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Operation voltage behavior of organic light emitting diodes with polymeric buffer layers doped by weak electron acceptor

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ABSTRACT

We present polymeric buffer materials based on poly[2,7-(9,9-dioctyl-fluorene)-co-(1,4-phenylene-((4-sec-butylphenyl)imino)-1,4-phenylene)] (TFB) for highly efficient solution processed organic light emitting diodes (OLEDs). Doped TFB with 9,10-dicyanoanthracene, a weak electron acceptor results in significant improvement of current flow and driving voltage. Maximum current- and power-efficiency value of 12.6 cd/A and 18.1 lm/W are demonstrated from phosphorescent red OLEDs with this doped polymeric anode buffer system.

1. Introduction

A uniform and robust polymer-based hole injection layer (HIL) could be formed by spin-casting process in an ambient air condition. From this approach, the rough surface of indium tin oxide (ITO) could be covered by this polymer-based HIL which plays an important role as a buffer layer. But, the buffer material such as poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) is strongly acidic and hygroscopic which gives failure modes in polymer light emitting diodes [1–3]. Thus, an introduction of a copolymer such as poly[9,9-dioctylfluorene-co-N,N-di(phenyl)-N,N-di(3-carboethoxyphenyl)-benzidine] (BFE) and poly[2,7-(9,9-dioctylfluorene)-co-(1,4-phenylene-((4-sec-butylphenyl)imino)-1,4-phenylene)] (TFB) was suggested as an alternative methodology to improve the device stability [1,4–6]. However, the utilization of such kinds of buffered HIL polymers resulted in high thickness sensitivity plausibly due to their low conductivity. Hence, we tried to introduce an electron acceptor to control the conductivity of the polymers. But, there have been limited reports about soluble acceptor due to their low solubility. Moreover, the electron acceptors with very high electron affinity (>5.0 eV) [e.g. tetrafluoro-tetracyanoquinodimethane (F4-TCNQ), 1,4,5,8,9,11-hexaazatriphenylene-hexacarbonitrile (HAT-CN)] normally show very low solubility [7–10]. However, there have been some reports which realized dramatically reduced operating voltage although the p-dopant has relatively weak accepting power, or hole transporting material has very high ionization potential [11–13]. Thus, we tried to utilize a relatively weak electron acceptor like 9,10-dicyanoanthracene (DCA) because it shows relatively high solubility. Meanwhile, DCA molecule which has relatively low electron affinity (~3.5 eV) was performed as a weak electron acceptor as a trapping agent which reduces a current level of polymer such as BFE [14], while it acted as a p-dopant which enhances a current level of the polymer such as TFB.

In the present paper, we report good current flow and operating voltage behaviors of red phosphorescent organic light emitting diodes (OLEDs) made with soluble TFB polymer. DCA was used as a p-doping material in such polymeric buffer layer although it is much weaker electron acceptor compared to F4-TCNQ or HAT-CN. We also investigated the energetic changes of those materials upon doping by ultraviolet photoelectron spectroscopy (UPS) experiments.

2. Experimental details

2.1. Materials

PEDOT:PSS (Baytron P CH8000, H. C. Starck) and TFB as a HIL and/or hole transport layer (HTL), DCA as an electron acceptor in HIL and/or HTL, bis(10-hydroxybenzo[h]quinolinato)beryllium ($Bebq_2$) as a red host in emitting layer (EML) as well as an electron transporting layer, bis(2-phenylquinoline)(acetyl-acetonate)iridium (III) [$Ir(2\text{-}phq)_2(acac)$] as a red dopant in EML, lithium fluoride (LiF) as an electron injection layer, aluminum (Al) as a cathode layer, were purchased from commercial suppliers and were used without purification.

2.2. Device fabrication

To fabricate OLED devices, clean glass substrates precoated with ITO layer were used to investigate bottom emission properties. Line patterns of anode material and organic insulating material for confinement of the aperture area were formed on glass by photo-lithography process. The ITO glasses were cleaned by sonification in an isopropyl alcohol and acetone, rinsed in deionized water, and finally irradiated in a UV-ozone

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chamber. Aqueous PEDOT: PSS and TFB solution in toluene were spun-coated and cured for 10 min at 90 °C in an oven. All spin-coating processes were performed at room temperature in the glove box. For doping of TFB polymer, we added DCA solution in 1,2-dicholoroethane (DCE) into TFB solution in toluene. All the other organic materials were deposited by the vacuum evaporation technique under a pressure of ~1.3 × 10^{-5} Pa. The deposition rate of organic layers was about 1 Å/s. Then, LiF and Al were deposited in another vacuum deposition system without breaking vacuum. Deposition rates of LiF, MoO_3 (molybdenum trioxide), and Al were 0.1, 0.1, and 5 ~ 10 Å/s, respectively.

2.3. Interface analysis

The changes in electronic structures and the energy level alignment at each interface were investigated using in situ UPS experiments [15,16]. The UPS measurements were performed using a hemispherical electron energy analyzer and a He I ultraviolet source ($\hbar\omega = 21.2$ eV) without monochromator. UPS spectra were obtained with a sample bias of −10 V for secondary electron cut-off region and highest occupied molecular orbital (HOMO) region spectra, respectively.

2.4. Measurements

The current density–voltage (J–V) and luminance–voltage (L–V) data of OLEDs were measured by Keithley SMU 238 and Minolta CS-100A, respectively. The OLED area was 4 mm^2 for all the samples studied in this work. Electroluminescence spectra and CIE coordinates were obtained using a Minolta CS-1000A spectroradiometer.

3. Results and discussion

In order to formulate a homogeneous solution, we added DCA solution in DCE into TFB solution in toluene and stirred for several hours. The resultant solution was spun-coated after microfiltration. The $bebq_2$ and Ir(2-phq)$_2$(acac) were selected as host and dopant materials, respectively. The TFB has a HOMO energy at about 5.3 eV (measured by cyclic voltammetry) and has a strong hole transporting characteristic [5]. The lowest unoccupied molecular orbital (LUMO) energy level of DCA calculated from the UV–visible absorption spectrum was about 3.5 eV, indicating that there is probably no or very little p-doping effect on TFB, i.e. DCA cannot capture electrons from TFB ground state, and thus should stay neutral in TFB layer. Nevertheless, the hole only devices with DCA-doped TFB layer showed enhanced hole current level compared to that prepared with non-doped TFB layer as shown in Fig. 1. This is very curious behavior because the hole current level was reduced when we doped the BFE polymer by same dopant. We thought that the reason of reduced current after doping of BFE polymer by DCA molecule was originated from the CT interaction in between hole carriers with partial negative charge on the nitrogen atom of cyano group [14].

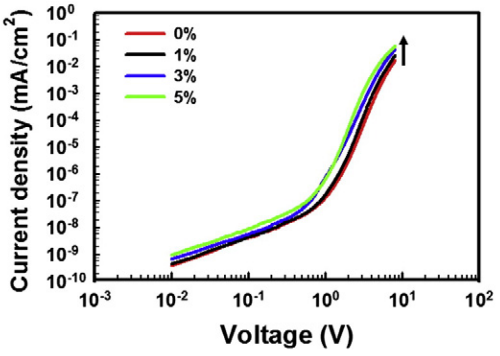

Fig. 1. Hole only devices with pure TFB and doped TFB layers: ITO/PEDOT:PSS(40 nm)/TFB:DCA (90 nm, 0,1,3,5%)/MoO_3 (10 nm)/Al(100 nm).

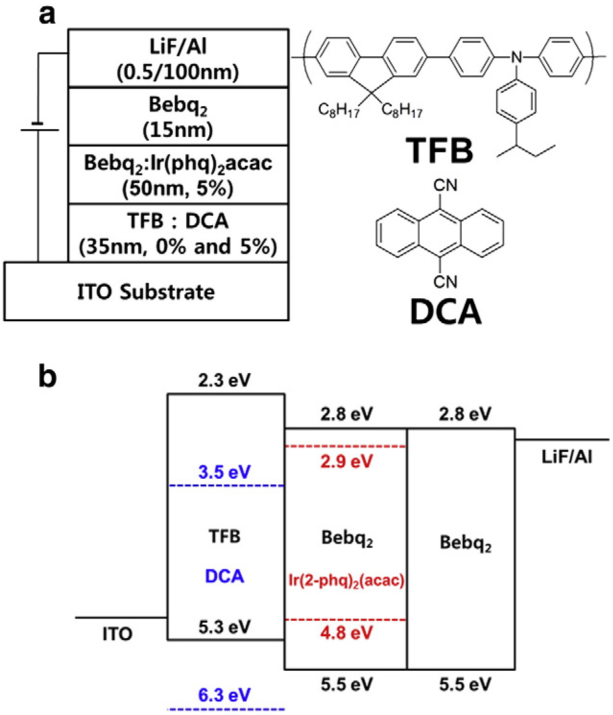

Fig. 2. (a) The device structure and (b) the energy band diagram of red phosphorescent OLED.

To verify the enhanced charge transport properties of TFB upon p-doping by DCA, we prepared full device as shown in Fig. 2. According to this device structure, electrons injected from the cathode move freely to the EML as the $bebq_2$ has LUMO energy level at 2.8 eV. A good electron transporting and a negligible electron trapping by dopant molecules are expected due to the very close LUMO level to that of host (2.9 eV) compared to that of dopant molecule

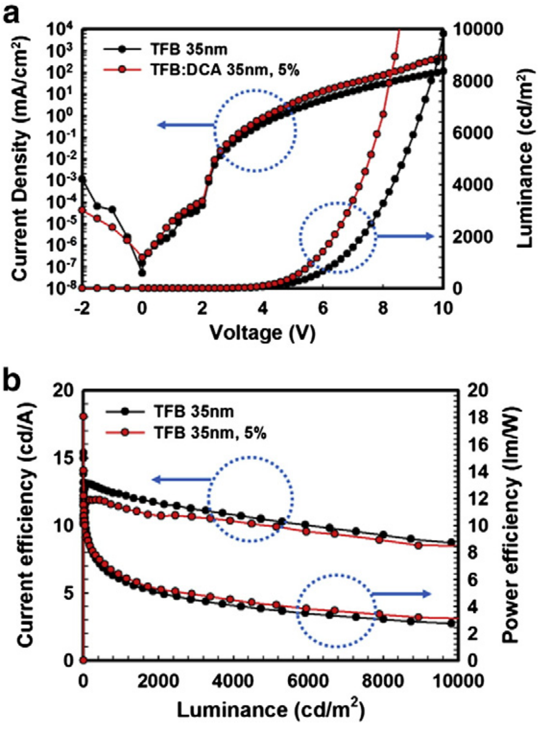

Fig. 3. (a) J–V vs. L–V characteristics and (b) Efficiency vs. L characteristics of fabricated OLED device A and B.