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Cross-couplings in the elaboration of luminescent bis-terpyridyl iridium complexes: the effect of extended or inhibited conjugation on emission

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The utility of Suzuki cross-coupling methodology for the *in situ* elaboration of bromo-functionalised bis-terpyridyl iridium(III) complexes has been explored. The complex $[Ir(tpy)(tpy\text{-}\phi\text{-}Br)]^{3+}$ {tpy-ϕ-Br = 4′-(4-bromophenyl)-2,2′:6′,2″-terpyridine} undergoes palladium-catalysed cross-coupling with aryl boronic acids to yield biaryl-substituted complexes directly. The biphenyl and 4-cyanobiphenyl-substituted products display relatively intense, long-lived ($\tau > 100$ μs) yellow emission in degassed aqueous solution at room temperature, assigned to a $^3\pi$–π^* state. A 4-aminobiphenyl-substituted analogue displays an additional low energy absorbance band, attributed to an intraligand charge-transfer (ILCT) excited state, and is scarcely emissive under the same conditions. The iridium(III) complex of 4′-mesityl-terpyridine is also reported. Its emission is much shorter-lived, with a spectral profile resembling that of unsubstituted $[Ir(tpy)_2]^{3+}$, confirming the need for the attainment of a roughly coplanar geometry for stabilisation of the $^3\pi$–π^* excited state.

Introduction

The rich photophysical and electrochemical properties of polypyridyl metal complexes render them of great interest in a wide variety of applications, ranging from photocatalysts to luminescent chemosensors, and from new electroluminescent display materials to devices for the conversion of light to electrical energy.[1a–d] Iridium(III) complexes with cyclometallating ligands, for example, developed in the 1980s by Watts and others,[2] have recently enjoyed renewed interest, following the demonstration that *tris*(2-phenylpyridine)iridium(III) is able to act as a "triplet harvester" when incorporated into electroluminescent devices, with accompanying large gains in efficiency.[1c,3] On the other hand, the longer lifetimes and appreciable quantum yields found in iridium(III) complexes with an N_6 coordination sphere have sparked interest in their application as luminescent sensors or labels amenable to time-resolved detection procedures.[4,5] With this latter application in mind, we have been investigating the chemistry and luminescence properties of bis-terpyridyl iridium(III) complexes.[4] Their preparation has proved challenging. Successful routes to date involve harsh conditions and laborious purification, reflecting the kinetic inertness of iridium(III) with respect to ligand substitution processes: temperatures of 160 °C or higher are required.[4–7] Compared to the more widely-studied ruthenium analogues (typically prepared at about 80 °C), these conditions are very harsh, and represent a hurdle to be overcome in the further development of this chemistry. This is especially important if more delicate functionality is required in the terpyridines, for example, in the case of responsive complexes as chemosensors. In this paper, we report on the possibility of using a simple, bromo-functionalised complex as a synthon in the preparation of larger, potentially more elaborate complexes, by palladium-catalysed cross-coupling with aryl boronic acids. Since the cross-coupling can be achieved under much milder conditions (80–85 °C) than those typically required for the complexation of the terpyridines to the metal (160–200 °C), this strategy could provide an attractive solution to the synthetic problem.

Previous work has shown that the luminescence lifetime of $[Ir(tpy)_2]^{3+}$ (tpy = 2,2′:6′,2″-terpyridine) is extended upon introduction of simple aryl groups into the 4′-positions of the terpyridine (*e.g.* 4-tolyl; 3,5-di-*tert*-butylphenyl[7]). The emission has been assigned to an excited state of predominantly $^3\pi$–π^* character,[4–7] as opposed to the shorter-lived MLCT states responsible for the luminescence of related cyclometallated compounds.[8] The complexes prepared during the present exploration of the cross-coupling synthetic strategy incorporate biphenyl-appended terpyridines, and hence offer an opportunity to investigate the effect of extended ligand conjugation on the luminesence properties. Also discussed is the effect of inhibiting conjugation, using a ligand carrying a 4′-mesityl substituent, itself prepared by a cross-coupling procedure.

Results and discussion

Synthesis and elaboration of complexes

The palladium-catalysed cross-coupling reaction of aryl boronic acids with aryl halides has become an important tool for C–C bond formation in organic chemistry, as it can tolerate a very wide variety of functionality in both substrates, without competitive homo-coupling of either of the reactants becoming an issue.[9] In the field of coordination chemistry, the procedure has been applied to the synthesis of new ligands,[10] but there are few instances of the use of pre-formed metal complexes themselves as substrates in Suzuki couplings.[11] The notable examples are the formation of dinuclear homometallic complexes with aryl spacers by cross-coupling of appropriate bromo-functionalised complexes with 1,4-benzene-diboronic acid: originally demonstrated for cyclometallated ruthenium complexes with terdentate ligands,[12a] this approach has also been applied very recently to bis-cyclometallated iridium(III) complexes.[12b] We have reported recently on the use of bis-terpyridyl ruthenium(II) complexes, that incorporate bromo- or boronic acid functionality in the ligands, in Suzuki-type cross-coupling reactions.[13] This strategy allows the *in situ* elaboration of both classes of complex, upon Pd-catalysed reaction with aryl boronic acids or aryl halides respectively. In the present work, we have sought to extend this methodology to analogous iridium(III) complexes.

In order to investigate this possibility, the bromo-functionalised complex $[Ir(tpy)(tpy\text{-}\phi\text{-}Br)](PF_6)_3$ (tpy-ϕ-Br = 4-bromophenyl-terpyridine; Scheme 1) was prepared by reaction of $[Ir(tpy)Cl_3]$ with tpy-ϕ-Br in refluxing ethylene glycol. The desired complex could be obtained in yields of 40–50% typically, following chromatography on silica. Cross-couplings with

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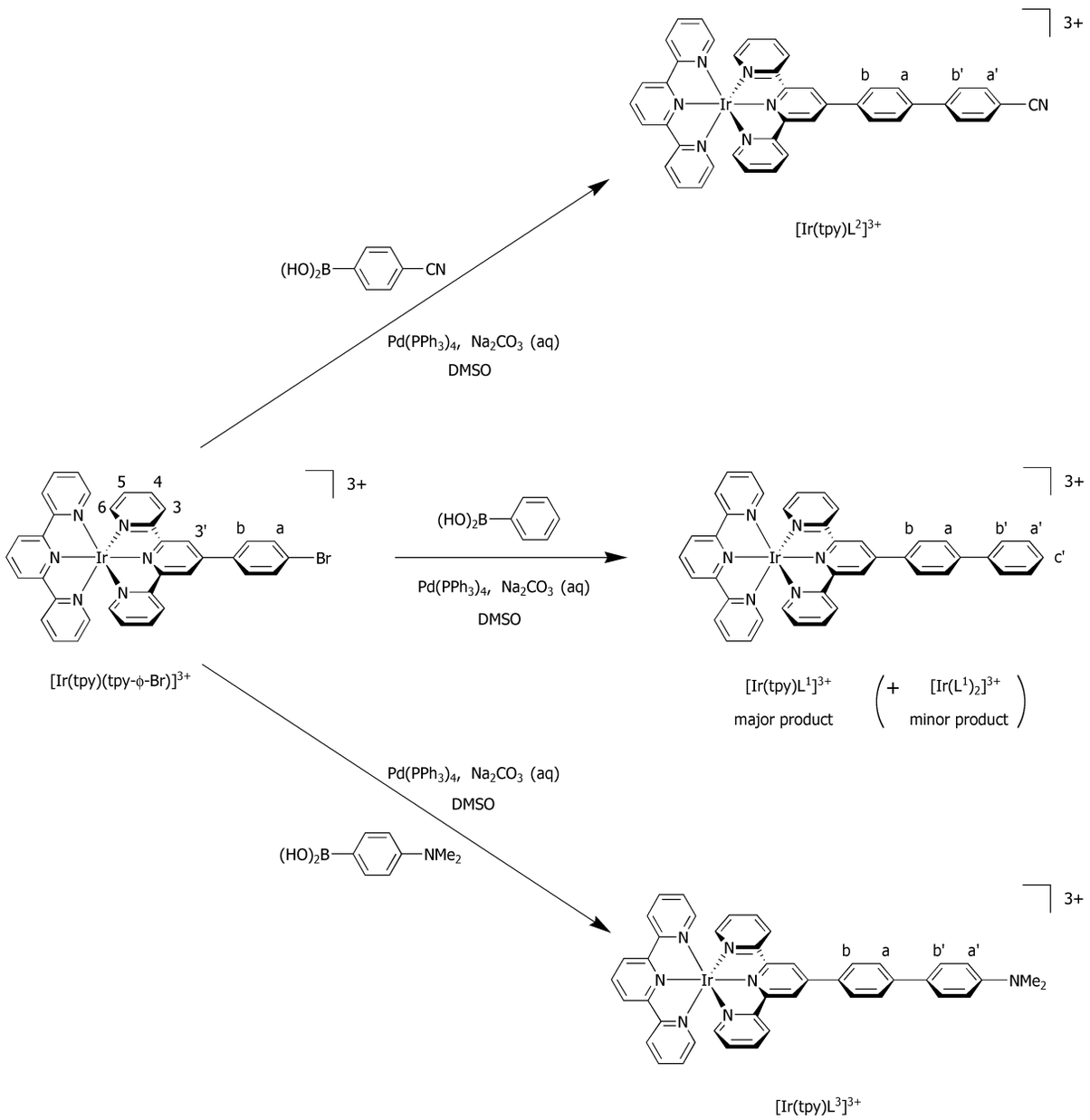


Scheme 1

phenylboronic acid, 4-cyanobenzene boronic acid and 4-(dimethylamino)benzene boronic acid were investigated, the latter two being chosen in order to verify the applicability of the method to systems with electron-withdrawing or -donating groups. Our earlier work on ruthenium had revealed that the widely-used catalyst $Pd(PPh_3)_4$, in combination with sodium carbonate as a base, offered satisfactory results, provided that DMSO was used as the solvent, as opposed to the less polar solvents normally used in cross-coupling reactions of organic substrates.[13] This is probably a reflection primarily of the low solubility of these rather highly-charged complexes in such solvents. Applying similar conditions to $[Ir(tpy)(tpy\text{-}\phi\text{-}Br)](PF_6)_3$ in DMSO allowed the cross-coupling reactions to proceed, leading to the desired complexes (Scheme 1). The reactions proceeded rapidly at 80 °C and all starting complex had been consumed within a few hours. This compares to considerably slower reaction times observed for comparable cross-couplings of uncomplexed tpy-ϕ-Br with the same boronic acids, where we found that, typically, reaction times of 24–48 h were required.[14] It is well-established that electron-withdrawing substituents in the aryl halide (especially those which are *ortho* or *para* to the halogen) will increase the rate of cross-coupling reactions (when the rate-determining step is the oxidative addition to the palladium centre), owing to the increased polarisation and lability of the carbon–halogen bond.[9] Thus, the faster rate of reaction of the complexes, compared to the free ligands, may be attributed to the presence of the electron-withdrawing $[Ir(tpy)_2^{3+}]$ core of the complex located *para* to the halogen. On the other hand, it is also possible that cross-couplings on the free ligands are somewhat retarded by competitive complexation of the catalytic palladium species to the terpyridine nitrogens, a possibility which clearly will not arise for the pre-formed complexes.

Following the coupling reactions, anion exchange with aqueous KPF_6 was carried out, to displace bromide anions and remove water-soluble material, followed by column chromatography on silica. The overall yields were of the order 25–35%; although rather low, it may be noted that these are the isolated product yields, which generally tend to suffer from the relatively inefficient nature of chromatographic purification of highly charged salts. Thus, they do not compare unfavourably with earlier work on such complexes,[4,6,7] and higher yields could be anticipated upon optimisation of reaction conditions. In the case of the coupling with phenylboronic acid, the formation of the desired heteroleptic complex, $[Ir(tpy)L^1]^{3+}$, was accompanied by a significant amount of the homoleptic complex,

$[Ir(L^1)_2]^{3+}$. Although these two complexes were readily separated by chromatography, the apparent scrambling that must have taken place during the coupling reaction, in order to lead to this side-product, is surprising, given the much higher temperatures that are normally required to introduce the terpyridines into the coordination sphere of iridium. For the other cross-couplings, the amount of the equivalent side-products formed was scarcely significant; however, in each case, thin layer chromatography revealed the presence of the corresponding "free" biphenyl ligand in solution after three hours (by comparison with the R_f values of samples of the pre-formed ligands[14]), indicating some minor dissociation of the newly-formed ligand. A control reaction, to examine whether the coupling conditions {DMSO, aqueous Na_2CO_3 in the presence of $Pd(PPh_3)_4$} favour ligand substitution processes around the iridium centre, was carried out using $[Ir(tpy)Cl_3]$ and 4′-tolyl-terpyridine (ttpy), but formation of $[Ir(tpy)(ttpy)]^{3+}$ did not occur at 85 °C, even after 72 h.

Given the success of this *in situ* coupling strategy in allowing 4′-bromophenylterpyridine to be elaborated whilst already bound to the metal ion, it would be of interest to investigate whether the analogous complex of 4′-bromoterpyridine, $[Ir(tpy)(tpy\text{-}Br)]^{3+}$, (*i.e.* omitting the phenyl ring interposed between the terpyridine unit and the bromo substituent), could be functionalised similarly. Unfortunately, however, the prepararation of this complex proved troublesome. Reaction of the intermediate, $[Ir(tpy)Cl_3]$, with 4′-bromoterpyridine (tpy-Br) under the usual conditions (ethylene glycol at reflux) gave a mixture of products, amongst which there was no evidence of the desired complex by ^{1}H NMR analysis or mass spectrometry. Bearing in mind the known instability of 4-bromopyridine with respect to substitution reactions to give oligomeric products, even under mild conditions,[15] it is possible that tpy-Br cannot itself tolerate these harsh, high temperature conditions. For the reverse strategy of reacting $[Ir(tpy\text{-}Br)Cl_3]$ with terpyridine (where tpy-Br is pre-coordinated to the metal under milder conditions, and hence protected from such possible side-reactions), the required product was detectable by electrospray mass spectrometry, but exhaustive chromatography was unsuccessful in separating it from the other components of the mixture to give a pure sample.

4′-Mesityl-terpyridine, L^4 and its iridium(III) complex $[Ir(L^4)_2]^{3+}$

This complex was of interest for study of its photophysical properties (see below) because, although it incorporates a 4′-aryl substituent, conjugation of this ring with the terpyridine will be inhibited due to the steric demand of the *ortho* methyl groups. The use of "classical" terpyridine synthetic methodology, starting from 2-acetylpyridine and the pertinent aryl aldehyde, in this case 2,4,6-trimethylbenzaldehyde, failed to provide the desired ligand, possibly because of steric inhibition of the Michael addition of the second equivalent of 2-acetylpyridine to the initially formed α,β-unsaturated ketone.† On the other hand, the ligand was readily prepared *via* a Suzuki cross-coupling reaction of tpy-Br with the neopentyl glycol ester of 2,4,6-trimethylbenzeneboronic acid in dimethoxyethane, catalysed by $Pd(PPh_3)_4$ and in the presence of a strong base, $Ba(OH)_2$ (Scheme 2).[14] A single crystal suitable for an X-ray diffraction study was obtained from an ethanol solution.

The molecule of L^4 in the crystal (Fig. 1) lies on a crystallographic twofold axis (passing through the N(1), C(4), C(5) and C(8) atoms) and has a *transoid* arrangement of the pyridine units about the interannular bonds C(2)–C(12) and C(2′)–C(12′). Such a configuration is commonly found in the solid state structures of terpyridines, as it minimises unfavourable electrostatic interactions between the nitrogen lone pairs.[19] The three pyridine rings which constitute the terpyridine moiety are not quite coplanar, with an angle of 9.3° between the planes of the lateral rings and that of the central pyridine ring. In this respect too, the compound is similar to previously studied systems, where an angle of 5–10° is typical. In contrast, the dihedral angle between the mesityl group and the central pyridine ring is large, 67.5°, compared to 11° between the central pyridine and the aromatic pendant in 4′-phenylterpyridine.[19] The mesityl ring is sandwiched between two lateral pyridyl rings of adjacent molecules (interplanar angles 8.2°, mean interplanar separations *ca.* 3.5 Å), but no *continuous* stacks exist in the structure.

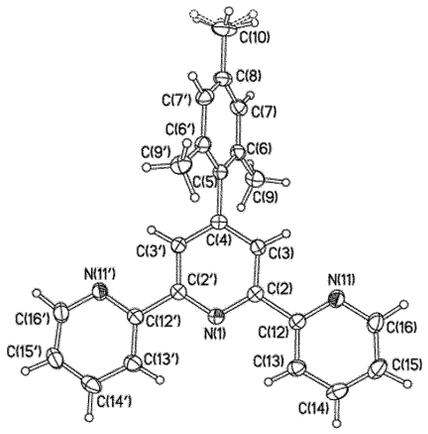


Fig. 1 The molecular structure of 4′-(2,4,6-trimethylphenyl)-terpyridine (mesityl terpyridine, L^4), showing thermal ellipsoids at the 50% probability level. Atoms generated by the twofold axis are primed.

The bis(4′-mesitylterpyridine)iridium(III) complex $[Ir(L^4)_2](PF_6)_2$ was prepared readily by reaction of $IrCl_3{\cdot}3H_2O$ with two equivalents of the ligand (L^4) in ethylene glycol at reflux (Scheme 2), and isolated as the hexafluorophosphate salt after anion exchange with aqueous KPF_6. Purification was achieved more readily than for related aryl-substituted complexes, by repeated recrystallisation from acetone/toluene.

Photophysical properties

Absorption and emission data for the complexes prepared in this study are collected in Table 1.

Absorption

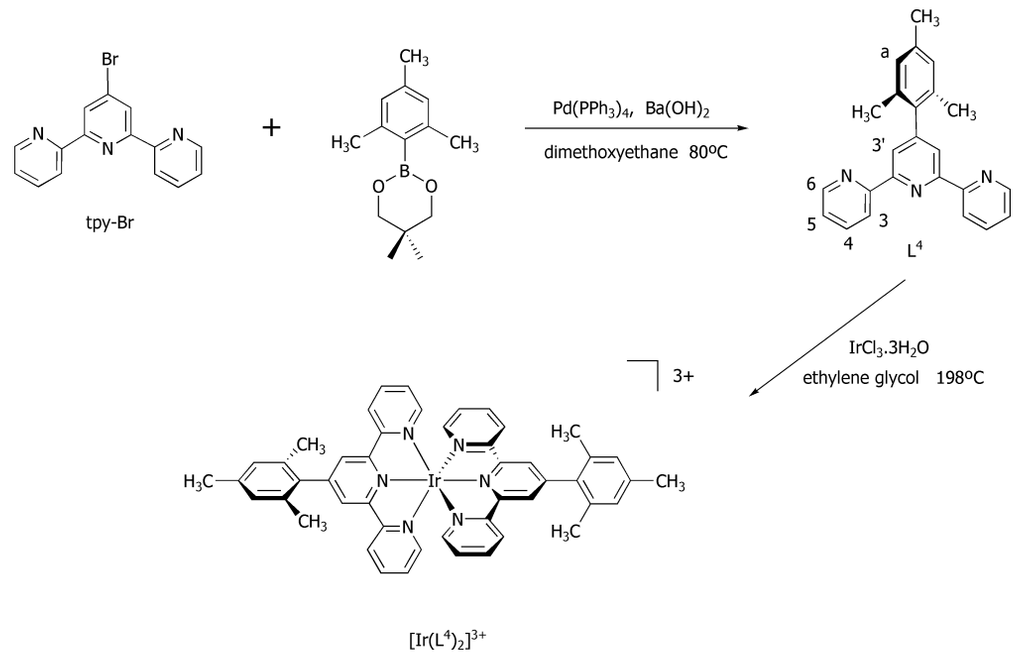
With the exception of $[Ir(tpy)L^3]^{3+}$, all of the complexes are yellow or pale yellow in colour, with strong absorption bands in the ultra-violet region tailing slightly into the visible (Fig. 2 and Table 1). The large extinction coefficients of 10^4–10^5 M^{-1} cm^{-1} are typical of ligand-centred ($^1\pi$–π^*) transitions, as normally observed in this region for iridium(III) complexes of bpy and tpy ligands. The biphenyl and cyano-biphenyl substituted complexes, $[Ir(tpy)L^1]^{3+}$ and $[Ir(tpy)L^2]^{3+}$, display pronounced absorption tails on the low-energy side, extending well beyond 400 nm, similar to those found previously for the tolyl-substituted complex $[Ir(ttpy)_2]^{3+}$ and related 4′-monoaryl-substituted compounds.[7] The tail is even more pronounced for the homoleptic, bis-biphenyl-substituted complex $[Ir(L^1)_2]^{3+}$ (Fig. 2), and the extinction coefficients of this complex are also significantly larger, as expected given the presence of two biphenyl units. On the other hand, the profile of the bis-mesityl complex $[Ir(L^4)_2]^{3+}$ is quite different from those of the other complexes at wavelengths > 330 nm, lacking the well-defined low energy maxima around 380–390 nm, and tailing off at

† Our attempts were based on the widely used "one-pot" procedure, which typically gives good results for simple 4′-aryl terpyridines (*e.g.* aryl = phenyl, tolyl, 4-bromophenyl, 4-methoxyphenyl).[16a] An alternative strategy involving initial deprotonation of 2-acetylpyridine with $KOBu^t$, to pre-form the enolate, has been found to promote reaction with unreactive α,β-unsaturated ketones formed from bulky aryl aldehydes,[17,18] which may have proved more successful in this instance.

Table 1 Photophysical parameters of the iridium(III) complexes[a]

	$[Ir(L^4)_2]^{3+}$	$[Ir(tpy)L^1]^{3+}$	$[Ir(L^1)_2]^{3+}$	$[Ir(tpy)L^2]^{3+}$
Absorption (H_2O) λ_{max}/nm (ε)[b]		253 (40 700)	255 (70 900)	252 (43 200)
	251 (34 300)	280 (45 600)	282 (85 400)	279 (49 400)
	280 (35 600)	317 (23 700)	321 (49 300)	316 (31 000)
	315 (16 800)	354 (18 000)	361 (41 700)	344 (25 500)
		375 (16 100)	381 (44 300)	367 (21 300)
Emission (H_2O) λ_{max}/nm	458, 491, 526, 564 (sh)	562	579	550, 582
Emission 77 K[c] λ_{max}/nm	461, 494, 532	517, 546 (sh), 604 (sh)	524, 557, 607 (sh)	514, 546 (sh), 604 (sh)
$\phi \times 10^2$ (H_2O)[d]	0.73	8.3	2.2	5.6
$\phi \times 10^2$ (CH_3CN)[d]	0.17	0.44	0.58	0.33
τ/μs in H_2O degassed (aerated)	0.37 (0.32)	107 (3.6[f])	61 (3.6)[e]	144 (3.7)
τ/μs in CH_3CN degassed (aerated)	0.40 (0.38)	6.0 (0.63)	17 (0.69)	6.2 (0.60)
τ/μs at 77 K[c]	9.5, 0.60	181	163	230

[a] At 295 K except where stated otherwise. [b] The Beer–Lambert law was obeyed at concentrations up to at least 5×10^{-5} M. Absorption spectra in CH_3CN were essentially identical to those in water, with the same λ_{max} values within the uncertainty of the measurement (±1nm). [c] In EtOH/MeOH (4:1 v/v), except for $[Ir(L^4)_2]^{3+}$, for which an EPA glass was used (EPA = ethanol/isopentane/diethyl ether, 2:5:5 v/v). [d] In degassed solution, measured using an excitation wavelength of 368 nm, excitation and emission band-passes of 2.5 nm, and using quinine sulfate as the standard ($\phi = 0.546$ in 1M H_2SO_4[27]); estimated uncertainty ±15%. [e] A short-lived minor component to the emission was also observed; the quoted value is that of the major component obtained by fitting the data to biexponential decay kinetics. [f] See also ref. 28.



Scheme 2

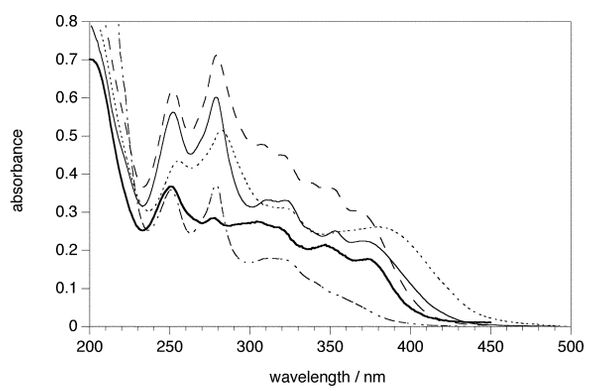
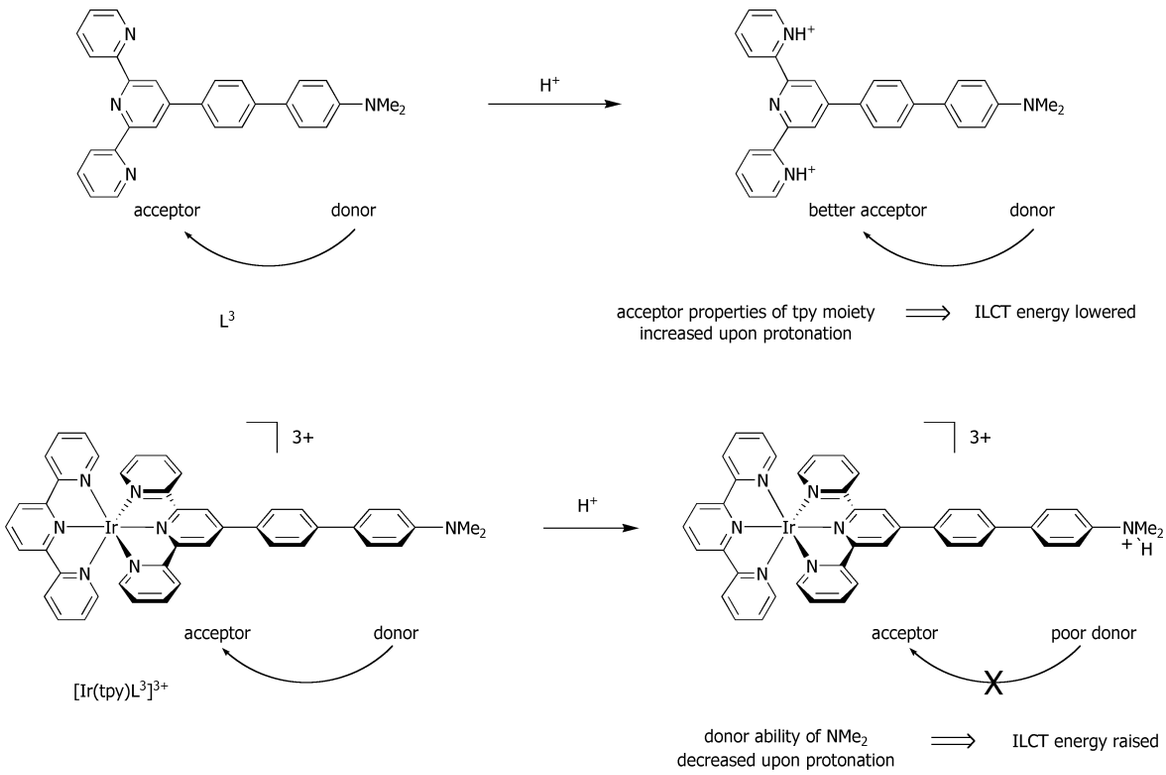


Fig. 2 UV-visible absorption spectra of $[Ir(tpy)L^1]^{3+}$ (thin solid line), $[Ir(L^1)_2]^{3+}$ (dotted line), $[Ir(tpy)L^2]^{3+}$ (dashed line) and $[Ir(L^4)_2]^{3+}$ (alternating dashed and dotted line) in aqueous solution. The spectrum of $[Ir(ttpy)_2]^{3+}$ (thick solid line) is shown for comparison. For each complex, the spectra in acetonitrile are almost identical to those in water.

shorter wavelengths. In this respect, it resembles much more closely the unsubstituted, parent complex $[Ir(tpy)_2]^{3+}$ [6,7] (albeit with somewhat enhanced absorption in the 360–400 nm region). It seems likely, therefore, that the low energy maxima and long wavelength tails are a consequence of additional conjugation at the 4′-position, which is only very limited in the mesityl system owing to the steric encumbrance of the *ortho* methyl groups.

In contrast to the other complexes, the amino-substituted compound, $[Ir(tpy)L^3]^{3+}$, is deep red in colour, owing to a broad, relatively intense absorption band centred at 420 nm in aqueous solution (Fig. 3). This is attributed to an intraligand charge transfer (ILCT) transition, in which the NMe_2 group acts as the electron donor and the metal-bound terpyridyl moiety as the electron acceptor. The free ligand L^3 displays a corresponding ILCT band around 350 nm (as reported in our previous study of the ligands[14]). The red-shift in the complex with respect to the ligand can be related to the increased acceptor properties of the terpyridyl π* orbitals upon coordination to the metal ion; shifts of comparable magnitudes have been observed upon coordination of zinc to L^3 and to 4′-(*p*-Me_2N–C_6H_4)-terpyridine (L^5),[14,20] and also in the iridium chloro complex $[IrL^6Cl_3]$ compared to the free ligand, where L^6 = 4′-(*p*-Bu_2N–C_6H_4–)-terpyridine.[21] Further support for the ILCT assignment comes from the substantial red-shift (50 nm) observed in acetonitrile compared to water (Fig. 3).



Scheme 3

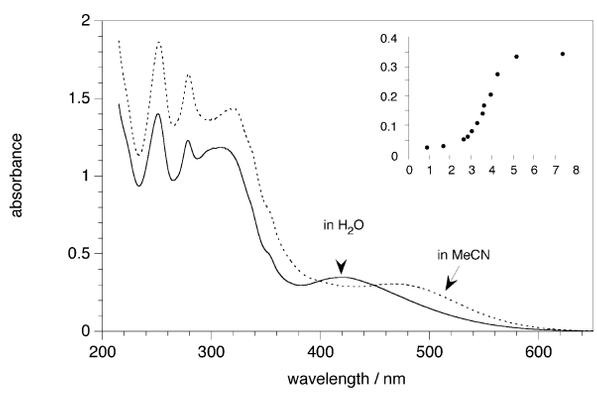


Fig. 3 UV-visible absorption spectra of $[Ir(tpy)L^3]^{3+}$ in water and in acetonitrile. The inset shows the change in absorption at 420 nm in aqueous solution as a function of pH.

This negative solvatochromic behaviour is indicative of a polar ground state and a less polar excited state, and is consistent with a charge-transfer axis which lies colinear with the dipole axis.[22] The behaviour is in marked contrast to that of the homoleptic analogues $[Ir(L^3)_2]^{3+}$ and $[Ir(L^5)_2]^{3+}$, which display only a very weak (and positive) solvatochromism in the corresponding band; in these complexes, there is no permanent dipole moment in the ground state (D_{2d} symmetry), and formation of the ILCT excited state will be accompanied by, at most, a small increase in the polarity of the system.[23]

Upon acidification of a solution of $[Ir(tpy)L^3]^{3+}$, this low energy absorption band disappears, owing to protonation of the -NMe_2 group, which inhibits its ability to act as a donor in the ILCT process (Scheme 3). This is very different from the effect of acidification of the free ligand L^3, where the band undergoes a red-shift. In that case, the site of initial protonation is the terpyridyl moiety, making it a better acceptor (Scheme 3).[14,20] Clearly, in the complex, the terpyridyl nitrogens are not available for protonation, leaving only the NMe_2 unit accessible. A pH titration in aqueous solution, obtained by monitoring the absorbance at 420 nm, gives an inflexion point at 3.8 (Fig. 3), significantly lower than the pK_a of *N*,*N*-dimethylaniline (5.2), which could be regarded as the simple model of the basic site. This reduced basicity of the amine is to be expected, given the presence of the electron-withdrawing metal–terpyridyl fragment in direct conjugation with it, and the fact that protonation will be inhibited by the +3 charge on the complex (related pyridyl-appended complexes display a comparable reduction in pK_a relative to pyridine[4a]).

Emission

Previous studies have attributed the luminescence from $[Ir(tpy)_2]^{3+}$ and 4′-aryl-substituted analogues to a state of primarily ligand-centred character.[4–7] The former displays a highly structured emission spectrum in solution at room temperature, whilst the introduction of aryl rings into the 4′ positions of the ligands leads to a red-shift and a rather less structured spectrum, which has been interpreted in terms of the effect of enhanced conjugation on the $^3\pi$–π^* excited state.[7] A higher-lying MLCT state may also be implicated in the luminescence behaviour.

Mesityl-substituted complex $[Ir(L^4)_2]^{3+}$

Despite possessing an aryl substituent at the 4′-position, the bis-mesityl substituted complex $[Ir(L^4)_2]^{3+}$ displays an emission spectral profile (Fig. 4) which is almost identical to that of the unsubstituted complex $[Ir(tpy)_2]^{3+}$, and quite different from those of all the previously reported aryl-substituted complexes, such as $[Ir(ttpy)_2]^{3+}$. From the position of the highest energy (0–0) band, the luminescent level of this complex is higher in energy by about 2000 cm^{-1} compared to other 4′-aryl substituted complexes. This result, which is in line with the absorption data, provides very strong evidence that it is indeed the additional conjugation offered by the 4′-aryl group that normally leads to the significantly different spectra exhibited by the aryl substituted systems compared to the parent complex: in the specific case of the mesityl system, the steric barrier to attainment of the necessary coplanar conformation will effectively prevent the aryl group from augmenting the conjugation in the excited state.

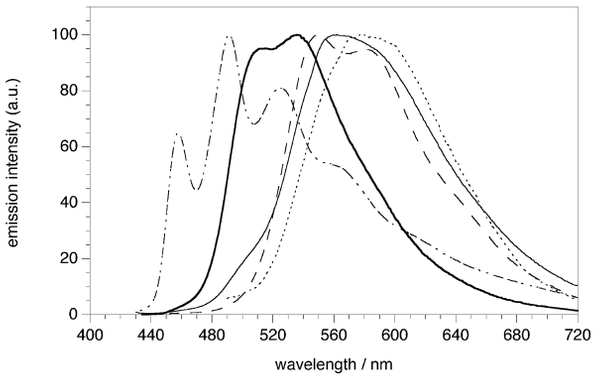


Fig. 4 Emission spectra of the complexes in aqueous solution at 295 K, λ_{ex} = 368 nm, excitation and emission band-passes set to 5 nm. The same legend as in Fig. 2 is employed: $[Ir(tpy)L^1]^{3+}$ (thin solid line), $[Ir(L^1)_2]^{3+}$ (dotted line), $[Ir(tpy)L^2]^{3+}$ (dashed line), $[Ir(L^4)_2]^{3+}$ (alternating dashed and dotted line), $[Ir(ttpy)_2]^{3+}$ (thick solid line).

The measured luminescence lifetime (*e.g.* 400 ns in MeCN, Table 1) is also more comparable to that of $[Ir(tpy)_2]^{3+}$ (τ = 1.2 μs under the same conditions[7]) than to the longer values found for the aryl-substituted systems ($\tau \geq 6$ μs[4,5,7]). On the other hand, it is intriguing that the introduction of the mesityl group actually shortens the lifetime compared to the unsubstituted system. Since the quantum yield is similarly lowered, it implies that the mesityl complex is subject to enhanced non-radiative decay pathways. This could be associated simply with the increased availability of proximate C–C stretching vibrations able to facilitate the deactivation of the excited state, but it could also reflect the inductively electron-donating nature of the 2,4,6-trimethylphenyl substituent, which may serve to raise the energy of the metal-centred orbital and thus lower the energy of the higher-lying MLCT state, promoting it as a pathway of decay.

Biphenyl-substituted complexes

The biphenyl, bis-biphenyl and cyano-biphenyl-substituted complexes all display moderately intense room temperature luminescence in degassed aqueous solution, with emission maxima in the range 550–590 nm (Fig. 4). This represents a significant red-shift relative to related complexes which have just one aryl ring at the 4′-position (as opposed to a biphenyl unit), such as $[Ir(ttpy)_2]^{3+}$, although the quantum yields of luminescence in degassed solution are of a similar magnitude (0.02–0.08). The cyano complex displays marginally the highest energy emission, and also retains the limited but nevertheless distinctive structure in the emission profile displayed by $[Ir(ttpy)_2]^{3+}$.

The increased conjugation offered by the additional phenyl ring will lead to stabilisation not only of the $^3\pi$–π^* states, but also of the MLCT excited states, since the ligand π^* energy will be lowered as the conjugation increases. However, on the basis of the lifetime data, we again assign the emission to a $^3\pi$–π^* state; indeed, the very long lifetimes in aqueous solution, substantially longer than those of $[Ir(ttpy)_2]^{3+}$, imply that any MLCT contribution to the excited state must now be small. Thus, the complexes $[Ir(tpy)L^1]^{3+}$ and $[Ir(tpy)L^2]^{3+}$ display monoexponential decay, with observed lifetimes of 107 and 144 (± 10) μs respectively in aqueous solution at room temperature, compared to 27 (± 3) μs for $[Ir(ttpy)_2]^{3+}$ under the same conditions. In line with their longer lifetimes and proposed greater triplet character, the new complexes also display higher sensitivity to oxygen. In air-equilibrated solution, for example, lifetimes and quantum yields are reduced by a factor of around 20, compared to much smaller effects (*ca.* 4-fold) for $[Ir(ttpy)_2]^{3+}$, with the result that the biphenyl complexes are significantly poorer emitters (in terms of quantum yield) than the monaryl-substituted systems, under these conditions. The bimolecular rate constants of quenching by molecular oxygen are of the order 9 × 10^8 $M^{-1}s^{-1}$, about twice as large as the value for $[Ir(ttpy)_2]^{3+}$ in aqueous solution, and more in line with values typically observed for polypyridine transition metal complexes.[24]

In a frozen glass at 77 K (in EtOH/MeOH, 4 : 1 by volume), these complexes display a significant hypsochromic shift in emission of around 1500 cm^{-1} relative to room temperature (Fig. 5). Such behaviour implies that the luminescent excited state is coupled with nuclear rearrangements which are affected by the state of the solvent. In contrast, the mesityl complex shows almost no change in emission energy or spectral shape. The differing behaviour is likely to be due to the torsional rearrangement that may be expected upon excitation of the biphenyl complexes, between the planes of the terpyridyl fragment and the biphenyl moiety, and between the two constituent rings of the latter. An approximately coplanar conformation of the three planes will be required to maximise the conjugation in the excited state whereas, in the ground state, the dihedral angle of a biphenyl fragment is around 30°.[25] The necesssary rearrangement to the more favourable conformation will be possible in fluid solution at room temperature, but not at 77 K, accounting for the higher energy emission under the latter conditions.

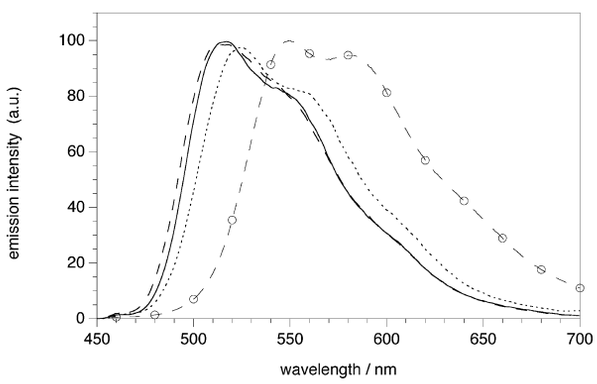


Fig. 5 Emission spectra of the biphenyl complexes at 77 K, in an ethanol/methanol (4 : 1 v/v) glass; λ_{ex} = 368 nm, band-passes of 5 nm. Legend: $[Ir(tpy)L^1]^{3+}$ (thin solid line), $[Ir(L^1)_2]^{3+}$ (dotted line), $[Ir(tpy)L^2]^{3+}$ (dashed line). The room temperature spectrum of $[Ir(tpy)L^2]^{3+}$ is also shown, to aid comparison (dashed line marked with open circles).

Interestingly, the complexes are substantially less emissive in acetonitrile than in aqueous solution, (*e.g.* the quantum yield of $[Ir(tpy)L^1]^{3+}$ is 18-times lower in acetonitrile than in water, in the absence of oxygen), even though the emission profiles in the two solvents are very similar. In air-equilibrated acetonitrile solutions, the emission intensity is very weak indeed (ϕ 5–7 × 10^{-4}). The lifetimes are also shortened, *e.g.* for $[Ir(tpy)L^1]^{3+}$, τ = 6.0 (±0.5) μs in CH_3CN compared to 107 (±10) μs in H_2O (degassed solutions), an 18-fold decrease. That the quantum yields and lifetimes are reduced by comparable factors (together with the similar forms of the spectra), suggests that the reduction is due to increased rates of non-radiative deactivation in acetonitrile, rather than to the radiative rate constant being substantially different in the two solvents (which might be expected if there were a switch to emission from a different type of excited state).

A similar trend to lower quantum yields and shorter lifetimes in acetonitrile has also been observed in the monoaryl series of complexes; however, the difference in that case was less pronounced (a factor typically of about 3).[26] An explanation for the more dramatic trend in the present instance possibly lies in the extent to which higher-lying ILCT states may influence the emission. As discussed earlier, in the amino-substituted complex $[Ir(tpy)L^3]^{3+}$, the presence of an ILCT state is revealed experimentally by the low energy band in absorption. This complex is scarcely emissive, suggesting that the charge-transfer

state is subject to efficient non-radiative deactivation. Analogous ILCT excited states are expected in the other complexes, albeit at higher energies (higher than the emitting $^3\pi$–π^* states), owing to the more weakly electron-donating nature of the biphenyl and cyanobiphenyl pendants. However, such ILCT states will be stabilised in acetonitrile compared to water (as observed experimentally for the amino system – see above), and may therefore mix with the emissive $^3\pi$–π^* state to a greater extent in the former solvent, possibly providing a pathway of non-radiative decay to the ground-state. Configurational mixing of ^{1,3}ILCT excited states into emissive $^3\pi$–π^* and MLCT states has been reported by McMillin and co-workers in a series of 4′-aryl substituted $[Pt(tpy)Cl]^+$ complexes although, in that case, it leads to an increase in lifetime and quantum yield over the parent, unsubstituted system which, itself, is almost non-emissive.[18]

Conclusion

Palladium-catalysed Suzuki-type cross-coupling methodology is successful in allowing the bromo-phenyl-substituted iridium bis-terpyridyl complex $[Ir(tpy)(tpy\text{-}\phi\text{-}Br)]^{3+}$ to be elaborated *in situ*, giving biphenyl-substituted complexes that are isolable in modest yield. Notably, the conditions employed (*e.g.* reaction temperature of 85 °C) are much milder than the aggressive conditions and high temperatures (≈200 °C) that are normally required to obtain such complexes. Thus, the approach offers a pathway for accessing a more diverse range of complexes, potentially including those appended with bioactive moieties such as peptides and nucleic acids. The long luminescence lifetimes of the biphenyl and cyano-biphenyl substituted complexes in degassed aqueous solution are consistent with an emissive state of primarily $^3\pi$–π^* character, stabilised compared to that of $[Ir(ttpy)_2]^{3+}$ by the additional conjugation of the biphenyl appendage. The mesityl-substituted complex supports these conclusions on the effect of conjugation, the inhibition of which, in this complex, leads to behaviour similar to that of $[Ir(tpy)_2]^{3+}$. Finally, the introduction of an amino susbtituent leads to a switch to a low-energy ILCT excited state. This new information on the way in which absorption and emission energies, lifetimes and quantum yields are influenced by ligand 4′ substituents should facilitate further exploration of the bis-terpyridyl class of iridium(III) complexes, the development of which has, to date, been largely overshadowed by the much more widely investigated cyclometallated systems.

Experimental

Synthetic details

4′-(4-Bromophenyl)-2,2′:6′,2″-terpyridine was prepared according to the one-pot procedure of Spahni and Calzaferri,[16a] and separated from the isomeric by-product, 6′-(4-bromophenyl)-2,2′:4′,2″-terpyridine, as previously reported.[16b] 4′-Bromo-terpyridine was prepared from 4′-triflate-terpyridine in almost quantitative yield upon treatment with a solution of HBr in acetic acid at 110 °C for 4 h;[14] the triflate was obtained as described by Potts.[29] $[Ir(tpy)Cl_3]$ was prepared as described previously.[7] Tetrakis(triphenylphosphine)-palladium(0) was obtained by hydrazine reduction of $PdCl_2$ in DMSO in the presence of triphenylphosphine.[30] Other reagents, including 2,2′:6′,2″-terpyridine and the boronic acids, were obtained from commercial sources and were used as supplied.

Proton and ^{13}C NMR spectra, including NOESY and COSY, were recorded on a Varian 500 MHz instrument, and referenced to residual protio-solvent resonances. Coupling constants are in Hertz. Electrospray ionisation mass spectra were acquired on a time-of-flight Micromass LCT spectrometer; high resolution spectra for accurate mass determinations were also carried out on this instrument or at the EPSRC National Mass Spectrometry Service Centre, Swansea.

4′-Mesityl-terpyridine L^4

An oven-dried Schlenk tube, equipped with a reflux condenser, was charged with 4′-bromoterpyridine (400 mg, 1.28 mmol), the neopentyl glycol cyclic ester of 2,4,6-trimethyl-benzeneboronic acid, (328 mg, 1.41 mmol, 1.1 equivalents), barium hydroxide (513 mg, 3 mmol, 2.4 equiv.) and $Pd(PPh_3)_4$ (74 mg, 0.06 mol, 5 mol%), and flushed with nitrogen. Degassed dimethoxyethane (13 mL) and water (2 mL) were added *via* cannula and the mixture heated at reflux for 24 h. The solvent was then evaporated under reduced pressure, and the residue partitioned between dichloromethane and water (30 mL of each). The organic layer was separated, washed with aqueous sodium hydroxide solution (0.1 M, 2 × 30 mL), and dried over anhydrous sodium carbonate. The solvent was removed to give a light brown residue, which was recrystallised from ethanol to give the desired compound as an off-white solid (275 mg, 61%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.64 (2H, d, ^3J 7.5, H^3), 8.62 (2H, d, ^3J 5.0, H^6), 8.26 (2H, s, $H^{3'}$), 7.83 (2H, td, ^3J 7.5, ^4J 1.5, H^4), 7.28 (2H, dd, ^3J 7.5, 5.0, H^5), 6.90 (2H, s, H^a), 2.29 (3H, s, *para*-CH_3), 2.03 (6H, s, *ortho*-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 156.2, 155.5, 151.6 (quats), 149.1 (C^6), 137.0 (quat), 136.7 (C^4), 136.6 (quat), 134.9 (quat), 128.0 (C^a), 123.6 (C^5), 121.9 ($C^{3'}$), 121.1 (C^3), 20.9 (*para*-CH_3), 20.6 (*ortho*-CH_3). MS (EI): 351 (M^+), 350 ($M^+ - H$), 335 ($M^+ - CH_3$), 273 (M^+ – py). HRMS (ES+): 352.1812 ($M + H^+$); calc. for $C_{24}H_{21}N_3+H^+$: 352.1813. Found C, 78.95, H, 5.90, N, 11.74; calc. for $C_{24}H_{21}N_3 \cdot H_2O$: C, 78.00, H, 6.27, N, 11.37%.

$[Ir(L^4)_2](PF_6)_3$

A mixture of iridium trichloride trihydrate (102 mg, 0.29 mmol) and 4′-(mesityl)-terpyridine (L^4) (200 mg, 0.57 mmol) in ethylene glycol (25 mL) was heated with stirring at 100 °C for 2.5 h, under an inert atmosphere of nitrogen. The temperature was then raised to 198 °C and heating continued for a further 1.5 h. After cooling to ambient temperature, the deep orange solution was added to a saturated aqueous solution of KPF_6, precipitating the hexafluorophosphate salt. Repeated recrystallisation from acetone and toluene yielded the desired complex as a pale yellow solid (150 mg, 40%). A sample for photophysical studies was chromatographed on a short column of alumina, gradient elution from CH_3CN to 80% CH_3CN/19% H_2O/1% KNO_3 (sat'd, aq). ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 9.16 (2H, s, $H^{3'}$), 9.02 (2H, d, ^3J 8.0, H^3), 8.39 (2H, t, ^3J 8.0, H^4), 8.21 (2H, d, ^3J 4.0, H^6), 7.66 (2H, dd, ^3J 8.0, 4.0, H^5), 7.19 (2H, s, H^a), 2.36 (6H, s, *ortho*-CH_3), 2.42 (3H, s, *para*-CH_3). ^{13}C NMR ($(CD_3)_2CO$): 143 (C^4), 130 (C^5), 129 (C^a), 128 ($C^{3'}$), 128 (C^6), 21.8 (*para*-CH_3), 21.0 (*ortho*-CH_3). ES-MS: *m*/*z* 298 (M^{3+}). HRMS-ES(+): *m*/*z* 1185.2384 $(M+2PF_6)^+$ (calcd for $C_{48}H_{42}N_6IrP_2F_{12}$: 1185.2378).

$[Ir(tpy)(tpy\text{-}\phi\text{-}Br)](PF_6)_3$

A mixture of $Ir(tpy)Cl_3$ (220 mg, 0.41 mmol) and 4′-bromophenylterpyridine (tpy-ϕ-Br) (159 mg, 0.41 mmol) in ethylene glycol (12 mL) was heated strongly until a clear red solution was obtained (15 min, oil temperature 215 °C). After cooling to ambient temperature, the solution was diluted with water (40 mL), and the small amount of red precipitate obtained {unreacted $Ir(tpy)Cl_3$} was separated off by centrifugation. The remaining solution was then treated with saturated aqueous KPF_6 (10 mL), precipitating the crude product as the hexafluorophosphate salt, which was collected and washed with water. Purification was achieved by column chromatography on silica, gradient elution from CH_3CN to 53% CH_3CN/45% H_2O/2% KNO_3 (sat'd, aq). Fractions containing the product were concentrated under reduced pressure and subject to a second metathesis with KPF_6, leading to the required complex (200 mg, 40%). ^{1}H NMR (500 MHz, CD_3CN): 9.05 (2H, s, $H^{3'}$ on tpy-ϕ-Br), 8.86 (2H, d, ^3J 8.5, $H^{3'}$ on tpy), 8.77 (1H, t, ^3J 8.5,

$H^{4'}$), 8.70 (2H, d, ^3J 8.0, H^3 on tpy-ϕ-Br), 8.59 (2H, d, ^3J 8.0, H^3 on tpy), 8.21 (4H, two overlapping t, H^4 on both terpyridines), 8.12 (2H, d, ^3J 8.5, H^b), 7.98 (2H, d, ^3J 8.5, H^a), 7.68 (2H, d, ^3J 5.5, H^6 on tpy or tpy-ϕ-Br), 7.59 (2H, d, ^3J 5.5, H^6 on tpy-ϕ-Br or tpy), 7.48 (4H, m, H^5 on both terpyridines). MS (ES+): *m*/*z* 813 (M^+), 407 (M^{2+}), 479 $(M+PF_6)^{2+}$. HRMS (EI): *m*/*z* 813.0939 (M^+), 271.0331 (M^{3+}); calc. for $C_{36}H_{25}BrN_6Ir$, M^+: 813.0955, M^{3+}: 271.0318.

$[Ir(tpy)L^1](PF_6)_3$

A Schlenk tube was charged with $[Ir(tpy)(tpy\text{-}ϕ\text{-}Br)](PF_6)_3$ (84 mg, 0.067 mmol), phenylboronic acid (17 mg, 0.14 mmol), sodium carbonate (22 mg, 0.20 mmol, dissolved in the minimum volume of water), and DMSO (6 mL) and the system was degassed *via* three freeze–pump–thaw cycles. $Pd(PPh_3)_4$ (5 mg, 4.2 μmol, 0.06 equiv.) was then added under a positive pressure of nitrogen and the mixture heated at 85 °C for 4 h, after which time, TLC indicated complete consumption of the starting material. A small amount of the free ligand L^1 was suspected to be present in the crude mixture, (based on comparison of the TLC with that for a previously prepared sample of the ligand [14]); this was readily removed by diluting the reaction mixture with water and washing with dichloromethane. Treatment of the aqueous solution with KPF_6 led to a precipitate, the NMR and ESMS of which revealed it to be a mixture of the desired product and a smaller amount of the homoleptic complex $[Ir(L^1)_2](PF_6)_3$. Separation was achieved using column chromatography on alumina; gradient elution from CH_3CN to 86.5% CH_3CN/12.0% H_2O/1.5% KNO_3 (sat'd, aq), eluting $[Ir(L^1)_2]^{3+}$, and subsequently to 77% CH_3CN/20% H_2O/3% KNO_3 (sat'd, aq), for elution of $[Ir(tpy)L^1]^{3+}$. Treatment with KPF_6 led to the complexes as their hexafluorophosphate salts: $[Ir(tpy)L^1](PF_6)_3$ (15 mg, 18%) and $[Ir(L^1)_2](PF_6)_3$ (8 mg, 9%).

Data for $[Ir(tpy)L^1](PF_6)_3$: ^{1}H NMR (500 MHz, CD_3CN): 9.13 (2H, s, $H^{3'}$ on L^1), 8.86 (2H, d, ^3J 8.0, $H^{3'}$ on tpy), 8.78 (1H, t, ^3J 8.0, $H^{4'}$ on tpy), 8.73 (2H, d, ^3J 8.0, H^3 on L^1), 8.59 (2H, d, ^3J 8.0, H^3 on tpy), 8.33 (2H, d, ^3J 8.5, H^b), 8.22 (4H, two overlapping t, H^4 both terpyridines), 8.10 (2H, d, ^3J 8.5, H^a), 7.87 (2H, d, ^3J 7.5, $H^{b'}$), 7.70 (2H, d, ^3J 5.5, H^6 on L^1), 7.59 (4H, overlapping m, H^6 on tpy and $H^{a'}$), 7.49 (5H, overlapping m, H^5 on both terpyridines and $H^{c'}$). MS (ES+): *m*/*z* 270 (M^{3+}), 478 $(M+PF_6)^{2+}$. HRMS (ES+): 270.4152 (M^{3+}). calc. for $C_{42}H_{30}N_6Ir$, M^{3+}: 270.4055.

Data for $[Ir(L^1)_2](PF_6)_3$: ^{1}H NMR (500 MHz, CD_3CN): 9.14 (2H, s, $H^{3'}$), 8.75 (2H, d, ^3J 8.0, H^3), 8.34 (2H, d, ^3J 8.5, H^b), 8.25 (2H, t, ^3J 8.0, H^4), 8.10 (2H, d, ^3J 8.5, H^a), 7.87 (2H, d, ^3J 7.5, $H^{b'}$), 7.73 (2H, d, ^3J 5.0, H^6), 7.59 (2H, t, ^3J 7.5, $H^{a'}$), 7.51 (3H, two overlapping m, H^5 and $H^{c'}$). MS (ES+): *m*/*z* 321 (M^{3+}).

$[Ir(tpy)L^2](PF_6)_3$ – method 1

The procedure was similar to that described above, in this case using 4-cyanobenzene boronic acid (8.8 mg, 0.06 mmol), $[Ir(tpy)(tpy\text{-}ϕ\text{-}Br)](PF_6)_3$ (40 mg, 0.032 mmol), sodium carbonate (9.5 mg, 0.09 mmol), $Pd(PPh_3)_4$ (2 mg, 1.8 μmol, 0.06 equiv.), in DMSO (5 mL). After 2 h at 80 °C, TLC indicated complete consumption of the starting material. Following anion exchange upon treatment with $KPF_{6(aq)}$, analysis of the crude product by ^{1}H NMR indicated that the desired complex was contaminated with the free ligand L^2, as well as a trace of $[Ir(tpy)_2]^{3+}$. The former was removed by passage through a small column of alumina (Brockman I), initially eluting with hexane/ethyl acetate to remove L^2, and then switching to acetonitrile/water, to elute the mixture of complexes. These two complexes were subsequently separated by chromatography on alumina (Brockman II–III); gradient elution from CH_3CN to 87% CH_3CN/12% H_2O/1% KNO_3 (sat'd, aq). After treatment with $KPF_{6(aq)}$, the desired complex was obtained as the hexafluorophosphate salt (15 mg, 36%).

^{1}H NMR (500 MHz, CD_3CN): 9.13 (2H, s, $H^{3'}$ on L^2), 8.86 (2H, d, ^3J 7.5, $H^{3'}$ on tpy), 8.78 (1H, t, ^3J 7.5, $H^{4'}$), 8.73 (2H, d, ^3J 8.0, H^3 on L^2), 8.59 (2H, d, ^3J 8.0, H^3 on tpy), 8.35 (2H, d, ^3J 8.5, H^b), 8.23 (4H, two overlapping t, H^4 on both terpyridines), 8.14 (2H, d, ^3J 8.5, H^a), 8.02 (2H, d, ^3J 8.5, $H^{b'}$), 7.95 (2H, d, ^3J 8.5, $H^{a'}$), 7.69 (2H, d, ^3J 5.0, H^6 on L^2 or tpy), 7.59 (2H, d, ^3J 4.5, H^6 on L^2 or tpy), 7.49 (4H, two overlapping dd, H^5 on both ligands). MS (ES+): *m*/*z* 278 (M^{3+}), 490 $(M^+ + PF_6)^{2+}$. HRMS (ES+): 270.7350 (M^{3+}). calc. for $C_{43}H_{29}N_7Ir$, M^{3+}: 278.7373.

$[Ir(tpy)L^2](PF_6)_3$ – method 2

A mixture of L^2 (prepared as described previously [14]) (55 mg, 0.13 mmol) and $Ir(tpy)Cl_3$ (74 mg, 0.14 mmol) in ethylene glycol (6 mL) was heated with stirring at 215 °C for 20 min. After cooling to ambient temperature, the clear red solution was diluted with water, and treated with $KPF_{6(aq)}$, to precipitate the crude product as a yellow solid, which was collected and washed with water. Purification was achieved by chromatography on silica, gradient elution from CH_3CN to 68% CH_3CN/30% H_2O/2% $KNO_{3(aq)}$; product-containing fractions were treated with $KPF_{6(aq)}$, leading to the desired complex (76 mg, 43%). ^{1}H NMR and ESMS data were consistent with those given above.

$[Ir(tpy)L^3](PF_6)_3$

The procedure was similar to that described above for $[Ir(tpy)L^1]^{3+}$, in this case starting from 4-(*N*,*N*-dimethylamino)-benzeneboronic acid, (26 mg, 0.16 mmol), $[Ir(tpy)(tpy\text{-}ϕ\text{-}Br)](PF_6)_3$ (100 mg, 0.080 mmol), sodium carbonate (25 mg, 0.24 mmol, dissolved in the minimum volume of H_2O) and $Pd(PPh_3)_4$ (5.4 mg, 4.8 μmol, 0.06 equiv.) in DMSO (12 mL). The mixture was heated at 85 °C for 12 h, the progress of the reaction being monitored by TLC. After anion exchange with potassium hexafluorophosphate, the crude product was found to contain the desired compound, together with small amounts of the two homoleptic complexes $[Ir(L^3)_2]^{3+}$ and $[Ir(tpy)_2]^{3+}$. The former was readily removed by chromatography on alumina, gradient elution from CH_3CN to 95% CH_3CN/5% H_2O; however, a further column was required to separate all traces of $[Ir(tpy)]_2^{3+}$, together with an unidentified, bright yellow fluorescent impurity; gradient elution from 50% CH_3CN/50% $(CH_3)_2CO$ to 41% CH_3CN/41% $(CH_3)_2CO$/16% H_2O/2% KNO_3. The fractions containing the product were concentrated and treated with $KPF_{6(aq)}$, leading to the desired complex as the hexafluorophosphate salt (17 mg, 26%). ^{1}H NMR (500 MHz, CD_3CN): 9.11 (2H, s, $H^{3'}$ on L^3), 8.86 (2H, d, ^3J 8.5, $H^{3'}$ on tpy), 8.77 (1H, t, ^3J 8.5, $H^{4'}$), 8.73 (2H, d, ^3J 8.0, H^3 on L^3), 8.59 (2H, d, ^3J 8.0, H^3 on tpy), 8.27 (2H, d, ^3J 8.5, H^b), 8.21 (4H, two overlapping t, approx. ^3J 8.0, H^4 on both terpyridines), 8.04 (2H, d, ^3J 8.5, H^a), 7.76 (2H, d, ^3J 8.5, $H^{b'}$), 7.70 (2H, d, ^3J 5.5, H^6 on L^3 or tpy), 7.59 (2H, d, ^3J 5.5, H^6 on tpy or L^3), 7.48 (4H, two overlapping dd, H^5 on both terpyridines), 6.91 (2H, d, ^3J 8.5, $H^{a'}$), 3.06 (6H, s, CH_3). MS (ES+): *m*/*z* 427 M^{2+}, 499 $(M+PF_6)^{2+}$.

Photophysical measurements

Absorption spectra were measured on a Biotek Instruments XL spectrometer, using quartz cuvettes of 1 cm path-length. Steady-state luminescence spectra at room tempertaure were measured using a Jobin Yvon FluoroMax-2 spectrofluorimeter and those at 77 K with a Perkin-Elmer LS50B instrument. Both instruments were fitted with red-sensitive Hamamatsu R928 photomultiplier tubes; the spectra shown are corrected for the wavelength dependence of the detectors, 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 less than 10^{-3} mbar, as monitored using a Pirani gauge.

Samples for time-resolved measurements were excited at 355 nm using the third harmonic of a Q-switched Nd:YAG laser and the luminescence detected with a Hamamatsu R928 photomultiplier tube and recorded using a digital storage oscilloscope, before transfer to a PC for analysis; estimated uncertainty in quoted lifetimes is ±10% or better. Low temperature measurements were made using an Oxford Instruments DN1704 cryostat, with helium as the inert atmosphere.

Crystallography

The X-ray diffraction experiment was carried out on a Bruker 3-circle diffractometer with a SMART 1K CCD area detector, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and a Cryostream (Oxford Cryosystems) open-flow N_2 cryostat. *Crystal data for* L^4*:* $C_{24}H_{21}N_3$, M = 351.44, T = 120 K, orthorhombic, space group *Pbcn* (no. 60), a = 8.217(1), b = 13.359(1), c = 17.167(1) Å, U= 1884.4(3) Å^3, Z = 4, D_c = 1.239 g cm^{-3}, μ = 0.07 mm^{-1}. A full sphere of reciprocal space was covered by 5 sets of narrow (0.3°) ω scans, each set with different ϕ and/or 2θ angles, yielding 19602 reflections with $2\theta \leq$ 55°, of which 2177 were independent (R_{int} = 0.050). The structure was solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL software. The refinement of 173 parameters converged at R = 0.046 [for 1728 reflections with $F^2 \geq \sigma(F^2)$] and w$R(F^2)$ = 0.119 [for all data].

CCDC reference number 222965.

See http://www.rsc.org/suppdata/dt/b3/b313638h/ for crystallographic data in CIF or other electronic format.

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