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Polymer Electroluminescent Devices of Poly(4,4'-triphenyl amine-diylvinylene-alt-4,4'-diphenyl-sulfone-vinylene) (PTASV)

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Polymer Electroluminescent Devices of Poly(4,4'-triphenyl amine-diylvinylene-*alt*-4,4'-diphenyl-sulfone- vinylene) (PTASV)

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PTASV was newly synthesized through the Wittig reaction and characteristics of various types of LEDs using this polymer were investigated. A single layer device (ITO/PTASV/Al) showed green emission at about 540 nm with the threshold voltage of 20 V. When a thin LiF layer was inserted to the PTASV/Al interface, the external quantum efficiency was increased about 10 times that of the single layer device with lower threshold voltage. The external quantum efficiency of the device with heterojunction structure (ITO/PTASV/Alq₃/LiF/Al) was 0.01 % at current density of 8 mA/cm², in air and at room temperature.

Keywords: electroluminescence; polymer; phenylenevinylene; sulfone

INTRODUCTION

Many kinds of polymeric EL devices have been investigated since Friend *et al.* first reported PPV-based LED ^[1]. Previous work reported that majority carrier in the PPV single layer device is the hole because of the low electron affinity. To achieve the high-efficiency light emission from the material, it is desirable to enhance the electron injection from metal electrode to polymer and the electron transport in the polymer ^[2]. For these purpose, we synthesized a novel EL polymer containing sulfonylene group (PPVS) ^[3]. Introduction of the sulfonylene group in the polymer not only improved the electron injection and transport in the material but also shifted the emission color to blue region because of the kink formation. It also allows the material to be processible. As an extension of this idea, triphenylamine moiety was introduced into the PPVS structure in this work to enhance the hole transport property in an EL device.

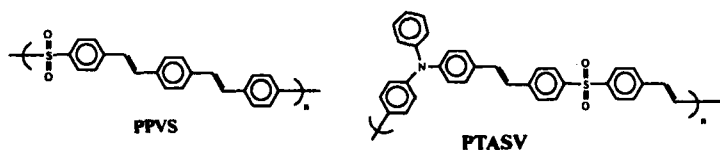


FIGURE 1. Chemical structure of PTASV and PPVS.

In this paper, we describe the characteristics of various types of LEDs using this novel EL polymer containing the sulfonylene group and triphenylamine moiety (PTASV). The devices include the single layer device, the device having a thin LiF layer at PTASV/Al interface, and the device with heterojunction structure (PTASV/Alq₃).

EXPERIMENTAL

Polymer synthesis

Novel class of arylenevinylene copolymer containing sulfonylene group in the main chain (PTASV) was synthesized through the Wittig reaction of bis(bromomethyl-*p*-phenyl)-sulfone triphenylphosphonium salt and 4,4'-diformyl triphenyl amine. The detailed synthetic procedures for monomers and polymer will be reported elsewhere.

Fabrication of EL Device

Three different light emitting devices of PTASV were fabricated on indium-tin-oxide coated glass substrates: (i) ITO/PTASV/Al, (ii) ITO/PTASV/LiF/Al, and (iii) ITO/PTASV/Alq₃/LiF/Al. The polymer films were obtained by spin coating and Alq₃, LiF and Al layers were deposited by the vacuum evaporation at the pressure of about 10^{-6} Torr.

RESULTS AND DISCUSSION

The weight average molecular weight of the polymer was about 7300 (PDI = 2.8) determined by GPC analysis. Glass transition temperature of PTASV was measured to be 180 °C. The polymer was very stable up to 400 °C as to show only 5 % weight loss. This excellent thermal stability of PTASV could suppress the reduction of EL emission from the heat produced during operation of the device.

Figure 2 shows UV-visible absorption, PL, and EL spectra of the PTASV polymer film. The EL device emits the green light of 540 nm.

The emission spectrum is red-shifted by 70 nm compared to PPVS, which is expected due to the intramolecular push-pull structure between triphenylamine moiety and sulfone group.

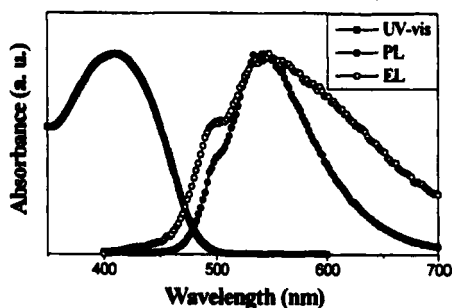


FIGURE 2. UV-visible absorption spectrum and PL / EL spectrum of PTASV film.

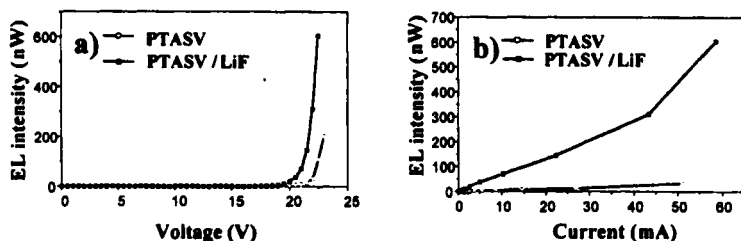


FIGURE 3. Voltage-luminance (a) and current-luminance (b) characteristics of PTASV and PTASV/LiF devices.

Figure 3 shows the voltage-luminance and current-luminance behaviors of LEDs for the single layer device and the ITO/PTASV/LiF (0.5 nm thick)/Al device. The single layer device showed the turn on voltage of 20 V. The high turn on voltage indicates that the LUMO level of the material is still quite high compared to the Al work function even with the introduction of the high electron affinity sulfonylene group in the polymer. The high LUMO level may result in the high injection barrier

for the electron from the Al cathode to increase the turn on voltage. The high LUMO level was confirmed by cyclic voltametry as shown in Table 1. The device performance was significantly improved by inserting the thin LiF layer between PTASV and Al cathode. It reduces the turn on voltage of the device and enhances the relative quantum efficiency by 10 times. The maximum intensity of the devices was also increased by inserting LiF layer. The improved efficiency may be attributed to the reduction of energy barrier at PTASV/LiF interface ^[4].

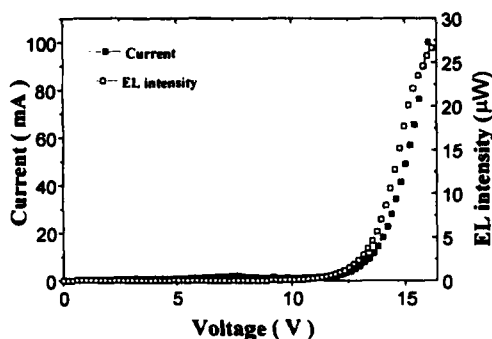


FIGURE 4. Voltage-current-luminance characteristics of ITO/PTASV(40nm)/Alq₃(40nm)/LiF(0.5nm)/Al device.

Even with the LiF layer, the turn on voltage is still quite high. The LUMO and the HOMO levels in Table 1 imply that the material can be used as a good hole transporting material. For this purpose, we fabricated ITO/PTASV/Alq₃/LiF/Al device, where the PTASV acts as the hole transporting layer. Figure 4 shows the current-voltage-luminance characteristics of the device. The emission with a luminance of 26 μ W was achieved at a driving voltage of 16 V and the external quantum efficiency was 0.01 % at current density of 8 mA/cm², in air and at room temperature. The luminance, driving voltage and external quantum

efficiency have been improved significantly in the device. Combined with the good thermal stability, this fact indicates that PTASV can be used not only as an emitting material but also as a hole transporting material.

TABLE 1. The HOMO-LUMO Energy Levels* of PTASV and Alq₃.

	HOMO (eV)	LUMO (eV)	E _g (eV)
PTASV	- 5.13	- 2.60	2.47
Alq ₃	- 5.70	- 3.10	2.60

* relative to the vacuum level.

Summary

We synthesized a novel light emitting arylene-vinylene polymer containing sulfonylene moiety. The material showed not only the good emitting characteristics but also good hole transporting properties for LED in addition to their excellent thermal stability.

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