Ditopic Bis-Terdentate Cyclometallating Ligands and their Highly Luminescent Dinuclear Iridium(III) Complexes

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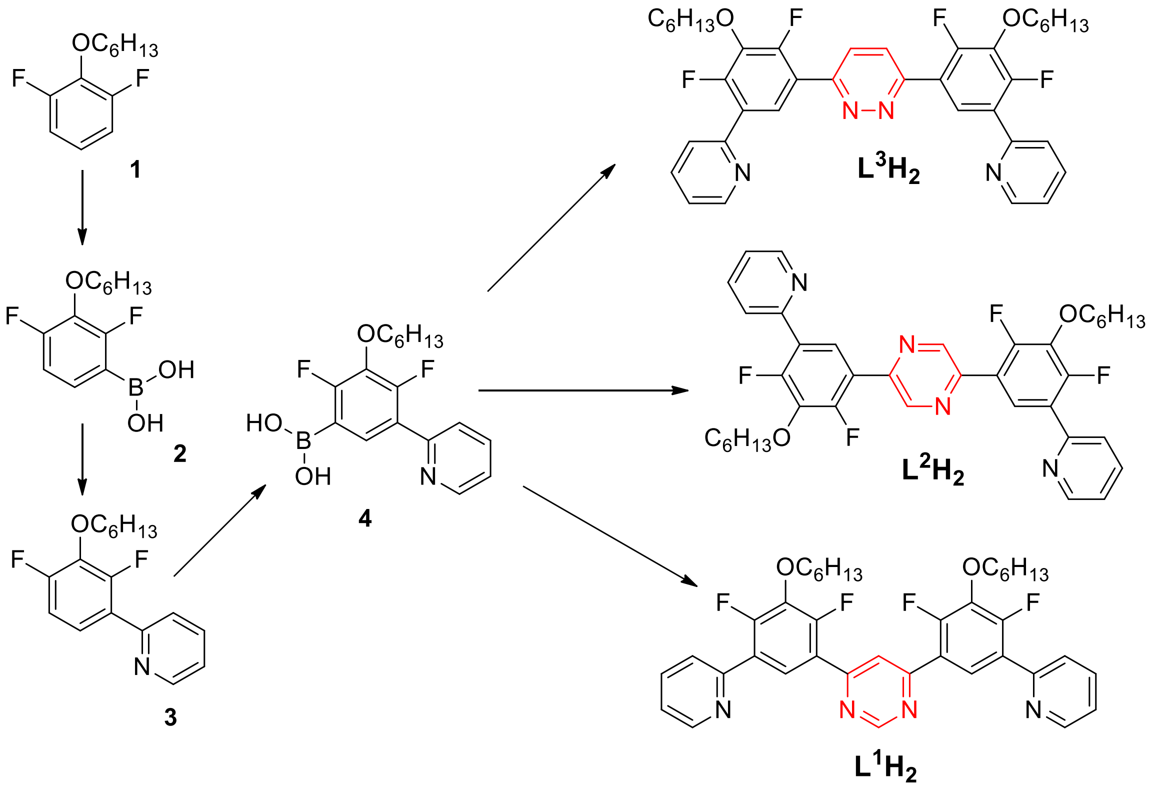
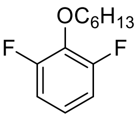
Electronic Supporting Information

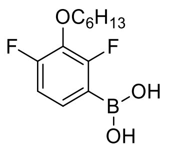
Synthetic and characterisation details

All chemicals and solvents were purchased from either Sigma Aldrich or Alfa Aeser and used as supplied, unless noted otherwise. ^{1}H,^{13}C and ^{19}F NMR spectra were recorded using a Jeol ECS400 (400 MHz for ^{1}H, 100 MHz for ^{13}C and 376 MHz for ^{19}F). Data are expressed in parts per million using tetramethylsilane as an internal standard or relative to the solvent used (chloroform-*d*). Assignments are made with the calculation of the constant coupling. HRMS were recorded using a Thermofisher LTQ Orbitrap XL spectrometer operating in high resolution with electrospray ionisation (ESI).

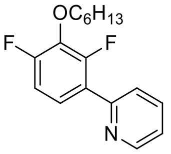




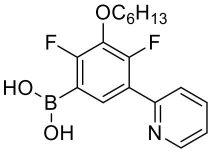
2,4-difluoro-3-hexyloxybenzene (1) : A mixture of anhydrous K_2CO_3 (53.86 g, 0.39 mol), 2,4-diflurophenol (16.91 g, 0.13 mol), 1-bromohexane (21.46 g, 0.13 mol) in acetonitrile (130 mL) was heated under reflux for 24 h. Petroleum ether (130 mL) and water (100 mL) were added to the reaction mixture. The organic layer was separated and the aqueous layer was washed with petroleum ether (2 × 20 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo to afford a colourless liquid which was used for the next step without further purification (23.36 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (m, 3H), 4.12 (t, 2H, J = 6.1 Hz); 1.76 (m, 2H), 1.47 (m, 2H); 1.33 (m, 4H), 0.90 (t, 3H, J = 6.1 Hz); ^{19}F NMR (400 MHz): δ –128.2 (m).



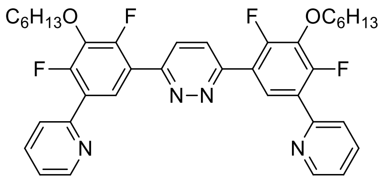
2,4-difluoro-3-*n*-hexyloxyphenyl boronic acid (2): To a stirred solution of 2,4-difluoro-3-*n*-hexyloxybenzene **1** (17.36 g, 81.0 mmol) in dry THF (90 mL), at -78°C, *n*-butyllithium (1.6 M solution in hexane, 61 mL, 97.2 mmol) was added slowly. The reaction mixture was stirred at -78°C for 2 hours. Triisopropylborate (28 mL, 121.5 mmol) was added slowly and the mixture was stirred at -78°C for 1 h. The mixture was left stirring overnight and allowed to warm to room temperature. The mixture was acidified with 1M hydrochloric acid (c.a 20 mL) and stirred at room temperature for 1 h. The organic layer was separated and the aqueous layer was extracted with hexane (2 × 20 mL). All combined organic layers were washed with brine (2 × 30mL), followed by water (15 mL). Evaporation of the organic solvents under vacuum afforded yellow oily liquid. The residue was treated with water (45 mL) and left at room temperature for 2 h. The white precipitate from the mixture was filtered, washed with water and petroleum ether and dried. (18.1 g, 87% yield), mp: 65.1-65.9°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, 1H, J = 14.4 Hz, J = 7.6 Hz), 6.92 (ddd, 1H, J = 9.2 Hz, J = 8.2 Hz, J = 1.4 Hz), 5.64 (d, 2H, J = 6.0 Hz), 4.09 (t, 2H, J = 6.6 Hz), 1.75 (quintet, 2H, J = 7.1 Hz), 1.45 (m, 2H), 1.31 (m, 4H), 0.89 (m, 3H).



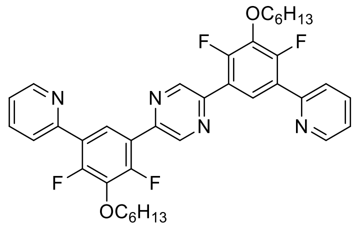
2-(2,4-difluoro-3-hexyloxyphenyl)pyridine (3): A mixture of 2,4-difluoro-3-hexyloxyphenyl boronic acid **2** (8.07 g, 31.3 mmol), 2-bromopyridine (3.95 g, 25.0 mmol) in 1,4-dioxane (95 mL) was deoxygenated by bubbling argon through the mixture for 20 min. A deoxygenated solution of potassium phosphate (15.92 g, 75.0 mmol) in water (32 mL) was then added to the reaction mixture, followed by addition of palladium acetate (280.6 mg, 1.25 mmol) and triphenylphosphine (655.7 mg, 2.5 mmol). The reaction mixture was heated under reflux for 24 h. Ethyl acetate (50 mL) was added and the organic layer was separated. The aqueous phase was extracted with hexane (3× 20mL). All organic layers were combined and washed with brine (2× 15 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo to give a dark yellow oily residue. The crude product was purified by column chromatography using silica gel (eluent petroleum ether/EtOAc, gradient eluted from 9/1 to 7/3, v/v), to give a colourless oil (6.2 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (1H, m), 7.72 (2H, m), 7.59 (1H, ddd, J = 14.6 Hz, J = 8.5 Hz, J = 6.2 Hz), 7.24 (1H, m), 6.99 (1H, m), 4.14 (2H, t, J = 6.6 Hz), 1.77 (m, 2H), 1.47 (m, 2H), 1.33 (m, 4H), 0.89 (m, 3H).



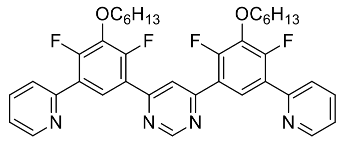
2,4-difluoro-3-hexyloxy-5-(2-pyridyl)phenyl boronic acid (4) : *n*-Butyllithium (1.6 M solution in hexane, 12.8 mL, 20.4 mmol,) was added slowly with stirring to a solution of 2-(2,4-difluoro-3-hexoxybenzene)pyridine (**3**) (5.390 g, 18.5 mmol) and *N,N,N'N',N*-pentamethyldiethylenetriamine (3.24 g, 20.4 mmol) in dry THF (65 mL) at -78 °C. On completion of addition, the mixture was stirred at -78 °C for 2 h. Triisopropylborate (6.5 mL, 27.8 mmol) was added slowly and the mixture was allowed to warm to room temperature over a period of 14 h. The mixture was added diluted HCl followed by neutralised with acetic acid until pH~ 7. Brine (15 mL) was added, layers separated and the aqueous layer was extracted with ethyl acetate (3 x 15 mL). Combined organic layers were dried over $MgSO_4$, filtered and all volatiles were removed under reduced pressure to afford a white powder which was used in the next step without further purification (3.35 g, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, 1H, J = 5.3 Hz), 8.31 (dd, 1H, J = 8.2 Hz), 8.01 (d, 1H, J = 7.8 Hz), 7.59 (m, 2H); 4.13 (t, 2H, J = 6.4 Hz), 1.72 (m, 2H); 1.43 (m, 2H), 1.33 (m, 4H), 0.86 (t, 3H, J = 7.0 Hz).



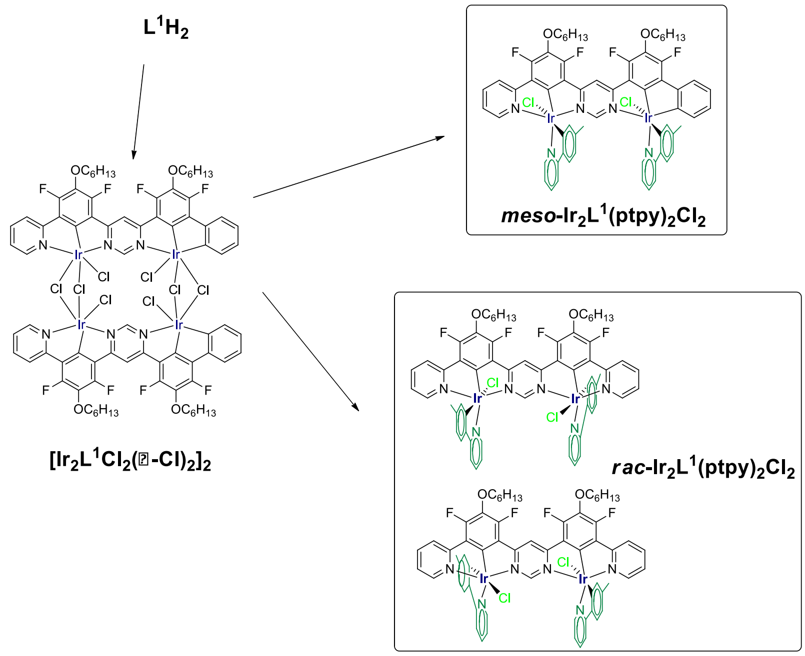
L^3H_2: A mixture of K_2CO_3 (3.3 g, 23.9 mmol), 2,4-difluoro-3-hexyloxy-5-(2-pyridyl)phenyl boronic acid **4** (2.0 g, 6.0 mmol) and 3,6-dichloropyridazine (372 mg, 2.5 mmol), water (20 mL), toluene (40 mL) and ethanol (2 mL) was deoxygenated by bubbling N_2 through the mixture for 20 minutes. $Pd(PPh_3)_4$ (250 mg, 0.24 mmol) was then added and the mixture was heated under refluxed for 15 h. Brine (15 mL) and ethyl acetate (20 mL) were added and the phases were separated. The aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and evaporated to dryness. The product was purified by column chromatography (SiO_2, petrol ether/EtOAc, 7/3) to give the desired product as a white solid (1.3 g, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (2H, m), 8.51 (2H, t, J = 8.4 Hz), 8.00 (2H, s), 7.74-7.81 (4H, m), 7.28 (2H, m), 4.23 (4H, t, J = 6.6 Hz), 1.82 (4H, m), 1.51 (4H, m), 1.33-1.39 (8H, m), 0.90 (6H, t, J =7.0 Hz); ^{19}F NMR (400 MHz): δ –128.4 (dd, J = 12.0 Hz, 8.2 Hz), –130.5 (dd, J = 12.0 Hz, 8.2 Hz).



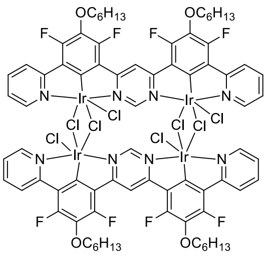
L^2H_2: A mixture of K_2CO_3 (3.4 g, 24.6 mmol), 2,4-difluoro-3-hexyloxy-5-(2-pyridyl)phenyl boronic acid (2.04 g, 6.1 mmol) and 2.5-dibromopyrazine (719 mg, 3 mmol), water (20 mL), toluene (40 mL) and ethanol (2 mL) was deoxygenated by bubbling N_2 through the mixture for 20 minutes. $Pd(PPh_3)_4$ (250 mg, 0.24 mmol) was then added and the mixture was heated under refluxed for 15 h. Brine (15 mL) and ethyl acetate (20 mL) were added and the phases were separated. The aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and evaporated to dryness. The product was purified by column chromatography (SiO_2, heptane/EtOAc, with gradient from 9/1 to 6/4) to give the desired product as a white solid (630 mg, 32%). ^1H NMR (400 MHz, $CDCl_3$) δ 9.16 (2H, d, *J* = 1.6 Hz), 8.74 (2H, br.d, *J* = 4.7 Hz), 8.39 (2H, t, *J* = 8.2 Hz), 8.30 (1H, br.s.), 7.73-7.82 (4H, m), 7.29 (2H, m), 4.23 (4H, t, *J* = 6.6 Hz), 1.82 (4H, br.q, *J*= 7.0 Hz), 1.53 (m, 4H), 1.33-1.40 (8H, m), 0.90 (6H, t, *J* =7.0 Hz); ^{19}F NMR (400 MHz): δ –128.7 (dd, *J* = 12.0 Hz, 8.2 Hz), –128.8 (dd, *J* = 12.0 Hz, 8.2 Hz).



L^1H_2: A mixture of K_2CO_3 (1.656 g, 12 mmol), 2,4-difluoro-3-hexyloxy-5-(2-pyridyl)phenyl boronic acid **4** (1 g, 3 mmol) and 4,6-dichloropyrimidine (186 mg, 1.25 mmol), water (5 mL), toluene (7mL) and ethanol (1 mL) was deoxygenated by bubbling N_2 through the mixture for 20 minutes. $Pd(PPh_3)_4$ (103 mg, 0.1 mmol) was then added and the mixture was heated under refluxed for 15 h. Brine (15 mL) was added and the phases were separated. The aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and evaporated to dryness. The product was purified by column chromatography (SiO_2, heptane/EtOAc, from 9/1 to 7/3) to give a desired product as a white solid (672 mg, 82%). ^1H NMR (400 MHz, $CDCl_3$) δ 9.38 (1H, d, *J* = 1.1 Hz), 8.76 (2H, m), 8.49 (2H, t, *J* = 8.2 Hz), 8.30 (1H, br.s.), 7.76-7.83 (4H, m), 7.31(2H, ddd, *J* = 6.2, 4.9, 2.3 Hz), 4.24 (4H, t, *J* = 6.6 Hz), 1.85 (4H, br.q, *J*= 7.0 Hz), 1.53 (m, 4H), 1.33-1.40 (8H, m), 0.90 (6H, t, *J* =7.0 Hz); ^{19}F NMR (400 MHz): δ –127.3 (s), –128.7 (s).



Dimer $[Ir_2L^1Cl_2(\mu\text{-}Cl)_2]_2$

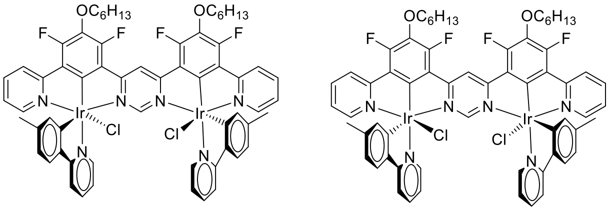


The ligand $\mathbf{L^1H_2}$ (1.77 g, 2.69) was dissolved in ethoxyethanol (30 mL) at 100°C. Water (10 mL) was added followed by $IrCl_33H_2O$ (2.15 g, 5.9 mmol, 2.2 eq). The mixture was heated under reflux for 14 h. Water (35 mL) was added and the mixture was allowed to cool to room temperature. The precipitated solid was filtered off, washed with water (3 x 20 mL) and methanol (2 x 10 mL) to give a bright-red solid; 3.06 g (96%). ^1H NMR (400 MHz, $CDCl_3$) δ 9.84 (2H, br.s), 8.98 (2H, br.s), 8.27 (4H, br.d, *J* = 5.3 Hz), 8.19 (4H,br.d, *J* = 7.9 Hz), 7.63 (4H, br.t, *J* = 7.8 Hz), 6.64 (4H, br.t, *J* = 7.8 Hz), 4.26 (t, 8H, *J* = 6.6 Hz), 1.93 (8H, br.q, *J* = 6.8 Hz), 1.53-1.63 (8H, m), 1.40-1.45 (16H, m), 0.97 (12H, t, *J* = 6.6 Hz); ^{19}F NMR (400 MHz): δ –117.7 (d, *J* = 19.3 Hz), – 119.3 (d, *J* = 19.4 Hz).

$Ir_2L^1(ptpy)_2Cl_2$

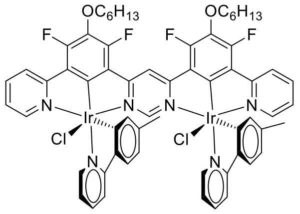
Di-chloro bridged Ir complex $\mathbf{[Ir_2L^1Cl_2(\mu\text{-}Cl)_2]_2}$ (344 mg, 0.29 mmol) was dissolved in hot toluene (25 mL). A solution of 2-(4-methylphenyl)pyridine (210 mg, 1.24 mmol, 4.3 eq) in toluene (5 mL) was added and the mixture was heated under reflux for 1 minute. A solution of silver triflate (7.4 mL, 0.74 mmol, 2.55 eq) in toluene was added and the mixture was heated under reflux for 14 h. Toluene was evaporated and the residue was dissolved in DCM (50 mL). The organic phase was washed with 2M HCl (2 x 25 mL), dried over $MgSO_4$, filtered and evaporated to dryness. The products were separated by column chromatography. (silica gel, DCM/ethylacetate, 4/1). Two products were isolated: ***rac*-$\mathbf{Ir_2L^1(ptpy)_2Cl_2}$** (180 mg, 43%, R_f 0.45), and ***meso*-$\mathbf{Ir_2L^1(ptpy)_2Cl_2}$** (104 mg, 25%, R_f 0.08).

***rac*-$\mathbf{Ir_2L^1(ptpy)_2Cl_2}$**



^{1}H NMR (CDCl$_3$, 400 MHz) δ 9.52 (2H, br.d, J = 5.4 Hz), 8.62 (1H, s), 8.03 (2H, d, J = 8.0 Hz), 7.95 (2H, d, J = 8.0 Hz), 7.86 (2H, ddd, J = 7.8 Hz, J = 7.8 Hz, J = 1.6 Hz), 7.56 (2H, ddd, J = 7.8 Hz, J = 7.8 Hz, J = 1.4 Hz,), 7.44 (2H, d, J = 7.9 Hz), 7.37 (2H, br.d, J = 5.6 Hz), 7.17 (m, 3H), 6.78 (2H, ddd, J = 7.0 Hz, J = 5.6 Hz, J = 1.3 Hz), 6.54 (br.d, 2H, J = 8.0 Hz), 5.60 (br.s, 1H), 4.17 (t, 4H, J = 6.6 Hz), 1.90 (6H, s), 1.87 (4H, m), 1.57 (4H, m), 1.40 (8H, m), 0.95 (6H, t, J = 6.5 Hz); Found C 51.03, H 4.06, N 5.78. $C_{62}H_{56}Cl_2F_4Ir_2N_6O_2$ requires C 51.41, H 3.90, N 5.80.

***meso*-$\mathbf{Ir_2L^1(ptpy)_2Cl_2}$**

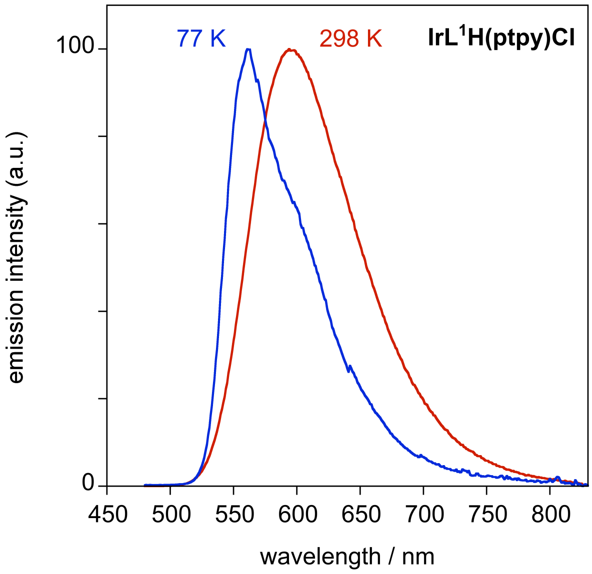


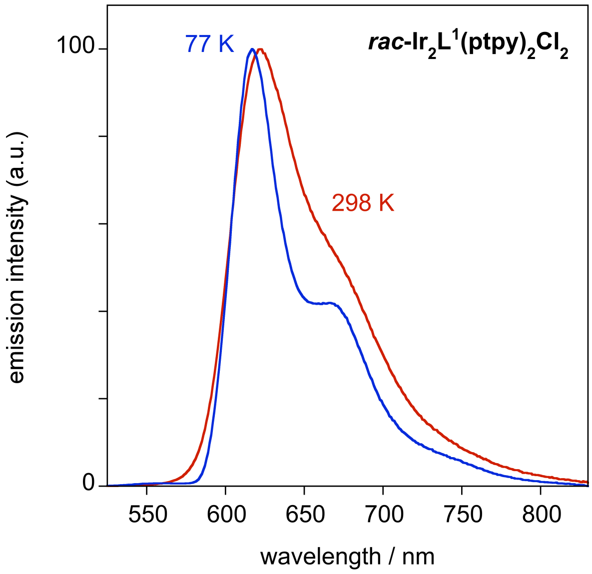
^{1}H NMR (CDCl$_3$, 400 MHz) δ 9.78 (2H, d, J = 5.6 Hz), 8.61 (1H, s), 8.02 (d, 2H, J = 8.0 Hz), 7.78 (4H, m), 7.55 (2H, br.t, J = 7.8 Hz), 7.31 (4H, m) 7.23 (2H, d, J = 8.0 Hz), 7.04 (s, 1H), 6.77 (2H, br.t, J = 6.6 Hz), 6.39 (2H, d, J = 7.8 Hz), 5.42 (2H, s), 4.19 (4H, m), 1.89 (4H, m), 1.78 (6H, s), 1.58 (8H, m), 1.43 (8H, m), 0.95 (6H, t, J = 6.5 Hz); HRMS(ES+) for $[M\text{-}Cl]^+$ calcd. 1409.3299, found 1409.3296.

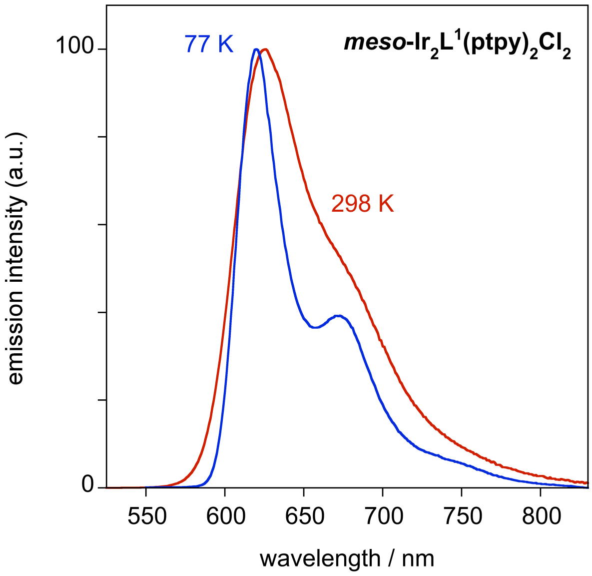
Details of instrumentation for absorption and emission spectroscopy

Absorption spectra in solution were measured on a Biotek Instruments XS spectrometer, using quartz cuvettes of 1 cm path length. Samples for emission measurements were contained within quartz cuvettes of 1 cm path length modified to allow connection to a high-vacuum line. Degassing was achieved *via* a minimum of three freeze-pump-thaw cycles whilst connected to the vacuum manifold; final vapour pressure at 77 K was $< 5 \times 10^{-2}$ mbar, as monitored using a Pirani gauge. Luminescence quantum yields were determined using [Ru(bpy)$_3$]Cl$_2$ in degassed aqueous solution (Φ = 0.042) as the standard and cross-checked against rhodamine B as a second standard; estimated uncertainty in absolute values of Φ is ± 20% or better, (the error on relative values amongst the three complexes is estimated to be 5%). The luminescence lifetimes of the complexes were measured by time-correlated single photon counting (TCSPC), following excitation at 374.0 nm with an EPL-375 pulsed-diode laser. The emitted light was detected at 90° using a Peltier-cooled R928 PMT after passage through a monochromator. The estimated uncertainty in the quoted lifetimes is ± 10% or better. Spectra at 77 K were recorded in a glass of EPA (= diethyl ether / isopentane / ethanol, 2:2:1 v/v).

Emission spectra of the three complexes in EPA at 77K (blue lines) together with corresponding spectra in CH_2Cl_2 at 298 ± 3 K.







Single crystal X-ray diffraction analysis

Crystals were obtained by vapour diffusion of hexane in dichloromethane.

Table S1. Crystal data and structure refinement for ***rac*-Ir$_2$L^1(ptpy)$_2$Cl$_2$**

Chemical formula (moiety)	$C_{62}H_{57}Cl_2F_4Ir_2N_6O_2\cdot0.5C_6H_{14}$	
Chemical formula (total)	$C_{65}H_{64}Cl_2F_4Ir_2N_6O_2$	
Formula weight	1492.52	
Temperature	120(2) K	
Radiation, wavelength	synchrotron, 0.68890 Å	
Crystal system, space group	triclinic, $P\bar{1}$	
Unit cell parameters	a = 13.2305(16) Å	α = 109.3506(12)°
	b = 13.3936(17) Å	β = 95.0445(14)°
	c = 18.760(2) Å	γ = 110.6617(12)°
Cell volume	2854.7(6) Å^3	
Z	2	
Calculated density	1.736 g/cm^3	
Absorption coefficient μ	4.431 mm^{-1}	
F(000)	1472	
Crystal colour and size	red, 0.04 × 0.04 × 0.001 mm^3	
Reflections for cell refinement	9863 (θ range 2.3 to 29.6°)	
Data collection method	Crystal Logic diffractometer and Rigaku Saturn 724+ CCD thick-slice ω scans	
θ range for data collection	3.4 to 24.2°	
Index ranges	h −12 to 15, k −15 to 15, l −22 to 22	
Completeness to θ = 24.2°	97.0 %	
Reflections collected	22574	
Independent reflections	9763 (R_{int} = 0.0353)	
Reflections with $F^2>2\sigma$	8743	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.8427 and 0.9956	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0650, 7.6599	
Data / restraints / parameters	9763 / 0 / 731	
Final R indices [$F^2>2\sigma$]	R1 = 0.0507, wR2 = 0.1276	
R indices (all data)	R1 = 0.0541, wR2 = 0.1296	
Goodness-of-fit on F^2	1.241	
Extinction coefficient	0.0293(7)	
Largest and mean shift/su	0.001 and 0.000	
Largest diff. peak and hole	2.21 and −2.72 e Å^{-3}	

Table S2. Crystal data and structure refinement for ***meso*-$\mathbf{Ir_2L^1(ptpy)_2Cl_2}$**

Crystals were obtained by vapour diffusion of ether in dichloroethane.

Identification code	nv3	
Chemical formula (moiety)	$C_{60}H_{56}Cl_2F_4Ir_2N_8O_2{\cdot}C_2H_4Cl_2{\cdot}H_2O$	
Chemical formula (total)	$C_{62}H_{62}Cl_4F_4Ir_2N_8O_3$	
Formula weight	1569.40	
Temperature	150(2) K	
Radiation, wavelength	synchrotron, 0.68890 Å	
Crystal system, space group	monoclinic, $P2_1/c$	
Unit cell parameters	a = 20.856(4) Å	α = 90°
	b = 18.490(3) Å	β = 109.229(2)°
	c = 17.084(3) Å	γ = 90°
Cell volume	6220.5(19) $Å^3$	
Z	4	
Calculated density	1.676 g/cm^3	
Absorption coefficient μ	4.148 mm^{-1}	
F(000)	3088	
Crystal colour and size	red, 0.20 × 0.05 × 0.05 mm^3	
Reflections for cell refinement	9866 (θ range 2.2 to 27.4°)	
Data collection method	Crystal Logic diffractometer and Rigaku Saturn 724+ CCD thick-slice ω scans	
θ range for data collection	3.4 to 23.9°	
Index ranges	h −24 to 24, k −21 to 21, l −19 to 14	
Completeness to θ = 23.9°	98.7 %	
Reflections collected	42960	
Independent reflections	10473 (R_{int} = 0.0412)	
Reflections with $F^2>2\sigma$	9059	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.4909 and 0.8194	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0495, 42.1012	
Data / restraints / parameters	10473 / 493 / 786	
Final R indices [$F^2>2s$]	R1 = 0.0429, wR2 = 0.1125	
R indices (all data)	R1 = 0.0507, wR2 = 0.1172	
Goodness-of-fit on F^2	1.073	
Extinction coefficient	0.00001(6)	
Largest and mean shift/su	0.002 and 0.000	
Largest diff. peak and hole	2.22 and −1.31 e $Å^{-3}$	