A Spectroscopic And Theoretical Investigation of Color Tuning in Deep Red Luminescent Iridium(III) Complexes

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Supporting Information

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Experimental

$^1\text{H}$, $^{19}\text{F}$,$^1\text{H}$ and $^{13}\text{C}$,$^1\text{H}$ NMR spectra were recorded on an NMR-FT Bruker 500 and 400 MHz spectrometer and recorded in CDCl$_3$, acetone-$d_6$, acetonitrile-$d_3$ and DMSO-$d_6$. $^1\text{H}$ and $^{13}\text{C}$,$^1\text{H}$ NMR chemical shifts ($\delta$) were determined relative to residual solvent peaks with digital locking and are given in ppm. Coupling constants are quoted in Hz. Low-resolution mass spectra were obtained by the staff at Cardiff University. High-resolution mass spectra were carried out at the EPSRC National Mass Spectrometry Facility at Swansea University. UV-Vis studies were performed on a Shimadzu UV-1800 spectrophotometer as CHCl$_3$ solutions ($1 \times 10^{-5}$ M). Photophysical data were obtained on a JobinYvon–Horiba Fluorolog spectrometer fitted with a JY TBX picosecond photodetection module as CHCl$_3$ solutions. Emission spectra were uncorrected and excitation spectra were instrument corrected. The pulsed source was a Nano-LED configured for 295 or 459 nm output operating at 1 MHz. Luminescence lifetime profiles were obtained using the JobinYvon–Horiba FluoroHub single photon counting module and the data fits yielded the lifetime values using the provided DAS6 deconvolution software. Quantum yield measurements were obtained on aerated CHCl$_3$ solutions of the complexes using $[\text{Ru(bpy)}_3](\text{PF}_6)_2$ in aerated MeCN as a standard ($\Phi = 0.016$).$^1$

**Transient absorption measurements**

Transient absorption measurements were carried out using an Edinburgh Instruments LP920 spectrometer. All spectra were collected using a pump wavelength of 355 nm (third harmonic of a Continuum Surelite II Nd:YAG laser system). The probe light for these measurements was a Xenon lamp, affording spectral generation between 300 $< \lambda <$ 800 nm. Wavelength dependent spectra were recorded with a 2.05 nm spectral resolution, collected using an Andor ICCD camera, and integrated over the first 500 ns after the pump laser pulse. The spectra are presented as $\Delta \text{OD}_{\text{Xe lamp}}$, which is simply referred to as $\Delta \text{OD}$. Lifetime data was generated using a photomultiplier to collect time resolved signals, with the bandwidth of these data being identical to the camera resolution (2.05 nm). The lifetime data is fit using the Origin 2017 software package,
and each data set is fit using a monoexponential function, with no evidence of multiexponential components. Uncertainties in lifetimes are taken from the Least-Squares fitting algorithm, and are not indicative of the uncertainties in multiple fits or data sets.

Cyclic voltammetry

Electrochemical studies were carried out using a Parstat 2273 potentiostat in conjunction with a three-electrode cell. The auxiliary electrode was a platinum wire and the working electrode a platinum (1.0 mm diameter) disc. The reference was a silver wire separated from the test solution by a fine porosity frit and an agar bridge saturated with KCl. Solutions (10 ml CH₂Cl₂) were 1.0 × 10⁻³ mol dm⁻³ in the test compound and 0.1 mol dm⁻³ in [NBu₄][PF₆] as the supporting electrolyte. Under these conditions, $E^0$ for the one-electron oxidation of [Fe(η⁵-C₅H₅)₂], added to the test solutions as an internal calibrant, is +0.46 V. Unless specified, all electrochemical values are at $\nu = 200$ mV s⁻¹.

Computational methods

Electronic structure calculations were all performed using density functional theory within the Gaussian 09 computational chemistry suite. All calculations were performed using the Stuttgart-Dresden (SDD) effective core potential and basis set in the treatment of the iridium, in combination with a 6-31G* basis set for all other light atoms. Full geometry optimizations were performed for the cationic complexes utilizing the self-consistent reaction field model (SCRF) which treats the solvent implicitly as a dielectric continuum. In all cases the solvent chosen was chloroform, consistent with that utilized in the both final synthesis and in the majority of the spectroscopic measurements. Chloroform is characterized by an electrical permittivity (ε) of 4.7113 within the calculations. This computational method models the solvent as surrounding a cavity in which the solute resides, and this cavity is characterized using an integral equation formalism for the polarizable continuum model (IEFPCM). This model represents the system in equilibrium during, for example, an optimization routine: in all excited state calculations a non-equilibrium solvent model is used.

All geometry optimizations were performed using an ultrafine grid and very tight convergence criteria, and the minima were confirmed as stationary points through the
computation of harmonic vibrational frequencies, each of which showed no imaginary components. These stationary points were used in single point TD-DFT calculations to compute vertical excitation energies. All TD-DFT calculations were undertaken using a linear response approach. All TD-DFT calculations were also performed with a long range corrected hybrid functional (CAM-B3LYP).

Phosphorescence and spin-forbidden absorption bands were investigated using unrestricted density functional theory to compute parameters associated with the first triplet state (T$_1$), using an identical methodology as for the singlet states. Decomposition of the molecular orbital character was performed using the GaussSum software package. Crystal structure overlays with optimised computational structures has been performed using the Chimera software package, which has also been used to calculate root mean squared deviation (RMSD) values for these comparative structures.

**X-ray crystallography**

**Data collection and processing**

Suitable crystals of [Ir(L7)$_2$(pic)] were selected and data collected following a standard method. A crystal 0.050×0.040×0.005 mm$^3$ was selected and mounted on a MITIGEN holder in perfluoroether oil on a Rigaku 007HF equipped with Varimax confocal mirrors and an AFC11 goniometer and HyPix 6000 detector diffractometer. The crystal was kept at a steady $T = 100(2)$ K during data collection. The structure was solved with the ShelXT$^9$ structure solution program using the Intrinsic Phasing solution method and by using Olex2$^{10}$ as the graphical interface. The model was refined with version 2018/3 of ShelXL$^{11}$ using Least Squares minimisation. CCDC 1957545 contains supplementary X-ray crystallographic data for [Ir(L7)$_2$(pic)]. This data can be obtained free of charge via [http://www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html), or from the Cambridge Crystallographic Data Centre, Union Road, Cambridge, CB2 1EZ; fax(+44) 1223-336-033 or email: deposit@ccdc.cam.ac.uk.
**Synthesis of the Ir(III) dimers, [[Ir(L)]_2(µ-Cl)]_2**

IrCl₃.xH₂O (1 eq.) and ligand, L (2 eq.) (where L = L1-7) were dissolved in 2-ethoxyethanol (10 mL) and the reaction mixture heated at reflux for 48 hours. The reaction was then cooled to room temperature and water (30 mL) was added to form a dark colored precipitate. The solid was collected by filtration to yield the dimer [[Ir(L)]_2(µ-Cl)]_2, which was subsequently used without further purification.

**Synthesis of [Ir(L1)]_2(pic)**

[[Ir(L2)]_2(µ-Cl)]_2 (100 mg, 0.08 mmol) and 2-picolinic acid (2 eq., 18 mg, 0.16 mmol) were dissolved in 2-ethoxyethanol (10 mL) along with potassium carbonate (2 eq., 22 mg, 0.16 mmol) and silver nitrate (4 eq., 51 mg, 0.32 mmol). The reaction mixture was heated at reflux under a nitrogen atmosphere in a covered flask for 24 hours. The reaction mixture was then cooled to room temperature before the addition of cold water (20 mL) to form a dark red precipitate. The solid was collected by filtration to yield the product as a red powder (yield = 107 mg, 97%).

1H NMR (400 MHz, CDCl₃): δH 8.55 (1H, d, 3J_HH = 8.56), 8.39 (1H, d, 3J_HH = 8.56), 8.21 (1H, d, 3J_HH = 8.56), 7.97 – 7.87 (4H, m), 7.77 (1H, d, 3J_HH = 7.79), 7.64 (1H, t, J_HH = 7.42), 7.61 – 7.55 (1H, m), 7.54 – 7.48 (1H, m), 7.42 (1H, app t), 7.34 – 7.30 (1H, m), 7.17 (1H, app. t), 7.02 (1H, app. t), 6.93 (1H, d, 3J_HH = 7.57), 6.90 – 6.85 (1H, m), 6.80 (1H, app. t), 6.60 (1H, app. t), 6.26 (1H, d, 3J_HH = 7.77), 3.36 (3H, s), 3.34 (3H, s) ppm. 13C {1H} NMR (100 MHz, CDCl₃): δC 145.5, 138.2, 137.1, 135.2, 131.1, 130.1, 129.9, 129.7, 129.5, 129.4, 128.9, 128.7, 127.9, 127.6, 127.5, 127.1, 124.5, 122.4, 121.7, 27.6 ppm. HRMS found m/z 754.1789, calculated m/z 754.1790 for [C₃₆H₂₆IrN₅O₂]. UV vis. (CHCl₃) λ_max (ε / dm³mol⁻¹cm⁻¹): 491 (3700), 373 (17300), 364 (15300), 274 (26100) nm. IR (solid) ν_max = 2962, 1630, 1507, 1578, 1564, 1526, 1481, 1451, 1425, 1387, 1334, 1321, 1289, 1260, 1219, 1194, 1165, 1015, 907, 841, 795, 758, 739, 662, 627, 592, 552, 407 cm⁻¹.

**Synthesis of [Ir(L2)]_2(pic)**

As [Ir(L1)]_2(pic) but with [[Ir(L2)]_2(µ-Cl)]_2 (100 mg, 0.07 mmol). Purified by column chromatography using dichloromethane:MeOH (96:4) and product collected as first red band. Red solid (yield = 13 mg, 12 %). 1H NMR (400 MHz, CDCl₃): δH 8.36 (1H, d, 3J_HH = 1.1), 8.36 – 8.31 (1H, m), 8.19 (1H, d, 3J_HH = 8.2), 7.96 – 7.92 (1H, m), 7.83
(1H, ddd, J_{HH} = 7.8, 1.5, 0.8), 7.69 (1H, s), 7.66 – 7.62 (2H, m), 7.32 (1H, ddd, J_{HH} = 7.4, 5.4, 1.5), 7.13 (1H, ddd, J_{HH} = 8.3, 7.0, 1.4), 7.03 (1H, s), 6.99 (1H, ddd, J_{HH} = 8.3, 7.1, 1.3), 6.86 (1H, dd, J_{HH} = 7.8, 1.3), 6.79 – 6.71 (1H, m), 6.64 (1H, app. td), 6.28 – 6.18 (1H, m), 2.38 – 2.36 (6H, m), 2.32 (6H, overlapping s), 2.29 – 2.27 (6H, m) ppm.

^{13}C\{^1H\} NMR (101 MHz, CDCl_3): δ_C 142.1, 137.8, 129.7, 129.4, 128.5, 127.6, 127.1, 126.3, 124.4, 122.0, 121.4, 27.9, 27.5, 20.3, 20.0, 19.7, 19.6 ppm. HRMS found m/z 810.2415, calculated m/z 810.2417 for [C_{40}H_{34}IrN_{5}O_{2}]. UV vis. (CHCl_3) λ_{max} (ε / dm^3 mol^{-1} cm^{-1}): 507 (3700), 381 (26000), 276 (116200) nm. IR (solid) ν_{max} = 3362, 2915, 1655, 1601, 1578, 1562, 1483, 1408, 1335, 1321, 1287, 1269, 1219, 1163, 1211, 1059, 1047, 1034, 1024, 991, 903, 878, 839, 795, 758, 743, 733, 702, 691, 658, 629, 567, 476, 430 cm^{-1}.

**Synthesis of [Ir(L3)_{2}(pic)]**

As for [Ir(L1)_{2}(pic)] but with [[Ir(L3)_{2}(µ-Cl)]_{2}] (100 mg, 0.06 mmol). Purified by column chromatography using dichloromethane:MeOH (95:5) and product collected as first red band. Red solid (yield = 20 mg, 18%). ^1H NMR (400 MHz, CDCl_3): δ_H 8.83 (1H, d, ^3J_{HH} = 12.5), 8.42 (1H, d, ^3J_{HH} = 8.3), 8.29 – 8.19 (1H, m), 8.06 (1H, s), 8.04 (1H, s), 7.96 – 7.90 (1H, m), 7.84 (1H, app. t), 7.76 (1H, app. td), 7.46 – 7.39 (1H, m), 7.38 (1H, s), 7.24 – 7.16 (1H, m), 7.04 (1H, ddd, J_{HH} = 12.7, 7.0, 3.3), 6.87 (2H, d, ^3J_{HH} = 3.8), 6.76 – 6.66 (1H, m), 6.17 (1H, app. dt), 3.47 – 3.23 (6H, m) ppm. ^13C\{^1H\} NMR (126 MHz, CDCl_3): δ_C 171.2, 164.3, 154.2, 152.2, 152.3, 152.3, 151.8, 145.5, 144.9, 143.8, 139.5, 139.2, 139.1, 138.8, 138.7, 136.6, 136.3, 134.9, 134.7, 134.2, 133.2, 131.0, 130.6, 130.3, 130.0, 128.7, 128.4, 128.2, 127.8, 125.4, 122.7, 122.2, 28.0, 27.7 ppm. HRMS found m/z 892.0191, calculated m/z 892.0195 for [C_{36}H_{22}Cl_{4}IrN_{5}O_{2}]. UV vis. (CHCl_3) λ_{max} (ε / dm^3 mol^{-1} cm^{-1}): 538 (2300), 389 (12500), 371 (11500), 300 (11500), 273 (21500) nm. IR (solid) ν_{max} = 3407, 3060, 1655, 1599, 1578, 1524, 1460, 1431, 1316, 1190, 1163, 1115, 1049, 1009, 963, 882, 855, 758, 725, 671, 646, 610, 556, 469, 436, 417 cm^{-1}.

**Synthesis of [Ir(L4)_{2}(pic)]**

As [Ir(L1)_{2}(pic)] but with [[Ir(L4)_{2}(µ-Cl)]_{2}] (80 mg, 0.05 mmol). Purified by column chromatography, dichloromethane used to elute ligand followed by dichloromethane:MeOH (9:1) to elute product as red band. The product was then
recrystallised from chloroform and hexane to give a red solid (yield = 27 mg, 30\%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$H 8.81 (1H, d, $^3$J$_{HH}$ = 0.4), 8.42 (1H, dd, $^3$J$_{HH}$ = 8.3, 1.0), 8.25 – 8.21 (1H, m), 8.06 (1H, d, $^3$J$_{HH}$ = 0.4), 8.04 (1H, d, $^3$J$_{HH}$ = 0.4), 7.93 (1H, ddd, $^3$J$_{HH}$ = 7.8, 1.5, 0.8), 7.85 (1H, ddd, $^3$J$_{HH}$ = 5.4, 1.6, 0.8), 7.76 (1H, app. td), 7.42 (1H, ddd, $^3$J$_{HH}$ = 7.6, 5.4, 1.5), 7.38 (1H, d, $^3$J$_{HH}$ = 0.4), 7.23 – 7.17 (1H, m), 7.04 (1H, ddd, $^3$J$_{HH}$ = 8.3, 7.2, 1.3), 6.87 – 6.84 (2H, m), 6.71 (1H, ddd, $^3$J$_{HH}$ = 0.4), 6.19 – 6.16 (1H, m), 3.33 (6H, overlapping s) ppm.

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$): $\delta$C 171.1, 153.9, 152.0, 145.4, 145.2, 144.1, 138.8, 136.7, 134.7, 130.7, 130.2, 129.9, 128.2, 128.0, 122.8, 122.2, 114.3, 31.6, 27.7, 27.5, 22.7, 14.2 ppm.

$^{19}$F($^1$H) NMR (376 MHz, CD$_3$CN): $\delta$F -131.81 (d, $^3$J$_{FF}$ = 21.3 Hz), -132.90 (d, $^3$J$_{FF}$ = 21.4), -133.67 (d, $^3$J$_{FF}$ = 18.8 Hz), -134.03 (d, $^3$J$_{FF}$ = 18.8 Hz) ppm. HRMS found m/z 826.1416, calculated m/z 826.1413 for [C$_{36}$H$_{22}$F$_4$IrN$_5$O$_2$]. UV vis. (CHCl$_3$) $\lambda_{\text{max}}$ (ε / dm$^3$mol$^{-1}$cm$^{-1}$): 501 (4000), 377 (26300), 272 (113200) nm. IR (solid) $\nu_{\text{max}}$ = 3410, 3001, 1634, 1601, 1578, 1530, 1501, 1414, 1327, 1294, 1256, 1233, 1196, 1163, 1125, 1051, 1034, 995, 880, 843, 793, 758, 743, 729, 706, 694, 660, 637, 586, 476, 459, 434 cm$^{-1}$.

**Synthesis of [Ir(L5)$_2$(pic)]**

As [Ir(L1)$_2$(pic)] but with [[Ir(L5)$_2$(μ-Cl)]$_2$] (100 mg, 0.06 mmol). Product purified by column chromatography using dichloromethane:MeOH (9:1) as the eluent. Product collected as the first red band and recrystallised from dichloromethane and hexane to give a red solid (yield = 25 mg, 23\%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$H 8.50 (1H, s), 8.39 (1H, d, $^3$J$_{HH}$ = 5.3), 8.03 – 7.87 (3H, m), 7.84 – 7.80 (1H, s), 7.76 (3H, m), 7.66 – 7.54 (6H, m), 7.54 – 7.45 (2H, m), 7.15 (1H, s), 7.10 – 7.02 (1H, m), 7.02 – 6.94 (1H, m), 6.75 – 6.41 (5H, m), 6.16 (1H, d, $^3$J$_{HH}$ = 7.5), 2.32 (6H, s), 1.84 (6H, s) ppm.

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$): $\delta$C 145.7, 144.3, 139.5, 134.5, 130.5, 129.6, 129.4, 128.9, 128.0, 127.3, 124.2, 121.3, 20.7, 20.0, 19.9, 19.7 ppm. HRMS found m/z 934.2731, calculated m/z 934.2731 for [C$_{50}$H$_{38}$IrN$_5$O$_2$]. UV vis. (CHCl$_3$) $\lambda_{\text{max}}$ (ε / dm$^3$mol$^{-1}$cm$^{-1}$): 501 (4700), 387 (28900), 300 (34200), 262 (60000) nm. IR (solid) $\nu_{\text{max}}$ = 3053, 1640, 1599, 1578, 1547, 1508, 1481, 1443, 1348, 1317, 1263, 1234, 1209, 1171, 1157, 1132, 1117, 1071, 1047, 1024, 1003, 974, 922, 876, 843, 833, 810, 774, 762, 743, 733, 698, 660, 640, 621, 608, 579, 540, 498, 490, 460, 440, 421 cm$^{-1}$. 


**Synthesis of [Ir(L6)2(pic)]**

As [Ir(L1)2(pic)] but [[Ir(L6)2(µ-Cl)]2]. Product purified by column chromatography using dichloromethane:MeOH (9:1) as the eluent. Product collected as the first red band and recrystallised from dichloromethane and hexane to give a red solid (yield = 37 mg, 34%). 1H NMR (400 MHz, CDCl3): δH 8.94 (1H, s), 8.32 (1H, d, 3JHH = 4.8), 8.20 (1H, s), 8.16 (1H, s), 8.08 (1H, d, 3JHH = 7.2), 7.98 (2H, s), 7.86 (1H, app. td), 7.79 (2H, s), 7.67 (3H, d, 3JHH = 2.2), 7.63-7.60 (4H, m), 7.52 (1H, s), 7.20 – 7.14 (1H, m), 7.07 (1H, dd, 3JHH = 8.0, 1.4), 6.77 – 6.71 (1H, m), 6.69 (2H, app. dt), 6.65 – 6.54 (2H, m), 6.10 (1H, dd, 3JHH = 7.5, 1.3) ppm. 13C{1H} NMR (126 MHz, CDCl3): δC 171.3, 165.7, 163.7, 155.7, 154.1, 152.6, 145.7, 144.6, 143.5, 139.8, 139.4, 139.3, 139.2, 139.1, 139.0, 138.9, 137.0, 136.2, 135.2, 134.9, 134.5, 133.5, 133.1, 131.5, 131.2, 130.0, 130.8, 130.5, 130.4, 129.5, 129.1, 128.9, 128.5, 128.3, 127.7, 125.3, 122.1, 121.6 ppm. HRMS found m/z 1017.0534, calculated m/z 1017.0537 for [C46H26Cl4IrN5O2].

**Synthesis of [Ir(L7)2(pic)]**

As [Ir(L1)2(pic)] but with [[Ir(L7)2(µ-Cl)]2] (90 mg, 0.05 mmol). Product purified by column chromatography using dichloromethane:MeOH (9:1) as the eluent. Product collected as the first red band. Product collected as a red solid (yield = 39 mg, 40 %). 1H NMR (400 MHz, CDCl3): δH 8.67 (1H, dd, 3JHH = 12.2, 8.1), 8.41 (1H, ddd, JHH = 5.4, 1.6, 0.8), 8.05 (1H, ddd, JHH = 7.8, 1.5, 0.7), 8.01 – 7.97 (2H, m), 7.90 – 7.84 (2H, m), 7.81 (2H, dd, JHH = 9.8, 7.9), 7.70 – 7.55 (8H, m), 7.22 – 7.18 (1H, m), 7.18 – 7.14 (1H, m), 7.07 – 7.03 (1H, m), 6.74 (1H, ddd, JHH = 8.2, 4.7, 3.9), 6.69 (2H, app. dd), 6.59 (2H, app. dtd), 6.10 – 6.07 (1H, m) ppm. 13C {1H} NMR (126 MHz, DMSO): δC 171.4, 153.5, 152.7, 151.8, 145.6, 145.1, 143.9, 139.1, 139.0, 136.4, 134.6, 131.1, 130.7, 130.6, 130.4, 130.2, 130.1, 129.1, 128.9, 128.4, 128.2, 122.2, 121.6 ppm. 19F {1H} NMR (376 MHz, CD3CN): δF -130.18 (d, 3JFF = 19.0 Hz), -131.51 (d, 3JFF = 18.8 Hz), -133.10 (d, 3JFF = 21.7 Hz), -133.59 (d, 3JFF = 21.3 Hz) ppm. HRMS found m/z 950.1726, calculated m/z 950.1728 for [C46H26F4IrN5O2]. UV vis. (CHCl3)
Synthesis of $[\text{Ir}(L2)_2(\text{pyz})]$ 
Firstly, $[\text{Ir}(L2)_2(\text{MeCN})_2]\text{BF}_4$ was synthesised according to previous procedures and then added (250 mg, 0.325 mmol) to pyrazine-2-carboxylic acid (50 mg, 0.4 mmol) and $[\text{Bu}_4\text{N}][\text{Cl}]$ (110 mg, 0.4 mmol) dissolved in a mixture of chloroform (20 mL) and ethanol (5 mL). The reaction mixture was heated at reflux for 48 hours. The reaction mixture was then filtered and a red solid collected. The solid was purified by silica gel chromatography using dichloromethane:methanol (95:5) as eluent and the first red band was collected. Reprecipitation from dichloromethane and diethyl ether gave the desired product as a red solid (yield = 32 mg, 12 %). $^1\text{H} \text{NMR (400MHz, CDCl}_3\text{)}$ δH 8.93 (1H, d, $^3\text{J}_{HH} = 1.1$), 8.53 (1H, d, $^3\text{J}_{HH} = 3.0$), 8.29 (1H, d, $^3\text{J}_{HH} = 7.8$), 8.22 (1H, s), 8.12 (1H, d, $^3\text{J}_{HH} = 7.7$), 7.84 (1H, dd, $^3\text{J}_{HH} = 3.0, 1.2$), 7.65 (1H, s), 7.61 (1H, s), 7.13-7.06 (1H, m), 6.97-6.90 (1H, m), 6.83 (1H, s), 6.80 (1H, dd, $^3\text{J}_{HH} = 7.8, 1.1$), 6.75-6.69 (1H, m), 6.61-6.56 (1H, m), 6.13 (1H, dd, $^3\text{J}_{HH} = 7.7, 1.0$), 3.26 (s, 3H), 3.24 (s, 3H), 2.32 (s, 3H), 2.25 (s, 3H), 2.23 (s, 3H), 1.72 (s, 3H) ppm. $^{13}\text{C}[^1\text{H}] \text{NMR (126MHz, CDCl}_3\text{)}$ δC 170.0, 163.6, 161.5, 151.7, 151.2, 150.1, 149.8, 149.5, 148.3, 146.0, 145.7, 144.6, 142.5, 141.2, 140.1, 139.6, 139.5, 139.4, 139.0, 138.7, 136.7, 129.9, 129.5, 129.1, 128.9, 127.4, 126.1, 123.9, 122.4, 122.0, 27.8, 27.5, 20.3, 20.00, 19.7, 19.6 ppm. HRMS found m/z of 811.2367, calculated m/z 811.2367 for $[\text{C}_{39}\text{H}_{33}\text{IrN}_6\text{O}_2 + \text{H}]$. UV-vis (CHCl$_3$) $\lambda_{\text{max}}$ (ε / dm$^3$mol$^{-1}$cm$^{-1}$) 480 (5100), 380 (27100), 267 (50200) nm. IR (solid) $\nu_{\text{max}} = 2360, 2337, 1651, 1577, 1523, 1450, 1319, 1165, 991, 875, 725, 624$ cm$^{-1}$. 

Synthesis of $[\text{Ir}(L5)_2(\text{pyz})]$ 
As for $[\text{Ir}(L1)_2(\text{pic})]$, but using $[[\text{Ir}(L5)_2(\mu-\text{Cl})]_2]$ (200 mg, 0.118 mmol), pyrazine-2-carboxylic acid (28 mg, 0.236 mmol), potassium carbonate (0.033g, 0.236mmol) and silver nitrate (80 mg, 0.472 mmol) dissolved in 2-ethoxyethanol (10 mL). Product purified by silica gel chromatography with dichloromethane:methanol 99:1 as eluent,
followed by 95:5 to elute the red band. Solvent was removed \textit{in vacuo} and then product reprecipitated from dichloromethane and diethyl ether to give a red solid (yield = 25 mg, 11 \%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$H 9.15 (1H, d, $^3$J$_{HH} = 1.1$), 8.78 (1H, d, $^3$J$_{HH} = 2.9$), 8.44 (1H, s), 8.31 (1H, dd, $^3$J$_{HH} = 3.0$, 1.3), 7.98-7.73 (6H, m), 7.67-7.56 (6H, m), 7.08 (1H, dd, $^3$J$_{HH} = 8.1$, 1.1), 7.02 (1H, s), 7.00 (1H, dd, $^3$J$_{HH} = 8.0$, 1.3), 6.75-6.61 (3H, m), 6.60-6.50 (2H, m), 6.13 (1H, dd, $^3$J$_{HH} = 7.5$, 1.1) 2.41 (s, 3H), 2.41 (s, 3H), 2.33 (s, 3H), 1.89 (s, 3H) ppm. $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$C 170.1, 163.0, 160.8, 153.5, 152.2, 150.7, 150.0, 149.9, 148.3, 146.6, 145.2, 144.1, 143.5, 141.5, 130.2, 129.9, 129.5, 129.4, 128.9, 128.3, 126.1, 123.7, 121.8, 121.4, 20.8, 20.1, 20.0, 19.8 ppm. HRMS found m/z 935.2684, calculated m/z 935.2683 for [C$_{49}$H$_{37}$IrN$_6$O$_2$ + H].

UV-vis (CHCl$_3$) $\lambda_{\text{max}}$ ($\varepsilon /$dm$^3$·mol$^{-1}$·cm$^{-1}$) 489 (4400), 386 (24000), 271 (49000) nm. IR (solid) $\nu_{\text{max}}$ = 3410, 3000, 1632, 1597, 1578, 1562, 1543, 1508, 1458, 1443, 1429, 1406, 1387, 1346, 1317, 1256, 1198, 1163, 1132, 1115, 1069, 1044, 1022, 997, 959, 887, 878, 845, 808, 758, 745, 735, 725, 696, 673, 665, 652, 633, 606, 571, 515, 488, 476, 436, 415, 403 cm$^{-1}$.

**Synthesis of [Ir(L7)$_2$(pyz)]**

As for [Ir(L5)$_2$(pyz)] but using [[Ir(L7)$_2$(μ-Cl)$_2$]] (250 mg, 0.145 mmol), pyrazine-2-carboxylic acid (41 mg, 0.290 mmol), potassium carbonate (42 mg, 0.290 mmol) and silver nitrate (98 mg, 0.58 mmol) dissolved in 2-ethoxyethanol (10 mL). Product purified by silica gel chromatography (dichloromethane:methanol, 99:1) to elute yellow band, followed by (dichloromethane:methanol, 95:5) to elute red band, solvent was removed \textit{in vacuo} to yield [Ir(L7)$_2$(pyz)] as a purple solid. Product was dissolved in dichloromethane and recrystallised from hexane to give the product as a purple crystalline solid (yield = 22 mg, 8 \%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$H 9.16 (1H, d, $^3$J$_{HH} = 1.2$), 8.85 (1H, d, $^3$J$_{HH} = 3.0$), 8.53 (1H, dd, $^3$J$_{HH} = 12.1$, 8.1), 8.30 (1H, dd, $^3$J$_{HH} = 3.0$, 1.3), 7.93 (2H, app. dd), 7.88-7.74 (4H, m), 7.65-7.53 (6H, m), 7.14-6.97 (3H, m), 6.74-6.62 (3H, m), 6.60-6.49 (2H, m), 5.98 (1H, dd, $^3$J$_{HH} = 7.6$, 1.0) ppm. $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$): $\delta$C 171.4, 165.7, 160.6, 154.0, 152.3, 151.6, 150.1, 148.2, 147.3, 143.1, 141.1, 139.9, 132.7, 131.5, 129.3, 128.2, 127.1, 125.2, 123.6, 121.7, 120.3 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$F -123.47 (d, $^3$J$_{FF} = 22.2$), -128.13 (d, $^3$J$_{FF} = 21.7$), -128.54 (d, $^3$J$_{FF} = 22.2$), -130.53 (d, $^3$J$_{FF} = 21.7$) ppm. HRMS found m/z 951.1677, calculated m/z 951.1677 for [C$_{49}$H$_{25}$F$_4$IrN$_6$O$_2$ + H]. UV-vis (CHCl$_3$) $\lambda_{\text{max}}$ ($\varepsilon /$dm$^3$·mol$^{-1}$·cm$^{-1}$)
1): 494 (2900), 383 (15500), 272 (41200) nm. $\nu_{\text{max}} = 3422, 3044, 1649, 1576, 1501, 1329, 1227, 1163, 1126, 1045, 980, 874, 808, 797, 758, 725, 700, 662, 640, 530, 419 \text{ cm}^{-1}$.

**Supporting Figures**

**Figure S1.** Comparison of the $^1$H NMR spectra of [Ir(L1)$_2$(pic)] (black) and [Ir(L1)$_2$(bipy)]PF$_6$. Inset shows the methyl resonances.
**Figure S2.** High-resolution mass spectrum recorded for [Ir(L4)$_2$(pic)]. Spectrum shows fragments, a protonated molecular ion peak, and a sodium adduct.
Figure S3. Comparison of the absorption spectra of [Ir(L2)2(pic)] (black) and its bipyridine analogue (red).

Figure S4. Comparison of the absorption spectra of [Ir(L3)2(pic)] (black) and its bipyridine analogue (red).
Figure S5. Comparison of the absorption spectra of $[\text{Ir(L4)}_2\text{(pic)}]$ (black) and its bipyridine analogue (red).

Figure S6. Comparison of the absorption spectra of $[\text{Ir(L5)}_2\text{(pic)}]$ (black) and its bipyridine analogue (red).
Figure S7. Comparison of the absorption spectra of [Ir(L6)$_2$(pic)] (black) and its bipyridine analogue (red).

Figure S8. Comparison of the absorption spectra of [Ir(L7)$_2$(pic)] (black) and its bipyridine analogue (red).
Figure S9. Comparison of the experimental (red) and simulated (black) absorption spectra for [Ir(L₂)₂(pic)]. The simulated spectrum is comprised of singlet and triplet transitions from the singlet ground state.

Figure S10. Comparison of the experimental (red) and simulated (black) absorption spectra for [Ir(L₃)₂(pic)]. The simulated spectrum is comprised of singlet and triplet transitions from the singlet ground state.
Figure S11. Comparison of the experimental (red) and simulated (black) absorption spectra for \([\text{Ir(L4)}_2(\text{pic})]\). The simulated spectrum is comprised of singlet and triplet transitions from the singlet ground state.

Figure S12. Comparison of the experimental (red) and simulated (black) absorption spectra for \([\text{Ir(L5)}_2(\text{pic})]\). The simulated spectrum is comprised of singlet and triplet transitions from the singlet ground state.
Figure S13. Comparison of the experimental (red) and simulated (black) absorption spectra for $[\text{Ir(L6)}_2\text{(pic)}]$. The simulated spectrum is comprised of singlet and triplet transitions from the singlet ground state.

Figure S14. Comparison of the experimental (red) and simulated (black) absorption spectra for $[\text{Ir(L7)}_2\text{(pic)}]$. The simulated spectrum is comprised of singlet and triplet transitions from the singlet ground state.
Figure S15. Comparison of the experimental (red) and simulated (black) absorption spectra for [Ir(L2)(pyz)]. The simulated spectrum is comprised of singlet and triplet transitions from the singlet ground state.

Figure S16. Comparison of the experimental (red) and simulated (black) absorption spectra for [Ir(L5)(pyz)]. The simulated spectrum is comprised of singlet and triplet transitions from the singlet ground state.
Figure S17. Comparison of the experimental (red) and simulated (black) absorption spectra for [Ir(L7)2(pyz)]. The simulated spectrum is comprised of singlet and triplet transitions from the singlet ground state.
Figure S18. Renderings of the $[\text{Ir(L2)}_2\text{(pic)}]$ MOs.
Figure S19. Renderings of the [Ir(L3)2(pic)] MOs.
Figure S20. Renderings of the [Ir(L4)₂(pic)] MOs.
Figure S21. Renderings of the [Ir(L5)2(pic)] MOs.
Figure S22. Renderings of the [Ir(L6)2(pic)] MOs.
**Figure S23.** Renderings of the [Ir(L7)$_2$(pic)] MOs.
Figure S24. Renderings of the [Ir(L2)₂(pyz)] MOs.
Figure S25. Renderings of the [Ir(L5)(pyz)] MOs.
Figure S26. Renderings of the [Ir(L7)₂(pyz)] MOs.
Figure S27. Low temperature (77 K) steady state emission spectra for [Ir(L2)(pic)] (left) and [Ir(L2)(pyz)] (right) recorded as frozen glasses (1:3 MeOH/EtOH) using excitation at 455 nm.
**Figure S28.** Emission corrected transient absorption spectrum of the [Ir(L2)_{2}(pic)], obtained in chloroform.

**Figure S29.** Emission corrected transient absorption spectrum of the [Ir(L3)_{2}(pic)], obtained in chloroform.
Figure S30. Emission corrected transient absorption spectrum of the \([\text{Ir(L4)}_2(\text{pic})]\), obtained in chloroform.

Figure S31. Emission corrected transient absorption spectrum of the \([\text{Ir(L5)}_2(\text{pic})]\), obtained in chloroform.
Figure S32. Emission corrected transient absorption spectrum of the [Ir(L6)2(pic)], obtained in chloroform.

Figure S33. Emission corrected transient absorption spectrum of the [Ir(L7)2(pic)], obtained in chloroform.
Figure S34. Emission corrected transient absorption spectrum of the \([\text{Ir(L2)}_2(\text{pyz})]\), obtained in chloroform.

Figure S35. Emission corrected transient absorption spectrum of the \([\text{Ir(L5)}_2(\text{pyz})]\), obtained in chloroform.
Figure S36. Emission corrected transient absorption spectrum of the [Ir(L7)2(pyz)], obtained in chloroform.
Figure S37. Kinetic traces of [Ir(L2)2(pic)] at major feature wavelengths, obtained with a PMT detector. Top 2 traces are emission, whilst the bottom 4 are Δ OD. All traces were fitted to mono-exponential functions and the lifetimes determined are reported next to each trace.
Figure S38. Kinetic traces of [Ir(L3)2(pic)] at major feature wavelengths, obtained with a PMT detector. The top 2 traces are emission, whilst the bottom 4 are Δ OD. All traces were fitted to mono-exponential functions and the lifetimes determined are reported next to each trace.
Figure S39. Kinetic traces of [Ir(L4)2(pic)] at major feature wavelengths, obtained with a PMT detector. Top 2 traces are emission, whilst the bottom 4 are Δ OD. All traces were fitted to mono-exponential functions and the lifetimes determined are reported next to each trace.
Figure S40. Kinetic traces of \([\text{Ir(L5)}_2\text{pic}]\) at major feature wavelengths, obtained with a PMT detector. The top 2 traces are emission, whilst the bottom 3 are \(\Delta\) OD. All traces were fitted to mono-exponential functions and the lifetimes determined are reported next to each trace.
Figure S41. Kinetic traces of [Ir(L6)2(pic)] at major feature wavelengths, obtained with a PMT detector. The top trace is emission, whilst the bottom 3 are Δ OD. All traces were fitted to mono-exponential functions and the lifetimes determined are reported next to each trace.
Figure S42. Kinetic traces of \([\text{Ir(L7)}_2\text{pic}]\) at major feature wavelengths, obtained with a PMT detector. The top traces is emission, whilst the bottom 3 are \(\Delta\) OD. All traces were fitted to mono-exponential functions and the lifetimes determined are reported next to each trace.
Figure S43. Kinetic traces of [Ir(L2)2(pyz)] at major feature wavelengths, obtained with a PMT detector. The top trace is emission, whilst the bottom 4 are Δ OD. All traces were fitted to mono-exponential functions and the lifetimes determined are reported next to each trace.
Figure S44. Kinetic traces of $[\text{Ir(L5)}_2\text{pyz}]$ at major feature wavelengths, obtained with a PMT detector. The top trace is emission, whilst the bottom 4 are $\Delta$ OD. All traces were fitted to mono-exponential functions and the lifetimes determined are reported next to each trace.
Figure S45. Kinetic traces of [Ir(L7)2(pyz)] at major feature wavelengths, obtained with a PMT detector. The top trace is emission, whilst the bottom 3 are Δ OD. All traces were fitted to mono-exponential functions and the lifetimes determined are reported next to each trace.
### Supporting Tables

| [Ir(L2)₂(pic)] | Moiety Contribution to Orbital (%) | Orbital Contribution to Excited State | Contributing Transitions |
|----------------|------------------------------------|--------------------------------------|--------------------------|
| Orbital        | Ir (5d)   | Picolinate | Q1 | Q2 | Excited State |                  |
| LUMO +4        | 1         | 1          | 72 | 26 | 1 (419.34 nm, f = 0.0504) | HOMO -1 → LUMO +1 (3.51%) |
|                |           |            |    |    | HOMO → LUMO (85.27%)     |                          |
|                |           |            |    |    | HOMO → LUMO +1 (4.34%)    |                          |
| LUMO +3        | 1         | 37         | 12 | 50 | 2 (411.06 nm, f = 0.1529) | HOMO -1 → LUMO (4.65%)   |
|                |           |            |    |    | HOMO → LUMO (4.82%)       |                          |
|                |           |            |    |    | HOMO → LUMO +1 (82.55%)   |                          |
| LUMO +2        | 2         | 96         | 2  | 0  | 3 (340.5 nm, f = 0.0887)  | HOMO -6 → LUMO (2.39%)   |
| LUMO +1        | 4         | 1          | 60 | 34 | 4 (327.66 nm, f = 0.0527) | HOMO -4 → LUMO +1 (5.84%)|
|                |           |            |    |    | HOMO -3 → LUMO (7.43%)    |                          |
|                |           |            |    |    | HOMO -3 → LUMO +1 (2.95%) |                          |
|                |           |            |    |    | HOMO -2 → LUMO +1 (31.72%)|
|                |           |            |    |    | HOMO -1 → LUMO +1 (33.53%)|
| HOMO           | 39        | 4          | 29 | 27 | 5 (323.41 nm, f = 0.3255) | HOMO -4 → LUMO +1 (6.93%)|
| HOMO -1        | 37        | 11         | 28 | 24 | 6 (323.4 nm, f = 0.3255)  | HOMO -4 → LUMO +1 (16.18%)|
| HOMO -2        | 12        | 7          | 49 | 32 | 7 (323.41 nm, f = 0.3255) | HOMO -4 → LUMO +1 (19%)  |
| HOMO -3        | 28        | 4          | 18 | 49 | 8 (323.41 nm, f = 0.3255) | HOMO -4 → LUMO +1 (19%)  |
| HOMO -4        | 21        | 7          | 43 | 29 | 9 (323.41 nm, f = 0.3255) | HOMO -4 → LUMO +1 (19%)  |

**Table S1.** Table of contributions to each MO from each part of [Ir(L2)₂(pic)], Q1 and Q2 are the quinoxalines. **Right:** First five singlet transitions of the complex and a breakdown of their corresponding formative transitions.
| Orbital   | Moiety Contribution to Orbital (%) | Orbital Contribution to Excited State |
|---------|------------------------------------|--------------------------------------|
| LUMO +4 | Ir (5d) Picolinate Q1 Q2           | Excited State                        |
|         | 1 1 75 22                          | 1 (439.97 nm, f = 0.0392)            |
|         |                                    | HOMO -1 → LUMO +1 (3.51%)            |
|         |                                    | HOMO → LUMO (87.01%)                 |
|         |                                    | HOMO → LUMO +1 (3.49%)               |
| LUMO +3 |                                    | 2 (431.02 nm, f = 0.1577)            |
|         |                                    | HOMO -1 → LUMO (4.57%)               |
| LUMO +2 |                                    | 2 (431.02 nm, f = 0.1577)            |
|         |                                    | HOMO -1 → LUMO (3.76%)               |
|         |                                    | HOMO → LUMO +1 (84.08%)              |
| LUMO +1 |                                    | 3 (351.22 nm, f = 0.08)              |
|         |                                    | HOMO -4 → LUMO (8.08%)               |
| LUMO    |                                    | 4 (337.03 nm, f = 0.0784)            |
|         |                                    | HOMO -4 → LUMO +1 (5.99%)            |
|         |                                    | HOMO -3 → LUMO (7.15%)               |
| HOMO    |                                    | 4 (337.03 nm, f = 0.0784)            |
|         |                                    | HOMO -3 → LUMO +1 (2.67%)            |
|         |                                    | HOMO -2 → LUMO +1 (18%)              |
|         |                                    | HOMO -1 → LUMO +1 (51.28%)           |
| HOMO -1 |                                    | 5 (330.3 nm, f = 0.2889)             |
|         |                                    | HOMO -4 → LUMO +1 (8.26%)            |
|         |                                    | HOMO -3 → LUMO (13.46%)              |
| HOMO -2 |                                    | 5 (330.3 nm, f = 0.2889)             |
|         |                                    | HOMO -3 → LUMO +1 (6.07%)            |
| HOMO -3 |                                    | 2 (431.02 nm, f = 0.1577)            |
|         |                                    | HOMO -2 → LUMO +1 (14.55%)           |
|         |                                    | HOMO -2 → LUMO +1 (25.73%)           |
| HOMO -4 |                                    | 2 (431.02 nm, f = 0.1577)            |
|         |                                    | HOMO -1 → LUMO (10.65%)              |
|         |                                    | HOMO -1 → LUMO +1 (5.14%)            |

**Table S2.** Table of contributions to each MO from each part of [Ir(L3)2(pic)], Q1 and Q2 are the quinoxalines. **Right:** First five singlet transitions of the complex and a breakdown of their corresponding formative transitions.
| [Ir(L4)₂(pic)] | Moiety Contribution to Orbital (%) | Orbital Contribution to Excited State | Contributing Transitions |
|----------------|-----------------------------------|--------------------------------------|--------------------------|
| Orbital        | Ir (5d)  | Picolinate | Q1 | Q2 | Excited State |                     |
| LUMO +4        | 1        | 1          | 79 | 19 | 1 (428.5 nm, f = 0.0373) | HOMO -1 → LUMO +1 (3.57%) |
|                |          |            |    |    |              | HOMO → LUMO (86.11%) |
|                |          |            |    |    |              | HOMO → LUMO +1 (4.2%) |
| LUMO +3        | 1        | 16         | 15 | 68 | 2 (420.47 nm, f = 0.1344) | HOMO -1 → LUMO (4.76%) |
|                |          |            |    |    |              | HOMO → LUMO (4.54%) |
|                |          |            |    |    |              | HOMO → LUMO +1 (83.26%) |
| LUMO +2        | 2        | 96         | 2  | 0  | 3 (342.9 nm, f = 0.0827) | HOMO -4 → LUMO (8.02%) |
| LUMO +1        | 4        | 1          | 56 | 39 | 4 (330.2 nm, f = 0.0823) | HOMO -4 → LUMO +1 (5.5%) |
| HOMO           | 39       | 4          | 29 | 28 | 4 (330.2 nm, f = 0.0823) | HOMO -3 → LUMO (7.67%) |
|                |          |            |    |    |              | HOMO -3 → LUMO +1 (2.53%) |
|                |          |            |    |    |              | HOMO -2 → LUMO +1 (23.91%) |
|                |          |            |    |    |              | HOMO -1 → LUMO +1 (45.01%) |
| HOMO -2        | 13       | 9          | 46 | 13 | 5 (325.06 nm, f = 0.2908) | HOMO -4 → LUMO +1 (6.26%) |
|                |          |            |    |    |              | HOMO -3 → LUMO (6.39%) |
| HOMO -3        | 23       | 4          | 22 | 51 | 6 (325.06 nm, f = 0.2908) | HOMO -4 → LUMO +1 (6.26%) |
|                |          |            |    |    |              | HOMO -3 → LUMO +1 (10.93%) |
| HOMO -4        | 24       | 18         | 46 | 13 | 5 (325.06 nm, f = 0.2908) | HOMO -4 → LUMO +1 (6.26%) |

**Table S3.** Table of contributions to each MO from each part of [Ir(L4)₂(pic)], Q1 and Q2 are the quinoxalines. **Right:** First five singlet transitions of the complex and a breakdown of their corresponding formative transitions.
| [Ir(L5)_2(pic)] | Moiety Contribution to Orbital (%) | Orbital Contribution to Excited State |
|-----------------|-----------------------------------|--------------------------------------|
| Orbital         | Ir (5d)  | Picolinate | Q1 | Q2 | Excited State | Contributing Transitions |
| LUMO +4         | 1        | 2          | 92 | 4  | 1 (424.82 nm, f = 0.0334) | HOMO -1 \(\rightarrow\) LUMO +1 (4.99%) |
|                 |          |            |    |    |               | HOMO \(\rightarrow\) LUMO (87.75%) |
| LUMO +3         | 1        | 5          | 4  | 91 | 2 (411.7 nm, f = 0.1952)  | HOMO -1 \(\rightarrow\) LUMO (8.18%) |
|                 |          |            |    |    |               | HOMO \(\rightarrow\) LUMO +1 (82.18%) |
| LUMO +2         | 2        | 94         | 3  | 1  | 3 (346.14 nm, f = 0.996)  | HOMO -6 \(\rightarrow\) LUMO (4.88%) |
| LUMO +1         | 4        | 1          | 57 | 38 | 4 (336.8 nm, f = 0.2223)  | HOMO -4 \(\rightarrow\) LUMO +1 (3.92%) |
| LUMO            | 4        | 1          | 38 | 57 |               | HOMO -3 \(\rightarrow\) LUMO (14.68%) |
|                 |          |            |    |    |               | HOMO -2 \(\rightarrow\) LUMO (12.45%) |
|                 |          |            |    |    |               | HOMO -2 \(\rightarrow\) LUMO +1 (9.51%) |
|                 |          |            |    |    |               | HOMO -1 \(\rightarrow\) LUMO (11.42%) |
|                 |          |            |    |    |               | HOMO -1 \(\rightarrow\) LUMO +1 (37.9%) |
| HOMO            | 38       | 4          | 30 | 28 | 5 (334.84 nm, f = 0.3983) | HOMO -3 \(\rightarrow\) LUMO (24.62%) |
| HOMO -1         | 21       | 5          | 46 | 29 |               | HOMO -3 \(\rightarrow\) LUMO +1 (13.09%) |
| HOMO -2         | 25       | 10         | 43 | 21 |               | HOMO -2 \(\rightarrow\) LUMO +1 (10.62%) |
| HOMO -3         | 5        | 2          | 30 | 63 |               | HOMO -1 \(\rightarrow\) LUMO (31.09%) |
| HOMO -4         | 37       | 4          | 23 | 36 |               | HOMO -1 \(\rightarrow\) LUMO +1 (2.25%) |

**Table S4.** Table of contributions to each MO from each part of [Ir(L5)_2(pic)], Q1 and Q2 are the quinoxalines. **Right:** First five singlet transitions of the complex and a breakdown of their corresponding formative transitions.
| [Ir(L6)2(pic)] | Moiety Contribution to Orbital (%) | Orbital Contribution to Excited State |
|---------------|-----------------------------------|--------------------------------------|
|               | Ir (5d) | Picolinate | Q1 | Q2 | Excited State | Contributing Transitions |
| LUMO +4       | 2       | 55         | 42 | 1  | 1 (445.39 nm, f = 0.0273) | HOMO -1 \(\rightarrow\) LUMO +1 (4.58%)  
 |               |         |            |    |    | HOMO \(\rightarrow\) LUMO (88.66%) |
| LUMO +3       | 1       | 37         | 45 | 16 | 2 (430.72 nm, f = 0.1950) | HOMO -1 \(\rightarrow\) LUMO (7.33%)  
 |               |         |            |    |    | HOMO \(\rightarrow\) LUMO +1 (83.14%) |
| LUMO +2       | 1       | 6          | 12 | 81 | 3 (356.62 nm, f = 0.1279) | HOMO -6 \(\rightarrow\) LUMO (3.7%)  
 |               |         |            |    |    | HOMO -4 \(\rightarrow\) LUMO (3.73%)  
 |               |         |            |    |    | HOMO -3 \(\rightarrow\) LUMO (46.6%)  
 |               |         |            |    |    | HOMO -2 \(\rightarrow\) LUMO (6.91%)  
 |               |         |            |    |    | HOMO -2 \(\rightarrow\) LUMO +1 (2.5%)  
 |               |         |            |    |    | HOMO -1 \(\rightarrow\) LUMO (24.7%)  
| LUMO +1       | 4       | 1          | 53 | 42 | 4 (347.51 nm, f = 0.2361) | HOMO -2 \(\rightarrow\) LUMO (30.68%)  
 |               |         |            |    |    | HOMO -2 \(\rightarrow\) LUMO +1 (3.29%)  
 |               |         |            |    |    | HOMO -1 \(\rightarrow\) LUMO (10.98%)  
 |               |         |            |    |    | HOMO -1 \(\rightarrow\) LUMO +1 (44.13%)  
| LUMO          | 4       | 1          | 42 | 53 | 5 (342.51 nm, f = 0.4185) | HOMO -4 \(\rightarrow\) LUMO (2.52%)  
 |               |         |            |    |    | HOMO -3 \(\rightarrow\) LUMO (23.94%)  
| HOMO          | 38      | 4          | 30 | 28 | 6 (347.51 nm, f = 0.2361) | HOMO -2 \(\rightarrow\) LUMO (30.68%)  
| HOMO -1       | 21      | 5          | 49 | 25 | 7 (347.51 nm, f = 0.2361) | HOMO -2 \(\rightarrow\) LUMO (30.68%)  
| HOMO -2       | 25      | 13         | 43 | 19 | 8 (347.51 nm, f = 0.2361) | HOMO -2 \(\rightarrow\) LUMO (30.68%)  
| HOMO -3       | 5       | 2          | 27 | 66 | 9 (347.51 nm, f = 0.2361) | HOMO -2 \(\rightarrow\) LUMO (30.68%)  
| HOMO -4       | 31      | 12         | 31 | 26 | 10 (347.51 nm, f = 0.2361) | HOMO -2 \(\rightarrow\) LUMO (30.68%)  

**Table S5.** Table of contributions to each MO from each part of [Ir(L6)2(pic)], Q1 and Q2 are the quinoxalines. **Right:** First five singlet transitions of the complex and a breakdown of their corresponding formative transitions.
| [Ir(L7)$_2$(pic)] | Moiety Contribution to Orbital (%) | Orbital Contribution to Excited State | Contributing Transitions |
|------------------|-----------------------------------|--------------------------------------|--------------------------|
| Orbital          | Ir (5d)  | Picolinate | Q1 | Q2 | LUMO +4 | 1 (434.13 nm, f = 0.0253) | HOMO -1 $\rightarrow$ LUMO +1 (4.6%) |
| LUMO +3          | 1       | 4         | 2  | 93 | 2 (420.48 nm, f = 0.1668) | HOMO -1 $\rightarrow$ LUMO (7.47%) |
| LUMO +2          | 2       | 90        | 8  | 1  | 3 (348.37 nm, f = 0.1302) | HOMO -4 $\rightarrow$ LUMO (2.94%) |
| LUMO +1          | 4       | 1         | 54 | 41 | 4 (341.03 nm, f = 0.2244) | HOMO -2 $\rightarrow$ LUMO (27.17%) |
| LUMO             | 4       | 1         | 41 | 54 | 5 (336.66 nm, f = 0.3471) | HOMO -4 $\rightarrow$ LUMO (2.26%) |
| HOMO             | 38      | 4         | 30 | 28 | 6 (336.66 nm, f = 0.3471) | HOMO -2 $\rightarrow$ LUMO (16.35%) |
| HOMO -1          | 16      | 4         | 54 | 26 | 7 (336.66 nm, f = 0.3471) | HOMO -2 $\rightarrow$ LUMO (16.35%) |
| HOMO -2          | 32      | 14        | 36 | 18 | 8 (336.66 nm, f = 0.3471) | HOMO -2 $\rightarrow$ LUMO (16.35%) |
| HOMO -3          | 5       | 2         | 28 | 65 | 9 (336.66 nm, f = 0.3471) | HOMO -2 $\rightarrow$ LUMO (16.35%) |
| HOMO -4          | 34      | 10        | 30 | 26 | 10 (336.66 nm, f = 0.3471) | HOMO -2 $\rightarrow$ LUMO (16.35%) |

**Table S6.** Table of contributions to each MO from each part of [Ir(L7)$_2$(pic)], Q1 and Q2 are the quinoxalines. **Right:** First five singlet transitions of the complex and a breakdown of their corresponding formative transitions.
| Orbital  | Moiety Contribution to Orbital (%) | Orbital Contribution to Excited State | Contributing Transitions |
|---------|-----------------------------------|--------------------------------------|--------------------------|
| LUMO +4 | Ir (5d) 1 Pyrazine 9 Q2 9 Q1 81   | 1 (416.4 nm, f = 0.0466)              | HOMO -1 → LUMO +1 (4.06%) |
| LUMO +3 |                     1 88 3 7         | 2 (407.26 nm, f = 0.1651)             | HOMO -1 → LUMO (5.59%)   |
| LUMO +2 |                     4 77 19 0     |                                      | HOMO → LUMO (4.37%)      |
| LUMO +1 |                     3 10 39 47   | 3 (347.97 nm, f = 0.016)              | HOMO → LUMO +2 (84.46%)  |
| LUMO    |                     4 10 38 48   | 4 (337.1 nm, f = 0.0897)              | HOMO -6 → LUMO (3.6%)    |
| HOMO    |                     38 4 30 28   |                                      | HOMO -5 → LUMO (3.29%)   |
| HOMO -1 |                     28 7 36 29   | 5 (325.11 nm, f = 0.0832)             | HOMO -4 → LUMO +1 (4.3%) |
| HOMO -2 |                     19 9 42 30   |                                      | HOMO -3 → LUMO (17.63%)  |
| HOMO -3 |                     22 4 23 51   |                                      | HOMO -3 → LUMO +1 (2.5%) |
| HOMO -4 |                     21 5 41 34   |                                      | HOMO -2 → LUMO +1 (21.11%)|

Table S7. Table of contributions to each MO from each part of $[\text{Ir(L}_2\text{)}_2\text{(pyz)}]$, Q1 and Q2 are the quinoxalines. Right: First five singlet transitions of the complex and a breakdown of their corresponding formative transitions.
| Orbital      | Ir (5d) | Pyrazine | Q1 | Q2 | Excited State | Contributing Transitions |
|--------------|---------|----------|----|----|---------------|--------------------------|
| LUMO +4      | 2       | 4        | 72 | 22 | 1 (421.51 nm, f = 0.032) | HOMO -1 → LUMO +1 (5.43%) |
|              |         |          |    |    |               | HOMO → LUMO +1 (9.3%)    |
| LUMO +3      | 1       | 34       | 8  | 57 | 2 (408.15 nm, f = 0.2089) | HOMO -1 → LUMO +1 (14.39%) |
|              |         |          |    |    |               | HOMO → LUMO +1 (79.48%)  |
| LUMO +2      | 4       | 76       | 20 | 1  | 3 (349.39 nm, f = 0.0223) | HOMO -1 → LUMO +1 (12.75%) |
|              |         |          |    |    |               | HOMO → LUMO +2 (80.64%)  |
| LUMO +1      | 3       | 14       | 35 | 48 | 4 (342.61 nm, f = 0.0938) | HOMO -1 → LUMO +1 (17.73%) |
|              |         |          |    |    |               | HOMO → LUMO +1 (30.27%)  |
|              |         |          |    |    |               | HOMO → LUMO +4 (2.29%)   |
| HOMO         | 37      | 4        | 31 | 28 |               |                          |
| HOMO -1      | 10      | 2        | 57 | 31 |               |                          |
| HOMO -2      | 31      | 11       | 36 | 22 | 5 (336.78 nm, f = 0.2254) | HOMO -2 → LUMO +1 (9.98%) |
| HOMO -3      | 6       | 2        | 29 | 64 |               |                          |
| HOMO -4      | 29      | 4        | 27 | 40 |               |                          |

**Table S8.** Table of contributions to each MO from each part of [Ir(L5)2(pyz)]. Q1 and Q2 are the quinoxalines. **Right:** First five singlet transitions of the complex and a breakdown of their corresponding formative transitions.
| [Ir(L7)₂(pyz)] | Moiety Contribution to Orbital (%) | Orbital Contribution to Excited State |
|----------------|-----------------------------------|--------------------------------------|
| Orbital        | Ir (5d)  | Pyrazine | Q1 | Q2 | Excited State | Contributing Transitions |
| LUMO +4        | 2        | 3        | 86 | 10 | 1 (430.81 nm, f = 0.0248) | HOMO -1 → LUMO +1 (4.97%) |
|                |          |          |    |    |               | HOMO → LUMO (88.25%)     |
| LUMO +3        | 1        | 16       | 6  | 77 | 2 (416.68 nm, f = 0.1779) | HOMO -1 → LUMO (8.42%) |
|                |          |          |    |    |               | HOMO → LUMO +1 (81.53%)  |
| LUMO +2        | 3        | 89       | 7  | 0  | 3 (344.58 nm, f = 0.1607) | HOMO -6 → LUMO (3.67%) |
|                |          |          |    |    |               | HOMO -4 → LUMO (3.78%)   |
|                |          |          |    |    |               | HOMO -3 → LUMO (46.24%)  |
|                |          |          |    |    |               | HOMO -2 → LUMO (2.96%)   |
|                |          |          |    |    |               | HOMO -2 → LUMO +1 (5.58%)|
|                |          |          |    |    |               | HOMO -1 → LUMO (24.74%)  |
|                |          |          |    |    |               | HOMO → LUMO +1 (2.01%)   |
| LUMO +1        | 4        | 4        | 46 | 46 | 4 (343.25 nm, f = 0.1002) | HOMO -2 → LUMO (15.02%)  |
| LUMO           | 4        | 4        | 44 | 49 |               | HOMO -1 → LUMO (2.34%)   |
|                |          |          |    |    |               | HOMO -1 → LUMO +1 (19.47%)|
|                |          |          |    |    |               | HOMO → LUMO +2 (50.87%)  |
| HOMO           | 37       | 4        | 31 | 28 | 5 (340.02 nm, f = 0.2894) | HOMO -3 → LUMO (5.54%)   |
| HOMO -1        | 8        | 2        | 63 | 27 |               | HOMO -2 → LUMO (12.85%)  |
|                |          |          |    |    |               | HOMO -2 → LUMO +1 (6.02%)|
|                |          |          |    |    |               | HOMO -1 → LUMO (11.89%)  |
|                |          |          |    |    |               | HOMO -1 → LUMO +1 (20.73%)|
|                |          |          |    |    |               | HOMO → LUMO +2 (25.41%)  |

**Table S9.** Table of contributions to each MO from each part of [Ir(L7)₂(pyz)], Q1 and Q2 are the quinoxalines. **Right:** First five singlet transitions of the complex and a breakdown of their corresponding formative transitions.
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