164 *Chem. Mater.* **2005,** *17,* 164−170

Mes_2B(*p*-4,4′-biphenyl-NPh(1-naphthyl)): A Multifunctional Molecule for Electroluminescent Devices

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Received August 18, 2004. Revised Manuscript Received October 15, 2004

Mes_2B(*p*-4,4′-biphenyl-NPh(1-naphthyl)), (BNPB) a novel luminescent molecule that contains part of the well-known NPB functionality (NPB = *N*,*N*′-di-1-naphthyl-*N*,*N*′-diphenylbenzidine) and a three-coordinate boron center has been synthesized. BNPB is a bright blue emitter with λ_{max} (emission) = 452 nm and a photoluminescent quantum yield of 95% in solution and 31% in the solid state. BNPB is an amorphous material and forms films readily via either solution casting or vacuum vapor deposition. A single layer EL device **A** with the device structure of ITO/BNPB/LiF/Al, two double-layer EL devices **B** and **C** with the device structure of ITO/NPB/BNPB/Ag for **B** and ITO/BNPB/Alq_3/LiF/Al for **C**, and a triple-layer device **D** with the structure of ITO/NPB/BNPB/Alq_3/LiF/Al have been fabricated and their performance has been evaluated. Device **A** produces a weak blue electroluminescence (EL). Device **B** produces a bright blue EL, identical to that of device **A**. Device **C** produces a green EL, typical of Alq_3. Device **D** produces a broadband whitish-blue EL attributable to dual emission from the BNPB zone and the Alq_3 zone. Devices **A**−**D** demonstrate that BNPB is capable of transporting both holes and electrons in addition to being a blue emitter for EL devices.

Introduction

Organic light-emitting diodes/devices (OLEDs) based on small molecules typically comprise three layers—the electron-transport layer, the emitter, and the hole-transport layer, to facilitate charge transport and charge recombination, and enhance the overall efficiency of the device.[1] The other commonly used strategy in enhancing device efficiency is to dope emitters into a hosting layer.[2] Although very bright and efficient OLEDs have been achieved by using multilayer device structures or the doping strategy, from a manufacturing point of view devices that have fewer layers and do not require doping are much more desirable because they simplify the fabrication process, allow better control of the uniformity of the device, and minimize the problems of interfacial diffusion—one of the common causes responsible for the degradation and poor long-term stability of OLEDs. One way to reduce the number of layers in OLEDs is to use molecules that are capable of functioning as efficient emitters as well as charge-transport materials, i.e., bifunctional or multifunctional molecules. Alq_3 is a well-known example of a bifunctional molecule, capable of acting as a bright green emitter as well as an electron-transport material in OLEDs, as demonstrated by the simple double-layer devices reported by Tang and co-workers.[3] Silole derivatives that are usually green emitters and capable of transporting electrons are recent examples of bifunctional molecules.[4] Stable blue emitters remain to be the most challenging and most sought-after materials in OLEDs, despite much recent research and many examples of blue emitters[5] reported in the literature, due to the well-known poor stability of blue emitters in OLEDs. Three-coordinate boron compounds have emerged recently as promising materials for OLEDs. Shirota and others have reported several three-coordinate boron compounds as electron-transport/hole-blocking materials for OLEDs.[6] We have reported recently that by introducing 2,2′-dipyridylamino or 7-azaindolyl functional groups in three-coordinate boron

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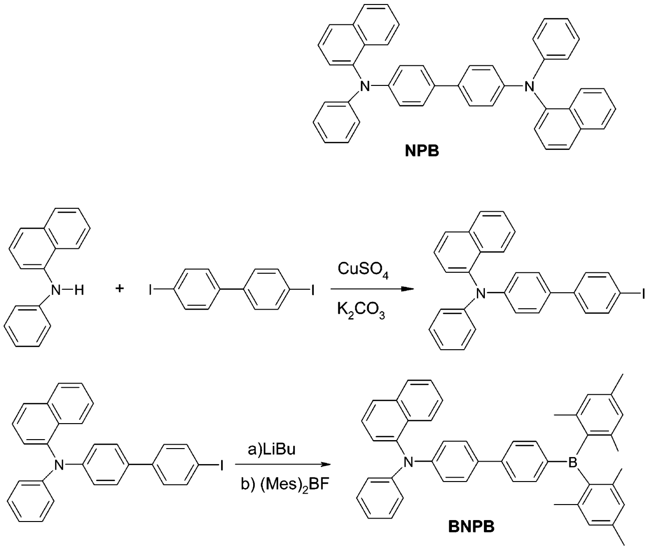
10.1021/cm048617t CCC: $30.25

Scheme 1



compounds, the resulting boron compounds can function as a blue emitter and an electron-transport material as well. As a result, no electron-transport layer is required for electroluminescent (EL) devices where these boron compounds are used as blue emitters.[7] One problem with our previously reported three-coordinate boron compounds is that the double-layer devices (ITO/NPB/Boron/LiF/Al) are either not efficient or produce exciplex emission between the boron and the NPB layer, and as a consequence, a blocking layer such as bicarbazole is required to achieve blue emission. In addition, 2,2′-dipyridylamino or 7-azaindolyl functionalized three-coordinate boron compounds are in general not capable of transporting holes. To improve the performance of our three-coordinate boron compounds in OLEDs, we have modified the boron molecule by attaching part of the NPB molecule to the boron center to produce a novel new molecule BNPB (Mes_2B[*p*-4,4′-biphenyl-NPh(1-naphthyl)]). The choice of the NPB functionality in the boron molecule is based on the well-known fact that NPB is a good hole-transport material (the structure of NPB is shown in Scheme 1), hence its inclusion in the emitter may facilitate hole-transport and may allow us to eliminate the standard hole-transport layer such as NPB in the device. Furthermore, due to the similarity of the NPB molecule and the NPB group in BNPB, it may be possible to eliminate exciplex emission by using BNPB as the emitter. The results of our investigation on BNPB and its usage in EL devices are reported herein.

Experimental Section

All starting materials were purchased from Aldrich Chemical Co. and used without further purification. Solvents were freshly distilled over appropriate drying reagents. All experiments were carried out under a dry nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. TLC was carried out on silica gel. Flash chromatography was carried out on silica (silica gel 60, 70−230 mesh). ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 300 or 500 MHz spectrometers. Excitation and emission spectra were recorded on a Photon Technologies International QuantaMaster model 2 spectrometer. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada. The melting point was determined on a Fisher-Johns melting point apparatus. All DSC measurements were performed on a Perkin-Elmer Pyris DSC 6. Cyclic voltammetry was performed using a BAS CV-50W analyzer with scan rates of 100 mV s^{-1}. The electrolytic cell used was a conventional three-compartment cell in which a Pt working electrode, a Pt auxiliary electrode, and a Ag/AgCl reference electrode were employed. The CV measurements were performed at room temperature using 0.10 M tetrabutylammonium hexafluorophosphate (TBAP) as the supporting electrolyte. The ferrocenium/ferrocene couple was used as the internal standard. 4-Iodo-4′-(1-naphthylphenylamino)biphenyl was synthesized by a modified literature method.[8]

***p*-(1-Naphthylphenylamino)-4,4′-biphenyldimesitylborane (BNPB).** To a solution of 4-Iodo-4′-(1-naphthylphenylamino)-biphenyl (0.497 g, 1 mmol) in Et_2O (60 mL) was added a hexane solution of *n*-BuLi (1.6 M, 0.69 mL, 1.1 mmol) at −78 °C, and the mixture was stirred for 1 h at this temperature. A solution of dimesitylboron fluoride (0.33 g, 90%, 1.1 mmol) in Et_2O (20 mL) was then added. The reaction mixture was stirred for another hour at −78 °C, allowed to slowly reach room temperature, and kept stirring overnight. The solvents were removed under reduced pressure. The residue was subjected to column chromatography on silica gel (CH_2Cl_2/hexane, 1:10) to afford colorless compound BNPB in 89% yield. T_g: 105 °C. ^{1}H NMR in CD_3Cl (δ, ppm, 25 °C): 8.01(d, $J = 8.5$, 1H), 7.95 (d, $J = 8.0$, 1H), 7.84 (d, $J = 8.0$, 1H), 7.59−7.63 (m, 4H), 7.50−7.55 (m, 4H), 7.42 (m, 2H), 7.26−7.30 (m, 2H), 7.17 (dd, $J = 8.5$, 1.0, 2H), 7.12 (dd, $J = 9.0$, 1.5, 2H), 7.04 (dd, $J = 7.0$, 1.5, 1H), 6.90 (s, 4H), 2.38 (s, 6H), 2.11 (s, 12H). ^{13}C NMR in $CDCl_3$ (δ, ppm, 25 °C): 148.8, 148.5, 144.3, 143.7, 142.3, 141.3, 138.9, 137.6, 135.8, 133.7, 131.7, 129.6, 128.9, 128.6, 128.2, 127.7, 127.1, 126.9, 126.8, 126.6, 126.2, 126.0, 124.7, 122.9, 122.7, 121.8, 23.9, 21.7. Anal. Calcd. for $C_{46}H_{42}BN$: C, 89.18; H, 6.79; N, 2.26. Found: C, 89.26; H, 6.73; N, 2.19.

Photoluminescent Quantum Yield Measurement of BNPB Films. UV−Vis absorption spectra were measured with a Cary 3E (Varian) spectrophotometer. Photoluminescence spectra were recorded with a Photon Technology International QuantumMaster model QM-1 equipped with an extra sample compartment containing an integrating sphere. The solid-state absolute quantum yields of luminescence efficiencies were obtained using an integrating sphere. Two excitation wavelengths were used: 390 and 420 nm. The 420 nm excitation line overlapped with the emission, therefore 390 nm was chosen. The sample compartment was flushed with nitrogen for thin film measurements. Fluorescent spectra of the thin films, spin-cast at 1500 rpm from $CHCl_3$ on quartz, had an optical density of 0.4. Fluorescent spectrum was recorded 22.5° normal to the incident light.

Fabrication of Electroluminescent Devices. The EL devices were fabricated using a K. J. Lesker OLED cluster tool with six high-vacuum process chambers. For the current experiments, 2 in. × 2 in. ITO-coated glass substrates were used. The patterned ITO surface was sequentially cleaned in acetone, methanol, deionized water, and UV ozone treatment. All the testing devices have an

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active area of 1 × 1 mm^2. The base pressures of the organic and metallization chambers are 5.9 × 10^{-9} Torr and 3.9 × 10^{-8} Torr, respectively. The pressures during the deposition process in the two chambers are lower than 7.0 × 10^{-7} Torr. The growth rates are ∼2 Å/s for organic materials, 0.1 Å/s for LiF, and ∼1.5 Å/s for metals (Al and Ag). Luminance−current density−voltage (*L*−*J*−*V*) characteristics were determined in ambient atmosphere using a HP 4140B pA meter and a Minolta LS-110 m. The dwell time for each testing point was 2 s. Electroluminescence (EL) spectra were recorded using an USB2000−UV−Vis miniature fiber optic spectrometer.

Results and Discussion

Synthesis and Properties of BNPB. The synthetic procedures for BNPB are shown in Scheme 1. The starting material 4-I-4′-(1-naphthylphenylamino)-biphenyl was synthesized from the coupling reaction of 4,4′-diodobiphenyl with 1-naphthylphenylamine using Ullmann condensation methods.[9] The reaction of 4-I-4′-(1-naphthylphenylamino)-biphenyl with butyllithium converted it to a lithium salt which subsequently reacted with $(Mes)_2BF$ to replace the fluoride and produce BNPB in good yield (89%). BNPB has been fully characterized by NMR spectroscopy and elemental analyses.

BNPB is an amorphous solid at ambient temperature with a T_g of 105 °C, which is in sharp contrast to previously known luminescent three-coordinate boron compounds, the majority of which are crystalline at ambient temperature. Another interesting property of BNPB is its high solubility in any organic solvent including hexane, benzene, THF, CH_2Cl_2, ethanol, and DMF. One unusual property of BNPB is that the solution of BNPB readily forms uniform and transparent films on glass surfaces by either dropping the solution directly on the surface or by spin-coating. This property is really unusual since small molecules have the tendency to form powders or microcrystalline particles on surfaces when deposited directly from solution. One major advantage of organic polymers for OLEDs is that they can form films readily, hence the possibility for processing by simple spin-casting. Earlier reports by Shirota and others have shown that branched molecules or starburst molecules often display good film-forming properties.[6,10] Some of the three-coordinate boron compounds reported by Shirota have also been found to form film readily.[10] However, most of the previously known compounds still require vacuum deposition to form amorphous films for OLEDs applications. BNPB is a fairly small molecule with a shape and a molecular weight resembling that of NPB. NPB however does not form films on a surface when deposited directly from solution. We do not understand yet why BNPB forms film readily. Nonetheless, the excellent film-forming properties of BNPB suggest many potential organic device applications, several of which are currently being explored in our laboratory.

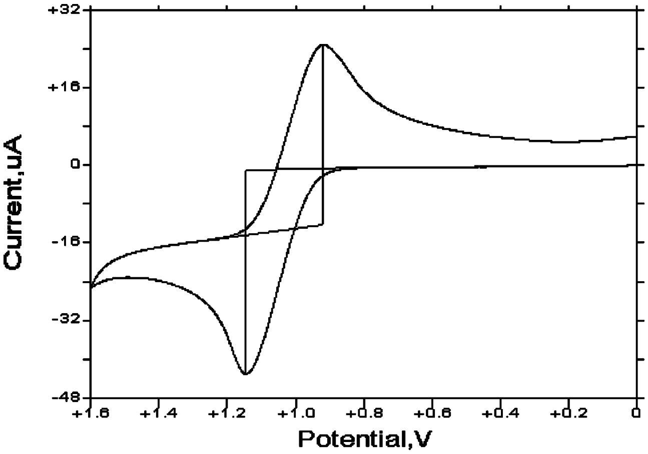

Figure 1. CV diagram showing the oxidation potential of BNPB in CH_2Cl_2.

Electronic Properties. The electrochemical properties of BNPB were investigated by cyclovoltammetry. BNPB displays a reversible oxidation peak in CH_2Cl_2 at 1.03 V (versus AgCl/Ag) (Figure 1). For NPB under the same experimental conditions, two reversible oxidation peaks at 0.75 and 1.05 V were observed, which can be attributed to the sequential oxidation of the two amino centers in NPB. Because of the presence of one amino center in BNPB, only a single reversible oxidation peak was observed for BNPB. The oxidation potential of BNPB is higher than the first oxidation potential of NPB, but similar to the second oxidation potential of NPB. The reduction potential for BNPB was measured in a THF solution. A pseudo-reversible reduction peak (the height of i_c and i_a is not symmetrical) at −1.88 V was observed, which can be attributed to the reduction of the boron center. Using the reduction and oxidation potentials of BNPB, the HOMO and LUMO energy levels of BNPB were calculated to be −5.30 eV and −2.44 eV, respectively, and the band gap was estimated to be 2.86 eV. The absorption edge of the UV−Vis spectrum of BNPB in CH_2Cl_2 is ∼430 nm, which corresponds to a band gap of 2.88 eV, similar to that obtained from the redox potentials. The LUMO level of BNPB is not as low as that of Alq_3. However, three-coordinate boron compounds have been demonstrated previously to be good electron-transport materials due to the availability of the empty p_π orbital on the boron center. Therefore, we anticipated that BNPB maybe able to transport electrons in OLEDs.

Luminescent Properties. BNPB emits a blue color in the solid state (as powders and films) when irradiated by UV light with the emission maximum at 451 nm. In solution, BNPB shows a strongly solvent-dependent emission band. The absorption and excitation spectra of BNPB in various solvents are similar (excitation λ_{max} = 377 nm). However, the emission spectrum of BNPB shifts toward a longer wavelength with the increasing polarity of the solvents. As shown by Figure 2, the shift of the BNPB emission maximum with solvents is quite dramatic. For example, in the nonpolar solvent hexane the emission λ_{max} of BNPB is 418 nm, while in CH_3CN the emission λ_{max} becomes 513 nm. Solvent-dependent emission has been frequently observed for three-coordinate organoboron compounds and has been attributed

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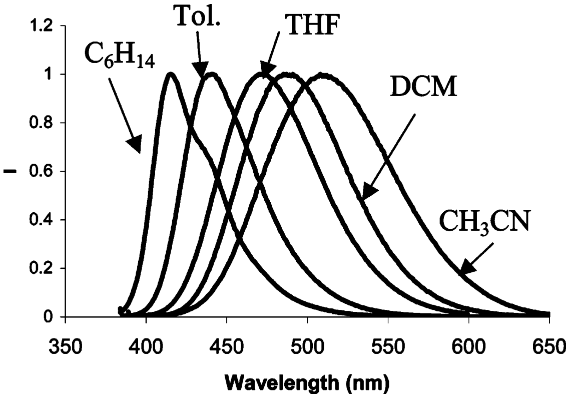
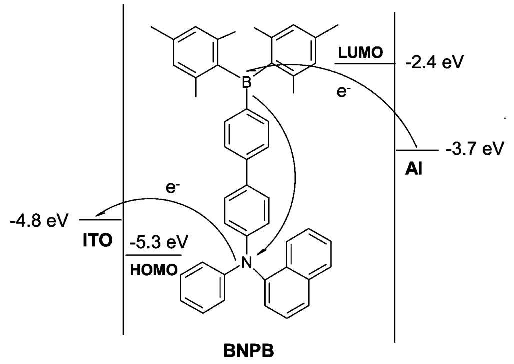


Figure 2. Emission spectra of BNPB in various solvents ($\lambda_{ex} = 377$ nm, $\sim 10^{-5}$ M).



Device A

Figure 3. Diagram showing the energy level and the role of BNPB in EL device **A**.

to the presence of a highly polarized excited state.[11] Our earlier investigation on related three-coordinate boron compounds showed that the LUMO is dominated by the empty p_π orbital of boron and the HOMO is dominated by the π orbitals of the diarylamino group.[7] The excitation process therefore involves charge transfer from the amino portion to the boron center, resulting in a highly polarized excited state. BNPB is a very bright emitter in both solution and the solid state. The quantum yield of BNPB in THF has been determined to be 0.95 (relative to that of 9,10-diphenylanthracence). The quantum efficiency of BNPB in films was determined to be 0.31 (±0.03) by using the integration sphere method.

Electroluminescent Properties. To evaluate the optoelectronic characteristics of BNPB, several EL devices have been fabricated. Our first attempt was to take advantage of the excellent film-forming properties of BNPB by fabricating a single-layer EL device of BNPB via spin-coating the solution of BNPB directly to the ITO substrate, followed by vacuum evaporation of the Al cathode layer on top of the BNPB layer. Various thicknesses of the BNPB layer were used. Although weak blue EL was observed for these devices, they all showed a very high turn-on voltage (~30 V), and as a consequence, the device only survived for a short time after it was turned on. To improve the efficiency, we attempted to co-deposit NPB with BNPB in various ratios by spin-coating the solution mixture. However, the films obtained lacked good homogeneity due to the tendency of solid formation by NPB. As a result, the performance of the single-layer NPB−BNPB device was not much better than that of the single-layer BNPB device. Our subsequent efforts therefore focused on the fabrication of BNPB EL devices by vapor-phase deposition under high vacuum.

Using vapor-phase deposition, a single-layer EL device **A** (Figure 3) was fabricated for BNPB (ITO/BNPB (90 nm)/LiF (0.5 nm)/Al). The device produced a blue EL that matches the PL spectrum of BNPB film (Figure 5). The turn-on voltage is 6.2 V. The device is, however, not bright as shown by Figure 6. In addition, device **A** was not stable. Nonetheless, device **A** demonstrates that BNPB is capable of functioning as an emitter, a hole-transport molecule, and an electron-transport molecule in EL devices. This behavior can be attributed to the coexistence of the three-coordinate boron center (an electron acceptor, transporting electrons), and the amino center (an electron donor, transporting holes) in BNPB and the high PL efficiency of BNPB, as shown by Figure 3. The poor stability of device **A** could be caused by several factors such as the poor interfacial stability between BNPB and LiF/Al layers (see discussion below). The low EL efficiency of device **A** is likely due to the poor matching of energy levels of BNPB with those of the cathode and the anode, and the lack of efficient emission zone where electron and hole are blocked. Such emission zone is generally realized at molecular heterojunction such as the classic NPB/Alq_3 interface.

To improve the efficiency of the device, two types of double-layer devices were fabricated. The first type of a double-layer EL device uses NPB as the hole-transport layer and BNPB as the emitter and the electron-transport layer with the structure of ITP/NPB (60 nm)/BNPB (90 nm)/LiF-(0.5 nm)/Al. However, this device was not stable. After the cathode layer (LiF/Al) was replaced by Ag metal, a stable double-layer device **B** (ITP/NPB (60 nm)/BNPB (90 nm)/Ag) was achieved successfully. This behavior of BNPB is peculiar and quite unexpected because previously we have used the LiF/Al cathode successfully for EL devices of related three-coordinate boron compounds. Effort is being taken by our laboratory to investigate and understand the origin of the poor interfacial stability of BNPB with LiF/Al. Although the work function of the Ag layer matches poorly with the LUMO of BNPB, device **B** produced fairly bright blue emission. The EL spectrum of device **B** is the same as that of the single-layer device **A**. The efficiency of **B** is several orders of magnitude higher than that of **A** as shown by Figure 7. The turn-on voltage of **B** is 7.4 V, somewhat higher than that of **A**—as expected for a Ag cathode OLED. The maximum luminance at 12 V is 840 Cd/m², and the

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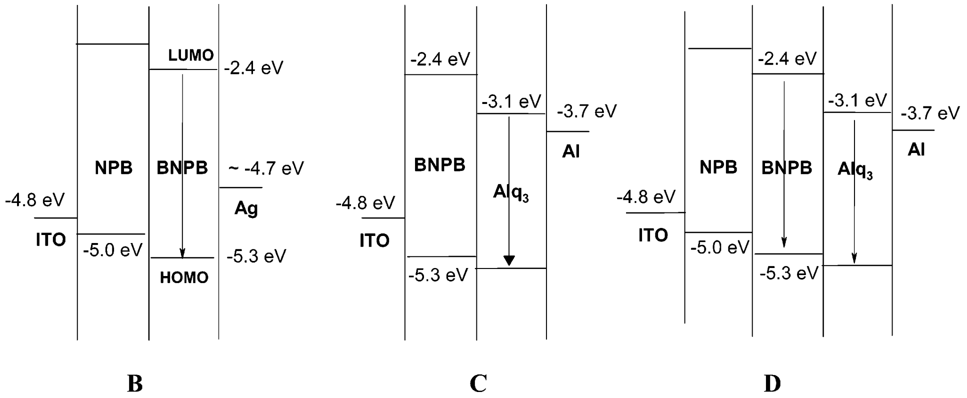

B **C** **D**

Figure 4. Diagram showing the EL device structures of **B**−**D**.

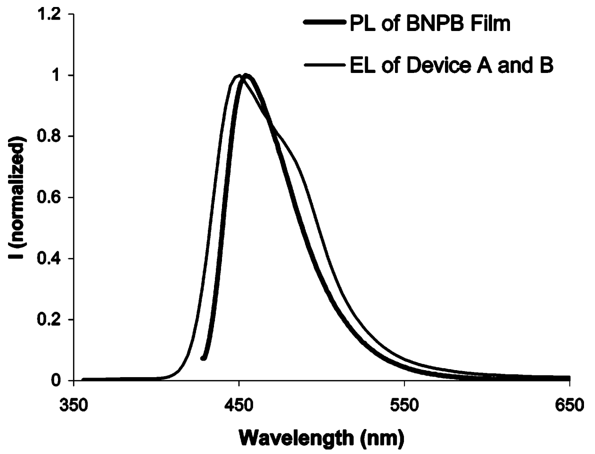

Figure 5. PL of BNPB film and the EL spectrum of devices **A** and **B** (they are identical).

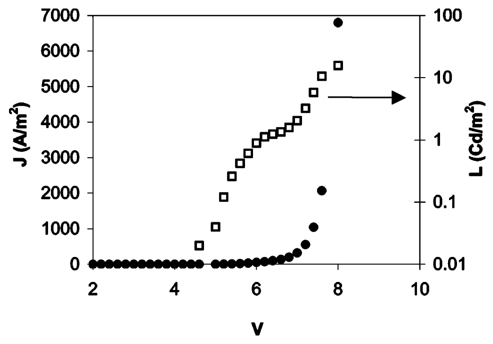

Figure 6. *J*−*L*−*V* characteristics of device **A**.

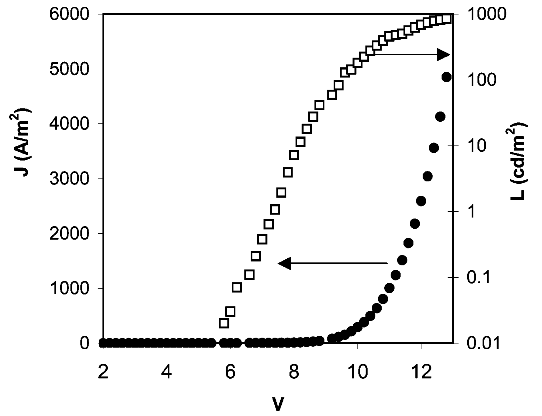

Figure 7. *J*−*L*−*V* characteristics of device **B**.

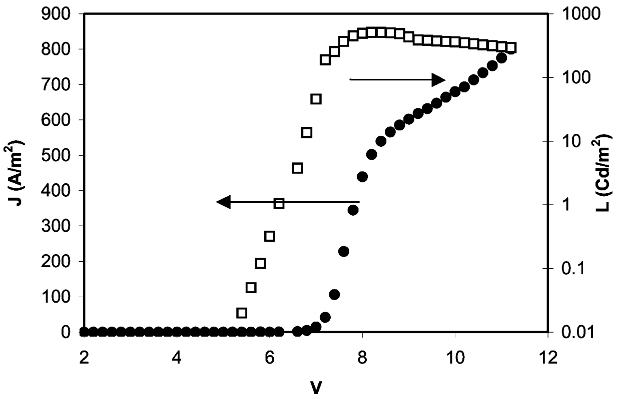

Figure 8. *J*−*L*−*V* characteristics of device **C**.

maximum efficiency is 1.0 Cd/A (at 9 V). The enhancement of efficiency of device **B** is clearly due to the fact that the HOMO level of NPB is midway between that of BNPB and ITO, thus enhancing hole transport. In addition, the NPB layer also likely acts as an electron-blocking layer, preventing the electrons from reaching the anode prior to the production of excitons. Device **B** demonstrates that bright blue EL devices could be produced using a simple double-layer structure where BNPB is used as both the emitter and the electron-transport layer.

To evaluate the utility of BNPB as a hole-transport material, a second double-layer device **C** using BNPB as the hole-transport layer and Alq_3 as the electron-transport layer (ITO/BNPB (60 nm)/Alq_3 (45 nm)/LiF (0.5 nm)/Al) was fabricated. Device **C** produces a green emission with an EL spectrum typical of Alq_3, an indication that the emission zone of device **C** is confined in the Alq_3 layer. This is not surprising since Alq_3 is the best known bifunctional molecule, being highly effective in both electron transport and light emission. Device **C** is bright and efficient as shown by the experimental data in Figure 8. The maximum efficiency is 4.5 Cd/A at 7 V. Device **C** demonstrates that BNPB can indeed function as a hole-transport material in OLEDs. However, although the maximum efficiency of device **C** is comparable to that of a standard double-layer device (ITO/NPB (60 nm)/Alq_3 (45 nm)/LiF-(0.5 nm)/Al) fabricated and characterized under the same condition as for device **C** in our laboratory, at high voltage (>7.5 V), the luminance of device **C** starts to decrease, an indication of poor stability of the device at a relatively high voltage. The fact that no BNPB emission was observed in device **C** can be attributed to the lack of the NPB layer,

Table 1. Data of Electroluminescent Devices

device structure	turn-on voltage (V)	EL (λ_{max}) nm	max. luminance (Cd/m^2)	max. efficiency (Cd/A)	efficiency at ~300 Cd/m^2
A: ITO/BNPB(90 nm)/LiF/Al	6.2	453	16 at 8 V		
B: ITO/NPB(60 nm)/BNPB(90 nm)/Ag	7.4	453	840 at 12 V	1.0 at 9 V	0.52 at 332 Cd/m^2
C: ITO/BNPB(60 nm)/Alq$_3$(45 nm)/LiF/Al	6.2	536	500 at 8 V	4.5 at 7 V	1.6 at 355 Cd/m^2
D: ITO/NPB(60 nm)/BNPB(60 nm)/Alq$_3$(45 nm)/LiF/Al	5.8	490	5053 at 12 V	6.0 at 8 V	5.1 at 352 Cd/m^2

which would otherwise serve as an electron-blocking layer. As shown by device **A**, in the absence of NPB, BNPB cannot emit effectively in an EL device. Furthermore, the lack of the electron-blocking NPB layer in device **C** may allow electrons to migrate directly from the BNPB layer to the anode without exciton formation and photon emission.

To further improve the device efficiency, a triple-layer device **D** where NPB is used as the hole transport, BNPB is the emitter, and Alq$_3$ is the electron transport (ITO/NPB(60 nm)/BNPB(60 nm)/Alq$_3$ (45 nm)/LiF(0.5 nm)/Al), has been fabricated. Compared to devices **C** and **B**, device **D** is very bright and highly efficient. As shown in Figure 9, the turn-on voltage of **D** is 5.8 V and the maximum brightness at 12 V is 5053 Cd/m^2. The maximum efficiency at 8 V is 6.0 Cd/A, one of the brightest EL devices indeed. For comparison purposes, the energy diagrams of devices **B**−**D** are shown in Figure 4. Data for EL devices **A**−**D** are summarized in Table 1.

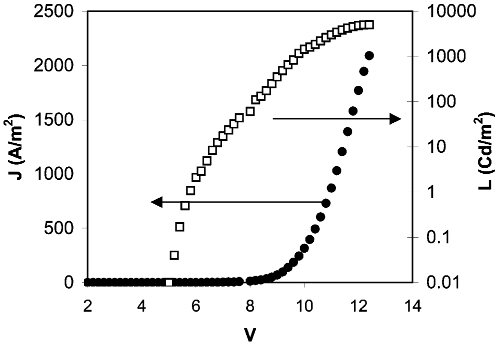

Figure 9. $J-L-V$ characteristics of device **D**.

The most interesting phenomenon is that device **D** emits a whitish blue color. The EL spectrum of device **D** is a broad emission band covering the entire 420−600 nm region with λ_{max} at 490 nm. This emission band is clearly not due to exciplex emission at either the NBP/BNPB interface or the BNPB/Alq$_3$ interface since a similar emission band was not observed in the corresponding double-layer devices **B** and **C**. Based on the EL spectra of devices **A**−**C**, we believe that the most plausible explanation for the broad EL spectrum of device **D** is that it is the result of dual emission bands, one from BNPB and the other from Alq$_3$. Indeed, as shown by the overlaying EL spectra in Figure 10, the broad emission band of device **D** appears to comprise two components, an EL band from device **B** and an EL band from device **C**. This unusual dual emission phenomenon is likely the direct consequence of the multifunctionality possessed by the BNPB molecule—its capability to transfer electrons, hence allowing the electron migration from the Alq$_3$ layer to the BNPB layer; its ability to emit photons effectively, hence allowing the charge recombination and exciton production to occur partially in the BNPB zone; and its ability to transfer holes to the Alq$_3$ layer, hence leading to partial exciton formation and consequently photon production within the Alq$_3$ layer.

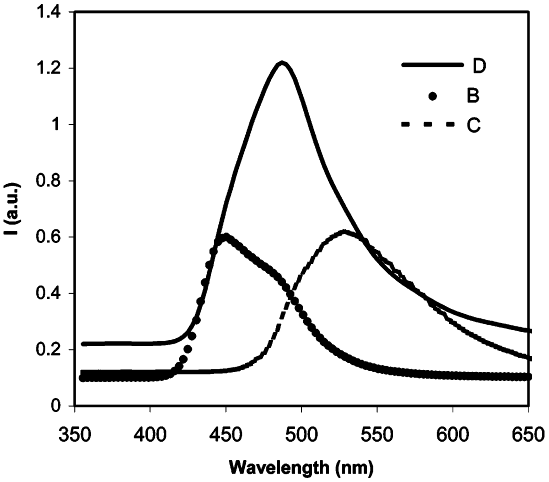

Figure 10. EL spectra of devices **B**, **C**, and **D**.

OLEDs that have multiple emission zones are often referred to as tandem OLEDs. Tandem OLEDs or dual-emission OLEDs are highly sought-after for achieving highly efficient broadband emission or white light emission.[12,13] This is typically realized through the insertion of an intermediate conducting layer between two emission layers[12] and the doping of two different color emitters into separate hosting layers.[13] Device **D** is a rare example of a dual-emission OLED that does not require the doping and an intermediate electrode method. Clearly the trifunctionality of BNPB made it possible for design and fabrication of the tandem device **D**. The utility of using BNPB in combination with emitters other than Alq$_3$ to achieve broadband or white light OLEDs is being investigated currently in our laboratories.

In summary, a new blue emitter BNPB has been obtained. This molecule has been demonstrated to be promising as a bifunctional molecule (blue emitter and electron transport) in a simple double-layer EL device to produce blue EL. Understanding of the interfacial interactions between BNPB

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and cathode materials is necessary for further optimization of the double-layer blue EL device. BNPB also appears to be able to act as a trifunctional molecule (blue emitter, electron-transport, and hole-transport) in a triple-layer EL device to produce dual (blue and green) emission. The full potential of BNPB as a trifunctional molecule to achieve dual emission in OLEDs will be further explored.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the Materials Manufacturing of Ontario for financial support. We thank Professor Steven Holdcroft at Simon Fraser University for providing the integration sphere facility for film emission quantum yield measurements.

CM048617T