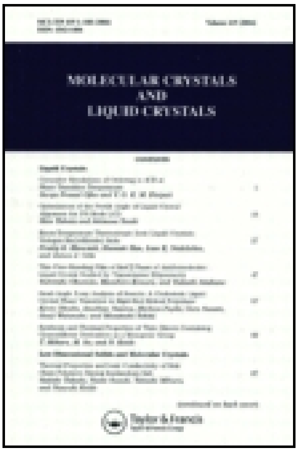

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Heterostructural Electroluminescent Devices Based on Poly (P-Phenylenevinylene) and Polyimide LB Films

Aiping Wu [a], Mitsutoshi Jikei [a], Masa-Aki Kakimoto [a], Yoshio Imai [a], Sadayuki Ukishima [b] & Yoshikazu Takahashi [b]

[a] Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro-ku, Tokyo, 152, JAPAN

[b] Institute for Super Materials, ULVAC Japan Ltd., Tohkodai, Tsukuba, 300-26, JAPAN

Version of record first published: 24 Sep 2006.

To cite this article: Aiping Wu, Mitsutoshi Jikei, Masa-Aki Kakimoto, Yoshio Imai, Sadayuki Ukishima & Yoshikazu Takahashi (1995): Heterostructural Electroluminescent Devices Based on Poly (P-Phenylenevinylene) and Polyimide LB Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 267:1, 441-446

To link to this article: http://dx.doi.org/10.1080/10587259508034029

Mol. Cryst. Liq. Cryst. 1995, Vol. 267, pp. 441–446
Reprints available directly from the publisher
Photocopying permitted by license only

HETEROSTRUCTURAL ELECTROLUMINESCENT DEVICES BASED ON POLY(P-PHENYLENEVINYLENE) AND POLYIMIDE LB FILMS

AIPING WU, MITSUTOSHI JIKEI, MASA-AKI KAKIMOTO, and
YOSHIO IMAI
Department of Organic and Polymeric Materials, Tokyo Institute of Technology,
Meguro-ku, Tokyo 152, JAPAN.

SADAYUKI UKISHIMA and YOSHIKAZU TAKAHASHI
Institute for Super Materials, ULVAC Japan Ltd., Tohkodai, Tsukuba 300-26,
JAPAN.

Abstract Several polymeric electroluminescent (EL) devices, possessing the poly(p-phenylenevinylene) (PPV) and polyimide LB films used as the light emitting layer and the hole transporting layer respectively, were fabricated by the LB technique. In these heterostructural EL devices, the luminance over 100 cd/m^2 was achieved, which was more than 10 times higher than that of the single layer (PPV LB film only) device. Furthermore, by incorporation of the hole transporting layer to the EL devices, remarkable improvements in charge injection and EL efficiency were observed. These improvements could be controlled by varying the thickness of the hole transporting layer.

INTRODUCTION

The remarkable electronic properties of conjugated polymers have attracted widespread research efforts in their use as active materials in various electronic devices.[1] Currently, the fabrication of conjugated polymer based EL devices has become a rapidly developing field because there is a potential applicability of these devices in large-area displays.[2]

Electroluminescence is the direct conversion of electrical energy into light without any intermediate process. In conjugated polymers, electroluminescence results from the radiative recombination of the injected electron in the conduction band with the injected hole in the valence band, which generates a photon with a wavelength corresponding to the energy level between the valence band and the conduction band. Therefore, conjugated polymer based EL devices have advantages in their use in full-color displays because the band gap of the polymers can be easily varied.

According to recent studies of PPV based EL devices, light emission in green-yellow,[3] yellow-orange[4] and red[5] regions, as well as blue-shifted electroluminescence[6] have been obtained by using substituted PPVs or copolymers as the light emitting material. In this field, recent works have also focused on improving the EL efficiency. Three approaches have shown effectiveness, namely (1) modification of the polymers,[4,6,7] (2) fabrication of heterostructural devices,[8-10] and (3) utilization of low work function electrodes.[4,8,11] The fabrication of heterostructural devices, using additional charge transporting layers between the light emitting layer and the electrodes, has significantly improved EL efficiency in the sublimed organic molecular EL devices.[12] Guided by this achievement, conjugated polymer based EL devices have also been made by incorporating an electron transporting layer (ETL) or a hole transporting layer (HTL) into the devices, which showed a remarkable improvement also.[8-10] In this work, novel heterostructural EL devices based on PPV LB films were fabricated. The increased efficiency was achieved by incorporation of a hole transporting polyimide LB film to the EL devices.

DEVICE STRUCTURE

We have developed a polymer processing technique called the "precursor method" to prepare polymeric LB films.[13-16] By this method, highly ordered thin films with precise control of film thickness could be achieved.

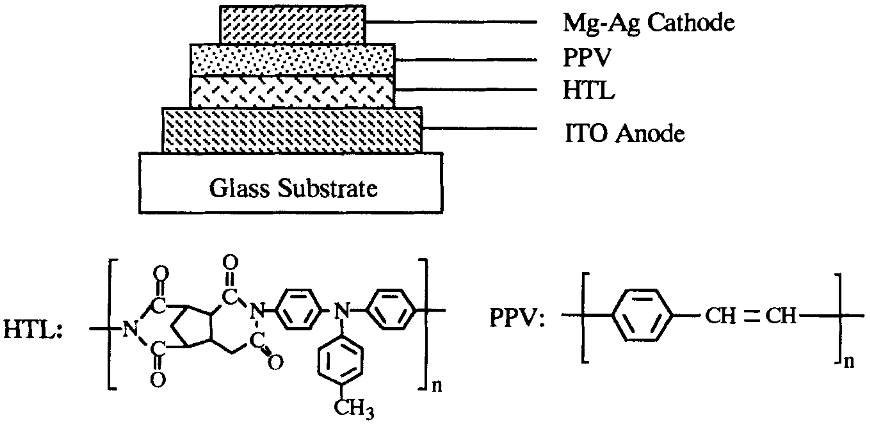

FIGURE 1. Device geometry and polymer structures.

In the present work, we fabricated PPV based EL devices with only polymeric LB films. The structure of the EL devices is shown in Fig. 1. The light emitting PPV layer and the hole transporting polyimide layer were sandwiched between the hole injection ITO anode and the electron injection Mg-Ag alloy cathode, and it was denoted as ITO/HTL/PPV/Mg-Ag. Here, a polyimide containing a triphenylamine group in its polymer backbone was expected to work as the hole transporting material, which was previously known as the electron donor in photo-current devices.[14] The polyimide LB film with the monolayer thickness of 0.5 nm was prepared by the chemical imidization of the precursor polyamic acid LB film.[14] The PPV LB film with the monolayer thickness of 0.34 nm was prepared by the thermal conversion of the precursor sulfonium salt LB film.[15,16] The Mg-Ag alloy electrode was deposited by vacuum evaporation at pressures about 2×10^{-6} Torr, creating an active area of 4 mm^2.

SPECTROSCOPIC PROPERTIES

The UV-Visible absorption characteristic of PPV LB film has been previously studied, which demonstrated a maximum absorption near 450 nm, corresponding to the π-π^* transition of π-conjugated PPV. A higher extended π-conjugation length compared with that of a conventional cast film was implied by the red-shifted absorption in the PPV LB film.[16] Strong photoluminescence in the PPV LB film was also observed by photo-excitation, which was similar to the photoluminescent (PL) spectrum of the usual PPV film.

Fig. 2 shows the typical UV-Visible absorption, PL and EL spectra of the heterostructural devices. Comparing with the UV-Visible absorption spectrum of the PPV LB film, a new strong absorption band near 315 nm was observed in the double-layered LB films. This new absorption corresponded linearly according to the thickness of the polyimide LB film. Thus, this absorption band was attributed to the absorption of the polyimide LB film. On the other hand, the shape of the PL spectrum did not show any change with or without the presence of the polyimide layers. This implied that the light emission came only from the PPV layer.

When forward bias was applied to these EL devices, yellow-green emissions were observed even under room light. As shown in Fig. 2, the EL spectrum of the ITO/HTL(51L)/PPV(50L)/Mg-Ag device was also similar to the PL spectrum of PPV. This similarity demonstrated that the same excited state was produced either by recombination of the injected electron and hole in the double-layered device or by photo-excitation of the PPV film. Also, it was notable that the EL spectrum did not change even with the presence of the polyimide LB film, which indicated that there was no exciplex between the polyimide and the PPV.

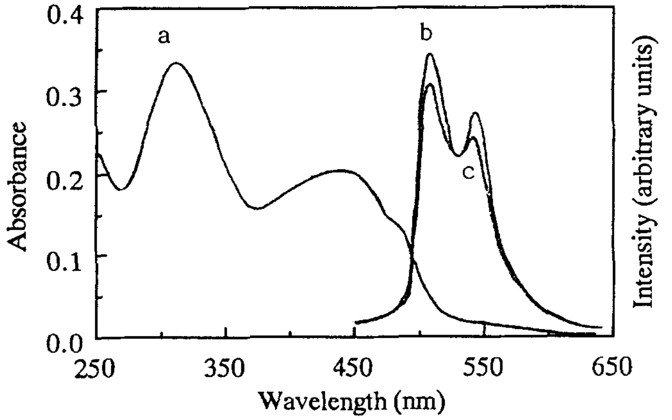

FIGURE 2. UV-Visible absorption (a) and PL spectra (b) of ITO/HTL(61L)/PPV(50L)/Mg-Ag device and EL spectrum (c) of ITO/HTL(51L)/PPV(50L)/Mg-Ag device.

EL EFFICIENCY

Although, the presence of the polyimide LB film seemed to have no influence to the shapes of the PL and EL spectra, its influence on the EL performance in the heterostructural devices was remarkable. Here, in order to investigate the effect of HTL on the EL efficiency, different heterostructural EL devices with PPV (50L) and varying thicknesses of the polyimide (21L, 41L, 61L and 81L) were prepared.

As the results shown in Table 1, it was exhibited that EL performance was highly dependent on the HTL. The drive field (threshold voltage/total polymer layer thickness) for these devices was found to be in the order of 10^6 V/cm. The introduction of the HTL caused a notable reduction in the drive field indicating that charge injection was improved with incorporation of HTL. Furthermore, when the applied voltage was below 20 V, the light output (luminance) increased approximately linearly with the input current density. The maximum luminance reached more than 100 cd/m^2 in the heterostructural devices, which was over 10 times higher than that in the single layer (PPV 50L) device. Similarly, EL efficiencies, which depended strongly on the thicknesses of the HTL, were improved significantly in the heterostructural devices at 10 V drive voltage. This dependence of the efficiency on the thickness of the HTL suggested that efficient charge injection and transportation in the polyimide HTL was improved by increasing the thickness of the HTL.

TABLE 1. Data of EL devices.

Structure of Devices	Field(V/cm)	Voltage(V)	J(mA/m^2)	L(cd/m^2)	η(lm/W,%)*
PPV(50L)	3.6×10^6	10	97.2	2.28	0.07
HTL(21L)/PPV(50L)	1.3×10^6	10	236.8	10.18	0.14
HTL(41L)/PPV(50L)	1.8×10^6	10	200.4	23.6	0.36
HTL(61L)/PPV(50L)	2.0×10^6	10	60.94	11.59	0.60
HTL(81L)/PPV(50L)	2.0×10^6	10	22.8	9.57	1.32

*Efficiency is calculated by following equation:

$\eta(\mathrm{lm/W}) = \pi L[\mathrm{cd/m^2}] / VJ\ [\mathrm{W/m^2}]$

η: EL efficiency, L: luminance, J: current density.

Efficient electroluminescence is known to be limited by the following three points: first, charge injection (both electron and hole) should be at similar rates, so that recombination of the opposite charges occurs in the light emitting layer; second, electron-hole capture must result in singlet excitons, which at a 1/4 probability compete with triplet excitons formation; and third is radiative decay of the singlet excitons, which competes with non-radiative decay of the excitons.[4]

The effectiveness of building up heterostructural EL device is well known either in a sublimed organic molecular system or in conjugated polymer system. Performance is improved by balancing the electron and hole injection rates and by confining excitons to the emissive layer, away from the injection electrodes.[4]

However in our work, improvement of EL efficiency was achieved in the different way. Since PPV is a semiconductor, electron injection is more difficult than hole injection. From this point, the introduction of HTL may cause an unbalancing of the charge injection. The influence of polyimide HTL in our work did not allow us to clearly understand exactly what occurred, but, it was believed that efficient charge injection was improved which resulted from the decrease in the leakage current. More detail investigations of this phenomenon are under way.

ACKNOWLEDGMENTS This work was supported by NEDO International Joint Research Grants.

REFERENCES

1. H. Stubb, E. Punkka, J . Paloheimo, Materials Science & Engineering **10 (3)**, 85 (1993).
2. D. D. C. Bradley, Synthetic Metals **54**, 401 (1993).
3. 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 **347**, 539 (1990).
4. D. Braun, A. J. Heeger and H. Kroemer, J. Electronic Materials **20 (11)**, 9 (1991).
5. N.C. Greenham, S. C. Moratti, D. D. C. Bradley, R. H.Friend and A. B. Holmes, Nature **365**, 628 (1993).
6. P. L. Burn, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown and R. H. Friend, J. Chem. Soc. Chem. Commun., 32 (1992).
7. P. L. Burn, A. B. Holmes, A. Kraft, D. D. C.Bradley, A. R. Brown R. H. Friend and R. W. Gymer, Nature **356**, 47 (1992)
8. R. Friend, D. Bradley and A. Holmes, Physics World, 42 (1992).
9. 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. **61 (23)**, 2793 (1992).
10. M. Uchida, Y.Ohmori, T.Noguchi, T.Ohnishi and K.Yoshino, Jpn. J. Appl. Phys. **32**, L921 (1993).
11. S. Doi, M. Kuwabara, T. Noguchi and T. Ohaishi, Synthetic Metals **55-57**, 4174 (1993).
12. C. W. Tang and S. A. Vanslyke, Appl. Phys. Lett. **51**, 913 (1987).
13. M. Kakimoto, M. Suzuki, T. Konishi, Y. Imai, M. Iwamoto and T. Hino, Chem. Lett. 823 (1986).
14. Y. Nishikata, S. Fukui, M. Kakimoto and Y. Imai, Thin Solid Film **210**, 296 (1992).
15. Y. Nishikata, M. Kakimoto, Y. Imai, Thin Solid Film **179**, 191 (1989).
16. A. Wu, S. Yokoyama, S . Watanabe, M. Kakimoto, Y. Imai, T. Araki and K. Iriyama, Thin Solid Film **244**, 750 (1994).