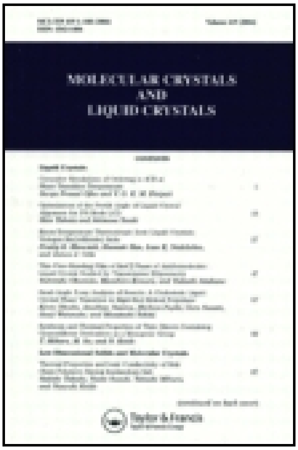

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# ELECTROLUMINESCENCE OF POLYMER BLENDS COMPOSED OF A PVK AND A COPOLYMER CONTAINING SiPh-PPV AND MEH-PPV UNIT

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# ELECTROLUMINESCENCE OF POLYMER BLENDS COMPOSED OF A PVK AND A COPOLYMER CONTAINING SiPh-PPV AND MEH-PPV UNIT

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*We report on the emission characteristics of the polymeric light-emitting diodes (PLEDs) with the blend of a copolymer containing MEH-PPV and SiPh-PPV unit (m-SiPh PPV-co-MEH PPV) and a polyvinylcarbazole (PVK). According to change of their blending ratio, the PLEDs showed the change of electroluminescence(EL) intensity and EL spectrum.*

*The EL characteristics were improved when the PVK was a small quantity. Most effective PLEDs with m-SiPh PPV-co-MEH PPV copolymer-rich blend for EL enhancement was when the blending ratio of m-SiPh PPV-co-MEH PPV : PVK equals to 70:30 by weight ratio. It is thought as the result of the m-SiPh PPV-co-MEH PPV's dilution effect and the role of the PVK with hole transport ability. On the other hand, we have attempted to tune the EL color of the m-SiPh PPV-co-MEH PPV EL cells by the blending with the PVK. According to*

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*increasing of PVK content, the emission peaks of the PLEDs have blue-shifted from red light. White emission which covers the full range of the visible region is realized when the weight ratio of m-SiPh PPV-co-MEH PPV : PVK equals to 4 : 96, which shows the CIE coordinates are $x = 0.3266$ and $y = 0.3438$.*

## 1. INTRODUCTION

Polymeric light-emitting diodes (PLEDs) with conjugated polymers [1–4] have attracted attention as a result of their potential for use in display technology after the report of Tang and Vanslyke [5]. In addition to relatively simple device fabrication and the ability to make such devices on flexible substrates, the color of the emission can be varied by using different conjugated structures and by using copolymers and polymer blends. The conjugated polymers as emitting materials like substituted poly (*p*-phenylenevinylene) or polyfluorine [6] have reached the milestone to fulfill the requirements for most display applications regarding brightness, efficiency and lifetime stability [7]. These materials can be deposited cost-efficiently by spin-coating or using doctor-blade technique.

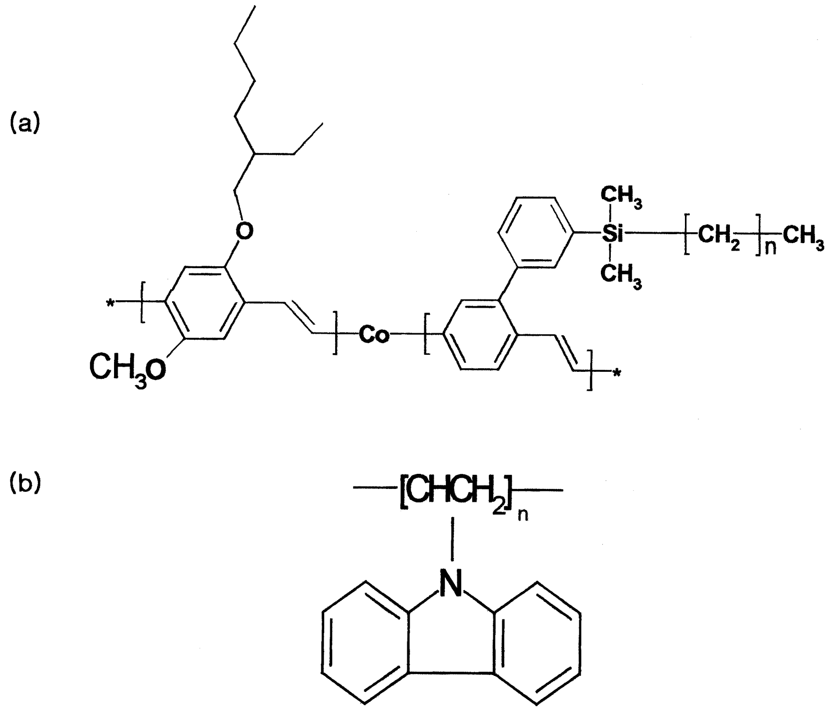
The color of the electroluminescence(EL) emission can be changed by using different main-chain molecular structures or modification of the side-chain structures like as poly(*p*-phenylene vinylene) (PPV) derivatives. EL color can also be tuned by utilizing polymer blends [8].

In this paper, we present the optical and electrical characteristics of PLEDs fabricated using the blends of a copolymer containing MEH-PPV and SiPh-PPV unit(m-SiPh PPV-co-MEH PPV) and a polyvinylcarbazole (PVK). The PVK plays a dual role in polymer blends. That is, the PVK is the hole-transporting matrix and exhibits a light-violet colored EL.

## 2. EXPERIMENTAL

Scheme 1 shows the chemical structures of m-SiPh PPV-co-MEH PPV, PVK and tris(8-hydroxyquinoline aluminum)(Alq3) used in this study. The copolymer, m-SiPh PPV-co-MEH PPV was synthesized [9]. The PVK, Alq3 and PEDOT/PSS were purchased from Aldrich chemical. Co. Inc., TCI Co. LTD and Bayer Co. Inc, respectively.

The configuration of the EL device is indium-thin oxide (ITO)-coated glass as an anode/PEDT:PSS as a buffer layer/blend of m-SiPh PPV-co-MEH PPV and PVK as an active layer/Alq3 as an electron transporting layer/LiF/Al as a cathode. The patterned ITO-coated glass (30 Ω/sq.) was sonicated in a detergent solution followed by a de-ionized water rinse and dipped into acetone, trichloroethylene and isopropyl alcohol in order. After drying, the PEDT was formed on the ITO-coated glass substrate by spin-cast technique.



**SCHEME 1** Molecular structures of (a) m-SiPh PPV-co-MEH PPV and (b) PVK.

The polymer blends were obtained by mixing the m-SiPh PPV-co-MEH PPV and the PVK with the weight ratio of 90:10, 80:20, 70:30 and 50:50, 17:83, 10:90, 4:96, 2:98 in chloroform. We prepared two kinds of blend. One is copolymer-rich blends in which the copolymer and the PVK are in weight ratio 90:10, 80:20, 70:30. And the other is PVK-rich blends which are in weight ratio 50:50, 17:83, 10:90, 4:96, 2:98. The pure m-SiPh PPV-co-MEH PPV, PVK and their blends were spin-coated onto ITO substrates coated with PEDT/PSS. Then Alq3(2 nm), LiF(0.5 nm), and Al(150 nm) were deposited in sequence by vacuum thermal evaporation under a vacuum of about $1 \times 10^{-6}$ torr. The active area of the device was 0.09 $\mathrm{cm}^2$.

The electroluminescence (EL) and photoluminescence (PL) spectra were taken with a monochrometer (PI instrument Spectra-pro 300i). The Commission International De L'Eclairage (CIE) coordinates were measured with Spectroradiometer (Minolta CS-1000). The current-voltage-luminance (I-V-L) characteristics were measured by Keithley 2400 source meter and Newport-1830C optical power meter. The energy levels of the materials were measured from cyclic voltammetry method and UV absorption spectrum.

## 3. RESULTS AND DISCUSSION

The UV absorption spectra of SiPh PPV-co-MEH PPV, PVK and their blend films are shown in Figure 1(a) and (b). Figure 1(a) is UV absorption spectra of the PVK-poor blend films and Figure 1(b) is UV absorption spectra of the PVK-rich blend films.

The maximum absorption peaks of m-SiPh PPV-co-MEH PPV and PVK are at 470 nm and at 340 nm, respectively. According to increase of PVK in blends, it can be seen the intensity of the absorption peaks from the copolymer becomes weak relatively.

PL spectra of pure m-SiPh PPV-co-MEH PPV, pure PVK, and their blend films are presented in Figure 2. Figures 2(a) and 2(b) correspond to the PL spectra of PVK-poor blend films and PVK-rich blend films, respectively. All films in the PL spectra were excited at 325 nm. The maximum peaks of m-SiPh PPV-co-MEH PPV and PVK films are at 586 nm and 420 nm, respectively. When the blend films have relatively small portion of PVK compared to the copolymer, there are no changes in the positions of emission peaks from the copolymer and the PVK, as can be seen in Figure 2(a). With increasing the PVK composition, however, the PL emission spectra originated from the copolymer were remarkably blue-shifted.

In the PLEDs with pure m-SiPh PPV-co-MEH PPV, and with PVK-poor blend as emitting layer, the characteristics of current density *vs.* applying voltage and luminance *vs.* applying voltage were shown in Figure 3(a) and (b), respectively.

In the PLED with pure copolymer, the EL output could be clearly seen at around 10 V in dark room and the maximum brightness of 16000 nW/cm$^2$ could be obtained at 17 V. Further increase in voltage causes rapid

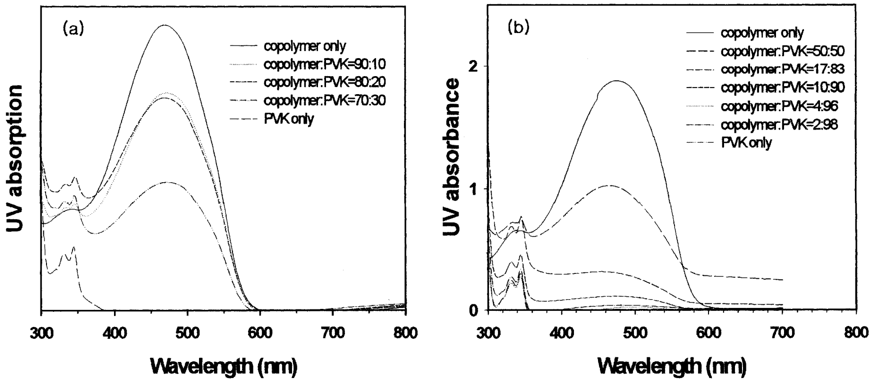


**FIGURE 1** UV-vis absorption spectra of m-SiPh PPV-co-MEH PPV, PVK, and their blend films (a) PVK-poor blends and (b) PVK-rich blends.

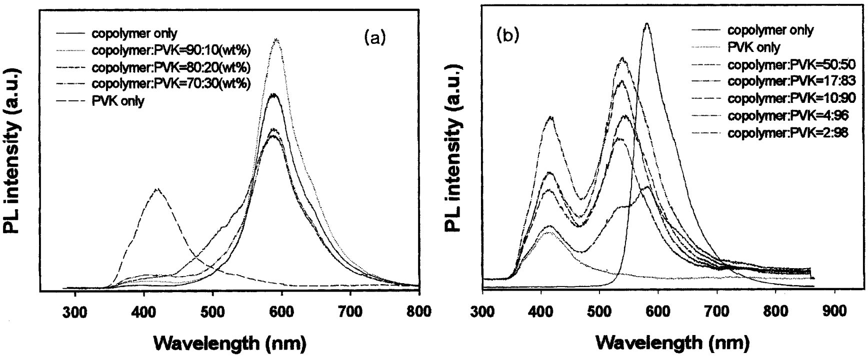


**FIGURE 2** PL spectra of m-SiPh PPV-co-MEH PPV, PVK and their blend films with different weight ratios. (a) PVK poor and (b) PVK rich, (Ex: 325 nm).

degradation of the device. In the case of the PLEDs with PVK-rich blend, however, the turn-on voltage was decreased and the brightness of the emitted light increased with increasing the PVK content. It was seen that the EL device with the composition of m-SiPh PPV-co-MEH PPV:PVK equals to 70:30 (wt%) has best efficiency.

As an another method to improve the EL efficiency, we fabricated the multi-layered EL devices with PEDOT as a buffer layer and Alq3 as an electron transport layer. Figure 4 shows the comparison on voltage-luminance-current density characteristics of the single layered PLED and the multi-layered PLED which structure is ITO/PEDOT/blend of m-SiPh PPV-co-MEH PPV:PVK(70:30)/Alq3/Al. The maximum brightness of the emitted

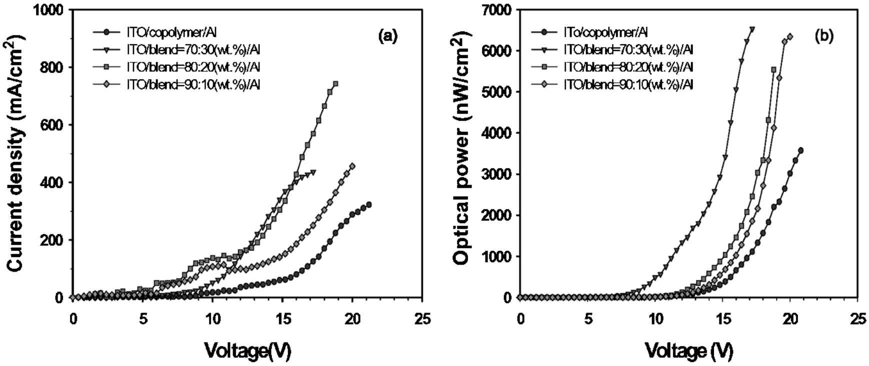


**FIGURE 3** Current density-voltage-luminance characteristic of the PLEDs with PVK-poor blends (a) Current-voltage characteristics (b) Luminance-voltage characteristics.

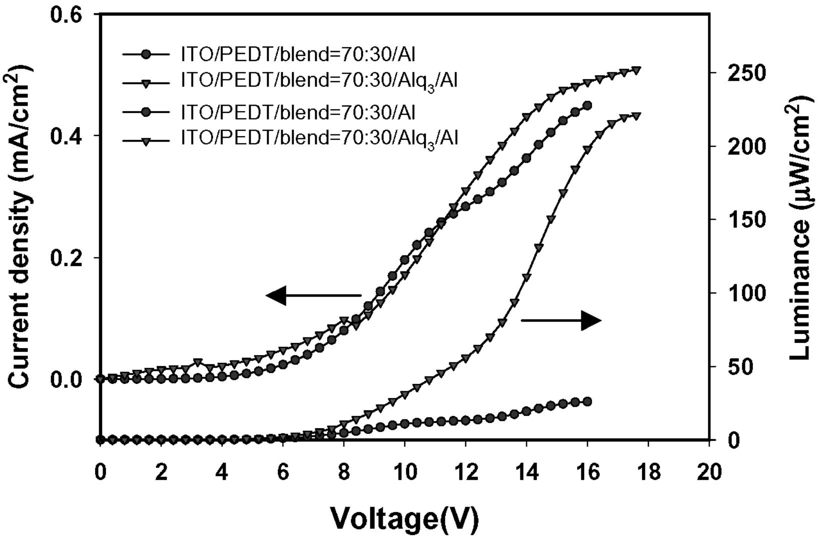


**FIGURE 4** Current density-voltage-luminance characteristic of the single-layered and the multi-layered PLEDs with PVK-poor blend (70:30 wt%).

light from the multi-layered EL device was increased about 10 times compared to the single layered device.

Figure 5 shows the EL spectra of the PLEDs with m-SiPh PPV-co-MEH PPV, blend of m-SiPh PPV-co-MEH PPV:PVK(70:30), and the multi-layer. There are no peaks from the PVK or Alq3, which is thought as the result of dilution effect on the copolymer and the roles of the PVK with hole transport ability and Alq3 with electron transport ability.

The energy levels (HOMO: highest occupied molecular orbital or ionization potential and LUMO: lowest unoccupied molecular orbital) of the materials were measured by cyclic voltammetry method and UV absorption spectra. The band gap of m-SiPh PPV-co-MEH PPV corresponds to absorption edge located at 585 nm (2.12 eV) in Figure 1. HOMO level of m-SiPh PPV-co-MEH PPV was measured to be 5.27 eV and LUMO level was 3.15 eV. Figure 6 shows the schematic model of the energy level of Ip (ionization potential) and Ea (electron affinity).

On the other hand, there were no effects on EL enhancement in the PLEDs with PVK-rich blends which compositions of copolymer : PVK were 50:50, 17:83, 10:90, 4:96, and 2:98 wt.%. Figures 7 (a) and (b) show the characteristics of voltage *vs.* current density and voltage *vs.* luminance of the PLED with PVK-rich blend. Even if the current density of some PLEDs with blend film were increased, the luminance of the PLEDs with blend film drastically decreased.

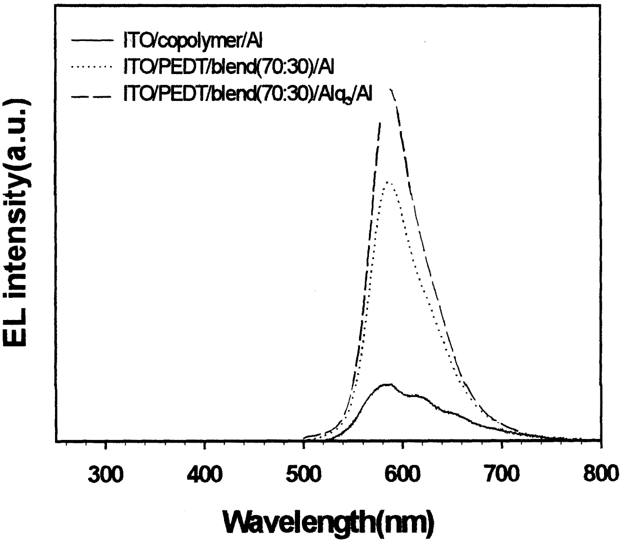


**FIGURE 5** Electroluminescence spectra of the PLEDs with m-SiPh PPV-co-MEH PPV, the single-layered PLED and the multi-layered PLED with PVK-poor blend (70:30 wt.%).

The EL spectra of the PLEDs with PVK-rich blend were shown in (Figure 8.) With increasing the PVK content, the intensity of the peaks at around 420 nm was slightly increased and the emission peak originated from the copolymer was blue-shifted.

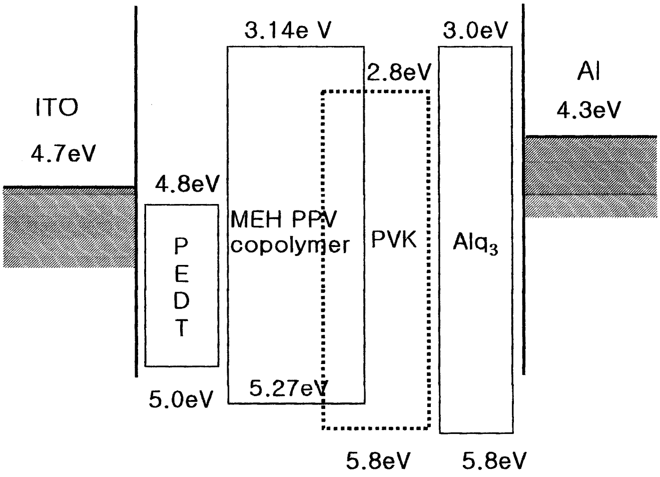


**FIGURE 6** Schematic model of the energy level of Ip and Ea for EL materials.

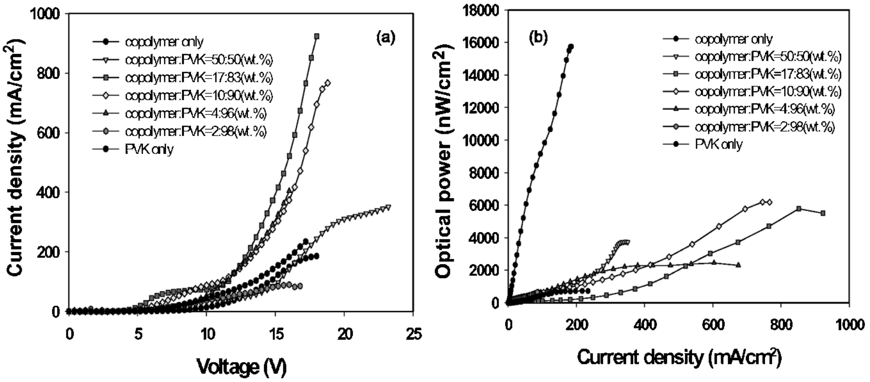


**FIGURE 7** Current density-voltage-luminance characteristic of the EL devices with PVK-rich blends (a) Current-voltage characteristics (b) Luminance-current characteristics

The emitted light from the PLEDs with the pure m-SiPh PPV-co-MEH PPV is orange-red with a maximum intensity at 586 nm. Further, the PLED with the blend containing m-SiPh PPV-co-MEH PPV:PVK = 4:96 wt% yielded an EL spectrum with a white emission which CIE coordinates are x = 0.3266 and y = 0.3438.

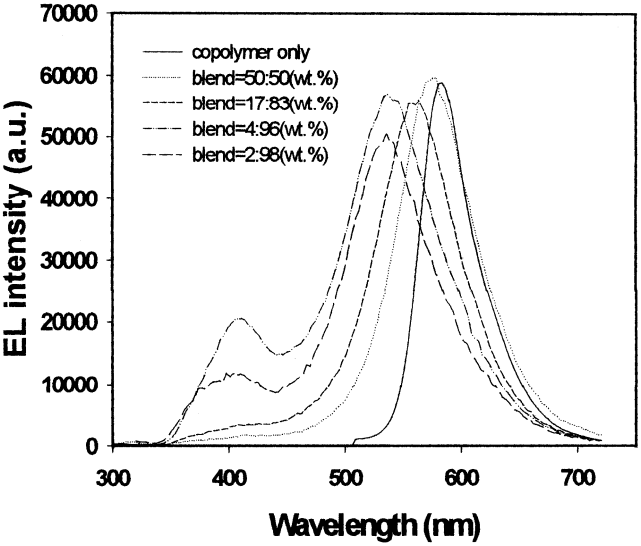


**FIGURE 8** Electroluminescence spectra of m-SiPh PPV-co-MEH PPV, PVK and their blend films with different weight ratios in PVK-rich blend PLEDs.

## 4. CONCLUSION

In this paper, we report on the emission characteristics of the PLEDs with the blend of a copolymer containing MEH-PPV and SiPh-PPV unit (m-SiPh PPV-co-MEH PPV) and a PVK. The EL characteristics were improved when the PVK was a small quantity, which is thought as result of m-SiPh PPV-co-MEH PPV's dilution effect and because of PVK has the hole transport ability. Most suitable blending ratio for EL enhancement was m-SiPh PPV-co-MEH PPV : PVK equals to 70:30 by weight ratio. On the other hand, the emission spectra can be tuned by varying the weight ratio of a blue light emitting PVK and a red light emitting m-SiPh PPV-co-MEH PPV. CIE coordinates changed from blue to red according to the weight ratio of m-SiPh PPV-co-MEH PPV and PVK. White light emission is realized when the m-SiPh PPV-co-MEH PPV:PVK weight ratio equals 1:30. In that condition, CIE coordinates are $x = 0.3266$ and $y = 0.3438$.

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