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Electroluminescent Characteristics of Conjugated Polymer/Ionomer Blend Devices According to Ionic Contents

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Fluorescent polymer and poly (sodium 4-styrenesulfonate) ionomer (PSS-ionomer) blends were used as emitting layers in polymer light-emitting diodes (LEDs). The two polymers were blended in the optimal ratio which shows the highest luminescent intensity due to dilution effect. We changed the ionic contents of ionomer from 5 mol% to 10 mol% with fixed optimal blended ratio. We obtained the narrow spectrum having high color purity in the blend system. The conjugated polymer/PSS-ionomer blend devices achieved a more enhanced luminescent efficiency as compared with that of the conjugated polymer/PS device due to polar groups in the PSS-ionomer, which enhance the electron injection from the cathode to the emitting molecules.

Keywords: electroluminescence; electron injection; ionomer

INTRODUCTION

There are a wide variety of reports that used ionic group as electron injecting layer in polymer electroluminescent (EL) devices or used

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organic dye salt as an emitting layer in organic light emitting diode (OLED) for improving the efficiency [1–5]. For elevating the quantum yield, electron injection should be enhanced in the polymer LED because a hole is the major carrier in the emitting layer. In order to do that, several attempts have been reported [6–8]. In a recent study it was reported that ionomers, as an electron injecting layer, increase the affinity with electrons and, thus, effectively lower the turn-on voltage and the driving voltage, which makes EL devices more efficient [3–5].

In this study, we investigated the optical properties and the current-voltage-luminance (I-V-L) characteristics of devices that utilize the blends of the light-emitting conjugated polymer and the ionic polymer. Especially, we focused on the point of view that the ionic contents of ionomer in conjugated polymer/ionomer blend films affect the properties of the blended EL devices.

EXPERIMENTAL

Polystyrene with a weight-averaged molecular weight of 230,000 and number-averaged molecular weight of 140,000 was purchased from Aldrich Co. The sulfonation of polystyrene and the synthesis of the PSS-ionomer was performed using a method described elsewhere [5]. The sulfonate content in the sulfonated polystyrene can be ranged from about 3.5 to 15.4 mole percent and we synthesized PSS-ionomers including ionic concentration of 5, 6.7, 8.3, and 10 mole percent. An polyfluorene-type blue LEP (Lumation BlueJ Light-Emitting Polymers, Trademark of Dow Chemical Company, BlueJ) was used as a luminescent polymer to blend with ionomers. BlueJ and the PSS ionomers were dissolved in chlorobenzene, at the fixed ratio of BlueJ 60 wt%/ionomer 40 wt%, which is the optimal ratio that shows the highest luminescent intensity due to dilution effect. This mixture, dissolved in chlorobenzene, was spin coated to a 100 nm thickness on PEDOT coated ITO glass substrates. And Al as a cathode was deposited by thermal evaporator under a pressure of 1×10^{-6} Torr.

The current-voltage-luminescence (I-V-L) characteristics of the devices were analyzed using a current/voltage source measurement unit (Keithley 236) and an optical powermeter (Newport 835) connected to a photodiode (Newport 818-SL). Photoluminescence (PL) spectra were measured by ISS PC1 Photon Counting Spectrofluorometer.

RESULTS AND DISCUSSION

Figure 1 shows the normalized PL spectra of the BlueJ/PSS-ionomer blend film and neat BlueJ polymer film. We obtained the narrow

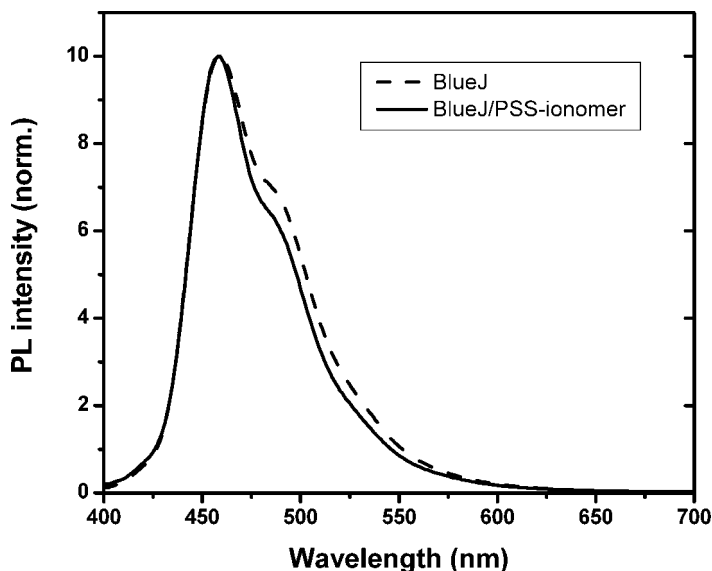


FIGURE 1 Normalized photoluminescence spectra of BlueJ polymer and BlueJ 60/PSS-ionomer 40 blend film.

spectrum having high color purity in the blend system because the rigid chains of PSS-ionomer reduced the interchain interactions of conjugated polymer. The blended films had higher PL intensity than the pure BlueJ film, and the PL efficiency of the BlueJ (60%)/PSS-ionomer (40%) film increased by 30%. This PSS-ionomer decreases the interchain interaction of the conjugated polymer and diminishes the exciton quenching, due to the packing of the conjugated polymer chains, thereby increasing the luminescent efficiency [9].

In Figure 2(a) the current density is plotted against the voltage, according to the ionic contents of the PSS-ionomers. And we compared these films with the BlueJ/polystyrene blend film to identify the electrical and optical properties of these devices. We can identify the electron injection and the mobility of carrier in Figure 2(a). The more ionic contents increase from 5 to 10 mol%, the more injected electrons and current density gradually increase. Under the electric field, local dipoles form in the emitting layer composed of the PSS-ionomer and BlueJ near the cathode. The local dipoles are arranged continuously from local dipoles formed near the cathode to the anode. These local dipoles strongly attract electrons and the injected electrons move into the anode quickly in the blended polymer layer. The role of ionomer

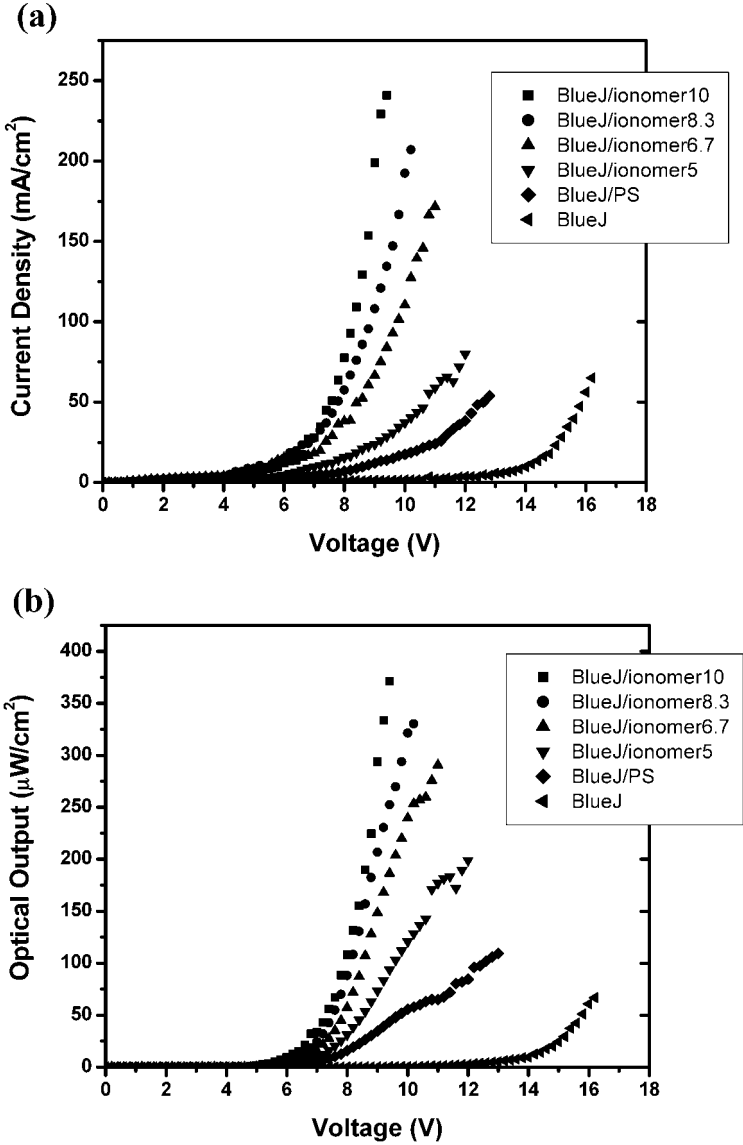


FIGURE 2 (a) Current density vs. voltage in ITO/PEDOT/BlueJ:PSS-ionomer blend/Al devices with a change of the sulfonic-ion concentration of the ionomers. (b) Optical output vs. voltage in ITO/PEDOT/BlueJ:PSS-ionomer blend/Al devices with a change of the sulfonic-ion concentration of the ionomers. The molar concentration of the sulfonic group in PSS-ionomer was changed from 5 to 10 mol%.

can be explained as bridging effect of counterions (Na^+) between the ionomer and Al existing at the electron injecting contact of polymer LEDs. Electron injection mainly depends on the local ionic dipoles within the ionomers, and these dipoles accelerate electron injection. Consequently, recombination probability with holes is improved and luminescent efficiency is also improved, by decreasing the quenching near the cathode. Therefore, while the currents flows plentifully, the luminance of the devices become brightened gradually, as the current density increases.

Figure 2(b) shows the optical output versus the voltage curve of the blended EL devices including the various ionic contents of PSS-ionomers. The optical output of the film of BlueJ/Ionomer 10 mol% is the brightest among those of the various ionic contents. While the EL intensity of the BlueJ/PS film roughly increased by 30%, compared with that of the pure BlueJ film, due to dilution effect, the EL intensity of the BlueJ/Ionomer 10 mol% device was more than 5 times brighter, when compared with the pure BlueJ device. Moreover, the turn-on voltage was decreased significantly from 10.2 V to 4.4 V, in the case of the BlueJ/Ionomer 10 mol% blended device. It is because

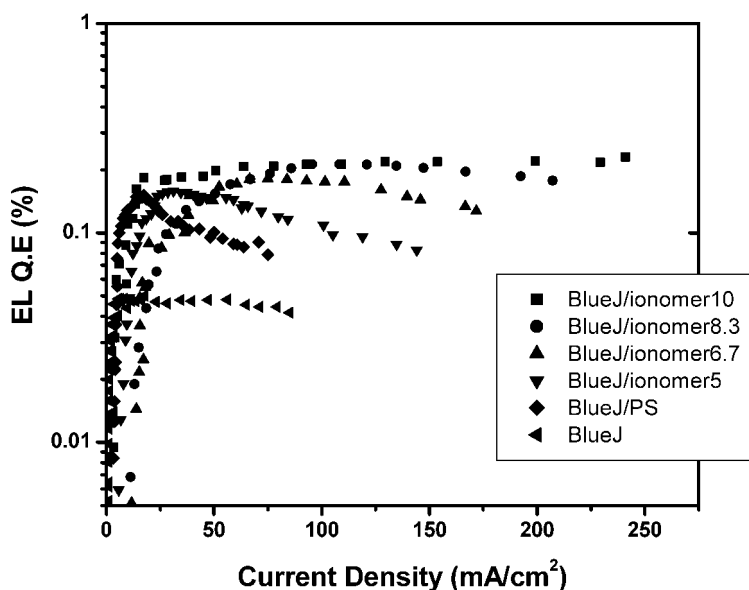


FIGURE 3 External quantum efficiency vs. current density in ITO/PEDOT/BlueJ:PSS-ionomer blend/Al devices with a change of the sulfonic-ion concentration of the ionomers.

band bending occurs, which lowers the energy band of BlueJ polymer, so that ionic groups of ionomer can induce electron injection into an emitting layer from the cathode.

In Figure 3 the EL quantum efficiency are plotted against the current density for the blended polymer LED. The BlueJ/Ionomer 10 mol% device is the most efficient. The device has the highest luminance when compared with the others, at a current level that can drive the devices, and its maximum EL quantum efficiency is 0.23%.

CONCLUSIONS

The enhanced luminescent properties of a conjugated polymer/PSS-ionomer blend devices were obtained. The blended film showed narrow spectrum having the high color purity due to the dilution effect. The local dipoles formed near the cathode enhanced electron injection, resulting low turn-on and driving voltage. The increase of ionic contents induced more current flow, so that the luminance of the devices gradually increased.

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