

Bright orange/red-emitting rhodium(III) and iridium(III) complexes: tridentate N[^]C[^]N-cyclometallating ligands lead to high luminescence efficiencies†

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Rhodium(III) complexes rarely display strong phosphorescence, in contrast to well-known iridium(III) complexes with cyclometallating ligands. This study shows how 1,3-bis(1-isoquinolyl)benzene cyclometallates to Rh(III) through N[^]C[^]N-coordination to give complexes with unprecedented phosphorescence quantum yields at room temperature. Their highly emissive Ir(III) analogues are also described.

The excited-state properties of cyclometallated iridium(III) complexes have attracted a great deal of interest over the past 15 years, owing particularly to the high quantum yields of emission from triplet excited states that have been found for many such compounds.¹ These properties have rendered them exciting molecular materials for application as emitters in organic light-emitting devices² and in biological stains and sensors suitable for time-resolved detection procedures.³ In contrast, rhodium(III) complexes have been much less explored for luminescence,⁴ their phosphorescence quantum yields being typically much lower. Thus, while bis-cyclometallated complexes of the form [Ir(N[^]C)₂(N[^]N)]⁺ are brightly luminescent,^{1a} emission from analogous Rh(III) complexes can scarcely be detected under such conditions⁵ (here N[^]C represents a ligand such as orthometallated phenylpyridine and N[^]N a diimine such as bipyridine).

The much weaker emission of rhodium complexes arises from the combination of a number of factors: (i) The lower spin-orbit coupling (SOC) constant of Rh compared to Ir will result in smaller triplet radiative rate constants, *k_r*. (ii) For a given type of complex, the Rh^{III}|Rh^{IV} couple will lie at higher potential than the corresponding Ir^{III}|Ir^{IV} couple, such that metal-to-ligand charge-transfer (MLCT) states will be raised in energy.⁵ Lowest-lying excited states are therefore more likely to

be predominantly ³π-π* in character and, since emission from triplet states requires mixing with higher-lying ¹MLCT states to introduce the necessary SOC,⁶ an increase in the energy of the latter will serve to reduce *k_r*. (iii) The weaker ligand-field splitting of 2nd versus corresponding 3rd row transition metals means that metal-centred d-d excited states – which are strongly distorted relative to the ground state and hence potentially highly deactivating for d⁶ complexes – are more likely to be thermally accessible for Rh(III) than for Ir(III).⁷

Amongst cyclometallated complexes, the brightest systems hitherto reported appear to be those of the form [Rh-(pba)₂(N[^]N)]⁺, where pba is 4-(2-pyridyl)benzaldehyde and N[^]N is a diimine ligand such as a 2,2'-bipyridine or 1,10-phenanthroline. This family of complexes were reported to have quantum yields of 1–3% and lifetimes of a few microseconds in solution at 298 K, rationalised in terms of the influence of the aldehyde group leading to a pba-localised state.⁸ Meanwhile, a family of rhodacyclopentadiene-based complexes display intense *fluorescence* from the singlet state, reflecting an unusually low rate of intersystem crossing.⁹

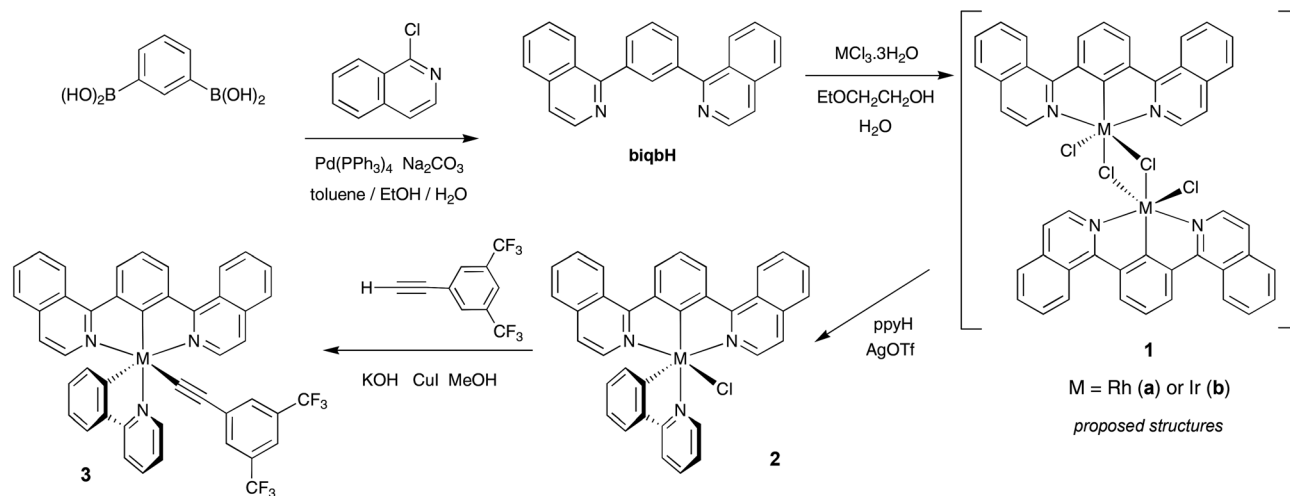
We have previously shown how the use of tridentate, N[^]C[^]N-cyclometallating ligands can provide access to exceptionally highly luminescent Ir(III) and Pt(II) complexes, probably due to the enhanced rigidity and the short M–C bonds imposed by the tridentate binding of the ligand.^{10,11} Here we show how such a ligand, namely 1,3-bis(1-isoquinolyl)benzene, can be used to generate unusually brightly-emitting rhodium complexes. We also describe the analogous Ir(III) complexes, which rival the most efficient deep-red triplet emitters reported.¹²

1,3-Bis(1-isoquinolyl)benzene (biqbH) was synthesised readily by Suzuki cross-coupling of benzene-1,3-diboronic acid with 2 equivalents of 1-chloroisoquinoline under standard conditions (Scheme 1). This method is attractive compared to the more commonly used Stille route to N[^]C[^]N-coordinating ligands,^{10a} as it avoids the use of the rather toxic heterocyclic stannane reagents. Moreover, heterocyclic substrates in which the carbon–halogen bond is *ortho* to the heteroatom are highly activated, such that chloro derivatives can be used. Reaction of

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†Electronic supplementary information (ESI) available: Synthesis and characterisation of all compounds; TD DFT; cyclic voltammograms; crystal structure data in CIF format. CCDC 937441–937443. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt51211h



Scheme 1 Synthesis of the proligand biqbH and of the rhodium and iridium complexes.

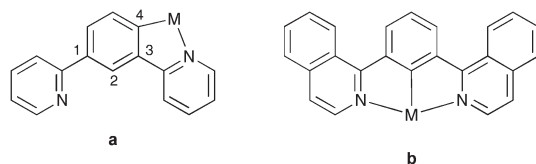


Fig. 1 Bidentate N^C^4 coordination is the predominant binding mode displayed by dpyb (**a**) whereas tridentate $N^C^2^N$ coordination predominates for biqb (**b**).

biqbH with $MCl_3 \cdot 3H_2O$ ($M = Rh$ or Ir) under the conditions typically used in the synthesis of $[M(ppy)_2(\mu-Cl)]_2$ dimers (ethoxyethanol–water at 80 °C) led to a precipitate, yellow for Rh and orange for Ir . Owing to their very low solubility in all common solvents, these products could not be characterised readily at this stage but – on the basis of subsequent reactions and our earlier work with substituted pyridyl analogues¹¹ – were deduced to be the chloro-bridged dimers $[M(biqb)Cl(\mu-Cl)]_2$ **1** (Scheme 1). This contrasts with the behaviour of 1,3-di(2-pyridyl)benzene (dpybH), where metallation with $Ir(III)$ or $Rh(III)$ occurs at the 4-position to give bidentate N^C -coordination (Fig. 1a), rather than at the 2-position to give tridentate $N^C^2^N$ coordination^{11a,b} – which can only be achieved by introducing blocking substituents at the 4 and 6 positions (*e.g.*, CH_3 , CF_3 , F).¹¹ Biqb apparently favours $N^C^2^N$ over N^C^4 binding, without the need for such substituents (Fig. 1b).

Treatment of dimers **1** with 2-phenylpyridine (ppyH) gave mononuclear complexes, $M(biqb)(ppy)Cl$, yellow for $M = Rh$ (**2a**)† and bright orange for $M = Ir$ (**2b**). Single-crystal X-ray diffraction study§ of **2a**·3CDCl₃ and **2b**·5/3MeOH·2/3H₂O obtained by slow evaporation of chloroform and methanol solutions respectively, showed very similar molecular geometry (Fig. 2, Table 1) with distorted octahedral coordination of the metal atom. The latter structure contains two symmetrically non-equivalent molecules of **2b**, one of which (**A**) has no crystallographic symmetry, like molecule **2a**, and the other (**B**) has C_s symmetry.

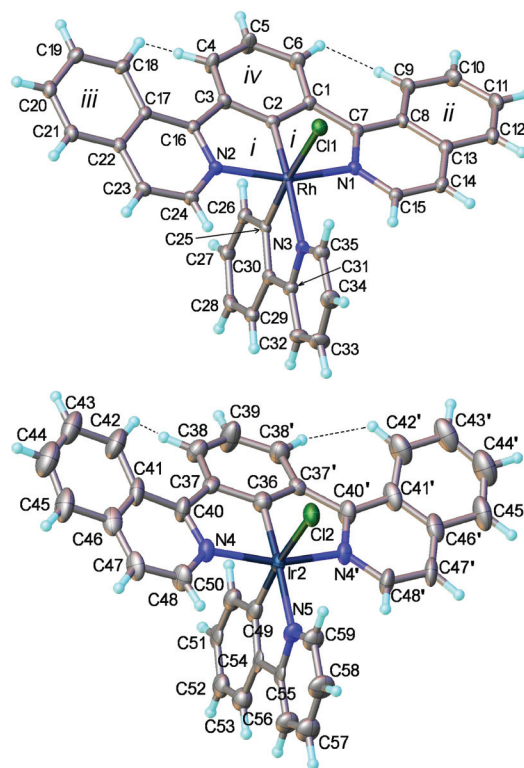


Fig. 2 X-ray structures of **2a** (top) and **2b** (molecule B, mirror plane passing through $Ir(2)$, $Cl(2)$, $C(36)$, $C(39)$ and the ppy ligand; molecule A has the same atom numbering as **2a**). Dotted lines show short $H \cdots H$ contacts. Thermal ellipsoids are drawn at 50% probability level. See also ESI.†

As in the related $Ir(III)$ complexes with 1,3-dipyridyl-benzene¹¹ and 1,3-bis(1-methylbenzimidazol-3-yl)-benzene,¹³ in **2** the two cyclometallating carbon atoms (of the ppy and biqb ligands) adopt a *cis* disposition, rather than *trans* which is disfavoured by their strong *trans* influence. The latter effect is apparent instead in lengthening of the $M-Cl$ bonds,

Table 1 Selected bond lengths (Å) and angles (°) in **2a** and **2b**

	2a	2b, A		2b, B
M–Cl(1)	2.479(1)	2.462(7)	Ir(2)–Cl(2)	2.461(9)
M–N(1)	2.050(3)	2.043(13)	Ir(2)–N(4)	2.041(13)
M–N(2)	2.049(3)	2.064(17)		
M–N(3)	2.178(3)	2.183(16)	Ir(2)–N(5)	2.13(2)
M–C(2)	1.907(4)	1.945(17)	Ir(2)–C(36)	1.95(3)
M–C(25)	1.993(4)	2.04(2)	Ir(2)–C(49)	1.96(4)
N(1)–M–N(2)	160.5(1)	159.7(6)	N(4)–Ir(2)–N(4')	160.5(8)
Cl(1)–M–C(25)	173.0(1)	172.5(6)	Cl(2)–Ir(2)–C(49)	170.3(9)
C(2)–M–N(3)	174.3(2)	172.9(8)	C(36)–Ir(2)–N(5)	174.8(11)
N(1)–M–C(2)	80.0(2)	79.6(7)	N(4)–Ir(2)–C(36)	80.3(4)
N(2)–M–C(2)	80.5(2)	80.2(6)		

cf. typical values of 2.31–2.38 Å in RhN₃Cl₃ and 2.34–2.39 Å in IrN₃Cl₃ chromophores.¹⁴

Whilst the crystal structure study,^{†,§} of biqbH revealed planar quinoline moieties inclined by 49° to each other and to the central benzene ring, in **2** two fused metallacycles *i* form a planar system and the resulting strain (short intra-biqb H···H contacts, see Fig. 2) is partly relieved by warping of the ligand. Thus, in **2a** rings *ii* and *iii* tilt to opposite sides of plane *i*, by 11.5° and 11.4° (Fig. 3). In **2b** these rings tilt in the same direction, by 4.0° and 14.1° in molecule A, and 14.6° in B, but ring *iv* tilts in opposite direction (towards the Cl ligand) by 8.2° and 13.2°, respectively.

These systems are unusual in that they comprise two different cyclometallating ligands, a feature difficult to attain in complexes based on bidentate ligands, such as the well-known Ir(N[^]C)₃ or Ir(N[^]C)₂(L[^]X) classes for example (L[^]X represents a

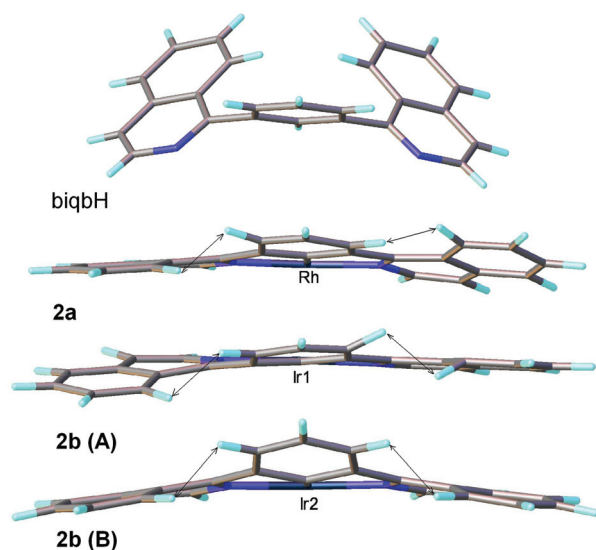


Fig. 3 Comparison of the molecular conformation of biqb in the crystal structures of biqbH, **2a** and two independent molecules of **2b**. Intra-ligand H···H contacts shown with arrows, measure 1.74–1.80 Å in **2a** and 1.89–1.90 Å in **2b**, assuming C–H bond distances of 1.08 Å (= internuclear distance established by neutron diffraction). Refinement of the direction (with fixed length) of these C–H bonds showed them bend out of the corresponding aromatic ring planes, so as to increase the H···H distance; however, the effect lies within the experimental error.

monoanionic, bidentate ligand such as acac). Moreover, the resulting structures also incorporate one terminal chloride ligand, which can undergo metathesis with other ligands. As an example, adducts **3** with a 3,5-bis(trifluoromethyl)phenyl-acetylide ligand in place of the chloride were prepared under Sonogashira-type conditions, by treating the parent complexes with the corresponding alkyne in the presence of base and copper(i) iodide (Scheme 1). In contrast to the field of platinum(II) chemistry, there are relatively few examples of acetylide adducts of cyclometallated iridium(III) complexes.^{13a,15}

The UV-visible absorption spectrum of **2b** (Fig. 4, Table 2) is typical of cyclometallated Ir(III) complexes, showing very intense absorption bands at <330 nm attributable to intra-ligand π – π^* transitions, and a set of bands at longer wavelengths with ϵ = 4000–7000 M^{–1} cm^{–1}, typical for spin-allowed charge-transfer transitions involving the metal. Some weaker, but nevertheless well-defined bands at longer wavelength (*e.g.*, λ = 591 nm, ϵ = 440 M^{–1} cm^{–1}) are likely to be due to corresponding spin-forbidden transitions to triplet excited states, promoted by the SOC associated with the metal ion. These visible-region bands are significantly red-shifted compared to complexes with simple arylpyridine ligands, *e.g.* Ir(ppy)₃, reflecting the more extended conjugation associated with the isoquinoline groups. Indeed, the spectrum is very similar to those of Ir(piq)₂(acac) and Ir(piq)₃, where piq = 1-phenyl-isoquinoline.^{12b,c,e} Time-dependent density functional theory calculations (B3LYP, with 6-311G and LanL2DZ basis sets for ligands and metal ion respectively) indicate that the lowest-lying singlet and lowest-lying triplet transitions both have primarily HOMO–LUMO character. The corresponding orbital plots (Fig. 5) show that the LUMO is based on the tridentate ligand, while the HOMO is delocalised over the metal, the cyclometallating phenyl ring of the ppy, and the chloride ligand. The excited state may thus be described as d/ π _{N[^]C} → π^* _{N[^]C[^]N} (mixed MLCT/L[^]LCT) in character.

The spectrum of **2a** is similar to that of **2b**, except for the absence of the weak, low-energy bands, and the blue-shift of the intense visible-region absorption bands by *ca.* 30 nm. The former can be explained by the smaller spin–orbit coupling

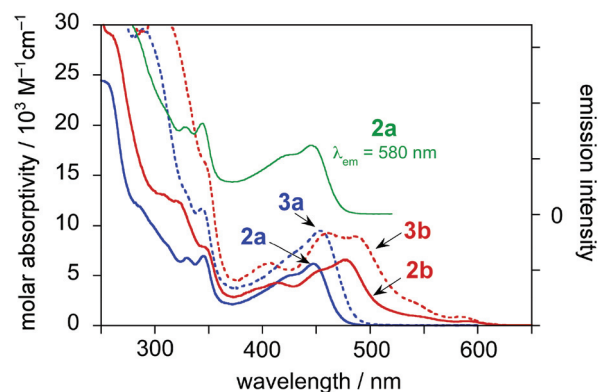
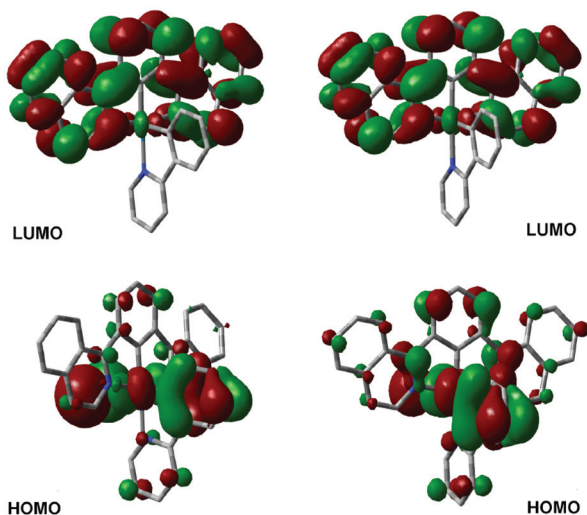


Fig. 4 UV-visible absorption spectra of complexes **2** and **3** in CH₂Cl₂ at 298 K (left scale), and the excitation spectrum of **2a** (green, right scale).

Table 2 Photophysical properties of the rhodium(III) and iridium(III) complexes in CH₂Cl₂ at 298 K except where indicated otherwise^a

Comp.	Absorption $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{ cm}^{-1}$)	Emission $\lambda_{\text{max}}/\text{nm}$	$\tau/\mu\text{s}$	Φ_{lum}	Emission at 77 K ^b	
					$\lambda_{\text{max}}/\text{nm}$	$\tau/\mu\text{s}$
2a	252sh (24 400), 330 (6790), 345 (6960), 426 (6200), 447 (6200)	575, 618, 678sh	16 [0.91]	0.10	564, 611, 667, 735	53
2b	259sh (29 100), 320sh (12 400), 347sh (7810), 414 (4280), 455sh (5590), 477 (6490), 549sh (870), 591 (440)	611, 653	1.7 [0.49]	0.40	593, 644, 703	2.8
3a	242 (47 700), 286 (29 400), 345 (11 700), 428 (7210), 453 (9490)	574, 616, 675sh	15.6 [0.95]	0.06	561, 608, 662, 729	49
3b	250 (52 200), 307 (32 000), 346sh (16 400), 406 (6270), 462 (9250), 488 (8880), 538sh (2450), 584 (880)	603, 644	1.7 [0.38]	0.51	585, 636, 698	3.2

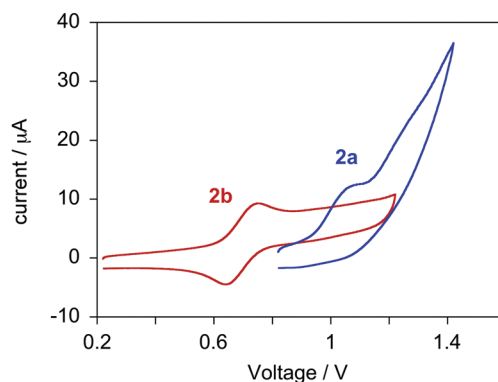
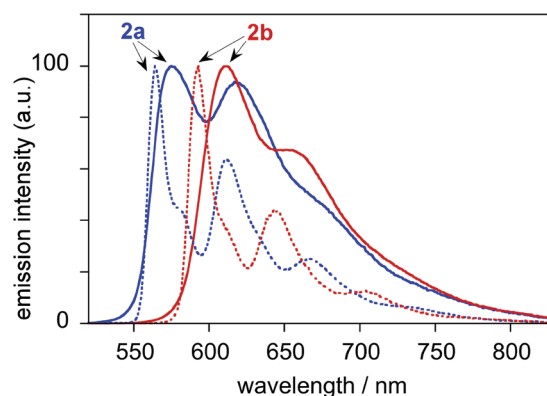
^a Experimental details are given in the ESI. ^b In diethyl ether–isopentane–ethanol (2 : 2 : 1 v/v).

**Fig. 5** Frontier orbital plots of the Rh(III) complex **2a** (left) and of the Ir(III) complex **2b** (right).

constant of Rh compared to Ir, so that the spin selection rule that inhibits the $S_0 \rightarrow T_1$ transition will not be relaxed to the same extent. The shift, observed earlier for cyclometallated Rh complexes,⁵ can be understood in terms of the lower energy of the Rh 4d compared to the Ir 5d orbitals, which will serve to raise the energy of those excited states that feature significant MLCT character. This interpretation is supported by electrochemical evidence: the cyclic voltammogram (*versus* $\text{Fc}|\text{Fc}^+$, in CH₂Cl₂ at 298 K, Fig. 6) of **2b** displays a reversible oxidation at +0.69 V, compared to +1.07 V for **2a**.

The absorption spectra of the acetylide adducts **3** resemble those of the parent complexes **2**, but show higher extinction coefficients throughout the spectra (Fig. 4, Table 2).

Upon irradiation into the visible or UV bands, **2a** displays intense orange-red luminescence in deoxygenated solution at room temperature (Fig. 7, Table 2). The quantum yield of phosphorescence of 0.10 is unprecedented for a cyclometallated rhodium complex and, indeed, apparently for any type of rhodium(III) complex. Moreover, the room temperature lifetime of 16 μs is exceptionally long, and contrasts with values of <10 ns for most complexes based on the Rh(ppy)₂ unit, for example (with the exception of those of ref. 8a). The long lifetime and high quantum yield of **2a** suggest that non-radiative

**Fig. 6** Cyclic voltammograms of M(biqb)(ppy)Cl, M = Rh (**2a**, blue) and Ir (**2b**, red). Recorded in CH₂Cl₂ at 298 K, in the presence of Bu₄NPF₆ (0.1 M) as supporting electrolyte; scale is relative to the $\text{Fc}|\text{Fc}^+$ couple.**Fig. 7** Normalised luminescence spectra of **2a** (blue) and **2b** (red) in CH₂Cl₂ at 298 K (solid lines) and in Et₂O–isopentane–ethanol (2 : 2 : 1 v/v) at 77 K (dotted lines).

decay is substantially reduced compared to Rh(III) complexes with bidentate cyclometallating ligands, an effect likely to be linked – at least in part – to the high rigidity associated with tridentate binding.¹⁶ However, given that an analogous Rh(III) complex of dpyb displays a quantum yield an order of magnitude lower than **2a**, other factors must also be involved.¹⁷ The spectrum recorded at 77 K is slightly blue-shifted compared to room temperature, and displays a well-resolved vibrational progression, $\nu \sim 1400 \text{ cm}^{-1}$. Such a spectrum is typical of an

emissive excited state that has significant ligand-centred character, as supported by the TD DFT calculations (Fig. 5).†

The acetylide adduct **3a** displays similar luminescence properties to the parent chloro complex (Fig. 8); there is no augmentation in efficiency of the type often observed in complexes of metals such as Pt(II) when there are low-lying d–d states present, which are displaced to higher energy on the introduction of a strong-field acetylide co-ligand.¹⁸

The Ir(III) complexes **2b** and **3b** both display very intense red luminescence in solution (Fig. 7 and 8). Again, some vibrational structure is apparent at room temperature, well-resolved at 77 K, suggestive of more ligand-centred character than Ir(ppy)₃ for example. The emission maxima and spectral profiles satisfy well the requirements for good red emitters for displays; e.g. C.I.E. colour coordinates for **2b** are (0.65, 0.34). Moreover, the luminescence quantum yields of around 0.5 (Table 2) are particularly high for red-emitting complexes, where the combined effects of increased non-radiative decay through vibrational deactivation and decreased radiative decay constants (which vary as ν^3) tend to limit efficiencies compared to structurally similar green emitters. The values are comparable to the most efficient red phosphors reported.¹²

In summary, bis(isoquinolyl)benzene is shown to bind as a tridentate N⁺C²N ligand to Rh(III) or Ir(III). Complexes incorporating this ligand in combination with a second, bidentate, cyclometallating ligand are highly luminescent in the orange or red region respectively. **2a** has higher phosphorescence quantum yield than any rhodium complex hitherto reported, whilst the Ir(III) complexes **2b** and **3b** are excellent red emitters. Given the recent successful demonstration of complexes of related dipyridylbenzene ligands as OLED emitters,^{11b,13b} and the ability to further fine-tune the emission wavelength through the bidentate ligand, these new compounds may be attractive in such applications, as well as in the area of time-resolved bioimaging, where intense, long-lived emission in the red region – to which biological tissue is most transparent – is particularly desirable.^{3d}

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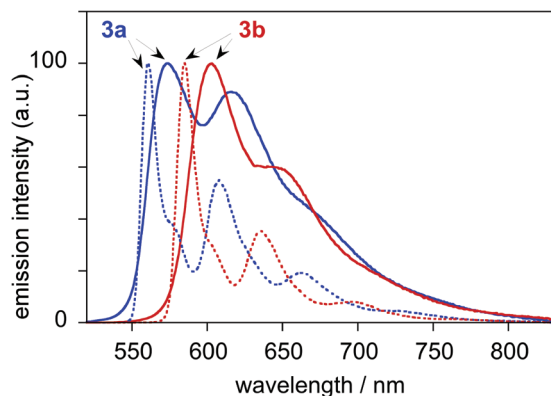


Fig. 8 Normalised luminescence spectra of **3a** (blue) and **3b** (red) in CH₂Cl₂ at 298 K (solid lines) and in diethyl ether–isopentane–ethanol (2 : 2 : 1 v/v) at 77 K (dotted lines).

Notes and references

†Synthesis and characterisation of **2a**. A suspension of 1,3-bis(1-isoquinolyl)benzene (0.050 g, 0.150 mmol) and rhodium trichloride trihydrate (0.053 g, 0.150 mmol) in 2-ethoxyethanol (7 mL) and water (3 mL) was heated to 80 °C for 24 h. After cooling to room temperature, the precipitate was collected *via* centrifugation and washed with water (3 × 5 mL), ethanol (3 × 5 mL) and diethyl ether (3 × 5 mL). Upon drying *in vacuo*, the crude product (**1a**) was obtained as a yellow solid; further product was obtained by repeating the procedure with the remaining solutions (0.059 g, 66%). The crude product, silver triflate (0.056 g, 0.22 mmol) and 2-phenylpyridine (200 μL, 1.78 mmol) were placed in a Schlenk tube, which was degassed three times *via* evacuating and backfilling with nitrogen. The mixture was heated at 110 °C under nitrogen for 20 h then cooled to room temperature and CH₂Cl₂ (35 mL) was added. Solid residue was removed by filtration and the filtrate washed with HCl (1 M, 3 × 35 mL), dried over MgSO₄ and the solvent removed under reduced pressure. Purification was carried out by column chromatography (silica, CH₂Cl₂–methanol, gradient elution from 100 : 0 to 99 : 1) to give the product as a yellow solid (0.065 g, 35%). ¹H NMR (CDCl₃, 700 MHz) δ = 10.27 (1H, d, ³J = 5.0, H⁶-ppy), 9.12 (2H, d, ³J = 7.7, H³-NCN), 8.62 (2H, d, ³J = 7.7, H⁴-NCN), 8.14 (1H, d, ³J = 11.2, H³-ppy), 8.10 (1H, td, ³J = 8.4, ³J = 1.4, H⁴-ppy), 7.63–7.70 (8H, m, H⁴-NCN and H⁵-ppy and H³-ppy and H⁵-NCN and H⁶-NCN, and H⁶-NCN or H⁷-NCN), 7.53–7.56 (3H, m, H²-ppy, and H⁶-NCN or H⁷-NCN), 7.22 (2H, d, ³J = 4.5, H⁵-NCN or H⁸-NCN), 6.74 (1H, td, ³J = 6.0, ⁴J = 1.0, H⁴-ppy), 6.51 (1H, td, ³J = 5.5, ⁴J = 1.0, H⁵-ppy), 5.91 (1H, d, ³J = 8.4, H⁶-ppy). ¹³C NMR (CDCl₃, 176 MHz) δ = 188.5, 167.9, 165.7, 157.9, 150.7, 143.8, 143.8, 142.7, 138.0, 136.8, 130.7, 129.8, 128.2, 127.7, 127.6, 125.9, 123.0, 122.6, 122.3, 121.9, 120.9, 119.0, 113.6, 110.2, 92.3, 92.1. MS (ASAP⁺) *m/z* 623.0 [M]⁺. HRMS (ASAP⁺) Calcd for C₃₅H₂₃³⁵ClN₃¹⁰⁸Rh: *m/z* 623.0636. Found: *m/z* 623.0643. Mp > 250 °C.

§CCDC 937441 (biqbH), 937442 (**2a**), 937443 (**2b**).

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