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COMMUNICATION

Blue-shifting the monomer and excimer phosphorescence of tridentate cyclometallated platinum(II) complexes for optimal white-light OLEDs[†]

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By using a tridentate N^C^N -coordinating ligand, the luminescence of a cyclometallated Pt(II) complex can be shifted into the blue region, without the problematic drop-off in quantum yield observed for bidentate analogues. The combination of blueshifted monomer and excimer allows white-emitting OLEDs with high colour rendering index to be produced.

The demonstration that luminescent metal complexes can be used as phosphors for organic light-emitting devices (OLEDs) has led to much interest in strategies for controlling the excited-state energy and optimising the emission efficiency of such complexes.¹ Green-emitting phosphors tend to be the most efficient. Good blue emitters are scarce, often owing in part to the energetic proximity of strongly distorted metalcentred states that can provide a deactivation pathway for the emissive states.² While the best available emitters are typically those based on iridium(III), there is increasing interest in platinum(I) complexes, particularly with respect to whitelight-emitting OLEDs (WOLEDs) for lighting applications.³

In contrast to the pseudo-octahedral geometry associated with d⁶ metal ions like Ir(III), complexes of the d⁸ Pt(II) ion are normally square-planar. This geometry favours face-to-face interactions between molecules, involving overlap of orbitals orthogonal to the molecular plane (*e.g.* $5d_{z2}$ and $6p_z$ on the metal, π and π^* orbitals of conjugated ligands). Such interactions in the ground-state lead to aggregate species that may display low-energy absorption and emission bands that are not observed in the isolated molecules, whilst the interaction between excited and ground-state monomers can lead to the concentration-dependent formation of excimers whose emission is also necessarily red-shifted.⁴ At an appropriate concentration in the emitting layer of an OLED, the combination of monomer emission in the blue/green region and excimer/aggregate emission in the red region of the spectrum can provide a means of obtaining white emission from a single triplet-emitting species.⁵ Here again, however, the need to blue-shift the emission bands sufficiently to obtain optimal white light emission has proved a challenge.

Cyclometallated complexes of N^C-coordinating aryl pyridines have been widely investigated as emitters, both with Pt(II) and Ir(III). In their landmark paper, Thompson and Forrest showed how a range of colours could be obtained from complexes based on Pt(ppy)(dpm) (for which λ_{max} = 486 nm in CH₂Cl₂), simply by introducing appropriate substituents into the ppy ligand (dpm = dipivaloyImethane).⁶ By inserting a strongly-donating amine into the pyridine ring and electron-withdrawing fluorine atoms into the aryl ring, a complex (Fig. 1a) emitting deep into the blue could be obtained, at least at low temperature ($\lambda_{max} = 440$ nm at 77 K). However, the shift was accompanied by a dramatic drop in the room-temperature photoluminescence quantum yield, reported to be $<10^{-3}$, compared to much higher values of 0.15 for Pt(ppy)(dpm) ($\lambda_{max} = 486 \text{ nm}$)⁶ and 0.36 for Pt(thpy)(acac) ($\lambda_{max} = 554$ nm).⁷ This is probably due to a combination of molecular distortion and the aforementioned d-d states promoting non-radiative decay.

Pt(II) complexes based on the tridentate, N[°]C[°]N-coordinating ligand 1,3-di(2-pyridyl)benzene (HL¹) (see caption to Fig. 1b), are amongst the brightest Pt-based emitters in solution at room temperature.⁸ They also form highly emissive excimers at elevated concentrations. Related N[°]C[°]N-coordinated complexes of bis(benzimidazol-2-yl)benzene ligands are likewise very good emitters.⁹ The high efficiency seems to be due to a combination of factors, primarily the rigidity imposed by tridentate coordination (*e.g.* the distortion from D_{4h} towards



Fig. 1 Structures of (a) the previously described bidentate complex that emits in the blue with very low quantum yield at ambient temperature, and (b) the intensely luminescent new blue-emitting complex $PtL^{30}Cl$. The complex $PtL^{1}Cl$ is the analogue with no substituents in the rings.

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 D_{2d} local symmetry open to bis-bidentate complexes is prohibited) and to the unusually short Pt–C bond enforced by the flanking heterocyclic rings.¹⁰ We reasoned that these factors should allow more efficient blue-emitting complexes to be obtained and, in combination with the excimer emission, high-quality white light.

The complex PtL³⁰Cl was targeted (Fig. 1b). The substitution pattern is rationalised as follows. Inspection of the frontier orbital plots of PtL¹Cl obtained from TD-DFT calculations in previous work (see Fig S1†)¹¹ reveals that the 4-position of the pyridyl rings plays a role in the LUMO but lies on a node in the HOMO, so that electron-donating amino groups at these positions should destabilise the former without affecting the latter. In contrast, the positions in the central aryl ring *meta* to the metal make a major contribution to the HOMO but not to the LUMO, and so electron-withdrawing fluorine atoms at these positions should independently allow the HOMO to be lowered without affecting the LUMO. The net effect should be a large increase in the HOMO–LUMO gap and hence blueshifted emission.

To date, dipyridylbenzene derivatives have been prepared by Pd-catalysed cross-coupling of dihalogenated benzenes with either pyridyl-zinc reagents (Negishi coupling)¹² or pyridylstannanes (Stille coupling).⁸ In the present case, 4-dimethylamino-2-tri-n-butylstannane was prepared from 4-di-methylamino-2-bromopyridine by lithiation followed by reaction with tri-n-butyl tin chloride. However, repeated attempts to prepare HL³⁰ by Pd-catalysed coupling of the stannane with 1,3-dibromo-4,6-difluorobenzene led to almost quantitative conversion of the stannane to 4-dimethylaminopyridine (DMAP). The introduction of the electron-donating amino substituent clearly renders the compound thermally unstable with respect to decomposition to DMAP.

We therefore applied a new approach to such ligands, namely through the intermediacy of a 1,3-benzene-diboronic ester to undergo Suzuki coupling with a halogenated pyridine (Scheme 1). Thus, Pd-catalysed reaction of 1,3-dibromo-4,6difluorobenzene with bispinacolatodiboron under the standard conditions established by Miyaura for aryl boronate ester synthesis {Pd(dppf)Cl₂ as the catalyst, in the presence of KOAc, DMSO solvent} led to the difluorinated diboronate ester in 86% yield (ESI†). This compound was then crosscoupled with 2 equiv. of 4-dimethylamino-2-bromopyridine to give HL³⁰ in 51% yield after purification. Finally, reaction of this proligand with K₂PtCl₄ in MeCN/H₂O led to the desired complex PtL³⁰Cl in 67% yield.



The new complex is intensely luminescent in degassed solution at ambient temperature. Dilute solutions display sky-blue luminescence ($\lambda_{max} = 453$ nm compared to 491 nm for PtL¹Cl) with a high quantum yield ($\Phi_{lum} = 0.60$; $\tau = 4.7 \,\mu s$). Clearly, the strategy of employing tridentate ligands is successful in allowing a large blue-shift to be induced without compromising the quantum vield. More concentrated solutions appear vividly white under UV irradiation. Under these conditions, the monomer emission is accompanied by strong excimer emission, centred at 596 nm. This represents a substantial shift to higherenergy compared to the excimer of PtL¹Cl (which is centred close to 700 nm). Apparently, the presence of the amino substituents destabilises the interaction between pairs of molecules that is responsible for the formation of the excimer. The clear consequence of this effect is that the excimer more effectively covers the mid-range part of the visible spectrum than PtL¹Cl, and much less energy is wasted in the NIR region.

The efficient coverage of the visible spectrum offered by the combination of monomer and excimer emission renders PtL³⁰Cl of particular interest as a phosphor for WOLEDs. Multi-layer devices have been prepared using PtL³⁰Cl as a phosphorescent guest within the emitting layer (EML). The device architecture-shown in Fig. S2⁺ together with full names of the components-comprises an ITO anode, holetransporting layers of TPD:PC and TCTA, an electron transporting layer of TAZ and an Al/LiF cathode. The 10 nm thick TCTA layer, characterized by a triplet-exciton energy E_T of 2.85 eV, has been used to block triplet-exciton transfer from the Pt complex ($E_T \sim 2.7 \text{ eV}$) to the non-radiative triplet of TPD ($E_T = 2.45$ eV). Meanwhile, the 25 nm-thick layer of TAZ ($E_T = 2.75$ eV) plays a similar role of inhibiting quenching of the triplet excitons at the cathode while at the same time blocking holes, thus enabling the recombination



Scheme 1 Synthesis of HL³⁰ via the diboronate ester.



Fig. 2 Absorption and emission spectra of PtL³⁰Cl (blue) and PtL¹Cl (red) in CH₂Cl₂ at 298 K. Concentration = 4×10^{-4} M for the emission spectra. The dotted lines show the weak $S_0 \rightarrow T_1$ bands on an expanded scale.



Fig. 3 Electroluminescence spectra and CIE diagram (inset) with different concentrations of $PtL^{30}Cl$ in the EML. The host material for the devices shown is a 1:1 mixture of TCTA and TCP by weight.

process to be confined to the EML layer. The choice of host is particularly important for blue-emitting phosphors: materials with high-energy triplet states are required to avoid guest-tohost energy transfer. A material with a low energy barrier for hole transport (TCTA), one with low energy barrier for electrons (TCP), and a 1:1 mixture (by weight) of the two were tested as hosts. Both materials have triplet energies which are sufficiently high not to quench the PtL³⁰Cl exciton by energy transfer (E_T = 2.85 and 2.95 eV respectively).

The electroluminescence efficiencies and spectra of OLEDs having 6 wt% PtL³⁰Cl in different hosts are reported in Fig. S3.[†] When the EML is a mixed matrix of TCTA and TCP, better charge-balancing properties are anticipated as the mixture combines low barriers for both holes and electrons and charge recombination is not restricted to a narrow zone close to the junctions with TAZ or TCTA buffer, but spreads over the entire EML (energy levels of the constituent materials of the device are shown in Fig. S2[†]). Hence, concentrationdependent quenching processes, such as exciton-exciton and exciton-charge interactions, and excitonic migrations toward the quenching TPD layer, are expected to be less effective. In fact, the overall electroluminescence efficiency when the mixed host is employed is higher through the entire current range examined than using either of the pure hosts, as shown in Fig. S3a.[†] The use of TCP alone is seen to give poor results: due to the same barrier for holes and electrons at the TCTA/ TCP junction (0.4 eV), charge recombination is not confined to the EML but can also occur in the TCTA and TPD layers. This is evident from the TPD emission band present in the EL spectrum (Fig. S3b[†]).

Having established its superiority, subsequent studies on the tuning of the blue-to-red ratio with guest concentration were performed using this mixed TCTA:TCP host system. Fig. 3 shows EL spectra and CIE coordinates for different PtL³⁰Cl concentrations in the EML. It is clear that a reduction in dopant concentration leads to a relative increase of the blue-light emission band originating from the radiative decay of molecular triplet excitons of the isolated Pt complex molecules, while increasing dopant concentration increases the contribution of the broad, red-light band emanating from the triplet excimers or aggregates that comprise two or more closely

associated Pt complexes. The EL spectrum of a neat film of the Pt complex (100%) is practically devoid of blue monomer emission (Fig. S3b†). The CIE coordinates show an apparent monotonic trend towards the red with increasing concentration of the phosphor dopant (see inset to Fig. 3). A remarkable increase in the colour rendering index (CRI) is observed between 12 and 25 wt% phosphor content in the EML, reaching values of 87 (at 20 wt%) and 88 (at 25 wt%) with CIE coordinates very close to white: (0.36, 0.37) and (0.37, 0.39), respectively. For the 20% doped device, the quantum efficiency is 3.7% ph/e and the luminous efficiency is 7.4 cd A^{-1} . Further device and performance characteristics are listed in Table S2.†

In summary, whilst green-emitting $Pt(\pi)$ complexes based on N^CN-coordinating ligands are known to be modestly superior, in terms of luminescence quantum yield, to analogues with bidentate ligands,⁸ we have shown here that the superiority of tridentate systems is much more dramatic in the blue region. PtL³⁰Cl is over 600 times more emissive than the analogue based on a similarly substituted phenylpyridine, probably due to the greater rigidity ensuring that deactivating d–d states are kept at higher energy. The complex also performs well as an OLED phosphor, and the accompanying blue-shift in the excimer of this complex ensures good cover-age of the visible region, such that the CRI values are the highest hitherto reported for triplet excimer-based WOLEDs.

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