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Synthesis and characterization of color tunable electroluminescent polymer by blending oxadiazole containing polymer

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Abstract

The electro-optical properties of novel polymers such as poly(phenylenevinylene-alt-*N*-hexylcarbazolevinylene) ([poly(PPV-*N*-hexylCvz)]) poly[1′,4′-phenylene-1″,4″-(2″-(2‴-ethylhexyloxy))phenylene-2,5-(1‴,4‴-phenylene)-1,3,4-oxadiazolyl] (PPEPPO) and their blends were characterized. The photoluminescence and electroluminescence (EL) spectra of the blend films composed of poly(PPV-*N*-hexylCvz) and PPEPPO were mainly contributed from the luminance of poly(PPV-*N*-hexylCvz) even at low poly(PPV-*N*-hexylCVz) ratios. Remarkably enhanced EL efficiency was observed as increase the ratio of PPEPPO. This probably results from the energy transfer in the excited state from PPEPPO, with a larger band gap, to poly(PPV-*N*-hexylCvz) with a smaller band gap. When the ratio of PPEPPO was increased, we observed color emission from green to blue and slightly increased the turn-on voltage compared to poly(PPV-*N*-hexylCvz). The forward bias turn-on voltage for the light emitting diodes are 5 V for poly(PPV-*N*-hexylCvz) and 40 V for PPEPPO, respectively.

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1. Introduction

Electroluminescent display [1–5] has advantages of a fast response time, driven at low voltage, obviation of a backlight, an excellent luminance as well as a wide viewing angle, so that many application have been studying in many ways. Diodes fabricated with organic dyes generally show higher efficiency and better performance compared to the ones with conjugated polymers. However, organic fluorescent dyes tend to recrystallize during the operation of the electroluminescence diodes (ELD) [6]. Conjugated polymer-based ELD appear to be very promising for the development of low-cost, multicolored, large-area active flat panel display. Polymer light emitting diodes (LEDs) have been widely studied, and the most efficient devices reported are multi-layered devices which comprise a sequence of a hole-transporting layers, emitting layers and electron-transporting layers [7,8]. The recombination of the injected electrons and holes in the polymer layer generates excitons which may radiatively decay. The characteristics of a polymer LED are determined by the balanced injected charges which is crucial in achieving high quantum efficiency.

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Multi-layered devices have been found to be more efficient than single-layer devices made from conjugated polymer layer in which hole injection is easier than that of electrons [9]. However, the fabrication of multi-layer devices is tedious and difficult to selection of the appropriate layers to optimize the device performance. To solve this problem, blended materials that contain mixtures of electron transporting and emitting materials are often used to form efficient single-layer devices with high quantum efficiency [10,11]. Recently, we have synthesized and reported the various types of a novel electroluminescent polymers [12–15].

In this paper, we report color tunable polymer LEDs using the blended materials by poly(*p*-phenylenevinylene-co-*N*-hexylcarbazolevinylene), poly(PPV-*N*-hexylCvz) as the emissive layer and oxadiazole-containing polymer poly[1′,4′-phenylene-1″,4″-(2″-(2″″-ethylhexyloxy))phenylene-2,5-(1‴,4‴-phenylene)-1,3,4-oxadiazolyl] (PPEPPO) as the electron transport layer.

2. Experimental

2.1. Synthesis of monomers

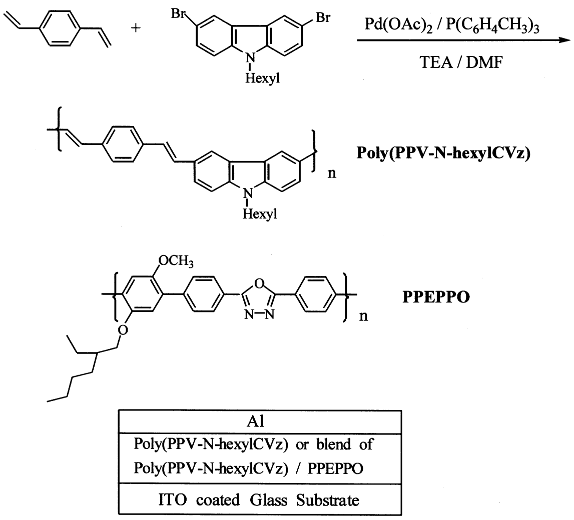
In a 500 ml three-neck flask fitted with a mechanical stirrer, reflux condenser and dropping funnel a solution of 33.4 g (0.2 mol) of carbazole in 150 ml of dry THF was added dropwise to a suspension of 6 g (0.25 mol) of NaH in 200 ml of THF. After refluxing for 2 h, 42 g (0.25 mol) of 1-bromohexane was added and the mixture refluxed overnight. After filtration and removal of THF, the product was recrystallized from methanol (yield: 75%, m.p. 53°C). 3,6-dibromo-*N*-hexylcarbazole was synthesized as follows: In a three-neck flask, 2.5 ml of bromine was slowly added to the mixture of 6 g of *N*-hexylcarbazole and 4 g of sodium acetate in 24 ml of acetic acid, while the temperature of the reaction mixture was maintained below 18°C. After stirring for 2 h, the mixture was poured into ice water and the product was isolated by filtration. After drying in vacuo the product was separated by column chromatography using *n*-hexane as an eluent. Yield: 56%, m.p. 81°C, ^{1}H-NMR ($CDCl_3$, ppm): 0.82 (t, 3H), 1.27 (broad, 6H), 1.87 (t, 2H), 4.2 (t, 2H), 7.2 (d, 2H), 7.5 (d, 2H), 8.1 (s, 2H). Divinylbenzene (Aldrich, 80%, mixture of isomers) was purified two isomers of *m*- and *p*-divinylbenzene by the literature procedure [16].

2.2. Characterization

^{1}H-NMR spectra were recorded with the use of Bruker AM-300 spectrometer, and chemical shifts are reported in ppm units with tetramethylsilane as internal standard. UV–VIS absorption spectra of the films were measured with JASCO spectrometer. Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) analysis with polystyrene standard calibration (Waters high-pressure GPC assembly Model M590 pump, μ-Styragel columns of 10^5, 10^4, 10^3, 500, and 100 Å refractive index detectors, solvent THF). Thermal analysis was carried out on a Dupont TGA 9900 thermogravimetric analyzer in a nitrogen atmosphere at a rate of 10°C/min. For fabrication of blend polymer films, the weight ratio of poly(PPV-*N*-hexylCvz)/ PPEPPO was varied as 100/0, 50/50, 17/83, 9/91 and 0/100. The formed films fabricated by spin casting with the thickness of about 100 nm were estimated with Alpha Step-200 profiler. EL spectra of the devices were recorded with an ISS PC spectrofluorometer under a constant current density. Photoluminescence (PL) spectra of the thin films were also recorded using the same spectrofluorometer. For the measurement of EL, the polymer LEDs was constructed as follows: an indium tin oxide (hereafter ITO) anode coated onto a glass substrate was patterned in stripe type with 3 mm wide, and which was cleaned in the order of a cleaning solution, deionized water, acetone and isopropyl alcohol. The polymer films were prepared by spin casting the blended polymer solution containing 1.5% by weight in THF and evaporated the solvent in a vacuum desiccator at 50°C for 3 h. Uniform and pinhole free films with a thickness around 100 nm were easily obtained from blended polymer mixture. Aluminum having purity of 99.99% was used for a cathode material, because it was stable in the air although the work function was high. After setting a shadow mask for cathode, and an Al wire was placed in a tungsten wire heater, and the vacuum pressure was kept to 4×10^{-6} Torr. After reaching the desirable vacuum pressure, the heater was heated to melt Al. The deposition rate and thickness of the layer was measured by means of a quartz resonator. The contact area of the light emitting part was 4 mm^2. The obtained sample was handled under nitrogen gas to avoid contacting with the air. The current–voltage (I–V) characteristics and the intensities of EL emission were simultaneously measured with a Keithley 236 SMU and a TOPCON-BM7 luminance meter. All processes and measurements mentioned above were carried out in N_2 at room temperature.

2.3. Polymerization

The polymerization with the reaction scheme as shown in Scheme 1 was carried out under an argon atmosphere using Heck reaction. A 25 ml glass pressure vessel was charged with 10 ml of DMF, 0.82 g (2 m mol) of 3,6-dibromo-*N*-hexylcarbazole, 0.26 g (2 mol) of divinylbenzene, 22 mg of palladium acetate(II) and 82 mg of tri-o-tolylphosphine. After a homogeneous solution was obtained, 2 ml of triethylamine was added to the reaction mixture. This mixture was heated for 24 h to



Scheme 1.

100°C. At the end of the reaction, the crude product was isolated by precipitation into methanol. After filtration, the crude polymer was purified using Soxhlet in methanol in order to remove the residual monomers and oligomers. After vacuum drying at 30°C for 1 day, a yellow colored poly(1,4-phenylenevinylene-alt-*N*-hexyl-3,6-carbazolevinylene) poly(PPV-*N*-hexylCvz) was obtained. Yield 80%.

3. Results and discussion

Scheme 1 shows the device configuration and the molecular structures of the poly(PPV-*N*-hexylCvz) and PPEPPO used in this study. Poly(PPV-*N*-hexylCvz) was composed of a phenylenevinylene unit as an emissive part and *N*-hexylcarbazole as an hole transporting part which was synthesized by using the Heck reaction. Molecular weight and glass transition temperature of the poly(PPV-*N*-hexylCvz) are $Mw = 7800$ and 147°C, respectively. Fig. 1 shows the (a) ^{1}H-NMR spectra of poly(PPV-*N*-hexylCvz) and (b) PPEPPO. As the polymerization proceeded, the vinylic proton peaks of the monomer present at 5.4 and 5.8 ppm disappeared and new vinylic proton peaks of poly(PPV-*N*-hexylCvz) appeared at 6.8–8.2 ppm along with aromatic protons. The assignment of the peaks as indicated in the spectra confirms the present polymer structure. In order to obtain a high efficiency in a single layer device, it is necessary to optimize the transporting balance of carriers such as holes or electrons. The EL polymer layer should be able to carry both of holes and electrons. Especially, the transportation of holes is much higher in π-conjugated polymer. To fabricate a polymer layer of the most ideal single layer device, there is a method of forming a polymer layer which is prepared from a single polymer carrying both hole and electron transporting parts. In other ways, there is a method of forming a polymer layer which is prepared by blending two polymers having both of characteristics above, or a polymer layer prepared from a molecular dispersed polymer. Therefore, it is expected that the polymeric analogues of PBD, oxadiazole-containing polymer, are also good electron-injection material [17]. In order to improve the above drawbacks, we had synthesized novel electron-transport polymer, poly[1,4-phenylene-1′,4′-(2′-methoxy-5′-ethylhexyloxy)phenylene-1″,4″-phenylene-2.5-oxadiazolyl], (PPEPPO) (Scheme 1), which synthetic method will be published elsewhere. The resulting polymers completely soluble in organic solvents such as THF, chloroform or 1,2-dichloroethane. A thin film is formed from the blended polymers which is soluble in an organic solvent, by dissolving 1.5 wt.% in THF solvent, and spin-coating onto the ITO coated substrate. The thin film formed by the above method is uniform and free of pinholes and has an excellent adhesion to a substrate. To enhance the PL, EL efficiency, we fabricated the EL devices consisting blend polymer films, which the blend ratio of poly(PPV-*N*-hexylCvz) and PPEPPO was varied as 100/0, 50/50, 17/83, 9/91 and 0/100 by weight. UV–VIS absorption spectra of poly(PPV-*N*-hexylCvz), PPEPPO and a blend of those were obtained. Poly(PPV-*N*-hexylCvz) had a maximum peak at 382 nm, PPEPPO had peaks at 330 and 366 nm, which showed UV absorption wavelength of bimodal shape. When the blend ratio of poly(PPV-*N*-hexylCvz) and PPEPPO was varied as 100/0, 50/50, 17/83, 9/91 and 0/100, the strength of each peak was proportioned to the concentration of the PPEPPO. According to the blend ratio, the position of the maximum absorption wavelength was not changed. It was

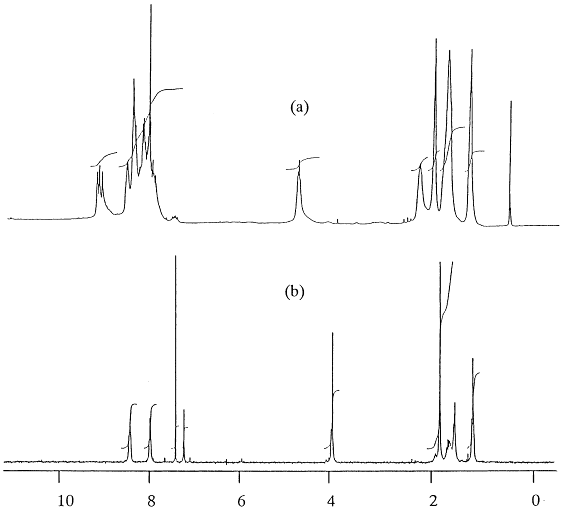


Fig. 1. ^{1}H-NMR spectra of (a) poly(PPV-*N*-hexylCvz) and (b) PPEPPO in $CDCl_3$.

Table 1
Electro-optical (PPV-*N*-hexylCVz), PPEPPO and their blends

Poly(PPV-*N*-hexylCVz)/PPEPPO (wt.%)	UV $\lambda_{\max}$	PL $\lambda_{\max}$	EL $\lambda_{\max}$
100/0	382	490, 520 (sh)[a]	533
50/50	370	490	492
17/83	367	482	451
9/91	367	480	461
0/100	330, 366 (sh)[a]	426	–

[a] sh: shoulder.

found that there were no changes of peaks between a new peak and an old peak, so that there were no interaction between poly(PPV-*N*-hexylCvz) and PPEPPO at the ground state. Table 1 summarizes the results of electro-optical characteristics obtained from poly(PPV-*N*-hexylCVz), PPEPPO and various conditions of their blends. The band gap of poly(PPV-*N*-hexylCvz) and PPEPPO (taken from the onset of the absorption spectrum) is 2.70 and 2.94 eV, respectively. The wide band gap of PPEPPO compared to poly(PPV-*N*-hexylCvz) is desirable for use a charge-injection material, because radiative electron–hole recombination is consequently confined to the emissive layer of narrow band gap. Fig. 2 shows the normalized PL spectra of the poly(PPV-*N*-hexylCVz), PPEPPO and their blend systems, which were excited at 370 nm. A film of poly(PPV-*N*-hexylCvz) (a) has maximum peaks at 490 and 520 nm with shoulder. A film of PPEPPO (e) showed a maximum light emitting peak at 426 nm. It was shown that a PL maximum peak wavelength of solid film state was red-shifted to about 10 nm, more than the PPEPPO solution using THF as a solvent. As shown in the PL spectrum of Fig. 2, in case of a blend film of poly(PPV-*N*-hexylCvz) and PPEPPO, the only light emitting peak from single component of poly(PPV-*N*-hexylCvz) could be observed, regardless of the content of the PPEPPO. According to increasing the content of PPEPPO, the maximum PL peak from poly(PPV-*N*-hexylCvz) was blue-shifted to about 10 nm, which was caused by the chain conformation effect. Fig. 3 shows the current density–voltage characteristics of ITO/poly(PPV-*N*-hexylCvz)/Al (a), ITO/PPEPPO/Al (d), and ITO/blend of poly(PPV-*N*-hexylCvz)-PPEPPO/Al devices (b,c). As can be seen in Fig. 3(d), the device comprising a PPEPPO film exhibited a clearly higher EL threshold voltage (40 V) and did not function at all or exhibited minimal light output at high voltage, when it was operated by pulse deriving. However, the EL threshold voltage was 5 V for the ITO/poly(PPV-*N*-hexylCvz)/Al device (Fig. 3(a)) from which a yellowish green emission can be seen. In the blend polymer devices, there was an increasing tendency in the turn-on voltage with the increasing the portion of PPEPPO. Fig. 4 shows a change of an EL spectrum according to the blend ratio of poly(PPV-*N*-hexylCvz):PPEPPO. As shown in Fig. 4(a), poly(PPV-*N*-hexylCvz) showed the maximum light emitting peak at 533 nm. The emitted light of poly(PPV-*N*-hexylCvz) was yellowish green with an EL spectrum. According to the blend ratio, an EL efficiency of the blend was suddenly increased, which is more than that of poly(PPV-*N*-hexylCvz) itself. It was believed that the oxadiazole group of PPEPPO functioned as an electron transporting material, so that the recombination effi-

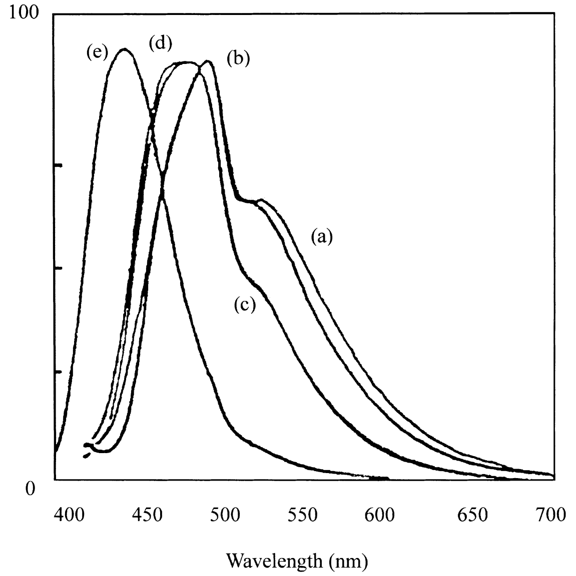


Fig. 2. PL spectra of poly(PPV-*N*-hexylCvz), PPEPPO and their blends thin films; blend ratio of poly(PPV-*N*-hexylCvz)/PPEPPO (wt.%): (a) 100/0, (b) 50/50, (c) 17/83, (d) 9/91, (e) 0/100.

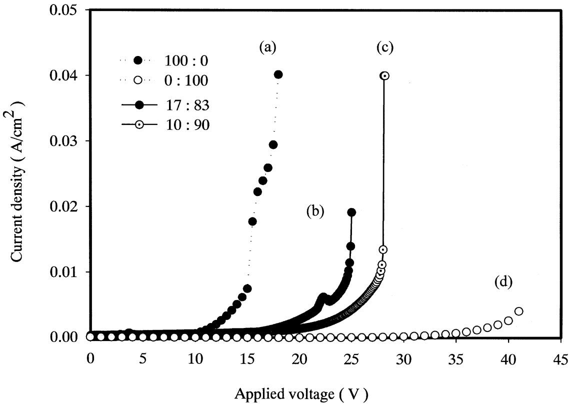


Fig. 3. *I–V* characteristics of ITO/poly(PPV-*N*-hexylCvz)/Al (a), ITO/PPEPPO/Al (d), and ITO/blend of poly(PPV-*N*-hexylCvz)-PPEPPO/Al devices: (b) 17/83, (c) 10/90.

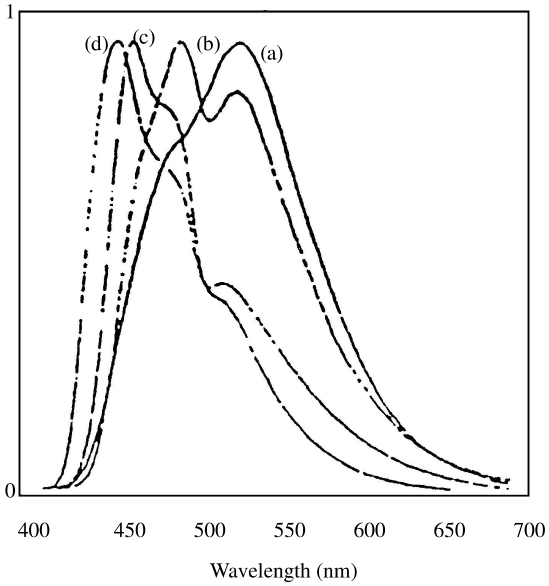


Fig. 4. EL spectra of ITO/poly(PPV-*N*-hexylCvz)/Al (a), and ITO/blend of poly(PPV-*N*-hexylCvz)-PPEPPO/Al devices; (b) 50/50, (c) 17/83, (d) 9/91.

ciency was raised by the appropriate balance of holes and electrons. The dilution effect was also worked for the EL efficiency. As increasing the content of the PPEPPO, it is possible to observe color emission from green to blue. When the ratio of poly(PPV-*N*-hexylCvz):PPEPPO was 9:91, the maximum EL efficiency was observed and in the range of over 90% PPEPPO, no more big difference was observed. In EL spectra, as increasing the PPEPPO content, the emission peaks of blended system are blue shifted about 40–70 nm compared to poly(PPV-*N*-hexylCvz). When the ratio of poly(PPV-*N*-hexylCvz): PPEPPO was 50:50, the emission light was green color. However, as the PPEPPO content increases up to 83%, the emission color changed from green to blue. The brightness at 10 V is about 490 and 280 cd/m^2, respectively. To optimize the diodes we can consider the use of metals with a lower work function or metal alloys known to facilitate the injection of electrons and multilayer structure using transport layer. Also, further studies on color tuning by blending are being investigated by spectroscopic method.

4. Conclusion

We have synthesized and characterized a color tunable light emitting polymer and oxadiazole containing polymer as an electron transport material. Characteristics of the resulting polymers and their blends are performed by ^{1}H-NMR, UV–VIS, PL and EL spectra. The efficient and high brightness color tunable polymeric EL devices have been demonstrated using blends with poly(PPV-*N*-hexylCvz) and PPEPPO depending on weight ratio. The EL intensity from poly(PPV-*N*-hexylCvz) is markedly enhanced and the optimal blend ratio of 9/91 [poly(PPV-*N*-hexylCvz)/PPEPPO] for the maximum EL efficiency output was obtained. As the ratio of PPEPPO was increased from 50% to 83%, the emission light was changed from green to blue color. The PL and EL spectra of the blend films could be mainly contributed from the luminance of poly(PPV-*N*-hexylCvz) even at low poly(PPV-*N*-hexylCvz) ratios. This probably results from the energy transfer in the exited state from PPEPPO, with a larger band gap, to poly(PPV-*N*-hexylCvz) with a smaller band gap.

Acknowledgements

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