

Blue emission from polymer light-emitting diodes using non-conjugated polymer blends with air-stable electrodes

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Abstract

By dispersing a non-conjugated luminescent polymer and an electron-transporting material, 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD), into a hole-transporting polymer, poly(9-vinylcarbazole) (PVK), we have achieved improved efficiencies for blue light-emitting diodes (LEDs) fabricated with a copolyester (CPE) containing isolated 1,2-dinaphthylethene units. Quantum efficiencies of the LEDs with the solid dispersion of CPE and PBD in PVK as electroluminescent layer and indium as the electron injection electrodes are about 0.1% photons per electron, better by factor of 10^2 than similar devices made with only the CPE. The LEDs turn on at about 30 V and have a peak emission wavelength in the blue at 485 nm.

Keywords: Blue emission; Light-emitting diodes; Electrodes

1. Introduction

Semiconducting and luminescent π -conjugated polymers are of interest for use in light-emitting diodes (LEDs). These materials offer significant processing advantages, mechanical advantages and size advantages, when compared with conventional semiconducting materials. Moreover, they emit over the full visible spectral range [1–13]. Although there has been rapid progress in research on polymer LEDs, the number of *soluble* conjugated polymers with relatively high luminescence efficiency remains limited; the principal examples being poly(2-methoxy-5-(2'-ethyl-hexyloxy)-*p*-phenylene vinylene) (MEH-PPV) [10], poly(2,5-bis(cholestanoxo)-1,4-phenylene vinylene) BCHA-PPV [11], and cyano-derivatives of PPV (CN-PPV) [12]. MEH-PPV, BCHA-PPV and CN-PPV are soluble in the conjugated form in common organic solvents; LEDs fabricated with MEH-PPV emit orange light [6], LEDs fabricated with BCHA-PPV emit yellow light [13], and LEDs fabricated with CN-PPV emit red light [12].

High efficiency polymer LEDs which have been previously reported utilize Ca as the rectifying contact; the low work function of Ca leads to enhanced electron injection into the conduction (π^*) band of the lumi-

nescent semiconducting polymer [6]. Since Ca is extremely air sensitive and is readily oxidized, such devices require surface passivation prior to use. Therefore, realization of high efficiency polymer LEDs using air-stable electrodes has remained an important goal.

Recent progress has shown that, by generalizing to heterojunction devices, the quantum efficiency and brightness can be significantly improved. By including an electron transport layer, devices with promising performance have been fabricated with BCHA-PPV (yellow emission) [14] or CN-PPV (red emission) [12] even with air-stable electrodes (such as Al or In) as the cathode material. Similarly, by using polyaniline (or bilayers of polyaniline on indium/tin oxide (ITO)), hole injection can be significantly improved [15].

Recently, we reported blue LEDs made with a polymer blend consisting of soluble poly(*p*-phenylphenylene vinylene) and the hole-transporting polymer, poly(9-vinylcarbazole) (PVK) [16]. By dispersing the electron-transporting molecule, 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD), into the semiconducting luminescent polymer, we demonstrated improved efficiencies for green LEDs with air-stable electrodes [17]. Blue electroluminescence was realized with air-stable electrodes using a novel soluble, non-conjugated copolyester, although the quantum efficiency was relatively low [18].

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In this paper, we describe procedures which lead to improved efficiency for blue LEDs fabricated with non-conjugated polymer blends and air-stable electrodes. By dispersing a non-conjugated luminescent polymer and an electron-transporting material, PBD, into a hole-transporting polymer, PVK, we have achieved improved efficiencies for blue LEDs fabricated with copolyester (CPE) containing isolated 1,2-dinaphthylethene units. External quantum efficiencies of LEDs fabricated with the solid dispersion of CPE and PBD in PVK and with indium as the electron injection electrode (cathode) are about 0.1% photons per electron, better by a factor of 10^2 than similar devices made with only the CPE. The LEDs turn on at about 30 V and have a peak emission wavelength in the blue at 485 nm (at room temperature).

2. Experimental details

Details of the synthesis of the CPE with molecular structure as shown in Fig. 1 have been published elsewhere [18]. PBD and PVK were obtained from Aldrich and used as received. CPE (50/50, 2 mg), PBD (20 mg) and PVK (20 mg) were dissolved in 2 ml chloroform. Films of the CPE/PBD/PVK polyblends can be spin-cast from the chloroform solution with excellent reproducibility; the films are colorless, homogeneous and uniform.

The LED structure consists of an In contact on the front surface of a CPE/PBD/PVK polyblend film which has been spin-cast onto a glass substrate partially coated with a layer of ITO as the hole-injecting contact (see Ref. 6 for a schematic diagram). The resulting colorless solid dispersion films have uniform surfaces with thicknesses in the range from 1000 to 3000 Å, depending on details (concentration of solution, spin rate, etc.).

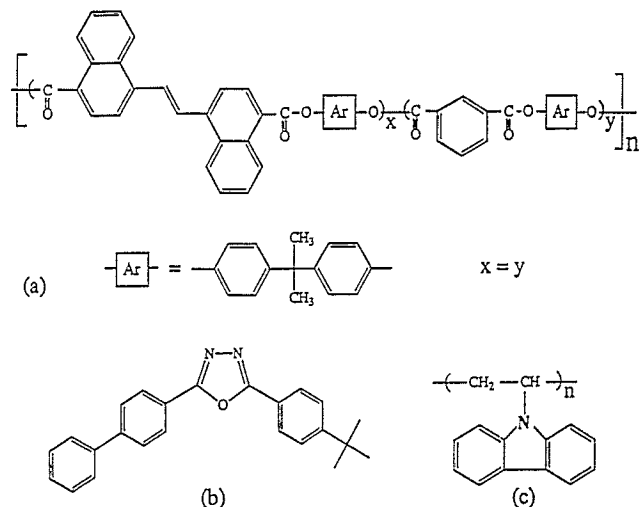


Fig. 1. Structure of (a) copolyester (CPE), (b) 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) and (c) poly(9-vinylcarbazole) (PVK).

Electron-injecting In contacts are deposited onto the surface of the solid dispersion by vacuum evaporation at pressures below 4×10^{-7} Torr, yielding active areas of 0.1 cm². All processing steps are carried out in a nitrogen atmosphere.

Spectroscopic measurements use a single-grating monochromator (Spex 340S) with a Photometrics CCD camera (Tektronix TK512 CCD) as a detector without correction for system response. Electroluminescence (EL) spectra were recorded while applying direct current. For photoluminescence (PL) spectra, the polymer is excited with ultraviolet light at 365 nm.

3. Results and discussion

The forward bias current is obtained when the ITO electrode is biased positive with respect to the In electrode, which is grounded. Fig. 2(a) shows the current versus voltage characteristics measured from a typical In/CPE-PBD-PVK (0.1/1/1)/ITO LED. The rectification ratio is typically 10^2 – 10^3 . The turn-on voltage of the polyblend device was around 25 V. Fig. 2(b) shows the current dependence of the emission intensity from the In/CPE-PBD-PVK (0.1/1/1)/ITO diodes. As is typical of polymer LED devices, the emission intensity exhibits an approximately linear increase with injected current. Blue light emission from the device is visible

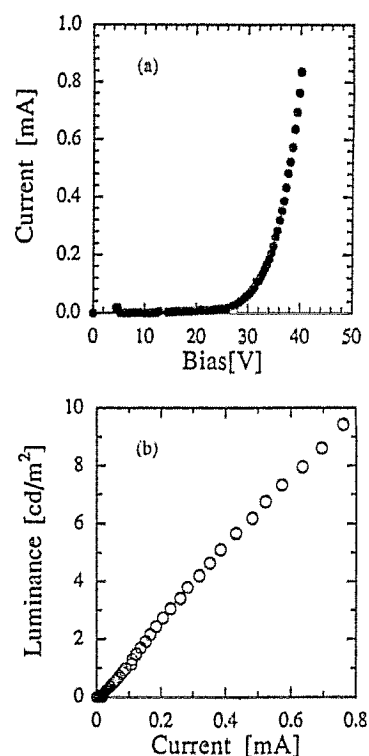


Fig. 2. Dependence of current on applied voltage (a) and emission intensity on injected current (b) for CPE/PBD/PVK (0.1/1/1) LEDs with In as electrodes.

in the normal room light of the laboratory above 30 V.

Fig. 3 compares the dependence of the emission quantum efficiency on current for devices of various blend compositions with In as electron injection electrode. As is typical of the polymer LED devices, the efficiency increases sharply with increasing injected current, followed by saturation. With In as the electron-injecting electrode, the external quantum efficiency of CPE/PBD/PVK (0.1/1/1) is approximately 0.1% photons per electron, 100 times higher than obtained from devices fabricated from CPE with In as the cathode. We have found good reproducibility from device to device.

Note that the quantum efficiencies of CPE/PVK (10%) and PBD/PVK (1/1) devices are two orders of magnitude lower than CPE/PBD/PVK (0.1/1/1) devices. This implies that the combination, including the luminescent polymer, the electron-transporting species and the hole-transporting matrix, is required to obtain a significant increase in EL efficiency. We also investigated the dependence of the efficiency on the concentration of the CPE. The maximum efficiency was achieved with CPE/PBD/PVK (0.1/1/1) devices, corresponding to a concentration of luminescent chromophores of about 2%, similar to the results obtained from the PPPV/PVK blend system [16]. Although blue emitting LEDs based on polyquinoline derivatives have yielded external efficiencies in excess of 2% with a Ca cathode [19], the 0.1% external quantum efficiency (photons per electron) with In as the electron-injecting electrode is the highest reported to date for blue-emitting polymer LEDs with *air-stable* electrodes.

Fig. 4 compares the room-temperature EL and PL spectra obtained from a CPE/PBD/PVK (0.1/1/1) film in a device configuration with an In electrode. The EL and PL spectra of the blend are virtually identical, a feature which is quite generally characteristic of polymer LEDs. Thus, the same excitations (presumably neutral bipolaron excitons) are involved in both cases. In PL, the neutral bipolaron excitons are formed by lattice

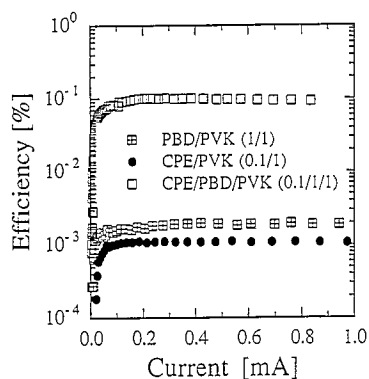


Fig. 3. Electroluminescent efficiency vs. device current (In/polyblend/ITO) for blend device with various compositions.

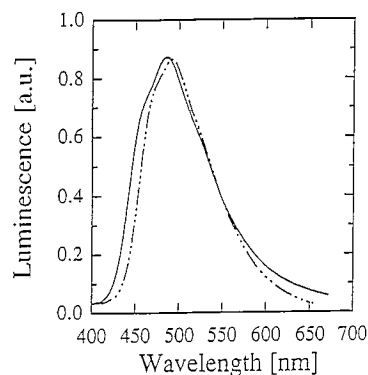


Fig. 4. EL (solid line) with In as the electrodes and PL (dashed line) from a CPE/PBD/PVK (0.1/1/1) blend at room temperature.

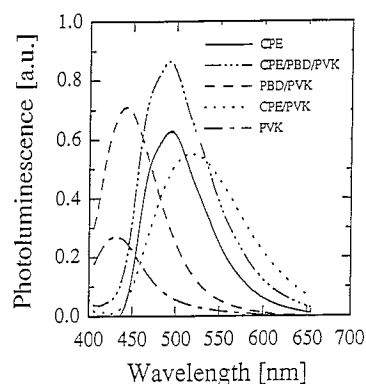


Fig. 5. PL of blend films with various compositions at room temperature.

relaxation following photoexcitation; in the case of EL, the same species are formed as the intermediate step in the recombination of an electron polaron and a hole polaron. The emission peak of the PL and EL spectra occurs in the blue at around 485 nm.

The PL spectra of various blend composition films are compared in Fig. 5. The CPE/PBD/PVK (0.1/1/1) film yields the highest PL intensity. The emission peak of CPE/PBD/PVK (0.1/1/1) composition is essentially identical with CPE, even though the concentration of CPE in the blend is only around 5%. This suggests that CPE acts as the dominant radiative combination site in the blend. These results suggest a general approach for achieving high-efficiency polymer electroluminescent diodes: design and synthesis of the electron-injecting/transporting polymer and hole-injecting/transporting polymer, respectively; then blending these active components together with the luminescent polymer (containing the specific luminescent species desired) to make the electroluminescent layer. Having identified good hole-transporting and electron-transporting polymers, it is relatively easy to tune the color of the emitting light by choosing various luminescent polymers.

4. Conclusions

We have demonstrated improved efficiencies for blue LEDs fabricated with a solid dispersion of a CPE containing isolated 1,2-dinaphthylethene units, an electron-transporting material (PBD) and hole-transporting material (PVK) as the electroluminescent layer and with In as the electron injection electrode. Typical external quantum efficiencies of these blue LEDs with In as the electrode are 0.1% photons per electron. These are the highest known efficiencies for blue-emitting polymer LEDs using air-stable electrodes.

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