Supporting Information

Dinuclear Iridium(III) Complexes of Cyclometalated Fluorenylpyridine Ligands as Phosphorescent Dopants for Efficient Solution-processed OLEDs

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General Details. Reactions that required an inert or dry atmosphere were performed under anhydrous argon which was dried by passage through a column of blue indicating silica gel and phosphorus pentoxide. All reagents were of standard reagent grade and were used as supplied unless otherwise stated from Aldrich, Fluka, Lancaster, Alfa Aesar or Alpha. Where an anhydrous solvent was employed it was dried through an HPLC column on an Innovative Technology Inc. solvent purification system. Petroleum ether refers to the fraction with a boiling point of 40-60 ^{o}C. Column chromatography was carried out using silica gel (40-60 μm). Thin layer chromatography was carried out using Polygram SilG/UV F_{254} TLC plates, with visualisation using ultraviolet light (254 or 365 nm). ^{1}H NMR spectra were recorded on either a Bruker Avance 400 at 400 MHz or a Varian Inova 500 instrument at 500 MHz. ^{13}C NMR spectra were recorded on the above spectrometers using broad-band decoupling at 100 MHz and 125 MHz, respectively. Chemical shifts are reported in ppm downfield of tetramethylsilane (TMS), using TMS or the residual non-deuterated solvent as the internal reference. Electrospray (ES^{+}) mass spectra were recorded on a Micromass LCT mass spectrometer. Matrix assisted laser desorption ionisation time of flight (MALDI-ToF) mass spectra were recorded on an Applied Biosystems Voyager-DE STR mass spectrometer. GC-MS mass spectra were recorded on a Thermo-Finnigan Trace mass spectrometer. Melting points were determined using a Stuart Scientific SMP3 melting point apparatus and are uncorrected. Elemental analyses were obtained on an Exeter Analytical Inc. CE-440 elemental analyser.

Synthetic Details.

Preparation of the Ligands 1a-e.

General procedure: To a mixture of 9,9-dihexylfluoren-2-yl-boronic acid[1] and the 2-halopyridine derivative in toluene and aqueous Na_2CO_3 solution a catalytic amount of tetrakis(triphenylphosphine)palladium(0) was added and the mixture was stirred and heated at 90 ^{o}C for 64 h. Upon cooling, the mixture was diluted with water and the organic products were extracted into CH_2Cl_2. The organic layer was separated and washed with brine, separated again, dried over $MgSO_4$ and then concentrated under reduced pressure to give a product. Purification by column chromatography over silica gel afforded the ligands.

2-(2-Pyridyl)-9,9-dihexylfluorene 1a was synthesised in 89% yield as described previously.[2]

2-(5-Fluoro-2-pyridyl)-9,9-dihexylfluorene 1b. 9,9-Dihexylfluoren-2-yl-boronic acid (2.80 g, 7.38 mmol), 2-bromo-5-fluoropyridine (1.00 g, 5.68 mmol), toluene (20 ml), aqueous Na_2CO_3 (2 M, 20 ml) and $Pd(PPh_3)_4$ (0.40 g, 6% mol equiv.) were used. Purification by column chromatography, elution with petroleum ether: DCM (9:1 v/v) then (7:3 v/v) yielded **1b** as a clear oil (1.75 g, 72%) which solidified on standing at room temperature: mp 78.2-79.0 ^{o}C; R_f=0.75 (DCM). ^{1}H NMR (700

MHz, $CDCl_3$) δ 8.56 (d, J = 2.9 Hz, 1H), 7.93 (d, J = 1.3 Hz, 1H), 7.91 (dd, J = 7.9, 1.6 Hz, 1H), 7.79 – 7.72 (m, 3H), 7.46 (td, J = 8.4, 2.9 Hz, 1H), 7.35-7.30 (m, 3H), 2.01 (qd, J = 13.5, 5.3 Hz, 4H), 1.16 – 0.93 (m, 12H), 0.73 (t, J = 7.3 Hz, 6H), 0.70 – 0.57 (m, 4H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 159.65, 158.19, 154.42, 154.40, 151.65, 151.44, 142.24, 140.72, 137.92, 137.79, 137.38, 127.57, 127.02, 125.88, 123.73, 123.62, 123.14, 121.56, 121.54, 121.27, 120.19, 120.13, 55.48, 40.63, 31.71, 29.93, 23.98, 22.79, 14.19. ^{19}F NMR (658 MHz, $CDCl_3$) δ -130.25 (dd, J = 8.0, 4.3 Hz). MS(ES^+) m/z 430.29 ([M+H]), 100%), 452.27 ([M+Na], 18%). Anal. Calcd. for $C_{30}H_{36}FN$: C, 83.87; H, 8.45; N, 3.26. Found: C, 83.88; H, 8.49; N, 3.17%.

2-(5-Methoxy-2-pyridyl)-9,9-dihexylfluorene 1c. 9,9-Dihexylfluoren-2-yl-boronic acid (2.61 g, 6.9 mmol.), 2-bromo-5-methoxypyridine (1.00 g, 5.32 mmol), toluene (20 ml), aqueous Na_2CO_3 (2 M, 20 ml) and $Pd(PPh_3)_4$ (0.368 g, 6% mol. equiv.) were used. Purification by column chromatography, elution with petroleum ether: DCM (1:1 v/v then 1:2 v/v) then pure DCM yielded **1c** as a clear oil (2.1 g, 90%) which solidified on standing at room temperature: mp 112.4-112.8 ^{o}C; R_f=0.48 (DCM). ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.42 (d, J = 2.9 Hz, 1H), 7.92 (d, J = 1.3 Hz, 1H), 7.89 (dd, J = 7.9, 1.6 Hz, 1H), 7.73 (m, 3H), 7.35 – 7.23 (m, 4H), 3.90 (s, 3H), 2.05 – 1.96 (m, 4H), 1.14 – 0.94 (m, 12H), 0.73 (t, J = 7.3 Hz, 6H), 0.70 – 0.55 (m, 4H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 154.89, 151.53, 151.38, 150.82, 141.52, 140.96, 138.13, 137.18, 127.29, 126.94, 125.42, 123.09, 121.58, 121.08, 120.86, 120.02, 55.93, 55.43, 40.66, 31.72, 29.94, 23.98, 22.80, 14.19. MS(ES^+) m/z 442.31 ([M+H], 100%), 464.29 ([M+Na], 6.7%). Anal. calcd. for $C_{31}H_{39}NO$: C, 84.31; H, 8.90; N, 3.17. Found: C, 84.12; H, 8.93; N, 3.03%.

2-(4-Fluoro-2-pyridyl)-9,9-dihexylfluorene 1d. 9,9-Dihexylfluoren-2-yl-boronic acid (4.10 g, 10.9 mmol), 2-chloro-4-fluoropyridine (1.10 g, 8.4 mmol), toluene (20 ml) aqueous Na_2CO_3 (2 M, 20 ml) and $Pd(PPh_3)_4$ (0.580 g, 6% mol. equiv.) were used. Purification by column chromatography, elution with petroleum ether:DCM (1:1 v/v) then pure DCM yielded **1d** as a clear oil (2.10 g, 59%) which solidified on standing at room temperature: mp 48.4-49.3 ^{o}C; R_f=0.69 (DCM). ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.74 (dt, J = 48.0, 24.0 Hz, 1H), 8.09 (d, J = 22.0 Hz, 1H), 8.05 (dd, J = 7.9, 1.4 Hz, 1H), 7.94 – 7.76 (m, 2H), 7.65 – 7.52 (m, 1H), 7.50 – 7.30 (m, 3H), 7.03 (ddd, J = 7.9, 5.6, 2.2 Hz, 1H), 2.24 – 2.01 (m, 4H), 1.25 – 1.00 (m, 14H), 0.82 (t, J = 7.3 Hz, 5H), 0.79 – 0.66 (m, 5H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 170.33, 168.85, 161.23, 152.06, 152.02, 151.63, 151.50, 143.02, 140.58, 137.16, 127.72, 127.03, 126.11, 123.11, 121.42, 120.29, 120.14, 109.87, 109.77, 108.28, 108.18, 55.48, 40.59, 31.68, 29.88, 23.95, 22.75, 14.15. ^{19}F NMR (658 MHz, $CDCl_3$) δ -102.64 (dd, J = 26.5, 8.9 Hz). MS(ES^+) m/z 430.3 ([M+H], 100%), 452.3 ([M+Na], 11%). Anal. calcd. for $C_{30}H_{36}FN$: C, 83.87; H, 8.45; N, 3.26. Found: C, 83.75; H, 8.56; N, 3.10%.

2-(4-Methoxy-2-pyridyl)-9,9-dihexylfluorene 1e. 9,9-Dihexylfluoren-2-yl-boronic acid (3.80 g, 9.9 mmol), 2-chloro-4-methoxypyridine (1.10 g, 7.6 mmol), toluene (20 ml), aqueous Na_2CO_3 (2 M, 20 ml) and $Pd(PPh_3)_4$ (0.5 g, 6% eq) were used. Purification by column chromatography, elution with DCM yielded a clear oil (1.50 g, 44%) which solidified on standing at room temperature: mp 82.5-83.4 ^oC; R_f=0.30 (DCM). ^1H NMR (700 MHz, $CDCl_3$) δ 8.56 (d, J = 5.6 Hz, 1H), 8.02 (d, J = 0.9 Hz, 1H), 7.97 (dd, J = 7.9, 1.4 Hz, 1H), 7.76 (dd, J = 32.5, 7.3 Hz, 2H), 7.42 – 7.27 (m, 5H), 6.75 (dd, J = 5.6, 2.3 Hz, 1H), 2.11 – 1.99 (m, 5H), 1.14 – 0.97 (m, 14H), 0.74 (t, J = 7.3 Hz, 7H), 0.72 – 0.59 (m, 5H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 166.51, 159.70, 151.41, 151.05, 142.32, 140.76, 138.35, 127.44, 126.92, 126.00, 123.03, 121.41, 120.09, 119.92, 107.85, 107.15, 55.41, 55.25, 40.57, 31.65, 29.86, 23.93, 22.72, 14.13. MS(ES^+) m/z 442.3 ([M+H], 100%), 464 ([M+Na], 4.5%). Anal. calcd. for $C_{31}H_{39}NO$: C, 84.31; H, 8.90; N, 3.17. Found: C, 83.97; H, 8.87; N, 3.09%.

Complex 2a was synthesised in 60% yield as described previously.[3]

Complex 2b. The ligand **1b** (1.37 g, 3.2 mmol), $IrCl_3 \cdot 3H_2O$ (0.24 g, 0.80 mmol), 2-ethoxyethanol (20 ml) and water (10 ml) were used. Purification by column chromatography, elution with DCM/hexane (1:3 v/v) yielded **2b** as a pale orange solid (0.55 g, 64%). ^1H NMR (700 MHz, $CDCl_3$) δ 9.21 (t, J = 2.5 Hz, 4H), 7.98 (dd, J = 9.1, 5.4 Hz, 4H), 7.79 – 7.65 (m, 4H), 7.38 (s, 4H), 7.15 (m, 8H), 7.13 – 7.06 (m, 8H), 6.35 (s, 4H), 1.86 – 1.72 (m, 16H), 1.04 – 0.82 (m, 48H), 0.61 (dt, J = 53.9, 7.2 Hz, 40H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 166.18, 157.54, 156.12, 151.98, 144.65, 143.06, 142.02, 141.64, 140.63, 140.49, 140.31, 127.02, 126.37, 124.78, 124.67, 122.96, 121.62, 119.73, 119.21, 119.18, 118.45, 54.32, 40.46, 31.58, 31.42, 30.06, 29.80, 23.91, 22.89, 22.67, 14.15, 14.06. ^{19}F NMR (658 MHz, $CDCl_3$) δ -126.97. MS(MALDI-TOF) m/z 2169.2 ([M+H, ^{191}Ir, ^{193}Ir, ^{35}Cl, ^{35}Cl], 100%). Anal. calcd. for $C_{120}H_{140}N_4Cl_2F_4Ir_2$: C, 66.43; H, 6.50; N, 2.58. Found: C, 66.20; H, 6.44; N, 2.40%.

Complex 2c. The ligand **1c** (1.41 g, 3.2 mmol), $IrCl_3 \cdot 3H_2O$ (0.24 g, 0.80 mmol), 2-ethoxyethanol (20 ml) and water (10 ml) were used. Purification by column chromatography, elution with DCM/hexane (1:1 v/v) yielded **2c** as a yellow solid (0.56 g, 63%). ^1H NMR (700 MHz, $CDCl_3$) δ 9.12 (d, J = 2.7 Hz, 4H), 7.91 (d, J = 9.0 Hz, 4H), 7.50 (dd, J = 8.9, 2.7 Hz, 4H), 7.33 (s, 4H), 7.18 – 7.13 (m, 4H), 7.10 (td, J = 8.6, 5.1 Hz, 16H), 6.33 (s, 4H), 3.66 (s, 4H), 1.78 (m, 16H), 1.07 – 0.86 (m, 48H), 0.63 (dt, J = 66.6, 7.1 Hz, 40H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 162.41, 153.61, 151.90, 144.17, 142.88, 142.60, 141.24, 140.79, 138.66, 126.39, 126.21, 123.25, 122.95, 121.41, 119.31, 118.61, 117.33, 56.34, 54.17, 40.39, 40.35, 31.58, 31.41, 30.05, 29.92, 29.80, 23.99, 23.89, 22.86,

22.66, 14.18, 14.07. MS(MALDI-TOF) m/z 2217.3 ([M+H, ^{191}Ir , ^{193}Ir, ^{35}Cl, ^{35}Cl], 100%). Anal. calcd. for $C_{124}H_{152}Cl_2N_4O_4Ir_2$: C,67.15; H,6.91; N,2.53. Found: C, 67.09; H, 6.87; N, 2.37%.

Complex 2d. The ligand **1d** (0.77 g, 1.8 mmol), $IrCl_3 \cdot 3H_2O$ (0.135 g, 0.45 mmol), 2-ethoxyethanol (10 ml) and water (5 ml) were used. Purification by column chromatography, elution with DCM/hexane (1:1 v/v) yielded **2d** as a pale orange solid (0.29 g, 60%), R_f=0.83 (DCM:hexane, 1:1 v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.32 (t, J = 6.8 Hz, 4H), 7.67 (dd, J = 9.3, 2.7 Hz, 4H), 7.38 (s, 4H), 7.24 (s, 4H), 7.19 – 7.06 (m, 16H), 6.75 (td, J = 6.7, 2.7 Hz, 4H), 6.33 (s, 4H), 1.83 – 1.74 (m, 16H), 1.00 – 0.84 (m, 48H), 0.61 (dt, J = 40.3, 7.1 Hz, 40H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.66, 172.60, 170.60, 168.50, 154.49, 154.42, 152.10, 144.69, 144.58, 142.92, 142.04, 140.42, 127.36, 126.44, 123.02, 121.78, 119.87, 118.80, 109.61, 109.45, 105.98, 105.81, 54.35, 40.53, 40.38, 31.60, 31.41, 30.03, 29.78, 23.89, 22.88, 22.68, 14.16, 14.05. ^{19}F NMR (658 MHz, $CDCl_3$) δ -100.64 (dd, J = 14.7, 6.8 Hz). MS(MALDI-TOF) m/z 2173.3 ([M+H, ^{191}Ir , ^{193}Ir, ^{37}Cl, ^{37}Cl], 100%). Anal. calcd. for $C_{120}H_{140}N_4Cl_2F_4Ir_2$: C, 66.43; H, 6.50; N, 2.58. Found: C, 66.62; H, 6.58; N, 2.55%. Crystals for X-ray diffraction analysis were grown by dissolving the sample in EtOAc and vapour diffusion of pentane.

Complex 2e. The ligand **1e** (0.37 g, 0.84 mmol), $IrCl_3 \cdot 3H_2O$ (0.063 g, 0.21 mmol), 2-ethoxyethanol (5 ml) and water (2.5 ml) were used. Purification by column chromatography, elution with DCM yielded **2e** as a dark orange solid (0.19 g, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.12 (d, J = 6.5 Hz, 4H), 7.42 (d, J = 2.8 Hz, 4H), 7.34 (s, 4H), 7.14 (m, 8H), 7.10 – 7.06 (m, 8H), 6.53 (dd, J = 6.5, 2.8 Hz, 4H), 6.41 (s, 4H), 4.17 (s, 12H), 1.82 – 1.73 (m, 16H), 1.02 – 0.86 (m, 48H), 0.61 (dt, J = 38.9, 7.2 Hz, 40H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.39, 166.27, 153.11, 151.95, 144.83, 143.82, 143.32, 141.81, 141.09, 126.68, 126.19, 122.86, 122.19, 119.72, 117.89, 109.15, 103.05, 56.05, 54.24, 40.64, 40.51, 31.60, 31.44, 22.91, 22.70, 14.17, 14.08. MS(MALDI-TOF) m/z 2218.0 ([M, ^{191}Ir , ^{193}Ir, ^{35}Cl, ^{37}Cl or ^{191}Ir , ^{191}Ir, ^{37}Cl, ^{37}Cl or ^{193}Ir , ^{193}Ir, ^{35}Cl, ^{35}Cl], 100%). Anal. calcd. for $C_{124}H_{152}N_4Cl_2O_4Ir_2$: C, 67.15; H, 6.91; N, 2.53. Found: C, 67.19; H, 6.91; N, 2.53%. Crystals for X-ray diffraction analysis were grown by dissolving the sample in EtOAc and vapour diffusion of pentane.

Complex 3a was prepared in 74% yield as described previously.[3] Crystals for X-ray diffraction analysis were grown by dissolving the sample in EtOAc and vapour diffusion of pentane.

Complex 3b. Complex **2b** (0.30 g, 0.14 mmol), tetrabutylammonium cyanate (0.49 g, 1.68 mmol) and dichloromethane (60 ml) were used. Purification by column chromatography, elution with

DCM:hexane (1:3 v/v) yielded **3b** as an orange solid (0.23 g, 76%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.41 (t, J = 2.6 Hz, 2H), 7.99 (dd, J = 9.1, 5.4 Hz, 2H), 7.71 (t, J = 9.1 Hz, 2H), 7.44 (s, 2H), 7.16 (t, J = 7.6 Hz, 4H), 7.14 – 7.08 (m, 4H), 6.37 (s, 2H), 1.82 (dd, J = 16.1, 7.8 Hz, 8H), 0.98 – 0.87 (m, 24H), 0.64 – 0.57 (m, 18H), 0.40 (m, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 166.62, 157.51, 156.09, 151.99, 144.68, 143.40, 142.48, 141.71, 140.70, 139.36, 139.18, 127.16, 126.38, 124.98, 124.87, 122.94, 121.75, 119.78, 119.38, 119.35, 118.88, 54.40, 40.76, 40.41, 31.39, 29.79, 24.02, 23.48, 22.74, 22.72, 14.08. ^{19}F NMR (658 MHz, $CDCl_3$) δ -126.54. MS(MALDI-TOF) m/z 2182.1 ([M, ^{191}Ir , ^{193}Ir], 100%). Anal. calcd. for $C_{122}H_{140}N_6F_4O_4Ir_2$: C, 67.13; H, 6.46; N, 3.85. Found: C, 67.04; H, 6.49; N, 3.68%.

Complex 3c. Complex **2c** (0.15 g, 0.071 mmol), tetrabutylammonuim cyanate (0.245 g, 0.842 mmol) and dichloromethane (30 ml) were used. Purification by column chromatography, elution with DCM:hexane 5:1 v/v, yielded **3c** as a dark orange solid (0.201 g, 75%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.32 (d, J = 2.4 Hz, 2H), 7.91 (d, J = 9.1 Hz, 2H), 7.44 (dd, J = 8.3, 1.9 Hz, 2H), 7.38 (s, 2H), 7.16 – 7.10 (m, 4H), 7.09 – 7.07 (m, 4H), 7.05 – 7.05 (m, 2H), 6.39 (s, 2H), 3.62 (s, 6H), 1.81 – 1.76 (m, 8H), 1.00 – 0.87 (m, 24H), 0.59 (d, J = 14.3 Hz, 18H), 0.52 – 0.46 (m, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 162.79, 153.73, 151.90, 144.28, 143.03, 142.48, 141.34, 136.93, 133.71, 126.53, 126.27, 124.00, 122.96, 121.59, 119.36, 118.76, 117.65, 56.16, 54.26, 40.53, 40.44, 31.51, 31.34, 29.92, 29.79, 24.03, 23.53, 22.73, 22.68, 14.11, 14.09. MS(MALDI-TOF) m/z 2231.2 ([M+H, ^{191}Ir , ^{193}Ir], 100%). Anal. calcd. for $C_{126}H_{152}N_6O_6Ir_2$: C, 67.83; H, 6.87; N, 3.77. Found: C, 68.12; H, 6.85; N, 3.57%.

Complex 4a was prepared in 23% yield as described previously.[2]

Complex 4b. Ligand **1b** (714 mg, 1.7 mmol), glycerol (15 ml) and $Ir(acac)_3$ (157 mg, 0.3 mmol) were used. Purification with column chromatography, elution with DCM/hexane 2:1 v/v then 1:1 v/v, yielded **4b** as an orange solid (91 mg, 20%); R_f=0.63(DCM:hexane; 1:1 v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (dd, J = 9.0, 5.1 Hz, 3H), 7.65 – 7.56 (m, 3H), 7.52 (s, 3H), 7.45 (t, J=2Hz, 3H), 7.44 – 7.36 (m, 3H), 7.23 – 7.06 (m, 9H), 6.97 (t, J = 7.4 Hz, 3H), 1.98 (t, J=8.5Hz 6H), 1.94 – 1.88 (m, 6H), 1.23-0.61 (m, 66H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.00, 163.97, 159.49, 157.91, 157.50, 151.59, 143.04, 143.00, 141.90, 141.73, 135.20, 134.97, 128.21, 126.66, 126.41, 123.77, 123.62, 122.45, 120.51, 120.28, 120.24, 118.44, 54.33, 41.35, 41.03, 31.70, 31.68, 30.16, 30.04, 24.02, 23.94, 23.15, 22.80, 14.29, 14.23. ^{19}F NMR (658 MHz, $CDCl_3$) δ -130.38 (t, J = 6.1 Hz). MS(MALDI-TOF) m/z 1476.9 ([M, ^{191}Ir], 74.37%), 1477.9 ([M+H, ^{191}Ir], 100%), 1478.9 ([M,^{193}Ir], 92%), 1479.8 ([M+H, ^{193}Ir], 74%); HRMS(MOLDI-TOF) calcd. for $C_{90}H_{105}F_3N_3Ir(^{193}Ir)$ 1478.7917,

found 1478.7933. Anal. calcd. for $C_{90}H_{105}F_3N_3Ir$: C, 73.14; H, 7.16; N, 3.86. Found: C, 73.72; H, 7.64; N, 2.66%.

Complex 4c. Ligand **1c** (734 mg, 1.7 mmol), glycerol (15 ml) and $Ir(acac)_3$ (157 mg, 0.3 mmol) were used. Purification with column chromatography over silica gel, elution with DCM/hexane 1:1 v/v, yielded **4c** as a yellow solid (115 mg, 25%); R_f=0.34 (DCM:hexane; 1:1 v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 9.5 Hz, 3H), 7.62 (s, 3H), 7.26 (s, 3H), 7.23 (dd, J = 7.2, 3.5 Hz, 9H), 7.12 (d, J = 7.4 Hz, 3H), 7.06 (t, J = 7.2 Hz, 3H), 6.97 (t, J = 7.4 Hz, 3H), 2.13 – 1.85 (m, 12H), 1.53 (s, 3H), 1.33 – 0.56 (m, 66H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.27, 151.59, 142.27, 135.23, 126.23, 126.19, 122.16, 120.49, 120.37, 119.98, 55.90, 42.21, 41.96, 31.72, 31.70, 30.18, 30.11, 24.13, 23.96, 23.16, 22.82, 14.30, 14.25. MS(MALDI-TOF) m/z 1512.8 ([M, ^{191}Ir], 47%), 1513.8 ([M+H, ^{191}Ir], 100%), 1514.9([M,^{193}Ir], 88%), 1515.9 ([M+H, ^{193}Ir], 44%). Anal. calcd. for $C_{93}H_{114}N_3O_3Ir$: C, 73.77; H, 7.59; N, 2.78 . Found: C, 73.76; H, 7.60; N, 2.71%.

Complex 4e. Ligand **1e** (734 mg, 1.7 mmol, 1.8 eq), glycerol (15 ml) and $Ir(acac)_3$ (157 mg, 0.3 mmol) were used. Purification with column chromatography, elution with DCM/hexane (2:1 v/v then 1:1 v/v) yielded **4e** as a yellow solid (110 mg, 24%); R_f=0.89 (DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 3H), 7.39 (s, 3H), 7.22 (d, J = 7.5 Hz, 3H), 7.14 – 7.04 (m, 12H), 6.95 (t, J = 7.4 Hz, 3H), 6.03 (s, 3H), 3.96 (s, 9H), 2.27 – 2.09 (m, 6H), 2.05 – 1.81 (m, 6H), 1.13 – 0.54 (m, 66H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.82, 151.55, 148.67, 142.72, 126.38, 122.24, 120.28, 110.46, 105.16, 55.50, 31.77, 31.74, 30.18, 30.14, 24.24, 24.06, 23.17, 22.86, 14.29. MS(MALDI-TOF) m/z 1512.8 ([M, ^{191}Ir], 66%), 1513.7 ([M+H, ^{191}Ir], 100%), 1514.7 ([M,^{193}Ir], 92%), 1515.7 ([M+H, ^{193}Ir], 66%). Anal. calcd. for $C_{93}H_{114}N_3O_3Ir$: C, 73.77; H, 7.59; N, 2.78 . Found: C, 73.82; H, 7.58; N, 2.82%.

^{1}H NMR Spectra of Complexes 2b, 2d and 3b.

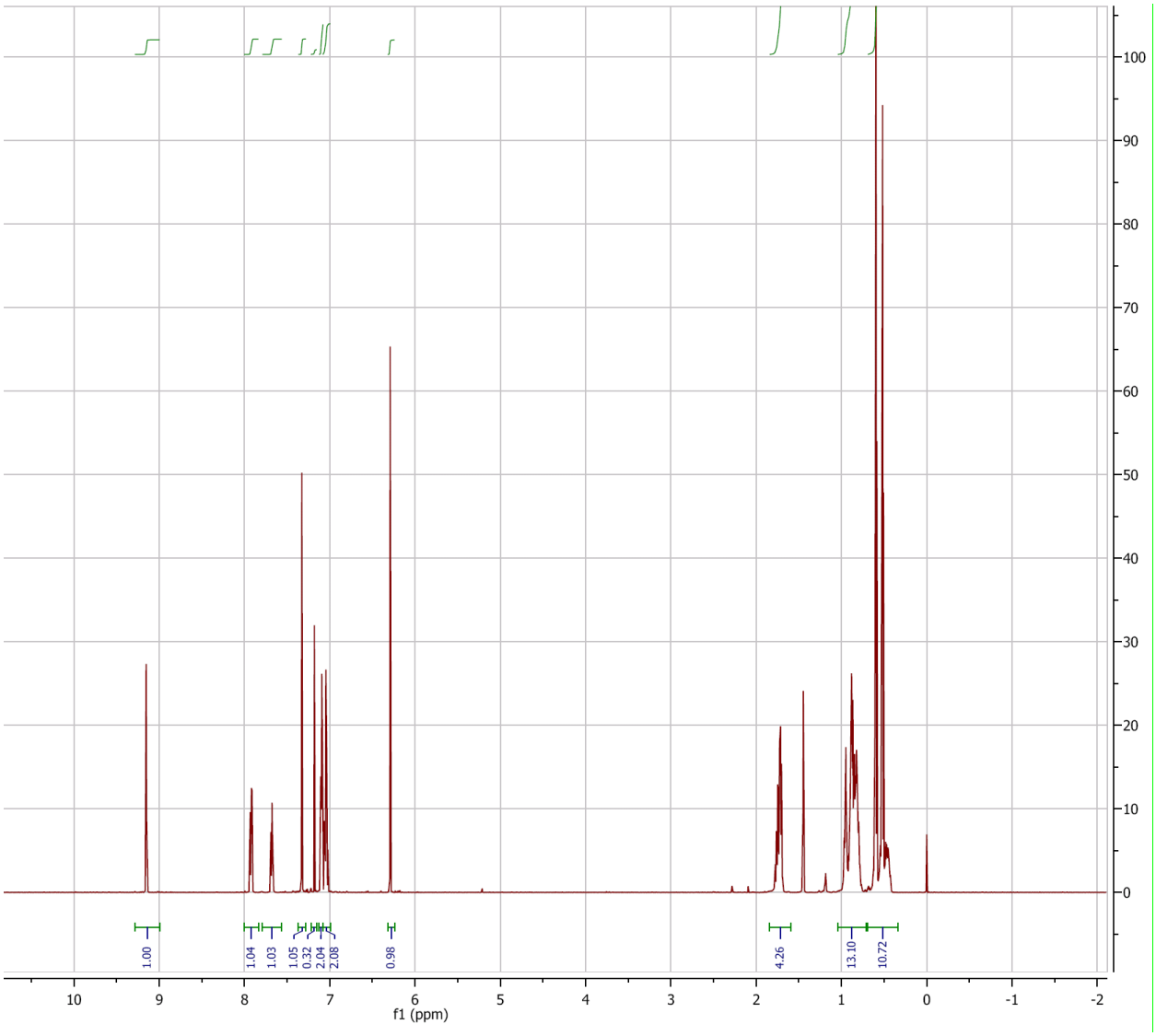

Fig. S1. ^{1}H NMR spectrum of complex **2b** in $CDCl_3$.

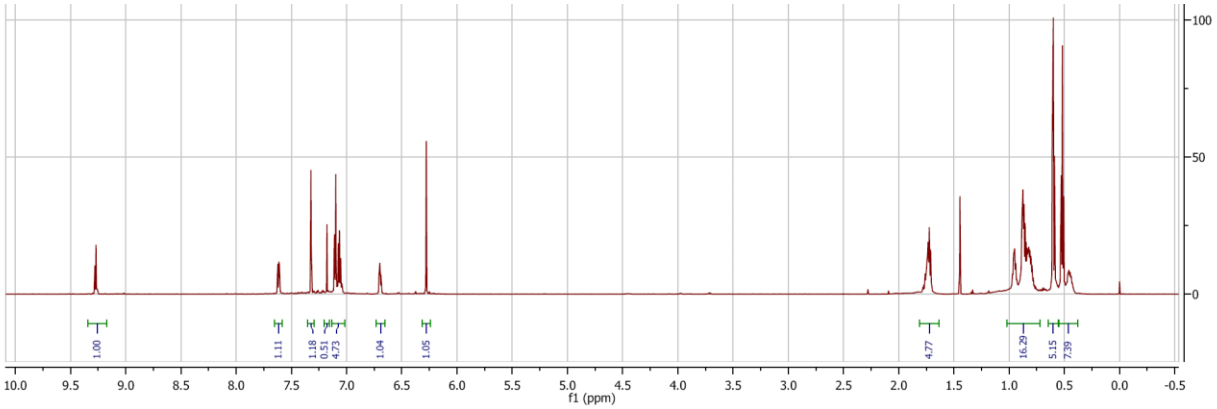

Fig. S2. ^{1}H NMR spectrum of complex **2d** in $CDCl_3$.

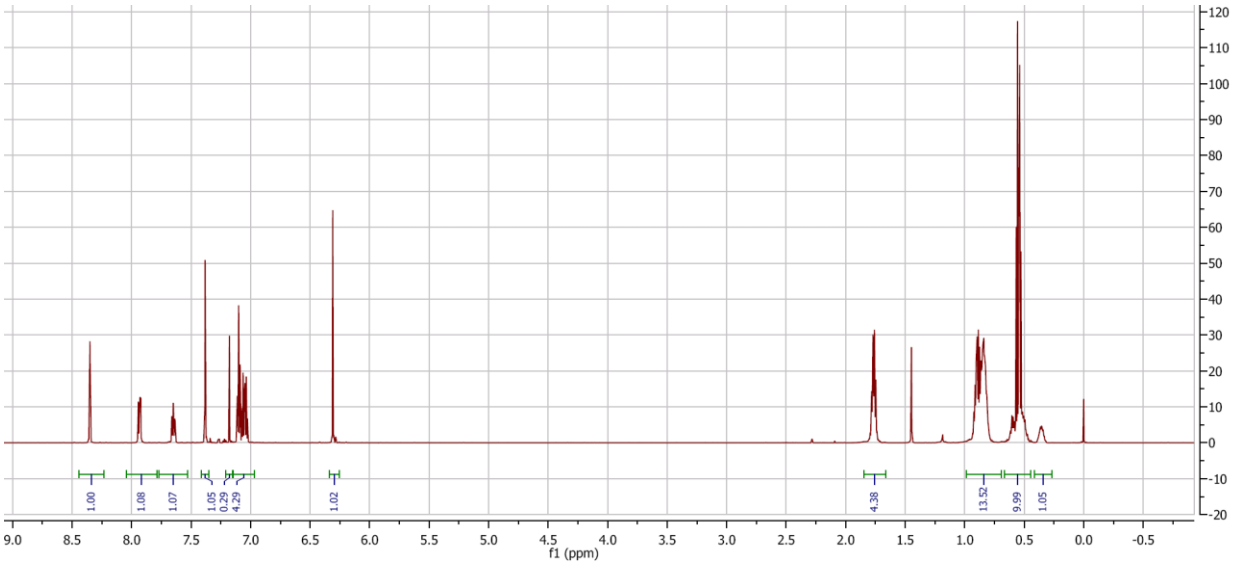

Fig. S3. ^{1}H NMR spectrum of complex **3b** in $CDCl_3$.

Cyclic Voltammograms of Complexes 2b and 3b.

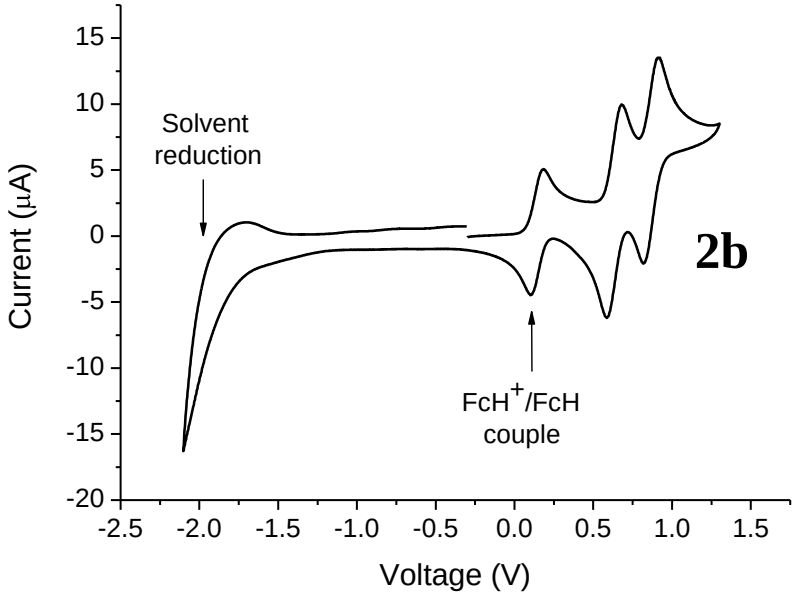

Fig. S4. CV of complex **2b** in dichloromethane.

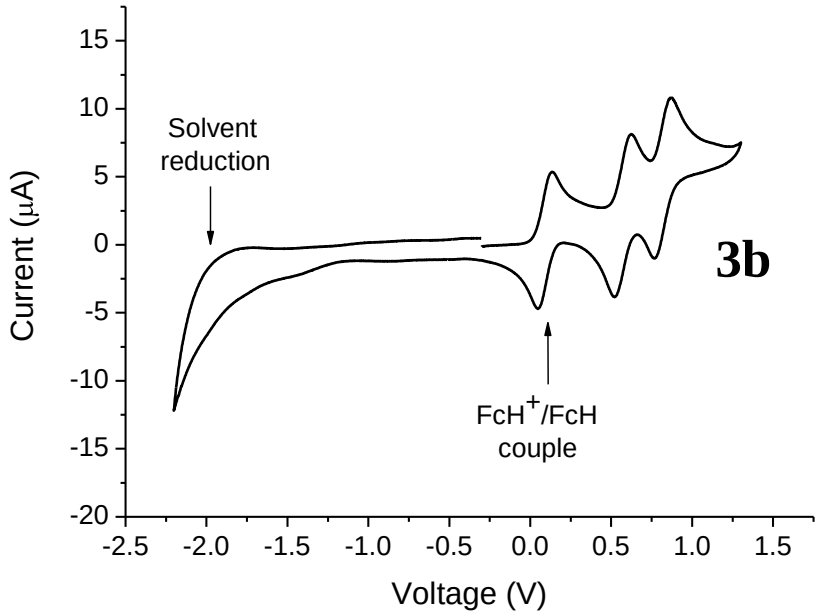

Fig. S5. CV of complex **3b** in dichloromethane.

X-Ray Crystal Structures

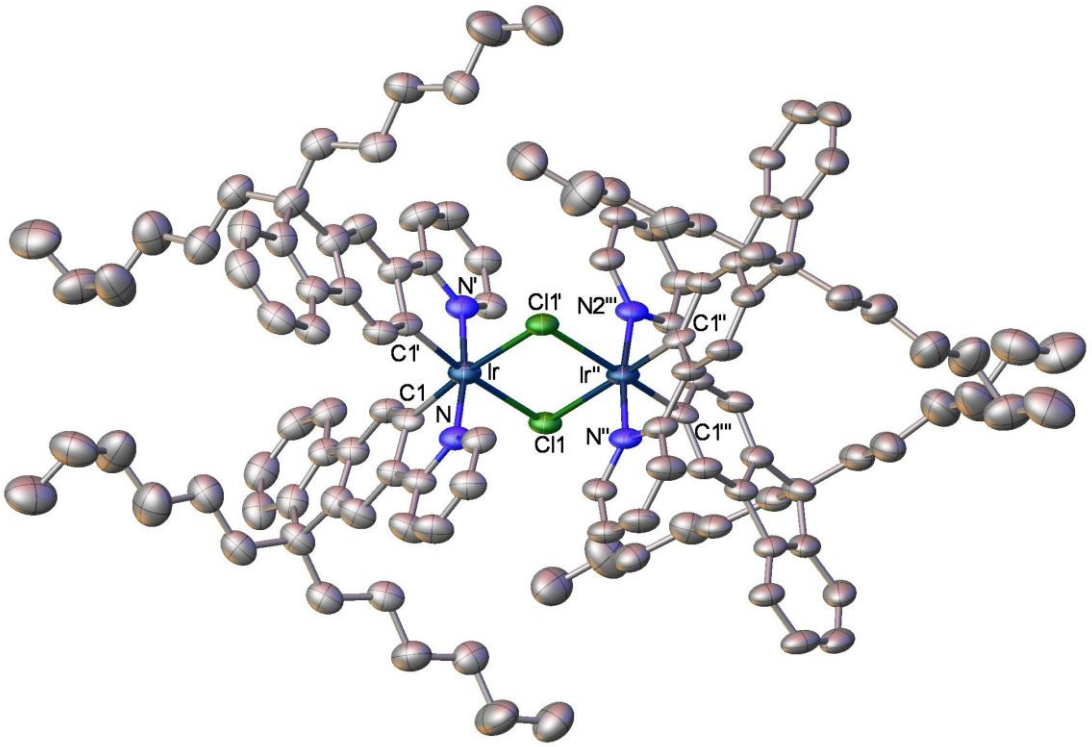

Fig. S6. X-ray molecular structure of **2a** in the crystal of **2a**·3/2PhCl. Thermal ellipsoids are drawn at the 50% probability level. Solvent molecules, disorder and H atoms are omitted for clarity.

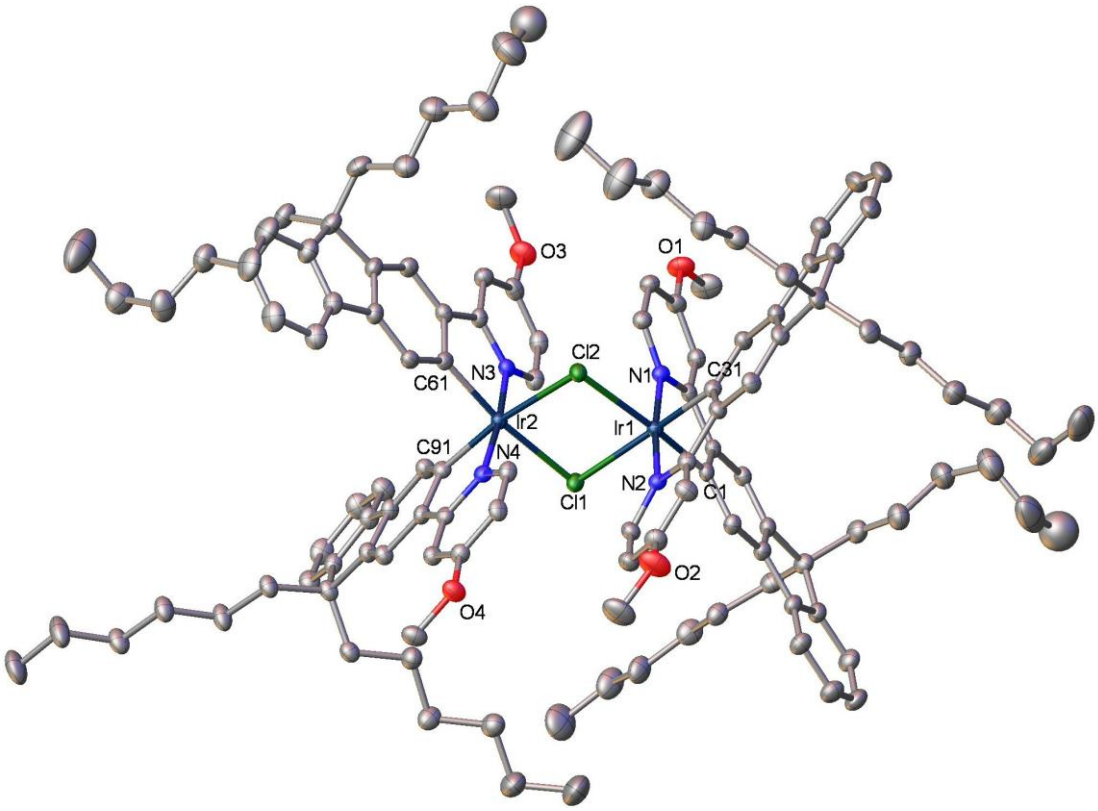

Fig. S7. X-ray molecular structure of **2e** in the crystal of **2e**·2PhCl·3C_5H_{12}. Thermal ellipsoids are drawn at the 30% probability level. Solvent molecules, disorder and H atoms are omitted for clarity.

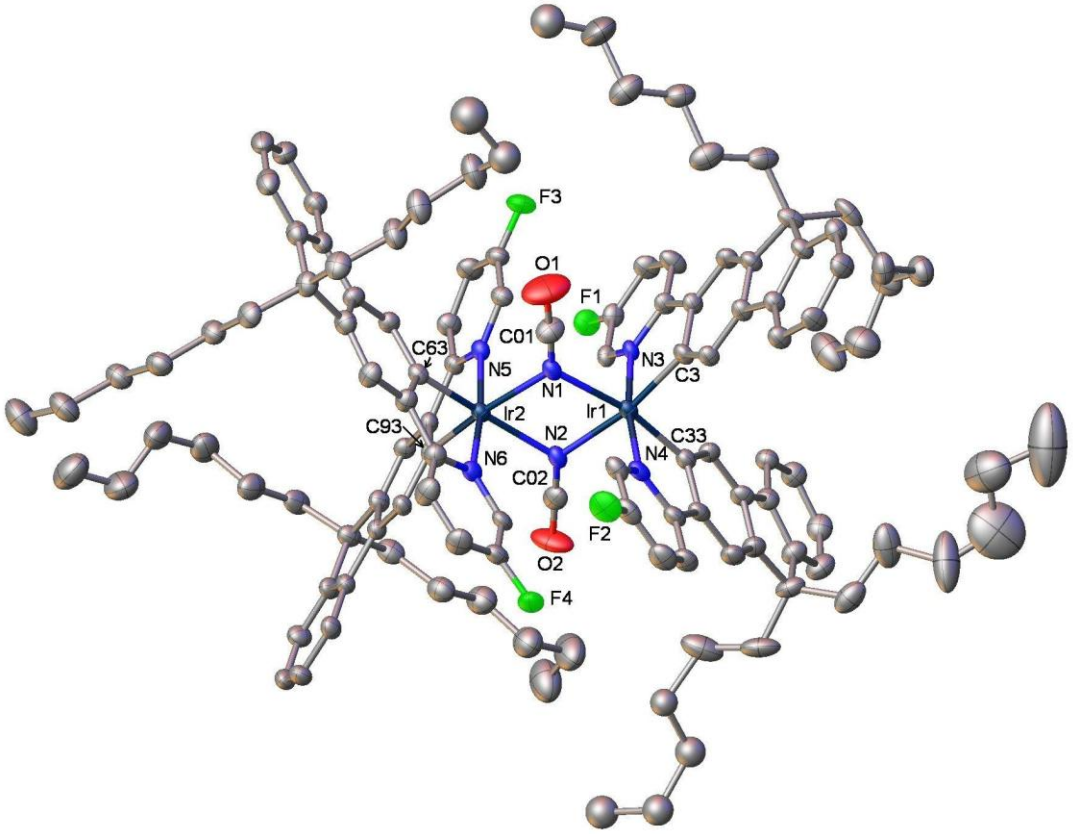

Fig. S8. X-ray molecular structure of **3b**. Thermal ellipsoids are drawn at the 50% probability level. Disorder and H atoms are omitted for clarity.

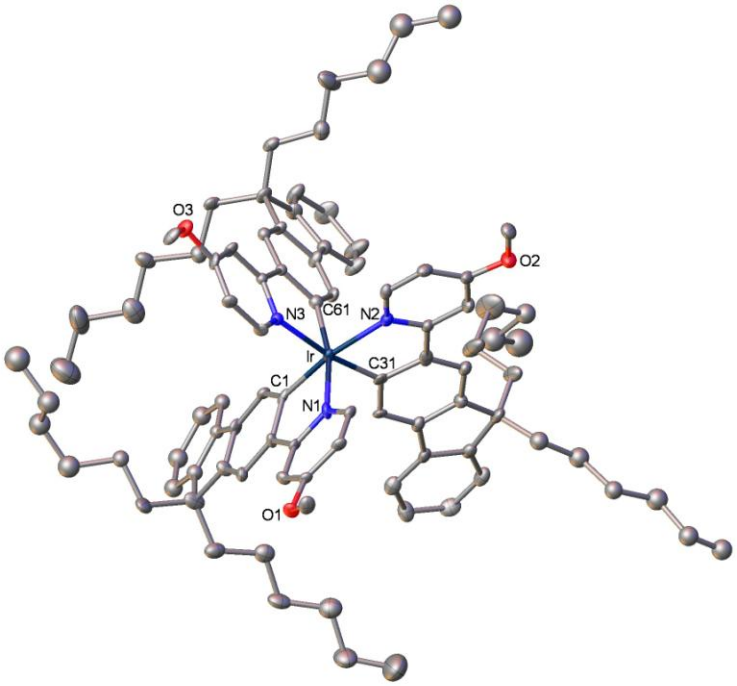

Fig. S9. X-ray molecular structure of **4e** in the crystal of **4e**·C_5H_{12}. Thermal ellipsoids are drawn at the 30% probability level. Solvent molecules, disorder and H atoms are omitted for clarity.

Table S1. Comparison of computed data from selected model chemistries with reported experimental data for $[Ir(ppy)_2Cl]_2$

	Expt	B3LYP	B3LYP	B3LYP	B3LYP	PBE0	MPW1K	CAM- B3LYP
Pseudopotential for Ir		LANL2DZ	LANL2DZ	LANL2DZ	LANL2DZ	LANL2DZ	LANL2DZ	LANL2DZ
Basis set for other atoms		LANL2DZ	6-31G	6-31G*	3-21G*	3-21G*	3-21G*	3-21G*
Ir…Ir distance (Å)	3.771[a]	4.079	4.083	4.013	3.930	3.813	3.794	3.853
Cl…Cl distance (Å)	3.388[a]	3.461	3.464	3.413	3.390	3.339	3.326	3.366
Ir-Cl bond length (Å)	2.535[a]	2.675	2.677	2.634	2.595	2.534	2.523	2.558
Ir-N bond length (Å)	2.091[a]	2.065	2.071	2.076	2.061	2.036	2.036	2.055
Ir-C bond length (Å)	2.020[a]	2.008	2.009	2.006	2.009	1.989	1.987	2.002
LUMO (eV)	(-3.1)[b]	-1.64	-1.43	-1.39	-1.41	-1.32	-0.77	-0.19
HOMO (eV)	-5.32[b]	-5.08	-4.92	-4.93	-4.98	-5.25	-6.02	-6.30
HLG (eV)	(2.23)[b]	3.44	3.49	3.54	3.57	3.93	5.35	6.11
$S_0 > T_1$ (absorption, nm)	484[c]	508	497	491	484	472	470	439
$S_0 > S_1$ (absorption, nm)	450[c]	462	453	444	443	421	358	361

[a] From X-ray diffraction data for $[Ir(tpy)_2Cl]_2$ tpy = 4'-methylphenylpyridine at 296 K; reference.[4]

[b] From CV data on $[Ir(ppy)_2Cl]_2$ in DCM and values in volts(V) based on 4.8 V for the FcH/FcH^+ couple – irreversible reduction wave; reference.[5]

[c] From absorption data for $[Ir(ppy)_2Cl]_2$ in DCM – these are very weak mixed MLCT bands 'assigned' as ^{3}MLCT and ^{1}MLCT for 484 and 450 nm, respectively; reference 5.

Table S2. Molecular Orbital Compositions (%) for **2b′**, **3b′** and **4b′**. Ir = iridium, Cl =chloride, Py = fluoropyridyl group, Fl = fluorenyl group, NCO = isocyanate.

2b′

MO		eV	Ir1	Cl1	Py1	Py2	Fl1	Fl2	Ir2	Cl2	Py3	Py4	Fl3	Fl4
341	L+4	-1.26	1	0	18	18	7	7	1	0	18	18	7	7
340	L+3	-1.51	2	0	15	15	9	9	2	0	15	15	9	9
339	L+2	-1.62	4	0	13	13	10	10	4	0	13	13	10	10
338	L+1	-1.71	3	0	18	18	6	6	3	0	18	18	6	6
337	LUMO	-1.71	2	1	17	17	6	6	2	1	17	17	6	6
336	HOMO	-5.03	18	2	2	2	13	13	18	2	2	2	13	13
335	H-1	-5.08	18	0	2	2	13	13	18	0	2	2	13	13
334	H-2	-5.48	7	1	4	4	17	17	7	1	4	4	17	17
333	H-3	-5.51	2	0	4	4	20	20	2	0	4	4	20	20
332	H-4	-5.70	6	1	2	2	19	19	6	1	2	2	19	19

3b′

MO		eV	Ir1	NCO1	Py1	Py2	Fl1	Fl2	Ir2	NCO2	Py3	Py4	Fl3	Fl4
345	L+4	-1.37	1	0	19	19	5	5	1	0	19	19	5	5
344	L+3	-1.57	2	0	16	16	8	8	2	0	16	16	8	8
343	L+2	-1.61	3	0	14	14	9	9	3	0	14	14	9	9
342	L+1	-1.76	2	0	16	16	7	7	2	0	17	17	7	7
341	LUMO	-1.78	3	0	18	18	6	6	3	0	18	18	6	6
340	HOMO	-5.03	20	0	2	2	12	12	20	0	2	2	12	12
339	H-1	-5.11	18	1	2	2	13	13	18	1	2	2	13	13
338	H-2	-5.42	17	9	3	3	9	9	17	9	3	3	9	9
337	H-3	-5.51	2	0	4	4	20	20	2	0	4	4	20	20
336	H-4	-5.61	27	15	2	2	2	2	27	15	2	2	2	2

4b′

MO		eV	Ir	Py1	Py2	Py3	Fl1	Fl2	Fl3
240	L+4	-0.99	1	20	50	8	6	14	2
239	L+3	-1.20	2	26	26	26	7	7	6
238	L+2	-1.45	5	31	0	35	13	0	16
237	L+1	-1.46	5	12	44	10	6	19	4
236	LUMO	-1.55	1	23	22	21	11	11	10
235	HOMO	-4.98	40	4	4	4	16	16	17
234	H-1	-5.17	29	3	3	7	7	15	35
233	H-2	-5.17	29	6	5	2	31	24	3
232	H-3	-5.58	16	2	2	4	14	13	49
231	H-4	-5.58	16	4	3	1	36	38	2

Table S3. Comparison of computed absorption and emission data with observed data.

Complex	$S_0 > S_1$ (S_0 geometry) (nm)	$S_0 > T_1$ (S_0 geometry) (nm)	$S_0 < T_1$ (T_1 geometry) (nm)	Complex	Abs Em. maxima (nm)	PL Em. maxima (nm)
2a′	461	523	587	**2a**	538	546
2b′	468	527	594	**2b**	539	545
2c′	453	517	534	**2c**	546	550
2d′	455	518	539	**2d**	539	544
2e′	450	511	622	**2e**	535	542
3a′	469	526	579	**3a**	541	548
3b′	478	530	568	**3b**	541	549
3c′	463	519	644	**3c**	546	552
4a′	454	504	626	**4a**	538	545
4b′	454	509	633	**4b**	536	542
4c′	453	512	651	**4c**	535	544
4e′	440	493	606	**4e**	535	544

Table S4. Predicted nature of $S_0 > T_1$ and $S_0 > S_1$ transitions for **2b′**, **3b′** and **4b′**.

	Energy (eV)	Wavelength (nm)	Osc. Strength	Major contributions	%Ir	%Py	%Fl	%Cl	%NCO
2b′									
$S_0 > T_1$	2.35	527	0	HOMO>LUMO (42%)	32>6 (-26)	12>64 (52)	56>32 (-24)	2>0 (-2)	
$S_0 > S_1$	2.65	468	0.0059	HOMO-1>LUMO (58%)	36>6 (-30)	8>64 (56)	52>32 (-20)	2>0 (-2)	
3b′									
$S_0 > T_1$	2.34	530	0	HOMO>LUMO (54%)	36>6 (-30)	8>64 (56)	52>32 (-20)		2>0 (-2)
$S_0 > S_1$	2.59	478	0.0063	HOMO>LUMO (81%)	40>4 (-36)	8>64 (56)	48>28 (-20)		0>0 (0)
4b′									
$S_0 > T_1$	2.44	509	0	HOMO>LUMO (65%)	36>3 (-33)	12>67 (55)	52>31 (-21)		
$S_0 > S_1$	2.73	454	0.0186	HOMO>LUMO (93%)	39>1 (-38)	9>66 (54)	50>32 (-18)		

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