

Bright blue electroluminescent devices utilizing poly(*N*-vinylcarbazole) doped with fluorescent dye

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Abstract

Bright blue electroluminescent devices have been fabricated using poly(*N*-vinylcarbazole) (PVK) doped with perylene as the emissive layer, poly(*p*-phenylenevinylene) (PPV) as the hole-transporting layer, 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD), tris(8-hydroxyquinoline)aluminum (Alq₃) as the electron-transporting layer, and Al as the cathode. A luminance of 700 cd/m² and a luminescent efficiency of 0.8% are achieved at a drive voltage of 36 V. In the experiment, it is found that the introduction of electron-transporting layer PBD has a great effect on the emissive color of the electroluminescent devices prepared by PVK doped with perylene. Yellow–green emission is observed from the device structure of glass substrate/indium–tin-oxide/PVK:perylene/Al. The possible emissive mechanisms are given. The effect of the transporting layer on the electroluminescence is also discussed. © 1997 Elsevier Science S.A.

Keywords: Molecularly doped polymers; Electroluminescence; Fluorescent dyes

1. Introduction

Organic electroluminescent (EL) devices have become one of the most important subjects because of their potential application as large-area flat-panel displays since Tang and VanSlyke [1,2] first reported bright organic electroluminescence at low voltages. Among the numbers of organic EL materials, molecularly doped polymers (MDPs) [3] with highly efficient fluorescent dyes are considered as a material system for obtaining highly luminescent efficiency and preventing the crystallization of small molecules. Because MDPs have good processibility and good mechanical properties of polymers [4], the devices can be fabricated by using the spin-casting method.

In this paper, we report the fabrication and characterization of multilayer-type blue EL devices using molecularly doped polymers, and discuss the effect of the electron- and hole-transporting layers on the EL device luminescence. A possible mechanism for the light emission is proposed.

2. Experimental

The molecularly doped polymer used in the study is molecularly dispersed perylene in poly(*N*-vinylcarbazole) (PVK).

The film was prepared by spin-casting from a chloroform solution of PVK and perylene with a weight ratio of 2:1. The hole-transporting layer poly(*p*-phenylenevinylene) (PPV) was obtained by heat conversion of the PPV sulfonium salt precursor on patterned indium–tin oxide (ITO) substrate. The electron-transporting layer tris(8-hydroxyquinoline)-aluminum (Alq₃) and cathodic Al were fabricated by vacuum evaporation. An electron-transporting layer was prepared by spin-casting from 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) in poly(methyl methacrylate) (PMMA) (0.02 g PMMA, 0.06 g PBD in 10 ml nitromethane). PVK, perylene and PBD were purchased from Aldrich. PPV, Alq₃ and PMMA were synthesized in our laboratory. We fabricated following types of devices in this experiment: Type I: ITO/PVK:perylene/Al; Type II: ITO/PPV/PVK:perylene/Al; Type III: ITO/PVK:perylene/Alq₃/Al; Type IV: ITO/PPV/PVK:perylene/Alq₃/Al; Type V: ITO/PVK:perylene/PBD:PMMA/Alq₃/Al; Type VI: ITO/PPV/PVK:perylene/PBD:PMMA/Alq₃/Al; Type VII: ITO/PVK:perylene:PBD/Al.

The electroluminescence and photoluminescence spectra were measured with a SPEX FL-2T2 spectrophotometer. The luminance was measured with an ST-900 photometer. All measurements were carried out at room temperature in air.

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Table 1
EL properties of the various devices fabricated

Number	Structure	Turn-on voltage (V)	Maximum brightness $B_{\max}$ (cd/m ²)	Color	Luminescent efficiency η (%)
1	Type I	25.2	14.0	y-g ^a	0.02
2	Type II	24.0	28.0	y-g ^a	0.07
3	Type III	15.0	240.0	y-g ^a	0.2
4	Type IV	12.0	320.0	y-g ^a	0.5
5	Type V	21.0	624.0	blue	0.6
6	Type VI	18.0	700.0	blue	0.8
7	Type VII	24.0	155.2	y-g ^a	0.2

^a Yellow–green.

3. Results and discussion

Table 1 gives the luminescent properties of the different EL devices based on PVK doped with perylene. It is seen from Table 1 that the hole-transporting layer PPV has only a slight effect on the turn-on voltage, maximum brightness and efficiency, and does not have any effect on the emissive color. This demonstrates that PPV only plays a role of transporting holes into the emissive layer. However, the electron-transporting layer Alq₃ has a great effect on turn-on voltage, maximum brightness and efficiency. In particular, the emissive color is changed from yellow–green to blue due to the introduction of the electron-transporting layer PBD between the MDP and Alq₃ layers.

The recombination region of the EL devices based on polymers is generally localized at the interface between the emissive layer and cathode, which plays a role as the nonradiative recombination center. This decreases luminance and efficiency. When an electron-transporting layer is introduced between the PVK:perylene emissive layer and the cathode, electrons injected into the emissive layer increase. Thus, the rate of recombination of holes and electrons increases, and the recombination zone is spatially isolated from the cathode due to the introduction of the electron-transporting layer, thus eliminating exciton quenching by the metal. So the luminance and efficiency are improved.

The energy transfer model [2] and the carrier trap model [5] are two typical models of the EL mechanism in dye-doped EL devices. It has been proved that the carrier trapping is the main process in MDPs [5] when the ionization potential (I_p) of the dopant is lower than that of the host, and the electron affinity (E_a) of the dopant is higher than that of the host. Thus, carrier trapping is the main process in our EL devices based on PVK doped with perylene without a PBD layer. Yellow–green emission is only from perylene in PVK, as shown in Fig. 1. The photoluminescence spectrum of PVK:perylene film and the electroluminescence spectrum of the Type I device are coincident. This suggests that the

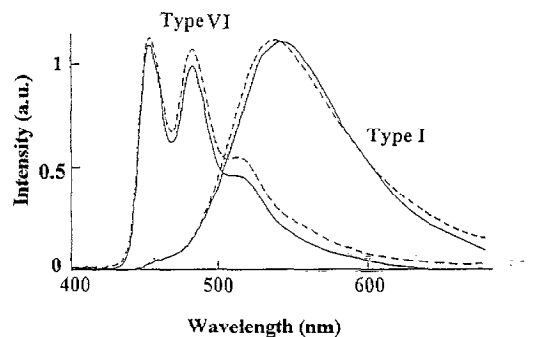


Fig. 1. Photoluminescence spectra (broken lines) of a PVK:perylene film and a PVK:perylene/PBD:PMMA film, and electroluminescence spectra (solid lines) of Type I device and Type VI device.

photoluminescence and electroluminescence originate from the same source. Fig. 1 also gives the photoluminescence spectrum of PVK:perylene/PBD:PMMA film and the electroluminescence spectrum of the Type VI device. They show blue emission with two peaks at 453 and 483 nm, respectively. We suggest that the blue emission is probably from another chromophore formed between the MDP layer and PBD layer, rather than perylene or PBD. The chromophore is generally named exciplex [6].

4. Conclusions

Bright blue EL devices based on MDPs have been fabricated by using multilayer structures. The effects of the electron- and hole-transporting layers on the luminescence properties of the EL devices are discussed and a mechanism for the light emission based on the exciplex formed between the two organic layers is proposed.

Acknowledgements

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