Highly Efficient White Organic Electroluminescence from a Double-Layer Device Based on a Boron Hydroxyphenylpyridine Complex**

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Organic electroluminescent (EL) devices are of growing interest in display applications because they can emit colors with high luminous efficiency throughout the visible spectrum. Extensive studies have been performed on the use of small molecular complexes to make organic EL devices with high brightness, multicolor emission, improved durability, and desirable efficiency.[1–16] While some applications require colored emission sources, others need a bright white-light source. Several methods of producing white light from polymer or small-molecule organic devices have been demonstrated.[17–21] To obtain white light efficiently with good color purity, complicated emitting material systems, multilayer structures, and precise fabrication technologies were often necessary.[22, 23] A simple approach for making efficient white electroluminescent devices is urgently required. Recently, we found some hydroxyphenylpyridine complexes to be ideal emitting materials for EL devices.[24–27] Here we report on high-efficiency white electroluminescence from a double-layer device based on a luminescent boron complex of the dianion of 1,6-bis(2-hydroxy-5-methylphenyl)pyridine ((mdppy)BF).

The ligand 1,6-bis(2-hydroxy-5-methylphenyl)pyridine (H_2mdppy) was prepared by the reaction of 2,6-dibromopyridine and the Grignard reagent from 2-bromo-4-methylanisole in THF with $[NiCl_2(dppe)]$ as catalyst (dppe = $Ph_2PCH_2CH_2PPh_2$). This was followed by demethylation in molten pyridinium chloride to give H_2mdppy. Reaction of H_2mdppy with one equivalent of BF_3 in benzene gave (mdppy)BF.

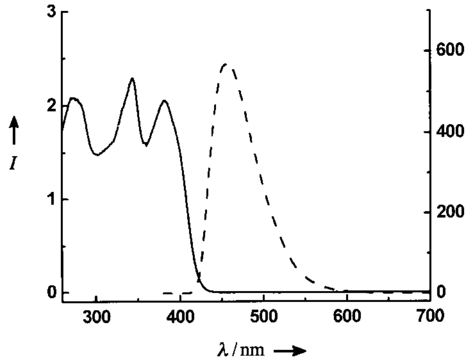

Figure 1. UV/Vis absorption (——) and emission (---) spectra of (mdppy)BF in dichloromethane.

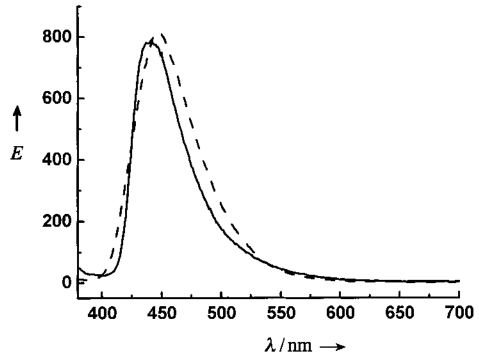

Figure 2. Photoluminescence spectra of solid thin films of (mdppy)BF (——) and NPB (---).

The UV/Vis and photoluminescence (PL) spectra of (mdppy)BF in dichloromethane are displayed in Figure 1. (mdppy)BF exhibits intensive blue luminescence in solution. The spectra of vacuum-evaporated films of *N,N*′-bis(α-naphthyl)-*N,N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) and (mdppy)BF are shown in Figure 2. The solid films of NPB and (mdppy)BF have similar photoluminescence properties, and they both emit blue light. To investigate the EL properties of (mdppy)BF, an organic electroluminescent device was fabricated by vacuum thermal evaporation of NPB and (mdppy)BF onto cleaned glass substrates precoated with conductive transparent indium tin oxide (ITO). The device consists of a 60 nm-thick layer of the hole-transporting material NPB, a 60 nm-thick layer of the emitting and electron-transporting material (mdppy)BF, a 1 nm-thick layer of LiF to enhance electron injection from aluminum, and a 200 nm-thick layer of aluminum metal. The device and the molecular structures of NPB and (mdppy)BF are presented in Figure 3. The device exhibited a significantly broader EL spectrum (Figure 4), ranging from 400 to 700 nm, which completely covers the total wavelength region of visible light emission, that is, high-quality white electroluminescence was obtained. The Commission Internationale de l'Eclairage (CIE) coordinates are (CIE; 0.30, 0.36); white is defined as (CIE; 0.33, 0.33). When the driving voltage was varied from 4 to 18 V, the CIE coordinates remained almost unchanged. The EL spectral component around 450 nm can be attributed to (mdppy)BF or NPB. The EL band beyond the blue region

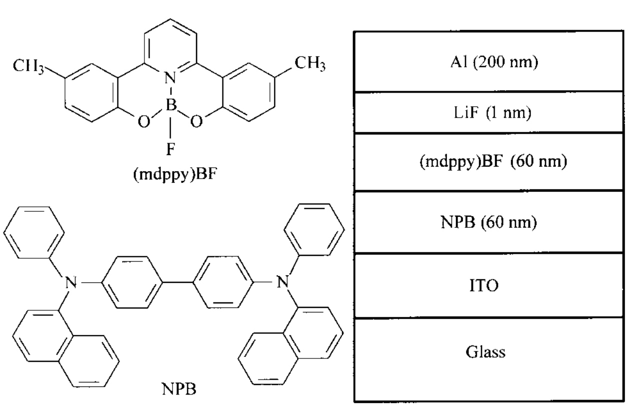

Figure 3. The EL device structure and molecular structures of (mdppy)BF and NPB.

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[**] This work was supported by the National Natural Science Foundation of China.

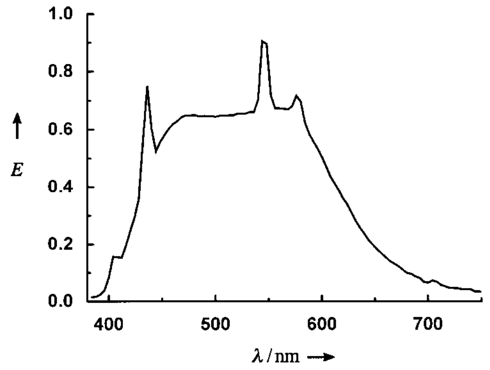

Figure 4. EL spectrum of the ITO/NPB/(mdppy)BF/LiF/Al device.

cannot be explained by singlet recombination in (mdppy)BF or NPB. We propose that this part of the EL band is due to exciplex emissions. The turn-on voltage of the device is 4.0 V and the maximum luminance is 3500 cd m^{-2} at a driving voltage of 18 V. The device showed a maximum EL efficiency of 3.6 lm w^{-1} (6.5 cd A^{-1}) with a luminance of 110 cd m^{-2} at a driving voltage of 5.5 V. To our knowledge, it is the highest efficiency for a white-light organic EL device that has been achieved until now. It reached an efficiency of 1.5 lm w^{-1} (3.3 cd A^{-1}) and a luminance of 620 cd m^{-2} at a current density of 20 mA cm^{-2} and a driving voltage of 7.0 V. Thus, the device exhibits high EL efficiency at higher luminances. Figure 5 presents the current–voltage and luminance–voltage characteristics of the device. We have not yet studied the lifetime of the device yet, but the unencapsulated device was stable, and the emission color did not change during the measurements of the EL spectrum, the CIE coordinates, and the luminance–voltage and current–voltage characteristics.

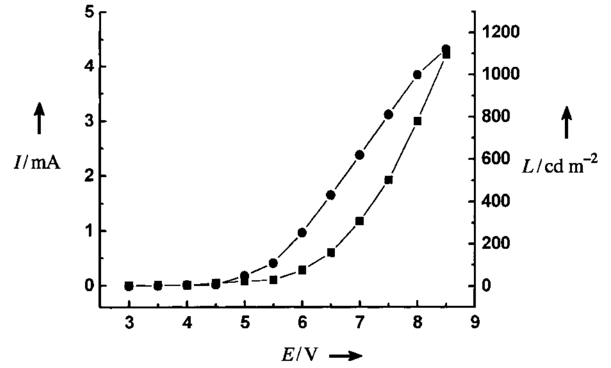

Figure 5. Current–voltage (■) and luminance–voltage (●) characteristics of the ITO/NPB/(mdppy)BF/LiF/Al device.

To investigate the exciplex emission properties of the NPB/(mdppy)BF system, a series of evaporated-film samples (Figure 6) were prepared on quartz substrates, and their PL spectra were recorded. The film samples consisted of a layer of NPB, a layer of (mdppy)BF, and an intermediate codeposited layer of NPB:(mdppy)BF (ca. 1:1 w/w). The thickness of the codeposited layer was varied from 0 to 120 nm. The total thickness of each film sample was 120 nm. The double-layer sample without a codeposited layer and the single-layer sample with only the codeposited layer represent the two extremes. Figure 7 presents the PL spectra of the film samples. The exciplex emissions beyond the blue region grew with increasing thickness of the codeposited layer. It can be concluded that the interaction between NPB and (mdppy)BF molecules results in exciplex emission. The single-layer film sample exhibits a significantly broader PL spectrum that ranges from 400 to 650 nm.

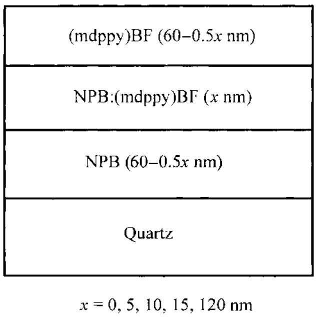

Figure 6. Schematic presentation of the film samples for PL measurements.

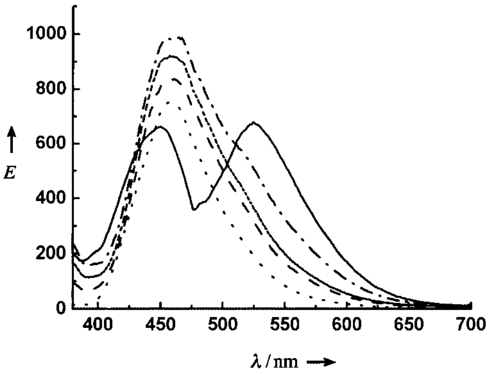

Figure 7. The PL spectra of film samples with structure NPB(60 − 0.5x nm)/NPB:(mdppy)BF(x nm)/(mdppy)BF(60 − 0.5x nm): x = 0 nm (••••); x = 5 nm (– – –); x = 10 nm (----); x = 15 nm (•–•–); x = 120 nm (——).

In the photoluminescence of an organic multilayer film, excitons are generated both in the bulk of each layer and at the interfaces. In a multilayer film without a blended layer, the PL properties are mainly determined by the bulk material, because the ratio of interface to bulk materials is small. In a multilayer film, the excitons that result from carrier injection and recombination are produced within a narrow interface region,[2] and the EL properties of the multilayer film are mainly determined by the interfacial characteristics. For a double-layer NPB/(mdppy)BF film, the electroluminescence is confined to the interfacial region and hence exhibits stronger exciplex emission characteristics than photoluminescence. Therefore, it is reasonable that the EL spectrum of the double-layer NPB:(mdppy)BF film is similar to the PL spectrum of the single-layer codeposited NPB:(mdppy)BF film, in which the ratio of interface to bulk of two materials is very high. The PL spectrum of the single-layer NPB:(mdppy)BF film and the EL spectrum of double-layer NPB/(mdppy)BF film have different line shapes. This may be because electron injection can sometimes generate excitons that cannot be induced by optical excitation.[20] Furthermore, the refractive, reflective, and absorptive properties of ITO and the metal cathode also can affect the EL spectrum.[21]

In summary, the new luminescent material (mdppy)BF was synthesized and its electroluminescent properties were investigated. Highly efficient white-light EL devices can be fabricated from this material. The white electroluminescence is caused by exciplex emissions at the interface between NPB and (mdppy)BF. This offers the opportunity for constructing high-performance white EL devices based on only one emitting material and with a simple device structure. In addition, the EL device reported here may have potential applications in microcavity EL devices for selectively enhancing individual or mutiple colors that lie within the EL spectrum band.[28]

Experimental Section

Synthesis of H_2mdppy: A solution of the Grignard reagent prepared from 2-bromo-4-methylanisole (6.0 g, 30 mmol) was added dropwise to an ice-cold mixture of [$NiCl_2$(dppe)] (0.52 g, 1 mmol) and 2,6-dibromopyridine (3.6 g, 15 mmol) in anhydrous THF (40 mL) under nitrogen. The mixture was stirred at room temperature for 12 h and then quenched with aqueous NH_4Cl. THF was removed under reduced pressure. The resulting white precipitate was filtered off, washed with water, and dried in air to give 1,6-bis(2-methoxy-5-methylphenyl)pyridine, which was used directly in the subsequent step without further purification. 1,6-bis(2-methoxy-5-methylphenyl)pyridine was added to molten pyridinium chloride (from 40 mL pyridine and 45 mL concentrated HCl) under nitrogen over 3 h at 200°C. After addition of water to the mixture and neutralization with aqueous KOH, the crude product was extracted with CH_2Cl_2 (3×60 mL). The organic phase was washed with water (2×30 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residual yellow solid was purified by chromatography (silica, CH_2Cl_2) to give the product as a white powder in 55% yield. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.00$ (t, $J = 8.0$ Hz, 1H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.47 (d, $J = 1.6$ Hz, 2H), 7.16 (dd, $J = 8.3, 1.9$ Hz, 2H), 6.96 (d, $J = 8.3$ Hz, 2H), 2.37 (s, 6H). MS: m/z (%): 291 (100) [M^+]; elemental analysis (%) calcd for $C_{19}H_{17}NO_2$: C 78.35, H 5.84, N 4.81; found: C 77.88, H 5.65, N 4.52.

Synthesis of (mdppy)BF: $BF_3 \cdot OEt_2$ (1.42 g, 10 mmol), H_2mdppy (2.91 g, 10 mmol), and NEt_3 (1 mL) were dissolved in 30 mL of benzene, and the reaction mixture was heated to reflux for 10 h. A light yellow solid precipitated from the solution. The solid product (75% yield) was collected by filtration and purified by recrystalization and sublimation. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.08$ (t, $J = 7.9$ Hz, 1H), 7.88 (d, $J = 8.2$ Hz, 2H), 7.58 (d, $J = 1.2$ Hz, 2H), 7.28 (dd, $J = 8.4, 1.70$ Hz, 2H), 7.10 (d, $J = 8.3$ Hz, 2H), 2.36 (s, 6H). MS: m/z (%): 319 (100) [M^+]; elemental analysis (%): calcd for $C_{19}H_{15}NO_2BF$: C 71.47, H 4.70, N 4.39; found: C 70.76, H 4.33, N 4.16.

Fabrication of electroluminescent devices: The device was built on glass which was precoated with ITO with a sheet resistance of 20 Ω cm^{-2}. The ITO glass was routinely cleaned by ultrasonic treatment in detergent solutions, rinsed with acetone, boiled in isopropyl alcohol, rinsed with methanol, and then with de-ionized water. The glass was dried in a vacuum oven between each cleaning step. The devices were fabricated by successive vacuum deposition of organic materials onto the ITO-coated glass substrate. Prior to deposition, all organic materials were purified by sublimation. A shadow mask with 2×3 mm^2 openings was used to define the cathodes. The EL spectrum, luminance, and CIE coordinates of the device were recorded on a PR650 spectrometer. Luminance–voltage and current–voltage characteristics were measured at room temperature under ambient atmosphere.

Received: August 9, 2001 [Z17698]

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