Electronic Supplementary Material (ESI) for Dalton Transactions

The synthesis and photophysics of tris-heteroleptic cyclometalated iridium complexes

Electronic Supporting Information

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Experimental

All starting reagents were purchased from Sigma Aldrich, with the exception of $IrCl_3.3H_2O$ which was purchased from Precious Metals Online, and were used as received. Solvent purification system (SPS) dried solvents and de-ionised water were used where appropriate. 4-(phenylethynyl)benzene boronic acid was synthesised according to the literature method.[1]

^{1}H-NMR spectra were recorded on a Varian Unity 300, Varian Mercury-400, Varian Inova-500 or Varian VNMRS-700 spectrometer. *J* coupling (^{1}H–^{1}H) values are given in Hz and chemical shifts, δ, in ppm, internally referenced to the residual protonated solvent. Assignment was aided, where necessary, by the following 2D-NMR experiments: ^{1}H–^{1}H gradient-selected correlation spectroscopy (gCOSY) and nuclear Overhauser effect spectroscopy (NOESY). Mass spectra (MS) were recorded on a Waters Xevo QTOF Atmospheric Solids Analysis Probe (ASAP) mass spectrometer or by GCMS. GCMS was performed using an Agilient Technologies 6890 N chromatograph equipped with a 5983 inert mass selective detector and a 10 m fused silica capillary column (5 % cross-linked phenylmethylsilicone) using UHP helium as the carrier gas with the following conditions: injector temperature 250 °C, detector temperature 300 °C, the oven temperature was ramped from 70 °C to 280 °C at 20 °C min^{-1}. HPLC analysis was performed through a XBridge 4.6 x 100 mm, 5 μm, C18 column with gradient elution 9:1 MeOH:water to 19:1 MeOH:water over 10 minutes at a flow rate of 1 ml min^{-1}.

All photophysical measurements were made using GPR grade solvents. Samples were kept dark between measurements as it has been observed in fluorimetry and NMR spectroscopy experiments that some cyclometalated iridium complexes can be photolytically degraded with prolonged irradiation. UV-visible absorption spectra were recorded in quartz cuvettes of path length l = 1 cm with an absorbance, A, < 0.3 at 400 nm were measured on a Unicam UV2-100 spectrometer operated with the Unicam Vision software. Baseline correction was achieved by reference to pure solvent in the same cuvette. Excitation and emission photoluminescence spectra were recorded on a Horiba Jobin Yvon SPEX Fluorolog 3-22 spectrofluorometer. Samples were held in quartz fluorescence cuvettes, l = 1 cm x 1 cm, degassed by repeated freeze-pump-thaw cycles using a turbomolecular pump until the pressure gauge showed no further movement upon a new pump phase, typically at 5 x 10^{-5} mbar, and sealed by way of a Teflon Young's tap. Solutions had A = 0.10-0.15 at the excitation wavelength to minimise inner filter effects. PLQYs were measured using the Fluorolog 3-22 and an integrating sphere using a published method.[2] DataMax software was used throughout. Excited state lifetime

measurements were made using the time-correlated photon counting method. Briefly this was achieved as follows: a N_2 laser (337 nm, 10 µJ, 10 Hz) was used as an excitation source with emission detected in a 90° geometry by a Perkin Elmer SPCM-AQR single-photon counting avalanche diode at a wavelength selected by a monochromator (Jobin-Yvon Triax 320) set to a 1 nm bandpass. The signal was digitised by a National Instruments (NI) USB-5133 (8 bit, 100 Ms/s) digitiser and processed and recorded by in-house NI LabVIEW software.

All calculations were carried out using the Gaussian-09 package.[3] Density functional theory (DFT) ground-state optimised structures were calculated using Becke's three parameter Lee-Yang-Parr (B3LYP) exchange-correlation functional with a mixed basis set of 6-31+G for light atoms (C, H, O, N) and the Los Alamos National Laboratories 2nd double zeta (LANL2DZ) basis set for both the valence and effective core potential functions of heavy atoms (Ir). Orbital surfaces generated from the DFT calculations were visualised in GaussView 4.1. Time-dependent (TD)-DFT calculations were performed on the B3LYP/6-31+G/LANL2DZ optimised ground-state geometries over 25 states (singlets and triplets) using the Coulomb-attenuating method-CAM-B3LYP/6-31+G/LANL2DZ level of theory. A trial calculation using the polarisable continuum model (PCM) and the united atom topological model UAKS with acetonitrile (ε = 35.688) on Ir(fppy)(ppy)(acac) at the same level of theory showed little influence on the calculated transition energies (< 0.05 eV) and thus was omitted in all reported calculations. The initial geometry input for optimisation was based on the crystallographic coordinates where possible or from a chemically intuitive geometry when experimental data were not available to maximise the probability of locating the global minimum on the potential energy surface.

Red, plate-habited crystals of Ir(fppy)(ppy)(acac) were grown by slow evaporation of a saturated acetonitrile solution. Crystals suitable for single crystal X-ray diffraction structure determination were selected, soaked in perfluoropolyether oil and mounted on a glass fiber. Crystallographic measurements were carried out at 120 K using a Bruker SMART CCD 6000 single crystal diffractometer equipped with an open flow N_2 Cryostream[4] (Oxford Cryosystems) device using graphite monochromated MoKα radiation (λ = 0.71073 Å). For data reduction, the SAINT suite was used; the structures were solved with SHELXS and refined with SHELXL.[5] All non-hydrogen atoms were treated anisotropically, the hydrogen atoms were calculated as riding models and refined isotropically.

Table S1 A comparison of the experimental (single-crystal X-ray diffraction) and calculated (DFT B3LYP/6-31+G/LANL2DZ) determined metal-ligand bond lengths of Ir(fppy)(ppy)(acac). Atom numbers refer to the numbering scheme used in the CIF.

Bond	**Experimental bond distance / Å**	**Calculated bond distance / Å**	**Difference / Å**	**% Difference**
Ir-O(2)	2.127(4)	2.196	0.069	3.2
Ir-O(6)	2.159(4)	2.200	0.041	1.9
Ir-C(8)	1.988(6)	2.013	0.025	1.3
Ir-C(19)	1.996(5)	2.009	0.013	0.7
Ir-N(4)	2.040(5)	2.056	0.016	0.8
Ir-N(10)	2.033(5)	2.060	0.027	1.3

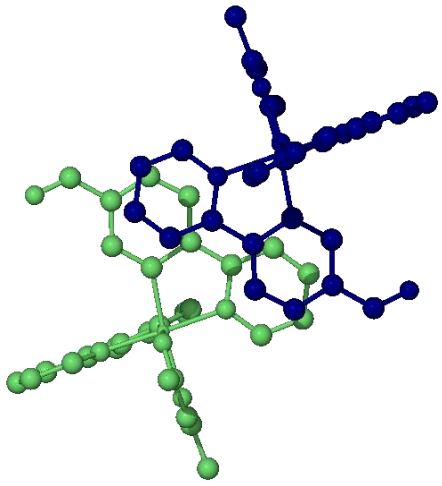
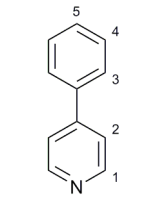


Figure S1 Head-to-tail π-stacking of the fppy ligand in Ir(fppy)(ppy)(acac) as determined by X-ray crystallography

Synthesis of compounds

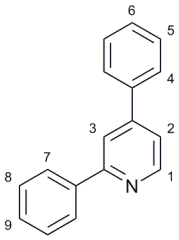
4-phenylpyridine



$C_{11}H_9N$
MW =155.2 g mol^{-1}

4-bromopyridine hydrochloride (1.95 g, 10 mmol) and benzeneboronic acid (1.36 g, 11 mmol) were dissolved in a mixture of THF (50 ml) and aqueous sodium hydroxide (20 ml, 2 M) and the solution purged with nitrogen. $Pd(PPh_3)_4$ (0.25 g, 2 mol%) was added and the solution was heated at 70°C for 16 h. The resultant dark brown solution was cooled to r.t. and the THF removed *in vacuo*. The organic product was extracted into DCM (3 x 15 ml), dried over $MgSO_4$ and reduced *in vacuo* to a light brown solid. The crude solid was run through a silica plug (DCM) affording a light brown solid (1.19 g, 77 %). δ_H (700 MHz; $CDCl_3$) 8.66 (2H, dd, J = 4.6, 1.4, H_1), 7.64 (2H, d, J = 7.6, H_3), 7.52-7.47 (4H, m, H_2 and H_4), 7.46-7.42 (1H, m, H_5); *m/z* (EI^+ GCMS) 155 (M^+).

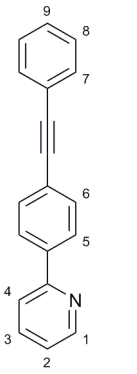
2,4-diphenylpyridine; dppyH



$C_{17}H_{13}N$
MW = 231.3 g mol^{-1}

4-phenylpyridine (1.05 g, 6.8 mmol) was dissolved in dry toluene (10 ml) and cooled to 0 °C. To this solution phenyllithium (4.0 ml, 1.8 M in di-*n*-butyl ether, 7.2 mmol) was added dropwise and stirred for 20 min. The mixture was then heated to 90 °C and stirred for 1 h. After the mixture was cooled to r.t., the reaction was quenched cautiously with water (15 ml). The toluene layer was separated, and the aqueous layer extracted with DCM (3 x 10 ml). The combined organic extracts were reduced *in vacuo* to leave a yellow-brown oil. This was dissolved in ether (15 ml), to which aqueous HCl (3 ml, 3 M) was added and the ether layer separated. The aqueous layer was neutralised with K_2CO_3, extracted with diethyl ether (3 x 10 ml), dried over anhydrous K_2CO_3 and reduced *in vacuo* to a light brown solid (0.61 g, 39 %). δ_H (700 MHz; $CDCl_3$) 8.74 (1H, dd, J = 5.11, 0.6, H_1), 8.06 (2H, dd, J = 8.1, 1.2, H_7), 7.94 (1H, dd, J = 1.6, 0.6, H_3) 7.72-7.68 (2H, m, H_4), 7.54-7.49 (4H, m, H_5 and H_8), 7.48-7.43 (3H, m, H_2, H_6 and H_9); *m/z* (EI^+ GCMS) 231 (M^+).

2-(4′-(phenylethynyl)phenyl)pyridine; 2-(pep)pyH



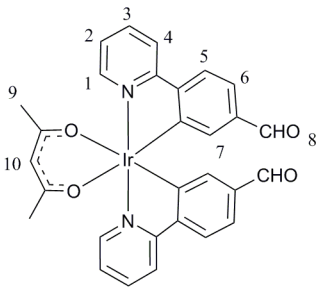
$C_{19}H_{13}N$
MW = 255.3 g mol^{-1}

4-(phenylethynyl)benzene boronic acid (1.0 g, 4.5 mmol), 2-bromopyridine (0.47 ml, 5.0 mmol) and K_2CO_3 (2 g) were dissolved in a mixture of dimethoxyethane (40 ml) and water (15 ml). The solution was purged with N_2 for 30 min before $Pd(OAc)_2$ (50 mg, 5 mol%) and triphenylphosphine (240 mg, 20 mol%) were added. The solution was heated to reflux for 15 h, cooled to r.t. and DCM added. The organic layer was separated dried over $MgSO_4$, filtered and reduced *in vacuo* to give a cream-white solid. The crude material was purified by column chromatography (SiO_2, DCM) and recrystallised from ethanol to give the product as a cream-white solid (0.869 g, 76 %). δ_H (300 MHz; $CDCl_3$) 8.72 (1H, d, J = 6.0, H_1), 8.02 (2H, d, 8.5, H_5), 7.77 (2H, m), 7.65 (2H, d, J = 8.5, H_6), 7.56 (2H, m), 7.37 (3H, m), 7.26 (1H, m); δ_C (75 MHz, $CDCl_3$) 156.8, 150.0, 139.2, 137.0, 132.2, 131.9, 128.6, 127.0, 124.1, 123.4, 122.6, 120.8, 90.9, 89.5; *m/z* (ASAP HRMS) 255.1074 (M^+), $C_{19}H_{13}N$ requires 255.1048.

Typical procedure for the synthesis of *bis*-heteroleptic complexes of the form $IrL_2(acac)$

$IrCl_3.3H_2O$ (350 mg, 0.99 mmol) was dissolved in 2:1 2-ethoxyethanol:water (15 ml) with L (2.2 eq.) The solution was heated to 110 °C for 10 h. The reaction mixture was then allowed to cool to r.t. and water (25 ml) added, affording a solid, which was filtered, washed with water (2 x 5 ml), dissolved in DCM (30 ml), dried over $MgSO_4$ and reduced in vacuo to leave a yellow-brown or orange solid. Flash column chromatography on silica gel (DCM with 1 % EtOH) was used to remove fore-running fractions. The crude material was dissolved in 2-ethoxyethanol (15 ml) with acetylacetone (0.1 ml, excess) and K_2CO_3 (100 mg) and heated to 65 °C for 1 h. Upon cooling to r.t., water (30 ml) was added giving a yellow suspension, which was filtered, washed with water (2 x 5 ml), dissolved in DCM, dried over $MgSO_4$ and reduced in vacuo to leave an oily solid. This was triturated with hexane (3 x 5 ml) and reduced in vacuo to leave a solid which was purified by column chromatography (see below).

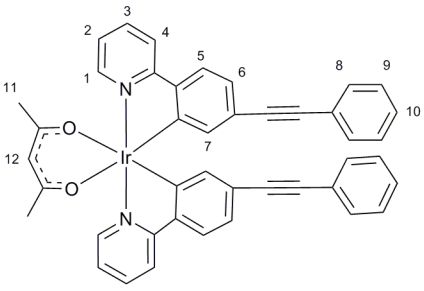
Ir(fppy)$_2$(acac)



$C_{29}H_{23}IrN_2O_4$
MW = 655.7 g mol^{-1}

Column chromatography on silica gel (DCM) afforded the title compound as a red solid (9 mg, 7 %). δ_H (300 MHz; $CDCl_3$) 9.64 (2H, s, H_8), 8.58 (2H, d, J = 5.1, H_1), 8.01 (2H, d, J = 7.8, H_4), 7.89 (2H, td, J = 7.4, H_3), 7.71 (2H, d, J = 8.1), 7.32 (4H, m), 6.71 (2H, d, J = 1.5, H_7), 5.27 (1H, s, H_{10}), 1.81 (6H, s, H_9); *m/z* (ASAP HRMS) 654.1262 (M^+), $^{191}IrC_{29}H_{23}N_2O_4$ requires 654.1264

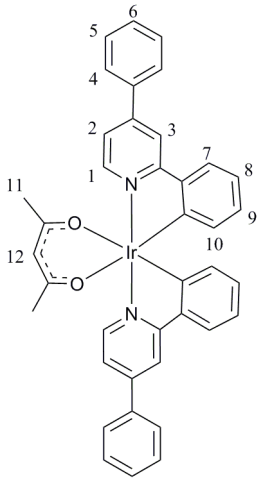
Ir(2-(pep)ppy)$_2$(acac)



$C_{43}H_{31}IrN_2O_2$
MW = 799.9 g mol^{-1}

Column chromatography on silica gel (DCM) afforded the title compound as a yellow solid (62 mg, 36 %). δ_H (700 MHz; CD_2Cl_2) 8.51 (2H, d, J = 5.6, H_1), 7.93 (2H, d, J = 8.1, H_4), 7.86-7.83 (2H, m, H_3), 7.61 (2H, d, J = 8.0, H_5), 7.42-7.40 (4H, m, H_8), 7.31-7.29 (6H, m, H_9 and H_{10}), 7.25 (2H, ddd, J = 7.1, 5.6, 1.4, H_2), 7.06 (2H, dd, J = 8.0, 1.6, H_6), 6.40 (2H, d, J = 1.6, H_7), 5.30 (1H, s, H_{12}), 1.81 (6H, s, H_{11}); *m/z* (ASAP HRMS) 799.2048 ($[M+H]^+$, $^{191}IrN_2O_2C_{43}H_{32}$ requires 799.2070).

Ir(dppy)$_2$(acac)



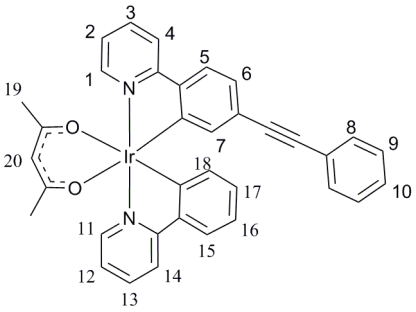
$C_{39}H_{31}IrN_2O_2$
MW = 751.9 g mol^{-1}

Column chromatography on silica gel (DCM with 5 % hexane) afforded the title compound as a yellow solid (118 mg, 53 %). δ_H (400 MHz; $CDCl_3$) 8.56 (2H, d, J = 6.0, H_1), 8.06 (2H, d, J = 1.9, H_3), 7.80 (4H, d, J = 7.4, H_4), 7.65 (2H, dd, J = 7.8, 0.9, H_7), 7.60-7.54 (4H, m, H_5), 7.52-7.47 (2H, m, H_6), 7.37 (2H, dd, J = 6.0, 1.9, H_2), 6.86-6.81 (2H, m, H_8), 6.74-6.70 (2H, m, H_9), 6.37 (2H, dd, J = 7.7, 0.9, H_{10}), 5.25 (1H, s, H_{12}), 1.82 (6H, s, H_{11}); *m/z* (ASAP HRMS) 750.1978 (M^+, $^{191}IrN_2O_2C_{39}H_{31}$ requires 750.1992).

Typical procedure for the synthesis of *tris*-heteroleptic complexes of the form Ir(ppy)L′(acac)

$IrCl_3.3H_2O$ (350 mg, 0.99 mmol) was dissolved in 2:1 2-ethoxyethanol:water (15 ml) with 2-phenylpyridine (0.23 ml, 1.5 mmol) and L′ (0.5 mmol). The solution was heated to 110 °C for 10 h. The reaction mixture was cooled to r.t. and water (25 ml) added, affording a solid, which was filtered, washed with water (2 x 5 ml), dissolved in DCM (30 ml), dried over $MgSO_4$ and reduced in vacuo to leave a yellow-brown or orange solid. Flash column chromatography on silica gel (DCM with 1 % EtOH) was used to remove fore-running fractions from the mix of dimers. This crude mixture was dissolved in 2-ethoxyethanol (15 ml) with acetylacetone (0.1 ml, excess) and K_2CO_3 (100 mg) and heated to 65 °C for 1 h. Upon cooling to r.t., water (30 ml) was added giving a yellow suspension, which was filtered, washed with water (2 x 5 ml), dissolved in DCM, dried over $MgSO_4$ and reduced in vacuo to leave an oily solid. This was triturated with hexane (3 x 5 ml) to remove excess acacH and reduced in vacuo to leave a solid which was purified by column chromatography (see below). In each case the desired product eluted as the second major component. Yields are based on the functionalised 2-phenylpyridine.

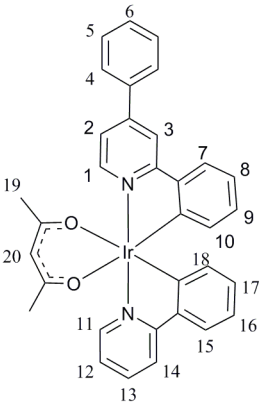
Ir(2-(pep)py)(ppy)(acac)



$C_{35}H_{27}IrN_2O_2$
MW = 699.8 g mol^{-1}

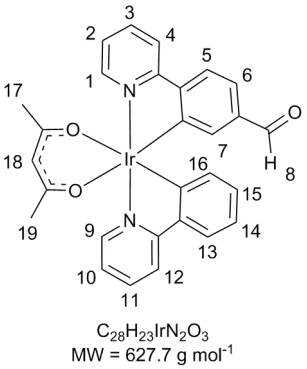
Column chromatography on silica gel (9:1 DCM:hexane) afforded the title compound (24 mg, 7 %) as a yellow solid. δ_H (500 MHz; CD_2Cl_2) 8.51-8.48 (1H, m, H_1 and H_{11}), 7.93-7.88 (2H, m, H_4 and H_{14}), 7.83-7.78 (2H, m, H_3 and H_{13}), 7.61 (1H, d, J = 7.8, H_{15}), 7.57 (1H, d, J = 8.0, H_5), 7.41-7.38 (2H, m, H_8), 7.31-7.28 (3H, m, H_9 and H_{10}), 7.25-7.20 (2H, m, H_2 and H_{12}), 7.04 (1H, dd, J = 8.0, 1.5, H_6), 6.88-6.85 (1H, m, H_{16}), 6.70 (1H, ddd, J = 8.5, 7.6, 1.2, H_{17}), 6.41 (1H, d, J = 1.5, H_7), 6.21 (1H, dd, J = 7.6, 0.6, H_{18}), 5.29 (1H, s, H_{20}), 1.97 (6H, s, H_{19}); *m/z* (ASAP HRMS) 698.1678 (M^+, $^{191}IrN_2O_2C_{35}H_{27}$ requires 698.1679); HPLC 100 %.

Ir(dppy)(ppy)(acac)



Column chromatography on silica gel (DCM) afforded the title compound (25 mg, 7 %) as a yellow solid. δ_H (700 MHz; $CDCl_3$) 8.55-8.53 (2H, m, H_1 and H_{11}), 8.05 (1H, d, J = 2.0, H_3), 7.86 (1H, d, J = 8.2, H_{14}), 7.80 (2H, dd, J = 8.0, 1.2, H_4), 7.74 (1H, ddd, J = 8.2, 7.5, H_{13}), 7.64 (1H, d, J = 7.7, H_7), 7.58-7.54 (3H, m, H_5 and H_{15}), 7.51-7.48 (1H, m, H_6), 7.36 (1H, dd, J = 5.9, 2.0, H_2), 7.14 (1H, ddd, J = 7.5, 5.7, 1.4, H_{12}), 6.84-6.79 (2H, m, H_8 and H_{16}), 6.72-6.68 (2H, m, H_9 and H_{17}), 6.35 (1H, dd, J = 7.7, 0.9, H_{10}), 6.28 (1H, dd, J = 7.6, 1.0, H_{18}), 5.23 (1H, s, H_{20}), 1.80 (6H, s, H_{19}); *m/z* (ASAP HRMS) 674.1695 (M^+, $^{191}IrN_2O_2C_{33}H_{27}$ requires 674.1679); HPLC 98 %.

Ir(fppy)(ppy)(acac)



Column chromatography on silica gel (50:1 DCM:ethanol) afforded the title compound (33 mg, 11 %) as a red solid. δ_H (400 MHz; d_6-acetone) 9.65 (1H, s, H_8), 8.65 (1H, ddd, J = 5.7, 1.6, 0.8, H_1), 8.58 (1H, ddd, J = 5.7, 1.6, 0.8, H_9), 8.28-8.25 (1H, m, H_4), 8.14-8.10 (1H, m, H_{12}), 8.03 (1H, ddd, J = 8.2, 7.5, 1.6, H_3), 7.97 (1H, ddd, J = 8.2, 7.5, 1.6, H_{11}), 7.88 (1H, d, J = 8.0, H_5), 7.69-7.66 (1H, m, H_{13}), 7.47 (1H, ddd, J = 7.5, 5.7, 1.4, H_2), 7.38 (1H, ddd, J = 7.5, 5.7, 1.4, H_{10}), 7.29 (1H, dd, J = 8.0, 1.5, H_6), 6.79 (1H, d, J = 1.5, H_7), 6.77 (1H, ddd, J = 7.7, 7.2, 1.2 . H_{14}), 6.62 (1H, ddd, J = 7.6, 7.2, 1.4, H_{15}), 6.18 (1H, ddd, J = 7.6, 1.2, 0.5, H_{16}), 5.30 (1H, s, H_{18}), 1.72 (3H, s), 1.71 (3H, s); *m/z* (ASAP HRMS) 626.1310 (M^+, $^{191}IrN_2O_3C_{28}H_{23}$ requires 626.1315); HPLC 92 %.

An alternative one-pot method for the synthesis of Ir(fppy)(ppy)(acac) was also demonstrated. Thus, on the same scale, the μ-chlorodimer was produced by heating $IrCl_3$ with the mixture of ppy ligands in aqueous 2-ethoxyethanol. After 4 h, acacH (10 eq.) and K_2CO_3 (10 eq.) were added to the mixture and heating continued for a further 0.5 h. The mixture of products could be isolated by the usual work-up, followed by careful column chromatography using the same solvent conditions as above gave material with identical analytical data. Although this method is quicker, we found that it is easier to obtain material of higher purity using the two-step procedure.

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