# Highly Improved Quantum Efficiency in Blend Polymer LEDs

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ABSTRACT: We report on light-emitting diodes (LEDs) made from blend polymers composed of two organic soluble and emittable conducting polymers, poly[2-methoxy-5-(2-ethylhexyloxy-1,4-phenylenevinylene] (MEH-PPV) and poly[1,3-propanedioxy-1,4-phenylene-1,2-ethenylene(2,5-bis(trimethylsilyl)-1,4-phenylene)-1,2-ethenylene-1,4-phenylene] (DSiPV), as the emitting layers. The emitting colors of the blend polymers were yellowish orange, which indicates that the emission is mainly due to MEH-PPV and DSiPV greatly contributes to the enhancement of the luminescence. The efficiencies of the blend polymers increase with decreasing MEH-PPV/DSiPV weight ratio. In blending MEH-PPV with DSiPV, DSiPV is believed to serve as an EL enhancing polymer rather than EL active in our devices. The quantum efficiency is measured as the function of MEH-PPV content in the blend. Especially, the maximum quantum efficiency of MEH-PPV/DSiPV(1/15) blend polymer is about 500 times greater than that of MEH-PPV homopolymer, and the luminance is up to 500 cd/m$^2$ at 30 V with 23.6 mA/cm$^2$ current density.

## Introduction

In recent years, two types of light-emitting diode (LED) have been reported. One type uses thin molecular films of fluorescent molecules as the light-emitting active layer,[1−4] and the other type uses conjugated or nonconjugated polymers (the polymer LEDs).[5−10] The luminescence is obtained by the recombination of electrons injected at the negative electrode and holes injected at the positive electrode in polymer thin films; the holes and electrons recombine in the polymer thin film, forming excited carriers (singlet excitons) which decay radiatively.[11−14] The light-emitting diodes (LEDs) using conjugated or nonconjugated polymers as the active luminescent layer are a promising application for semiconducting polymers. The polymer LEDs have many advantages compared with inorganic LEDs. One of the important advantages over inorganic LEDs lies in the ability to construct polymer LEDs on flexible substrates promising to enable the fabrication of displays in a variety of unusual shapes. Other advantages include the ability to provide colors which span the visible spectrum by altering the $\pi-\pi^*$ energy gap through controlled change of molecular structure. The quantum efficiency, however, is more or less low compared with that of inorganic LEDs; therefore, the research of this field is still the focus of many scientists. To increase the quantum efficiency of the polymer LEDs, Heeger et al. utilized the high work function polymer (polyaniline) as a hole injection electrode[15] and the low work function metal (Ca) as an electron injection electrode,[16] giving highly improved efficiency of the polymer LEDs. Also the multilayer structure is used to increase the quantum efficiency of the polymer LEDs. The electron-transporting layers are placed between the luminescent layer and the negative electrode, which enhanced electroluminescent efficiency through charge carrier confinement.[17,18] Other efforts are performed on blending electron- or hole-transporting molecules with luminescent polymers. The efficiencies of these blend polymers are also improved owing to a decrease in the energy barriers between the electrodes and the luminescent polymers.[19−23] In the research of new materials for polymer LEDs, we have investigated a novel polymer blend as the emitting layer; the blend is composed of an organic soluble, confined conjugated polymer, poly[1,3-propanedioxy-1,4-phenylene-1,2-ethenylene-(2,5-bis(trimethylsilyl)-1,4-phenylene)-1,2-ethenylene-1,4-phenylene] (DSiPV), and a fully conjugated poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV). The initial devices utilized aluminum as an electron-injection electrode and indium/tin oxide (ITO) as a hole-injection electrode. We present and discuss the results of optical measurements and electroluminescent behavior of the device characteristics. The synthetic route and polymer structures are shown in Schemes 1 and 2.

## Experimental Section

**Instrumentation.** The synthesized compounds were identified by $^1$H-NMR spectra that were obtained by using a Bruker AM 200 spectrometer. The elemental analyses were performed by the Analytical Department of the Korea Research Institute of Chemical Technology. The UV−visible spectra of the MEH-PPV, DSiPV, and blend polymers were measured by using a Shimadzu UV-3100S. The photoluminescence spectra of the blend polymers were obtained by using a Perkin-Elmer LS-50 luminescence spectrometer. The electroluminescence (EL) spectra were measured by using a dual-grating monochromator (Spex 270M) with the photomultiplier tube (Hammamatzu R955) as a detector. The EL spectra were recorded at 3-nm resolution by computer through the photon counter (SR400) averaging the signal from PMT while applying direct current from the current/voltage source (Keithley 238). For the measurement of device properties, current−voltage ($I-V$) and light intensity−current ($L-I$) characteristics were measured by using the current/voltage source and the optical powermeter (Newport 835). The injected current was measured by the voltage supply while applying forward bias. And the emitted light was collected with a Si photodetector (Newport 818SL) placed in front of the device and recorded by computer. All the measurements mentioned above were performed in air and at room temperature.

**Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV).** The MEH-PPV was synthesized by the

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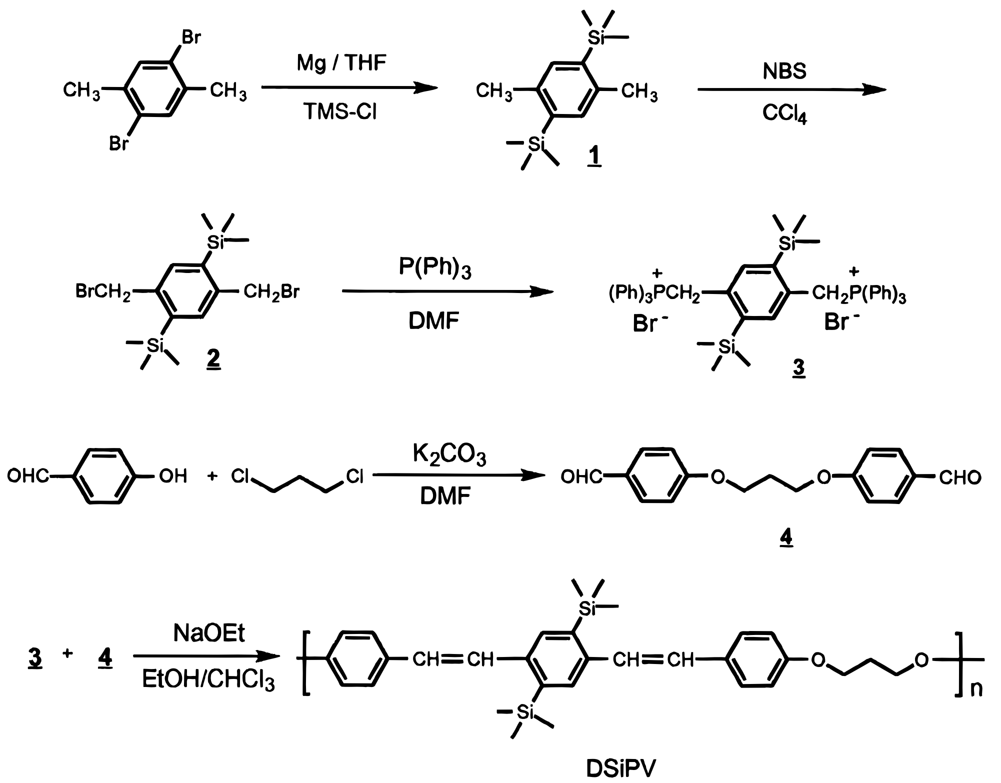
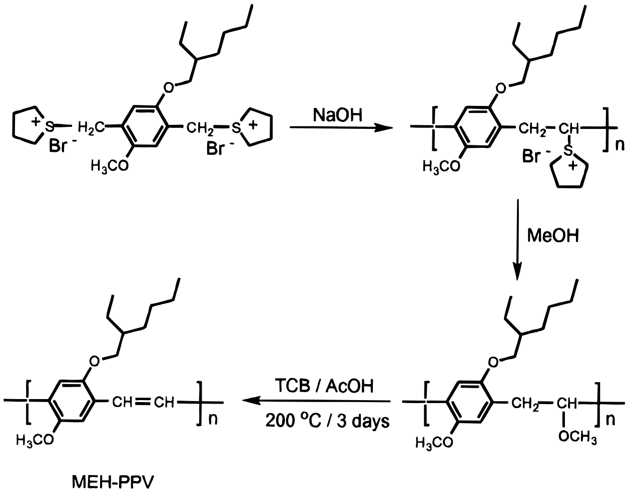
Scheme 1



Scheme 2



method of Wudl et al.[24] The final polymer was soluble in common organic solvents.

**Poly[1,3-propanedioxy-1,4-phenylene-1,2-ethenylene-(2,5-bis(trimethylsilyl)-1,4-phenylene)-1,2-ethenylene-1,4-phenylene] (DSiPV).** The DSiPV polymer was synthesized by the following procedures.[25]

**2,5-Bis(trimethylsilyl)-*p*-xylene (1).** A solution of 4.61 g (190.0 mmol) of magnesium in 5 mL of tetrahydrofuran was stirred and heated to 70 °C and then was added 0.3 mL (5 mol %) of dibromoethane. When the reaction mixture was initiated, 20 g (76.0 mmol) of 2,5-dibromo-1,4-xylene dissolving in 50 mL of tetrahydrofuran was added to the reaction mixture. After 3 h, 19.0 g (174.0 mmol) of chlorotrimethylsilane was added to the reaction mixture and heated to reflux for 10 h. The resulting mixture was extracted with dichloromethane/water and then precipitated from methanol. The product yield was 14.1 g (74%); mp 56−57 °C: $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.23 (s, 2 H), 2.41 (s, 6 H), 0.31 (s, 18 H). $^{13}$C NMR ($CDCl_3$) $\delta$ 139.50, 139.14, 135.57, 22.55, −0.16. Anal. Calcd: C, 67.07; H, 7.98. Found: C, 66.53; H, 7.83.

**2,5-Bis(trimethylsilyl)-1,4-bis(bromomethyl)benzene (2).** Compound **2** was prepared by reacting 5.0 g (20.0 mmol) of compound **1** with 7.1 g (40.0 mmol) of *N*-bromosuccinimide (NBS) in 40 mL of carbon tetrachloride A small amount of benzoyl peroxide was added as an initiator. The reaction mixture was refluxed at 90 °C for 3 h under a nitrogen atmosphere. The completion of the reaction was indicated by the appearance of succinimide on the surface of the reaction solution. A yellow-colored solution was obtained after filtration of succinimide. The solution was concentrated and precipitated from methanol. The product yield was 5.1 g (62%); mp 96−97 °C: $^1$H NMR ($CDCl_3$) $\delta$ 7.53 (s, 2 H), 4.61 (s, 4 H), 0.40 (s, 18 H). $^{13}$C NMR $\delta$ 142.12, 140.89, 137.40, 34.08, 0.28. Anal. Calcd: C, 41.18; H, 5.92. Found: C, 40.91; H, 5.73.

**2,5-Bis(trimethylsilyl)-1,4-xylenebis(triphenylphosphonium bromide) (3).** A solution of 7.4 g (7.4 mmol) of 2,5-bis(trimethylsilyl)-1,4-bis(bromomethyl)benzene and 4.3 g (16.3 mmol) of triphenylphosphine in 30 mL of DMF was stirred and heated to reflux for 24 h. The resulting mixture was poured into diethyl ether. After filtration and vacuum drying, the monomer **3** was obtained as a white powder. The product yield was 6.1 g (89%); mp 299−300 °C (dec): $^1$H NMR (DMSO-$d_6$) $\delta$ 7.94−7.55 (m, 30 H), 7.05 (s, 2 H), 5.01 (d, 4 H), −0.31 (s, 18 H). Anal. Calcd: C, 64.35; H, 5.79. Found: C, 64.02; H, 6.04.

**1,3-Bis(4-formylphenoxy)propane (4).** To synthesize the monomer **4**, 1,3-bis(4-formylphenoxy)propane, a solution of 10 g (81.9 mmol) of 4-hydroxybenzaldehyde, 8.3 g (41.0 mmol) of 1,3-dibromopropane, and 6.2 g (45.1 mmol) of potassium carbonate in 100 mL of DMF was stirred and refluxed for 24 h. The resulting mixture was poured into cold water. The precipitate was collected and dried in a vacuum desiccator. The pure white solid product was obtained by recrystallizing from ethanol. The product yield was 8.8 g (76%); mp 129−130 °C: $^1$H NMR (200 MHz, $CDCl_3$) d 7.91 (s, 2 H), 7.79 (d, 4 H), 6.83 (d, 4 H), 4.22 (t, 4 H), 2.30 (q, 2 H). $^{13}$C NMR ($CDCl_3$) d 190.71, 163.73, 131.92, 130.01, 114.64, 64.45, 28.82. Anal. Calcd: C, 71.82; H, 5.67. Found: C, 71.43; H, 5.60.

**Polymerization.** A solution of 0.3 g of sodium ethoxide in 10 mL of anhydrous ethanol was added to a stirred solution of 0.5 g (1.6 mmol) of the dialdehyde monomer **4** and 1.4 g (1.6 mmol) of 2,5-bis(trimethylsilyl)-1,4-xylenebis(triphenylphos-

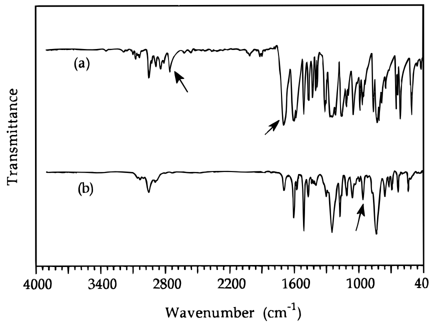


**Figure 1.** FT-IR spectra of (a) monomer **4** and (b) DSiPV polymer.

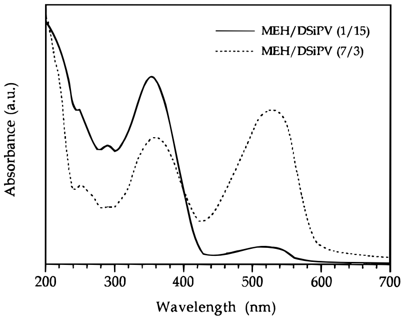


**Figure 2.** Absorption spectra of MEH-PPV/DSiPV(1/15) and MEH-PPV/DSiPV(7/3) blend polymers.

phonium bromide) (**3**) in a mixed solvent of 10 mL of ethanol and 10 mL of chloroform at room temperature. Soon, a yellow-green precipitate was formed and the mixture was stirred for 10 h after the addition. The reaction mixture was extracted with dichloromethane and water. After drying and removing the solvent, crude polymer product was obtained. Then, the product was redissolved in dichloromethane and precipitated in methanol. After filtration and vacuum drying, a yellow-green DSiPV was obtained. The product yield was 0.5 g (14.3%): $M_n$, 2100; $M_w$, 7200.

**Blend Polymers.** Our synthesized MEH-PPV and DSiPV are soluble in common organic solvents such as dichloroethane, THF, xylene, and so on. The MEH-PPV and DSiPV polymer were mixed by changing the weight ratios of the two polymers in dichlororthane. The MEH-PPV content of the blend polymers could be varied over the full range from 100 to 6% (by weight). The films of the blend polymers could be spin-cast from dichloroethane solution with excellent reproducibility. AFM (atomic force microscopy) and SEM images showed no indication of phase separation or layer formation due to the immiscibility of two polymers. The LED structures consist of an aluminum rectifying contact on the blend polymers which have been spin-cast onto ITO glass as a hole-injecting contact. The film thickness ranged from 60 to 80 nm. The electron-injecting aluminum contacts were deposited by vacuum evaporation at pressure below $10^{-6}$ Torr, giving active areas of 0.195 cm$^2$.

## Results and Discussion

Figure 1 shows the FT-IR spectra of the dialdehyde monomer **4** and the polymer film of DSiPV. In Figure 1a, the dialdehyde monomer **4** shows a strong absorption peak of the aldehyde carbonyl group at 1701 cm$^{-1}$ and also the characteristic absorption peak of aldehydic hydrogen at 2730 cm$^{-1}$. But in Figure 1b, these absorption peaks drastically decreased after polymerization; at the same time, a weak but sharp absorption peak at 960 cm$^{-1}$ corresponding to the out-of-plane bending mode of the *trans*-vinylene groups appeared, suggesting that the generated double bonds are mainly trans configuration.

The optical absorption spectra of the blend polymers are shown in Figure 2. The $\pi-\pi^*$ transition peaks of DSiPV and MEH-PPV appear at about 340 and 520 nm, respectively. The absorption intensities are varied by changing weight ratios of the two polymers. The absorption maximum of DSiPV-rich blend polymer, MEH-PPV/DSiPV (1/15), was blue shifted by 10 nm, the blue shift of the blend polymer probably resulting from the change in chain conformation.[26] This result cuold affect the photoluminescence and electroluminescence.

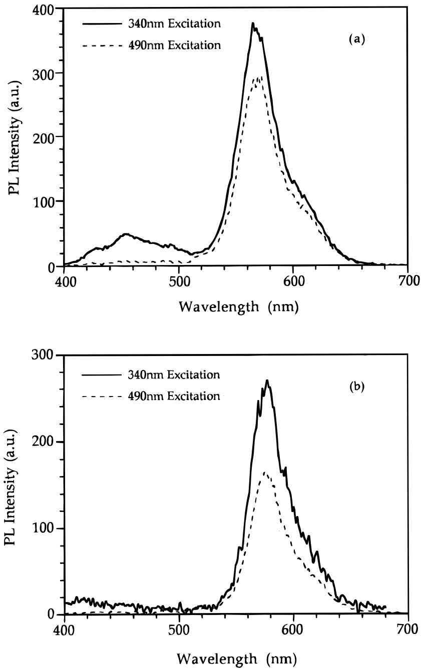


**Figure 3.** Photoluminescence spectra of the blend polymers (a) MEH-PPV/DSiPV(1/15) and (b) MEH-PPV/DSiPV(7/3).

The photoluminescence (PL) spectra of the blend polymers are shown in Figure 3. For PL spectra, the blend polymers were excited at 340 and 490 nm, which are in the ranges of the optical absorption maxima for DSiPV and MEH-PPV, respectively. Interestingly, when the blend polymers are excited at 340 nm, both MEH-PPV/DSiPV(1/15) and MEH-PPV/DSiPV(7/3) exhibited very strong emission at about 570 and 580 nm, respectively. The emission of the DSiPV-rich blend polymer, MEH-PPV/DSiPV(1/15), was blue shifted by 10 nm. This result was consistent with absorption spectra. The blend polymer containing a large amount of DSiPV, MEH-PPV/DSiPV(1/15), showed a very weak emission at 450 nm (Figure 3a), and MEH-PPV/DSiPV(7/3) blend polymer which contains much more MEH-PPV exhibited no emission at around 450 nm (Figure 3b). Regardless of the composition of blend polymers, they showed strong emission maxima at around 570–580 nm and the emission of DSiPV was not found. From these results, we can guess that the energy transfer occurred from DSiPV to MEH-PPV polymer. This fact is very interesting in an electroluminescence (EL) study. More detailed experiments were investigated, using temperature-dependent and time-resolved photoluminescence.

The EL spectra of blend polymers are shown in Figure 4. The emission peak of MEH-PPV occurs at around 600 nm, which is in good agreement with other reported results,[6] and those of the blend polymers ranged from 560 to 580 nm as the blend ratios are changed. The EL spectra of the blend polymers are very similar to their PL counterparts. The energy transfer also exists at the DSiPV and MEH-PPV interface; therefore, all blend polymers exhibit similar emission maxima. The EL emission peaks of the blend polymers are blue shifted by 20–40 nm with respect to MEH-PPV homopolymer. The blue shifts of the blend polymers should result from the change in chain conformation[26] like the optical absorption spectra as shown in Figure 2.

The forward bias current was obtained when ITO is a positive electrode and the Al electrode is the grounded. Figure 5 shows the voltage vs current characteristics measured from MEH-PPV and the blend polymers. The forward current increases with increasing forward bias voltage for all devices.

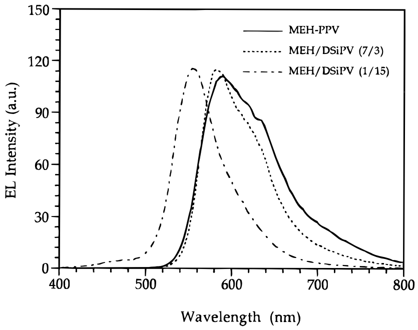


**Figure 4.** Electroluminescence spectra of the MEH-PPV and the blend polymers.

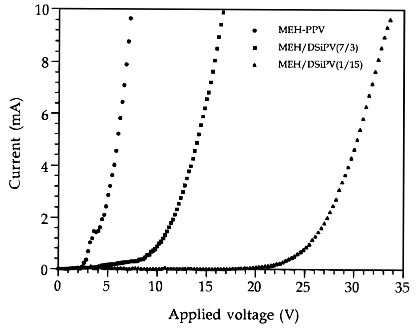


**Figure 5.** Voltage−current characteristics of the MEH-PPV, MEH-PPV/DSiPV(7/3), and MEH-PPV/DSiPV(1/15).

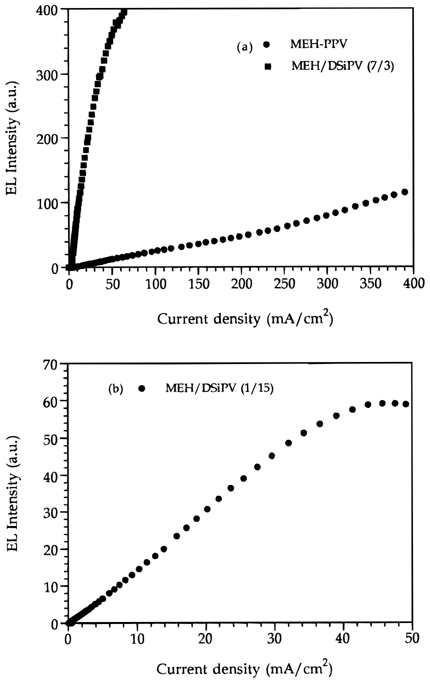


**Figure 6.** Current density−intensity characteristics of (a) MEH-PPV and MEH-PPV/DSiPV(7/3) and (b) MEH-PPV/DSiPV(1/15).

The turn-on voltages of the blend polymer devices increase as the composition of DSiPV increases. Parts a and b of Figure 6 show the emission intensity dependence on current density from MEH-PPV, MEH-PPV/DSiPV(7/3), and MEH-PPV/DSiPV(1/15) polymer devices, respectively. The light emission became visible at a bias of just under 5 mA/cm$^2$ for a typical blend polymer device, MEH-PPV/DSiPV(1/15), and 100 mA/cm$^2$ for a MEH-PPV device. The bright yellowish-red light from the device of the MEH-PPV/DSiPV(1/15) is visible at above 30 V in the normal room light of the laboratory (Figure 5). The light intensities of the blend polymers are much stronger than that of MEH-PPV.

**Table 1. Relative Quantum Efficiencies of MEH-PPV and Blend Polymers**

| polymer(wt/wt) | rel efficiency |
|---|---|
| MEH | 1 |
| MEH/DSiPV(9/1) | 2 |
| MEH/DSiPV(7/3) | 11 |
| MEH/DSiPV(3/7) | 19 |
| MEH/DSiPV(1/15) | 484 |
| MEH/PMMA(1/9) | 7.5 |
| DSiPV | 44 |

The relative quantum efficiencies of the MEH-PPV and blend polymer devices are listed in Table 1. The relative quantum efficiencies of blend polymers increase with increasing DSiPV content. Surprisingly, the efficiency of this blend polymer is about 500 times higher than that of MEH-PPV. From these results, we can deduce that the energy transfer from DSiPV to MEH-PPV also exists in the EL device; therefore, the blend polymer devices emit yellowish-red lights at about the 560−580-nm wavelength region and their efficiencies are also dramatically improved. The improvement in quantum efficiencies of the blend polymers compared with MEH-PPV may be explained by the following factors. First, the excited DSiPV polymers transfer their energies to MEH-PPV, thereby enhancing the luminescent intensity of the blend polymers. The relative EL intensities were dramatically increased from MEH-PPV to blend polymers in our EL measurement. In these results, we could propose that the excitons were generated from DSiPV transfer to MEH-PPV and thus there is an increase in concentration of excitons which enhance the EL intensity of blend polymer. Second, the dilution effect influences the efficiencies of blend polymer devices. As the EL active MEH-PPV is diluted by DSiPV, the intermolecular nonradiative decay is diminished by blocking of the charge carriers. Therefore, the luminescent intensity is increased by increasing the DSiPV portion in the blend polymer. The dilution effect is proved by blending MEH-PPV with EL inactive poly(methyl metacylate), PMMA (Table 1). In this case, the quantum efficiency of the blend polymer is also increased about 8 times compared to than that of MEH-PPV. In these results, we propose that the DSiPV acts as an EL enhancing polymer rather than an EL active polymer in our devices. More detailed experiments on the polymer−polymer interface and microdomain structure of blend polymers are necessary for understanding the results of these blend polymer LEDs.

## Conclusion

The improvement of quantum efficiency of the devices made by blending MEH-PPV with DSiPV is demonstrated above. The efficiency is dramatically increased in the MEH-PPV/DSiPV(1/15) blend polymer, which may be due to the energy transfer from DSiPV to MEH-PPV and the dilution of the EL active MEH-PPV lumophore by DSiPV. The quantum efficiency of the MEH-PPV/DSiPV(1/15) blend polymer is about 500 times larger than that of the MEH-PPV homopolymer in our EL measuring system.

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## References and Notes

(1) Frederiksen, P.; Bjornholm, T.; Madsen, H. G.; Bechgard, K. *J. Mater. Chem.* **1994**, *4* (5), 675.
(2) Tang, C. W.; Vanslyke, S. A. *Appl. Phys. Lett.* **1987**, *5*, 913.
(3) Adachi, C.; Saito, S. *Appl. Phys. Lett.* **1990**, *56*, 799.
(4) Dodabalapur, A.; Rothberg, L. J.; Miller, T. M. *Electron. Lett.* **1994**, *30* (12), 1000.
(5) Burroughs, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

(6) Braun, D.; Heeger, A. J. *Appl. Phys. Lett.* **1991**, *58*, 1982.
(7) Burn, D.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, *47*, 356.
(8) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477.
(9) Yang, Z.; Karasz, F. E.; Geise, H. J. *Macromolecules* **1993**, *26*, 6570.
(10) Yan, M.; Rothberg, L. J.; Papadimitrakopoulos, M. E.; Galvin, M. E.; Miller, T. M. *Phys. Rev. Lett.* **1994**, *73* (5), 744.
(11) Yan, M.; Rothberg, L.; Hsieh, B. R.; Alfano, R. R. *Phys. Rev. B* **1994**, *49* (14), 9419.
(12) Bassler, H.; Gailberger, M.; Mahrt, R. F.; Oberski, J. M.; Weiser, G. *Synth. Met.* **1992**, *49*−*50*, 341.
(13) Dudis, D. S. *Synth. Met.* **1992**, *49*−*50*, 353.
(14) Chandross, M.; Mazumdar, S.; Jeglinski, S.; Wei, X.; Vardeny, V.; Kwock, E. W.; Miller, T. M. *Phys. Rev. Commun.* **1994**, *50* (19), 14702.
(15) Yang, Y.; Heefer, A. J. *Appl. Phys. Lett.* **1994**, *64* (10), 1245.
(16) Parker, I. D. *J. Appl. Phys.* **1994**, *75* (3), 1656.
(17) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628.
(18) Brown, A. R.; Bradley, D. D. C.; Burroughes, J. H.; Friend, R. H.; Greenham, N. C.; Burn, P. L.; Holmes, A. B.; Kraft, A. *Appl. Phys. Lett.* **1992**, *61* (23), 2793.
(19) Aratani, S.; Zhang, C.; Pakbaz, K.; Hoger, S.; Wudl, F.; Heeger, A. J. *J. Electron. Mater.* **1993**, *22* (7), 745.
(20) Zhang, C.; Hoger, S.; Pakbaz, K.; Wudl, F.; Heeger, A. J. *J. Electron. Mater.* **1994**, *23* (5), 453.
(21) Hu, Z.; Yang, Y.; Karasz, F. E. *J. Appl. Phys.* **1993**, *72* (4), 2419.
(22) Zhang, C.; Seggern, H. V.; Pakbaz, K.; Kraabel, B.; Schmidt, H. W.; Heeger, A. J. *Synth. Met.* **1994**, *62*, 35.
(23) Parker, I. D.; Pei, Q. *Appl. Phys. Lett.* **1994**, *65* (10), 1272.
(24) Wudl, F.; Allemand, D. M.; Srdanov, G.; Ni, Z.; Mcbranch *Materials for Nonlinear Optics*; ACS Symposium Series 455; American Chemical Society: Washington, DC; Chapter 46; p 683.
(25) Zyung, T. H.; Hwang, D. H.; Kang, I. N.; Shim, H. K.; Hwang, W. Y.; Kim, J. J. *Chem. Mater.* **1995**, *7* (8), 1449.
(26) Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* **1987**, *20*, 212.

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