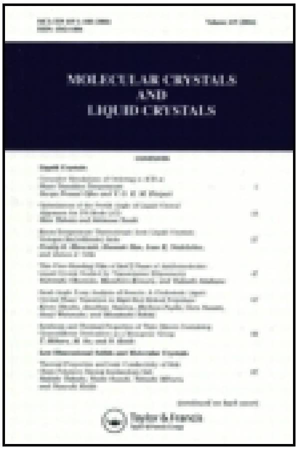

Molecular Crystals and Liquid Crystals

Green Emitting PLED Having Polymeric Host and Dopant in Emissive Layer

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Version of record first published: 22 Sep 2010

To cite this article: Yoon Soo Han, Hoyoung Kim, Byeong Dae Choi, Jeong Han Song, Younghwan Kwon, Youngjune Hur, Giseop Kwak, Soon Hak Kim, Lee Soon Park & Byeong-Dae Choi (2007): Green Emitting PLED Having Polymeric Host and Dopant in Emissive Layer, Molecular Crystals and Liquid Crystals, 470:1, 329-340

To link to this article: http://dx.doi.org/10.1080/15421400701497647

Mol. Cryst. Liq. Cryst., Vol. 470, pp. 329–340, 2007
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701497647

Green Emitting PLED Having Polymeric Host and Dopant in Emissive Layer

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Poly(1,1′-biphenyl-4,4′-ylene vinylene-alt-*2,5-bis(2-ethylhexyl)-1,4-phenylene vinylene] [poly(BPV*-alt-*BEHPV)] as a polymeric dopant, was synthesized by Honer-Emmons condensation from corresponding dialdehyde and diphosphonate*

This work was supported by the DGIST Basic Research Program of the MOST, and the Regional Innovation Center (ADMRC) Program of the Ministry of Commerce, Industry, and Energy of Korea.

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*monomers. Synthesized alternating polymer was used to fabricate single layer (ITO/Host:Dopant/Al) PLEDs with poly(vinyl carbazole) (PVK) as a host. Conjugated poly(BPV-*alt*-BEHPV) showed green emission from single layer ITO/poly(BPV-*alt*-BEHPV)/Al device. Emission colors from doped PLEDs were changed by energy transfer from blue originated from PVK to green with increasing the content of poly(BPV-*alt*-BEHPV).*

Keywords: energy transfer; polymeric dopant; polymeric host; polymer light emitting diode (PLED)

INTRODUCTION

Organic light emitting diodes (OLEDs) are under active research lately because of their low-operating voltage, low power consumption, the ease of fabrication and low cost. A number of conjugated polymers have been synthesized for use as more efficient emitting materials, since the first report of the polymer light emitting diodes (PLEDs) from poly(*p*-phenylene vinylene) by Cambridge group [1–4]. Conjugated polymers are especially useful in PLEDs since they could be readily incorporated in OLED devices by simple spin-coating or ink-jet printing method. Because of these advantages it is envisaged that PLEDs may provide the platform for the next generation of displays [5].

However, the luminance and color purity are not as high as small molecular OLEDs which have adopted a doping system in emissive layer to increase luminance. Recently, the efforts to enhance quantum efficiency by adopting doping system in PLEDs have been conducted by many researchers [6–9]. In case of OLEDs using low molecular weight emitting materials, each organic layer is generally fabricated by vacuum deposition method. However, this method is cost ineffective and the performance of OLEDs was greatly affected by thermal properties of organic materials and deposition conditions employed.

PLEDs are also considered as the best candidate for the flexible display such as wearable, rollable and paper-like display because of their excellent flexibility. In order to obtain the best flexibility in flexible display, all materials and parts of device should be replaced with organic materials, especially polymeric materials.

In this work, we synthesized a conjugated polymeric dopant, poly(BPV-*alt*-BEHPV), containing both biphenylene and alkoxyphenylene vinylene unit. Doped PLEDs were fabricated with different ratio of poly(BPV-*alt*-BEHPV) to the host polymer (PVK) and evaluated in terms of the energy transfer, color coordinates and luminance.

EXPERIMENTAL

Materials

2-Nitropropane, hydroquinone, 2-ethylhexyl bromide, sodium ethoxide, triethylphosphite, paraformaldehyde, hydrogen bromide (33 wt%) in acetic acid, and potassium *tert*-butoxide were purchased from Aldrich Chemical Co., and used as received. 4,4-Bischloromethylbiphenyl was purchased from Tokyo Chemical Industry Co. Ltd. Solvents such as dimethysulfoxide (DMSO), ethyl alcohol, methyl alcohol, and tetrahydrofurane (THF) were reagent grades and purified prior to use. Indium-tin oxide (ITO) coated glass with a sheet resistance of 30 $\Omega/\square$ was obtained from Samsung Corning Co. Aluminum (99.99%, CERAC, USA) was used to deposit cathode electrode. Poly(vinyl carbazole) (PVK) with $Mn = 48{,}800$ and $Mw/Mn = 1.68$ used as a host material was purchased from Aldrich Chemical Co.

Synthesis of Polymeric Dopant

The synthetic route to the polymeric dopant studied in this work is shown in Figure 1.

4,4′-Biphenyldicarboxaldehyde (BPCA)

The procedures used for the preparation of PHBP were the same as reported [10].

1,4-Diethylhexyloxybenzene (DEHB)

Hydroquinone (3.3 g, 0.02 mol) and 2-ethylhexylbromide (12.68 g, 0.022 mol) were dissolved in 60 mL of methanol, and KOH (3.7 g, 0.024 mol) was added to the solution, and then refluxed for 12 hr. After cooling, the reaction mixture was extracted with ethylether and distilled water several times. DEHB was obtained in 79% yield from column chromatography using n-hexane/ethyl acetate = 9/1 as eluent. ^{1}H-NMR ($CDCl_3$), δ: 6.94 (d, 4H, Ar H), 3.4 (m, 6H, $-CH_2O-$), 2.04 (m, 2H, CH), 1.56–1.27 (m, 8H, $-CH_2-$), 0.88 (m, 2H, CH_3). IR (KBr), cm^{-1}: 3046 (Ar CH), 2928 ($-CH_3$), 1508 (Ar C=C), 1228 (Ar$-$O). Elemental Anal, Calcd. for $C_{22}H_{38}O_2$: C (78.99), H (11.45); Found: C (80.02), H (10.96). Molecular weight, Calcd. for $C_{22}H_{38}O_2$: 334.54, Found: 334.40.

1,4-Bisbromethyl-2,5-bis(2-ethylhexyloxy)benzene (BEHB)

The synthesized DEHB (8.36 g, 0.025 mol) and paraformaldehyde (1.62 g, 0.054 mol) were dissolved in 40 mL of acetic acid, and the 33 wt% of hydrogen bromide (14.58 g, 0.054 mol) in acetic acid was added dropwise. The reaction mixture was heated to 70°C and stirred

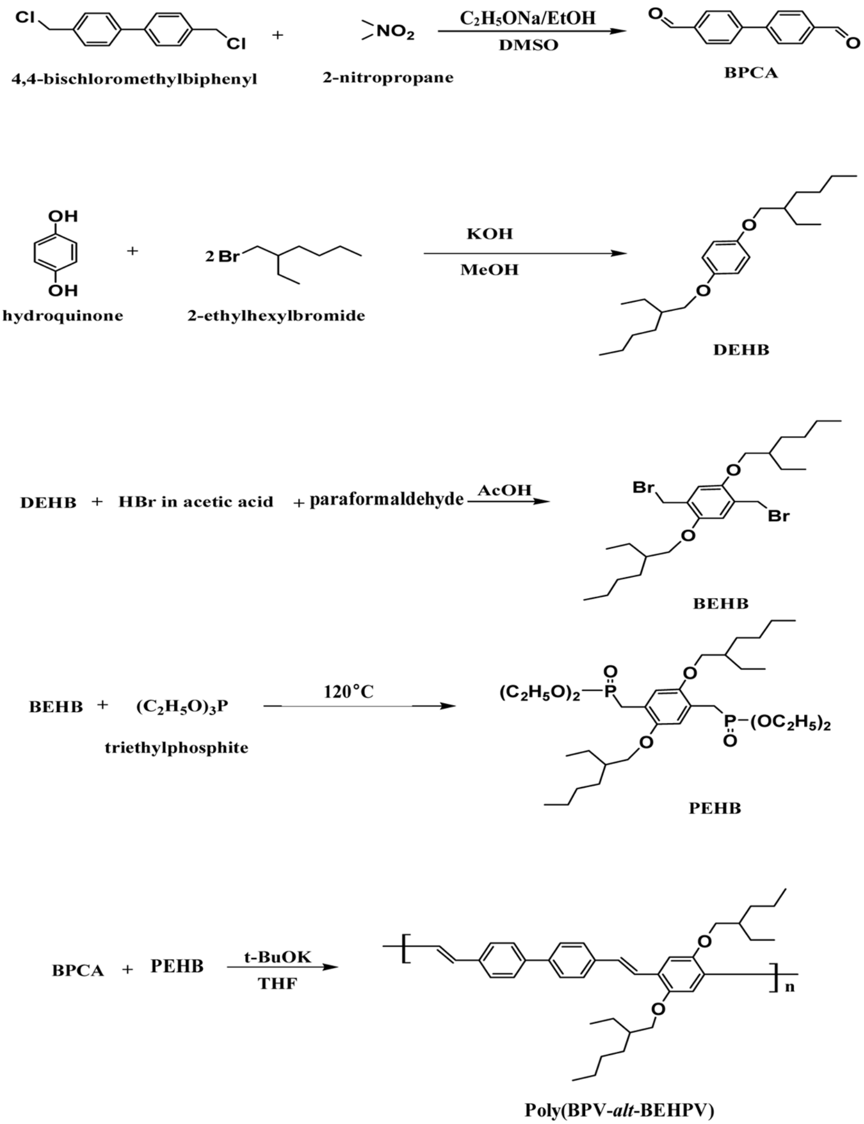

FIGURE 1 Synthetic route to poly(BPV-*alt*-BEHPV).

for 4 hr with N_2 flow. The cooled reaction mixture was treated with aqueous $NaHCO_3$ solution to adjust pH = 7, and extracted with water and chloroform several times. The collected organic layer was concentrated under reduced pressure, and the residue was purified with a silicagel column(n-hexane:ethylacetate = 12:1). After the evaporation of the eluent, BEHB was obtained in 72% yield. ^{1}H-NMR ($CDCl_3$), δ: 6.85 (s, 2H, Ar H), 4.52 (s, 4H, $-CH_2Br$), 3.88 (d, 4H, $-CH_2O-$), 2.17 (s, 2H, CH), 1.53–1.33 (m, 8H, CH_2), 0.91 (m, 2H, CH_3). IR (KBr), cm^{-1}: 3046 (Ar CH, weak signal), 2925 ($-CH_3$), 1508 (Ar C=C), 1227 (CH_2-Br). Br). Elemental Anal. Calcd. for $C_{24}H_{40}O_2$: C (55.39), H (7.75); Found: C (55.52), H (7.54). Molecular weight, Calcd. for $C_{24}H_{40}O_2$: 520.38, Found: 520.50.

1,4-Bis(diethoxyphosphinylmethyl)-2,5-di(ethylhexyloxy)benzene (PEHB)

PEHB was synthesized by the reaction of BEHB (1.6 g, 0.003 mol) with triethyl phosphate (5.46 g, 0.03 mol) at 120°C for 12 hr (Arbuzov reaction) [11,12]. This reaction mixture was cooled at room temperature, and then ethyl ether was added to the solution to precipitate product. After filteration, the filtered cake was recrystallized from mixed solvent of ethanol and ethyl acetate. PEHB was obtained in 90% yield. IR (KBr), cm^{-1}: 2929 ($-CH_3$), 1488 (Ar C=C), 1255 (P=O). Molecular weight, Calcd. for $C_{32}H_{60}O_8P_2$: 634.76, Found: 634.40.

Poly(1,1′-biphenyl-4,4′-ylene vinylene-alt-2,5-bis(2-ethylhexyl)-1,4-phenylene vinylene] [poly(BPV-alt-BEHPV)]

Polymeric dopant, poly(BPV-*alt*-BEHPV), was synthesized by Honer-Emmons condensation [13,14] from corresponding dialdehyde BPCA and diphosphonate PEHB monomers. To a solution of BPCA (1.59 g, 0.0076 mol) and PEHB (4.8 g, 0.0076 mol) in anhydrous THF (50 ml) was added dropwise to a solution of potassium *tert*-butoxide (^{t}BuOK) (4.47 g, 0.38 mol) in dry THF (10 ml) at room temperature under nitrogen atmosphere. After the addition of ^{t}BuOK the solution was stirred for 24 hr to give a polymer product as precipitate. The resulting mixture was poured into n-hexane, and filtered. The filterate was washed with methanol and acetone. After filtration and vacuum drying the poly(BPV-*alt*-BEHPV) was obtained in 75% yield. IR (KBr), cm^{-1}: 3024 (Ar CH), 2922 (aliphatic CH), 1496 (Ar C=C), 1200 (Ar−O).

Fabrication of PLEDs

Doped single layer PLEDs were fabricated using PVK as host and poly(BPV-*alt*-BEHPV) as dopant. Indium-tin oxide (ITO) coated glass with a sheet resistance of 30 Ω/□ was cut into 2.0 × 2.0 cm^2, and electrode area was prepared by photoetching technique. It was sequentially cleaned with acetone, methanol, and mixture of isopropyl alcohol and water (1:1 by vol.) in an ultrasonic bath.

A solution of PVK:poly(BPV-*alt*-BEHPV) in THF after filtration using MFS filter (0.45 μm pore size) was spin-coated on the ultrasonically cleaned ITO glass and dried at 80°C for 1 hr to give an emissive layer with a thickness of about 600–800 Å. After drying the emission layer Al electrode was deposited at a rate of 20 Å/sec by thermal evaporation to give single layer [ITO/PVK:poly(BPV-*alt*-BEHPV) (99:1 ~ 70:30 w:w)/Al] PLEDs. The area of deposited Mg was approximately 0.4 cm^2. For comparison undoped single layer PLEDs such as ITO/PVK/Al and ITO/poly(BPV-*alt*-BEHPV)/Al were also fabricated.

Measurements

The ^{1}H-NMR and FT-IR spectra of synthesized polymeric dopant were taken on a Varian Unity Plus 300 and Jasco FT/IR-620 spectrometer, respectively. UV-visible absorption spectrum of synthesized poly(BPV-*alt*-BEHPV) were obtained by Shimadzu UV-2100. PL spectra were obtained by optical multichannel analyzer (OMA system, laser photonics, USA). Excitation source was He-Cd laser. EL spectra were recorded by Spectroscan PR 704 (Photoresearch Inc.) at 2 nm resolution and color coordinates were determined by the same instrument. Current and luminance vs. voltage profiles were obtained by using a dc power supply connected with Model 8092 A Digital Multimeter (Hyun Chang Product Co. Ltd) and luminance meter (Minolta LS-100) equipped with close-up lens (No. 110, Φ 40.5 mm) at room temperature, respectively.

RESULTS AND DISCUSSION

Synthesis and Characterization of Polymeric Dopant

The polymeric dopant, poly(BPV-*alt*-BEHPV), was synthesized by Honer-Emmons condensation to investigate energy transfer from blue emitting PVK to the dopant. As presented in experimental section, all the intermediates to synthesize poly(BPV-*alt*-BEHPV) were characterized by using ^{1}H-NMR or FT-IR. The out-of-plane bending mode of trans vinylene unit and the C=C stretching mode were appeared in FT-IR spectrum of poly(BPV-*alt*-BEHPV) at about 960 cm^{-1} and 1600 cm^{-1}, respectively. The weight-average molecular weight of the polymeric dopant determined by gel permeation chromatography with THF as an eluent was 42,000 g/mol. TGA result revealed that the synthesized polymeric dopant was stable up to about 370°C under nitrogen. DSC thermogram of the synthesized dopant showed no thermal transition from room temperature up to 300°C.

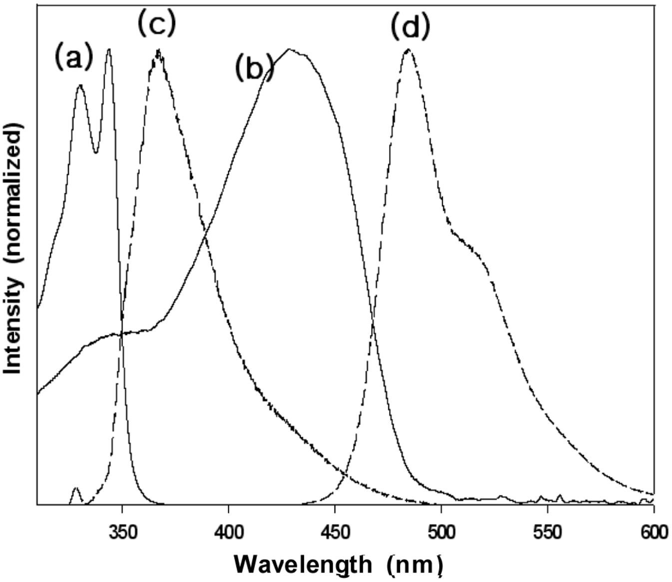

FIGURE 2 UV-visible absorption spectra of (a) PVK and (b) poly(BPV-*alt*-BEHPV), and PL spectra of (c) PVK and (d) poly(BPV-*alt*-BEHPV).

Optical Properties of PVK and Poly(BPV-*alt*-BEHPV)

Energy transfer can be achieved from the excited state of host to that of dopant due to good spectral overlap between the emission of host and the absorption of the dopant [9]. In order to evaluate the possibility of energy transfer from PVK to poly(BPV-*alt*-BEHPV), UV-Visible absorption and PL emission spectra of PVK and poly(BPV-*alt*-BEHPV) were measured, as presented in Figure 2. The absorption maxima ($\lambda_{\mathrm{max,UV}}$) were measured to be 330 and 344 nm for PVK, and 428 nm for poly(BPV-*alt*-BEHPV), respectively. PL maximum ($\lambda_{\mathrm{max,PL}}$) values of PVK and poly(BPV-*alt*-BEHPV) were observed at 367 and 484 nm, when excited at their own $\lambda_{\mathrm{max,UV}}$, respectively. The absorption spectrum of synthesized poly(BPV-*alt*-BEHPV) was ranged from about 250 nm to 510 nm, which was overlapped to a relatively large extent with PL spectrum of PVK. Poly(BPV-*alt*-BEHPV) showed $\lambda_{\mathrm{max,PL}}$ at 484 nm, but PL was not observed when excited at 330 nm, $\lambda_{\mathrm{max,UV}}$ of PVK. These optical properties including Stoke's shifts [15,16] and absorption edges ($\lambda_{\mathrm{edg,UV}}$) corresponding to band gap energies [17] were summarized in Table 1.

PL spectra of PVK/poly(BPV-*alt*-BEHPV) mixtures, excited at 330 nm, were measured as a function of the poly(BPV-*alt*-BEHPV)

TABLE 1 Optical Properties of Polymeric Host and Dopant

Materials	$\lambda_{\mathrm{max,UV}}$ (nm/eV)	$\lambda_{\mathrm{edg,UV}}{}^{a}$ (nm/eV)	$\lambda_{\mathrm{max,PL}}$ (nm/eV)	Stoke's shift^{b} (nm)
PVK	330/3.76, 344/3.60	370/3.35	367/3.38	23
Poly((BPV-*alt*-BEHPV)	428/2.90	510/2.43	484/2.56	56

^{a}onset point of UV-visible absorption spectrum.
$^{b}\lambda_{\mathrm{max,PL}} - \lambda_{\mathrm{max,UV}}$.

content in mixtures (Fig. 3). As the content of poly(BPV-*alt*-BEHPV) dopant was increased in the PVK/poly(BPV-*alt*-BEHPV) mixture solution, the PL intensity of poly(BPV-*alt*-BEHPV) at 484 nm steadily increased while PL intensity of PVK decreased, suggesting energy transfer between poly(BPV-*alt*-BEHPV) dopant and PVK host polymer.

Electro-Optical Properties of PLEDs

Figure 4 shows EL spectra of single layer PLEDs made with PVK/poly(BPV-*alt*-BEHPV) blend. Likewise the PL spectra, PVK emission fraction decreased with increasing poly(BPV-*alt*-BEHPV) content. Although the emission from host PVK was reduced, and emission from

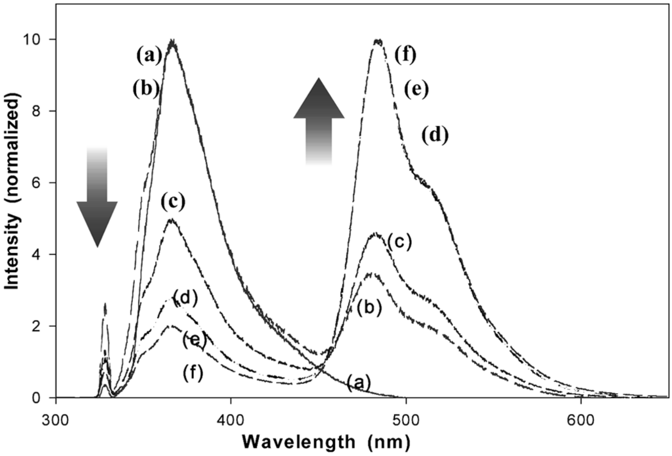

FIGURE 3 PL spectra of (a) 0, (b) 1, (c) 5, (d) 10, (e) 20, and (f) 30 wt% of poly(BPV-*alt*-BEHPV) in PVK: poly(BPV-*alt*-BEHPV) mixture solved in TCE. Zero wt% of poly(BPV-*alt*-BEHPV) means to use only PVK.

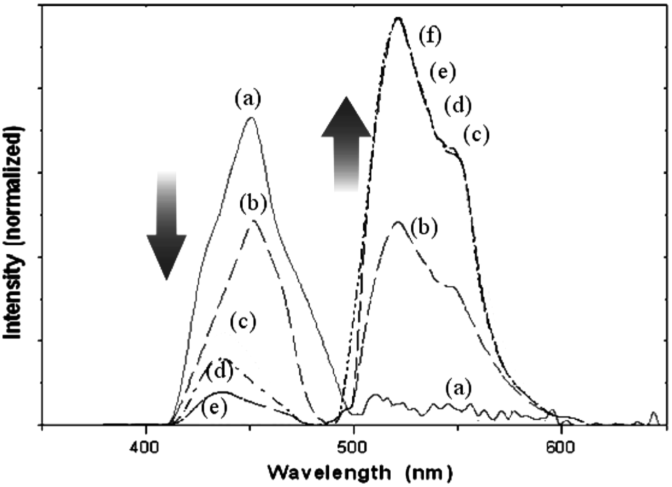

FIGURE 4 EL spectra of PLEDs made with (a) 1, (b) 5, (c) 10, (d) 20, (e) 30 and (f) 100 wt% of poly(BPV-*alt*-BEHPV) in PVK: poly(BPV-*alt*-BEHPV) mixture. One hundred wt% of poly(BPV-*alt*-BEHPV) means to use only poly(BPV-*alt*-BEHPV).

dopant poly(BPV-*alt*-BEHPV) became more dominant with increasing dopant concentration, the emission from PVK still appeared. This result suggests partial energy transfer from PVK to poly(BPV-*alt*-BEHPV).

Color coordinates of single layer PLEDs were compared with those of standard red, green, blue, and white color established by NTSC (national television system committee) [18] in Figure 5. The emission color could be determined from these color coordinates as measured by Spectroscan PR-704 (Photoresearch Inc.) and Kelly's map [19] in CIE (Commission Internationale de l'Eclairage) 1931 chromaticity diagram [20]. The EL light of PVK-based PLED(ITO/PVK/Al) showed blue emission with color coordinates of x = 0.19 and y = 0.19, and the EL colors from PLEDs with 1 and 5 wt% of poly(BPV-*alt*-BEHPV) in PVK/poly(BPV-*alt*-BEHPV) blend were blue (CIE coordinates of x = 0.18 and y = 0.21) and blue green (x = 0.21, 0.33) respectively. In the case of 10, 20 and 30 wt% of poly(BPV-*alt*-BEHPV), the PLEDs showed green emission with CIE color coordinates (x, y) of (0.21, 0.41), (0.21, 0.48) and (0.210.51), respectively. The single layer PLED fabricated with poly(BPV-*alt*-BEHPV) showed also green emission with color coordinates of x = 0.22 and y = 0.58 that was adjacent to the NTSC green.

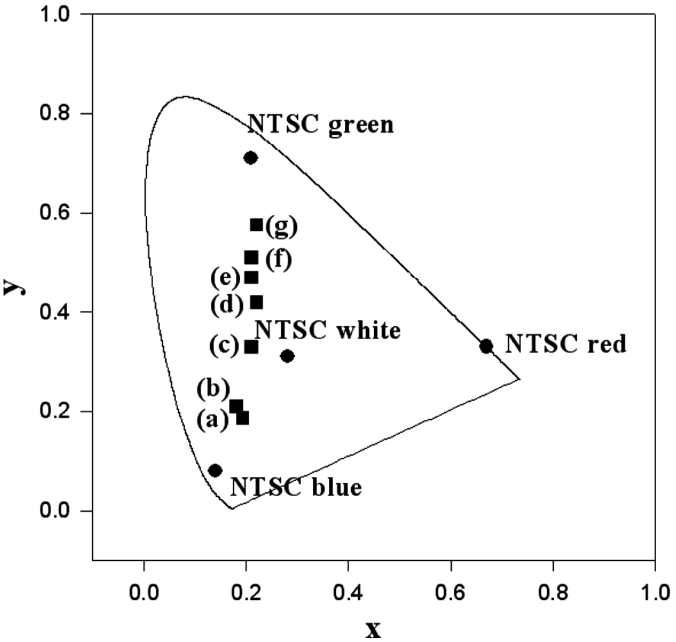

FIGURE 5 CIE 1931 chromaticity diagram showing color coordinates of PLEDs fabricated with (a) 0, (b) 1, (c) 5, (d) 10, (e) 20, (f) 30, and (g) 100 wt% of poly(BPV-*alt*-BEHPV) in PVK: poly(BPV-*alt*-BEHPV) mixture.

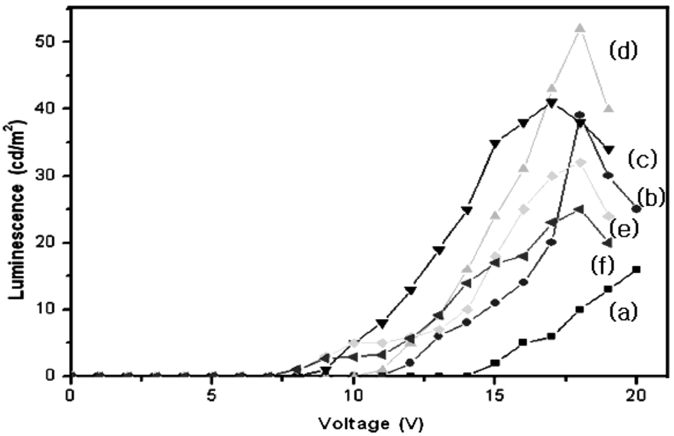

FIGURE 6 Luminance-voltage profiles of PLEDs fabricated with (a) 0, (b) 1, (c) 5, (d) 10, (e) 20, and (f) 100 wt% of poly(BPV-*alt*-BEHPV) in PVK: poly(BPV-*alt*-BEHPV) mixture.

The luminance-voltage profiles are shown in Figure 6. PLED fabricated with PVK as emitting layer showed lower luminance than those of PLEDs made with PVK/poly(BPV-*alt*-BEHPV) blend, due to energy transfer from blue emitting PVK to green emitting poly(BPV-*alt*-BEHPV). The highest luminance was 52 cd/m^2 at 15 V from ITO/PVK: poly(BPV-*alt*-BEHPV) (90:10 w:w)/Al device.

CONCLUSIONS

In summary, green emitting polymer, poly(BPV-*alt*-BEHPV), was synthesized, and used as dopant in PLEDs with PVK as host. The spectral overlap between UV-Visible absorption of dopant and PL emission of host was observed. The existence of energy transfer from PVK to poly(B-*alt*-BEHPV) was identified from the PL spectra of PVK/poly(BPV-*alt*-BEHPV) mixture, and also EL spectra of single layer PLEDs. For example, while undoped ITO/PVK/Al device showed blue emission of high color purity, doped ITO/PVK:poly(BPV-*alt*-BEHPV) (90:10 w:w)/Al Al device exhibited green emission, implying energy transfer from PVK to poly(BPV-*alt*-BEHPV) dopant. However, even the ITO/PVK:poly (BPV-*alt*-BEHPV) (70:30 w:w)/Al device exhibited blue emission originated from PVK. This result indicated that energy transfer from PVK to poly(BPV-*alt*-BEHPV) was incomplete.

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