



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

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Version of record first published: 20 Aug 2006

To cite this article: Jai Kyeong Kim, Soo-Hyoung Lee & Taeyong Noh (2006): Improved Performance of Polymeric Light-Emitting Diodes with an Electron Blocking Layer, Molecular Crystals and Liquid Crystals, 444:1, 103-106

To link to this article: <http://dx.doi.org/10.1080/15421400500365268>

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Improved Performance of Polymeric Light-Emitting Diodes with an Electron Blocking Layer

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In this paper, we describe a new approach for fabrication of high efficient polymeric light-emitting diodes (PLEDs). In the device configuration of ITO/HTL/EBL/EML/BaF₂:Ca:Al (ITO: indium tin oxide, HTL: hole transport layer, EBL: electron blocking layer, EML: emitting layer), EBL contains cross-linkable moieties in order to make the layer which is insoluble to layering of an additional emitting polymer. The devices with EBL exhibit strong blue emissions and higher efficiency values than those in devices without EBL. The synthesis, characterization, device fabrication, and electroluminescence (EL) properties of devices will be presented.

Keywords: cross-link; electron blocking; organic light-emitting diodes

INTRODUCTION

In recent years, organic light-emitting devices (OLEDs) have received much attention for their application as full-color flat-panel displays [1,2]. Since the basic structure of OLED which has a sandwiched organic emitting layer between two electrodes has been reported, there have been extensive studies on introducing of multiple functional organic layers, such as hole transporting, hole injection, electron

This research was supported by a grant (code#: 04K1501-01210) from 'Center for Nanostructured Materials Technology' under 21st Century Frontier R&D Programs' of the Ministry of Science and Technology, Korea.

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transporting, electron injection and hole blocking layers, to further improve the devices performances [3,4]. Recently, the insertion of a thin layer known to be an electron blocking layer (EBL) between hole transporting (or injecting) and emitting layer has been more attracted [5]. This thin layer is blocking electrons from cathode, accumulating, and giving them more chance to meet holes in the emitting layer resulting better device performances. In this report, highly efficient and bright PLEDs with a stable EBL have been developed by simple polymer blend approach [6]. The EBL has been prepared with a cross-linkable siloxane compound and a polymer which has functions of blocking electrons as well as transporting holes. The resulting layer contains a heavily cross-linked siloxane networking structure embedded within the polymer chains which is more adherent and mechanically robust as well as impervious to spin coating of next emitting polymer layer. The PLEDs with EBL developed in this study show better device performances in a brightness and efficiency than those without EBL.

EXPERIMENTAL

The emitting polymer, poly(alkylfluorene) derivative (PF, Fig. 1(a)), was synthesized by the method in the literature [7]. Poly[(9,9-dihexylfluoren-2, 17-diyl)-co-(N,N'-di(4-butylphenyl)-N,N'-diphenyl-4,4'-diyl-1,4-diaminobenzene)] (F6-PFB, Fig. 1(b), molecular weight ~ 100000 g/mole) was

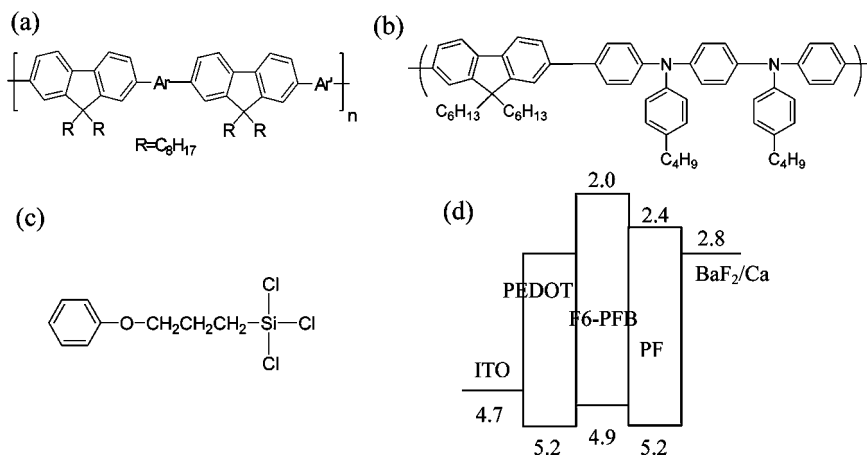


FIGURE 1 The molecular structure of (a) PF, (b) F6-PFB, (c) PPTS, and (d) the schematic energy diagram of multilayer PLED employed.

obtained from H.W. SANDS CORP. and 3-phenoxypropyltrichlorosilane (PPTS, (Fig. 1(c)) was purchased from Gelest Inc. PEDOT (Baytron-P) was purchased from Bayer. The UV-Vis absorption spectra were measured with a HP 8453 spectrophotometer. Photoluminescence (PL) spectra were collected with a spectrofluorometer (Jobin-Yvon Spec Corp.). Cyclic voltametry (CV) experiments were performed with a BAS-100 electrochemical analyzer. The device configuration is ITO/PEDOT(65 nm)/PPTS:F6-PFB(10–20 nm)/PF(70 nm)/BaF₂(2 nm)/Ca(50 nm)/Al(300 nm). PEDOT was spin coated onto the ITO substrate with baking at 110°C for 10 min. A blended solution of PPTS and F6-PFB (PPTS:F6-PFB, 1:4 mass ratio) in toluene was spin coated onto the surface of PEDOT with baking at 90°C for 1 hr. The emitting polymer was then spun onto the PPTS:F6-PFB layer with baking at 130°C for 1 hr. The BaF₂/Ca/Al cathode was deposited on the emitting polymer by thermal evaporation at 3×10^{-7} torr. A device in the similar structure without PPTS:F6-PFB layer was also fabricated in parallel as a control. The luminescence-voltage and current efficiency-voltage characteristics were measured using a Keithley 238 source measurement unit and PR650 (Photo Research Corp.).

RESULTS AND DISCUSSION

Figure 1(a) shows the generic molecular structure of the emitting polymer PF. Ar and Ar' denote the aromatic structure which was connected with poly(octylfluorene) units by Suzuki coupling reaction [7]. The electrochemical characteristics of polymer PF and F6-PFB were investigated by the CV method. The first oxidation potential was used to determine the highest occupied molecular orbital (HOMO) energy level. This was then used to obtain the lowest unoccupied molecular orbital (LUMO) energy level with the absorption band edge from UV-vis absorption spectra. Figure 1(d) schematically depicts the relative HOMO and LUMO energies of the emitting polymer PF and F6-PFB with other layer sequences. Based on these data, F6-PFB can make electrons effectively blocked and holes easily passed by the positions of its LUMO and HOMO energy levels relative to the neighboring layers, PF and PEDOT.

It is necessary to verify that the PPTS:F6-PFB layer is not dissolved during spin coating of the emitting polymer layer. The baked PPTS:F6-PFB film on the glass substrate was rotated on the spin coater and slowly rinsed by toluene (the solvent for the emitting polymer). After rinsing with toluene, the optical absorption of the PPTS:F6-PFB film remains essentially unchanged indicating the layer is not dissolved by the solvent (data are not shown). In addition, the

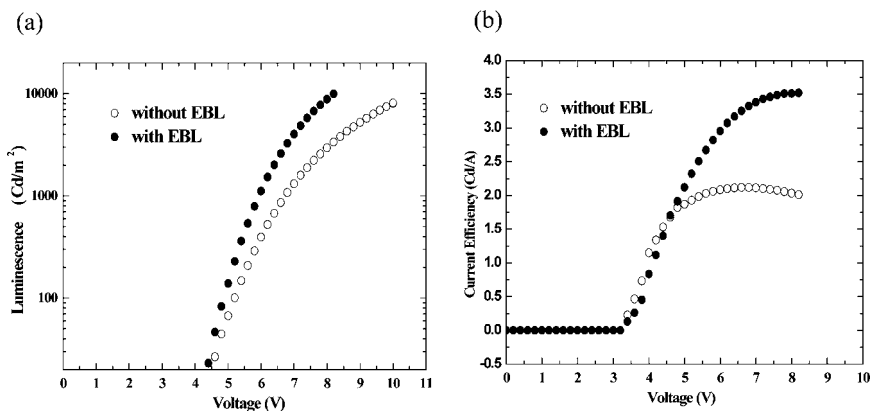


FIGURE 2 (a) Luminescence-voltage, (b) Current efficiency-voltage characteristics of the PLED.

surface uniformity of PPTS:F6-PFB film is not changed after rinsing as well. The same root mean square (RMS) roughness values are obtained before and after the solvent treatment (data are not shown).

The EL characteristics of the present PLEDs are shown in (Fig. 2(a) and 2(b) for luminescence-voltage (L-V) and current efficiency-voltage, respectively. Figure 2(a) shows that the device with EBL of PPTS:F6-PFB exhibits comparable turn-on voltage and can reach maximum luminescence over 10000 cd/m^2 at about 8 V, which is 3 times greater than that without EBL. The device containing EBL also shows over 70% greater current efficiency compared to that without EBL at the same voltage as shown in Figure 2(b). We believe that the enhancements in luminescence and efficiency are attributed to the electron blocking ability of PPTS:F6-PFB layer which is durable.

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