

Voltage-Dependent Luminescence Properties of Molecularly Doped Polymer System

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Single-layer light-emitting diodes (LEDs) are fabricated using a mixture of a blue-emitting polymer and green-emitting 9,10-bis(phenylethynyl)anthracene as emitting layer. The blend device with these two components in the emitting layer exhibits voltage-induced evolution of the electroluminescence. But when polystyrene is also blended into the emitting layer, the EL spectra show emission bands from both ether-PPV and BPEA in proportion to concentrations of the two materials, and the spectra exhibit no change with applied voltage. This implies that doping inert polymer is helpful in suppressing voltage-induced evolution of electroluminescence in LED blends. © 2001 Academic Press

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Tuning the color of electroluminescent (EL) devices is one of the most attractive topics in the fabrication of organic light-emitting diodes (LEDs). It makes voltage control of pictures possible because it provides a way to select color. In recent years, several kinds of color-variable LEDs, such as polymer-based LEDs, inorganic nanometer-sized particles, or small organic-molecule-doped polymer LEDs have been studied (1–5). Color change from orange to greenish-yellow or from red to green has been observed in multilayer LEDs or single-layer LED blends. The phenomena are attributed to the variation of the recombination zone (2, 6). The field-induced quenching of emitting states has been pointed out to be inevitably included in explaining the results (2, 7).

In this communication, we report single-layer LED blends with a mixture of two emitting materials and one optic-electric inert polymer as emitting-layer in an effort to understand the mechanism of voltage-induced evolution of the EL spectra in molecularly doped polymer system.

Poly(1,2-ethandioxy-1,4-phenylene-1,2-ethenylene-2,5-didecanoxy-1,4-phenylene-1,2-ethenylene-1,4-pheny-

lene) (ether-PPV) and 9,10-bis(phenylethynyl)anthracene (BPEA) are used as emitting materials and polystyrene (PS) is used as an inert dopant in our study. Ether-PPV is synthesized in our laboratory according to published method (8, 9). It can be dissolved in common organic solvents such as chloroform. BPEA and PS are purchased from Aldrich. The structures of ether-PPV and BPEA are shown in Fig. 1.

The structure of ITO/ether-PPV + BPEA + PS/Al is employed. Mixtures of ether-PPV, BPEA, and PS at different weight ratios are dissolved in chloroform. The solution is spin coated on the ITO electrode at a rate of 2500 rpm, giving a homogeneous film. The top aluminum electrode is prepared by thermal evaporation under 2×10^{-5} Pa. Devices with structures of ITO/ether-PPV/Al and ITO/BPEA/Al are fabricated the same way for comparison. The thickness of all emitting layers of these devices is controlled to be about 100 nm. The photoluminescent (PL) films are made the same way on quartz. The PL and EL are measured with a Shimadzu RF-5000 spectrofluorophotometer at room temperature under air.

Figure 2 displays normalized PL spectra of thin films of ether-PPV, BPEA, and their blends (30%BPEA). Since the PL spectrum of the blended film reveals emission mainly from ether-PPV when excited at 350 nm, where only absorption by ether-PPV can be found, the energy transfer from ether-PPV to BPEA should be impossible or very weak, even if it exists.

The normalized EL spectra of devices with structures of ITO/ether-PPV/Al, ITO/BPEA/Al, and ITO/ether-PPV + BPEA + PS/Al in different ratios and the spectral variation at different applied voltages are shown in Fig. 3, 4. The EL spectrum of a single-molecule device for ether-PPV or BPEA corresponds to the PL spectrum, indicating the same mechanism of EL and PL. The ether-PPV device emits blue light with a peak at 470 nm. The BPEA device emits green light with a peak at 535 nm. For a blend device containing only ether-PPV and BPEA with a low content of BPEA (1% and 5%), the EL spectrum exhibits blue emission

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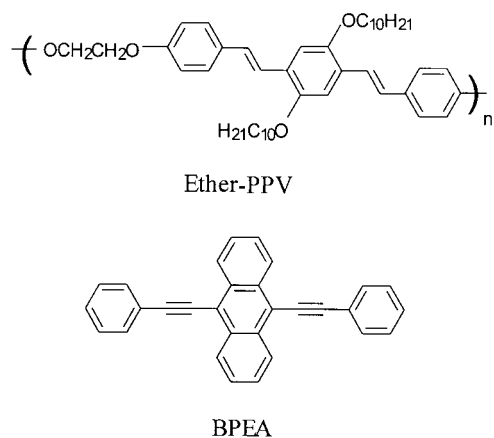


FIG. 1. Molecular structures of ether-PPV and BPEA.

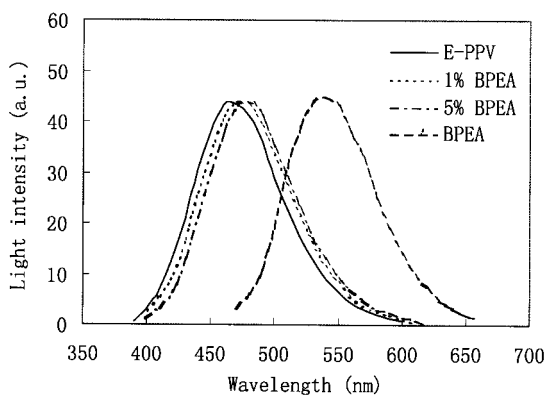


FIG. 3. Normalized EL spectra of single-layer ether-PPV, BPEA, and LED blends with different average BPEA content (1% and 5%).

characteristic of ether-PPV independent of the applied voltage. But for blend device with higher concentration of BPEA (30%), the EL spectrum varies under different applied voltages. When the applied voltage is 15 V, the EL spectrum exhibits only green emission from BPEA (Fig. 4a). At 18 V, the EL spectrum exhibits emission from both ether-PPV and BPEA (Fig. 4b). At a higher voltage, 25 V, the spectrum exhibits only blue emission from ether-PPV (Fig. 4c). In other words, the peak shifts from green emission of BPEA to blue emission of ether-PPV upon increased applied voltage. But it is not the situation for devices with PS doped in the emitting layer. The EL spectrum with higher concentration of BPEA (35% ether-PPV, 15% BPEA, and 50% PS) exhibits emission from both ether-PPV and BPEA and no spectrum change has been found upon increased applied voltage, although the ratio of ether-PPV to BPEA is the same as that in the device with only the two emitting materials in the emitting layer (Fig. 4d). The EL spectrum with a lower concentration of BPEA (48% ether-PPV, 2% BPEA, and 50% PS) exhibits

emission from ether-PPV only and no spectrum change has been found upon increased applied voltage.

As is known, the generation of light is a consequence of the recombination of electrons and holes injected from the electrodes. In a blended device, phase separation occurs in the active layer although the blend solution has high homogeneity (10). Once the BPEA-ether-PPV mixture is composed of the separated phase domains (most probably on a submicrometer size scale), they can form microdiodes connecting individually anode and cathode. This is the situation resembling that for an Alq3-ROPPV mixture (1). The emission originates from individual BPEA and ether-PPV microdiodes. An increasing field involves more blue-emitting ether-PPV domains because of its larger band gap, as is the situation in samples (30% BPEA). The emission from ether-PPV is enhanced so quickly with increased applied voltage that emission from BPEA is hardly observed when the applied voltage is high enough. Decreasing concentration of BPEA prevent formation of BPEA

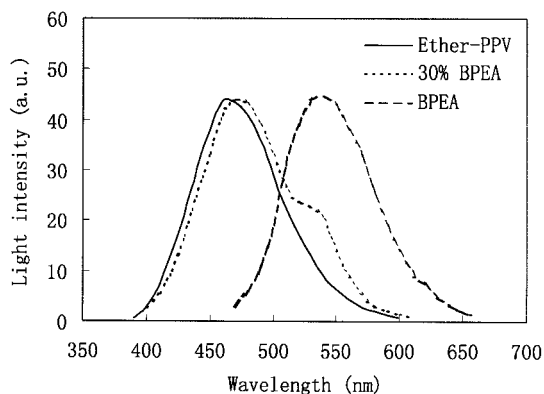


FIG. 2. Photoluminescence spectra of thin films of ether-PPV ($\lambda_{\text{ex}} = 350$ nm), BPEA ($\lambda_{\text{ex}} = 450$ nm), and blends (30% BPEA, $\lambda_{\text{ex}} = 350$ nm).

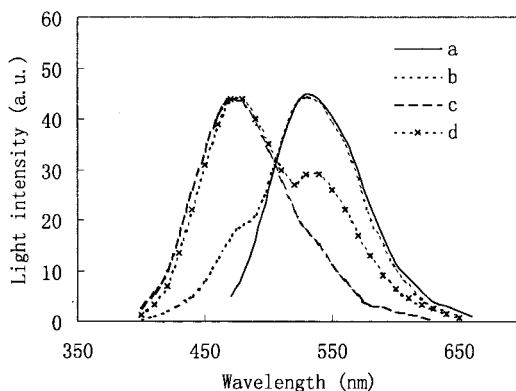


FIG. 4. Normalized EL spectra of LED blend (70% ether-PPV and 30% BPEA) at different voltages (a, 15 V; b, 18 V; c, 25 V) and LED blend with PS doped in the emitting layer (35% ether-PPV, 15% BPEA, and 50% PS) (d).

microdiodes. When the concentration of BPEA is decreased to 1% or 5% BPEA, only the emission of ether-PPV can be detected. This implies that the emission comes from the interface between ether-PPV and BPEA in the bulk at low concentrations of BPEA.

The different sensitivity of the emissive components to applied voltage-induced quenching effects has been used in the interpretation of voltage-induced evolution of the EL spectra in multilayer LEDs or single-layer LED blends. But this is not the situation for a mixture of BPEA and ether-PPV, because it cannot explain the result that the EL spectrum of LED and blend with PS doped in the emitting layer exhibits emission from ether-PPV and BPEA and no spectrum change upon increased applied voltage. It is because blending the two materials with PS prevents formation of BPEA microdiodes showing two emission bands following proportions between ether-PPV and BPEA.

In summary, single-layer LED based on the blend of ether-PPV and BPEA has been fabricated by spin-coating technology. The voltage-induced evolution of EL spectra has been observed in LED blend with only ether-PPV and BPEA in the emitting layer. But the device with PS doped in the emitting layer exhibits emission from both ether-PPV and BPEA, showing two emitting bands, following the proportions of the two materials, and the spectra exhibit no

change with applied voltage. This is because decreasing the concentration of BPEA or blending ether-PPV with PS prevents formation of BPEA microdiodes so that the emission comes from interface in the bulk at low concentrations of BPEA and from microdiodes connecting electrodes at higher concentrations.

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