

PII: S0038–1098(97)00138-5

## LIGHT-EMITTING DIODE BASED ON OLIGO-PHENYLENE VINYLENE AND BUTYL-PBD BLENDS

Jae-Gyoung Lee,<sup>a</sup> Byoungchoo Park,<sup>a</sup> Hyung-Suk Woo,<sup>a</sup> Youngkyoo Kim,<sup>b</sup> Chang-Sik Ha,<sup>b</sup> Choong-Man Lee,<sup>c</sup>  
Kwangho Jeong,<sup>c</sup> Jeong-Hyon Ha<sup>d</sup> and Yong-Rok Kim<sup>d</sup><sup>a</sup>Electronic Materials Lab., Institute for Advanced Engineering, Yongin P.O. Box 25, Kyonggi-Do, Korea<sup>b</sup>Dept. of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea<sup>c</sup>Dept. of Physics, Yonsei University, Seoul 120-749, Korea<sup>d</sup>Dept. of Chemistry, Yonsei University, Seoul 120-749, Korea

(Received and accepted 10 March 1997 by Z.Z. Gan)

We have fabricated light-emitting diodes (LEDs) using organic materials; a polymer blend dispersing oligo-phenylene vinylene (oligo-PV), 1,4-disubstituted benzene and 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (butyl-PBD) as emissive materials into a soluble polyimide mixed with polyaniline (PANI) of emeraldine salt used as a hole transport material. These polymer dispersed materials were sandwiched between In and indium-tin-oxide (ITO) electrodes. In order to increase the electron injection into the emissive material, we have inserted a thin Mg layer between In and polymer blends. The electroluminescence (EL) spectra of LEDs showed noticeable enhancement of the oscillator strength of oligo-PV peak at 2.76 eV. This implies improved quantum efficiency of this blue light-emitting diode, resulting from the excitonic migration from butyl-PBD to oligo-PV. We have found that the EL device with host polymers, polyimide and PANI, displayed increasing device performance, lowering the turning point in  $I$ - $V$  characteristics, compared to that of LED without PANI. Under normal illumination conditions, our devices with PANI showed visible blue-violet color at room temperature after applying a bias exceeding 8 V. © 1997 Elsevier Science Ltd

Keywords: A. organic LEDs, B. PANI, C. electroluminescence, D. quantum efficiency.

Organic materials have attracted in recent years much interest, both basic and applied point of view, extending the possibility of applications to many electronic and opto-electronic devices including light-emitting diodes (LEDs). Since the discovery of electroluminescence (EL) in poly(para phenylene vinylene) (PPV), conjugated polymers have been used as the active emissive layer in devices [1–4]. Light emission is thought to arise from the singlet polaronic exciton resulting from the recombination of negative polaron ( $P^-$ ) and positive polaron ( $P^+$ ), generated from electron and hole injected within emissive layer. The efficiencies of EL device can be improved by the use of good materials (e.g. conjugated polymers, semi-conjugated oligomers [5] and organic dyes [6, 7], etc.), variation of the metal contacts [8, 9]

and the use of good structures (e.g. multistructure [10], heterostructure, etc.). Many efforts to synthesize  $\pi$ -conjugated polymers with different energy gap, their derivatives and copolymers containing several segments have been performed. Recently, organic blends dispersed polymer matrix have acted to focus attention on the color tuning and improvement of efficiency by selecting the component organic dyes and controlling the amounts of organic dyes in blends. As specified, in organic thin film EL device emission occurs by way of the following processes: (a) double charge carrier injection from anode and cathode electrodes into organic layers, (b) charge carrier transport crossing organic layers, (c) recombination of transported charge carriers and creation of singlet polaronic excitons, (d) migration of singlet

polaronic excitons and (e) radiative decay of polaronic excitons. Processes (a), (b), (c) and (d) involve the efficiency of production of singlet polaronic excitons, which is the one of the major factors that control total quantum efficiency of EL. We focus our attention on these processes in this paper. First, in order to improve quantum efficiency of this blue light-emitting diode, we will attempt to blend two organic materials dispersed polymer matrix, as a kind of soluble polyimide and obtain EL spectra resulting from the excitonic migration from one organic material (butyl-PBD) to the other (oligo-PV). Second, as expected, it will be seen that the EL device with PANI in host polymers displayed increasing of device performance compared to that of LED without PANI [11, 12].

We used organic materials; a polymer blend dispersing oligo-phenylene vinylene (oligo-PV), 1,4-distyrylbenzene and 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (butyl-PBD) as emissive materials. The mixing ratio of these organic light-emitting dyes is 1 : 1 by weight. These materials are dispersed into a soluble polyimide, poly(ether imide) (PEI), mixed with polyaniline (PANI) of emeraldine salt used as a charge transport material. The mixing ratio of PEI and PANI is 2 : 1 by weight. Figure 1 shows the molecular structures of oligo-PV (a), butyl-PBD (b), PEI (c) and PANI of

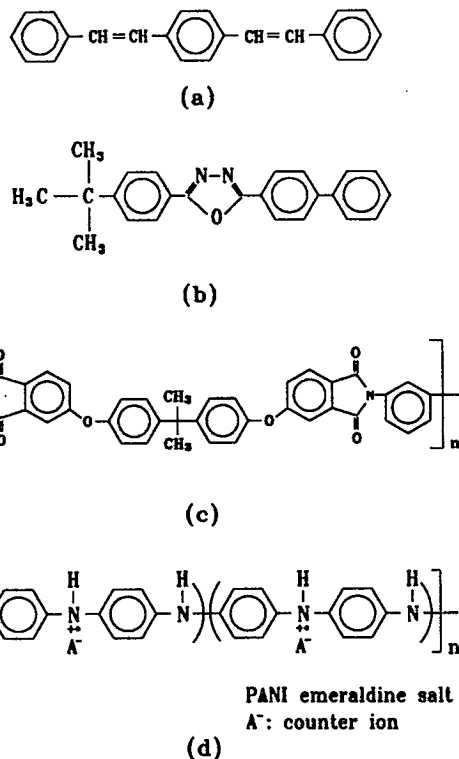
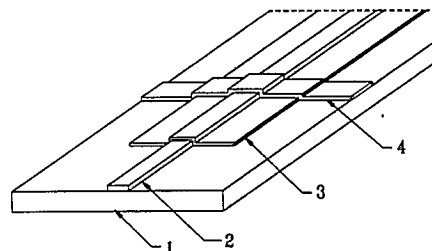


Fig. 1. Molecular structures of oligo-PV (a), butyl-PBD (b), PEI (c) and PANI (emeraldine salt form) (d).



1	- Glass
2	- Anode part indium-tin-oxide (ITO)
3	- emissive layer (spin or vacuum evaporation) (polymer dispersed matrix form)
4	- Cathode part Mg & In

Fig. 2. Structure of LEDs.

emeraldine salt form (d). These polymer dispersed materials were spin coated on to the indium-tin-oxide (ITO) glass substrate from a chloroform solution with 1 : 2 mixing ratio, by weight, of emissive dyes (guest materials) and polymers (host materials). The film thickness of emissive layer was about 2000 Å after 20 min of spinning at 2000 r.p.m. With the following process we thermally evaporated magnesium (Mg) and indium (In), one by one, in vacuum state of  $5 \times 10^{-6}$  torr. Therefore, these polymer dispersed layer was sandwiched between In and ITO electrodes. In order to increase the electron injection into the emissive materials, we have inserted a thin Mg layer between In and polymer blends. This structure is shown in Fig. 2. We investigated *I-V*

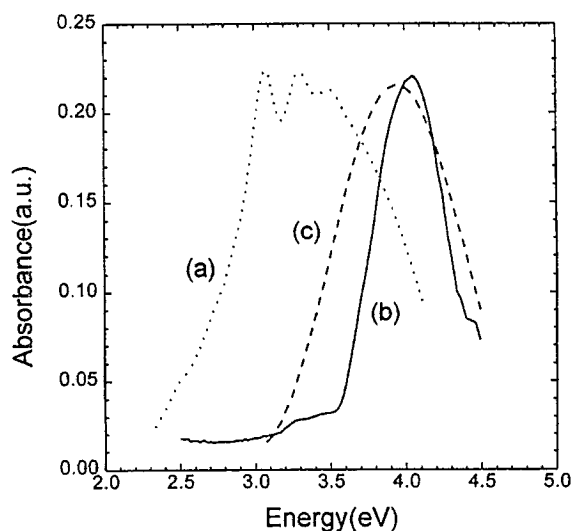


Fig. 3. Absorption spectra of oligo-PV (a), butyl-PBD (b) and blended form (c).

characteristics of LEDs with source-measure unit (SMU) (Keithley 237). Optical properties – absorbance, photoluminescence (PL) and electroluminescence (EL) – of LEDs were measured by UV spectrometer (Hewlett-Packard 8452A) and luminescent spectrometer (Perkin-Elmer LS50B).

In order to determine the exciting source which generate the PL of oligo-PV, butyl-PBD and blended form, we investigated absorption spectra using the UV spectrometer. Figure 3 shows the absorption spectra of oligo-PV (a), butyl-PBD (b) and blended form (c). As shown in Fig. 3, these materials have the peak positions of absorption spectra at 3.08 eV, 3.98 eV and 4.02 eV, respectively. The measurements of PL spectra of each sample were followed using the measured exciting source with a energy of maximum peak intensity. Figure 4 shows that the PL spectra of oligo-PV (a), butyl-PBD (b) and blended form (c) have peaks at 2.62 eV, 3.02 eV and 2.77 eV, respectively. The PL spectra of blended form showed noticeable enhancement of the oscillator strength of oligo-PV peak at 2.76 eV. This implies improved quantum efficiency of PL, resulting from the excitonic migration from butyl-PBD to oligo-PV.

After measured the absorption and PL data, we have fabricated LEDs using these materials. Figure 5 shows the  $I$ - $V$  characteristics of the devices for both cases, with (a) and without (b) using PANI for supplement of hole and increment of electrical conductivity at emissive layer. As shown in Fig. 5, it can be seen that the EL device with PANI in host polymers displayed increasing of device performance, lowering the turning point in  $I$ - $V$  characteristics, compared to that of LED without PANI. In the normal illumination condition, our devices

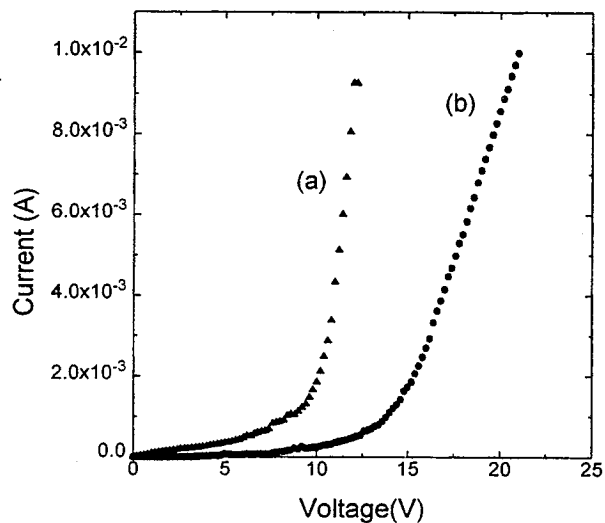


Fig. 5.  $I$ - $V$  characteristic curves with (a) and without (b) using PANI.

with PANI showed visible blue-violet color at room temperature after applying a bias exceeding 8 V. Figure 6 represents PL (a) and EL (b) spectra of polymer blend dispersing oligo-PV and butyl-PBD with PANI. The EL spectra of blended form showed noticeable enhancement of the oscillator strength of oligo-PV peak at 2.77 eV (high energy part), with applied voltage of 10 V. As for the case of PL, this implies improved quantum efficiency of EL, resulting from the excitonic migration as mentioned before. We have found, however, that the main peak positions of EL spectra were unchanged irrelevantly with PANI. It can be viewed, as we expected, that the PANI can act as a hole transport material and helps the electrical conductivity in emissive material without any contribution of excitonic migration. We

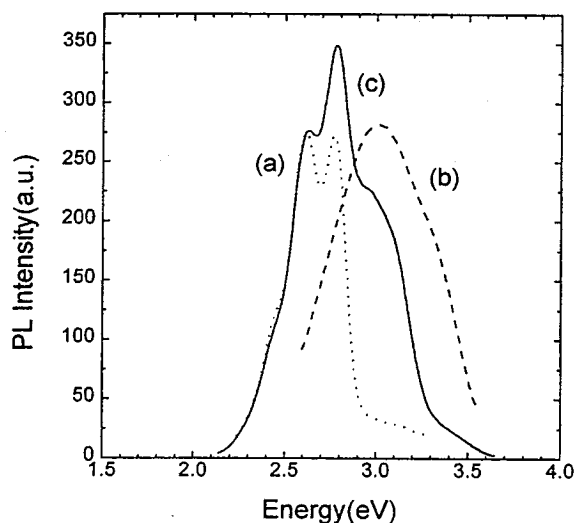


Fig. 4. Photoluminescent spectra of oligo-PV (a), butyl-PBD (b) and blended form (c).

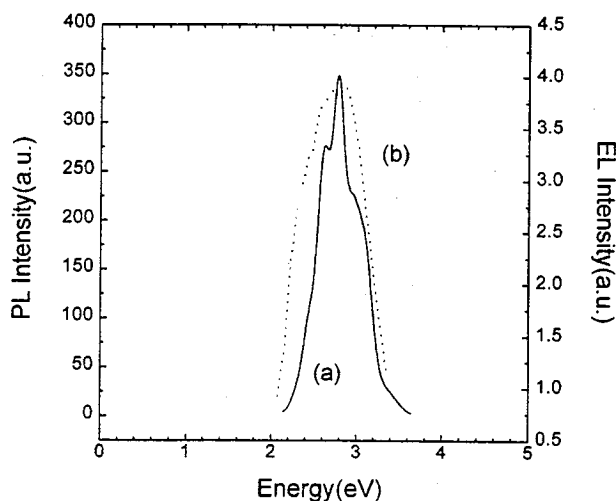


Fig. 6. Comparison of PL (a) and EL (b) spectra.

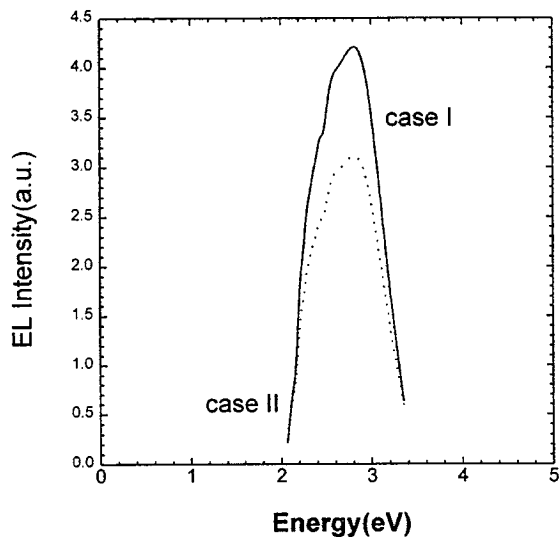


Fig. 7. EL spectra of blended structure (case I) and double-layered structure (case II).

have seen, after comparing the PL and EL spectra, that the spectral line broadening is more dominant in EL. We propose this phenomenon as a result of larger scattering of injected charges at the interface between metal electrode and emissive layer compared to the relatively smaller scattering effect of photons in bulk system.

In order to explain the excitonic migration effect occurring more seriously in blended system, as we believed, we compared the electroluminescence (EL) of blended structure (butyl-PBD + oligo-PV) to that of double-layered structure (butyl-PBD/oligo-PV). Figure 7 shows that the oscillator strength of EL in blended case (I) is larger than that in double-layered case (II), which implies that the excitonic migration effect in blended system occur more seriously than that in double-layered system due to larger collision area. As shown in Fig. 8, we have found that the change of oscillator strength of EL spectra as function of applied voltage was in excellent agreement with the curvature of  $I-V$  characteristics. This implies that the energy loss in this device, due to improper ohmic contact between emissive layer and electrodes, was minimized within operating voltage range.

Using PANI in the host polymeric material helps to increase the device efficiency due to its hole transporting property and to lower the operating voltage because of high conductivity. Blended system can increase the efficiency of LED as well due to the migration of excitations, singlet polaronic excitons in this case. We have seen, after comparing the PL and EL spectra, that the spectral line broadening is more dominant in EL. We propose that this phenomenon is a result of larger scattering of injected charges with phonons in emissive layer of LED compared to the relatively smaller

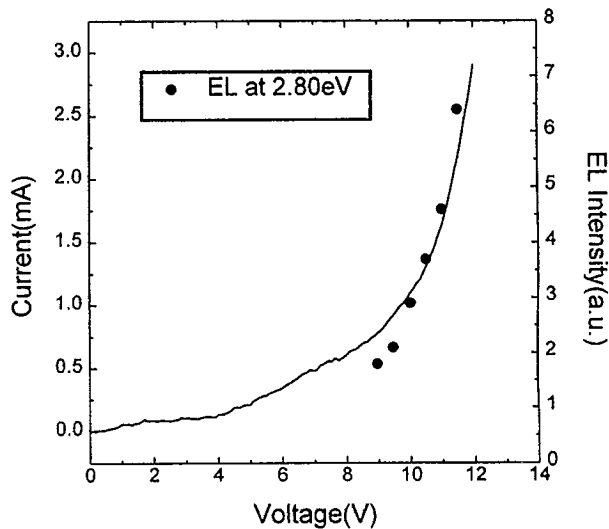


Fig. 8. Comparison of  $I-V$  characteristic curve and EL intensity for applied voltage.

scattering effect of photons in the bulk system. Further study of electronic structures at interfaces between organic thin films and metal electrodes is needed.

*Acknowledgements*—We would like to thank Y.Y. Jung, J.Y. Bae and D.K. Choi for their contributions to this work.

#### REFERENCES

1. Hamaguchi, M. and Yoshino, K., *Jpn. J. Appl. Phys.*, **34**, 1995, L712.
2. Peng, J., Yu, B.Y., Pyun, C.H., Kim, C.H., Kim, K.Y. and Jin, J.I., *Jpn. J. Appl. Phys.*, **35**, 1996, L317.
3. Hamaguchi, M. and Yoshino, K., *Appl. Phys. Lett.*, **69**, 1996, 143.
4. Moratti, S.C., Cervini, R., Holmes, A.B., Baigent, D.R., Friend, R.H., Greenham, N.C., Gruner, J. and Hamer, P.J., *Synth. Met.*, **71**, 1995, 2117.
5. Woo, H.S., Lee, J.G., Min, H.K., Oh, E.J., Park, S.J., Lee, K.W., Lee, J.H., Cho, S.H., Kim, T.W. and Park, C.H., *Synth. Met.*, **71**, 1995, 2173.
6. Aminaka, E.I., Tsutsui, T. and Saito, S., *Jpn. J. Appl. Phys.*, **33**, 1994, 1061.
7. Kido, J., Ikeda, W., Kimura, M. and Nagai, K., *Jpn. J. Appl. Phys.*, **35**, 1996, L394.
8. Jung, D.R., Czanderna, A.W. and Herdt, G.C., *J. Vac. Sci. Technol.*, **A14**, 1996, 1779.
9. Ulman, A., *Chem. Rev.*, **96**, 1996, 1533.
10. Mori, T., Obata, K. and Mizutani, T., *Jpn. J. Appl. Phys.*, **35**, 1996, L849.
11. Park, Y.J., Lee, J.G., Hwang, H.K., Kim, H.S., Park, B., Woo, H.S., Kim, T.W., Min, H.K. and Oh, E.J., *Mol. Cryst. Liq. Cryst.*, **280**, 1996, 385.
12. Wang, H.L., MacDiarmid, A.G., Wang, Y.Z., Gebler, D.D. and Epstein, A.J., *Synth. Met.*, **7**, 1996, 33.