Supporting Information

A cross-coupling strategy for the synthesis of dimetallic assemblies containing mixed bipyridine–terpyridine bridging ligands: luminescence and energy transfer properties

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General synthetic details

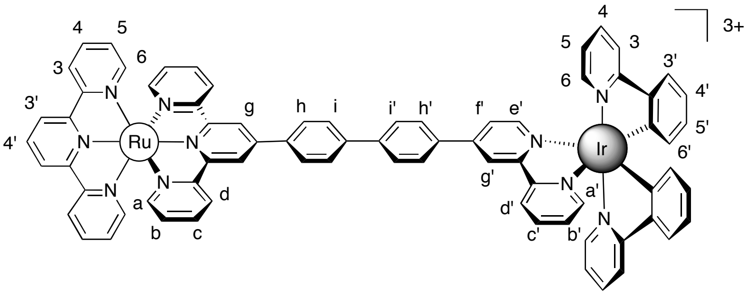
The bromo-substituted terpyridyl complexes, $[Ir(tpy)(tpy\text{-}\phi\text{-}Br)](PF_6)_3$ and $[Ru(tpy)(tpy\text{-}\phi\text{-}Br)](PF_6)_2$, were prepared by reaction of $M(tpy)Cl_3$ with 4'-(bromophenyl)terpyridine, as described previously.[S1,S2] The boronate complexes were prepared by reaction of $[Ru(bpy)_2(Me_2CO)_2]^{2+}$ or $[Ir(ppy)_2\mu\text{-}Cl]_2$ with bpy-ϕ-Bneo (neo = neopentylglycloate), as reported in our earlier work.[S3]

^{1}H NMR resonances are referenced relative to residual protiosolvent resonances, and coupling constants are in Hertz. Spectra were assigned using a combination of ^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY NMR spectroscopy. Strictly, the two bpy ligands in **^{t}Ir–Ru^b** are inequivalent, as are the two ppy ligands in **^{t}Ru–Ir^b**. However, even at 500 MHz, this led only to additional fine structure in some resonances. In the spectral assignments given in the footnote to the paper and below, such ligands are therefore treated as being equivalent. Mass spectra were recorded using electropsray ionisation, with samples introduced in methanol solution.

Synthetic procedure and characterisation data

(details for ^{t}Ir–Ru^b are provided in the footnote to the printed paper)

^{t}Ru–Ir^b $[(tpy)Ru(tpy\text{-}\phi\text{-}\phi\text{-}bpy)Ir(ppy)_2][PF_6]_3$



A Schlenk tube was charged with $[Ru(tpy)(tpy\text{-}\phi\text{-}Br)][PF_6]_2$ (51 mg, 0.050 mmol), $[Ir(ppy)_2(bpy\text{-}\phi\text{-}B(OH)_2)][PF_6]$ (92 mg, 0.10 mmol), Na_2CO_3 (16 mg in 200 μL water, 0.15 mmol) and DMSO (10 mL). The solution was thoroughly degassed via three freeze-pump-thaw cycles before adding

$Pd(PPh_3)_4$ (4 mg, 0.003 mmol) under a positive pressure of nitrogen. The solution was stirred at 80 - 85°C for 18 h. After this time, the DMSO solution was diluted with acetonitrile (6 mL) and filtered into a saturated aqueous solution of KPF_6. The precipitate was collected using a centrifuge and transferred in acetonitrile (128 mg). Purification was achieved via column chromatography on silica gel, using a gradient elution from 100% CH_3CN to 88% CH_3CN / 11.8% H_2O / 0.2% $KNO_{3(aq)}$. After evaporation of solvent, the desired product was isolated as the PF_6 salt by precipitation from $KPF_{6\,(aq)}$; (42 mg, 0.02 mmol, 46%). ^{1}H NMR (500 MHz, CD_3CN): δ 9.06 (s, 2H, H^f and H^g), 8.85 (d, 1H, $J = 1.5$, $H^{g'}$), 8.79 – 8.74 (m, 3H, $H^{d'}$ and tpy-$H^{3'}$), 8.67 (d, 2H, $J = 8.1$, H^d), 8.50 (d, 2H, $J = 8.2$, tpy-H^3), 8.42 (t, 1H, $J = 8.2$, tpy-$H^{4'}$), 8.35 (d, 2H, $J = 8.5$, H^h), 8.19 (td, 1H, $J = 7.8, 1.5$, $H^{c'}$), 8.16 – 8.01 (m, 10H, ppy-H^3, $H^{a'}$, $H^{e'}$, $H^{h'}$, H^i and $H^{i'}$), 7.98 – 7.82 (m, 9H, H^c, $H^{f'}$, tpy-H^4, ppy-H^4 and ppy-$H^{3'}$ or ppy-H^6), 7.73 – 7.67 (m, 2H, ppy-$H^{3'}$ or ppy-H^6), 7.56 (t, 1H, $J = 6.5$, $H^{b'}$), 7.43 (d, 2H, $J = 5.6$, H^a or tpy-H^6), 7.36 (d, 2H, $J = 5.6$, H^a or tpy-H^6), 7.21 – 7.15 (m, 4H, H^b and tpy-H^5), 7.11 – 7.05 (m, 4H, ppy-$H^{4'}$ and ppy-H^5), 6.99 – 6.93 (m, 2H, ppy-$H^{5'}$), 6.34 and 6.32 (two overlapping d, 2H, ppy-$H^{6'}$). Elemental analysis for $[C_{74}H_{52}F_{18}IrN_{10}P_3Ru]3H_2O$: found C 47.2, H 2.8, N 7.2; calc. C 47.6, H 3.1, N 7.5 %. MS ES$^+$: m/z = 458.4 $[(M - 3PF_6)^{3+}/3]$, 760.1 $[(M - 2PF_6)^{2+}/2]$. HRMS ES$^+$: m/z = 458.43586 measured, 458.43443 calculated for $[C_{74}H_{52}N_{10}{}^{193}Ir^{102}Ru]^{3+}/3$, 760.13808 measured, 760.13401 calculated for $[C_{74}H_{52}N_{10}F_6{}^{193}IrP^{102}Ru]^{2+}/2$. TLC ($SiO_2$, 2% KNO_3 (aq), 18% H_2O, 80% CH_3CN): $R_f = 0.55$.

References

S1. W. Leslie, A.S. Batsanov, J.A.K. Howard and J.A.G. Williams, *Dalton Trans.*, 2004, 623.

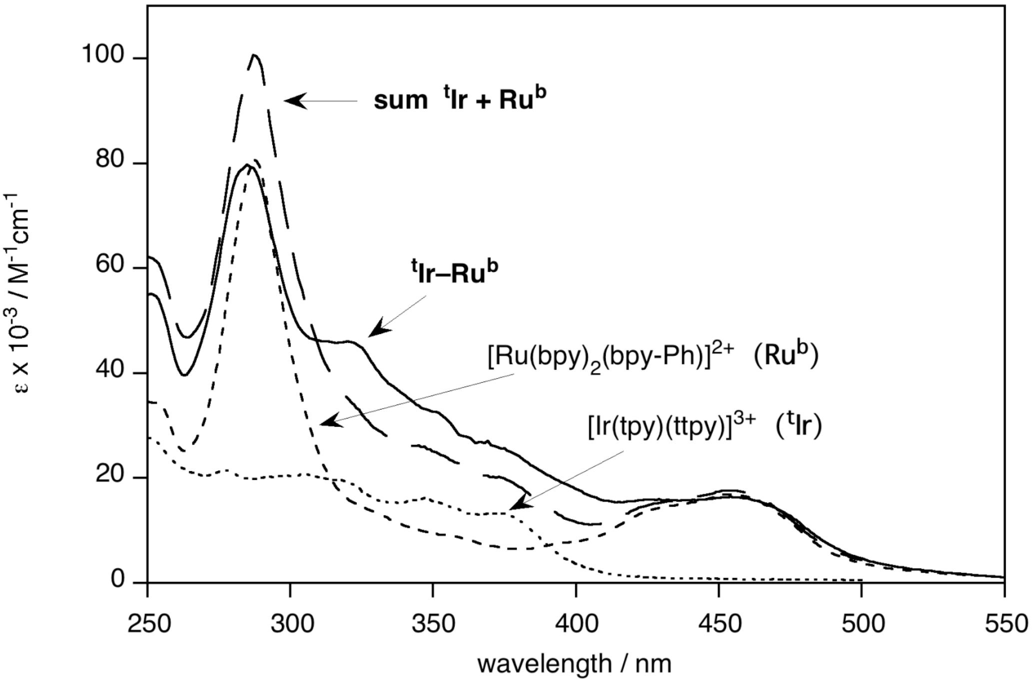
S2. C.J. Aspley and J.A.G. Williams, *New J. Chem.*, 2001, **25**, 1136.

S3. K.J. Arm and J.A.G. Williams, *Chem. Commun.*, 2005, 230.

Optical spectroscopy

Absorption spectra were recorded on a Biotek Instruments XS spectrometer, in 1 cm pathlength quartz cuvettes. Steady-state emission spectra were recorded using a Jobin-Yvon FluoroMax-2 instrument, equipped with a red-sensitive Hamamatsu R928 photomultiplier tube. Spectra were corrected for the wavelength dependence of the emission monochromator and detector using a correction curve generated from a standard lamp. The low temperature spectra were obtained using an Oxford Instruments variable temperature liquid nitrogen cryostat (DN1704), with Intelligent Temperature Controller. Lifetimes were obtained following excitation using the third harmonic of a Nd:YAG laser; the emission was detected with an R928 PMT and recorded using a digital storage oscilloscope. In all cases, samples were degassed by three freeze-pump thaw cycles to a base pressure of $< 10^{-2}$ mm Hg.

UV-visible absorption spectra of the dimer ^{t}*Ir–Ru*^{b}, together with the spectra of the individual building blocks and their summation (in CH_3CN at 295K)



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