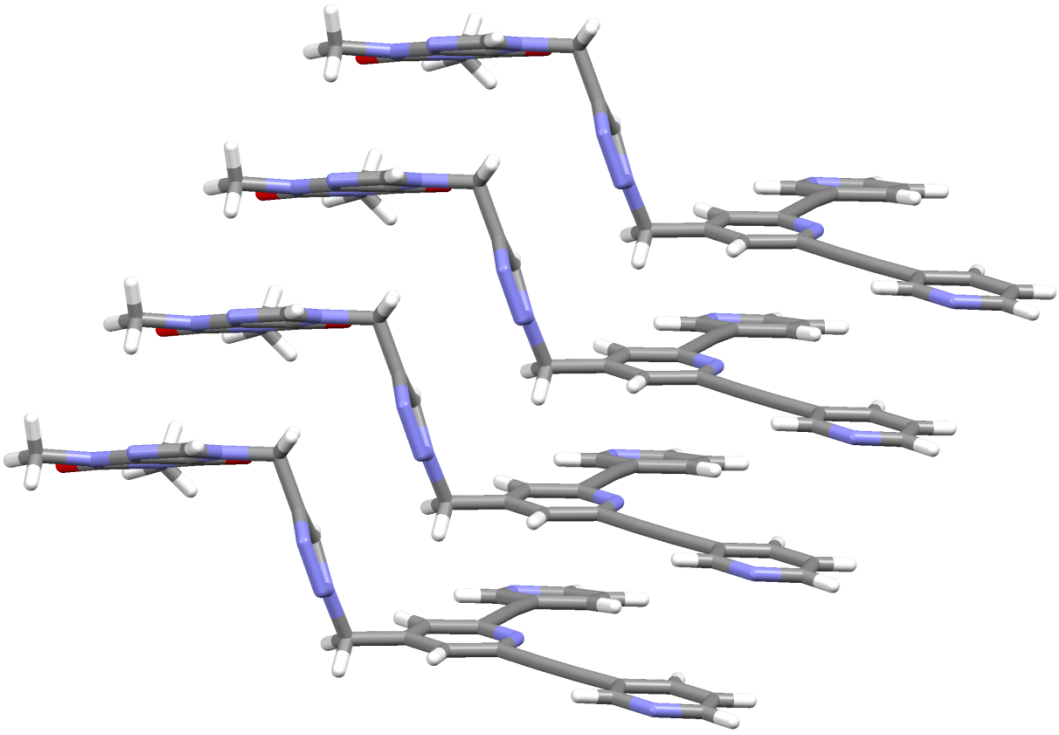


Figure 84 Capped-sticks model showing π-stacked one dimensional tapes throughout the crystal lattice of **5c**.

7.6 Crystal data and structure refinement for 6b⊃(cisplatin)$_2$·6b

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}	

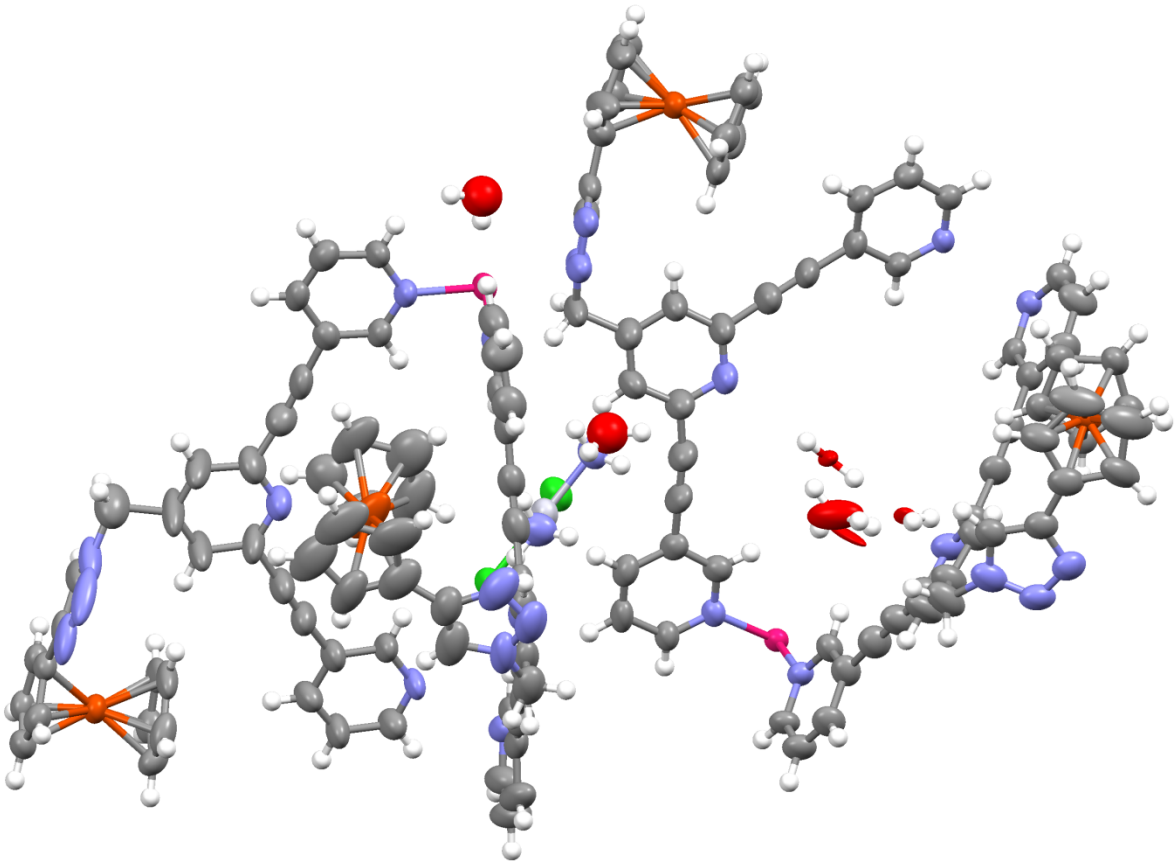


Figure 85 Ellipsoid plot of the asymmetric unit of **6b⊃(cisplatin)$_2$·6b**. Ellipsoids are shown at the 50% probability level.

The crystal lattice contained diffuse electron density that could not be appropriately modelled. The SQUEEZE routine within PLATON was employed to resolve this, giving a void electron count of 519 that was assigned to disordered tetrafluoroborate counteranions and solvent molecules.

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.;

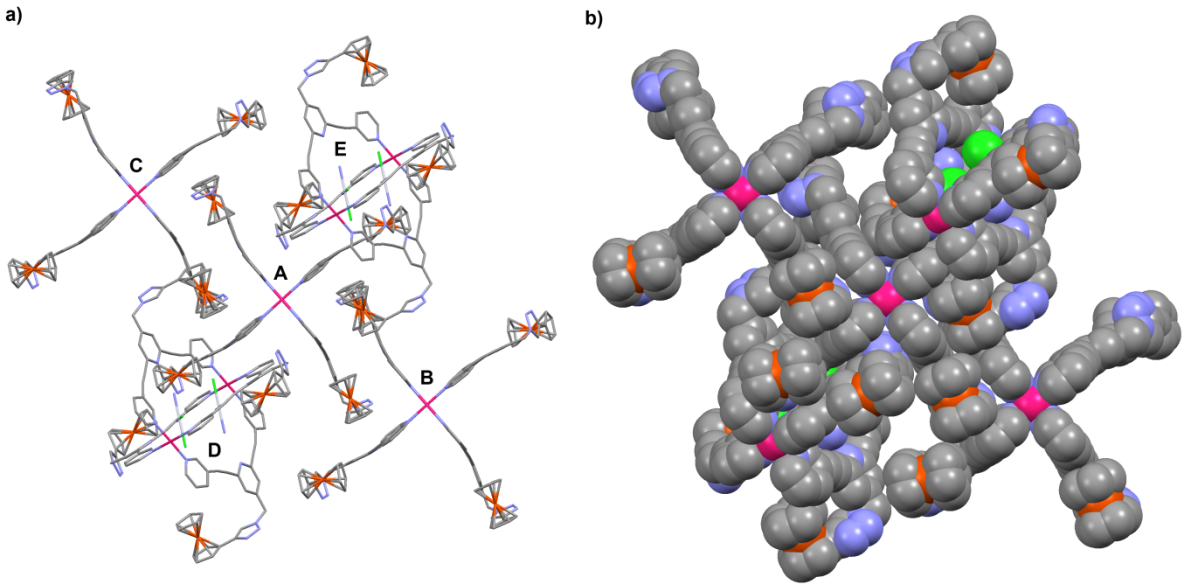


Figure 86 Mercury diagrams of a) capped-stick view and b) space-fill view showing intercalation of cages adjacent to **6b** (**A**), largely filling the internal cavity. The cage (**A**) is flanked by two **6b** moieties (**B** and **C**) and two [**6b**⊃(cisplatin)$_2$] moieties (**D** and **E**).

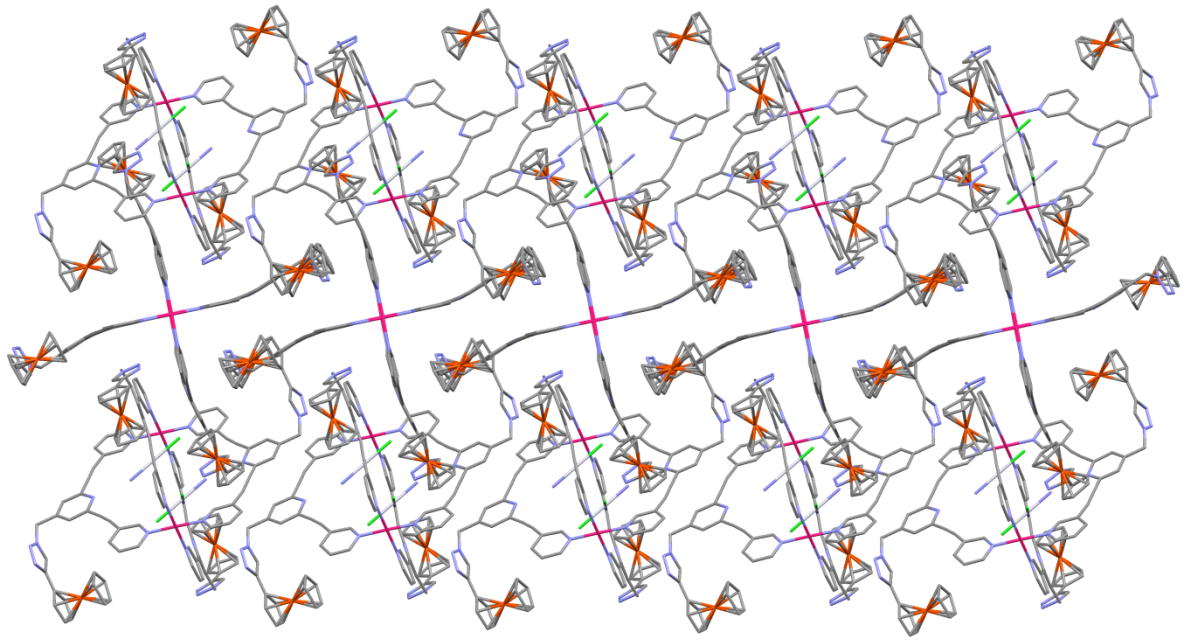


Figure 87 Capped-stick Mercury diagram showing the intercalating 1D chains of **6b** and [**6b** ⊃(cisplatin)$_2$] moieties which stack to form a 2D lattice structure.

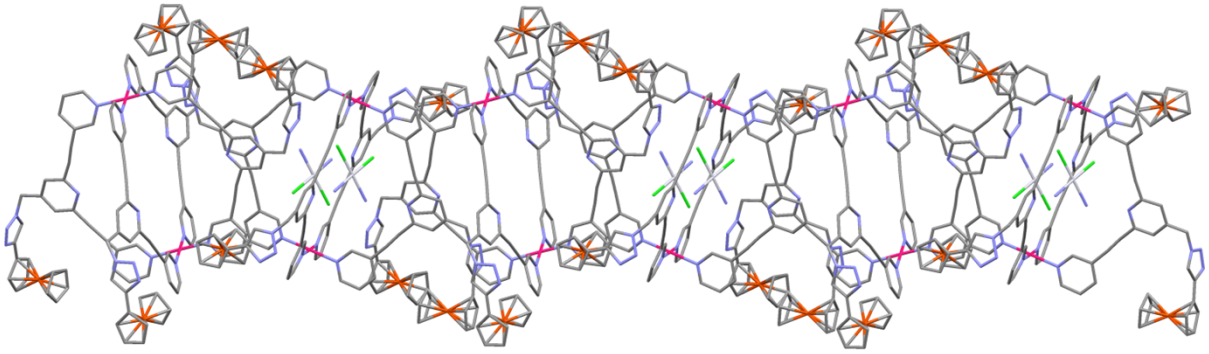


Figure 88 Capped-stick Mercury diagram (side view) showing 1D chains of alternating [**6b** ⊃(cisplatin)$_2$] and **6b** moieties.

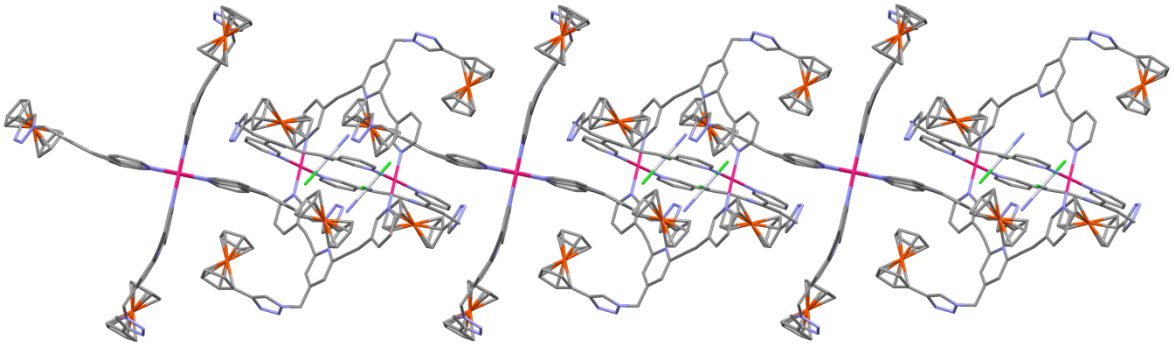


Figure 89 Capped-stick Mercury diagram (top view) showing 1D chains of alternating [**6b** ⊃(cisplatin)$_2$] and **6b** moieties.

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