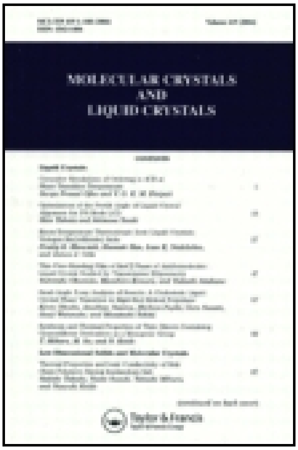

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Electroluminescent Behaviour in Multilayer Structure Device Using Poly(P-Phenylenevinylene) Derivative

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ELECTROLUMINESCENT BEHAVIOUR IN MULTILAYER STRUCTURE DEVICE USING POLY(P-PHENYLENEVINYLENE) DERIVATIVE

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Abstract We observe a new electroluminescent(EL) peak from a two-layer polymer device, which does not appear in EL spectra of each layer. The polymers of both layers are poly(p-phenylenevinylene) derivative with monoalkoxy substituents, poly(2-methoxy-1,4-phenylene-vinylene, abbreviated as PMPV derivatives), but dialyzed for different periods respectively. A new peak is located at 590 nm and has comparable intensity. The origin of this peak is attributed to the emissive transition at the interface between two emitting layers, which is supported by the transient EL experiment. The multilayer device showed typical diode characteristics and large enhancement of quantum efficiency.

INTRODUCTION

Researches on EL from organic polymers have been expanded rapidly[1-6], since the polymer EL devices have the large potential for information displays and light emitting diodes. Several advantages of the polymer EL devices are wavelength controllability, large area processibility, and high luminous efficiency. Recently, utilization of the low work function metals for cathode improved the quantum efficiency remarkably[7,8], so that the future of polymeric EL device becomes more promising.

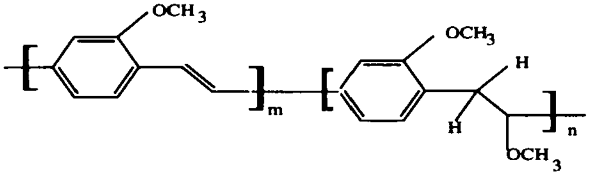
One of the strengths of organic EL devices is the controllability of emission color. EL color from organic semiconducting polymers can be easily tuned by modifying the chemical structure of polymers. For example, poly(p-phenylenevinylene) gives green color[1], poly(p-phenylene) for blue color[3] and the red color can be obtained using polythiophene[4]. One way of color tuning is to change the substituents attached to main chain. Introduction of the substituents leads to change of energy gap between the highest occupied molecular orbital (HOMO) energy level and the lowest occupied molecular orbital (LUMO) energy level resulting in change of emission color. Color can be also tuned by controlling the conjugation length of main chain[9-11], and dispersing the various fluorescent dyes in polymer matrix[12].

Multilayer structure EL devices have been studied mostly to improve the device efficiency[13-15]. A hole or electron transport layer is introduced between the electrodes and the light-emitting layer to balance the carrier injection from the electrodes resulting in the enhancement of device efficiency. In some of the multilayer structure devices, mixed colors emitted from more than one layer were observed[16]. Broad range of emission color can also be obtained by dispersing several dyes in conducting or nonconducting polymer matrices[12].

In this paper, we report the observation of a new EL peak from the two-layer structure consisting of PMPV derivatives for the first tme to our knowledge. Both polymer layers were synthesized with the same starting materials via the same route, but dialyzed for different periods. The new EL peak is not present in the EL spectra of each polymer layer and the origin of this peak is discussed.

EXPERIMENTAL

The chemical structure of PMPV derivative used in this study is shown below. The precursor polymers of PMPV derivatives were synthesized[17] and was dialyzed in cosolvent of methanol/water (9/1) for two different periods, one for short period (one week) and another for much longer period (one month). Hereafter, the former is called material A and the latter material B, respectively. It is expected that the larger amount of nonconjugated part in main chain is formed during the longer period of dialysis. The PMPV derivatives thin films were obtained by elimination reaction of the organic soluble precursor polymers. For the fabrication of an EL device, material B was spin coated at 5000 rpm on a glass substrate with transparent electrode and heated in vacuum for elimination reaction at 200 °C for several hours. After then, material A was spin-coated at the same revolution speed and also treated for the same thermal process. Finally, aluminum was deposited by thermal evaporation at about 10^{-6} torr for the cathode. The aluminum electrode has a diameter of 5 mm. The schematic diagram of the multilayer electroluminescence device and the details of optical and electrical measurements were described previously[18].



RESULTS AND DISCUSSION

EL spectra of the material A and the material B are shown in Fig. 1. The peak wavelength of the material B is blue shifted by about 20 nm from that of the material A located at about 560 nm. This blue shift is also observed in absorption and photoluminescence(PL) spectra (Fig. 2). The absorption edges are shifted from about 540 nm for material A to about 520 nm for material B. The peak wavelengths of PL spectra of both samples were observed to be almost the same as those of the corresponding EL peaks. The blue shift may be due to the shortening of conjugation length during long dialysis. Longer dialysis will increase the methoxylation of the sulfonium group of the precursor polymer resulting in shortening the conjugated part.

EL spectrum of the multilayered ITO/B/A/Al structure device shows a peak at 550 nm and an additional peak at 590 nm with comparable intensity as shown in Fig. 3 which also includes the PL spectrum of the same device. PL spectrum exhibits a strong peak at 550 nm and a very weak shoulder at 590 nm. The appearance of the peak at 590 nm in EL spectra may be due to the new optical transition between the levels at the interface of two polymer layers, or due to a new compound formed at the interface by interaction between two polymer layers. However, no additional peaks corresponding to a new compound were observed in the absorption spectrum. The absorption maximum of the overcoated device is located between those of the materials A and B. If there is a compound corresponding to the peak of 590 nm, there must be an additional peak at longer wavelength or a red shift of absorption maximum of overcoated sample in the absorption spectrum. Furthermore, the EL and PL spectra of the multilayer device of ITO/A/B/Al do not show this additional peak. Therefore, the possibility of the formation of a new compound was excluded and the peak at 590 nm may be attributed to the new optical transition at the interface.

The I - V of the double layer device showed the rectification and the threshold voltage was about the 10 V which is little bit larger than those of the material A or the material B (Fig. 4). Based on the I - V characteristics of the single layer device of each polymer, we obtained the band offsets using Fowler-Nordheim plot and featured the energy band diagram as shown in Fig. 5. According to Fig. 5, HOMO and LUMO levels of the material A are lower than those of the material B. Since HOMO level of the material A is lower than that of the material B, holes injected into the material B move toward the cathode and are blocked at the interface between the materials A and B by the energy barrier in the HOMO level. On the similar manner, electrons injected into the material A will be blocked by the material B. The blocked electrons and holes at the interface make the radiative recombination across the interface be possible. The peak at 590 nm

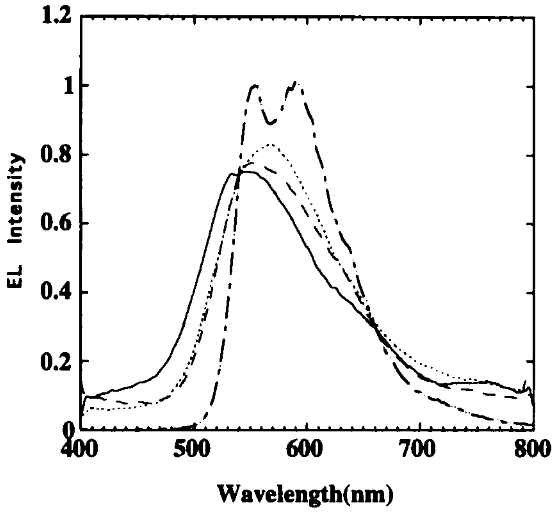


FIGURE 1 Electroluminescence of multi- and single- layered PMPV devices

—— ITO/B/Al ······ ITO/A/Al – – ITO/A/B/Al — - ITO/B/A/Al

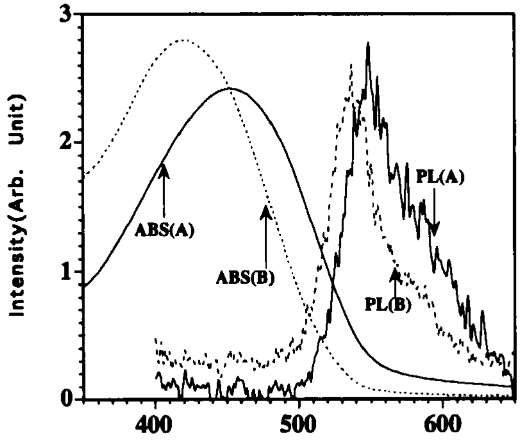


FIGURE 2 Absorption and photoluminescence spectra of PMPV derivative polymers

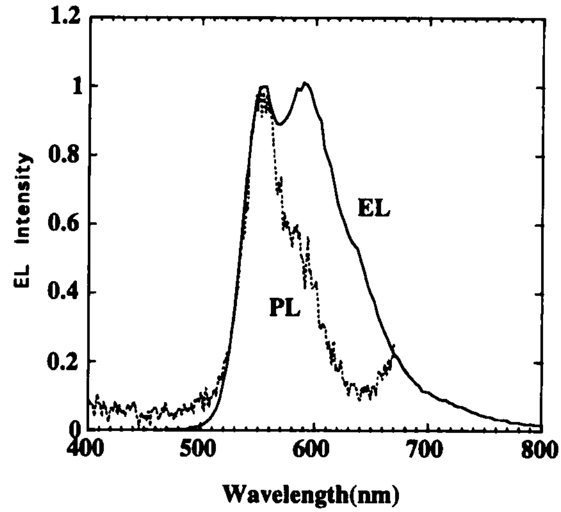


FIGURE 3 Comparison of electroluminescence and photoluminescence of ITO/B/A/Al device

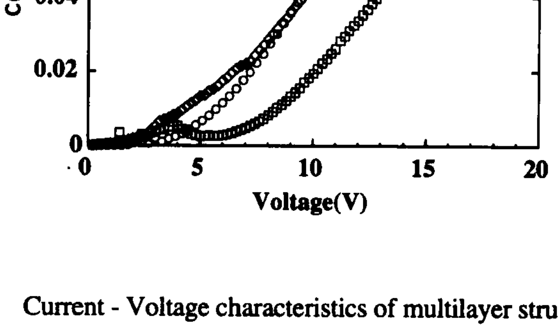


FIGURE 4 Current - Voltage characteristics of multilayer structure devices

○ ITO/A/Al, ▢ ITO/B/A/Al, ◇ ITO/B/Al

corresponds to the optical transition taking place between HOMO level of material B and LUMO level of material A across the interface, indeed. The fact that no observation of the additional peak at 590 nm for the device of ITO/A/B/Al and the enhancement of the quantum efficiency for ITO/B/A/Al device (Fig. 6) supports our deduction of the origin of the new EL peak based on the energy band alignment. The optical transition at the interface between two emissible layers was also observed in a polythiophene multilayer device[19].

Quantum efficiency of the ITO/B/A/Al device was remarkably enhanced than the single layer device of ITO/A/Al, as shown in Fig. 6. Because of the hole blocking at the interface and the lowering of electron injection barrier from the cathode, more balanced charge injection into the emissive layer is expected resulting in higher quantum efficiency. This behaviour is consistent with the energy band diagram in Fig. 5. The dependence of emission light intensity of the double layer device on the injection current shows linear increase at initial stage with injection current tending to slight saturation at high injection current (Fig. 6). The slight saturation of the emission intensity may be due to the increase in nonradiative recombination[20].

Possibility of a new optical transition is clearly supported when we see the transient EL behaviour. Transient EL signals were obtained by applying 3 μs electrical square pulses with 6V at the repetition rate of 100 KHz. The device itself shows 1 nF at 20 KHz with 50 Ω. Therefore, the RC time constant of the device is negligible in our measurement. Fig. 7 shows the temporal behaviour of two multilayer devices, in which the rise time of the device ITO/B/A/Al is longer than that of the device ITO/A/B/Al by about 500 ns. The rise times are taken from the period between 10% and 90% of the signal. Rise time of the EL signal is related to the injected carrier transit time[21].

Lengthening of the rise time can be explained with the energy band diagram shown in Fig. 5. In the device ITO/A/B/Al, once holes are injected, the holes move to the cathode and recombine with the injected electrons near the cathode since there are no barriers against movement of the injected holes to the cathode as seen in Fig. 5. It is well known that the mobility of holes is much larger than that of electrons[22] in polymer. However, in the device ITO/B/A/Al, the injected holes are blocked by the material A and the injected electrons from cathode move to the interfaces between two polymer layers to recombine with the blocked holes. Since the electrons move more slowly than the holes, the transit time should be longer than that of the device ITO/A/B/Al. We also observed that the transit times increase with the thickness of the layers and are independent upon the detection wavelengths of ITO/B/A/Al device for constant thickness.

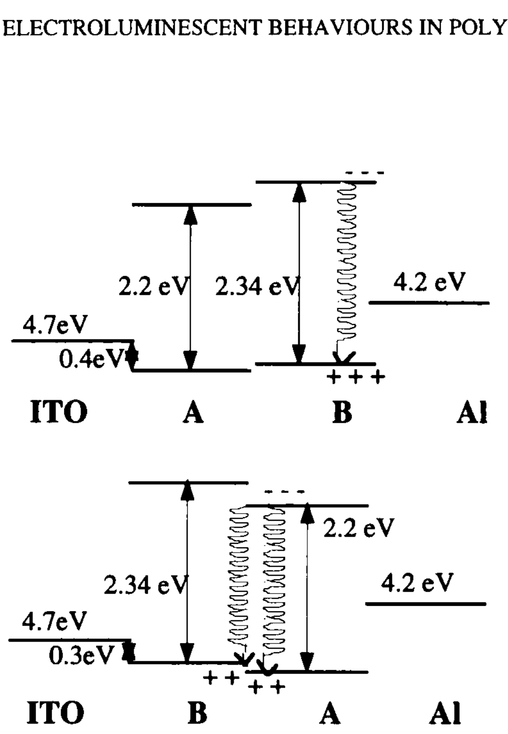


FIGURE 5 Energy band diagram of multilayer structure devices and emission procedure in EL

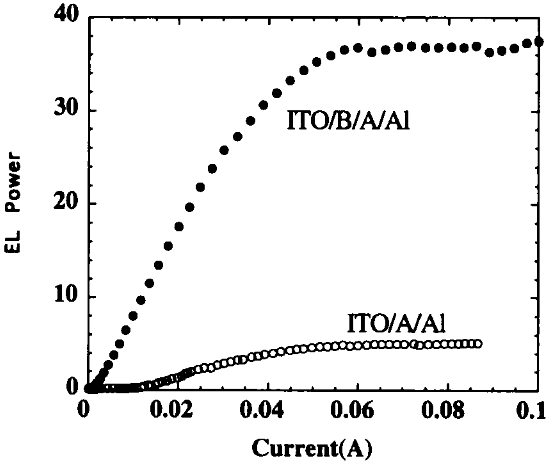


FIGURE 6 Luminescence - current characteristic curve of EL devices

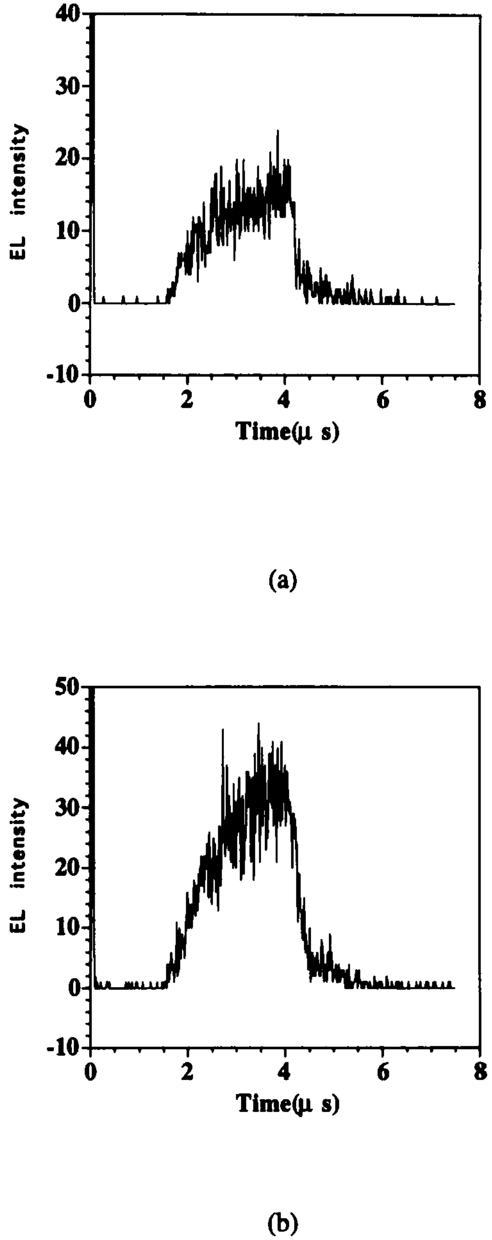


FIGURE 7 Transient EL behavior of the devices (a) ITO/A/B/Al (b) ITO/B/A/Al

CONCLUSION

We observed a new electroluminescence, which does not appear in EL spectra of each layer, from a two layer polymer device. The additional peak has longer wavelength than the peak of each layer and is assigned to the radiative recombination through the optical transition across the interface between two emitting layers. The transition occurs through the blocking of hole and electron transport at the interface by the energy barriers in HOMO and LUMO levels, respectively. Because of the blocking of the charge transport at the interface, remarkable enhancement of quantum efficiency was achieved by the multilayer device. The transition is supported by the observation of no appearance of the additional peak in a reversely stacked structure device and transient behaviour of EL signal. Possibility of the formation of a new compound at the interface is excluded from the observation.

ACKNOWLEDGEMENT

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REFERENCES

1. J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burns and A.B. Holmes, Nature, V.347, pp.539-541, 1990
2. D. Braun and A.J. Heeger, Appl. Phys. Lett., V.58, pp.1982-1984, 1991
3. G. Grem, G. Leditzky, B. Ullrich and G. Leising, Adv. Mater., V.4, pp.36-37, 1992
4. D. Braun, G. Gustafsson, D. McBranch and A.J. Heeger, J. Appl. Phys., V72, pp.564-568, 1992
5. Y. Ohmori, M. Uchida, K. Muro and K. Yoshino, Jpn. J. Appl. Phys., V.30, pp.L1941-L1943, 1991
6. S.C. Moratti, D.D.C. Bradley, R.H. Friend, N.C. Greenham and A.B. Holmes, Mat. Res. Soc. Symp. Proc., V.328, pp.371-376, 1994
7. D. Braun and A.J. Heeger, Thin Solid Films, V.216, pp.96-98, 1992
8. N.C. Greenham, S.C. Moratti, D.D.C. Bradley, R.H. Friend and A.B. Holmes, Nature, V.365, pp.628-630, 1993
9. P.L. Burn, A.B. Holmes, A. Kraft, D.D.C. Bradley, A.R. Brown, R.H. Friend and R.W. Gymer, Nature, V356, pp.47-49, 1992
10. C. Zhang, D. Braun and A.J. Heeger, J. Appl. Phys., V.73, pp.5177-5180, 1993
11. T. Zyung, D.H. Hwang, I.-N. Kang, H.-K. Shim, W.-Y. Hwang, and J.-J. Kim, Chem. Mater. V. 7, 1499(1995)
12. P. Frederikson, T. Bjornholm, H.G. Madson and K. Bechgaard, J. Mater. Chem., V.4, pp.675-678, 1994
13. S. Aratani, C. Zhang, K. Pakbaz, S. Hoger, F. Wudl and A.J. Heeger, J. Electron. Mater., V.22, pp.745-749, 1993
14. A.R. Brown, D.D.C. Bradley, J.H. Burroughes, R.H. Friend, N.C. Greenham, P.L. Burn, A.B. Holmes and A. Kraft, Appl. Phys. Lett., V.61, pp.2793-2795, 1992
15. J. Kido, C. Ohtaki, K. Hongawa, K. Okuyama and K. Nagai, Jpn. J. Appl. Phys., V.32, pp.L917-L920, 1993
16. A.R. Brown, N.C. Greenham, J.H. Burroughes, D.D.C. Bradley, R.H. Friend,

P.L. Burn, A. Kraft and A.B. Holmes, Chem. Phys. Lett., V.200, pp.46-54, 1992
17. T. Zyung, J.-J. Kim, W.-Y. Hwang, D.H. Hwang and H.K. Shim, Synth. Metals, V.71, pp.2167-2169, 1995
18. T. Zyung, I.-N. Kang, D.H. Hwang and H.K. Shim, Optical and photonic applications of electroactive and conducting polymers, SPIE(San Diego, 1995)
19. O. Inganas, M. Berggren, M.R. Andersson, G. Gustafsson, T. Hjertberg, O. Wennerstrom, P. Dyreklev and M. Granstrom, Synth. Metals., 71, 2121(1995)
20. J. Singh, Semiconductor devices, Chap. 11, McGraw-Hill, New York, 1994
21. Y. Ohmori, C. Morishima, M. Uchida and K. Yoshino, Jpn. J. Appl. Phys., 31, L568 (1992)
22. C. Hosokawa, H. Tokailin, H. Higashi and T. Kusumoto, Appl. Phys. Lett., 60, 1220 (1992)