Boronic acid-substituted metal complexes: versatile building blocks for the synthesis of multimetallic assemblies†

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Polypyridyl complexes of Ru(II) and Ir(III) incorporating a boronic acid substituent undergo cross-coupling with bromo-substituted complexes, and a sequential coupling–bromination–coupling strategy permits the controlled synthesis of a luminescent Y-shaped heterometallic assembly, in which efficient energy transfer to the terminus occurs.

The covalent linkage of metal complexes to generate multimetallic assemblies is an important theme within contemporary coordination chemistry. Such products may offer potential as photochemical molecular devices, (*e.g.* in solar energy conversion, electroluminescence and information storage), and in the fundamental study of photoinduced energy- and electron-transfer processes.[1] The preparation of heterometallic assemblies generally requires prior synthesis of multitopic ligands, followed by stepwise metal complexation. Although this strategy has led to a diverse range of complexes, it is limited by a need for ligands that can complex reliably in a stepwise manner and, frequently, by incomplete control over the structure and composition of the final assembly.[1] Moreover, the presence of such bridging ligands often leads to reduced performance of the constituent units, in terms of quantum efficiency and lifetime, compared to simpler mononuclear complexes {*e.g.* 2,3-bis(2-pyridyl)-pyrazine (dpp) *versus* bpy}.[2] Two elegant approaches that seek to circumvent these problems have appeared recently. Hanan *et al.* and Juris *et al.* introduce a new binding site onto the back of a suitably functionalised, pre-coordinated ligand, allowing subsequent coordination to a second metal ion,[3,4] whilst Tor *et al.* have demonstrated that pre-formed complexes of Ru(II) and Os(II), one incorporating a bromo substituent in one of its ligands and the other an ethynyl group, can undergo Pd-catalysed cross-coupling to give dimers or trimers linked (necessarily) by –C≡C– units.[5]

We have been investigating the synthesis and reactivity of boronic acid-substituted polypyridyl complexes, a hitherto scarcely explored class of compound.[6] In this contribution, we describe for the first time how such complexes can be used as building blocks in the controlled synthesis of heterometallic assemblies by means of Suzuki-type cross-couplings. Moreover, by exploiting the ease with which a bis-cyclometallated iridium complex can undergo electrophilic bromination, we show that cross-coupling reactions of a single complex with different partners can be carried out *sequentially*, allowing a Y-shaped tetrameric complex to be prepared containing three different types of metal environment.

The complexes and the overall synthetic strategy employed are shown in Scheme 1. The choice of component building blocks was determined by the desire to obtain a well-defined gradient of excited state energy levels, in such a way that excitation of any site within the assembly would be followed by a "funnelling" of the energy to the terminus of the structure, (the base of the Y-shape). The ^{3}MLCT excited state energies of [Ir(ppy)$_2$(phbpy)]$^+$, **Ir**, and [Ru(bpy)$_2$(phbpy)]$^{2+}$, **Ru**, lie at approximately 16 300 and 16 000 cm^{-1} respectively (phbpy = 4-phenylbipyridine), whilst we have also shown during this study that [Ir(F$_2$ppy)$_2$(phbpy)]$^+$, **Ir^{F4}**, {F$_2$ppyH = 2-(2,4-difluoro-phenyl)-pyridine}, emits at higher energy (18 500 cm^{-1}) (Fig. 1), such that the structure **(Ir^{F4})$_2$–Ir–Ru** was an attractive target.

The boronate-substituted ligand bpy-ϕ-Bneo {4-(4-neopentylglycolatoboronphenyl)-2,2′-bipyridine} was synthesised by Pd-catalysed cross-coupling of 4-(4-bromophenyl)-2,2′-bipyridine (bpy-ϕ-Br) with bis(neopentylglycolato)diboron. A heteroleptic trisbipyridyl ruthenium(II) complex incorporating one boronic acid-substituted bpy ligand was then prepared by treating [Ru(bpy)$_2$Cl$_2$] with AgBF$_4$ in acetone, to generate [Ru(bpy)$_2$(Me$_2$CO)$_2$]$^{2+}$, followed by reaction with bpy-ϕ-Bneo at room temperature. The boronate ester hydrolyses during work-up to give the desired boronic acid-substituted complex, [Ru(bpy)$_2${bpy-ϕ-B(OH)$_2$}](PF$_6$)$_2$, **Ru–B**. The bromo-substituted complex [Ir(ppy)$_2$(bpy-ϕ-Br)]PF$_6$, **Ir–Br**, was prepared by cleavage of the chloro-bridged dimer [Ir(ppy)$_2$μ-Cl]$_2$ with bpy-ϕ-Br, using well-established methodology.[7] The fluorinated complex [Ir(F$_2$ppy)$_2${bpy-ϕ-B(OH)$_2$}]PF$_6$, **Ir^{F4}–B**, was similarly accessible by reaction of [Ir(F$_2$ppy)$_2$μ–Cl]$_2$ with bpy-ϕ-Bneo.

Cross-coupling of **Ru–B** with **Ir–Br** proceeded readily in DMSO solution at 80 °C, using Pd(PPh$_3$)$_4$ as the catalyst (3–6 mol%), in the presence of Na$_2$CO$_3$ (3 equiv.). The dimetallic product **Ir–Ru** was isolated as its hexafluorophosphate salt, by precipitation from KPF$_6$(aq). The reaction proceeds remarkably cleanly; typically, the main side-product after washing the crude product with water is a small amount of the deboronated starting material, [Ru(bpy)$_2$(phbpy)]$^{2+}$, which is readily removed by chromatography on silica, along with any remaining traces of starting materials or phosphine. The structure of the dimer (isolated as a mixture of diastereoisomers), was confirmed by ^{1}H-^{1}H COSY and NOESY NMR spectroscopy and by high-resolution electrospray mass spectrometry.†

In order to allow subsequent elaboration of this dimetallic complex to give the Y-shaped tetramer by a second cross-coupling

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† Electronic supplementary information (ESI) available: details of synthetic procedures and characterisation data for key compounds; UV-vis data. See http://www.rsc.org/suppdata/cc/b4/b414929g/

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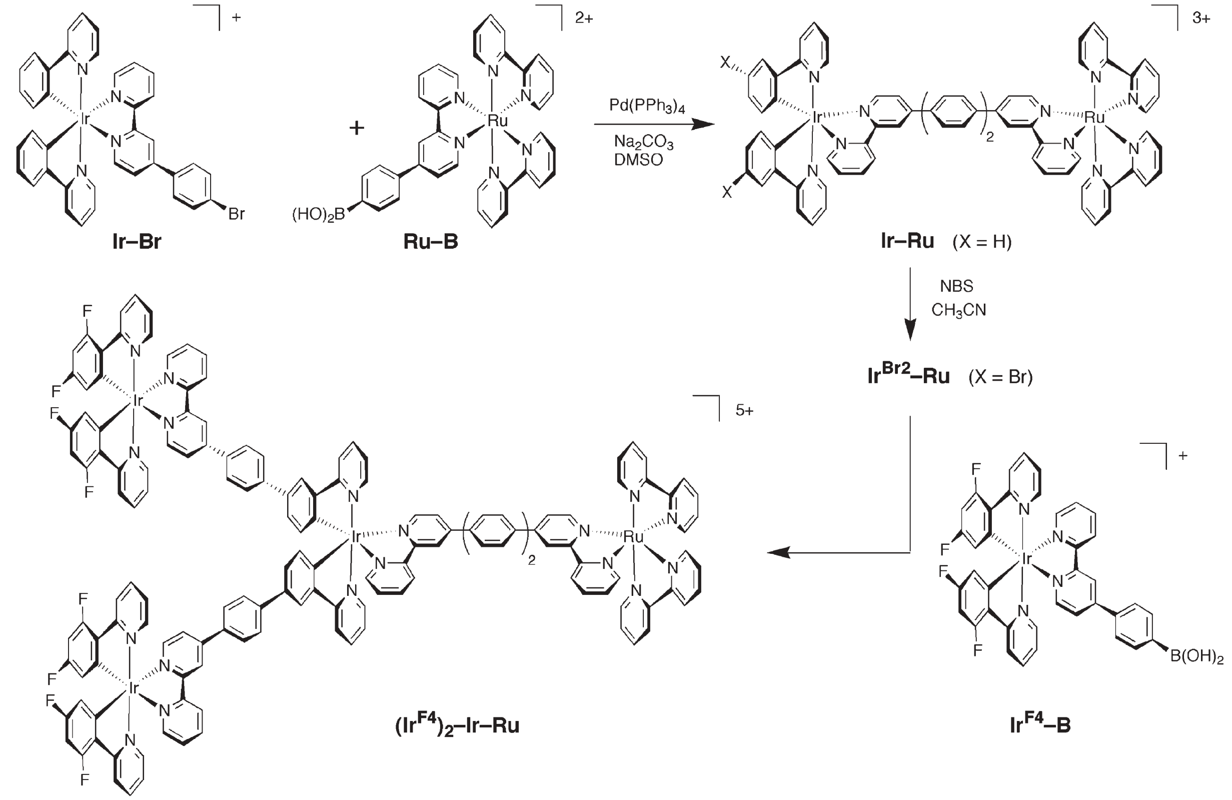

Scheme 1

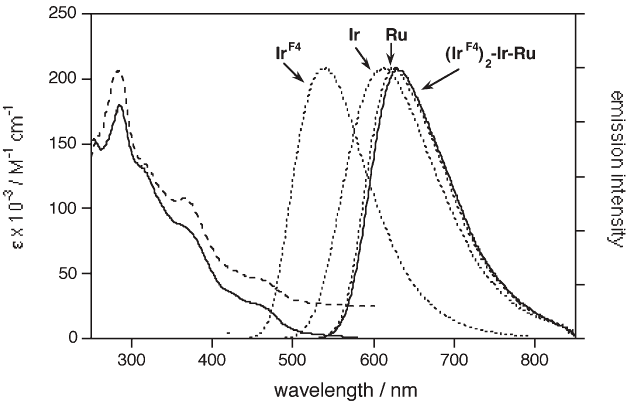

Fig. 1 Absorption (solid line, left), excitation spectrum (dashed line; λ_{em} = 629 nm) and corrected emission spectrum (solid line, right, λ_{ex} = 360 nm) of **(Ir^{F4})$_2$–Ir–Ru**, in CH_3CN at 295 K. The corrected emission spectra of the individual constituent building blocks are also shown.

reaction, halogen substituents must first be introduced. Coudret *et al.* have shown that cyclometallation of 2-phenylpyridine (ppy) to Ru(II), as in $[Ru(bpy)_2(ppy)]^+$, activates the 4′-position of the phenyl ring to electrophilic bromination by NBS under mild conditions, leading to the mono-bromo functionalised complex, upon which further chemistry can be carried out.[8] A similar activation was anticipated for the dimer **Ir–Ru**, which incorporates two such cyclometallated ppy units, albeit coordinated to Ir(III) rather than to Ru(II). Treatment of **Ir–Ru** with NBS (2.2 equiv.) in acetonitrile at room temperature for 18 h led specifically to the desired dibrominated complex **Ir^{Br2}–Ru** in quantitative yield. Analysis of the coupling patterns in the ^{1}H-^{1}H COSY spectrum confirmed the C4′ positions in the two ppy ligands as the exclusive sites of bromination.

The dimer, now primed for further reaction, was then cross-coupled with two equivalents of **Ir^{F4}–B**, under the same conditions as those used for the first cross-coupling reaction above. Again, the coupling partners reacted smoothly, to give the tetrameric product, **(Ir^{F4})$_2$–Ir–Ru** in 40% yield.†

The UV-visible absorption spectrum of the tetramer displays strong absorption bands up to 500 nm. Compared with the sum of the absorption spectra of the four individual components, the molar absorptivity in the 320–400 nm region is enhanced, attributable to the more extended conjugation in the product in comparison to the building blocks.† Upon excitation at any wavelength within the range 300–500 nm, a single emission band is observed in acetonitrile solution at room temperature, centred at 629 nm, very close to that displayed by **Ru** (626 nm; Fig. 1). No emission bands are observed at higher energy, in the region where the mononuclear units **Ir^{F4}** and **Ir** emit (Fig. 1). The excitation spectrum registered at the emission maximum matches the profile of the absorption spectrum, and the luminescence quantum yield of 0.12 (degassed CH_3CN, 295 K) is independent of excitation wavelength. The emission decay follows monoexponential kinetics; τ = 1.6 μs under the same conditions.

These observations provide conclusive evidence that excitation into either of the **Ir** components is followed by rapid energy transfer to the **Ru** centre, in line with the ordering of the energy levels of the three constituent units.[9] Thus, the tetramer behaves as a light-harvesting device in which the absorbed energy is channelled efficiently into a single component. A detailed study of the photophysical properties of the assemblies and individual building blocks is in progress.

In conclusion, this first report of the use of the Suzuki cross-coupling reaction to link different polypyridyl metal complexes under mild conditions demonstrates the power of new boronic acid-substituted complexes as versatile building blocks in the construction of large, multimetallic assemblies. No preformed bridging ligands are required, the linking units in the final products are simple aryl groups, and the excited state properties may be predicted on the basis of simple model building blocks.

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