

Blue-to-green electrophosphorescence of iridium-based cyclometallated materials†

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The photo- and electroluminescence properties of a series of novel, heteroleptic, *mer*-cyclometallated iridium complexes have been fine-tuned from green to blue by changing the substituents on the pyridyl ring of the phenylpyridyl ligand. The X-ray crystal structures of two Ir-based triazolyl complexes are reported.

Research on electrophosphorescence in polymer light emitting diodes (PLEDs) has received much attention in recent years.¹ Using the triplet as well as the singlet excitons formed in electroluminescent devices through energy transfer onto emitters with strong spin-orbit coupling (also referred to as 'triplet harvesting') raises the theoretical limit for the internal quantum efficiency from 25 to 100%, thus greatly increasing device efficiency.² Neutral iridium cyclometallated complexes have attracted considerable attention in photonic applications due to their reasonably short emission lifetime compared with other heavy metal complexes. Their emission energy can be fine-tuned over the visible spectrum by simply manipulating the substituents on the ancillary ligands.³ Although electrophosphorescent PLEDs in the red and green spectral region have been demonstrated in numerous studies,¹ reports on solution-processable blue phosphorescent LEDs (as opposed to vacuum-deposited organic LEDs⁴) are still sparse. An exception is the excellent blue dendritic material described by Burn and Samuel.^{3c}

In this communication, we report the luminescent properties of a series of heteroleptic, blue to green emitting, iridium-based cyclometallated complexes in PLEDs. The design principles behind the new ligands anticipate the opportunity to link them directly to conjugated polymer backbones through Suzuki coupling at the bromo substituents.^{1a} The long chain alkyl groups (R) would mimic a chain for the analogous non-conjugated, covalent attachment of the phosphor to a host polymer.^{1d} In addition, these ligands have the important advantage that the labile *acac* ligand has been replaced by the more stable pyridyl triazolyl

alternative. It has been previously demonstrated that complexes containing *acac* ligands are sensitive to the presence of poly(3,4-ethylenedioxythiophene) : poly(styrene sulfonic acid) (PEDOT : PSS) in working EL devices.⁵

The heteroleptic complexes were prepared from the corresponding dichloro-bridged diiridium bis(arylpyridyl) precursors in the presence of base and 2-[3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl]pyridine (for **1a–f**) and potassium tetrakis(1-pyrazolyl)borate (for **2a,b**) according to the principles laid down by Thompson^{3c} and Igarishi.⁶ During the course of the present work the core complex **1a** was described by Yeh *et al.*^{6b}

An important aspect of the present work has been the determination of the crystal structures of, and the unambiguous assignment of the *mer*- configuration to, the iridium containing 2-[3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl]pyridine (N[^]N) complexes **1a** and **1d**.‡ The perspective view of the structures of **1a** and **1d** is shown in Fig. 1. The geometry about the Ir metal centre is a distorted octahedron and the three cyclometallated ligands (two C[^]N ligands and one N[^]N ligand) are arranged in a meridional (*mer*-) configuration with respect to the three pyridine rings on the ligands. The *mer*- conformation is expected to be the kinetically favoured product from the *trans* dichloro-bridged dimer precursor^{3b} since there is no bond breaking and spatial rearrangement needed. The two nitrogen atoms on the N[^]N ligand coordinating the Ir centre are both *trans*-standing with respect to the phenyl groups on the other ligands. The Ir–N bond lengths in this case are significantly longer than Ir–N4 (**1a**) and Ir–N6 which are arranged *trans* to each other. It is suggested that this Ir–N bond lengthening is caused by a stronger *trans* influence of the phenyl group as opposed to the pyridyl group.^{3b} The Ir–N1 bond to the triazolyl ring is 59 pm shorter than the Ir–N5 for the pyridyl even though both stand *trans* to phenyl groups. This may be due to electronic coupling of the electron-withdrawing trifluoromethyl group on the triazolyl ring with the Ir metal centre.

The thin film electronic absorption and photoluminescence spectra of all complexes were measured by blending 5 wt.% of the metal complex in polystyrene. All complexes exhibit weak absorption bands in the range 350–470 nm that are assigned to spin-allowed and spin-forbidden metal to ligand charge transfer (MLCT) transitions. A very strong absorption band peaking at around 275 nm originates from an intra-ligand π - π^* transition. The luminescence properties of the complexes can be easily tuned by varying the structure of the ligands. The strong blue to green emissions with maxima spanning the range from 455 nm to 530 nm are assigned to ³MLCT/ π - π^* transitions (Fig. 2). The small Stokes shift between the ³MLCT absorption and emission bands indicates

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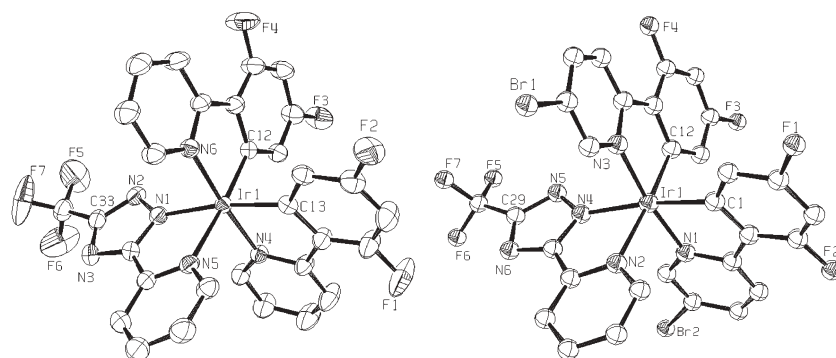


Fig. 1 ORTEP drawings of **1a** (left) and **1d** (right). Solvent molecules and hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

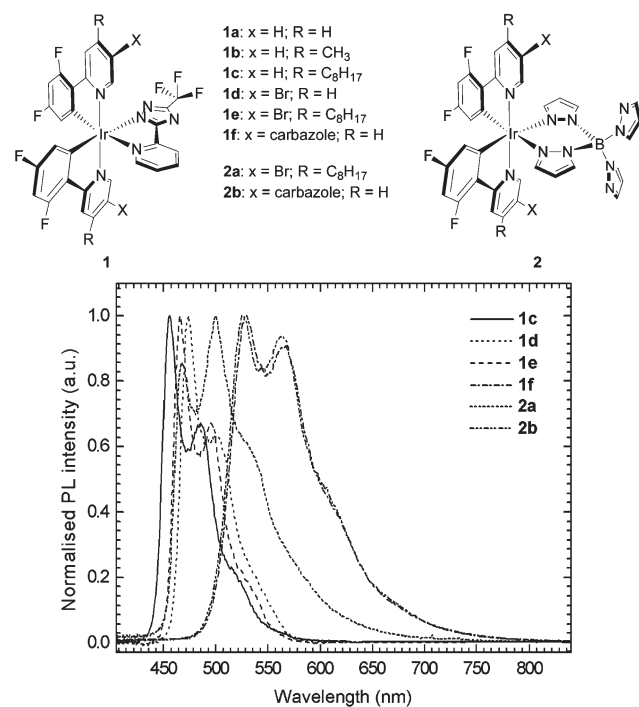


Fig. 2 Chemical structures of **1–2** and normalised photoluminescence spectra of Ir complexes at 5 wt.% in polystyrene films at RT.

that the lowest excited state is predominantly MLCT in nature.⁷ However, unlike the broad and featureless ³MLCT emission band from *fac*-Ir(ppy)₃,⁸ well-defined band structures are observed. The vibronic splitting of 1200 cm⁻¹ (ν_{0-1}) corresponds to the aromatic stretching of the cyclometallated ligands which is diagnostic of the involvement of the intra-ligand $\pi-\pi^*$ transition in the emission. The emissive state is thus an admixture of MLCT and ³ $\pi-\pi^*$ excited states. When an octyl chain is introduced at the 4-position of the pyridyl ring (*para* to the N coordinating the metal centre) a slight spectral blue shift results (*cf.* **1a** with **1c**, a shift of 4 nm/30 meV). An electron-donating group at the 4-position increases the LUMO energy and thus increases the HOMO–LUMO gap.⁹ By extending the π -conjugation of the ligand, on the other hand, a strong red shift can be achieved. This is particularly apparent for complexes substituted by a *meta*-carbazole unit in the 5-position of the pyridyl ring (**1f** and **2b**). A red shift of 71 nm (360 meV) with respect to complex **1a** is observed in this case.

However, even the introduction of a single Br atom in the 5-position (**1d**) with its lone pair coupling with the π electronic system of the ligand results in a significant red shift of 15 nm (80 meV).

The EL spectra of complexes **1–2** blended into poly-(*N*-vinylcarbazole) (PVK) were measured at room temperature in a device configuration of ITO/PEDOT : PSS/PVK : PBD : complex/Ca/Al (PVK : PBD 80 : 20, 5 wt.% of Ir complex) where PBD was added to facilitate the electron transport in the devices [PBD is 2-(4-biphenyl)-5-(*t*-butylphenyl)-1,3,4-oxadiazole]. No host emission is observed even at high current density for any of the emitters; this indicates that charge trapping on the emitter dominates in the recombination process,^{1c,10} and/or the occurrence of complete energy transfer from the host to the emitter. The fact that the current densities at a given voltage vary significantly between devices made from different emitters suggests the metal complexes indeed play an important role in the charge transport instead of purely accepting excitons once charge recombination has occurred on the host polymers. Nevertheless, additional Förster energy transfer of singlet excitons as well as Dexter energy transfer of triplet excitons from the polymer host to the triplet emitter is possible and appears to be complete in the materials presented here. Fig. 3 shows the EL device properties of the two triazolyl-containing Ir complexes exhibiting the highest and lowest emission energies. The spectral features and emission energies in EL resemble those in PL very closely, indicating that the emission originates from the same species in both EL and PL. The EL CIE coordinates for **1c** and **1f** are (0.14, 0.26) and (0.38, 0.59), respectively.

In summary, a series of novel, blue to green light emitting Ir cyclometallated complexes have been synthesised, and the X-ray crystal structures of representative examples are reported. Thin film PL spectra were obtained, and the emission energy has been fine-tuned by modifying the substituents on the ancillary ligands. We have demonstrated blue to green PLEDs using PVK blends containing the novel Ir complexes. The brightness for the bluest complex is 110 cd m⁻² at 18 V and the luminous efficiency at 100 cd m⁻² is 0.06 cd A⁻¹. Direct charge trapping on the triplet emitter is found to be the dominant recombination process in these electrophosphorescent devices.

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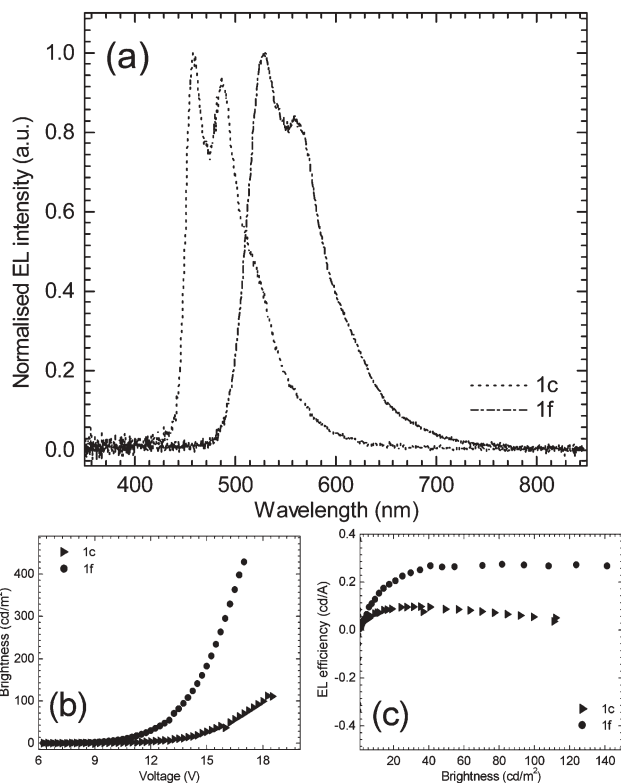


Fig. 3 (a) The EL spectra of the Ir complexes **1c** and **1f** doped in PVK, (b) the plot of luminance as a function of applied bias and (c) the plot of EL efficiency as a function of luminance.

Table 1 PL emission wavelength, quantum yield and CIE coordinates of complexes **1–2**^a

Complex	PL λ_{max} /nm (eV)	Φ^b	CIE coordinates (x, y)
1a	459 (2.70)	ND ^c	0.16, 0.17
1b	455 (2.73)	ND	0.12, 0.15
1c	455 (2.73)	0.38	0.17, 0.29
1d	474 (2.62)	0.53	0.13, 0.34
1e	467 (2.66)	0.57	0.13, 0.25
1f	530 (2.34)	0.61	0.40, 0.57
2a	468 (2.65)	0.63	0.22, 0.42
2b	525 (2.36)	0.70	0.40, 0.57

^a All the data were obtained from Ir complexes doped at 5 wt.% in polystyrene films. ^b $\pm 5\%$ error. ^c ND Not determined.

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Notes and references

‡ Crystallographic data for **1a** $\text{C}_{30}\text{H}_{16}\text{F}_7\text{IrN}_6 \cdot 0.5\text{CH}_2\text{Cl}_2$: $M = 785.70$, monoclinic, space group $C 2/c$, $a = 31.9711(13)$ Å, $b = 10.4764(4)$ Å, $c = 15.9719(7)$ Å, $\beta = 91.6650(10)^\circ$, $V = 5347.4$ Å³, $Z = 8$, $D_c = 1.952$ g cm⁻³, $\lambda = 0.6904$ Å, $\mu = 5.077$ mm⁻¹, $F(000) = 3024$. Of 29052 reflections measured, 8135 were independent ($R_{\text{int}} = 0.06$). Final $R = 0.0223$ (5407 reflections with $I > 3\sigma(I)$) and $wR = 0.0264$. Crystallographic data for **1d** $\text{C}_{30}\text{H}_{14}\text{Br}_2\text{F}_7\text{IrN}_6 \cdot 2\text{CHCl}_3$: $M = 1182.25$, monoclinic, space group $P 2_1/c$, $a = 10.2543(1)$ Å, $b = 21.6017(3)$ Å, $c = 17.3654(3)$ Å, $\beta = 101.4341(6)^\circ$, $V = 3770.3$ Å³, $Z = 4$, $D_c = 2.083$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 6.156$ mm⁻¹, $F(000) = 2248$. Of 64642 reflections measured, 8289 were independent ($R_{\text{int}} = 0.06$). Final $R = 0.0665$ (6168 reflections with $I > 3\sigma(I)$) and $wR = 0.0704$. CCDC 256587 and 256588. See <http://www.rsc.org/suppdata/> for crystallographic data in CIF or other electronic format.

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