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Lithium salt doped conjugated polymers as electron transporting materials for highly efficient blue polymer light-emitting diodes

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Highly efficient blue polymer light-emitting diodes (PLEDs) are fabricated using a conjugated polymer, poly[9,9-bis(2-(2-(2-diethanol-amino-ethoxy) ethoxy) ethyl) fluorene-*alt*-4, 4′-phenylether] as an electron transporting layer (ETL). It was found that the performance of these blue-emitting devices could be greatly improved if the ETL was doped with LiF or Li_2CO_3 salts. A bis[[(4,6-di-fluorophenyl)-pyridinato-N, C^2] (picolinate) Ir(III) (FIrpic) complex based blue phosphorescent PLED exhibited a maximum luminance efficiency of 20.3 cd/A with a luminance of 1600 cd/m^2 at the current density of 7.9 mA/cm^2 and drive voltage of 8.0 V. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3050452]

The research in polymer light-emitting diodes (PLEDs) is one of the most successful areas among organic electronics, where significant improvements in efficiency, brightness, and drive voltage have all been realized to lead to highly efficient full-color and white-light PLEDs.[1] In order to achieve high efficiency PLEDs, efficient and balanced electron and hole injection and transport from cathode and anode is essential. However, most of the organic semiconductors possess lower carrier concentration and mobility than those of inorganic semiconductors.[2] In order to overcome these deficiencies, chemical doping has been adapted in small molecule-based organic light-emitting diodes (OLEDs) to enhance charge transport. It was proved to be an effective way to lower the operating voltages.[3] For solution processed PLEDs, although the *p*-doped poly(3,4-ethylene-dioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) has been widely used to improve hole injection and transport in devices, the development of *n*-doped materials for efficient electron injection and transport remains to be a significant challenge due to a lack of suitable hosts and dopants.

In this letter, we report highly efficient blue-emitting PLEDs based on a conjugated polymer, poly[9,9-bis(2-(2-(2-diethanol-amino-ethoxy) ethoxy) ethyl) fluorene-*alt*-4, 4′-phenylether] (PDFPE), which can be dissolved in alcohol and is a good electron injecting material for solution processable PLEDs (Scheme 1). PDFPE comprises a conjugated main chain and surfactantlike side chains. The polar ethanolamino groups on PDFPE's side chains not only could render the polymer with good solubility in polar solvents (such as methanol) for multilayer solution processing, but also should endow it with good electron injecting ability from high work-function metal cathodes (such as Ag and Au).[4] The PDFPE was obtained by treating a precursor conjugated polymer with excess amount of diethanolamine in a post-functionalization reaction, where the precursor conjugated polymer was synthesized by Suzuki cross-coupling reaction.[4,5] Due to confined conjugation length, PDFPE has a very large band gap (around 3.3 eV). The energy level of the

polymer was investigated by cyclic voltammetry.[5] The highest occupied molecular orbital (HOMO) energy level of PDFPE is calculated to be −5.9 eV by using the ferrocene value of −4.8 eV below the vacuum level (E_{FOC}=0.12 V versus Ag/Ag$^+$) as the internal standard. The lowest unoccupied molecular orbital energy level (−2.6 eV) of PDFPE can only be estimated from its optical band gap and HOMO energy.

The alcohol soluble feature of PDFPE prevents interfacial mixing between the emissive layer and the adjacent electron injection layer, which is one of the most challenging problems in fabricating multilayer PLEDs by solution process. Moreover, the unique solubility of PDFPE also offers the possibility to enhance electron injection and conduction by doping it with water-soluble alkali or alkaline earth metal salts, which have been used as *n*-type dopants in OLEDs.[6] Two lithium salts (LiF and Li_2CO_3) were chosen as dopants for PDFPE to improve its electron transporting ability in PLEDs. Atomic force microscopy (AFM) was used to examine the surface quality of the doped PDFPE layer. The main concern for the doped layer is the possible crystallization of the salts that may lead to phase separation and create rough surface features. As shown in Fig. 1, the Li_2CO_3 doped PDFPE films exhibit only a slightly rougher morphology (rms=1.2 nm) than that of the undoped PDFPE film (rms=0.8 nm), suggesting Li_2CO_3 was well dispersed in PDFPE film. However, the surface morphology of LiF doped PDFPE film is quite rough (rms=2.0 nm), possibly due to some aggregate formation on the surface. It appears that Li_2CO_3
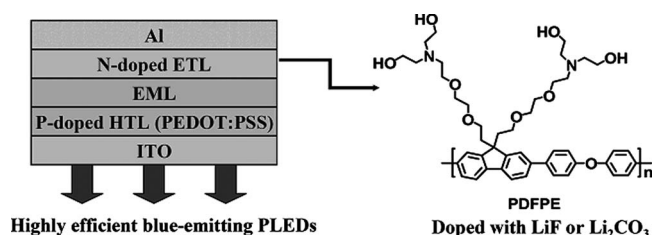
SCHEME 1. Chemical structure of PDFPE and schematic of the device structure based on the doped PDFPE ETL.

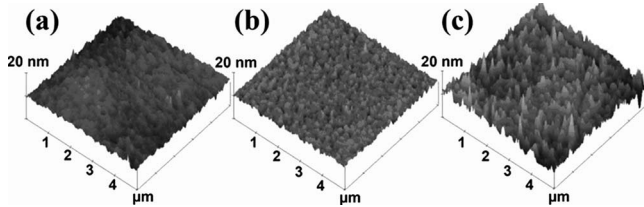[a]Author to whom correspondence should be addressed. Electronic mail: ajen@u.washington.edu.

FIG. 1. AFM images (5×5 μm^2 scale) of the PDFPE films spin-coated on top of the emissive layer. (a) PDFPE, (b) PDFPE doped with 5% Li$_2$CO$_3$, and (c) PDFPE doped with 5% LiF.

doped PDFPE film is a better choice for use as the electron transporting layer (ETL) for PLEDs.

The combined electron injecting and transporting ability of the undoped and doped PDFPE ETLs was evaluated in the typical bis[(4,6-di-fluorophenyl)-pyridinato-N, C^2] (picolinate) Ir(III) (FIrpic) based blue-emitting PLEDs with the configuration of indium tin oxide (ITO)/PEDOT: PSS (H. C. Starck, 35 nm)/FIrpic(7 wt %):PVK:OXD-7(30 wt %) (70 nm)/ETL (30 nm)/Al (100 nm),[7] where undoped PDFPE or doped PDFPE (with 5% LiF or Li$_2$CO$_3$) cast from the methanol/water (4:1) mixed solvent is used as the ETL. All the devices were fabricated and characterized according to the routine procedure described earlier.[4,5] An analogous device with no ETL exhibited very poor device performance and there was almost no light detected due to the poor elec-
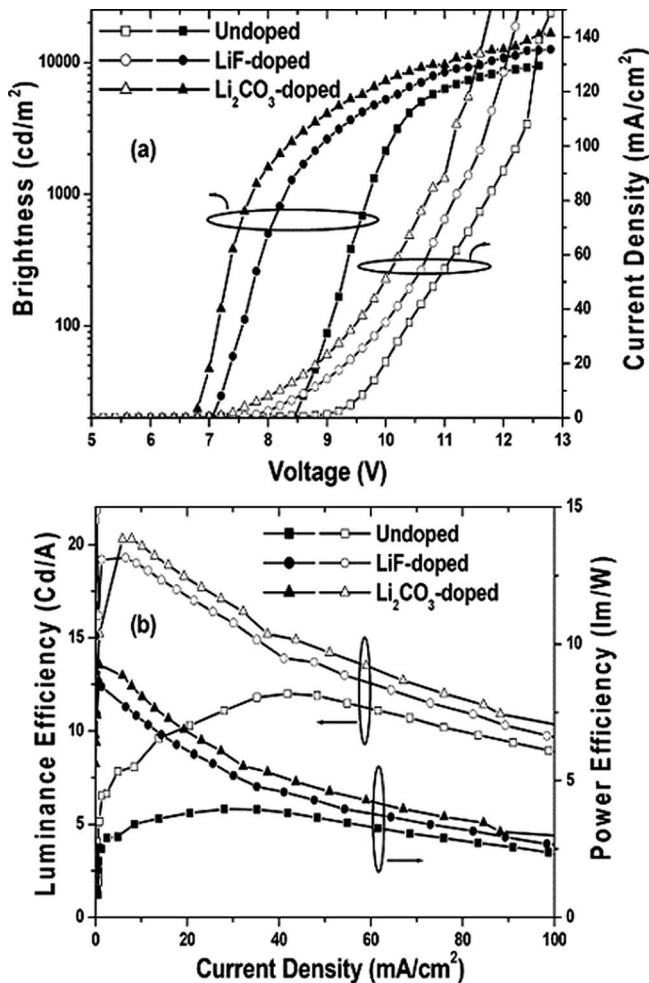

FIG. 2. *J-L-V* characteristics (a) and LE and PE vs current density characteristics (b) of the devices with different ETLs.
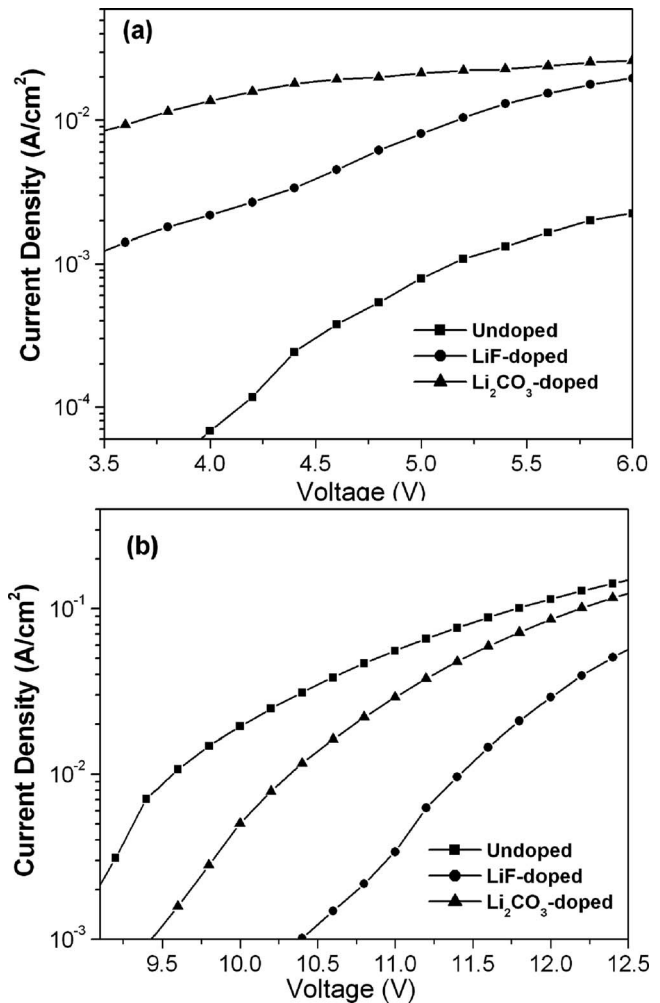

FIG. 3. Current density vs driving voltage characteristics of the single carrier devices: (a) electron-dominated device and (b) hole-dominated device.

tron injection from Al cathode. By using PDFPE as an ETL, the device's performance was greatly improved. The device with undoped PDFPE as an ETL showed a turn-on voltage (corresponding to a brightness of 1 cd/m^2) at $\sim$8.2 V, a maximum external quantum efficiency (EQE) of 5.23%, and a luminance efficiency (LE) of 11.8 cd/A at a luminance of 4150 cd/m^2, current density of 35.2 mA/cm^2, and drive voltage of 10.4 V. Interestingly, the performance of devices can be further improved by using LiF or Li$_2$CO$_3$ doped ETL. Under the same driving voltage, the devices with a lithium salt doped ETL showed a significantly enhanced current density and brightness compared to that of the undoped device [Fig. 2(a)]. In spite of the rough morphology, the device with a LiF doped ETL showed a decreased turn-on voltage to 6.8 V, while the maximum EQE increased to 8.59% and a LE of 19.3 cd/A at a luminance of 1280 cd/m^2, current density of 6.6 mA/cm^2, and drive voltage of 8.4 V. With the Li$_2$CO$_3$ doped ETL, the turn-on voltage further decreased to 6.4 V and the EQE increased to 9.03% with a LE of 20.3 cd/A at a luminance of 1600 cd/m^2, current density of 7.9 mA/cm^2, and drive voltage of 8.0 V. Moreover, the power efficiency (PE) of the devices also showed a significant improvement upon doping [Fig. 2(b)]. The maximum PE improved from 4.0 lm/W for the undoped device to 8.6 and 9.2 lm/W for the LiF and Li$_2$CO$_3$ doped devices, respectively. These results

are comparable to those reported for the state-of-the-art blue-emitting phosphorescent PLEDs.[7]

In order to understand the reason for the remarkable improvements in the device performance with a lithium salt doped ETL, the electron-dominated device ITO/Al (100 nm)/ PVK:OXD-7 (30 wt %) (70 nm)/ETL (30 nm)/Ba (4 nm)/Al (100 nm) and the hole-dominated device ITO/PEDOT (30 nm)/PVK:OXD-7 (30 wt %) (70 nm)/ETL (30 nm)/Au (100 nm) were fabricated. As shown in Fig. 3(a), in the electron-dominated device, the electron current densities of the devices with a LiF or Li_2CO_3 doped ETL are much higher than that of the device with an undoped ETL. This means the electron injecting/transporting ability of PDFPE is indeed significantly enhanced upon doping. More interestingly, the results of the hole-dominated device clearly showed that the hole-current density of the PDFPE ETLs significantly decreased upon doping. Therefore, all these results clearly indicate that LiF or Li_2CO_3 doped PDFPE ETL possesses enhanced electron injection/transporting ability compared to that of undoped PDFPE ETL, resulting in much improved device performance. These results are comparable to those of the recently reported LiF doped tris(8-hydroxyquinoline) aluminum (Alq_3) ETL where the conductivity of the Alq_3 layer can be significantly improved by the formation of Alq_3 radical anion.[6] Similar results have also been demonstrated in a very recently published article that the Cs_2CO_3 doped polyethylene oxide can be used as a highly efficient hole-blocking/ETL in PLEDs, where the Cs_2CO_3-rich region in the blend films offers a good channel for electron transporting.[8] It is possible that lithium salts exhibit similar unique electron injecting/transporting properties such as Cs_2CO_3, which can greatly enhance the electron injecting/transporting abilities of the PDFPE ETL. The detailed mechanism for the lithium salt doped PDFPE ETL is not clear and it warrants further studies to clarify this.

In summary, the electron transporting ability of the PDFPE ETL can be significantly improved by doping with lithium salts. By using Li_2CO_3 doped PDFPE as an ETL and *p*-doped PEDOT:PSS as a hole transporting layer, a highly efficient blue-emitting phosphorescent PLED with a maximum LE of 20.3 cd/A and PE of 9.2 lm/W has been realized. Our results offer a new strategy to realize novel *n*-type doping in PLEDs, which can be applied to most of the newly developed water-soluble conjugated polymer electron-injecting materials.[9]

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