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Supramolecular photochemistry

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Cyclometallated, bis-terdentate iridium complexes as linearly expandable cores for the construction of multimetallic assemblies[†]

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Cyclometallated iridium complexes comprised of two terdentate cyclometallating ligands, of the form $[Ir(N^C^N)(N^N^C)]^+$, have been explored for the preparation of multimetallic systems by palladium-catalysed cross-coupling reactions. An N^N^C-coordinating ligand carrying a boronate ester group has been prepared and complexed to iridium to give a boronic acid appended complex of this type, **3**. This complex has been subjected to cross-coupling with a bromo-substituted bis-terpyridyl iridium complex to give a dinuclear iridium compound **6**, in which one of the two iridium centres is N₆-coordinated and the other has an N₄C₂-coordination sphere. Meanwhile, a bromo-substituted complex **4** has been coupled with a boronic acid-appended ruthenium complex, to give a dinuclear heterometallic complex **8** that can be activated to a second coupling by *in situ* bromination, offering access to a linear Ir–Ir–Ru trimetallic assembly **11**. The electrochemical and luminescence properties of these systems are investigated. In the case of **8** and **11**, the behaviour can be rationalised in terms of a supramolecular description: efficient energy transfer occurs from the Ir terminus to the Ru. In contrast, for compound **6**, an excited state with significant bridge character appears to play a key role in determining the emission properties.

Introduction

Within the field of supramolecular photochemistry, a prevailing theme of research has been the question of how to construct molecular assemblies in a controlled and efficient manner from individual units, in such a way that the photophysical properties of the final assembly can be predicted reliably on the basis of the "building blocks" from which it is comprised. Indeed, one of the definitions of the term "supramolecular photochemistry", as proposed by Balzani, relates to photoactive multi-component systems held together by covalent bonds, where the components have distinct spectroscopic and photophysical identities.¹ Intercomponent processes, such as long-range directional energyand/or electron-transfer and charge separation, can then frequently be achieved through appropriate choice of units.²⁻⁴ Polypyridyl complexes of the transition metals Ru(II) and Ir(III) are widely regarded as attractive components in such assemblies, owing partly to their relatively long excited state lifetimes, which allow energy- or electron-transfer to compete with usual deactivation pathways, and to the relative ease with which their key photophysical properties-in particular, excited state energies-can be controlled through ligand modification.5,6 Interest in iridiumbased complexes, in particular, is blossoming at present owing to diverse applications.7 These include the use of mononuclear complexes as triplet-harvesting dopants in OLEDs,^{8,9} luminescent probes for biological systems,10 photovoltaics,11 and photocatalysts for water splitting.¹² Further potential may be opened up through incorporation into multimetallic systems.

Pioneering work in the 1990s made use of bridging aromatic ligands (*e.g.* hexaazaphenanthrene and triazoles) to construct heterometallic Ru/Ir assemblies, in which each metal was chelated in a tris-bidentate fashion.^{13–15} Assemblies displaying energy transfer from Ir to Ru or vice versa could be constructed, although the quantum efficiencies of systems based on pyrazine bridges, for example, are compromised by severe non-radiative decay.¹⁵ More recent studies have made use of bridging *para*-phenylene-bridged bis-bipyridines of the form $N^{\circ}N-(\phi)_{n}-N^{\circ}N$.¹⁶

The conventional approach to such (poly)aryl-bridged systems involves the prior synthesis of multitopic ligands, followed by stepwise metal complexation.¹⁷ Although this strategy has led to a diverse range of complexes, it is frequently limited by incomplete control over the structure and composition of the final assembly. A number of research teams have been developing a "building block" approach to the formation of multimetallic assemblies, involving chemistry on suitably functionalised complexes.¹⁸⁻²⁰ In our case, we have been exploring the utility of boronic acidappended complexes in Pd-catalysed cross-coupling reactions with halo-substituted complexes as a reliable route to heterometallic assemblies, and have constructed systems containing three or more different types of tris-bidentate metal centres in this way.^{21,22}

Tris-bidentate complexes are intrinsically chiral (D_3 or C_2 symmetry with Λ and Δ enantiomers), which leads to mixtures of diastereomeric products when incorporated into multimetallic assemblies. The diastereomers may have different photophysical properties, for example arising from different distances between units. The *cis*-disposition of the cyclometallated carbon atoms in $[Ir(ppy)_2(bpy)]^+$ complexes²³ alleviates the problem to the extent that linear assembly is assisted, for instance by substitution at the pyridyl 4-position of the ppy ligands, but does not remove the chirality. An attractive alternative is the use of achiral D_{2d}

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bis-terdentate components, which are particularly appealing for the construction of linear assemblies when elaborated at the central position (*e.g.* the 4' of terpyridines).^{24–26} However, rather fewer such complexes have been established to date, and they sometimes have vastly inferior properties; *e.g.* the well known case of [Ru(tpy)₂]²⁺, which suffers from very rapid non-radiative decay at room temperature ($\tau_{em} \sim 1$ ns), in contrast to the desirable properties of [Ru(bpy)₃]²⁺ ($\tau_{em} \sim 1$ µs).²⁷

Our group has been investigating the chemistry and excited state properties of iridium(III) complexes with terdentate ligands.²⁶ Very recently, we described the preparation of iridium(III) complexes comprising N^C^N and N^N^C-coordinating ligands, e.g. 1 (Fig. 1), which are bis-terdentate analogues of the well-known class of complexes of the type $[Ir(N^{A}C)_{2}(N^{A}N)]^{+}$.²⁸ The latter of which $[Ir(ppy)_2(bpy)]^+$ 2 (Fig. 1) is the archetypal example have attractive photophysical properties similar to those of $[Ru(bpy)_3]^{2+}$.^{6,29,30} We found that, in contrast to $[Ru(tpy)_2]^{2+}$, these desirable properties are retained—indeed sometimes augmented in the bis-terdentate systems (e.g. for 1, $\lambda_{max} = 632$ nm, $\Phi_{lum} =$ 0.023, $\tau_{lum} = 120$ ns in MeCN at 298 K). We also demonstrated that complexes of this type are amenable to extension with organic groups, in a stepwise manner, by a sequence of successive crosscoupling-bromination-cross-coupling reactions. In this contribution, we explore the potential of such complexes as building blocks in the construction of multimetallic assemblies using this methodology.

Results and discussion

Synthesis

1. Boronate-ester substituted complex. In the first instance, we sought to prepare an $[Ir(N^{C}N)(N^{N}C)]^+$ complex incorporating boronic acid functionality. The boronic acid group is widely used in palladium-catalysed cross-couplings, as originally pioneered by Suzuki and now a central tool in synthetic organic chemistry for aryl–aryl bond formation.³¹ The classical route to aryl boronic acids involves conversion of haloaromatics to aryl lithium derivatives, and treatment with trialkylborates. In previous work on terpyridines and bipyridines, we found that this method gave very poor results, whereas palladium-catalysed cross-coupling with bis-boron esters such as bis(pinacolato)diboron gave far superior yields of the boronate ester.^{32,33} In the case of the bis-

neopentylglycolate ester, the boronate product can be hydrolysed readily to the corresponding boronic acid.

In the present work, we found that the N^N^C-coordinating proligand 4-(p-bromophenyl)-6-(m-tolyl)bipyridine (mtbpyH-Br) could be readily converted to the boronate ester derivative mtbpyH- ϕ -B upon palladium-catalysed reaction with bisneopentylglycolato diboron (B2neo2) in the presence of potassium acetate. This ligand was then used to prepare an $[Ir(N^{A}C^{N})(N^{A}N^{C})]^{+}$ complex, by reaction with the chloro bridged dimer $[Ir(dpyx)Cl(\mu-Cl)]_2$ (Scheme 1), which is in turn generated by the cyclometallation of iridium to the dipyridylxylene ligand, dpyxH.34,35 In our previous work, the introduction of the N^N^C-coordinating ligand was achieved by reaction at high temperature (refluxing ethylene glycol at 198 °C) for a short period of time (30-60 min).28 However, the relatively weak and labile nature of the C-B bond renders aryl boronates susceptible to thermally activated hydrodeboronation, and the new ligand did not tolerate complexation at such high temperatures. We found that complexation could be achieved successfully, without significant competing deboronation, by using a lower temperature of 140 °C in conjunction with a longer reaction time of 3 h. In a similar way, Collin et al. were able to achieve the selective complexation of a terpyridine to $Ir(tButpy)Cl_3$, in the presence of a phenanthroline pendant, by reducing the temperature to 140 °C.36 The resulting orange bis-terdentate complex [Ir(dpyx)(mtbpyH- ϕ -B)]Cl 3 was converted to the hexafluorophosphate salt and purified by column chromatography on silica, using CH₂Cl₂/MeOH as the eluant. ¹H NMR spectroscopy and mass spectrometry revealed that the expected hydrolysis of the boronate ester occurred during chromatography, and that the main component isolated, in high yield, was the monomethyl ester, as shown in Scheme 1.

The alternative and potentially attractive method of preparing such a boronate ester-substituted complex *in situ*, *i.e.* by carrying out a palladium-catalysed cross-coupling reaction on a bromo substituted *complex*, was also investigated. The complex $[Ir(dpyx)(mtbpyH-\phi-Br)]^+ 4$ was treated with an excess of B₂neo₂ in the presence of Pd(dppf)Cl₂ in DMSO solution, a medium that offers solubilisation of both the complex and reactants. However, none of the desired boronated complex was isolated, the main product being identified as the hydro-debrominated complex by ¹H-NMR spectroscopy and mass spectrometry. Similarly, attempts to boronate the N^C^N-coordinating ligand of [Ir(dpyx-Br)(mtbpy- ϕ -ph)]⁺ at the C⁴-position gave a mixture of unreacted



Fig. 1 The parent structures of complexes of the type $[Ir(N^{C^N})(N^{N^*C})]^+$ and $[Ir(N^{C})_2(N^{N})]^+$: $Ir(dpyx)(phbpy)]^+$ 1 and $[Ir(ppy)_2(bpy)]^+$ 2, and the structure of the biphenyl-appended complex 12 used as a model in interpreting the emission properties of the multimetallic compounds.



[lr(dpyx)₂Cl(µ-Cl)]₂

and hydrodebrominated complexes. We note that although such a strategy in previous work on ruthenium(II) terpyridines did allow conversion of $[Ru(tpy)(tpy-Br)]^{2+}$ to $[Ru(tpy)\{tpy-B(OH)_2\}]^{2+}$, the yield was greatly inferior to that obtained by direct complexation of the terpyridine boronate to ruthenium.³² Apparently, therefore, hydrodehalogenation is promoted when the ligand is coordinated to the metal ion.

2. Cross-coupling using the boronate-substituted complex. To test the utility of the new boronate-substituted complex in the preparation of a multimetallic derivative by cross-coupling, we selected the reaction shown in Scheme 2, in which a coupling was carried out with a bromo-substituted bis-terpyridyl complex. This was chosen because the product would represent a structure that would be especially difficult to prepare through conventional methods involving the pre-synthesised bridging ligand. Thus, although the bridging ligand itself would be accessible, the *selective* complexation of the terpyridine terminus to the N^N^N-bound iridium, and likewise the 6-tolylbipyridine unit to the N^C^N-bound iridium, would be difficult—and probably impossible—to achieve, and the synthesis would have to resort to purification of a statistical mixture of products.

The complex $[Ir(tpy)(tpy-\phi-Br)]^{3+}$ **5** was prepared by reaction of $Ir(tpy)Cl_3$ with *p*-(bromophenyl)terpyridine.³⁷ The Suzuki crosscoupling with **3** was carried out using the standard catalyst $Pd(PPh_3)_4$ in the presence of sodium carbonate as the base. The use of DMSO as the solvent—rarely used for cross-couplings of organic compounds—was previously shown to facilitate the dissolution of the charged reagents allowing reaction to proceed readily.³⁷ In the present instance, cross-coupling proceeded to generate the target complex $[Ir(tpy)(\mu-tpy-\phi-\phi-mtbpy)]Ir(dpyx)]^{4+}$, 6, which was isolated as an orange solid following anion exchange with KPF_{6(aq)}. Purification by column chromatography was necessary to remove less polar species such as traces of the hydrodebrominated and hydrodeboronated complexes. The identity of 6 was confirmed by mass spectrometry and by a combination of ¹H–¹H COSY and NOESY spectroscopy in conjunction with the spectra of the corresponding monometallic species.

3. Stepwise linear elaboration of bis-terdentate Ir complex as a route to linear multimetallic assemblies. The concept of stepwise cross-couplings of haloaromatics in a controlled fashion relies either on (i) different reactivities of halogen substituents in an aromatic ring (e.g. 2,5-dibromopyridine can be cross-coupled first at the 2 position and then at the 5 position owing to their relative reactivities), or (ii) on being able to introduce a halogen atom under mild conditions following the first cross-coupling. In a purely organic system, the second option is unusual, because of the forcing conditions typically needed for halogenation of aromatics. We previously demonstrated that bis-cyclometallated, tris-bidentate complexes of the type $[Ir(ppy)_2(bpy)]^+$ 2 are susceptible to facile electrophilic bromination of the cyclometallating phenyl rings, which occurs selectively at the positions para to the metal ion.²¹ This remarkable reactivity, similar to that observed by Coudret et al. for [Ru(bpy)₂(ppy)]⁺,³⁸ can be attributed to the increase in the electron density in the phenyl rings that accompanies cyclometallation.

In a similar manner, we found that treatment of 1 with NBS in MeCN at RT leads to bromination of the N^{\wedge}C^{\wedge}N ligand at



Scheme 2 Cross-coupling of a bis-terpyridyl iridium(III) complex 5 with the boronic-acid substituted complex 3 to generate the homodinuclear system $[Ir(tpy)(\mu-tpy-\phi-\phi-mtbpy)Ir(dpyx)]^{4+} 6$.

the 4'-position *trans* to the metal but—not surprisingly—also at the equivalent position of the phenyl ring of the N^N^C ring.²⁸ The modified complex [Ir(dpyx)(mtbpy- ϕ -Br)]⁺ **4** (Scheme 3) was selected for study, as it carries a methyl group at the latter position, restricting the site of potential bromination to the N^C^N ligand. It also carries a bromo substituent in the N^N^C ligand from the outset, and is therefore an ideal candidate for a sequence of cross-coupling–bromination–cross-coupling (Scheme 3).

Complex 4 was first subjected to cross-coupling with a tris-bipyridyl ruthenium(II) complex appended with a boronic acid group, $[Ru(bpy)_2(bpy-\phi-B)]^{2+}$ 7, using the standard conditions {Pd(PPh₃)₄ catalyst, Na₂CO₃(aq) as base, DMSO solvent at 80 °C}. The heterometallic dimer $[Ir(dpyx)(\mu-mtbpy (\phi-\phi-bpy)Ru(bpy)_2^{3+}$ 8 was isolated as an orange-red solid in 43% yield after ion exchange with $\text{KPF}_{6(aq)}$ and purification by column chromatography. The ¹H NMR spectrum, assigned on the basis of ¹H-¹H COSY and NOESY spectra and reference to corresponding mononuclear complexes, is shown in Fig. S1 (see ESI[†]). Bromination of the dimer, specifically at the 4'-position of the N^AC^AN ligand, was then accomplished by treatment with NBS in MeCN at room temperature, followed by ion exchange and washing of the product hexafluorophosphate salt with water to remove N-hydrosuccinimide. The brominated complex 9 was obtained in essentially quantitative yield. Now primed for a second cross-coupling reaction, 9 was reacted with the boronic acid

appended iridium complex $[Ir(F_2ppy)_2(bpy-\phi-B)]^{2+}$ **10**, leading to the heterotrimetallic complex $[Ir(F_2ppy)_2(\mu-bpy-\phi-dpyx)Ir(\mu$ $mtbpy-\phi-\phi-bpy)Ru(bpy)_2]^{4+}$ **11**, isolated as an orange–red solid in 62% yield after anion exchange with KPF_{6(aq)} and chromatographic purification. The choice of constituent building blocks is discussed in Section 5.

Naturally, the incorporation of the third metal complex and the presence of 80 aromatic protons (70 inequivalent environments) leads to a rather complicated ¹H NMR spectrum. However, notwithstanding some overlapping signals, most peaks could be assigned unambiguously with the aid of ¹H-¹H COSY and NOESY spectra, ¹⁹F NMR, and the spectra of the constituent building blocks (see Experimental section). Perhaps more definitive proof of identity for such large assemblies is offered by electrospray mass spectrometry, faciliated by the high net charge leading to m/z peaks (z = 1-4) and adducts with $n \operatorname{PF}_6^-$ ions (n = 0-4). High resolution electrospray mass spectrometry showed excellent correlation between the measured and theoretical masses $\Delta m < 1$ ppm for z = 1). On the other hand, the large size of such species means that several molecular formulae containing only the atoms in the desired complex often closely match the measured mass. Isotope peak matching provides additional and arguably more conclusive and reliable support of structure. The isotope peak matching for the trimetallic complex **11** is shown in Fig. S2 (see ESI[†]), showing the excellent match between experimental and simulated spectra.



[lr(F2ppy)2(µ-bpy-q-dpyx)lr(µ-mtbpy-q-q-bpy)Ru(bpy)2]⁴⁺

Scheme 3 The cross-coupling–bromination–cross-coupling sequence used in the preparation of the trinuclear assembly $[Ir(F_2ppy)_2(\mu-bpy-\phi-dpyx)]r(\mu-mtbpy-\phi-\phi-bpy)Ru(bpy)_2]^{3+}$ **11** *via* the heterodinuclear complex $[Ir(dpyx)(\mu-mtbpy-\phi-\phi-bpy)Ru(bpy)_2]^{3+}$ **8**.

4. Electrochemistry. Electrochemical studies of the multimetallic systems were carried out in acetonitrile solution at 298 \pm 3 K using Bu_4NBF_4 (0.1 M) as the supporting electrolyte. Results are compiled in Table 1, together with those of pertinent mononuclear complexes that can be regarded as the constituent units of the assemblies. The dinuclear iridium compound $[Ir(tpy)(\mu$ tpy- ϕ - ϕ -mtbpy)Ir(dpyx)]⁴⁺ 6, which comprises a bis-terpyridyl iridium centre and a doubly cyclometallated iridium ion, displays reversible oxidation waves at 1.08 and 1.67 V. The first of these is only a little higher than that displayed by the cyclometallated monometallic complex 12 (the structure of 12 is shown in Fig. 1)²⁸ suggesting that the first oxidation process occurs at this unit. The second wave could be associated with a second oxidation at this site or perhaps with the bridge. It seems unlikely to involve the Ir(tpy)₂ unit, given that the corresponding tricationic mononuclear complexes do not normally display oxidation within accessible windows.³⁹ The first and second reduction processes observed are probably associated with one of the terpyridyl units of the $Ir(tpy)_2$ centre and with the bpy unit of the N^N^C ligand respectively, by comparison with data for the respective mononuclear complexes in Table 1. That the values in the multimetallic complexes differ quite significantly from the respective building blocks does imply that there is significant interaction between the metal centres by communication through the biphenylene bridge.

The heterometallic dimer $[Ir(dpyx)(\mu-mtbpy-\phi-\phi-bpy)Ru-(bpy)_2]^{3+}$ 8 displays reversible oxidation waves at 0.81 and 0.98 V. One might tentatively attribute these to oxidation processes at the Ir and Ru centres respectively, based on the data for the monometallic species, although both oxidations are more facile than anticipated on this basis, presumably reflecting the additional stabilisation of the resultant higher positive charge through delocalisation. In contrast, the reduction waves observed, which could reasonably correspond to the phenylene-substituted bipyridine units and terminal bipyridines respectively, are cathodically shifted relative to the building blocks. The trimetallic assembly **11** similarly displays two oxidation and two reduction waves within the region studied (-2.5 to + 2.0 V). Given that the monometallic complex $[Ir(F_2ppy)_2(bpy)]^+$ is oxidised at considerably higher potentials than either **12** or $[Ru(bpy)_3]^{2+}$, it seems likely that the oxidations are again associated with the bis-terdentate iridium and ruthenium centres respectively. This interpretation is supported by the report of De Cola and co-workers that a series of dinuclear species of the type $[Ir(F_2ppy)_2Ir(\mu-bpy-\phi_n-bpy)Ru(bpy)_2]^{3+}$ exhibit only a ruthenium-based oxidation within this range.³ On the other hand, the presence of five different N^N-bipyridyl-based sites within molecule **11** renders it difficult to make reliable assignments about the site of reduction.

5. Electronic absorption and emission spectroscopy.

(i) Heterodinuclear complex $[Ir(dpyx)(\mu-mtbpy-\phi-\phi$ bpy $Ru(bpy)_2 l^{3+}$ 8. The absorption spectrum of 8 in acetonitrile solution at room temperature displays peaks characteristic of the monometallic complexes of which it can be considered to be comprised, namely $[Ir(dpyx)(mtbpy-\phi-Ph)]^+$ 12 and [Ru(bpy)₂(bpy-Ph)]²⁺ (see Fig. S3 in ESI[†] and Table 1). Although the overall profile is quite similar to the simulated spectrum based on summation of these two components, it can be seen that there is enhanced absorption in the region between 325-400 nm, probably attributable to the bridging polyphenylene unit. Similar observations have previously been reported for $[Ir(tpy)(\mu-tpy-\phi-\phi-bpy)Ru(bpy)_2]^{5+}$ from our laboratory²² and for the $[Ir(F_2ppy)_2(\mu-bpy-\phi_n-bpy)Ru(bpy)_2]^{3+}$ complexes of De Cola and co-workers,3 where absorption spectra were similar to those of the sum of the monometallic components, in line with the supramolecular description in terms of properties of constituent units being retained.

Table 1 Ground state UV-visible absorption and electrochemical data for the multimetallic assemblies and for pertinent monometallic model complexesin MeCN at 298 \pm 3 K^a

Compound	$E_{1/2}^{\text{ox}}$ / V ^c (ΔE / mV)	$E_{1/2}^{\rm red}$ / V ^c (ΔE / mV)	Absorbance ^{<i>b</i>} λ_{max} / nm (ϵ /M ⁻¹ cm ⁻¹)
$\overline{[\mathrm{Ir}(\mathrm{tpy})(\mu-\mathrm{tpy}-\phi-\phi-\mathrm{mtbpy})\mathrm{Ir}(\mathrm{dpyx})]^{4+}}6$	1.08 (120)	-1.21 (150)	382 (62000), 354 (56000), 308 (96800), 280 (109000), 250 (116000)
$[Ir(tpy)(ttpy)]^{3+d}$	1.67 (100) —	-2.01 (110) -0.81, -0.97	372 (13200), 354 (18000), 340 (23300), 322 (29500), 310 (31900), 279 (43200),
$[Ir(dpyx)(mtbpy-\phi-Ph)]^+$ 12	0.96 (90)	-1.54 (80)	251 (52000) 479 (1940), 412sh (13200), 375 (23200), 293 (60900)
$[Ir(dpyx)(\mu\text{-mtbpy-}\phi\text{-}\phi\text{-}bpy)Ru(bpy)_2]^{3+} 8$	0.81 (140)	-2.25 (90) -1.67 (170)	451 (27600), 426 (30600), 373 (47600), 327 (71800), 288 (96400)
[Ru(bpy) ₂ (bpy-Ph)] ²⁺ e	0.98 (160) 1.31 ^f	-2.42 (70) -1.34 ^r	454 (16900), 430 (14000), 399 (7030), 288 (84100), 253 (35000)
$[Ir(F_2ppy)_2(\mu\text{-bpy-}\phi\text{-dpyx})Ir(\mu\text{-mtbpy-}\phi\text{-}\phi\text{-bpy})Ru(bpy)_2]^{4+} 11$	1.16 (140)	-1.54 (60)	453 (27000), 426 (29900), 379 (50100), 288 (147000)
[Ir(F ₂ ppy) ₂ (bpy-Ph)] ^{+ g}	1.31 (120) 1.65 ^h	-2.07 (120) -1.29 ^h	446 (600), 417 (1300), 359 (7860), 333 (12100), 313 (23500), 300 (28100), 262 (49100)
		-1.97^{h}	(1)100)

^{*a*} Complexes as their hexafluorophosphate salts at 10⁻³ M, using B₄NBF₄ (0.1 M) as the supporting inert electrolyte. ^{*b*} For bands > 250 nm. ^{*c*} ΔE^{ox} and ΔE^{red} are the peak-to-peak separation of the reversible oxidation and reduction processes respectively. ^{*d*} Data from ref. 39. ^{*e*} Data from ref. 22. ^{*f*} For [Ru(bpy)₃]²⁺. ^{*s*} Data from ref. 21. ^{*b*} For [Ir(F₂ppy)₂(bpy)]⁺, ref. 3.

 Table 2
 Luminescence data for the multimetallic systems 6, 8 and 11 together with data for relevant monometallic complexes for comparison. Data refers to the complexes as their hexafluorophosphate salts in dilute solutions in MeCN at 298 ± 3 K, except where stated otherwise

Complex	$\lambda_{\rm max}/{\rm nm}$	$\Phi_{\rm lum}{}^a imes 10^2$	τ/ns^{b}	$k_{\rm r}{}^c/10^4~{ m s}^{-1}$	$\sum k_{\rm nr}{}^{c}/10^{5}~{ m s}^{-1}$	$k_{\rm Q}^{\rm O2} d/10^9 {\rm s}^{-1}$	$\lambda_{\rm max}/{\rm nm}^e$ 77 K	τ/μs ^e 77 K
$\overline{[\mathrm{Ir}(\mathrm{tpy})(\mu-\mathrm{tpy}-\phi-\phi-\mathrm{mtbpy})\mathrm{Ir}(\mathrm{dpyx})]^{4+}}6$	607	0.3	3200 (700)	0.08	3.1	0.58	570, 597	3.4, 160
$[Ir(tpy)(ttpy)]^{3+f}$	506	2.6	5800 (2300)	1.1	4.2	0.14	490	37
$[Ir(dpyx)(mtbpy-\phi-Ph)]^+$ 12 g	636	6.3	150 (57)	42	63	5.7	553, 590	4.0
$[Ir(dpyx)(\mu-mtbpy-\phi-\phi-bpy)Ru(bpy)_2]^{3+} 8$	630	12	1200	10	7.3	1.6	604, 644	4.9
[Ru(bpy)(bpy-Ph)] ^{2+ h}	627	9.0	1300	6.9	7.0	2.2	_	—
$[Ir(F_2ppy)_2(\mu-bpy-\phi-dpyx)-Ir(\mu-mtbpy-\phi-\phi-bpy)Ru(bpy)_2]^{4+}$ 11	632	7.7	(200) (1200) (220)	6.4	7.7	2.0	614, 664	5.1
$[Ir(F_2ppy)_2(bpy-Ph)]^{+h}$	539	66	1400 (140)	47	2.4	3.4	_	_

^{*a*} Luminescence quantum yield measured using [Ru(bpy)₃]Cl₂ in H₂O as the standard. ^{*b*} $\lambda_{ex} = 374$ nm. ^{*c*} Radiative and non-radiative decay rate constants estimated from τ and Φ_{tum} values at 298 K. ^{*d*} Bimolecular rate constant for quenching by O₂, estimated from τ in degassed and aerated solutions, and assuming [O₂] = 1.9 mmol dm⁻³ at 1 atm air. ^{*c*} In an ether/isopentane/ethanol (2:2:1 v/v) glass. ^{*f*} Data from ref. 39. ^{*s*} Data from ref. 28. ^{*h*} Data from ref. 22.

Upon excitation of 8 in degassed acetonitrile, a single structureless emission band centred at 630 nm was observed, irrespective of the excitation wavelength (Fig. 2, Table 2). The excitation spectrum registered at 630 nm matches closely the absorption spectrum, and the luminescence decay follows mono-exponetial kinetics, with a lifetime of 1.2 µs. These observations indicate that the emission arises from a single excited state. The excited state energies of the two constituent monometallic units would be essentially identical (~15800 cm⁻¹) based on the emission data for the individual complexes [Ir(dpyx)(mtbpy- ϕ -Ph)]⁺ 12 and [Ru(bpy)₂(bpy- ϕ -Ph)]²⁺. However, the observed luminescence lifetime of 1.2 μ s for **8** is much longer than that of the former under the same conditions ($\tau = 190$ ns), whereas it is very similar to that of the Ru complex ($\tau = 1.3 \,\mu s$). Thus, we conclude that the emitting state is probably localised on the ruthenium moiety, and that energy absorbed by the iridium unit is rapidly transferred to this end of the molecule. Further support for this assignment comes from the emission spectrum at 77 K, $\lambda_{max} = 604$ and 644 nm (Fig. 2), which contrasts with the substantially higher energy



Fig. 2 Absorption, excitation ($\lambda_{em} = 630$ nm) and emission ($\lambda_{ex} = 410$ nm) spectra of [Ir(dpyx)(μ -mtbpy- ϕ - ϕ -bpy)Ru(bpy):]³⁺ 8 in MeCN at 298 K. The emission spectrum in an EPA glass at 77 K is also shown.

spectrum displayed by **12** at this temperature, indicating that the energy transfer to the ruthenium terminus must be fast also under these conditions.

(ii) Trinuclear complex $[Ir(F_2ppy)_2(\mu-bpy-\phi-dpyx)Ir(\mu-mtbpy-\phi-\phi-bpy)Ru(bpy)_2]^{3+}$ 11. The absorption, excitation and emission spectra of the heterotrinuclear assembly 11 are shown in Fig. 3. The choice of the $[Ir(F_2ppy)_2(bpy-Ph)]^+$ unit to append onto the dimetallic complex 8 was based on the known higher excited state energy of this unit, a green emitter (~18900 cm⁻¹). The absorption spectrum of 11 is similar to that of the sum of the constituent "building blocks" 8 and $[Ir(F_2ppy)_2(bpy-Ph)]^+$, indicating that the polyphenylene bridge formed between the two iridium centres does not significantly influence the ground state absorption. The steric influence of the flanking methyl groups of the dpyx unit probably inhibits ground state delocalisation across the bridge.



Fig. 3 Absorption, excitation ($\lambda_{em} = 630 \text{ nm}$) and emission ($\lambda_{ex} = 410 \text{ nm}$) spectra of $[Ir(F_2ppy)_2-(\mu-bpy-\phi-dpyx)Ir(\mu-mtbpy-\phi-\phi-bpy)Ru(bpy)_2]^{3+}$ **11** in MeCN at 298 K. The emission spectrum of $[Ir(F_2ppy)(bpy-Ph)]^+$ under the same conditions is also shown.

Excitation of **11** in MeCN at 298 K results in a single structureless emission band centred at 632 nm, irrespective of

the excitation wavelength in the range 275-500 nm. The emission energy, lifetime of 1.2 µs and quantum yield of 0.077 are all similar to those of [Ru(bpy)₂(bpy-Ph)]⁺. Moreover, there is no evidence of any detectable emission in the region around 530 nm, where $[Ir(F_2ppy)_2(bpy-Ph)]^+$ emits (Fig. 3), and the excitation spectrum registered at 632 nm corresponds closely to the absorption profile. Thus we conclude that there is essentially quantitative energy transfer to the ruthenium terminus of the assembly, which then emits. The approach of forming a trinuclear assembly from constituent units of appropriate excited state energies thus allows access to a linear "funnel" of energy to a single terminus of the molecule. Although the emission in terms of the quantum yield is not significantly improved compared to that of the tris-bipyridyl runthenium(II) model complex, being limited by the same decay processes, the quantity $\varepsilon \times \Phi_{lum}$, which takes into account both the absorbance and emission, is improved.

complex (iii) Binuclear $[Ir(tpy)(\mu-tpy-\phi-\phi-mtbpy)]$ Ir- $(dpvx)]^{4+}$ 6. Although the absorption spectrum of the homodinuclear complex 6 shows some resemblance to the sum of the spectra of its constituent monometallic units, the absorption is enhanced throughout (see Fig. S4, ESI[†]). This suggests a significant influence of the formation of the bridge. Excitation of this complex in MeCN at room temperature leads to weak emission centred at 607 nm, but with evidence of some structured bands superimposed on the higher-energy side of the main band (Fig. 4). In this system, the building blocks [Ir(tpy)(ttpy)]³⁺ and [Ir(dpyx)(mtbpy- ϕ -Ph)]⁺ 12 have very different excited state energies, and the former displays a structured spectrum in contrast to the structureless nature of the latter. The lack of resemblance of the predominant emission band of 6 to either of the constituent units suggests that the bridging polyphenylene may be playing a significant role. The luminescence decay kinetics at the emission maximum gave a lifetime of 3.2 µs, much longer than that of 12 (150 ns). The quantum yield of emission ($\Phi_{lum} = 2.5 \times 10^{-3}$) is much less than that of either the terpyridyl or cyclometallated mononuclear complexes under the same conditions, apparently due to a particularly small radiative decay constant (Table 2). Such a small value would be consistent

> 6 $\tau = 3.2 \, \mu s$ 160 molar absorptivity / 10³ M⁻¹ dm³ cm⁻¹ 100 [lr(tpy)(ttpy)] 120 80 emission intensity (a.u.) 12 absorption 60 80 40 40 20 0 0 200 300 500 600 700 800 400 wavelength / nm

Fig. 4 Absorption and emission spectra of $[Ir(tpy)(tpy-\phi-\phi-mtbpy)Ir-(dpyx)]^{4+}$ **6** in degassed MeCN at 298 K, together with the spectra of $[Ir(tpy)(ttpy)]^{3+}$ and **12** under the same conditions. The dashed line is the emission spectrum in air-equilibrated solution.

with an excited state associated with the bridge, having lower metal character to promote triplet decay. The structure on the high-energy side of the emission band could then tentatively be attributed to some emission from the $[Ir(tpy)(tpy-\phi)]$ unit, indicative of incomplete energy transfer to the lower state. We were not able to obtain any convincing indication of a second, longer decay component when monitoring the emission at the shorter wavelengths associated with the structured bands, and the data quality was hampered by the weakness of the emission. However, we note that upon aeration of the solution, these higher-energy bands become less apparent (Fig. 4), suggesting that they are quenched more efficiently by O_2 and hence may be characterised by a longer lifetime. The more effective oxygen quenching of the higher-energy emission bands is similar to that of other iridium complexes recently reported to display dual emission.40 Unfortunately, the low emission intensity ($\Phi_{lum} = 3 \times 10^{-3}$ in MeCN) hampered efforts to obtain good quality time-resolved spectra, but the high-energy bands are undoubtedly resolved more clearly at longer time intervals after excitation (Fig. S5, ESI[†]).

Changing from acetonitrile to water as the solvent for 6 was found to have a dramatic influence on the emission (Fig. 5). In pure water, the emission is an order of magnitude brighter $(\Phi_{\text{lum}} = 1.4 \times 10^{-2})$ and a single structureless emission band is observed. Strikingly, the luminescence lifetime is now much longer, $\tau = 75 \,\mu s$. A similarly augmented lifetime on going from MeCN to aqueous solution was previously observed for bis-terpyridyl complexes appended with biphenyl tails, which we attributed to modulation of the relative energies of the excited states such that a π - π * state largely localised on the biphenyl tail becomes the lowestenergy excited state.^{37,41} In the present instance, the corresponding implication is that in H₂O, the emission emanates from an excited state associated largely with the bridge, with relatively little metal character to promote radiative decay. The lack of vibrational structure is not inconsistent with a ligand-centred assignment, since the presence of a thermal distribution of conformers having different torsion angles between the aryl rings will naturally lead to a blurring-out of the spectrum, for example, as seen in the effect of 4-aryl substituents on the emission of $[Ir(tpy)_2]^{3+1}$ complexes.39,26,7



Fig. 5 Absorption and emission spectra of $[Ir(tpy)(tpy-\phi-\phi-mtbpy)Ir(dpyx)]^{4+}$ 6 in degassed H₂O at 298 K (solid lines), and the emission spectrum in air-equilibrated solution (dashed line).

Interestingly, the use of mixtures of MeCN/H₂O leads to intermediate values of τ , which increase with the increasing proportion of water (Fig. 6), even though the emission energy remains essentially constant. Since, the emission intensity increases concomitantly with the lifetime, the most likely explanation is that non-radiative decay is progressively reduced as the proportion of water increases.



Fig. 6 Emission decays of the dinuclear complex 6 in the acetonitrile/water mixtures indicated; registered at 580 nm.

Such a non-innocent bridge has also been noted in the case of De Cola's symmetric dinuclear complexes of the type $[{Ir(F_2ppy)_2}_2(\mu$ -bpy- ϕ_n -bpy)]²⁺, where biexponential decay kinetics were attributed to an additional long component from the bridge.⁴² Similarly, in symmetrical dimers of the type $[{Ir(dpyx)_2}_2(\mu$ -mtbpy- ϕ -mtbpy)]²⁺, we observed biexponential decay at 77 K, in which a long component of 70 µs was assigned to a π - π * state of the bridging unit.

Conclusions

In summary, cyclometallated iridium complexes comprised of two terdentate cyclometallating ligands, of the form $[Ir(N^{A}C^{N})(N^{A}N^{C})]^{+}$, have been used in the preparation of multimetallic systems. Access to a complex of this type carrying a boronic acid functional group allows palladium-catalysed crosscoupling with complexes bearing halogens. Equally, a halogenated complex can be coupled with a boronic acid-substituted complex. Owing to the susceptibility of the cyclometallating ligand to bromination under mild conditions at the central C4' of the N[^]C[^]N ligand, a second cross-coupling can be carried out with a third complex, offering stepwise generation of a linear A-B-C assembly. The luminescence properties of the Ir-Ir-Ru system indicate that it can be regarded as a supramolecular system: the properties of the individual units are largely retained, and excitation at any wavelength leads to exclusive emission from the lower energy terminus, indicative of fast energy transfer. On the other hand, for the system comprised of $[Ir(N^{A}N^{A}N)_{2}]$ and $[Ir(N^{A}C^{N})(N^{A}N^{C})]$ units linked together via the N^C^N ligand, an excited state with significant bridge character seems to play a

key role in determining the emission properties. Overall, the results demonstrate the versatility of this new class of iridium complex and their potential in the design of linear multimetallics offering unidirectional energy transfer.

Experimental

Proton and ¹³C NMR spectra, including NOESY and COSY, were recorded on Varian 300, 400 or 500 MHz instruments. Chemical shifts (δ) are in ppm, referenced to residual protiosolvent resonances, and coupling constants are in Hertz. Electron ionisation (EI) mass spectra were recorded with a Micromass AutoSpec spectrometer. Electrospray ionisation (ES) mass spectra were acquired on a time-of-flight Micromass LCT spectrometer with methanol or acetonitrile as the carrier solvent. All solvents used in preparative work were at least Analar grade, and water was purified using the Purite[®] system. Acetonitrile used for optical spectroscopy was HPLC grade.

4-(*p*-Bromophenyl)-6-(*m*-tolyl)bipyridine (mtbpyH- ϕ -Br),²⁸ 1,3-di(2-pyridyl)-4,6-dimethyl-benzene (dpyxH),³⁴ and bis(μ -chloro)-bis[1,3-di(2-pyridyl)-4,6-dimethylbenzene- N, C^2, N -iridium chloride], [Ir(dpyx)₂Cl(μ -Cl)]₂,³⁴ were prepared as described previously. The complexes [Ir(tpy)(tpy- ϕ -Br)]³⁺ **5**,³⁷ [Ir(dpyx)(mtbpy- ϕ -Br)]⁺ **4**,²⁸ [Ru(bpy)₂(bpy- ϕ -B)]²⁺ **7**,²² and [Ir(F₂ppy)₂(bpy- ϕ -B)]⁺ **10**²² were prepared according to procedures described in our earlier work.

4'-(p-neopentylglycolatoboron)-phenyl-6'-(m-tolyl)-bipyridine: mtbpyH-**Φ**-B

A mixture of mtbpyH- ϕ -Br (0.10 g, 0.25 mmol), bis(neopentylglycolato)diboron (0.68 g, 0.30 mmol) and potassium acetate (0.068 g, 0.30 mmol) in DMSO (6 mL) was degassed by four freeze-pump-thaw cycles. Pd(dppf)Cl₂ (0.074 g, 0.075 mmol) was added under a positive pressure of N₂ and the reaction mixture heated at 80 °C, under a N₂ atmosphere, for 16 h. The resultant black solution was diluted with DCM (20 mL), washed with water (5 × 100 mL) and dried over sodium sulfate. The solvent was then removed under reduced pressure and the product dried under vacuum giving a brown/black solid (0.15 g). The product was used without further purification.

¹H-NMR (CDCl₃, 500 MHz) $\delta = 8.73-8.64$ (2H, m, H³ and H⁶), 8.63 (1H, s, H³), 8.02–7.93 (3H, m, H^{4"} and H^a), 7.91 (1H, d, ³*J* = 8.0, H^{5'}), 7.85 (1H, t, ³*J* = 8.0, H⁴), 7.82–7.78 (3H, m, H^{2"} and H^b), 7.38 (1H, t, ³*J* = 7.5, H^{5"}), 7.32 (1H, t, ³*J* = 5.0, H⁵), 7.24 (1H, d, ³*J* = 9.0, H^{6"}), 3.79 (4H, s, CH₂), 2.48 (3H, s, CH₃), 1.03 (6H, s, CH₃-Bneo). ¹³C-NMR (CDCl₃, 126 MHz) $\delta = 207.3$ (C), 157.6 (C), 156.6 (C), 150.5 (C), 149.2 (C³), 140.9 (C), 139.7 (C), 138.7 (C), 138.6 (C), 137.2 (C⁴), 134.8 (C^b), 130.2 (C), 130.1 (C^{6"}), 128.9 (C^{5"}), 128.0 (C^{2"}), 127.9 (C), 126.6 (C^a), 124.5 (C^{4"}), 124.0 (C⁵), 121.9 (C⁶), 118.9 (C), 117.7 (C^{3'}), 72.6 (CH₂), 21.9 (CH₃-Bneo), 21.8 (CH₃). MS (MALDI, DCTB matrix) *m*/*z* = 453.3 [M + H]⁺. HRMS (ES⁺) *m*/*z* = 434.22672 [M + H]⁺; 434.22747 calculated for [C₂₈H₂₈¹⁰BN₂O₂]⁺.

[Ir(dpyx)(mtbpy- ϕ -B)]⁺ 3

A suspension of $[Ir(dpyx)Cl(\mu-Cl)]_2$ (0.052 g, 0.050 mmol), mtbpyH- ϕ -B (0.076 g, 0.18 mmol) and silver triflate (0.051 g,

0.20 mmol) in ethylene glycol (4 mL) was stirred at room temperature under a N₂ atmosphere for 1 h, before being heated to 140 °C for a further 3 h. After cooling to room temperature, the precipitated AgCl was collected by centrifuge and washed with acetonitrile $(2 \times 1 \text{ mL})$. The washings and filtrate were combined, added to saturated aqueous KPF_6 solution (25 mL) and the resulting orange precipitate collected by centrifuge, washed with water $(3 \times 5 \text{ mL})$ and dried under vacuum. Purification was achieved by flash column chromatography (silica, DCM/methanol, gradient elution from 100/0 to 93/7) to give the desired product as an orange solid (0.087 g, 89%). ¹H-NMR (d₆-acetone, 400 MHz) $\delta = 9.07$ (1H, d, ${}^{4}J = 1.6$, H^{3'}-NNC), 8.99 (1H, d, ${}^{3}J = 8.0$, H³-NNC), 8.90 (1H, d, ${}^{4}J = 1.2$, H^{5'}-NNC), 8.33 (2H, d, ${}^{3}J =$ 4.4, H³-NCN) 8.28 (2H, d, ${}^{3}J = 8.0$, H^b-NNC), 8.14 (1H, td, ${}^{3}J = 7.6, {}^{4}J = 1.6, H^{4}$ -NNC), 8.07 (2H, d, ${}^{3}J = 8.4, H^{a}$ -NNC), 7.96 (1H, s, $H^{3''}$ -NNC), 7.85 (2H, ddd, ${}^{3}J = 8.4$, 7.6, ${}^{4}J = 1.6$, H⁴-NCN), 7.79 (2H, dd, ${}^{3}J = 5.6$, ${}^{4}J = 1.2$, H^{6"}-NNC), 7.69 $(1H, dd, {}^{3}J = 5.6, {}^{4}J = 1.6, H^{6}$ -NNC), 7.42 (1H, ddd, {}^{3}J = 1.6, H^{6}-NNC), 7.42 (1H, ddd, ${}^{3}J = 1.6, H^{6}$ -NNC), 7.42 (1H, ddd, H^{6}) 7.6, 5.6, ${}^{4}J = 1.2$, H⁵-NNC), 7.23 (1H, s, H^{4'}-NCN), 6.96 (2H, ddd, ${}^{3}J = 7.6$, 5.6, ${}^{4}J = 1.2$, H⁵-NCN), 6.51 (1H, dd, ${}^{3}J = 8.4$, ${}^{4}J = 1.2, \text{ H}^{5''}$ -NNC), 5.84 (1H, d, ${}^{3}J = 7.2, \text{ H}^{6''}$ -NNC), 4.49 (3H, s, OMe) 2.99 (6H, s, CH₃-NCN), 2.18 (3H, s, CH₃-NNC). MS (MALDI, DCTB matrix) m/z = 817.3 [Ir(dpydmb)(mtbpy- ϕ -B(OH)₂]⁺, 831.3 [Ir(dpydmb)(mtbpy- ϕ -B(OH)(OMe)]⁺ and 847.3 $[Ir(dpydmb)(mtbpy-\phi-B(OMe)_2]^+$. HRMS (ES⁺) m/z = 830.25034[Ir(dpydmb)(mtbpy-\phi-B(OH)(OMe)]+; 830.25133 calculated for $[C_{42}H_{35}^{10}B^{193}IrN_4O_2]^+$. TLC (silica) $R_f = 0.26$ in DCM/methanol, 90/10. Mp > 250° C.

[Ir(tpy)(μ-tpy-φ-φ-mtbpy)Ir(dpyx)]⁴⁺ 6

A mixture of $[Ir(dpydmb)(mtbpy-\phi-B(OH)(OMe)]^+$ 3 (0.030 g, 0.031 mmol), [Ir(tpy)(tpy-\$\phi-Br)]³⁺ 5 (0.039 g, 0.031 mmol) and Na₂CO₃ (0.0099 g, 0.093 mmol in 100 µL water) in DMSO (5 mL) was degassed by three freeze-pump-thaw cycles. Pd(PPh₃)₄ (0.0043 g, 0.0037 mmol) was added under a positive pressure of N_2 and the mixture heated for 24 h. The solution was added to an aqueous solution of KPF₆, and the resulting precipitate collected by centrifuge and washed with water. Purification of the crude product was achieved by flash column chromatography (silica, acetonitrile/water/KNO3(aq), gradient elution from 100/0/0 to 78.0/20.7/1.3). Following evaporation of the solvent, the product was ion exchanged to the PF_6^- salt to give the product as an orange solid (0.011 g, 16%). ¹H-NMR (CD₃CN, 500 MHz) δ = 9.21 (2H, s, $H^{3'}$ -tpy- ϕ), 8.91 (2H, d, ${}^{3}J = 8.0, H^{3'}$ -tpy), 8.84–8.79 (4H, m, H³tpy-\u03c6, H^{3'}-NNC and H^{4'}-tpy), 8.73 (1H, s, H^{5'}-NNC), 8.68 (1H, d, ${}^{3}J = 8.0, H^{3}$ -NNC), 8.64 (2H, d, ${}^{3}J = 8.0, H^{3}$ -tpy), 8.45 (2H, d, ${}^{3}J = 8.5, \text{H}^{a}\text{-NNC}$, 8.38 (2H, d, ${}^{3}J = 8.5, \text{H}^{b'}\text{-tpy-}\phi$), 8.33–8.24 (10H, m, H³-NCN, H⁴-tpy, H⁴-tpy- ϕ , H^{a'}-tpy- ϕ and H^b-NNC), 8.04 (1H, t, ${}^{3}J = 8.0$, H⁴-NNC), 7.91 (1H, s, H^{3"}-NNC), 7.81–7.75 (4H, m, H4-NCN, H6-tpy and H6-tpy-\$), 7.66-7.61 (4H, m, H6tpy, H6-tpy-\$\$\phi\$ and H6-NCN), 7.59-7.51 (5H, m, H5-tpy, H5-tpy-\$\$\$\phi\$ and H⁶-NNC), 7.29 (1H, t, ³J = 6.0, H⁵-NNC), 7.22 (1H, s, H⁴-NCN), 6.90 (2H, t, ${}^{3}J = 6.0$, H⁵-NCN), 6.58 (1H, d, ${}^{3}J = 7.0$, H⁵''-NNC), 5.83 (1H, d, ${}^{3}J = 8.0$, H^{6"}-NNC), 2.97 (6H, s, CH₃-NCN), 2.26 (3H, s, CH₃-NNC). MS (MALDI, DCTB matrix) m/z =1939.4 $[M + 3PF_6]^+$. HRMS (ES⁺) $m/z = 375.59682 [M]^{4+}/4$; 375.59699 calculated for $[C_{77}H_{56}^{191}Ir_2N_{10}]^{4+}/4$. TLC (silica) $R_f =$ 0.15 in MeCN/H₂O/KNO_{3(aq)}, 80/18/2. Mp > 250°C.

A mixture of [Ir(dpyx)(mtbpy- ϕ -Br)]⁺ 5 (0.030 g, 0.030 mmol), [Ru(bpy)₂(bpy-\$\phi-B)]²⁺ (0.031 g, 0.030 mmol) and Na₂CO₃ (0.0095 g, 0.090 mmol in 100 µL water) in DMSO (5 mL) was degassed by three freeze-pump-thaw cycles. $Pd(PPh_3)_4$ (0.0042 g, 0.0035 mmol) was added under a positive pressure of N_2 and the same reaction procedure employed as for 6. The crude product was purified by flash column chromatography (silica, acetonitrile/water/KNO_{3(aq)}, gradient elution from 100/0/0 to 89.0/10.8/0.4). Following evaporation of the solvent, the product was ion exchanged to the PF_6^- salt to give the product as an orange solid (0.024 g, 43%). ¹H-NMR (CD₃CN, 500 MHz) $\delta =$ 8.86 (1H, s, $H^{3'}$ -bpy- ϕ), 8.77 (1H, d, ${}^{3}J = 9.0$, H^{3} -bpy- ϕ), 8.76 (1H, s, $H^{3'}$ -NNC), 8.68 (1H, s, $H^{5'}$ -NNC), 8.65 (1H, d, ${}^{3}J = 8.0$, H³-NNC), 8.56 (4H, t, ${}^{3}J = 9.0$, H³-bpy) 8.31 (2H, d, ${}^{3}J = 8.5$, $H^{b'}$ -bpy- ϕ), 8.26 (2H, d, ${}^{3}J = 8.5$, H³-NCN), 8.15–8.07 (10H, m, H⁴-bpy, H⁴-bpy-\, H^{6'}-bpy-\, H^{a'}-bpy-\, and H^b-NNC), 8.02 (1H, t, ${}^{3}J = 7.0$, H⁴-NNC), 7.88 (1H, s, H^{3"}-NNC), 7.87 (1H, d, ${}^{3}J =$ 6.5, H⁶-bpy-φ), 7.84–7.75 (9H, m, H⁴-NCN, H^{5'}-bpy-φ, H⁶-bpy and H^a-NNC), 7.59 (2H, d, ${}^{3}J = 5.0$, H⁶-NCN), 7.55 (1H, d, ${}^{3}J = 5.5, \text{ H}^{6}\text{-NNC}$, 7.49–7.44 (5H, m, H⁵-bpy and H⁵-bpy- ϕ), 7.27 (1H, t, ${}^{3}J = 7.0$, H⁵-NNC), 7.21 (1H, s, H^{4'}-NCN), 6.88 (2H, t, ${}^{3}J = 6.5$, H⁵-NCN), 6.56 (1H, d, ${}^{3}J = 8.5$, H^{5"}-NNC), 5.81 $(1H, d, {}^{3}J = 8.0, H^{6''}$ -NNC), 2.96 (6H, s, CH₃-NCN), 2.24 (3H, s, CH₃-NNC). MS (MALDI, DCTB matrix) m/z = 1707.3 [M + PF_6^{-} +. HRMS (ES⁺) $m/z = 777.15976 [M + PF_6^{-}]^{2+}/2; 777.15794$ calculated for $[C_{77}H_{58}F_6^{191}IrN_{10}P^{96}Ru]^{2+}/2$. TLC (silica) $R_f = 0.59$ in MeCN/H₂O/KNO_{3(aq)}, 80/18/2. Mp > 250°C.

[Ir(dpyx-Br)(µ-mtbpy-φ-φ-bpy)Ru(bpy)₂]³⁺ 9

A mixture of $[Ir(dpyx)(\mu-mtbpy-\phi-\phi-bpy)Ru(bpy)_2]^{3+}$ 8 (0.029 g, 0.029 mmol) and N-bromosuccinimide (0.0034 g, 0.019 mmol) was stirred in acetonitrile (5 mL) for 18 h. The solution was then added to saturated aqueous KPF₆ solution (20 mL), forming a precipitate which was collected by centrifugation, washed with water $(3 \times 2 \text{ mL})$ and dried under vacuum to give the product as a red solid (0.036 g, 97%). ¹H-NMR (CD₃CN, 400 MHz) δ = 8.86 (1H, s, H^{3'}-bpy- ϕ), 8.77 (1H, d, ³*J* = 7.2, H³-bpy- ϕ), 8.76 (1H, s, $H^{3'}$ -NNC), 8.69 (1H, s, $H^{5'}$ -NNC), 8.65 (1H, d, ${}^{3}J = 8.0, H^{3}$ -NNC), 8.56 (4H, t, ${}^{3}J = 8.0$, H 3 -bpy), 8.59–8.53 (4H, m, H ${}^{b'}$ -bpy- ϕ and H3-NCN), 8.17-8.06 (10H, m, H4-bpy, H4-bpy-, H6-bpy-, $H^{a'}$ -bpy- ϕ and H^{b} -NNC), 8.02 (1H, td, ${}^{3}J = 6.8, 1.6 H^{4}$ -NNC), 7.89–7.86 (2H, m, H^{3"}-NNC and H⁶-bpy- ϕ), 7.85–7.76 (9H, m, H⁴-NCN, H^{5'}-bpy- ϕ , H⁶-bpy and H^a-NNC), 7.65 (2H, d, ³*J* = 6.0, H⁶-NCN), 7.58 (1H, d, ${}^{3}J = 4.8$, H⁶-NNC), 7.50–7.43 (5H, m, H⁵-bpy and H⁵-bpy- ϕ), 7.27 (1H, t, ³*J* = 6.4, H⁵-NNC), 6.93 (2H, td, ${}^{3}J = 7.2$, ${}^{4}J = 1.2$, H⁵-NCN), 6.57 (1H, d, ${}^{3}J = 8.0$, H^{5"}-NNC), 5.83 (1H, d, ${}^{3}J = 7.6$, H^{6"}-NNC), 3.18 (6H, s, CH₃-NCN), 2.24 (3H, s, CH₃-NNC). MS (MALDI, DCTB matrix) m/z = 1758.3 $[M + 2PF_6^{-}]^+$. HRMS (ES⁺) $m/z = 498.42015 [M]^{3+}/3$; 498.42025 calculated for $[C_{77}H_{57}^{79}Br^{191}Ir^{193}IrN_{10}]^{3+}/3$. TLC (silica) $R_{\rm f} = 0.65$ in MeCN/H₂O/KNO_{3 (aq)}, 80/18/2. Mp > 250° C.

$[Ir(F_2ppy)_2(\mu-bpy-\phi-\phi-dpyx)Ir(\mu-mtbpy-\phi-\phi-bpy)Ru(bpy)_2]^{3+}$ 11

A mixture of $[Ir(dpyx-Br)(\mu-mtbpy-\phi-\phi-bpy)Ru(bpy)_2]^{3+}$ **9** (0.030 g, 0.016 mmol), $[Ir(ppy-F_2)_2(bpy-\phi-B)]^+$ (0.016 g, 0.016 mmol) and Na₂CO₃ (0.0051 g, 0.048 mmol in 100 µL water) in DMSO (5 mL) was degassed by three freeze-pump-thaw cycles. Pd(PPh₃)₄ (0.0022 g, 0.0019 mmol) was added under a positive pressure of N_2 and the same reaction procedure employed as for 6. The crude product was purified by flash column chromatography (silica, acetonitrile/water/KNO3(aq), gradient elution from 100/0/0 to 89.0/10.8/0.4). Following evaporation of the solvent, the product was ion exchanged to the PF₆⁻ salt to give the desired product as an orange/red solid (0.028 g, 62%). ¹H-NMR (CD₃CN, 500 MHz) $\delta = 8.95$ (1H, s, H^{3'}-Ir-bpy- ϕ), 8.87 (1H, s, H^{3'}-Ru-bpy- ϕ), 8.84 (1H, d, ${}^{3}J = 8.0$, H³-Ir-bpy- ϕ), 8.79 (1H, s, H^{3'}-NNC), 8.78 (1H, d, ${}^{3}J = 10.0$, H³-Ru-bpy- ϕ), 8.71 (1H, s, H^{5'}-NNC), 8.68 $(1H, d, {}^{3}J = 8.5, H^{3}$ -NNC), 8.56 (4H, t, ${}^{3}J = 9.0, H^{3}$ -Ru-bpy), 8.40 (2H, t, ${}^{3}J = 9.5$, H^{b'}-Ru-bpy- ϕ), 8.34–8.25 (4H, m, H³-NCN, H⁴-Ir-bpy-\$\$\phi\$ and H⁵-Ir-bpy-\$\$\phi\$\$, 8.19-8.07 (15H, m, H⁴-Ru-bpy, H⁴-Ru-bpy- ϕ , H⁶-Ir-bpy- ϕ , H⁶-Ru-bpy- ϕ , H^a-Ir-bpy- ϕ , H^{a'}-Ru-bpy- ϕ , H^b-Ir-bpy- ϕ and H^b-NNC), 8.05 (1H, t, ${}^{3}J = 8.0$, H⁴-NNC), 8.02– 7.96 (3H, m, H³-Ir-ppy and H^{5'}-Ir-bpy- ϕ), 7.91 (1H, s, H^{3'}-NNC), 7.87 (1H, d, ${}^{3}J = 5.5$, H⁶-Ru-bpy- ϕ), 7.85–7.74 (11H, m, H⁴-NCN, H⁴-Ir-ppy, H^{5'}-Ru-bpy-ø, H⁶-Ru-bpy and H^a-NNC), 7.70 (2H, d, ${}^{3}J = 9.0, H^{6}$ -Ir-ppy), 7.67–7.59 (4H, m, H⁶-NCN, H⁶-NNC and H⁶-Ir-bpy-φ), 7.50–7.44 (5H, m, H⁵-Ru-bpy and H⁵-Ru-bpy-φ), 7.33 (1H, t, ${}^{3}iJ = 6.5$, H⁵-NNC), 7.20–7.15 (2H, m, H⁵-Ir-ppy), 6.91 (2H, t, ${}^{3}J = 6.5$, H⁵-NCN), 6.82–6.74 (2H, m, H^{4'}-Ir-ppy), 6.62 (1H, d, ${}^{3}J = 8.0$, H^{5"}-NNC), 5.95 (1H, d, ${}^{3}J = 7.5$, H^{6"}-NNC), 5.85–5.80 (2H, m, H^{6'}-Ir-ppy), 2.65 (6H, s, CH₃-NCN), 2.27 (3H, s, CH₃-NNC). ¹⁹F-NMR (CD₃CN, 658 MHz) $\delta = -73.0$ $(24F, d, J_{F-P} = 707.1, PF_6^{-}, -108.3 \text{ to } -108.2 \text{ (2F, m, } F^{5'}), -110.1$ $(2F, t, J_{F-P} = 13.2, F^{3'})$. MS (MALDI, DCTB matrix) m/z = 2655.5 $[M + 3PF_6^-]^+$. HRMS (ES⁺) $m/z = 53.12276 [M]^{4+}/4$; 553.12290 calculated for $[C_{115}H_{80}F_4^{191}Ir^{193}IrN_{14}^{96}Ru]^{4+}/4$. TLC (silica) $R_f =$ 0.62 in MeCN/H₂O/KNO_{3 (aq)}, 80/18/2. Mp > 250°C.

Electrochemistry

Cyclic voltammetry was carried out using a μ Autolab Type III potentiostat with computer control and data storage *via* GPES Manager software. Solutions of concentration 1 mM in 90% CH₃CN/10% CH₂Cl₂ were used, containing [Bu₄N][BF₄] as the supporting inert electrolyte. A three-electrode assembly was employed, consisting of a platinum working electrode, platinum wire counter electrode and platinum flag reference electrode. Solutions were purged for 5 minutes with solvent-saturated nitrogen gas with stirring, prior to measurements being taken without stirring. The voltammograms were referenced to a ferrocene–ferrocenium couple as the standard ($E^{\circ} = 0.40 \text{ vs SCE}$).

Photophysical measurements

Absorption spectra were measured on a Biotek Instruments XS spectrometer, using quartz cuvettes of 1 cm pathlength. Steady-state luminescence spectra were measured using a Jobin Yvon FluoroMax-2 spectrofluorimeter, fitted with a red-sensitive Hamamatsu R928 photomultiplier tube; the spectra shown are corrected for the wavelength dependence of the detector, and the quoted emission maxima refer to the values after correction. Samples for emission measurements were contained within quartz cuvettes of 1 cm pathlength modified with appropriate glassware 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 < 5×10^{-2} mbar, as monitored using a Pirani gauge. Luminescence quantum yields were determined using [Ru(bpy)₃]Cl₂ in airequilibrated aqueous solution ($\phi = 0.028^{43}$) as the standard; estimated uncertainty in ϕ is $\pm 20\%$ or better.

The luminescence lifetimes of the complexes were measured by time-correlated single-photon counting, 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 $\pm 10\%$ or better. Bimolecular rate constants for quenching by molecular oxygen, k_Q , were determined from the lifetimes in degassed and air-equilibrated solution, taking the concentration of oxygen in CH₂Cl₂ at 0.21 atm O₂ to be 2.2 mmol dm⁻³.⁴⁴

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