

Highly efficient orange electrophosphorescence from a trifunctional organoboron–Pt(II) complex†

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Received 21st September 2010, Accepted 22nd October 2010

DOI: 10.1039/c0cc04014b

High efficiency orange OLEDs have been achieved using a trifunctional Pt(II) complex that contains an electron-transporting triarylborane and a hole-transporting triarylamine.

Triarylboron compounds have been the subject of considerable research due to their ability to act as powerful electron acceptors, facilitated by the empty p_π orbital on the boron centre. When the boron atom is protected by appropriate bulky substituents, highly stable materials can be synthesized with impressive charge-transporting properties.¹ In addition, the electron-accepting boron centre readily facilitates intramolecular charge-transfer, providing highly luminescent materials in the presence of an electron donor. We and others have previously demonstrated that by combining an electron-transporting triarylborane with a hole transporting triarylamine, trifunctional molecules can be prepared that show strong luminescence as well as the ability to effectively transport charge, making them attractive for using in OLEDs.² One example of such molecules is BNPB, (Scheme 1) which has been used to fabricate highly efficient blue electroluminescent devices.^{2d,e}

More recently, our group and others have shown that the triarylboron moiety is capable of enhancing charge-transfer from metal centres, including Ir(III),³ Re(I),⁴ and Pt(II).⁵ In the case of Pt(II), the low-lying CT state afforded by the boron functionality greatly increases the energy separation between the emissive state and radiatively quenching d–d states,

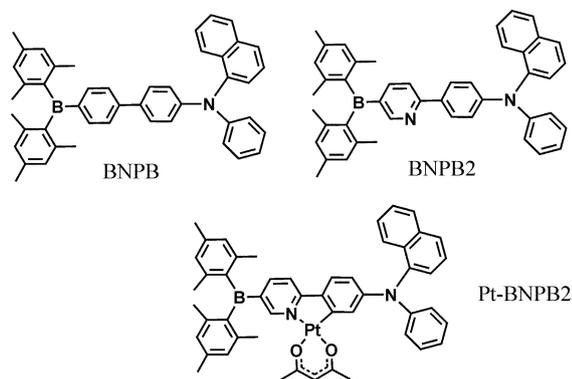
thereby providing large increases in Φ_P and emission brightness in some cases. As a result, we have shown that functionalization with triarylboron can be used to fabricate OLEDs based on Pt(II) emitters with greatly improved efficiencies.^{5b}

Although several examples of highly efficient green electrophosphorescent devices based on Pt(II) compounds have been reported recently,^{5b,6} high performance orange or red Pt(II) based EL devices remain rare. Herein we report the synthesis, photophysical properties and device performance of a trifunctional Pt(II) phosphor, incorporating electron-transport, hole-transport and high-efficiency phosphorescence into a single material. This compound has been used to fabricate a series of orange electrophosphorescent devices with performance among the highest observed for Pt(II)-based OLEDs.⁶

This compound, Pt-BNPB2, was designed as a successor to the highly fluorescent BNPB, able to take advantage of the much higher efficiencies achievable using triplet emitters in OLEDs due to spin statistics. Replacement of the phenyl spacer adjacent to the boron centre with an electron-deficient pyridine moiety not only enhances donor–acceptor charge-transfer, but also allows this compound to act as a cyclometalating ligand to Pt(II). The strong ligand field provided by this rigid N–C chelate raises the energy of deactivating d–d excited states, reducing their interaction with the emissive state and increasing Φ_P .⁷ Acetylacetonate (acac) is a good ancillary ligand, providing excellent solution and solid-state stability. In addition, its highly rigid structure and high triplet level help to ensure efficient phosphorescence from the N–C chelate. The advantages of the boron moiety are threefold: in addition to supporting reversible reduction and promoting MLCT phosphorescence, this bulky group also aids in the formation of amorphous films, greatly reducing exciplex emission that is often problematic from square-planar Pt(II) compounds. The donor moiety was incorporated from the well-known hole-transport material *N,N'*-di-[(1-naphthalenyl)-*N,N'*-diphenyl]- (1,1'-biphenyl)-4,4'-diamine (NPB), and readily facilitates oxidation and hole transport. In addition, this moiety promotes charge-transfer to triarylboron with a high quantum efficiency that is also preserved in the metal complex despite the large red shift in the emission spectrum. This complex is similar to an earlier trifunctional complex reported by our group, but displays improved quantum efficiency and is the first to be evaluated in OLEDs.

The ligand BNPB2 was prepared by selective Suzuki coupling of 2,5-dibromopyridine with *p*-(1-naphthylphenyl-amino)phenyl pinacolborane, which can be synthesized in two steps from 1-naphthylphenylamine.

Subsequent metal–halogen exchange and reaction with FBMes_2 at low temperature affords BNPB2 in good yield. Conventional methods for cyclometalation to form the Pt acac



Scheme 1

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† Electronic supplementary information (ESI) available: Complete experimental and EL performance details and spectral data. See DOI: 10.1039/c0cc04014b

Table 1 Photophysical properties of BNPB2 and its Pt complex

Compound	Abs ^a , $\lambda_{\text{max}}/\text{nm}$, $\epsilon^a/\text{cm}^{-1} \text{ M}^{-1}$	$\lambda_{\text{EM}}^a/\text{nm}$	$\Phi^{a,b}$	$E_{1/2}^{\text{red } c}/\text{V}$	$E_{1/2}^{\text{ox } c}/\text{V}$
BNPB2	396 (42 700)	509	1.0	-2.19	0.56
Pt-BNPB2	456 (37 100)	590	0.91	-1.97	0.49

^a Measured in CH₂Cl₂ at 1×10^{-5} M at 298 K. ^b Fluorescence QY measured relative to anthracene ($\Phi_{\text{F}} = 0.36$),¹⁰ phosphorescent QY measured relative to Ir(ppy)₃ ($\Phi_{\text{P}} = 0.97$).¹¹ All QYs are $\pm 5\%$. ^c In DMF relative to FeCp₂^{0/+}.

complex,⁸ which typically involve heating the ligand at high temperatures (≥ 80 °C) are unsuitable for the synthesis of the complex in this case, as the pyridine–boron bond is unstable in solution at these temperatures. Using a recently developed strategy based on the method of Crespo, reaction of the ligand with 1 equivalent of PtCl(DMSO)(acac) and NaOAc in refluxing methanol affords the desired complex which can then be isolated in high purity by column chromatography.^{5b,9}

Both the ligand and the complex are capable of reduction and oxidation by cyclic voltammetry (Table 1, also see ESI†), highlighting the electron- and hole-transport capabilities of the triarylboron and triarylamine moieties. In addition, these compounds show strong, broad absorption bands in their UV-visible spectra characteristic of B ← N donor–acceptor charge-transfer (Fig. 1). This is consistent with TD-DFT calculations carried out on the complex at the B3LYP level of theory, which indicate that the lowest energy electronic transition is primarily between the electron-rich amino group (HOMO) and the electron-deficient boron centre (LUMO), with high oscillator strength and some contribution from the Pt d orbitals (see ESI†).

The BNPB2 molecule shows bright fluorescent emission in the solid state and in solution ($\Phi_{\text{F}} \approx 1.0$ in CH₂Cl₂). This emission is highly dependent on solvent polarity, with the emission maximum shifting from 431 nm in hexanes to 531 nm in MeCN owing to the highly polarized nature of the charge-transfer excited state. The emission spectra of BNPB2 are red-shifted relative to BNPB ($\lambda_{\text{max}} = 418$ nm in hexanes, 513 in MeCN), due to the increased planarity afforded by the phenylpyridine linker.^{2a} Upon cyclometalation, the complex shows bright orange phosphorescence with remarkably high quantum efficiencies in both solid state ($\Phi_{\text{P}} = 0.46$) and solution ($\Phi_{\text{P}} = 0.91$, $\tau_{\text{P}} = 40.1$ μs in CH₂Cl₂). Its emission maximum shows almost no solvent dependence despite the

polar charge-transfer excited state, suggesting that this is cancelled by the large ground state dipole typical of Pt(II) complexes.¹²

This compound shows impressive performance when doped into a host material and used as the emissive layer in phosphorescent OLEDs. We have recently shown that a transition metal oxide hole injection layer, such as MoO₃, raises the work function of the ITO anode sufficiently so as to allow direct charge injection into the host material. This eliminates the need for a discrete hole-transport layer (HTL) entirely, instead requiring simply a layer of un-doped host material.¹³ Using CBP (4,4'-N,N'-dicarbazolebiphenyl) as HTL and host, and 1,3,5-tris(N-phenylbenzimidazole-2-yl)-benzene (TPBI) as the electron-transport layer (ETL), we first evaluated the EL performance of Pt-BNPB2 by fabricating a series of devices in which the position of the doped emission zone between the electrodes was varied (Fig. 2).

We evaluated a 20 nm double emission zone of 10% Pt-BNPB2 doped into both CBP and TPBI (device A) as well as devices in which the emitter was doped into TPBI (device B) and CBP (device C) individually. Devices with Pt-BNPB2 doped into TPBI had lower efficiencies, most likely due to poor carrier balance. Furthermore, a series of devices we fabricated incorporating an additional hole-blocking layer of BCP, CBP or BAiq (see ESI†) also showed reduced efficiency, likely due to exciton quenching at the EML/HBL interface due to accumulation of charge.

The highest efficiency devices were thus obtained using CBP as host in the absence of any HBL (device C). With this structure, orange electrophosphorescence was achieved with maximum current and power efficiencies of 35.0 cd A⁻¹ and 36.6 lm W⁻¹ and a maximum external quantum efficiency of 10.6%, the highest reported for a device using a triarylboron-based phosphorescent EML and among the highest reported using Pt(II) in OLEDs. Furthermore, these devices show

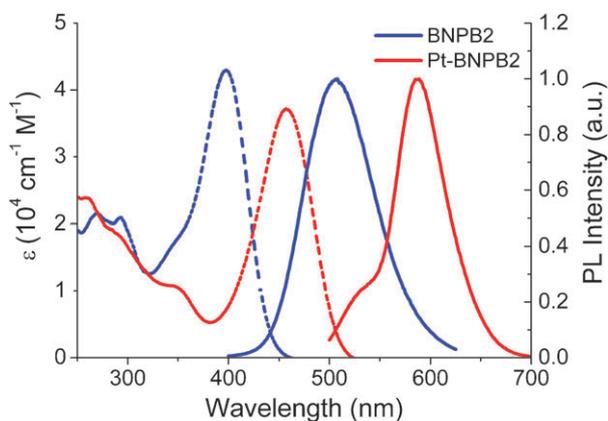


Fig. 1 Absorption (---) and emission (—) spectra at 1.0×10^{-5} M in CH₂Cl₂. $\lambda_{\text{EX}} = 365$ nm for BNPB2 and 470 nm for Pt-BNPB2.

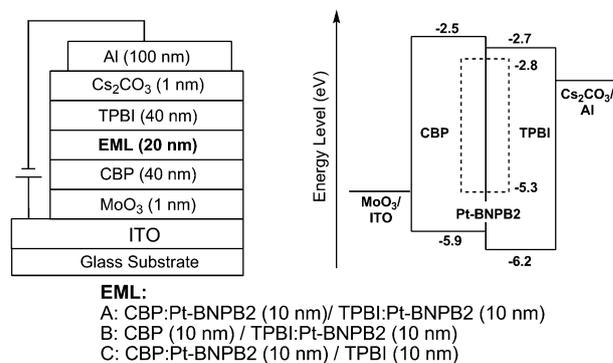


Fig. 2 Device structure and energy level diagram of OLEDs fabricated using Pt-BNPB2 as the emitter at a doping concentration of 10 wt%.

Table 2 EL device performance

Device	V_{on}/V	Luminance ^a /cd m ⁻²	$\eta_{\text{ext,max}}$ [%]	$\eta_{\text{L}}^a/\text{cd A}^{-1}$	$\eta_{\text{P}}^a/\text{lm W}^{-1}$	$\lambda_{\text{max}}/\text{nm}$ (CIE) ^b
A	3.0	4966 (10.2)	10.1	35.0 (3.0)	36.6 (3.0)	581 (0.52, 0.47)
B	3.0	2134 (10.0)	7.5	24.8 (3.0)	26.0 (3.0)	529 (0.38, 0.50)
C	3.0	5590 (10.4)	10.6	33.2 (3.0)	34.8 (3.0)	580 (0.51, 0.48)

^a Voltages at which the values were obtained are shown in brackets. ^b CIE chromaticity coordinates.

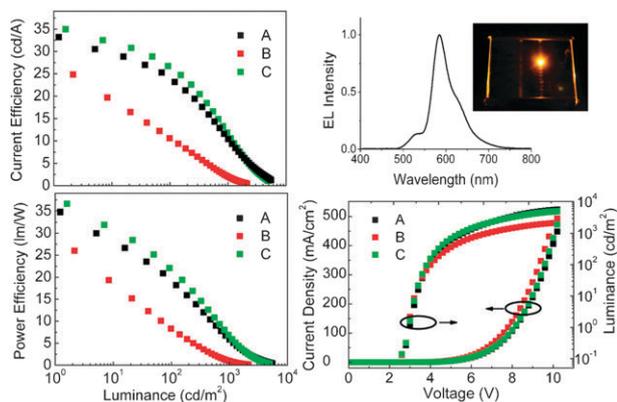


Fig. 3 Luminance–current density–voltage characteristics and efficiency data for devices A, B and C. Also shown is the EL spectrum and the device C photo, operating at 5 V.

impressive performance at higher luminance, making this material a promising candidate for use in commercial devices (Table 2, Fig. 3).

In conclusion, a trifunctional donor–acceptor Pt(II) compound that displays bright phosphorescence from a mixed LC/MLCT excited state promoted by the triarylboron group has been achieved. When incorporated into the emissive layer of organic light-emitting diodes, high-efficiency orange electroluminescence is obtained that ranks among the highest obtained using a Pt(II) complex as emissive material. This high performance may be attributed in part to the presence of both electron and hole transport functional groups in the molecule.

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

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