Multi-layer Polymer Light-emitting Diodes with 2,3-Dialkoxy-\(p\)-phenylene Vinylene and its Blends

Takeshi Sano, Chi-Shen Tuan,* Rainer E. Martin* and Andrew B. Holmes*

Materials and Devices Development Center, SANYO Electric Co., Ltd.,
1-18-13 Hashiridani, Hirakata, Osaka, 573-8534 Japan
*Melville Laboratory for Polymer Synthesis, Department of Chemistry,
University of Cambridge, Pembroke Street, Cambridge, CB2 3RA U.K.

A green-fluorescent polymer, poly(2,3-dibutoxy-1,4-phenylene vinylene) (DB-PPV), was synthesized and used in electroluminescent (EL) devices. By introducing a small molecular electron-transport layer in a device, the EL efficiencies were improved up to 1.26 cd/A. A polymer-blend with DB-PPV and poly(9,9-diocctylfluorene) (PF8) was also examined. The EL peak wavelength was blue-shifted to 503 nm and the EL efficiencies were improved in the polymer-blend device. A layered structure and a polymer-blend system both have shown contribution to the improvements of the polymer light-emitting diodes using DB-PPV.

Keywords: electroluminescence, polymer light-emitting diodes, PPV

1. Introduction

Polymer light-emitting diodes (PLEDs) have a number of attractive features including low driving voltage, ease of fabrication, and then allow the possibility for large-area emitting devices.\(^1\)\(^2\) Poly(p-phenylene vinylene) (PPV, 1) is the first successful light-emitting polymer (LEP) for PLEDs.\(^3\) PPV analogues have been studied extensively due to their strong fluorescence and the color tunability. The first yellow-green PPV film for the device was prepared by thermal conversion of a precursor film. A solution-processable PPV, poly(2-methoxy, 5-(2'-ethyl-hexoxy)-1,4-phenylene vinylene) (MEH-PPV, 2),\(^4\) was then developed, which was able to spin-coat on glass substrates or even on flexible plastic films. However, the 2,5-dialkoxy substitution of PPV resulted in a significant red-shift of the luminescence yielding the emission colors from orange to red.

Chuah reported a solution-processable poly(2,3-dibutoxy-1,4-phenylene vinylene) (DB-PPV, 3), which provided a significant blue-shift in emission \(^5\) compared to 2,5-substituted PPVs. The crystal structure of the model compound, distyryl-2,3-dibutoxybenzene 4, revealed that the benzene rings on both sides were twisted at 30°, having the alkoxy chains as the ortho-position slightly out of the plane of the benzene rings, whilst the three benzenes of distyryl-2,5-dimethoxybenzene 5 were coplanar in the crystal structure. The model compound 4 showed very high PL quantum yield (ca. 80% in solid state) with the PL maximum at 477 nm, which was the motivation to investigate the related 2,3-dialkoxy-PPVs.

Chuah reported that DB-PPV exhibited strong green fluorescence with a high PL quantum yield. A single-layer EL device with DB-PPV showed EL efficiencies of up to 0.07 cd/A, which corresponds to 0.02% EL quantum yield. This value (0.02%) is quite low compared to the PL efficiency (22%) in solid state. One of the possible reasons for that is the unbalance of the charge injections. The recombination yield in

Received April 30, 2002
Accepted May 30, 2002
the active layer can be improved by introducing a proper multi-layer structure to control the charge-injection balance. The examples of this approach include [PPV / PBD: PMMA], [PPV / CN-PPV] double-layer structures in which PBD is an oxadiazole derivative, PMMA is poly(methyl methacrylate), CN-PPV is a cyano-substituted PPV. In these examples, the first polymer layer, PPV, did not dissolve with the solvent of the second spin-coating process; therefore it was possible to fabricate a double-layer structure by consequent spin-coating. The resulting LEDs showed remarkable improvement, which was reported about 0.6 cd/A and 0.8% for the [PPV / PBD: PMMA] device. In this work, DB-PPV 3 was soluble in organic solvents therefore small molecular evaporated films were used as an electron-transport layer.

Another investigation is a polymer-blend system to improve EL efficiencies of PLEDs. Berggren and co-workers showed PLEDs with variable colors using polythiophene derivatives and blends with these polymers. In contrast, Halls and co-workers reported an efficient photodiode with a polymer-blend active layer which consisted of a hole-transport polymer, MEH-PPV, and an electron-transport polymer, CN-PPV. In our case, DB-PPV is strongly colored and the absorption spectrum partially covers the emission spectrum, therefore self-absorption of the film may decrease the EL efficiencies. In order to avoid this effect, DB-PPV was dispersed in another blue-emitting polymer and the EL and photovoltaic characteristics of the polymer-blend device have been studied.

2. Preparation of poly(2,3-dialkoxy-p-phenylene vinylene) and the EL devices

DB-PPV 3 was synthesized via a dehydro-halogenation polymerisation route using 2,3-dibutoxy-1,5-bis(bromomethyl) benzene and potassium t-butoxide in dry THF (Scheme 1). The product was purified by reprecipitation (3 times) to obtain DB-PPV 3 as yellow fibres. The molecular weights of DB-PPV were $M_p = 520,000$, $M_n = 90,000$ and $M_w = 580,000$ ($PDI = 6.4$). The PL peak wavelength in solution was 492 nm. The PL quantum yield in chloroform was 72% relative to a quinine sulfate solution as a reference standard. The PL peak wavelength in a spin-coated film of DB-PPV was 522 nm, and the PL quantum yield of a film was 22% measured using an integrated sphere and a 457 nm excitation by laser.

Other carrier-transport materials were prepared as follows. Poly(3,4-ethylenedioxythiophene): poly(styrene sulfonic acid) blend (PEDOT:PSS, 12) was purchased from Bayer Corp. as an aqueous solution and used as a buffer layer or a hole-transport layer. An oxadiazol derivative, 1,3-bis[5-(p-t-butyl-phenyl)-1,3,4-oxadiazol-2-yl]benzene (OXD-7, 13) and tris(8-hydroxy quinolinato) aluminum (Alq3, 14) were synthesized, purified by sublimation, and used as electron-transport materials.

The PLED devices were fabricated as follows. Indium-tin-oxide (ITO) coated (2000 Å) glass substrates were purchased from Sanyo Vacuum Industry and ITO was patterned as 2 mm stripes. After patterning and washing of the substrates, PEDOT:PSS (600 Å) was spin-coated on ITO. Remaining water was removed by heating on a hotplate. Next, DB-PPV (1000 Å) was spin-coated from xylene solution. OXD-7 (400 Å) or Alq3 (400 Å) was deposited on DB-PPV by thermal vapor deposition in high vacuum (1 x 10^-6 torr). Finally, Ca (500 Å) and Al (2000 Å) were thermally deposited in
sequence using a shadow mask. The EL devices were immediately encapsulated with epoxy-resin and glass. The EL characteristics were evaluated using Topcon BM-8 Luminance Meter, Keithley 2000 Digital Multimeter, Hewlett-Packard E3631A DC Power Supply, and Aminco-Bowman Series 2 Fluorescence Spectrometer. The photoelectron yield spectroscopy of the organic/polymer films was measured using Riken-keiki AC-1.

3. EL results of the layered EL devices

Four devices were fabricated as follows. The number of organic/polymer layers between electrodes was one to three depending on the device configuration.

Device 1 [ITO / DB-PPV 3 / Ca / Al] (single layer)
Device 2 [ITO / PEDOT:PSS 12 / DB-PPV 3 / Ca / Al] (double layers)
Device 3 [ITO / PEDOT:PSS 12 / DB-PPV 3 / OXD-7 13 / Ca / Al] (three layers)
Device 4 [ITO / PEDOT:PSS 12 / DB-PPV 3 / Alq3 14 / Ca / Al] (three layers)

The EL characteristics of the devices are shown in Table 1. The emission peak wavelengths of the four devices were almost identical to the PL peak wavelength of the DB-PPV film (522 nm), but vary slightly due to the difference in thickness and possibly due to a small amount of emission from the exciplex at the interfaces or from Alq3. The single-layer device 1 showed quite low EL efficiency, but the other devices 2-4 have shown remarkably improved EL efficiencies by incorporating a hole-transport layer and an electron-transport layer. The double-layer device 2 showed very high luminance of 14,000 cd/m² at 11 V, but the efficiency at low current-density region decreased due to the imbalance of carrier injection (Fig. 1). The three-layer device 3 showed much better luminance-current characteristics, but the operating voltage was too high, probably due to the large energy-barrier gap at the OXD-7 / Ca interface. The three-layer device 4 with Alq3 as an electron-transport layer showed higher efficiencies, 1.26 cd/A and 0.62 lm/W, compared to the other device performance.

Photoelectron yield measurements have revealed that the HOMO level of the DB-PPV film appears at -5.0 eV which was similar to that of MEH-PPV, while Alq3 at -5.7 eV. This means that DB-PPV has a hole-transport nature. When Alq3 is employed as an electron-transport layer, holes will be blocked at the DB-PPV / Alq3 interface due to the large energy barrier. The improvement in the EL efficiencies can be explained by the good injection of electrons and the good hole-blocking function of the Alq3 layer.

4. Electroluminescence study on a polymer blend system

Another problem of a DB-PPV film is self-absorption of the emission. There is a large Stokes' shift observed in a film (PL λmax = 522 nm, ABS λmax = 450 nm), whilst the Stokes' shift in solution was small (PL λmax = 492 nm, ABS λmax = 444 nm). It is considered from the wmax absorption and the PL spectra that the self-absorption of the DB-PPV film has quenched the PL peak at 492 nm. The PL quantum yield was also decreased in a film. One idea to solve this problem is to blend DB-PPV with another light-emitting polymer. By dispersing highly colored DB-PPV in a colorless polymer, it may be possible to avoid self-quenching of the emission. When choosing a host polymer,

![Fig. 1 Luminance-current characteristics of the PLED devices.](image-url)
carrier-transport property is quite important as studied before in the layered EL devices. A blue fluorescent polymer, poly(9,9-dialkylfluorene), has been used in this experiment to blend with DB-PPV since an excellent carrier-transport property was reported by Sheffield University. Poly(9,9-dioctylfluorene) (PF8, 15) was synthesized by a Pd-catalysed Suzuki cross-coupling (Suzuki-coupling) conditions and carefully purified by reprecipitations (4 times). The product was white (slightly greenish) fibres and showed strong blue fluorescence (PL λmax (in CHCl3) = 417 nm, relative PL quantum yield (in CHCl3) = 67%, PL λmax (film) = 423 nm), and the GPC assay was Mp 93,000, Mn 38,000, Mw 210,000 and PDI 5.5. Toluene solutions of PF8 and DB-PPV were blended (10:1 w/w, DB-PPV 9 wt.%), and the mixture was used in the EL device of the following structure.

![Chemical structure of PF8](image)

**Device 5** [ITO / PEDOT:PSS 12 / PF8 15: DB-PPV 3 (9 wt.%)/Ca / Al]

The EL spectrum of the device 5 is shown in Fig. 2 in comparison with that of the normal double-layer device 2. Remarkably, the emission peak was changed from 522 nm (for the DB-PPV only system) to 503 nm (for the polymer-blend system). By comparing the EL spectra with the PL spectra, it is found that the EL spectrum of the device 5 has a similar shape to the PL spectrum in solution, while the EL spectrum of the device 2 was almost identical to the PL spectrum of the film. It is considered that the emission at around 500 nm was self-absorbed by the DB-PPV film and in the device 2, which might have decreased the EL efficiency. On the other hand, DB-PPV was diluted by PF8 in the polymer blend system; therefore the emission at around 500 nm had not been fully self-absorbed in the device 5 which showed a solution-like emission spectrum.

The maximum luminance of the polymer-blend device 5 was 5,900 cd/m² at 17 V, and the EL efficiencies at 100 cd/m² were 0.93 cd/A, 0.22 lm/W and 0.30% for the external quantum efficiency. The reference device 2 showed higher luminance (14,000 cd/m²) than the device 5, but the EL efficiencies at 100 cd/m² were much lower (0.26 cd/A, 0.16 lm/W and 0.08% for the external quantum yield) compared to the polymer-blend device 5. It is clearly shown that the polymer-blend system effectively improved the EL efficiencies.

An interesting feature of the polymer-blend system is the charge-separation upon excitation by light. Blends of polymers with different electronic properties are promising materials for the active layer in a photovoltaic cell. DB-PPV 3 is a highly colored material and therefore it is a possible candidate material in polymer photodiodes. The same structure as the device 5 was used to examine the photovoltaic property of the PF8:DB-PPV blend. A larger size for each pixel, 1 cm x 1 cm, was employed to obtain sufficient output current. The cell was tested under irradiation of a 6W UV-lamp (366 nm). The cell showed an open-circuit voltage of 0.29 V and a short-circuit current of 0.19 x 10⁻⁶ A upon irradiation of light. The performance of the cell was lower than the theoretical value estimated from the difference of the work functions of the electrodes, but it can be improved by further optimization.
5. Conclusion

In conclusion, the EL efficiencies of the devices using poly(2,3-dibutoxy-1,4-phenylene vinylene) (DB-PPV, 3) were significantly improved by incorporating a polymeric hole-transport layer and a small molecular electron-transport layer. The EL efficiencies were also improved by blending DB-PPV with poly(9,9-dioctylfluorene) (PF8, 15). By using a layered structure and a polymer-blend system, it is possible to improve EL efficiencies in PLEDs dramatically.

Acknowledgement

We thank Dr. B. S. Chuah, Dr. G. Frey, Mr. U. Hennecke, Dr. J. Frey, Mr. J. Li and Dr. I. Rees in University of Cambridge for the useful advice, and Universities UK for the Overseas Research Students Awards to TS.

References

15 M. T. Bernius, M. Inbasekaran, J. O’Brien

Fig. 2 UV-Vis and PL spectra of DB-PPV and the EL spectra of the devices 2 and 5.