

**Luminescent bis-tridentate iridium(III) complexes:
Overcoming the undesirable reactivity of *trans*-disposed metallated rings
using $N^{\wedge}N^{\wedge}N^{\wedge}$ -coordinating bis(1,2,4-triazolyl)pyridine ligands**

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Abstract

Nine new iridium(III) complexes featuring two tridentate ligands have been synthesised of the form $\text{Ir}(N^{\wedge}C^{\wedge}N)(N^{\wedge}N^{\wedge}N^{\wedge})$, where $N^{\wedge}C^{\wedge}N$ represents a cyclometallating ligand based on 1,3-di(2-pyridyl)benzene and $N^{\wedge}N^{\wedge}N^{\wedge}$ is a doubly deprotonated bis(1,2,4-triazolyl)pyridine. Three examples of each ligand have been used, with different substituents in the central aryl ring of the former and *para*-substituted aryl groups in the 5-positions of the triazole rings of the latter. Two of the complexes have been structurally characterised in the solid-state by X-ray diffraction, confirming the mutually orthogonal arrangement of the two ligands. Unlike related tris-cyclometallated complexes of the type $\text{Ir}(N^{\wedge}C^{\wedge}N)(C^{\wedge}N^{\wedge}C)$, which are unstable with respect to photoactivated cleavage of the *trans*-disposed Ir–C bonds, the new complexes show no evidence of instability. They are phosphorescent in the green region of the spectrum with lifetimes around 200 ns and quantum yields up to 3%, apparently limited by non-radiative decay processes in particular. Although there is some variation in performance with substitution pattern, the only discernible trend is that complexes of the 4-methoxy-substituted $N^{\wedge}C^{\wedge}N$ ligand are the better emitters. Three examples of related complexes of the form $\text{Ir}(N^{\wedge}C^{\wedge}N)(N^{\wedge}N^{\wedge})\text{Cl}$ – incorporating a bidentate 1,2,4-triazolylpyridine – have also been prepared. They show no room-temperature emission but the properties at 77 K are similar to those of the bis-tridentate systems.

Keywords

Iridium; cyclometalated; tridentate ligand; triazole; luminescence; crystal structure.

Introduction

Research into the light-emitting properties of iridium(III) complexes with cyclometallating ligands has been intense over the last two decades. The use of Ir(III) provides access to phosphorescent complexes that emit with almost 100% efficiency from triplet states, thanks to the efficient spin-orbit coupling induced by the presence of the metal ion.¹ Much of the interest has centred around organic light-emitting diodes (OLEDs)² and light-emitting electrochemical cells (LEECs)³ though other applications have been envisaged too, such as in time-resolved bio-imaging,⁴ photodynamic therapy,⁵ photocatalysis,⁶ and light-to-chemical energy conversion.⁷ The vast majority of studies have focused on tris-bidentate complexes, often based on the archetypal structure *fac*-Ir(*N*[^]*C*-ppy)₃ in which iridium is cyclometallated to three 2-phenylpyridine ligands.⁸ A range of other monoanionic bidentate ligands have also been investigated,⁹ including those based on a variety of azoles in which deprotonation of an N–H unit occurs upon complexation to the metal ion.¹⁰

There has been far less investigation of Ir(III) complexes featuring tridentate ligands, though interest in them is certainly increasing. Early examples included [Ir(*N*[^]*N*[^]*N*-tpy)₂]³⁺ and derivatives, whose preparation required arduous purification,¹¹ and the bis-cyclometallated [Ir(*C*[^]*N*[^]*C*-dppy)(*N*[^]*N*[^]*N*-tpy)]⁺.¹² Neither of these classes of complex are in the same league as *fac*-Ir(ppy)₃ in terms of emission efficiency. In the first instance, the tricationic nature of the complex results in the metal orbitals being too low in energy to mix well with the ligand orbitals, so the emissive excited state has predominantly ligand-centred character. In the latter, the HOMO and LUMO are localised on different parts of the molecule (the dppy and tpy ligand respectively) resulting in little orbital overlap and a low radiative rate constant. Some *N*[^]*N*[^]*C*-coordinated complexes displayed more promising performance.¹³ We showed that some much more brightly luminescent complexes could be prepared by using *N*[^]*C*[^]*N*-

coordinating ligands based on 1,3-di(2-pyridyl)benzene (dpybH).¹⁴ Whilst dpyb itself binds as an N^2C ligand through the C^4 position of the central ring, the incorporation of substituents such as CH_3 , CF_3 , or F at the $C^{4/6}$ positions forces the ligand into an N^2C^2N binding mode (Fig. 1).¹⁵ Even a single substituent such as *t*-butyl or CF_3 at the C^5 position is sufficient to sterically disfavor the competitive metallation at C^4 .¹⁶ Indeed, it has recently been shown that dpyb itself can also be made to bind to Ir(III) in the N^2C^2N mode through the use of a mercurated precursor.¹⁷

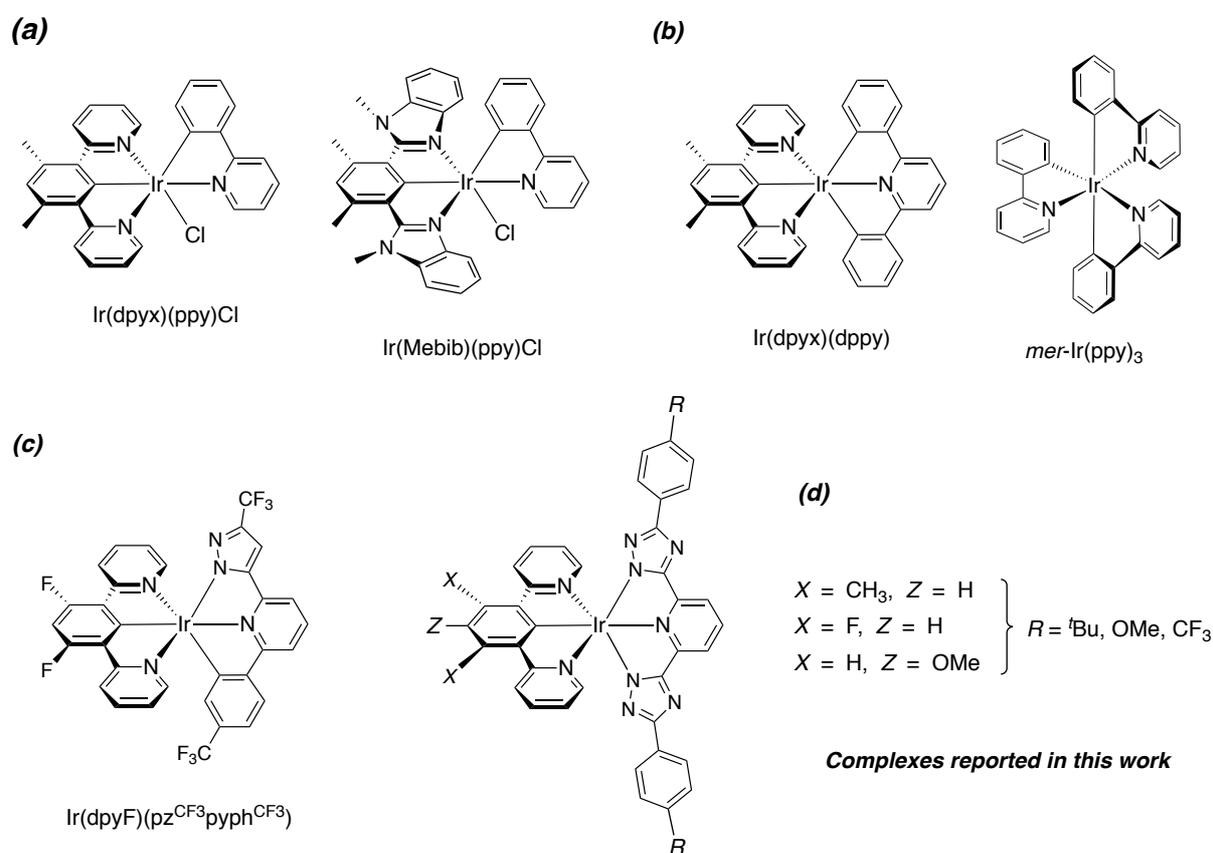


Figure 1 (a) Complexes of the form $Ir(N^2C^2N)(N^2C)Cl$ featuring an N^2C^2N -coordinating dipyridylbenzene or bis(benzimidazole)benzene. (b) $Ir(N^2C^2N)(C^2N^2C)$ complexes, such as $Ir(dpyx)(dppy)$ shown here, are unstable due to the presence of *trans*-diposed Ir–C bonds, an effect also observed for the same reason for *mer*- $Ir(ppy)_3$ (also shown). (c) An example of a brightly emissive $Ir(N^2C^2N)(C^2N^2N)$ complex from the group of Chi. (d) General formula of the new class of $Ir(N^2C^2N)(C^2N^2N)$ complexes reported in this work, and the substitution pattern in the nine examples described.

Charge-neutral complexes of the form $\text{Ir}(N^{\wedge}C^{\wedge}N)(N^{\wedge}C)\text{Cl}^{15\text{b,c}}$ (Fig. 1a), as well as dinuclear analogues,¹⁸ have been prepared using this strategy and shown to have high photoluminescence quantum yields in solution and in OLED devices. Related complexes based on 1,3-bis(benzimidazole)benzene, as opposed to 1,3-dipyridylbenzene, have been explored by Haga and co-workers.¹⁹ Yet, the presence of the monodentate halide is undesirable for many practical applications where chemical stability is key. Bis-tridentate complexes might therefore be expected to be more attractive in that respect. Nevertheless, the obvious target, $\text{Ir}(N^{\wedge}C^{\wedge}N)(C^{\wedge}N^{\wedge}C\text{-dppy})$ (Fig. 1b), proved to have profound drawbacks. The high *trans* influence of the *trans*-disposed Ir–C bonds (in the $C^{\wedge}N^{\wedge}C$ ligand) facilitates the photoactivated cleavage of one of these bonds, which not only compromises emission efficiency but also leads to irreversible degradation.^{15a} This behaviour is reminiscent of that of *mer*- $\text{Ir}(\text{ppy})_3$, which likewise has a pair of photolabile, *trans*-disposed Ir–C bonds (Fig. 1b).^{8b}

Recently, Chi and co-workers have made great progress in the design of related complexes, using dianionic $C^{\wedge}N^{\wedge}N$ -coordinating ligands in place of the dianionic $C^{\wedge}N^{\wedge}C$ -binding ligand dppy.^{16,20} These ligands are based on 2-pyrazol-3-yl-6-phenylpyridine with substituents in the pyrazole or phenyl ring. The *trans* influence associated with the deprotonated, coordinated pyrazole is not as strong as that of a metallated phenyl ring: the resulting complexes are stable and highly luminescent, and some have been tested successfully as OLED emitters.²⁰ Further improvements, giving impressive devices with EQE > 20%, were subsequently achieved by using monoanionic $:C^{\wedge}C^{\wedge}C:$ carbene ligands in place of the $N^{\wedge}C^{\wedge}N$ ligands.²¹ Very recently, the pyrazolyl-based ligands have also been used in conjunction with $N^{\wedge}N^{\wedge}C$ -coordinating phenylbipyridines in a study by Tong and co-workers.²²

In this contribution, we describe our investigations into the viability of 2,6-bis(1,2,4-triazolyl)pyridines as $\text{N}^-\text{N}^-\text{N}^-$ -coordinating alternatives to dppy in the preparation of charge-neutral, bis-tridentate Ir(III) complexes that are more stable than $\text{Ir}(\text{N}^-\text{C}^-\text{N}^-)(\text{C}^-\text{N}^-\text{C}^-)$ -dppy). These studies were motivated in part by our recent work on Pt(II) complexes with bidentate pyridyltriazole ligands, wherein a set of charge-neutral $\text{Pt}(\text{N}^-\text{N}^-)_2$ complexes were developed and incorporated successfully into OLEDs.²³ That work revealed a mutually *trans* disposition of the deprotonated azoles in the crystal structures of the complexes, suggesting that the *trans* influence of triazoles is relatively weak and should not compromise stability. Furthermore, a number of Pt(II) complexes with bis-(1,2,4-triazolyl)pyridine ligands have previously been reported, of the form $\text{Pt}(\text{N}^-\text{N}^-\text{N}^-)\text{L}$ (where *L* is a neutral ligand such as a pyridine or isonitrile).²⁴ They are stable despite featuring *trans*-related deprotonated triazoles.

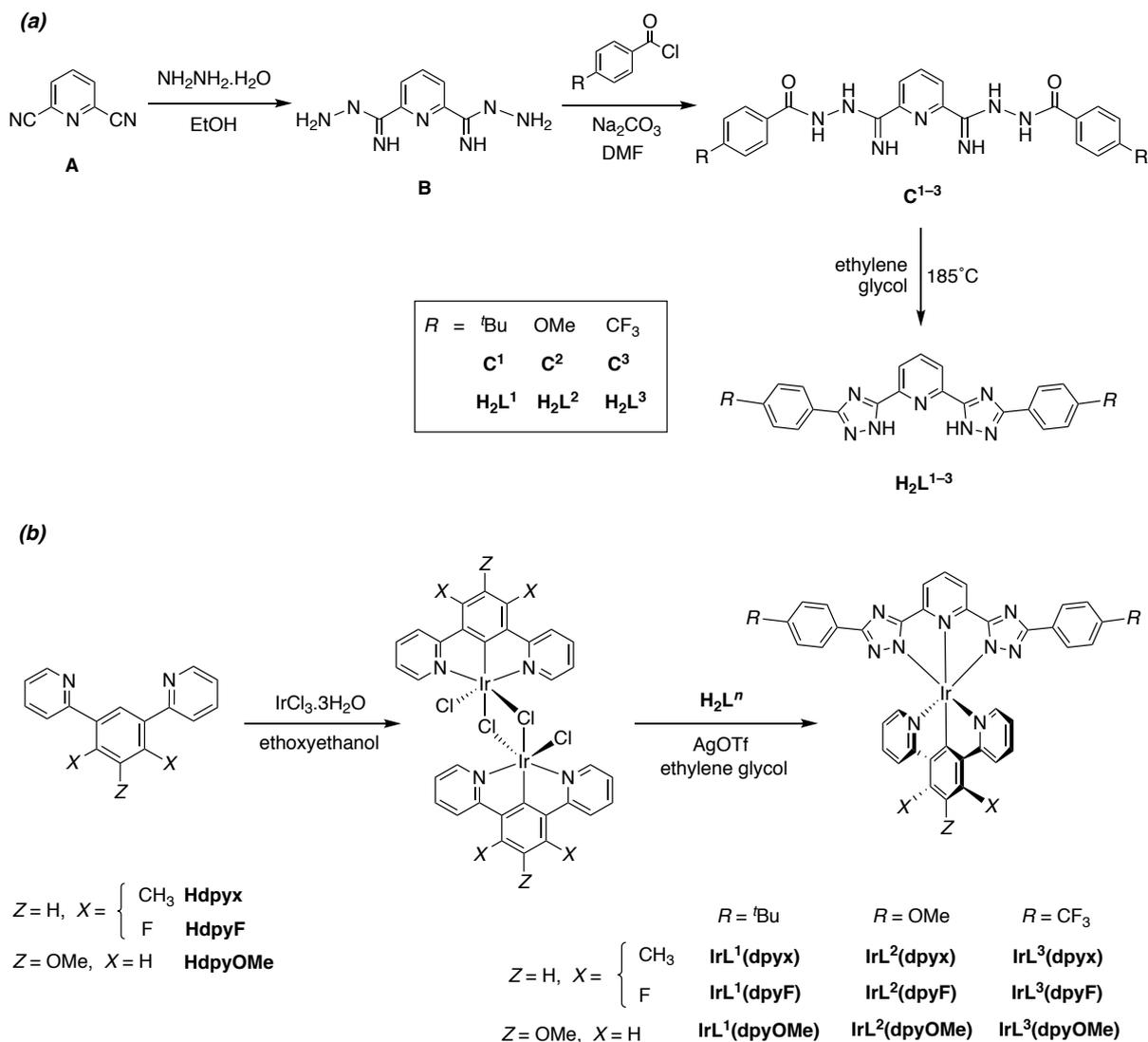
Results and Discussion

Synthesis of proligands and complexes

The complexes chosen for synthesis have the generic structure $\text{Ir}(\text{N}^-\text{C}^-\text{N}^-)(\text{N}^-\text{N}^-\text{N}^-)$, where $\text{N}^-\text{C}^-\text{N}^-$ represents a 1,3-dipyridylbenzene derivative and $\text{N}^-\text{N}^-\text{N}^-$ is a bis-(1,2,4-triazolyl)-pyridine appended with functionalised aryl groups at the 5-positions of the triazoles. In order to facilitate an assessment of the influence of each type of ligand on the excited state properties, we selected three different derivatives of each ligand, giving a total of nine target complexes as summarised in Fig. 1(d). The dpyb derivatives are (i) 1,3-dipyridyl-*meta*-xylene (dpyx), to allow comparison with the original studies on $\text{Ir}(\text{N}^-\text{C}^-\text{N}^-)$ systems that used this ligand;¹⁵ (ii) the fluorinated analogue, dpyF, incorporating two electron-withdrawing F atoms in place of the methyl groups of dpyx;²⁵ and (iii) a 5-methoxy derivative, dpyOMe,²⁶ that has not previously been reported in combination with Ir(III). Meanwhile, the bis-(1,2,4-triazolyl)pyridine ligands carry *t*-butyl, methoxy (electron-donating), or trifluoromethyl

(electron-withdrawing) substituents (L^1 , L^2 , and L^3 respectively) at the *para* positions of the phenyl rings.

The bis-(1,2,4-triazolyl)pyridine proligands H_2L^1 , H_2L^2 and H_2L^3 were prepared using a 3-step procedure based on that described by Hergenrother for the synthesis of the parent compound with unsubstituted phenyl pendants (Scheme 1a).²⁷ Treatment of pyridine-2,6-dicarbonitrile **A** with hydrazine gives the bis-imidrazone **B**, which reacts readily with the appropriate *para*-substituted acyl halide $R-C_6H_4COCl$ ($R = 'Bu, OMe$ or CF_3) to form an imino hydrazide intermediate **C**¹⁻³. A thermally-activated cyclo-condensation at 185°C in ethylene glycol then generates the two triazole rings and thus the desired proligands. The dipyridylbenzene derivatives Hdpyx, HdpyF and HdpyOMe were prepared by Pd-catalysed Stille cross-coupling of the appropriately functionalised dibromobenzene with 2-(tri-*n*-butylstannyl)pyridine, as reported previously.^{15a,e}

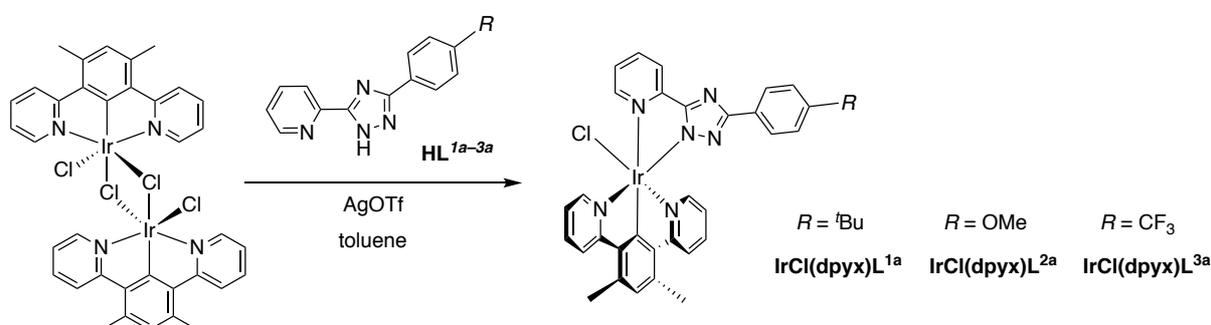


Scheme 1 (a) Synthetic route to the bis-triazolylpyridine proligands H_2L^1 , H_2L^2 , and H_2L^3 via the corresponding intermediates C^1 , C^2 , and C^3 . (b) Preparation of the nine new Ir(III) complexes via $[\text{Ir}(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})\text{Cl}(\mu\text{-Cl})]_2$.

The nine new iridium complexes were prepared via the intermediacy of chloro-bridged dimers of the form $[\text{Ir}(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})\text{Cl}(\mu\text{-Cl})]_2$, obtained upon treatment of the dipyridylbenzene-based proligands with $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (Scheme 1b). Cleavage of the chloro bridges with H_2L^{1-3} to generate the desired complexes in good yields was achieved in ethylene glycol at high temperatures (185°C) in the presence of AgOTf as a chloride scavenger. No reaction was observed in lower-boiling solvents such as toluene, despite the fact that cyclometallating ligands such as ppy can be introduced in this way.^{15b,e} The complexes were isolated by

precipitation from water and purified by a sequence of washes followed by chromatography on a short column of silica. The yields were in excess of 50% in all but one case. The observation that these complexes showed no evidence of degradation – neither during chromatography nor over prolonged periods in solution in ambient light – directly supports our starting hypothesis: the *trans* effect associated with the deprotonated azoles is evidently weaker in these complexes compared to the structurally analogous $\text{Ir}(N^{\wedge}C^{\wedge}N)(C^{\wedge}N^{\wedge}C)$ systems, which decomposed rapidly under comparable conditions.^{15a,b}

Three analogues of the dpyx complexes were also prepared that incorporate a bidentate $N^{\wedge}N$ -coordinating ligand, in place of the corresponding tridentate $N^{\wedge}N^{\wedge}N$ ligand, with the coordination sphere completed by a monodentate chloride ligand in each case (Scheme 2). These complexes – $\text{IrCl}(\text{dpyx})\text{L}^{1a}$, $\text{IrCl}(\text{dpyx})\text{L}^{2a}$, and $\text{IrCl}(\text{dpyx})\text{L}^{3a}$ – were prepared by reaction of $[\text{Ir}(\text{dpyx})\text{Cl}(\mu\text{-Cl})]_2$ with the bidentate ligands HL^{1a-3a} in refluxing toluene in the presence of AgOTf . Whilst the yield of the first of these was high, the formation of the other two complexes was accompanied by the formation of a number of unidentified side products. Multiple recrystallizations were required in order to obtain analytically pure material, leading to poor overall isolated yields.



Scheme 2 Preparation of $\text{IrCl}(\text{dpyx})\text{L}^{1a-3a}$, analogues of $\text{Ir}(\text{dpyx})\text{L}^{1-3}$ that feature one tridentate, one bidentate and one monodentate ligand.

Structural characterisation of representative complexes

Single crystals of the bis-bidentate complexes $\text{IrL}^1(\text{dpyx})$ and $\text{IrL}^1(\text{dpyF})$, suitable for X-ray diffraction analysis, were obtained by slow diffusion of hexane into solutions of the complexes in dichloromethane. The bis-tridentate nature of $\text{IrL}^1(\text{dpyF})$ with mutually orthogonal chelates is confirmed (Fig. 2). The Ir–C bond is shorter than the central Ir–N^{py} bond to the $\text{N}^{\wedge}\text{N}^{\wedge}\text{N}^-$ ligand, in line with the high *trans* influence associated with the Ir–C bond and as observed in numerous cyclometallated complexes. For the $\text{N}^{\wedge}\text{N}^{\wedge}\text{N}^-$ ligand, the Ir–N^{trz} bonds are slightly shorter than the Ir–N^{py}. The N–Ir–N angle for this ligand is 5° smaller than the corresponding angle for the $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ ligand, consistent with coordination to 5- as opposed to 6-membered heterocyclic rings. The complexes pack head-to-tail in the crystal and the planes of the ligands in neighbouring complexes are parallel to one another (Fig. S1 in the Supporting Information). The quality of X-ray data for $\text{IrL}^1(\text{dpyx})$ was not sufficient to allow full quantitative analysis, but it does unequivocally confirm the identity of the complex and the mutually orthogonal ligand planes (Fig. S2 in the Supporting Information).

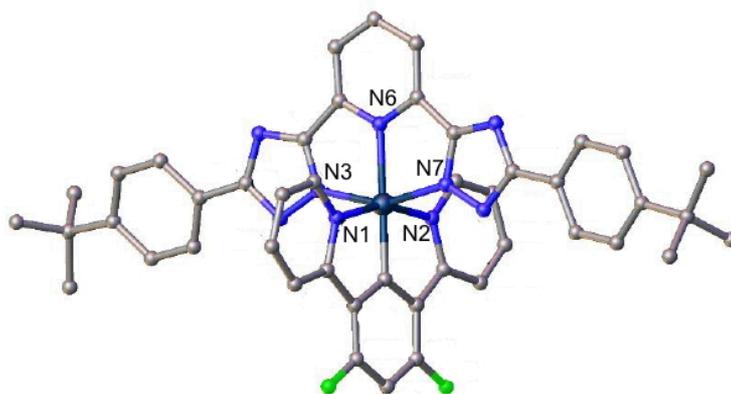


Figure 2. Molecular structure of $\text{IrL}^1(\text{dpyF})$ with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ir–N1 2.049(3); Ir–N2 2.050(3); Ir–N3 2.032(3); Ir–N6 2.066(3); Ir–N7 2.033(3); Ir–C7 1.937(4); N1–Ir–N2 160.02(12); N7–Ir–N3 155.05(12); 178.95(14).

Photophysical properties

The UV-visible absorption and emission spectra of the complexes in dichloromethane solution at room temperature are shown in Figures 3 and 4, and associated data are compiled in Table 1. The identity of the substituents on the $N^{\wedge}C^{\wedge}N$ ligand has a much more significant influence on the optical properties than those on the $N^{\wedge}N^{\wedge}N$ ligand. The spectra have therefore been grouped accordingly in Figures 3 and 4, to highlight the effect of the $N^{\wedge}C^{\wedge}N$ ligand whilst the L^n ligand remains constant within each group of three complexes.

The absorption spectra (Fig. 3) are quite typical, in their general form, of cyclometallated complexes of aromatic ligands, with a set of very intense bands at $\lambda < 330$ nm (ϵ of the order $40,000 \text{ M}^{-1} \text{ cm}^{-1}$) due to π - π^* transitions within the ligands, accompanied by a set of somewhat weaker bands ($\epsilon < 10,000 \text{ M}^{-1} \text{ cm}^{-1}$) at longer wavelength that are absent from the spectra of the proligands. The latter are typically attributed to charge-transfer transitions of mixed $d_M | \pi_L \rightarrow \pi_L^*$ character (*i.e.*, MLCT/LLCT).²⁸ Within each group of complexes with a given L^n ligand, the bands at $\lambda > 350$ nm shift further to the red in the order dpyF < dpyx < dpyOMe. Such a trend is anticipated for transitions in which the central aryl ring of the $N^{\wedge}C^{\wedge}N$ ligand and the metal participate in the filled molecular orbital involved in the underlying transition, reflecting the increasingly electron-donating nature of the substituents which destabilise the filled orbitals. Indeed, this trend mirrors that observed in $\text{Ir}(N^{\wedge}C^{\wedge}N)(\text{ppy})\text{Cl}$ complexes^{15e} and many of the large number of $\text{Ir}(\text{ppy})_3$ -based complexes that have been studied with electron-withdrawing and -releasing substituents in the aryl ring.²⁹

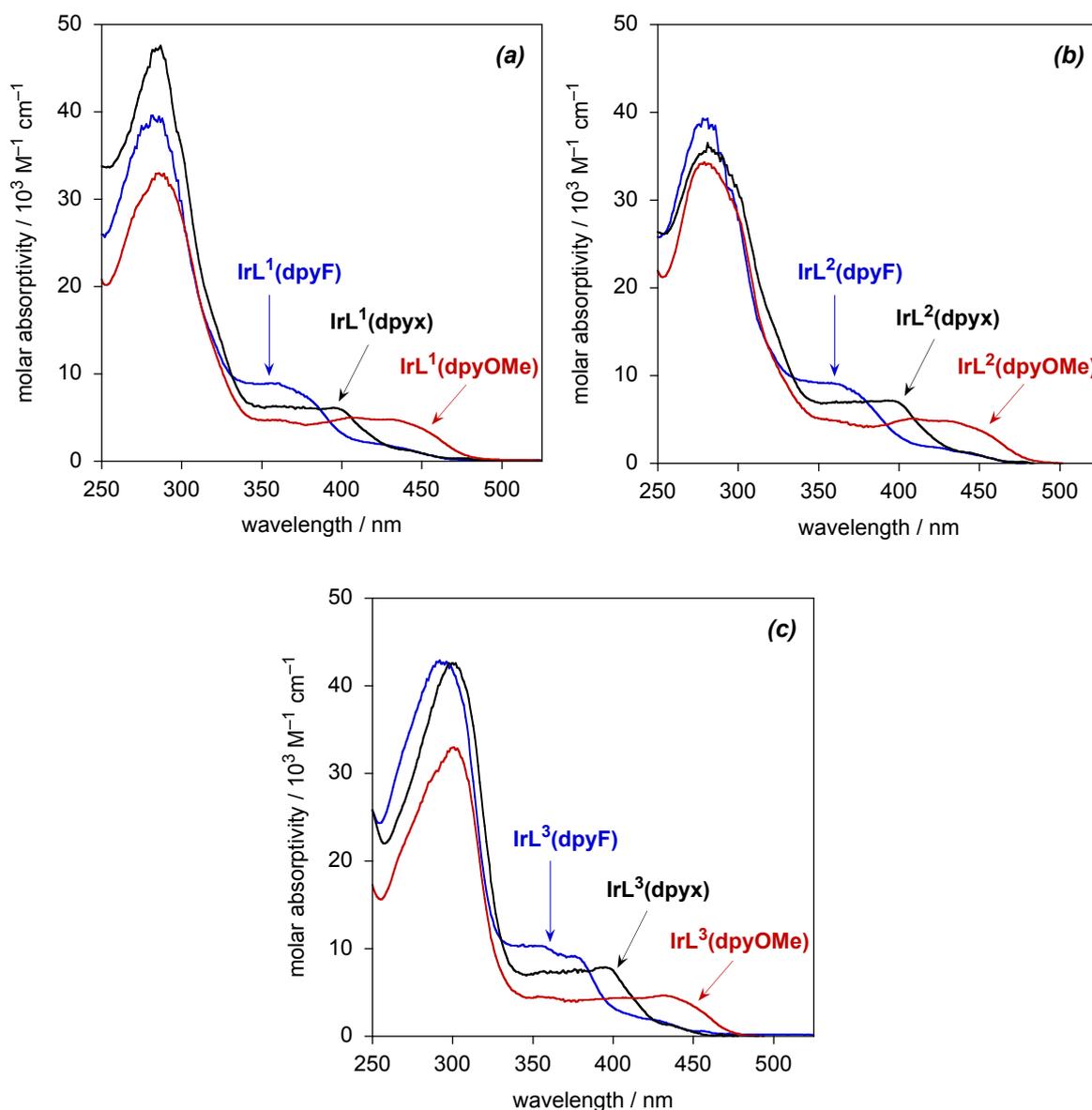


Figure 3 UV-visible absorption spectra of (a) the L^1 series of bis-tridentate complexes, (b) the L^2 series, and (c) the L^3 series, in solution in dichloromethane at 295 ± 3 K.

All nine complexes are luminescent in deoxygenated dichloromethane solution at room temperature (Figure 4 and Table 1); the perceived colour is blue-green for those of dpyF and dpyx, and green-yellow for the three dpyOMe complexes. The spectra of the dpyOMe complexes show quite well-defined vibrational structure with the 0,0 component being the most intense. The structure is less clear-cut for the other complexes, and the 0,0 component appears as a shoulder to the high-energy side of the emission maximum. At 77 K (Figure 4d-

f), the vibrational structure becomes well-resolved for all of the complexes, with a small blue-shift in the 0,0 band relative to that at room temperature. The emission maxima of the dpyOMe complexes are noticeably red-shifted relative to those of the other two N[^]C[^]N ligands, reflecting the trend in absorption, though there is little difference between the dpyF and dpyx complexes for a given Lⁿ ligand.

There is no evidence of the rapid photodecomposition exhibited by Ir(dpyx)(dppy), confirming that the problematic *trans* labilisation effect of the metallated aryl rings in that system is alleviated. But, this does not translate into a superior quantum yield. On the contrary, the values for the new complexes are an order of magnitude lower. The best performance is observed for the complexes with the dpyOMe ligand (up to 3%) and for IrL²(dpyF), but the values are inferior to many cyclometallated iridium(III) complexes. Moreover, the luminescence lifetimes are shorter, of the order of a few hundred nanoseconds. Taken together, these data are indicative of emission being compromised by rapid, competitive non-radiative decay. Estimates of the radiative k_r and non-radiative Σk_{nr} rate constants can be made, assuming that the emitting state is formed with unit efficiency, through the relationships $k_r = \Phi / \tau$ and $k_{nr} = (1-\Phi) / \tau$. The k_r values are in the range 10^4 – 10^5 s⁻¹, rather smaller than typical values for efficient green-emitting Ir(III) emitters in the range 10^5 – 10^6 s⁻¹.^{9,10,30} But, more strikingly, Σk_{nr} are all $> 2 \times 10^6$ s⁻¹, far higher than those of the best Ir(III) emitters; *e.g.*, for *fac*-Ir(ppy)₃, the value is around 100× lower than that.³⁰ At 77K, all of the complexes emit brightly with similar lifetimes to one another, in the range 10 – 18 μs.

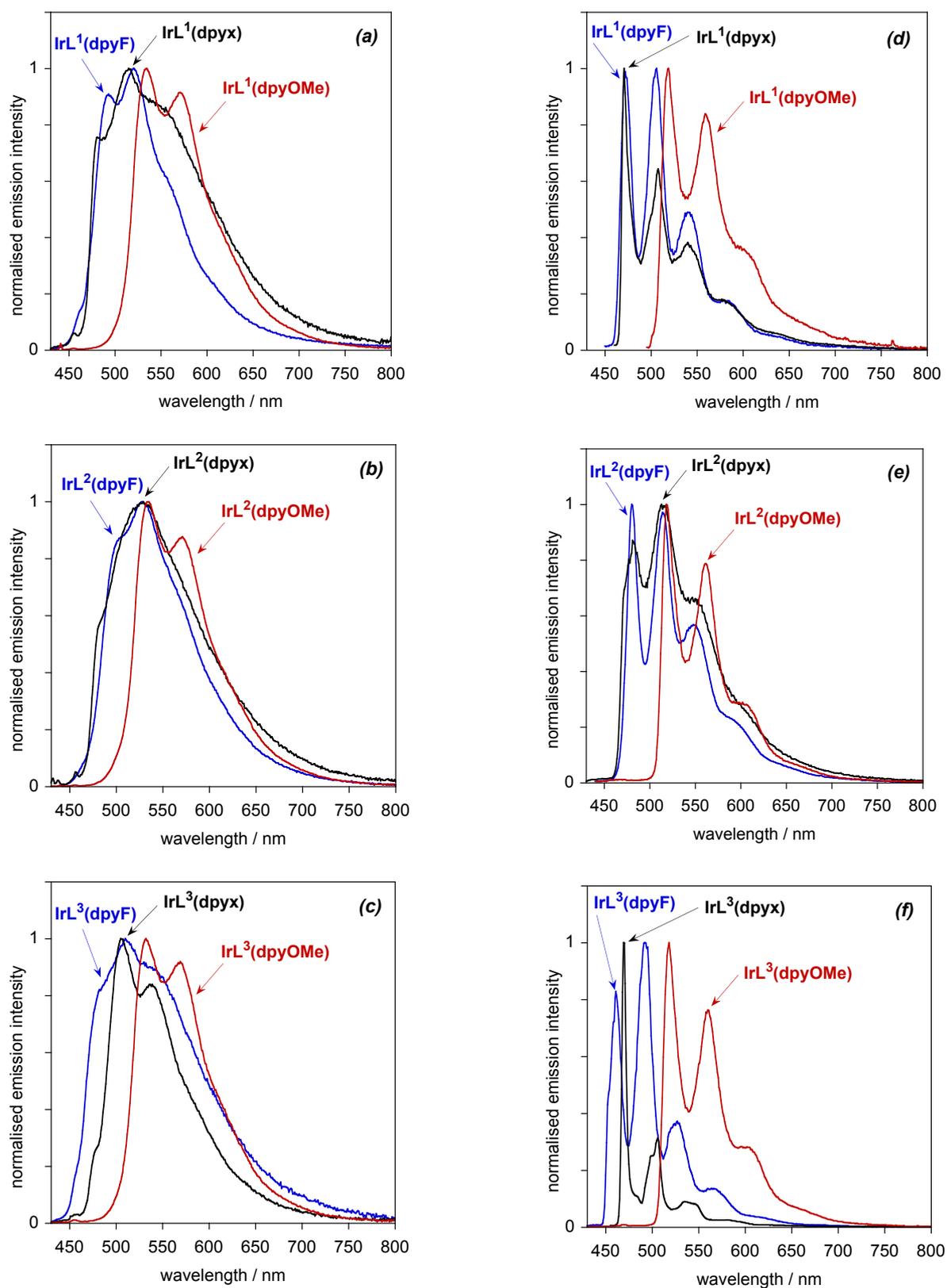


Figure 4 Photoluminescence spectra of (a) the L^1 series of complexes, (b) the L^2 series, and (c) the L^3 series, in deoxygenated dichloromethane solution at 295 K. The corresponding spectra at 77 K in butyronitrile are shown in plates (d) – (f).

Table 1 Photophysical properties of the bis-tridentate Ir(III) complexes in dichloromethane solution at 295 K except where stated otherwise.

Complex	Absorption at 295 K λ_{\max} / nm (ϵ / $\text{M}^{-1} \text{cm}^{-1}$)	Emission at 295 K						Emission at 77 K ^(e)	
		λ_{\max} / nm	Φ_{lum} ^(a) /10 ⁻²	τ / ns ^(b)	k_r ^(c) / 10 ³ s ⁻¹	Σk_{nr} ^(c) / 10 ³ s ⁻¹	$k_Q^{\text{O}_2}$ ^(d) / 10 ⁹ M ⁻¹ s ⁻¹	λ_{\max} / nm	τ / ns
IrL ¹ (dpyx)	285 (47000), 395 (6100), 439sh (1280)	479, 515, 547sh	0.38	110 [76]	34	9100	1.8	472, 508, 539, 580	12000
IrL ¹ (dpyF)	284 (39000), 355 (8920), 424sh (1930)	491, 520, 556sh	0.80	74 [55]	110	13000	2.1	472, 505, 540, 581	14000
IrL ¹ (dpyOMe)	286 (32900), 406 (5000), 427sh (4740)	535, 571	2.9	470 [190]	62	2100	1.4	519, 560, 604	16000
IrL ² (dpyx)	283 (36000), 394 (7140), 443sh (1220)	480sh, 528	0.38	200 [120]	19	5000	1.5	481, 513, 549	13000
IrL ² (dpyF)	280 (39100), 354sh (9150), 427sh (1700)	502sh, 529	1.7	180 [100]	94	5500	2.0	481, 514, 550, 591	14000
IrL ² (dpyOMe)	279 (34300), 410 (5080), 426 (4810)	534, 571	3.0	460 [200]	65	2100	1.3	519, 562, 603	18000
IrL ³ (dpyx)	300 (42600), 394 (7800), 435sh (1280)	506, 538	0.45	280 [140]	16	3600	1.6	470, 506, 535, 581	10000
IrL ³ (dpyF)	293 (42500), 352 (10300), 427 (1830)	484sh, 510, 540sh	0.45	240 [90]	19	4100	3.2	461, 493, 527, 564	13000
IrL ³ (dpyOMe)	300 (32900), 430 (4620)	532, 568	1.2	170 [120]	71	5800	1.1	518, 560, 604	17000
IrCl(dpyx)L ^{1a}	264 (38400), 286 (34200), 392 (7300)	--	--	--				471, 507, 538, 578	12000
IrCl(dpyx)L ^{2a}	265 (37700), 292 (27500), 361 (6500)	--	--	--				472, 509, 546	12000
IrCl(dpyx)L ^{3a}	275 (36500), 379 (6500)	--	--	--				470, 505, 536	13000

(a) Luminescence quantum yield in deoxygenated solution, recorded using $\text{Ru}(\text{bpy})_3\text{Cl}_2$ in air-equilibrated aqueous solution as the standard. (b) Luminescence lifetime in deoxygenated solution; values in parenthesis refer to the corresponding air-equilibrated solution. (c) Radiative k_r and non-radiative Σk_{nr} rate constants estimated from the lifetimes and quantum yields as described in the text. (d) Bimolecular rate constant for quenching by molecular oxygen estimated from the lifetimes in deoxygenated and air-equilibrated solutions, assuming $[\text{O}_2] = 2.2 \text{ mmol dm}^{-3}$ in CH_2Cl_2 under 1 atm of air. (e) In butyronitrile.

For the series of complexes incorporating the bidentate triazolypyridine ligands, $\text{IrCl}(\text{dpyx})\text{L}^{1a-3a}$, the absorption spectra extend less far into the visible, with the lowest-energy absorption maxima < 400 nm (Fig. 5a). This is intuitively consistent with the presence of only one as opposed to two σ -donating triazole ligating units in the coordination sphere of the metal, and mirrors the previously observed blue-shift of $\text{Ir}(\text{N}^{\wedge}\text{C}^{\wedge}\text{N}\text{-dpyx})(\text{C}^{\wedge}\text{N}\text{-ppy})\text{Cl}$ versus $\text{Ir}(\text{N}^{\wedge}\text{C}^{\wedge}\text{N}\text{-dpyx})(\text{C}^{\wedge}\text{N}^{\wedge}\text{C}\text{-dppy})$, for example.^{15b,e} Interestingly, however, no convincing luminescence is detectable from any of these three complexes in solution at room temperature. At 77 K, the complexes do emit brightly, displaying structured spectra with a principal vibrational progression of 1400 cm^{-1} , similar to the bis-tridentate complexes though with some additional structure discernible, and with lifetimes of around $12\ \mu\text{s}$. The similarity of the 77 K properties to those of the bis-tridentate complexes suggests that the triplet states have similar character. Apparently, non-radiative decay at room temperature is even faster than for the bis-tridentate complexes, to such an extent that emission is not observable.

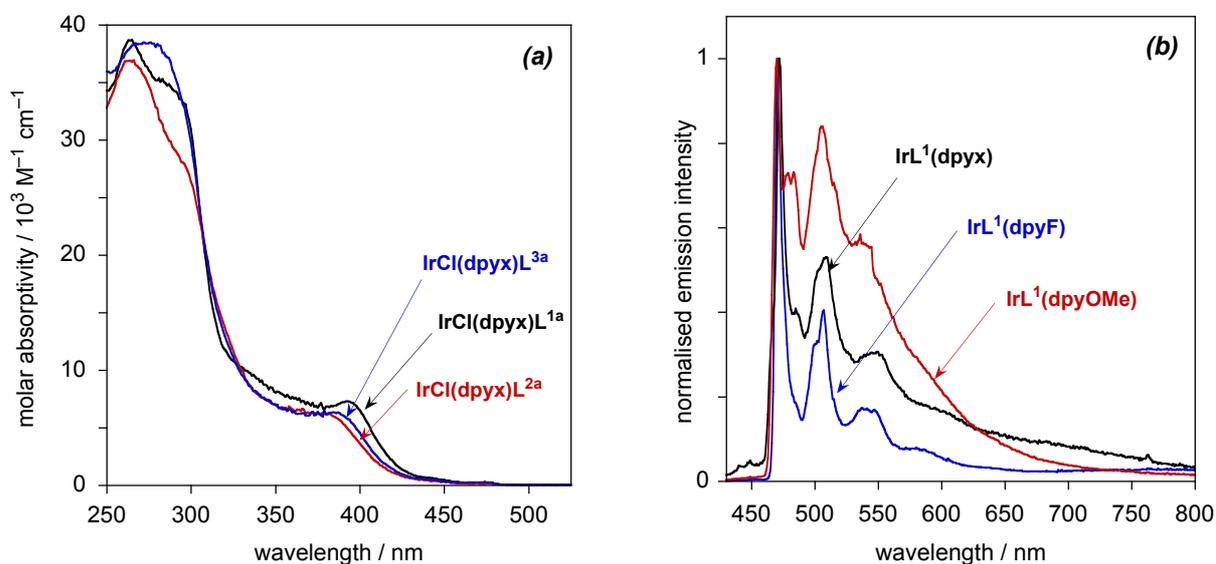


Figure 5 (a) Absorption spectra of $\text{IrCl}(\text{dpyx})\text{L}^{1a-3a}$ in dichloromethane solution at 295 K and (b) their photoluminescence spectra in butyronitrile at 77 K.

Conclusions

In summary, the present study shows how 2,6-bis-(1,2,4-triazolyl)pyridines can be used as proligands to form bis-tridentate iridium(III) complexes, in combination with a monoanionic, N^C^N -cyclometallating ligand. The binding of these ligands is shown to be accompanied by deprotonation of *both* of the azole rings, at least under the conditions used here, such that the final complexes are charge-neutral, similar to tris-cyclometallated Ir(III) complexes. The mutually *trans* disposition of the deprotonated azoles in the complexes does not lead to the instability found for corresponding complexes incorporating bis-cyclometallated diphenylpyridine, associated with the strong *trans* influence of metallated aryl rings. Nevertheless, the downside of the azoles is apparently that non-radiative decay processes are much more efficient in the resulting complexes. It is likely that the ligand field they offer is weaker, exacerbating non-radiative decay via d-d states at ambient temperature. Such a hypothesis is supported by the fact that the analogues with bidentate triazolylpyridines are essentially non-emissive under the same conditions.

The rather poor performance of these new bis-tridentate complexes contrasts with the much brighter emission displayed by the $Ir(N^C^N)(C^N^N)$ complexes reported by Chi and co-workers, which feature ligands offering a combination of one metallated aryl ring and one deprotonated pyrazole ring (*e.g.*, Fig. 1c). The presence of only one metallated aryl ring in the coordination sphere of Ir(III) – as in the new complexes reported here – may not be sufficient for intense room-temperature emission. It is likely that improved performance could be achieved by using asymmetric ligands based on 2-(1,2,4-triazolyl)-6-phenylpyridine. Indeed, such ligands have recently led to highly luminescent Pt(II) complexes,³¹ and they will likely be investigated with Ir(III) in the future.

Experimental

General

Reagents were obtained from commercial sources and used without further purification unless stated otherwise. All solvents used in preparative work were at least Analar grade and water was purified using the Purite^{STILL} plusTM system. Dry solvents were obtained from HPLC grade solvent that had been passed through a Pure Solv 400 solvent purification system and stored over activated 3 or 4 Å molecular sieves. For procedures involving dry solvent, glassware was oven-dried for at least 8 h prior to use. Oxygen-free argon cylinders (BOC, UK) were used to provide an inert atmosphere where required. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance-400 spectrometer. Two-dimensional NMR (COSY, NOESY, HSQC and HMBC) spectra were acquired on Varian VNMRS-600 (600 MHz) or VNMRS-700 (700 MHz) instruments. Chemical shifts (δ) are in ppm, referenced to residual protio-solvent resonances, and coupling constants are given in Hertz. Mass spectra were obtained by electrospray ionisation (positive and negative ionisation modes) on a Waters TQD mass spectrometer interfaced with an Acquity UPLC system with acetonitrile as the carrier solvent. Measurements requiring the use of an atmospheric solids analysis probe (ASAP) for ionisation were performed on Waters Xevo QToF mass spectrometer.

X-ray crystallography

The X-ray single crystal data have been collected using λ MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker D8Venture (Photon100 CMOS detector, I μ S-microsource, focusing mirrors) diffractometers equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostats at 120.0(2)K. Both structures were solved by direct method and refined by full-matrix least squares on F^2 for all data using Olex2 [32] and SHELXTL [33] software. All non-disordered non-hydrogen atoms were refined anisotropically; the hydrogen atoms were placed in the calculated positions and refined in riding mode. Disordered atoms in both structures were refined isotropically with fixed SOF. Severely disordered solvent molecules (presumably DCM) in structure Ir(dpyx)L¹ could not be modelled properly and were taken into account by applying the MASK procedure of OLEX2 program package. The table of crystal data and refinement parameters are listed in Table S1 in the ESI. Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 2113372-2113373.

Solution-state photophysics

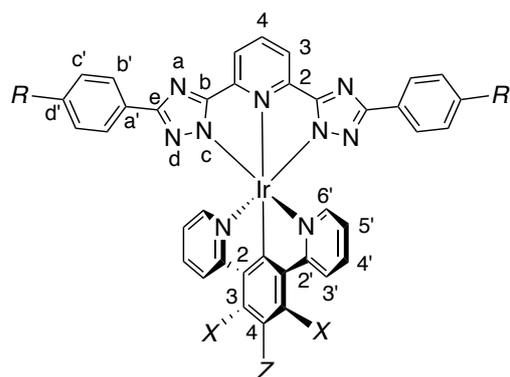
UV-vis absorption spectra were recorded on a Biotek Instruments UVIKON XS spectrometer operating with LabPower software in matched 1 cm pathlength quartz cuvettes. Emission spectra were acquired on a Jobin Yvon Fluoromax-2 spectrometer equipped with a Hamamatsu R928 photomultiplier tube. All samples were contained within 1 cm pathlength quartz cuvettes modified for connection to a vacuum line. Degassing was achieved by three freeze-pump-thaw cycles whilst connected to the vacuum manifold: final vapour pressure at 77 K was $< 5 \times 10^{-2}$ mbar. Emission was recorded at 90° to the excitation source, and spectra were corrected after acquisition for dark count and for the spectral response of the detector. The quantum yields were determined relative to an aqueous solution of $[\text{Ru}(\text{bpy})_3]\text{Cl}_3$ for which $\Phi_{\text{lum}} = 0.040$.³⁴ Spectra at 77 K were recorded using the same instrument, with the samples held in 4 mm quartz tubes within a quartz dewar.

Luminescence lifetimes of the complexes in solution were measured by time-correlated single-photon counting, using a 405 nm pulsed-diode laser as the excitation source. The emission was detected at 90° to the excitation source, after passage through a monochromator, using a Peltier-cooled R928 detector. Lifetimes at 77 K were measured using the same detector operating in multichannel scaling mode following excitation with a microsecond pulsed xenon lamp.

Synthetic details and characterisation of compounds

The synthesis and characterisation of the proligands H_2L^{1-3} and HL^{1a-3a} is described in the Supporting Information, together with the intermediates C^{1-3} . The three chloro-bridged Ir dimers, $[\text{Ir}(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})\text{Cl}(\mu\text{-Cl})_2]$, were synthesised as described previously¹⁵ by reaction of the corresponding proligand with $\text{IrCl}_3 \cdot \text{H}_2\text{O}$ in ethoxyethanol/ H_2O reflux for 24 h, from which they precipitate.

Bis-tridentate iridium(III) complexes



Atom labelling system for NMR assignments

IrL¹(dpyx). A suspension of [Ir(dpyx)Cl(μ -Cl)]₂ (32 mg, 0.03 mmol) and **H₂L¹** (29 mg, 0.06 mmol) in ethylene glycol (2 mL) was degassed by three freeze-pump-thaw cycles and then refluxed at 185 °C for 24 h under a nitrogen atmosphere. After cooling to ambient temperature, the precipitate was separated by filtration and washed with water. This material product was subjected to column chromatography on silica, using a gradient elution from DCM/MeOH 100:0 to 95:5, and giving the product as a yellow solid (15 mg, 52%). $R_f = 0.45$ (95:5 DCM/MeOH). ¹H NMR (700 MHz, DMSO-*d*₆) δ 8.37 (t, $J = 7.8$ Hz, 1H, H^{4triz}), 8.21 (d, $J = 8.2$ Hz, 2H, H^{6'}), 8.19 (d, $J = 7.7$ Hz, 2H, H^{3triz}), 7.80 (t, $J = 8.0$ Hz, 2H, H^{5'}), 7.61 (d, $J = 8.7$ Hz, 4H, H^{b'}), 7.40 (d, $J = 5.8$ Hz, 2H, H^{3'}), 7.25 (d, $J = 8.7$ Hz, 4H, H^{c'}), 7.18 (s, 1H, H⁴), 7.04 (d, $J = 6.8$ Hz, 2H, H^{4'}), 2.90 (s, 6H, H^{Me}), 1.18 (s, 18H, H^{tBu}); MS (ES⁺) $m/z = 928.3$ [M+H]⁺; HRMS (ES⁺) $m/z = 926.3439$ [M+H]⁺; calculated for [C₄₇H₄₅N₉¹⁹¹Ir]⁺ 926.3404.

IrL²(dpyx) was prepared using the same procedure from [Ir(dpyx)Cl(μ -Cl)]₂ (24 mg, 0.02 mmol) and **H₂L²** (20 mg, 0.05 mmol) in ethylene glycol (1 mL), giving the product as a yellow solid (5 mg, 25%). $R_f = 0.27$ (90:10 DCM/MeOH); MS (ES⁺) $m/z = 876.2$ [M+H]⁺; HRMS (ES⁺) $m/z = 874.2365$ [M+H]⁺; calculated for [C₄₁H₃₃N₉O₂¹⁹¹Ir]⁺ 874.2363. The poor solubility of this compound hampered attempts to acquire quality NMR spectra, but elemental analysis is consistent with the expected formulation: anal. calcd for C₄₁H₃₃N₉O₂Ir: C, 56.28; H, 3.69; N, 14.41 %; found: C, 55.76; H, 3.09; N, 14.78 %.

IrL³(dpyx) was prepared using the same procedure from [Ir(dpybMe₂)Cl(μ -Cl)]₂ (50 mg, 0.05 mmol) and **H₂L³** (48 mg, 0.10 mmol) in ethylene glycol (3 mL), giving the product as a yellow solid (30 mg, 63%). $R_f = 0.32$ (95:5 DCM/MeOH); ¹H NMR (700 MHz, DMSO-*d*₆) δ 8.42 (t, $J = 7.7$ Hz, 1H, H^{4triz}), 8.27 (d, $J = 8.0$ Hz, 2H, H^{3triz}), 8.22 (d, $J = 8.5$ Hz, 2H, H^{6'}), 7.90 (d, $J = 8.2$ Hz, 4H, H^{c'}), 7.81 (t, $J = 7.7$ Hz, 2H, H^{5'}), 7.60 (d, $J = 8.3$ Hz, 4H, H^{b'}), 7.42

(d, $J = 5.8$ Hz, 2H, H^{3'}), 7.18 (s, 1H, H⁴), 7.04 (t, $J = 6.6$ Hz, 2H, H^{4'}), 2.90 (s, 6H, H^{Me}); ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -62.47; MS (ES⁺) $m/z = 951.8$ [M+H]⁺; HRMS (ES⁺) $m/z = 950.1907$ [M+H]⁺; calculated for [C₄₁H₂₇N₉F₆¹⁹¹Ir]⁺ 950.1900.

IrL¹(dpyF) was prepared using the same procedure from [Ir(dpyF)Cl(μ -Cl)]₂ (100 mg, 0.09 mmol) and **H₂L¹** (90 mg, 0.19 mmol) in ethylene glycol (3 mL), giving the product as a yellow solid (30 mg, 63%). R_f 0.51 (95:5 DCM/MeOH); ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.44 (dd, $J = 8.4, 7.5$ Hz, 1H, H^{4triz}), 8.26 (d, $J = 7.9$ Hz, 2H, H^{6'}), 8.22 (d, $J = 8.2$ Hz, 2H, H^{3triz}), 7.94 (dd, $J = 7.9, 1.4$ Hz, 2H, H^{5'}), 7.67 (d, $J = 8.6$ Hz, 4H, H^{b'}), 7.54 – 7.46 (m, 3H, H⁴ and H^{4'}), 7.30 (d, $J = 8.6$ Hz, 4H, H^{c'}), 7.17 (ddd, $J = 7.4, 5.7, 1.4$ Hz, 2H, H^{3'}), 1.22 (s, 18H, H^{tBu}); ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -107.48 (d, $J = 14.2$ Hz); MS (ES⁺) $m/z = 936.3$ [M+H]⁺; HRMS (ES⁺) $m/z = 934.2894$ [M+H]⁺; calculated for [C₄₅H₃₉N₉F₂¹⁹¹Ir]⁺ 934.2903;

IrL²(dpyF) was prepared similarly from [Ir(dpyF)(μ -Cl)Cl]₂ (125 mg, 0.12 mmol) and **H₂L²** (100mg, 0.24 mmol) in ethylene glycol (2 mL), giving the product as a yellow solid (24 mg, 23 %); R_f=0.4 (95:5 DCM/MeOH); ¹H NMR (700 MHz, DMSO-*d*₆) δ 8.40 (t, $J = 8.0$ Hz, 1H, H^{4triz}), 8.20-8.17 (m, 4H, H^{3triz} and H^{6'}), 7.90 (td, $J = 7.9, 1.6$ Hz, 2H, H^{5'}), 7.64 (d, $J = 8.9$ Hz, 4H, H^{b'}), 7.47 (d, $J = 5.6$ Hz, 2H, H^{3'}), 7.44 (t, $J = 11.6$ Hz, 1H, H⁴), 7.14 (ddd, $J = 7.4, 5.8, 1.4$ Hz, 2H, H^{4'}), 6.80 (d, $J = 8.9$ Hz, 4H, H^{c'}), 3.68 (s, 6H, H^{OMe}); ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -107.49 (d, $J = 12.0$ Hz); MS (ES⁺) $m/z = 884.1$ [M+H]⁺; HRMS (ES⁺) $m/z = 882.1857$ [M+H]⁺; calculated for [C₃₉H₂₇N₉O₂F₂¹⁹¹Ir]⁺; 882.1862.

IrL³(dpyF) was prepared similarly from [Ir(dpyF)Cl(μ -Cl)]₂ (100 mg, 0.09 mmol) and **H₂L³** (95 mg, 0.19 mmol) in ethylene glycol (2 mL), giving the product as a yellow powder (35 mg, 39 %). ¹H NMR (700 MHz, DMSO-*d*₆) δ 8.47 (t, $J = 8.1$ Hz, 1H, H^{4triz}), 8.30 (d, $J = 7.9$ Hz, 2H, H^{3triz}), 8.19 (d, $J = 8.2$ Hz, 2H, H^{6'}), 7.93 (d, $J = 8.4$ Hz, 4H, H^{c'}), 7.91 (d, $J = 7.7$ Hz, 2H, H^{5'}), 7.61 (d, $J = 8.4$ Hz, 4H, H^{b'}), 7.51 (d, $J = 6.0$ Hz, 2H, H^{3'}), 7.46 (t, $J = 11.6$ Hz, 1H, H⁴), 7.14 (ddd, $J = 7.4, 5.9, 1.4$ Hz, 2H, H^{4'}); ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -60.99, -107.30 (d, $J = 13.1$ Hz); MS (ES⁺) $m/z = 960.0$ [M+H]⁺; HRMS (ES⁺) $m/z = 958.1384$ [M+H]⁺; calculated for [C₃₉H₂₁N₉F₈¹⁹¹Ir]⁺ 958.1398.

IrL¹(dpyOMe) was prepared similarly from [Ir(dpyOMe)Cl(μ -Cl)]₂ (50 mg, 0.05 mmol) and **H₂L¹** (46 mg, 0.10 mmol) in ethylene glycol (3 mL), giving the product as a yellow-orange solid (33 mg, 74 %). MS (ES⁺) $m/z = 930.2$ [M+H]⁺; HRMS (ES⁺) $m/z = 928.3202$ [M+H]⁺; calculated for [C₄₆H₄₃N₉O¹⁹¹Ir]⁺ 928.3197. The poor solubility of this compound hampered attempts to acquire quality NMR spectra, but elemental analysis is consistent with the expected formulation: anal. calcd for C₄₆H₄₂N₉OIr: C, 59.47; H, 4.56; N, 13.57 %; found: C, 59.23; H, 4.48; N, 12.93 %.

IrL²(dpyOMe) was prepared similarly from [Ir(dpyOMe)Cl(μ -Cl)]₂ (50 mg, 0.05 mmol), and **H₂L²** (41 mg, 0.10 mmol) in ethylene glycol (3 mL), giving the product as a yellow-orange solid (25 mg, 59%). $R_f=0.2$ (95:5 DCM/MeOH); ¹H NMR (700 MHz, DMSO-*d*₆) δ 8.36 – 8.33 (m, 3H, H^{4triz} and H^{6'}), 8.15 (d, $J = 7.9$ Hz, 2H, H^{3triz}), 7.96 (s, 2H, H³), 7.84 (ddd, $J = 8.1, 7.4, 1.5$ Hz, 2H, H^{5'}), 7.61 (d, $J = 9.0$ Hz, 4H, H^{b'}), 7.38 (d, $J = 5.9$ Hz, 2H, H^{3'}), 7.04 (ddd, $J = 7.3, 5.8, 1.4$ Hz, 2H H^{4'}), 6.78 (d, $J = 9.0$ Hz, 4H, H^{c'}), 4.06 (s, 3H, H^{OMe(NCN)}), 3.67 (s, 6H, H^{OMe(triz)}); MS (ES⁺) $m/z = 878.1$ [M+H]⁺; HRMS (ES⁺) $m/z = 876.2155$ [M+H]⁺; calculated for [C₄₀H₃₀N₉O₃¹⁹¹Ir]⁺ 876.2156.

IrL³(dpyOMe) was prepared similarly from [Ir(dpyOMe)Cl(μ -Cl)]₂ (50 mg, 0.05 mmol) and **H₂L³** (48 mg, 0.10 mmol) in ethylene glycol (3 mL), giving the product as a yellow-orange solid (34 mg, 71%). $R_f=0.26$ (95:5 DCM/MeOH); ¹H NMR (700 MHz, DMSO-*d*₆) δ 8.42 (t, $J = 7.9$ Hz, 1H, H^{4triz}), 8.36 (d, $J = 8.1$ Hz, 2H, H^{6'}), 8.27 (d, $J = 7.9$ Hz, 2H, H^{3triz}), 7.98 (s, 2H, H³), 7.91 (d, $J = 8.2$ Hz, 4H, H^{c'}), 7.85 (t, $J = 7.7$ Hz, 2H, H^{5'}), 7.59 (d, $J = 8.4$ Hz, 4H, H^{b'}), 7.42 (d, $J = 5.8$ Hz, 2H, H^{3'}), 7.05 (t, $J = 6.5$ Hz, 2H, H^{4'}), 4.07 (s, 3H, H^{OMe}); ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -60.96; MS (ES⁺) $m/z = 953.9$ [M+H]⁺; HRMS (ES⁺) $m/z = 952.1714$ [M+H]⁺; calculated for [C₄₀H₂₄N₉O₁F₆¹⁹¹Ir]⁺ 952.1692.

Ir(N[^]C[^]N) complexes with one bidentate ligand and Cl

The atom labelling system for NMR assignment of these complexes below is as for L¹⁻³ above, but numbering the now asymmetrically-substituted pyridine ring through to positions 5 and 6.

IrCl(dpyx)L^{1a} A suspension of [Ir(dpyx)Cl(μ -Cl)]₂ (50 mg, 0.05 mmol), **HL¹** (27 mg, 0.10 mmol) and AgOTf (56 mg, 0.22 mmol) in toluene (3 mL) was degassed via three freeze-pump-thaw cycles and then refluxed for 24 h under a nitrogen atmosphere. After cooling to ambient temperature, the solvent was removed under reduced pressure. The residue was extracted into CH₂Cl₂ and then recrystallized from methanol / hexane to give the product as a yellow powder (30 mg, 82 %). ¹H NMR (400 MHz, Methanol-*d*₄) δ 8.41 (d, $J = 8.3$ Hz, 2H, H^{2'}), 8.27-8.20 (m, 3H, H^{6triz} and H^{b'}), 7.89 (d, $J = 5.6$ Hz, 2H, H^{3'}), 7.83 – 7.70 (m, 3H, H^{5'} and H^{3triz}), 7.47 (d, $J = 8.2$ Hz, 2H, H^{c'}), 7.23 (d, $J = 5.8$ Hz, 1H, H^{4triz}), 7.15 (s, 1H, H^{4dpyb}), 7.01 (td, $J = 6.9, 1.67$ Hz, 1H, H^{5triz}), 6.98-6.90 (m, 2H, H^{4'}), 2.91 (s, 6H, H^{Me}), 1.37 (s, 9H, H^{tBu}); MS (ES⁺) $m/z = 763.0$ [M+H]⁺; HRMS (ES⁺) $m/z = 763.2071$ [M+H]⁺; calculated for [C₃₅H₃₃N₆Cl¹⁹¹Ir]⁺ 763.2061.

IrCl(dpyx)L^{2a} was prepared using the same procedure but using **HL²** (24 mg, 0.10 mmol) in place of **HL¹**. Additional recrystallisations were required for purification, giving the product as a yellow solid (5 mg, 14 %). ¹H NMR (700 MHz, DMSO-*d*₆) δ 9.55 (d, $J = 5.4$, 1H,

H^{6triz}), 8.63 (d, $J = 7.9$, 1H, H^{3triz}), 8.30 (t, $J = 7.9$, 1H, H^{5triz}), 8.14-7.99 (m, 3H, H^{4triz} and H^{2'}), 7.85 (t, $J = 8.0$ Hz, 2H, H^{3'}), 7.55 (d, $J = 5.2$ Hz, 2H, H^{5'}), 7.29 (d, $J = 7.7$ Hz, 2H, H^{c'}), 7.14 (t, $J = 7.1$, 2H, H^{4'}), 6.40 (s, 1H, H^{4dpyb}), 6.35 (d, $J = 7.7$ Hz, 2H, H^{b'}), 3.68 (s, 6H, H^{OMe}), 2.51 (s, 6H, H^{Me}); MS (ES⁺) $m/z = 737.1$ [M+H]⁺; HRMS (ES⁺) $m/z = 737.1580$ [M+H]⁺; calculated for [C₃₂H₂₇N₆OCl¹⁹¹Ir]⁺ 737.1541.

IrCl(dpyx)L^{3a} was prepared similarly but using HL³ (28 mg, 0.10 mmol) in place of HL¹. Additional recrystallisations were again required for purification, giving the product as a yellow solid (7 mg, 18 %). ¹H NMR (700 MHz, DMSO-*d*₆) δ 9.57 (dt, $J = 5.2$, 1.3 Hz, 1H, H^{6triz}), 8.48 (dt, $J = 7.9$, 1.2 Hz, 1H, H^{3triz}), 8.42 (td, $J = 7.9$, 1.6 Hz, 1H, H^{5triz}), 8.05-8.00 (m, 3H, H^{4triz} and H^{2'}), 7.85 (ddd, $J = 8.5$, 7.4, 1.7 Hz, 2H, H^{3'}), 7.58 (d, $J = 5.7$ Hz, 2H, H^{5'}), 7.22 (d, $J = 7.8$ Hz, 2H, H^{c'}), 7.14 (ddd, $J = 7.2$, 5.6, 1.3 Hz, 2H, H^{4'}), 6.46 (s, 1H, H^{4dpyb}), 6.35 (d, $J = 7.7$ Hz, 2H, H^{b'}), 2.53 (s, 6H, H^{Me}); ¹³C NMR (176 MHz, DMSO-*d*₆) δ 169.08 (C^{6'}), 163.32 (C^{b/e}), 162.75 (C^{b/e}), 161.86 (C^{a'}), 151.78 (C^{5'}), 148.94 (C^{d'}), 148.63 (C^{6triz}), 140.45 (C^{5triz}), 139.31 (C^{3'}), 137.99 (C^{3dpyb}), 136.98 (C^{2dpyb}), 130.79 (C^{4dpyb}), 129.12 (C^{b'}), 127.13 (C^{4triz}), 124.07 (C^{c'}), 123.37 (C^{2'}), 123.22 (C^{4'}), 121.90 (C^{3triz}), 22.04 (C^{Me}); ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -61.84; MS (ES⁺) $m/z = 775.1$ [M+H]⁺; HRMS (ES⁺) $m/z = 775.1348$ [M+H]⁺; calculated for [C₃₂H₂₄N₆F₃Cl¹⁹¹Ir]⁺ 775.1309.

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Supporting Information

Synthesis and characterisation of proligands and intermediates leading to them; figures illustrating the packing of molecules of IrL¹(dpyF) in the crystal and of the structure of IrL¹(dpyx); additional crystallographic details. Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 2113372 - 2113373.

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