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We report that high efficiency blue polymer light-emitting diodes obtained by adding a thin interlayer between a poly(3,4-ethylene dioxythiophene)-poly(styrene sulfonic acid) (PEDT:PSS) hole transporter and emissive polymer. The one of OLED hole transporters, N,N′-bis(4-methylphenyl)-N,N′-diphenyl-1,4′-phenylenediamine (PDA), was modified with cross-linkable trichlorosilyl groups and used for the interlayer material. The devices, with configuration of indium tin oxide (ITO)/PEDT:PSS (65 nm)/interlayer (10–20 nm)/emitting polymer layer (70 nm)/BaF_2 (2 nm)/Ca (50 nm)/Al (300 nm), were fabricated by spin coating and thermal evaporation. In this device structure, the cross-linkable interlayer is more adherent and mechanically robust as well as impervious to spin coating of next emitting polymer layer and shows a better stability. In addition, the devices with the interlayer exhibit a higher luminescence and current efficiency than those in devices without the interlayer.

Keywords: cross-link; interlayer; organic light-emitting diodes

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INTRODUCTION

Much attention for conjugated polymers over the past decade has been received into their various applications such as polymer based light-emitting diodes (PLEDs) and photovoltaics [1–4]. Present-generation PLED structures usually have a p-doped water soluble conductive polymer, such as poly(3,4-ethylene dioxythiophene)-poly(styrene sulfonic acid) (PEDT-PSS) as a hole-transport layer (HTL) [5,6]. While PEDT-PSS acts as high performance HTL by maximizing hole injection from anode, it is also known to have serious drawbacks such as corrosion of indium tin oxide (ITO) anode [7] and quenching of radiative excitons at the interface between emissive and PEDT-PSS layer [8] leading to a large decrease in the luminescence quantum yield of PLEDs.

Recently, an adding of thin interlayer between PEDT:PSS (HTL) and a semiconductor emissive layer (EML) in order to minimize damages from PEDT:PSS has been reported in PLEDs. Morgado *et al*. has shown that the current efficiency of PLED was nearly doubled by inserting a poly(p-phenylene vinylene) (PPV) electron confinement layer between the PEDT:PSS and the emissive polymer [9]. In the recent work of Kim *et al.*, a thin (∼10 nm) conjugated polymer interlayer, poly(2,7-9,9-di-n-octylfluorene)-alt-(1,4-phenylene-((4-sec-butylphenyl)imi-no)-1,4-phenylene) (TFB), leads to a significant improvement of device efficiency of R, G, B color PLEDs by preventing severe quenching of radiative excitons at the PEDT:PSS interface and acting as an efficient exciton blocking layer [10]. However, in Kim's study, interlayer may have undefined layer structure due to the inter-diffusion between interlayer and subsequent EML because they are fabricated by simple physical absorption process (spin coating) and interlayer doesn't have any stable functions (which can be, for example, crosslinkable).

Herein, we report the method which can make a well-controlled interlayer structure between PEDT:PSS and emissive polymer layer by crosslinked-network deposition approach without previous mentioned problems. The interlayer material (PDA-Si) is prepared with modification of N,N′-bis(4-methylphenyl)-N,N′-diphenyl-1,4′-phenylenediamine (PDA), which is one of HTLs, by appending crosslinkable trichlorosilyl groups. This interlayer results in not only stable layer qualities to spin coating of next polymer layer due to a strong solvent resistance but also dramatic enhancements of device performance by blocking electron overflow from, and confining electrons and excitons within the EML. The devices with interlayer in our approach show higher luminescence and efficiency than those without interlayer.

EXPERIMENTAL

The hole transporting material, PEDT:PSS in aqueous solution was purchased from H. C. Starck (a Bayer company) and used without additional modification (Baytron-P). The emitting polymer, poly(octylfluorene) derivative (PF), was synthesized by conventional Suzuki coupling methodology and procedures similar to those described in the literature [11]. The electron blocking material, (PDA-Si), was synthesized by the similar method reported in the literature, but with a different starting material [12]. The UV-vis absorption spectra were measured with a HP 8453 spectrophotometer. Cyclic voltametry (CV) experiments were performed with a BAS-100 electrochemical analyzer. All measurements were carried out a glassy carbon working electrode, a platinum auxiliary electrode and a non-aqueous $Ag/AgNO_3$ reference electrode.

The devices were prepared in configuration of ITO/PEDT:PSS (65 nm)/PDA-Si (10–20 nm)/PF (70 nm)/BaF_2 (2 nm)/Ca (50 nm)/Al (300 nm). PEDT:PSS was spin coated onto an ITO glass and baked at 110°C for 10 min. A solution of PDA-Si in toluene was spin-coated onto the surface of PEDT:PSS. This film was baked at 90°C for 1 hr. In the same way, the emitting polymer was then spun onto PDA-Si layer followed by baking at 130°C for 1 hr. The BaF_2/Ca/Al cathode was deposited on the emitting polymer by thermal evaporation. A device in the similar structure without PDA-Si layer was also fabricated in parallel as a control to compare. The surface morphology of this film was analyzed by atomic force microscopy (AFM, Nanoscope IIIa, Digital Instruments Co.). The current-voltage-luminescence (I-V-L) and current efficiency-voltage characteristics were measured using a Keithley 238 source measurement unit and PR650 (Photo Research Corp.).

RESULTS AND DISCUSSION

The chemical structures of all the materials used in this study are shown in Figures 1(a)–(c). Ar and Ar′ in the generic molecular structure of the emitting polymer PF denote the aromatic structure which was connected with poly(octylfluorene) units by Suzuki coupling reaction. In this study, interlayer (PDA-Si) requires a relatively higher lowest unoccupied molecular orbital (LUMO) energy level than the emitting polymer layer (PF) in order to block electrons from cathode and to confine excitons effectively in the EML. Also, it should have a comparable highest occupied molecular orbital (HOMO) with a hole transporting layer (PEDT:PSS) to get holes from anode. Therefore, it is necessary

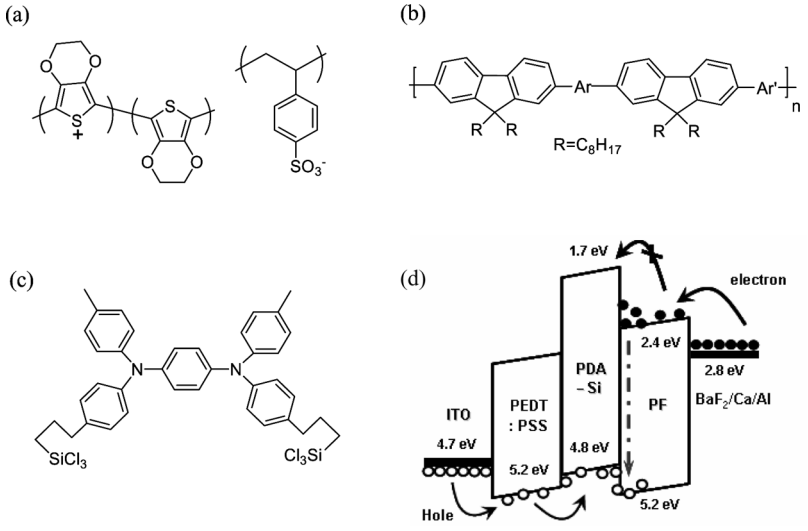

FIGURE 1 The molecular structures of (a) PEDT:PSS, (b) PF and (c) PDA-Si and (d) the schematic energy diagram of multilayer PLED employed.

to verify energy levels of PDA-Si as well as PF. To get insight into these energy levels, the electrochemical characteristics of PDA-Si and PF were investigated by the CV method. The first oxidation potential was used to determine HOMO energy level. This was then used to obtain 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 PF and PDA-Si with other layer sequences. As shown in Figure 1(d), PDA-Si has a relatively good position in LUMO and HOMO energy levels to neighboring PF and PEDT:PSS layers and it can make electrons and excitons effectively blocked and holes easily passed.

It is necessary to verify that the PDA-Si layer is not dissolved during spin coating of the EML. In order to test the solvent resistance of PDA-Si layer, the baked PDA-Si film on the glass substrate was rotated on the spin coater and slowly rinsed by toluene (the solvent for the emissive polymer). After rinsing with toluene, the optical absorption of the PDA-Si film measured by UV-vis spectrophotometer remains essentially unchanged as shown in Figure 2(a), indicating the layer is not dissolved by the solvent. In addition, the morphology of PDA-Si film after rinsing by toluene was further investigated by AFM. The almost same root mean square (RMS) roughness values, 1.31 and 1.28 nm, are obtained before and after the solvent treatment

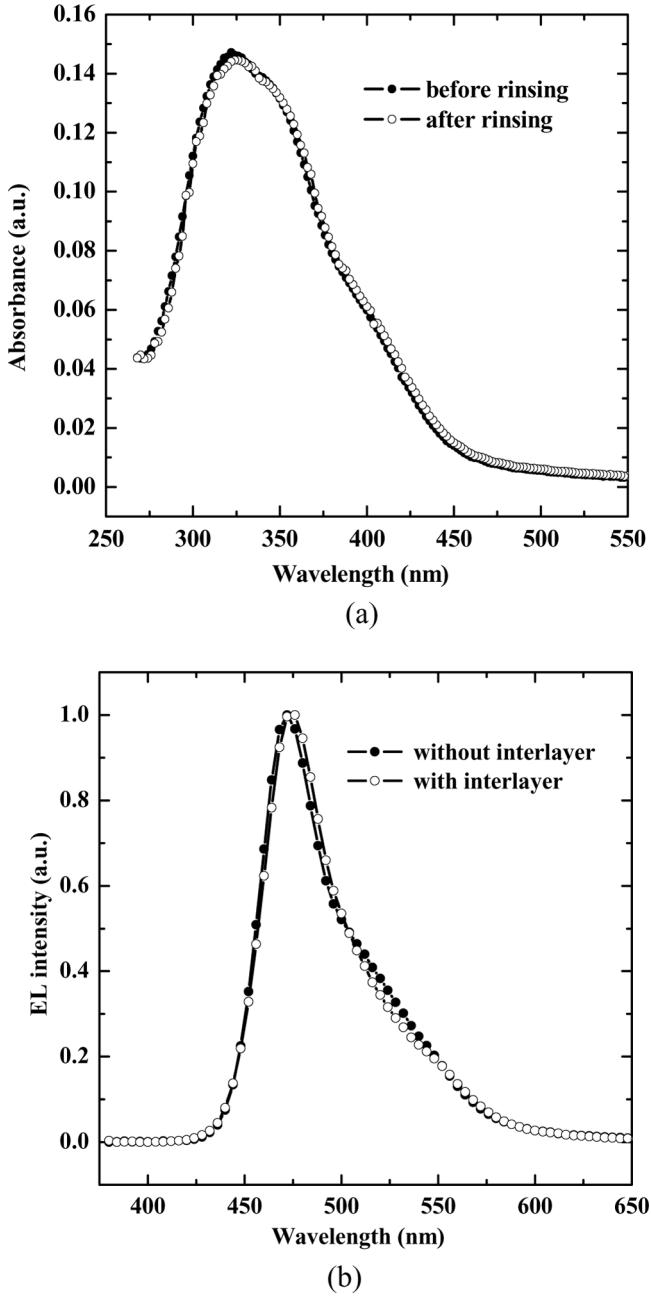

FIGURE 2 (a) UV-vis spectra of PDA-Si film before and after rinsing by toluene and (b) EL spectra from devices with and without an interlayer.

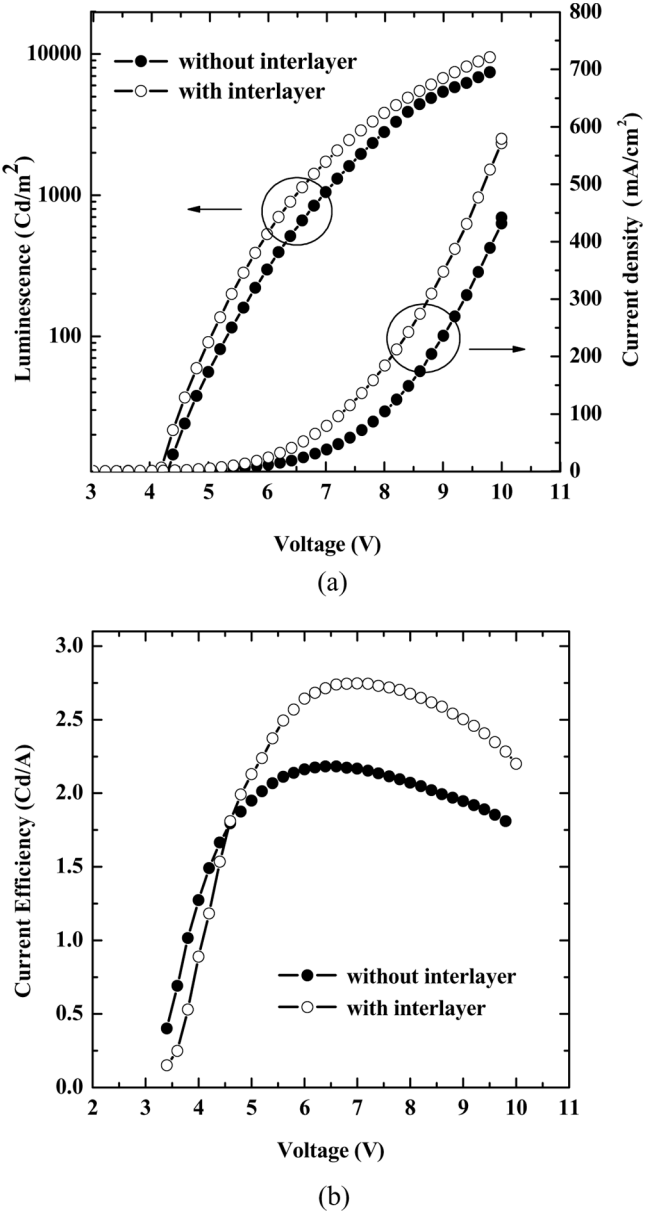

FIGURE 3 (a) Current-voltage-luminescence (I-V-L) and (b) current efficiency-voltage characteristics of the PLED.

indicating the surface uniformity of PDA-Si film is not changed after rinsing. Based on the results from the optical absorption measurement and morphological study, devices were fabricated without dissolving the interlayer employing toluene as suitable solvents for emissive polymer. Figure 2(b) shows EL spectra with and without interlayer. As can be seen, similar spectra were obtained and there exists the blue emission centered at around 474 nm, which comes from emitting polymer PF not from an interlayer material. The EL characteristics of the present PLEDs are shown in Figures 3(a) and 3(b) for current-voltage-luminescence (I-V-L) and current efficiency-voltage, respectively. Figure 3(a) shows that the device with interlayer of PDA-Si exhibits comparable turn-on voltage and more luminescence than that without interlayer. Similarly, the current efficiency is also greatly increased due to the introduction of the PDA-Si layer as shown in Figure 3(b). The device containing interlayer shows over 30% greater current efficiency compared to that without interlayer at the same voltage.

In summary, the high performance PLEDs containing interlayer have been successfully developed by inserting of PDA-Si layer between PEDT:PSS and EML. Since PDA-Si layer has a heavily cross-linked siloxane networking structure, the highly impervious interlayer can be fabricated without severe morphological defects due to spin coating of next EML. The device with PDA-Si layer shows improved device performances in luminescence and current efficiency and these enhancements are attributed to the electron and exciton blocking ability of PDA-Si layer. We believe that this approach can be simply extended to other layer fabrications to make multilayered PLEDs.

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