

MULTILAYER ORGANIC LEDS BASED ON A NEW DYE-DOPED POLYMER*

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Abstract A blue dye, 1-benzothiazoly-3-phenyl-pyrazoline (BTTP) was found to function as bright light emitting dye in organic electroluminescent devices. This heterocyclic compound exhibits good characteristics of blue photoluminescence and electroluminescence, which has emission peak at 445 nm. The thin films of fluorescent dye dispersed in poly(*N*-vinylcarbazole) (PVK) could serve as light-emitting layers in multilayer organic LEDs. 2-(4-Biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) and *tris*-(8-hydroxyquinoline) aluminum (Alq₃) were introduced into double-layer and three-layer devices respectively. The introduction of electron transport material Alq₃ enhanced the electron injection and luminous efficiency, as compared with double-layer devices. Maximum brightness and luminous efficiency can be reached up to 190 cd/m² and 0.31 m/W, respectively.

Keywords Heterocyclic compound, Hole block layer, Electron transport layer, Organic EL devices

INTRODUCTION

Organic electroluminescent (EL) devices were expected to serve as a new type of flat display^[1-3] since Tang and Van Slyke first reported high-performance organic EL devices. Red, blue, green and white light emissions from organic EL devices have been achieved. Compared with other color devices, blue luminescence from molecular and polymeric materials are especially attractive due to low efficiency of inorganic blue light-emitting diodes. Some blue luminescent organic materials including 1,3-bis[4-*N,N*-dimethylaminophenyl]-1,3,4-oxadiazolyl-benzene^[4], 4,4'-bis(2,2-diphenylethenyl)biphenyl^[5] and 1,1,4,4-tetraphenyl-1,3-butadiene^[6] have been studied for use as light emitting materials in organic LEDs.

We report here that a kind of amorphous material containing heterocyclic group, 1-benzothiazoly-3-phenyl-pyrazoline (BTTP), can function as bright blue light-emitting material for organic devices, which is doped into poly(*N*-vinylcarbazole) (PVK) as light emitting layer. Three-layer and double-layer devices are fabricated using 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) and *tris*-(8-hydroxyquinoline) aluminum (Alq₃) as hole blocking layer and electron transporting layer, respectively. Bright blue light emission was observed in three-layer devices.

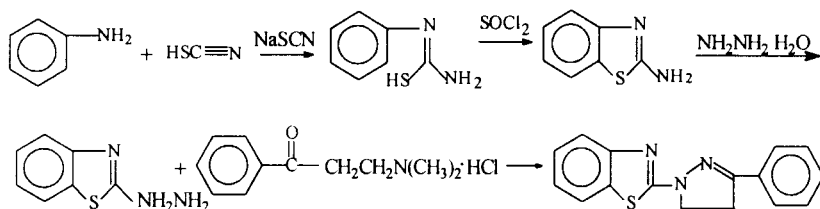
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EXPERIMENTAL

The blue fluorescent dye BTPP was synthesized according to the method shown in Scheme 1^[7]. The results of elemental analysis of BTPP were shown in Table 1. The measured contents of C, N, H elements were in good agreement with the calculated values of the proposed molecular structure. The results of ¹H-NMR measurement show that there are three kinds of H atoms in BTPP molecule: [3.37 δ (2H, *t*, *J* = 10), 4.32 δ (2H, *t*, *J* = 10), 7.05~7.8 δ (9H, *t*, *m*)], which is also consistent with the proposed molecular structure. PVK and PBD were supplied from Aldrich Co. Inc. and used as received. The organic materials used were shown in Fig. 1. The structures of double-layer and three-layer devices were ITO/PVK:BTPP/PBD/Al and ITO/PVK:BTPP/PBD/Alq₃/Al, respectively. Air stable aluminum (Al) and indium-tin-oxide (ITO) were used as the electron and hole injection electrodes. The ITO coated glass plate was typically 40 μ m thick with a sheet resistance of about 60 $\Omega/\square$. Prior to the spin coating of the PVK:BTPP solution, ITO substrates were thoroughly cleaned by swabbing and ultrasonic cleaning with toluene, acetone and methanol consecutively, finally the substrate were treated by oxygen plasma. The light emitting layer of BTPP dispersed in PVK (10% in chloroform) was spin-coated onto glass substrate, which was partially coated with ITO. For double-layer or three-layer devices, it was prepared by sequentially depositing onto the light-emitting layer (PVK:BTPP), hole blocking layer PBD (30 nm), electron transport layer Alq₃ (40 nm), finally aluminum (Al) electrode was deposited onto Alq₃ or PBD layer, yielding active light emitting areas of 4 mm². All measurements were carried out at room temperature.



Scheme 1 The synthesis route of BTPP

Table 1 The results of C, H, N elemental analysis

	C (%)	H (%)	N (%)
Calculated value	68.80	4.70	15.05
Measured value	68.94	4.70	15.14

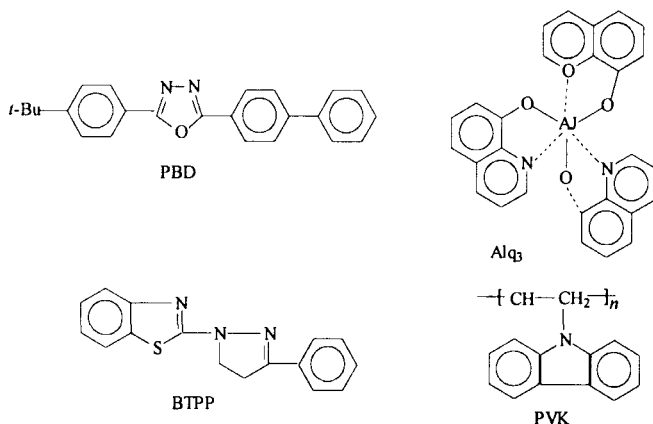


Fig. 1 Molecular structures for organic materials used

RESULTS AND DISCUSSION

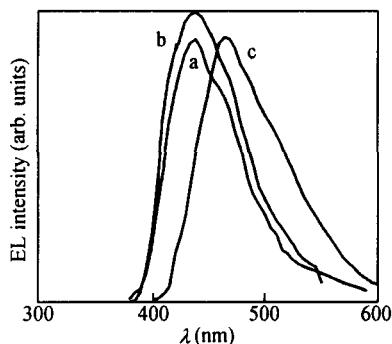


Fig. 2 PL spectrum of BTTP EL spectra of double-layer and three-layer LEDs

- a) PL spectrum of BTTP;
- b) EL spectrum of double-layer LEDs;
- c) EL spectrum of three-layer LEDs

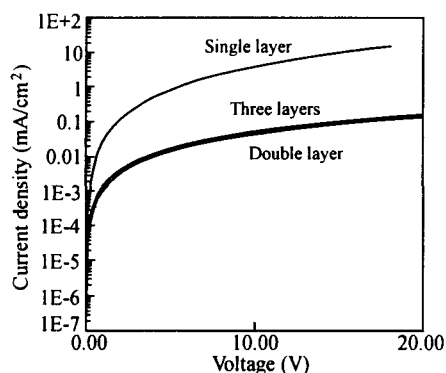


Fig. 3 I-V Characteristics of single, double and three-layer LEDs

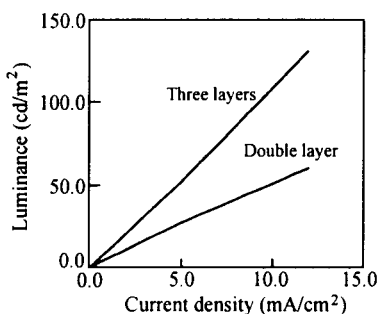


Fig. 4 Luminance-current density curves for double-layer and three-layer LEDs

Figure 2 shows the photoluminescent (PL) spectrum of BTTP (curve a), and the electroluminescent (EL) spectra of double-layer (curve b) and three-layer (curve c) LED, respectively. BTTP has emission peak at 445 nm. The introduction of pyrazoline groups enhanced the degree of planar conjugation and made the emission wavelength shift red, as compared with 2-aminobenzothiazole (whose emission peak was at 420 nm). The PL emission peaks of both BTTP and BTTP:PVK were at 445 nm, from which we knew that the luminescence of BTTP was dominant due to faster energy transfer from PVK to BTTP in PVK:BTTP thin films. The emission of PVK was at 418 nm. The EL spectra of double-layer and three-layer devices were also shown in Fig. 2 together with the PL spectrum of BTTP. The EL of double-layer LED was virtually identical to the PL of BTTP, which demonstrated that the blue emission completely originated from the radiation decay of singlet excited states of BTTP. The EL spectrum of three-layer LED shifted red, as compared with that of the double-layer LED. This is because that the PBD layer does not block hole transporting completely, and the emission of Alq_3 also contributed to the whole spectrum. Figure 3 shows the weak current-voltage characteristics of single-layer (ITO/PVK:BTTP/Al), double-layer and three-layer devices. The introduction of PBD blocked the hole transport to cathodes, in which hole was the major carrier. The current was decreased by 1-2 orders of magnitude and balanced the electron and hole injection. The current density-luminance curves of double-layer and three-layer LEDs were shown in Fig. 4. The introduction of Alq_3 decreased the electron injection barrier and

improved the luminous efficiency. Maximum brightness and luminous efficiency values were 190 cd/m² and 0.31 m/W, respectively.

CONCLUSION

We fabricated bright blue LEDs using BTPP as a new kind of blue electroluminescent dye. The heterocyclic compound exhibits advantages in the electric and optical characteristics, and provides a novel material series for the research of the blue organic LEDs.

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