Electronic Supplementary Information for Dalton Transactions

Supplementary Information for

Tuning emission wavelength and redox properties through position of the substituent in iridium(III) cyclometallated complexes†

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Experimental

General information and materials

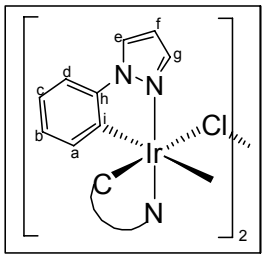
All reactions were carried out under an inert atmosphere of nitrogen and under microwave irradiation unless stated otherwise. After work up all the complexes were air stable. Microwave reactions were carried out in a *CEM-Discover* commercial microwave reactor. ^{1}H, and $^{13}C–\{^{1}H\}$ NMR spectra were obtained using a DRX 400 MHz spectrometer. Chemical shifts were recorded in ppm (on δ scale with tetramethylsilane as internal reference), and coupling constants are reported in Hz. FAB mass spectra were obtained on a Kratos concept mass spectrometer using NOBA as matrix. The electrospray (ES) mass spectra were recorded using a micromass Quattra LC mass spectrometer in HPLC grade acetonitrile except methanol for **2d**. UV – Vis absorption measurements were carried out on a Shimadzu UV – 1600 series spectrometer in a range 230-800 nm in dry dichloromethane at a concentration of 1 x 10^{-5} M. Luminescence studies were performed in solution in dry dichloromethane at 1 x 10^{-5} M concentration using a Jobin Yvon Horiba Fluoromax–P spectrofluorimeter in a range 450-800 nm. Electrochemical measurements were performed with an Eco Chemie Autolab. All measurements were carried out in a one-compartment cell under N_2 gas, equipped with a Pt disc working electrode, a Pt gauze counter electrode and a silver wire reference electrode. The supporting electrolyte was Et_4NClO_4 (0.1 mol L^{-1}) in acetonitrile. Elemental analyses were performed at London Metropolitan University. All starting materials were obtained from Aldrich or Alfa Aesar.

General procedure for synthesis of $[Ir(ppz\text{-}R_1)_2Cl]_2$ (1a-e)

K_2IrCl_6 or $IrCl_3.(H_2O)_3$, and the appropriate cyclometallating ligand (2.4-3 equiv.) were placed in a microwave vial along with a mixture of propan–2–ol/water (4 ml, 3:1). Nitrogen was bubbled through the solution for 2 mins and the vial was then sealed with a septum cap. The vial was placed in the microwave reactor and heated under microwave irradiation at 110˚C for 90 minutes, at a maximum pressure of 250 psi. After this time the solvent was removed *in vacuo* leaving behind a solid which was dissolved in dichloromethane (40 ml) and passed through celite. The filtrate was reduced in volume and hexane was added slowly to induce precipitation. The precipitate was isolated,

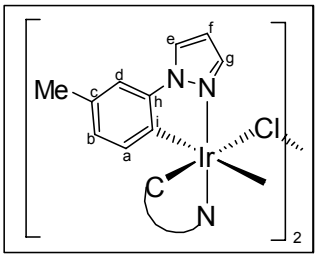
washed with hexane and dried *in vacuo*. The compounds could be recrystallised from DCM/hexane.

Synthesis of $[Ir(ppz)_2Cl]_2$ (1a)



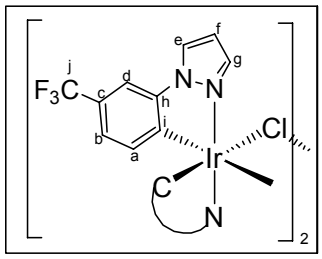
This was prepared from K_2IrCl_6 (400 mg, 0.828 mmol) and 1-phenyl-1H-pyrazole (Hppz) (358.2 mg, 0.328 ml, 2.484 mmol) and after work up gave **1a** as a grey solid (409 mg, 96%). The data is consistent with the literature (ref) but full assignment of the NMR and MS is given here. ^{1}H NMR (CD_2Cl_2): δ 8.19 (4H, dd, J = 3.2, 0.8, H_e), 7.82 (4H, dd, J = 2.4, 0.8, H_g), 7.19 (4H, dd, J = 7.8, 1.2, H_d), 6.84 (4H, td, J = 7.4, 1.6, H_c), 6.69 (4H, m, H_f), 6.57 (4H, td, J = 7.4, 1.2, H_b), 5.95 (4H, dd, J = 7.8, 1.2, H_a). ^{13}C NMR: 141.65 (C_i), 139.00 (C_g), 130.97 (C_a), 125.88 (C_h), 124.94 (C_e), 123.71 (C_b), 120.43 (C_c), 109.12 (C_d), 105.22 (C_f). MS (FAB): *m/z* 1028 $[M]^+$, 991 $[M\text{-}Cl]^+$. MS (ES): *m/z* 561 $[Ir(ppz)_2(MeCN)_2]^+$

Synthesis of $[Ir(ppz\text{-}Me)_2Cl]_2$ (1b)



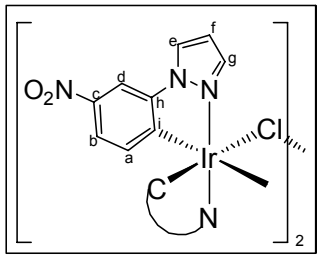
This was prepared from $IrCl_3(H_2O)_3$ (300 mg, 0.850 mmol) and 1-*m*-tolyl-1H-pyrazole (Hppz-Me) (323 mg, 2.040 mmol) and after work up gave **1b** as a pale yellow solid (441 mg, 96%). Anal. Calcd for $C_{40}H_{36}Cl_2Ir_2N_8$: C, 44.32, H, 3.35, N, 10.34. Found: C, 44.42, H, 3.44, N, 10.19%. ^{1}H NMR ($CDCl_3$): δ 8.08 (4H, d, J = 2.7, H_e), 7.82 (4H, d, J = 2.3, H_g), 6.92 (4H, d, J = 1.2, H_d), 6.60 (4H, t, J = 2.3, H_f), 6.36 (4H, dd, J = 7.8, 0.8, H_b), 5.85 (4H, d, J = 7.8, H_a), 2.14 (12H, s, Me). ^{13}C NMR: 142.86 (C_i), 140.26 (C_g), 132.20 (C_a), 130.97 (C_h), 126.22 (C_b), 125.55 (C_e), 123.07 (C_c), 111.40 (C_d), 106.14 (C_f), 20.92 (Me). MS (FAB): *m/z* 1084 $[M]^+$, 1047 $[M\text{-}Cl]^+$. MS (ES): *m/z* 589 $[Ir(ppz\text{-}Me)_2(MeCN)_2]^+$

Synthesis of $[Ir(ppz\text{-}CF_3)_2Cl]_2$ (1c)



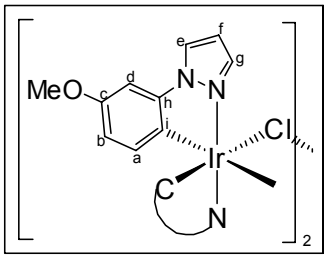
This was prepared from $IrCl_3(H_2O)_3$ (200 mg, 0.567 mmol) and 1-(3-(trifloromethyl)phenyl)-1H-pyrazole (Hppz-CF_3) (360 mg, 1.701 mmol) and after work up gave **1c** as a grey solid (321 mg, 87%). Anal. Calcd for $C_{40}H_{24}Cl_2F_{12}Ir_2N_8$: C, 36.96, H, 1.86, N, 8.62. Found: C, 37.11, H, 1.83, N, 8.53%. ^{1}H NMR ($CDCl_3$): δ 8.24 (4H, d, J = 2.7, H_e), 7.85 (4H, d, J = 2.0, H_g), 7.35 (4H, d, J = 1.2, H_d), 6.81 (4H, dd, J = 7.8, 0.8, H_b), 6.76 (4H, t, J = 2.3, H_f), 6.09 (4H, d, J = 7.8, H_a). ^{13}C NMR: 142.99 (C_h), 141.00 (C_g), 126.95 (C_a), 125.47 (C_j), 125.03 (C_c), 122.13 (C_i), 122.10 (C_b), 107.38, 107.34 ($C_{d,\ f}$). MS (FAB): *m/z* 1300 $[M]^+$, 1265 $[M-Cl]^+$. MS (ES): *m/z* 697 $[Ir(ppz\text{-}CF_3)_2(MeCN)_2]^+$

Synthesis of $[Ir(ppz\text{-}NO_2)_2Cl]_2$ (1d)



This was prepared from $IrCl_3(H_2O)_3$ (100 mg, 0.284 mmol) and 1-(3-(nitrophenyl)-1H-pyrazole (Hppz-NO_2) (160.7 mg, 0.852 mmol) and after work up gave **1d** as a pale green solid (321 mg, 87%). Anal. Calcd for $C_{36}H_{24}Cl_2Ir_2N_{12}O_8$: C, 35.79, H, 2.00, N, 13.91. Found: C, 35.60, H, 1.87, N, 13.88%. ^{1}H NMR ($CDCl_3$): δ 8.37 (4H, d, J = 2.7, H_e), 8.05 (4H, d, J = 2.5, H_d), 7.88 (4H, d, J = 2.0, H_g), 7.48 (4H, dd, J = 8.6, 2.3, H_b), 6.87 (4H, t, J = 2.3, H_f), 6.12 (4H, d, J = 8.6, H_a). ^{13}C NMR: 144.61 (C_h), 143.75 (C_c), 142.01 (C_g), 140.09 (C_i), 132.91 (C_a), 128.63 (C_e), 120.52 (C_b), 108.74 (C_f), 106.00 (C_d). MS (FAB): *m/z* 1208 $[M]^+$. MS (ES): *m/z* 633 $[Ir(ppz\text{-}NO_2)_2(MeOH)_2]^+$

Synthesis of $[Ir(ppz\text{-}OMe)_2Cl]_2$ (1e) major isomer (A)



This was prepared from $IrCl_3(H_2O)_3$ (200 mg, 0.567 mmol) and 1-(3-(methoxyphenyl)-1H-pyrazole (Hppz-OMe) (295.8 mg, 1.701 mmol) and after work up gave **1e** as a grey solid (276 mg, 85%). Anal. Calcd for $C_{40}H_{36}Cl_2Ir_2N_8O_4$: C, 41.85, H, 3.16, N, 9.76. Found: C, 41.80, H, 3.18, N, 9.77%. ^{1}H NMR ($CDCl_3$): δ 8.07 (4H, d, J = 3.1, H_e), 7.83 (4H, d, J = 1.5, H_g), 6.74 (4H, d, J = 2.7, H_d), 6.62 (4H, t, J = 2.3, H_f), 6.24 (4H, dd, J = 8.6, 2.7, H_b),

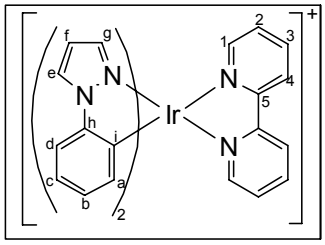
5.87 (4H, d, J = 8.2, H_a), 3.66 (12H, s, Me). MS (FAB): *m/z* 1148 $[M]^+$. MS (ES): *m/z* 621 $[Ir(ppz\text{-}OMe)_2(MeCN)_2]^+$.

Minor isomer (B): ^{1}H NMR ($CDCl_3$): δ 8.11 (1H, d, J = 2.7), 8.01 (1H, d, J = 2.7), 7.87 (1H, d, J = 1.9), 7.86 (1H, d, J = 1.9), 7.78 (1H, d, J = 1.9), 7.74 (1H, d, J = 1.9), 6.85 (1H, d, J = 7.8), 6.79 (1H, d, J = 7.8), 6.65 (1H, t, J = 2.3), 6.58 (1H, t, J = 2.3), 6.56, 6.55 (2H, 2 X t, J = 2.3), 6.20 (1H, dd, J = 7.8, 2.0), 6.04 (1H, d, J = 7.8), 5.84 (1H, d, J = 8.2), 5.72 (1H, d, J = 8.2), 3.66 (9H, s, Me), 3.13 (3H, s, Me). The remaining 8H are under the signals of major isomer, hence a detailed assignment of the minor isomer was not possible.

General procedure for synthesis of bipy complexes $[Ir(ppz\text{-}R_1)_2(bipy)]PF_6$ (2a-e)

The appropriate dimer **1a-e**, 2,2'-bipyridyl (2.2-2.4 equiv) and KPF_6 (2.4 equiv) were placed in a microwave vial and methanol (3 ml) was added. Nitrogen was bubbled through the solution for 2 mins and the vial was then sealed with a septum cap. The tube was placed in the microwave reactor and heated under microwave irradiation at 60˚C for 20 mins, at a maximum pressure of 250 psi. After this time the solvent was removed *in vacuo* leaving behind a solid which was dissolved in DCM (15 ml) and passed through celite. The filtrate was reduced in volume and hexane was added slowly to induce precipitation. The precipitate was isolated, washed with hexane and dried *in vacuo*. The compounds could be recrystallised from DCM/hexane.

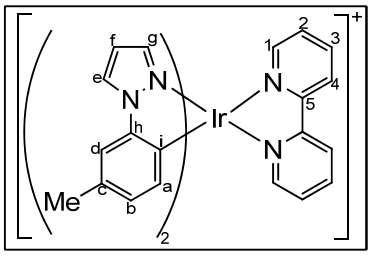
Synthesis of $[Ir(ppz)_2(bipy)]PF_6$ (2a) This is a known complex,(ref) the NMR data is included here for the comparison (the ^{1}H NMR shifts are out by 0.09 ppm relative to literature).



This was prepared from $[Ir(ppz)_2Cl]_2$ **1a** (50 mg, 0.048 mmol), 2,2'-bipyridyl (18.2 mg, 0.116 mmol) and KPF_6 (21.3 mg, 0.116 mmol) and after work up gave **2a** (60 mg, 81%) as a yellow solid. ^{1}H NMR (CD_2Cl_2): δ 8.40 (2H, dd, J = 8.2, 0.8, H_4), 8.10 (2H, dd, J = 5.4, 1.5, H_1), 8.08 (2H, d, J = 2.7, H_e), 8.06 (2H, td, J = 8.1, 1.7, H_3) 7.39 (2H, ddd, J = 7.8, 5.5, 1.2, H_2), 7.27 (2H, dd, J = 7.8, H_d), 7.01 (2H, td, J = 8.9, 1.6, H_c), 6.82 (2H, td, J = 8.6, 1.2, H_b),

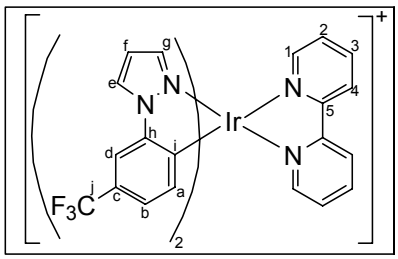
6.77 (2H, d, J = 2.3, H_g), 6.47 (2H, t, J = 2.3, H_f), 6.24 (2H, dd, J = 7.4, 1.2, H_a). MS (FAB): *m/z* 635 $[M]^+$. UV-Vis (ε_{max}[$dm^3mol^{-1}cm^{-1}$]): 263 sh (44600), 311 (22100), 410 sh (2700).

Synthesis of [Ir(ppz-Me)$_2$(bipy)]PF$_6$ (2b)



This was prepared from [Ir(ppz-Me)$_2$Cl]$_2$ **1b** (40 mg, 0.037 mmol), 2,2'-bipyridyl (13.8 mg, 0.088 mmol) and KPF_6 (16.2 mg, 0.088 mmol) and after work up gave **2b** as a yellow solid (47 mg, 80%). Anal. Calcd for $C_{30}H_{26}F_6IrN_6P$: C, 44.61, H, 3.24, N, 10.40. Found: C, 44.70, H, 3.16, N, 10.38%. ^{1}H NMR (CD_2Cl_2): δ 8.46 (2H, d, J = 8.2, H_4), 8.21 (2H, ddd, J = 5.5, 1.6, 0.8, H_1), 8.15 – 8.11 (4H, m, $H_{3,\,e}$), 7.47 (2H, ddd, J = 7.4, 5.5, 1.2, H_2), 7.18 (2H, s, H_d), 6.83 (2H, d, J = 2.3, H_g), 6.74 (2H, dd, J = 7.4, 1.6, H_b), 6.53 (2H, t, J = 2.3, H_f), 6.18 (2H, d, J = 7.4, H_a), 2.31 (6H, s, Me). ^{13}C NMR: 156.79 (C_5), 151.54 (C_1), 143.22 (C_h), 139.82 (C_e), 138.34 (C_g), 133.62 (C_c), 133.27 (C_a), 128.20 (C_b), 128.19 (C_2), 127.83 (C_i), 127.27 (C_3), 124.57 (C_4), 112.98 (C_d), 108.46 (C_f), 21.15 (Me). MS (FAB): *m/z* 663 $[M]^+$. UV-Vis (ε_{max}[$dm^3mol^{-1}cm^{-1}$]): 270 sh (53000), 310 (25300), 330 (15000), 448 sh (1700).

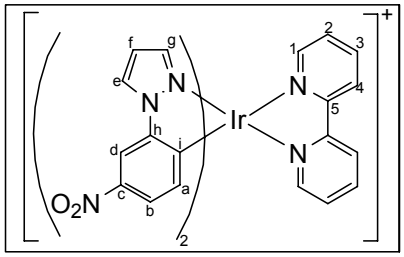
Synthesis of [Ir(ppz-CF$_3$)$_2$(bipy)]PF$_6$ (2c)



This was prepared from [Ir(ppz-CF$_3$)$_2$Cl]$_2$ **1c** (50 mg, 0.038 mmol), 2,2'-bipyridyl (14.4 mg, 0.092 mmol) and KPF_6 (16.9 mg, 0.092 mmol) and after work up gave **2c** as a yellow solid (59 mg, 84%). Anal. Calcd for $C_{30}H_{20}F_{12}IrN_6P$: C, 39.35, H, 2.20, N, 9.18. Found: C, 39.42, H, 2.15, N, 9.15%. ^{1}H NMR (CD_2Cl_2): δ 8.54 (2H, d, J = 8.2, H_4), 8.24 (2H, d, J = 3.1, H_e), 8.20 (2H, td, J = 8.2, 1.6, H_3), 8.11 (2H, ddd, J = 5.5, 1.6, 0.8, H_1), 7.57 (2H, s, H_d), 7.52 (2H, ddd, J = 7.8, 5.5, 1.2, H_2), 7.16 (2H, dd, J = 7.8, 0.8, H_b), 6.95 (2H, d, J = 2.3, H_g), 6.65 (2H, t, J = 2.3, H_f), 6.47 (2H, d, J = 7.8, H_a). ^{13}C NMR: 156.58 (C_5), 151.40 (C_1), 143.54 (C_h), 140.59 (C_3), 139.61 (C_g), 137.85 (C_i), 134.18 (C_a), 128.58 (C_2), 128.43 (C_e), 126.38

(C_j), 126.12 (C_c), 123.82 (C_4), 123.79 (C_b), 109.56 (C_f), 108.87 (C_d). MS (FAB): *m/z* 771 $[M]^+$. UV-Vis (ε_{max}[$dm^3mol^{-1}cm^{-1}$]): 298 sh (30600), 310 sh (27600), 398 sh (2000).

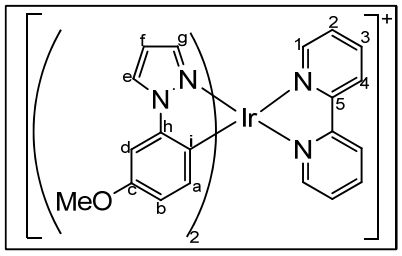
Synthesis of [Ir(ppz-NO_2)$_2$(bipy)]PF_6 (2d) major isomer (A)



This was prepared from [Ir(ppz-NO_2)$_2$Cl]$_2$ **1d** (50 mg, 0.041 mmol), 2,2'-bipyridyl (14.2 mg, 0.091 mmol) and KPF_6 (16.7 mg, 0.091 mmol). In this case heating for 65 mins was required for complete conversion and after work up gave **2d** as a greenish yellow solid (61 mg, 86%). Anal. Calcd for $C_{28}H_{20}F_6IrN_8O_4P$: C, 38.67, H, 2.32, N, 12.88. Found: C, 38.58, H, 2.27, N, 12.92%. ^{1}H NMR (CD_2Cl_2): δ 8.56 (2H, d, *J* = 8.2, H_4), 8.34 (2H, d, *J* = 3.1, H_e), 8.23 (2H, td, *J* = 7.8, 1.6, H_3), 8.21 (2H, d, *J* = 2.3, H_d), 8.08 (2H, ddd, *J* = 5.5, 1.6, 0.8, H_1), 7.76 (2H, dd, *J* = 8.2, 2.3, H_b), 7.54 (2H, ddd, *J* = 7.8, 5.5, 1.2, H_2), 7.02 (2H, d, *J* = 2.3, H_g), 6.71 (2H, t, *J* = 2.3, H_f), 6.52 (2H, d, *J* = 8.2, H_a). ^{13}C NMR: 156.43 (C_5), 151.32 (C_1), 145.75 (C_h), 143.92 (C_c), 143.69 (C_i), 141.00 (C_3), 140.30 (C_g), 134.08 (C_a), 129.09 (C_2), 128.79 (C_e), 125.39 (C_4), 121.93 (C_b), 110.13 (C_f), 107.09 (C_d). MS (FAB): *m/z* 725 $[M]^+$. UV-Vis (ε_{max}[$dm^3mol^{-1}cm^{-1}$]): 261 (23860), 314 (11290), 347 (9200)

Minor isomer (B): ^{1}H NMR (CD_2Cl_2): δ 8.49, 8.48 (2H, 2 X d, *J* = 7.8), 7.84 (1H, dd, *J* = 5.5, 1.6), 7.72 (1H, t, *J* = 2.0), 7.29 (1H, t, *J* = 8.2), 6.91 (1H, d, *J* = 2.7), 6.88 (1H, d, *J* = 2.3), 6.83 (1H, d, *J* = 2.3), 6.80 (1H, d, *J* = 2.3), 6.73 (1H, d, *J* = 2.3), 6.69 (1H, t, *J* = 2.3), 6.64 (1H, t, *J* = 2.3), 6.57 – 6.55 (2H, m), 6.56 (1H, dd, *J* = 7.8, 2.0), 6.22 (1H, d, *J* = 7.8). The remaining 4H are under the signals of the major isomer Hence a detailed assignment of the minor isomer was not possible.

Synthesis of [Ir(ppz-OMe)$_2$(bipy)]PF_6 (2e)



This was prepared from [Ir(ppz-OMe)$_2$Cl]$_2$ **1e** (40 mg, 0.035 mmol), 2,2'-bipyridyl (13.1 mg, 0.084 mmol) and KPF_6 (15.5 mg, 0.084 mmol) and after work up gave **2e** as a yellow solid (43 mg, 74%). Anal. Calcd for $C_{30}H_{26}F_6IrN_6O_2P$: C, 42.91, H, 3.12, N, 10.01. Found: C, 43.14, H, 3.04, N,

9.90%. ^{1}H NMR (CD_2Cl_2): δ 8.46 (2H, d, *J* = 8.2, H_4), 8.23 (2H, d, *J* = 5.0, H_1), 8.16 – 8.11 (4H, m, $H_{3, e}$), 7.48 (2H, m, H_2), 6.96 (2H, d, *J* = 2.3, H_d), 6.84 (2H, d, *J* = 1.8, H_g), 6.59 – 6.53 (4H, m, $H_{b,f}$), 6.19 (2H, d, *J* = 8.2, H_a), 3.79 (6H, s, Me). MS (FAB): *m/z* 695 $[M]^+$. UV-Vis (ε_{max}[$dm^3mol^{-1}cm^{-1}$]): 241 (52500), 342 (8500), 476 (500)

Minor isomer (B): ^{1}H NMR ($CDCl_3$): δ 8.08 – 8.06 (2H, m), 7.95 (1H, d, *J* = 2.7), 7.07 (1H, t, *J* = 7.8), 6.98 (1H, d, *J* = 7.0), 6.89 (1H, d, *J* = 2.7), 6.74 – 6.73 (2H, m), 6.51 – 6.50 (2H, m), 6.42 (1H, t, *J* = 2.3), 6.40 (1H, d, *J* = 7.8), 6.06 (1H, d, *J* = 8.2), 3.79 (3H, s, Me), 3.25 (3H, s, Me). The remaining 7H are under the signals of the major isomer, hence a detailed assignment of the minor isomer was not possible.