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A mixed pyridine–phenol boron complex as an organic electroluminescent material

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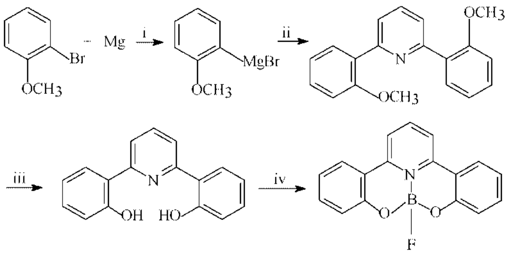
A blue light emitting 1,6-bis(2-hydroxyphenyl)pyridine boron complex has been synthesized and used as an emitting material to fabricate electroluminescent devices.

The electroluminescence (EL) of Alq_3 (q = 8-hydroxyquinolinate) and its derivatives and also of other metal chelate complexes[1–14] have attracted a great deal of attention since the first light-emitting devices (LEDs) fabricated from Alq_3 were reported by Tang and VanSlyke.[1] This report describes the synthesis and EL properties of a 1,6-bis(2-hydroxyphenyl)pyridine boron complex.

The pyridine–phenol ligand dppy and its boron complex were prepared following the synthetic route shown in Scheme 1.† The dppy ligand was obtained by the reaction of 2-bromopyridine with the Grignard reagent from 2-bromoanisole in THF with $[NiCl_2(dppe)]$ as catalyst at room temperature, followed by demethylation in molten pyridinium chloride.[15] The reaction of dppy with 1 equivalent of BF_3 in benzene at 60 °C resulted in the formation of (dppy)BF. An X-ray diffraction study shows that in the solid state (dppy)BF molecules exhibit intermolecular $\pi\cdots\pi$ interactions,‡ leading to columnar aromatic stacks as shown in Fig. 1. The average intermolecular $\pi\cdots\pi$ interaction distance is 3.28 Å. Our earlier report demonstrated that the higher electron mobility of tris(8-hydroxyquinolinato)-gallium is due to intermolecular $\pi\cdots\pi$ stacking interactions.[16] Munakata *et al.* confirmed that strong intermolecular interactions as well as intermolecular aromatic stacking could assist charge-transfer pathways.[17] We believe that the strong intermolecular $\pi\cdots\pi$ interactions in solid (dppy)BF are beneficial in terms of charge mobility.



Scheme 1 Synthetic route towards dppy and (dppy)BF. *Reagents and conditions*: i, THF, 25 °C; ii, $[NiCl_2(dppe)]$, 2,6-dibromopyridine, 25 °C, 12 h, 75%; iii, py·HCl, 200 °C, 3 h, 85%; iv, BF_3, benzene, 60 °C, 5 h, 70–85%.

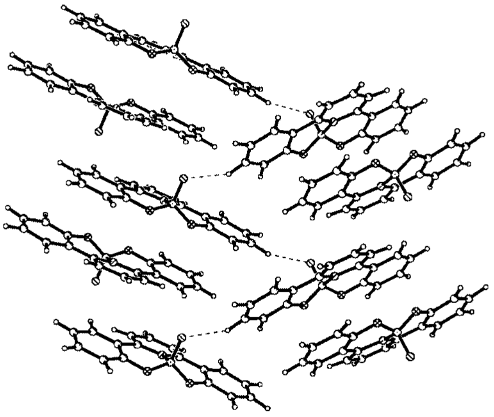


Fig. 1 Intermolecular $\pi\cdots\pi$ interactions in (dppy)BF.

(dppy)BF exhibits strong blue emission at *ca*. 445 nm. The PL spectra of (dppy)BF in $CHCl_3$ solution, the solid state and as an evaporated film are compared in Fig. 2 while Fig. 3 shows the PL and EL spectra of devices of structure [ITO/TPD (500 Å)/(dppy)BF (400 Å)/Al (2000 Å)].§ The EL spectrum are dramatically different from the PL spectra of pure (dppy)BF or solid TPD films, shifting to longer-wavelength (λ_{max} = 550 nm). This suggests that exciplex formation takes place at the organic solid-state interface between TPD and (dppy)BF, resulting in a yellow emission. The devices exhibit a maximum luminance (*L*) of 500 cd m^{-2} with an efficiency of 0.0013 lm w^{-1} and achieve a maximum efficiency of 0.01 lm W^{-1} at 18 cd m^{-2}. In order to investigate the relationship between the interface state and EL properties of boron complexes, PVK (*N*-vinylcarbazole) was employed as hole transport layer to

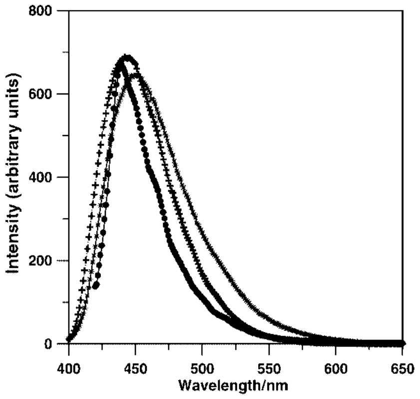


Fig. 2 The PL spectra of (dppy)BF in $CHCl_3$ (+), the solid state (●) and evaporated film (×).

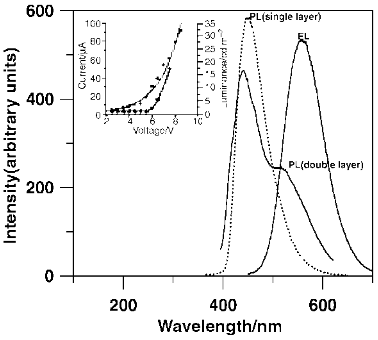


Fig. 3 EL and PL spectra for [ITO/TPD/(dppy)BF/Al] together with the PL spectrum of an evaporated single layer film of (dppy)BF; the inset shows the *I–V* (●) and *L–V* (+) characteristics for the devices.

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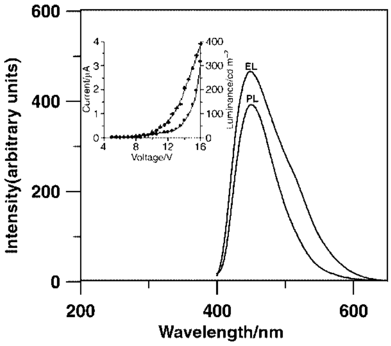

Fig. 4 The EL and PL spectra for [ITO/PVK/(dppy)BF/Al]; the inset shows the *I*–*V* (●) and *L*–*V* (+) characteristics for the devices.

fabricate emitting devices with structure [ITO/PVK (1000 Å)/(dppy)BF (500 Å)/Al (2000 Å)].§ Fig. 4 presents the EL spectrum of [ITO/PVK (1000 Å)/(dppy)BF (500 Å)/Al (2000 Å)] together with its PL spectrum. The EL spectrum exhibits a strong peak at 450 nm accompanied by a weaker shoulder at 500 nm. The above experimental results suggest that there are very little or no exciplex formation at the interface between PVK and (dppy)BF. An alternative explanation may be electroluminescence of PVK is favored by the fact that (dppy)BF acts as an electron transport material. When PVK was used as the hole transport material, the devices showed a dramatic improvement in performance. Each device exhibited a maximum luminance of 400–600 cd m^{-2} with an efficiency of 0.012 lm W^{-1} at a driving voltage of *ca*. 12.5 V and showed a maximum efficiency of 0.1 lm W^{-1} at a luminance of 26 cd m^{-2}. The devices [ITO/TPD/(dppy)BF/Al] and [ITO/PVK//(dppy)BF/Al] exhibited obviously different EL properties. Our experimental results also demonstrated that, frequently, the organic–solid interface can determine the EL properties of organic light emitting devices.[18] At present we have yet to elucidate the mechanism and further investigation is in progress.

The complexes (dppy)B(OMe) and (dppy)B(OEt) have also been synthesized and exhibited similar EL behavior as (dppy)BF. X-Ray structural studies show that there are strong intermolecular $\pi\cdots\pi$ interactions in the solid state of (dppy)-B(OEt) and detailed results will be reported in due course.

In conclusion, we have demonstrated that a pyridine–phenol ligand can be used as to synthesize strong blue phtoluminescent boron complexes. The pyridine–phenol boron complexes show novel electroluminescent properties. We also found that the interface state determines the EL color of the devices based on the boron complexes.

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Notes and references

† Mass, ^{1}H NMR Spectroscopic and elemental analysis: dppy: EIMS: *m*/*z* 263. δ_H(CDCl$_3$, 80 MHz) 9.41 (s 2H), 7.99–7.53 (m, 5H), 7.36–6.80 (m, 6H). Anal. Calc. for $C_{17}H_{13}NO_2$: C, 77.6; H, 4.9; N, 5.3. Found: C, 77.2; H 4.6; N, 5.6%.

(bpy)BF: EIMS: *m*/*z* 291. δ_H(CDCl$_3$, 80 MHz) 8.20–7.72 (m, 5H), 7.57–6.88 (m, 6H). Anal.: Calc. for $C_{17}H_{11}NO_2BF$: C, 70.1; H, 3.8; N, 4.8. Found: C, 70.3; H, 3.6; N, 4.5%.

‡ *Crystal data*: (dppy)BF: $C_{17}H_{11}NO_2BF$, M_r = 291, monoclinic, space group $P2_1/c$, a = 7.5482(7), b = 7.9581, c = 22.422 Å, β = 98.227(9)°, V = 1333.0(2) Å^3, Z = 4, D_c = 1.450 g cm^{-3}, F(000) = 600. Reflection data were collected on a Siemens R3 four-cicle diffractometer using graphite-monochromated Mo-Kα radiation and ω scans at room temperature, giving 3365 unique reflections. The structure was solved by direct methods (SHELXTL Version 5). All atoms were refined anisotropically using full-matrix least squares to give R_1 = 0.066 for 2340 reflections with $F > 4\sigma(F)$. CCDC 182/1716.

§ The devices of [ITO/TPD/(dppy)BF/Al] were fabricated by successive vacuum deposition of organic materials onto the ITO coated glass substrate. Then a layer of aluminum was deposited onto the layer of (dppy)BF. For devices [ITO/PVK/(dppy)BF/Al], the PVK layer was formed by spin coating a 10 mg ml^{-1} chloroform solution, and (dppy)BF was deposited on the PVK layer by thermal evaporation, followed by deposition of the aluminum cathode *in vacuo*.

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