

Synthesis, characterization and Electroluminescence of $\text{BPh}_2(2\text{-(benzimidazol-2-yl) pyridinato})$ compound

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ABSTRACT: A novel luminescent boron compound, $\text{BPh}_2(2\text{-(benzimidazol-2-yl) pyridinato})$ (**B-BIP**), have been synthesized by reactions of triphenylboron with appropriate ligands, 2-(2-pyridyl)benzimidazole (**BIP**). For the three-layer OLED with the structure ITO/NPB/**B-BIP** /Alq₃/Mg-Ag, an emission band covering the whole visible region from 400 to 650 nm with the maximum brightness of 50 cd/m² was observed, indicating a perfect white light OLED (CIE = 0.32, 0.37). [Journal of American Science 2009: 5(1), 77-82](ISSN: 1545-1003)

Keywords: white light; electroluminescence; imidazole; boron;

1. INTRODUCTION

The chemistry of organoboron compounds have attracted much more attention recently because they are of interest for practical applications [1-3]. Since an organic light emitting diode (OLED) was reported by Tang and Vanslyke [4], LEDs based on organic materials have generated considerable interest and enabled the development of low-cost, full-color, flat-panel displays [5-8]. The best-known EL metal complex used in OLED is Alq₃ which is not only a good emitter but also a highly efficient electron-transporting material, where q is the 8-hydroxyquinolinato ligand [9-12]. Via the modification of the ligands of metal complexes, the emission spectra of devices and other properties, such as thermo stability and carrier mobility, can be tuned. The imidazoles have

been known as good chelating ligands [13] and the attachment of the pyridyl group at 2-position of imidazole would allow the new ligand to form stable compounds with the other atoms. In the present work, the syntheses, structures, and electroluminescent properties of two new boron compounds $\text{BPh}_2(2\text{-(benzimidazol-2-yl) pyridinato})$ (**B-BIP**) is reported.

2. EXPERIMENTAL METHOD

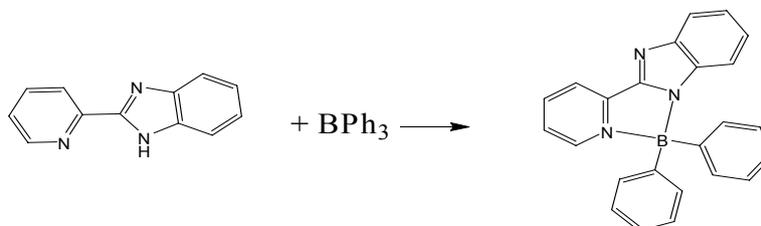
The synthesis of the title compound was accomplished by following processes, as shown in Scheme 1. The triphenylboron (1.45g, 6.0 mmole) was slowly added to 100 ml of THF solution containing 2-(2-pyridyl)benzimidazole (2.63g, 13.5 mmole) at 0°C under N₂. After the resulting mixture was stirred at room

temperature for 6 hours, 5 ml isopropyl alcohol was added to quench the reaction. The solvents were removed under vacuum condition at 5×10^{-3} Torr, and the residual solid was sublimed to purify the final product. Light green of **B-BIP** was obtained in 90% yield. The organic light emitting device, Fig. 1, using **B-BIP** as the emitting and electron-transporting layer were fabricated on the transparent conductive indium-tin oxide (ITO) glass substrate. The organic layers and the cathode were sequentially deposited by conventional vacuum vapor deposition in the same chamber without breaking the vacuum under 3×10^{-6} Torr. The cathode composed of magnesium silver alloy (Mg:Ag = 10:1) were deposited onto the top layer of organic materials by co-evaporation of Mg and Ag from different source. Before the deposition, all of the organic materials were purified by the train sublimation method. In the

present work, the

N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) was used as the hole-transport material (HTM), and tris (8-quinolinolato) aluminum (Alq₃) was employed as the electron-transporting material (ETM). The EL spectrum and the Commission Internationale de l'Eclairage (CIE) co-ordinates were measured by Pro-650 Spectroscanner (step size is 1.0 nm and bandpass is 4nm), the current-voltage (I-V) characteristic was measured by Keithley 2400 Source meter.

Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer thermogravimeter (Pyris 1) under a dry nitrogen gas flow at the heating rate of 20°C/min. Glass transition temperature (T_g) and melting point (T_m) of materials were determined by differential scanning calorimetry of the Perkin-Elmer differential scanning calorimeter (DSC-7).



Scheme 1. Synthesis process for the title compound

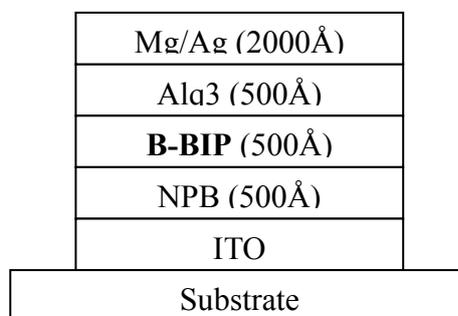


Fig 1: Device structure of organic light emitting device (OLED) fabricated in this work

3. RESULTS AND DISCUSSION

A new boron compound

$\text{BPh}_2(2\text{-(benzimidazol-2-yl) pyridinato})$ (**B-BIP**) was prepared by reacting triphenylboron with appropriate imidazole in dry THF (Scheme 1). Both of the compounds are air-stable in the solid state and in solution. The Thermogravimetric analyses (TGA) scans under nitrogen for **B-BIP** powder showed weight loss of 10% at 301 °C, respectively, which reveal that **B-BIP** is quite stable in the atmosphere of nitrogen. The DSC results indicate that the compound **B-BIP** possess a very high melting temperatures, 289°C, respectively, which may serve as an advantage for OLED device fabrication because the materials having high transition temperature could provide the device with greater longevity

[14, 15]. The thin films of **B-BIP** used for the analyses of UV-vis and photoluminescence spectra were obtained by depositing **B-BIP** onto quartz substrates under vacuum condition. At room temperature and low concentration (1×10^{-5} M), the absorption spectral features of **B-BIP** in N,N' -dimethylformamide (DMF) consist of two discrete bands (Fig. 2). The strong absorptions centered at 280 nm for **B-BIP**, respectively, can be assigned to the $\pi\text{-}\pi^*$ transition. The other intense band centered at 348 nm shows a vibrational separation of 1000 cm^{-1} with the $\nu_{0,0}$ transition at $2.94 \times 10^3\text{ cm}^{-1}$. This lower energy band possesses a reasonably high absorptivity ($\epsilon \sim 3 \times 10^4\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$) and a red shift with increasing polarity of solvent, which is typical for a $\pi\text{-}\pi^*$ transition [16-18].

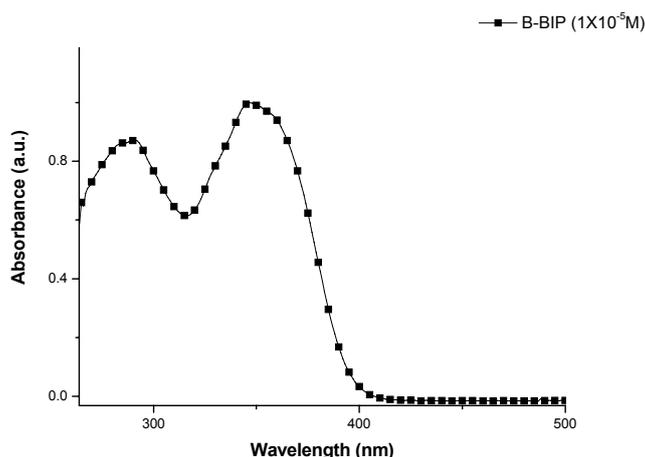


Fig 2: UV-vis spectra of **B-BIP** in N,N' -dimethylformamide

Fig. 3 show the photoluminescence (PL) spectra of the solutions and neat film of **B-BIP** excited with 355 nm laser line. All concentration in DMF, only one emission band was observed with a maximum at 455 nm. Compound **B-BIP** possess the appreciable PL quantum yield, with $\Phi_f = 0.66$ respectively, 10^{-6} M in DMF relative to

3-(2-benzothiazolyl)-7-diethyl-aminocoumarin (C540). To investigate the electroluminescent properties of **B-BIP** typical three-layer device

with the configuration of

ITO/NPB/**B-BIP**/Alq3/MgAg was fabricated by using NPB as the hole-transporting layer and **B-BIP** as the emitter and Alq3 is electron-transporting layer. The EL spectrum of organic light emitting device at the bias voltage of 10 V, Fig. 4, shows the broader emission bands ranging from 400 to 650 nm were observed, indicating that the three-layer LED device emitted white light covering the whole visible light region. The band around 455 nm in

EL spectrum can be attributed to emission of **B-BIP**, because its emission position is almost identical with that in PL spectrum of **B-BIP**. The emission band at 535 is Alq₃ emission position. The emission is almost fixed in the white region in the CIE coordinate of $x = 0.32$ $y = 0.37$. For the small molecular organic materials, to develop the double layer of device with white

emission is very important because this kind of material is very seldom prepared so far, and it is very important for the fabrication of display panels. At the same time important role here may play electron-vibration interactions determining the spectral broadening of the emission lines. So the future strategy of the materials design may be in this way also.

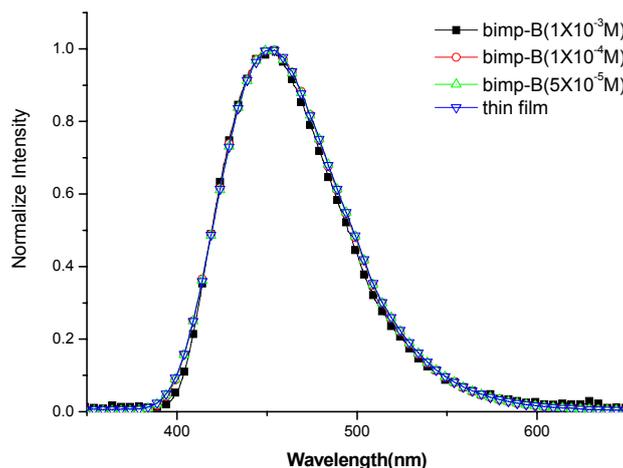


Fig 3: PL spectra of the **B-BIP** in solutions and neat film

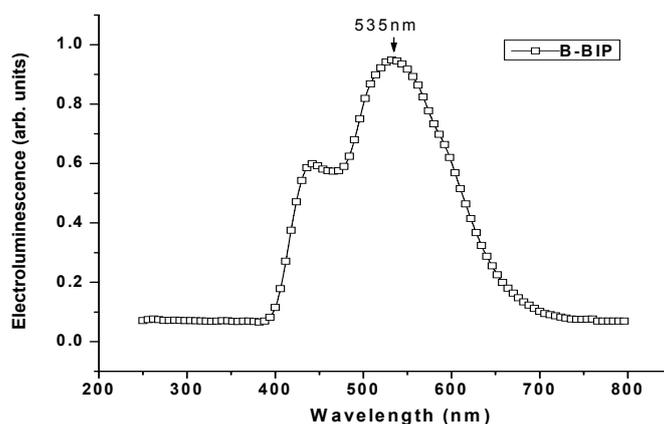


Fig 4: EL spectrum of OLED fabricated in this work.

Figure 5. shows the energy level diagram of the HOMO and LUMO of the different organic materials and the work function of cathode and anode. By using cyclic voltammetry (CV) method obtaining LUMO energy of **B-BIP** is

3.4eV and the optical band gap estimated from the absorption onset, we can determine the HOMO energy at 6.5eV. In Comparison with the energy level of **B-BIP** and NPB, **B-BIP** has much higher hole injection barrier than that of

NPB. As a matter of fact, it is impossible for the hole injection from ITO into **B-BIP** without the assistance of NPB or some HTLs. This diagram pointed out Alq₃ has lower electron injection barrier than that of **B-BIP**. Therefore, the electron injection from the MgAg into **B-BIP** will be enhanced and confines the recombination zone at the interface between NPB and **B-BIP**. Fig.6 shows the current-voltage and luminance-voltage characteristics of this device having a low turn on voltage of about 4.5V for current and luminance. This device shows a brightness of 50 cdm⁻² at the driving voltage of 12V with current density of 390 mA/cm², decaying to 25 cdm⁻² in 100 hours.

4. CONCLUSION

A new compound of emitter for OLED, BPh₂(2-(benzimidazol-2-yl)pyridinato) (**B-BIP**), has been successfully synthesized and investigated. It has been shown that the novel ligands BIP is capable of chelating to B(III) centers and the resulting compounds possess appreciable photoluminescent efficiency and very high thermal stabilities. This study further indicates that the emission band of the devices could be modified by changing the composition of emitting layer and therefore, OLEDs with different colors could be obtained.

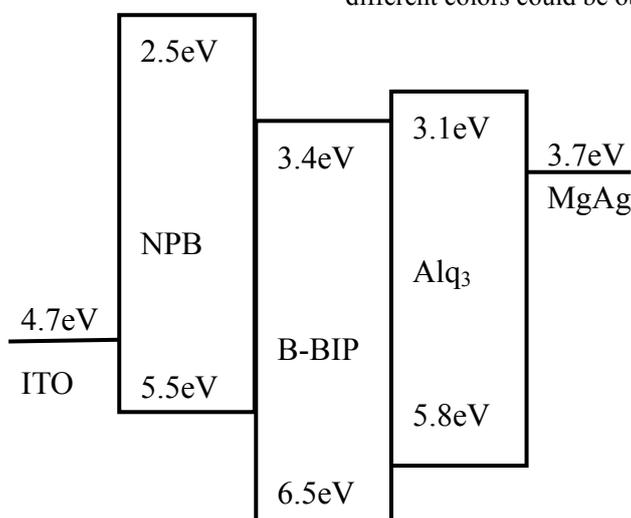


Fig 5: Energy level diagram of OLED materials, ITO, and Mg-Ag alloy

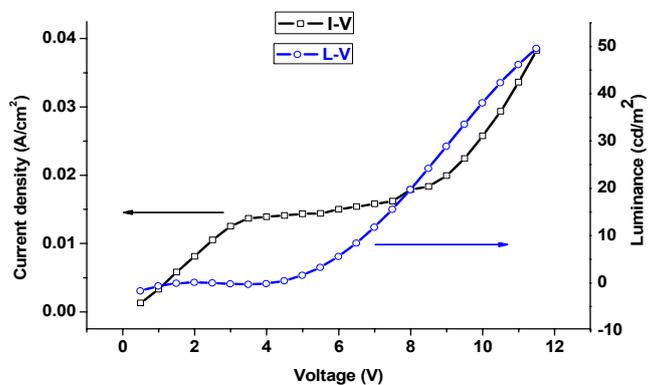


Fig 6: Current-voltage and luminance- voltage characteristics of OLED fabricated in this work

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