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An optimized *p*-doped hole injection structure to improve the performance of organic light emitting diodes

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ABSTRACT

Organic light emitting diodes (OLEDs) have been fabricated using various *p*-doped hole injection structures based on MoO_3 doped 4,4′-*N*,*N*′-dicarbazole-biphenyl (CBP:MoO_3) and 2,3,5,6-Tetrafluoro-7,7,8,8,-tetracyanoquinodimethane doped 4,4-bis[*N*-1-naphthyl-*N*-phenylamino]biphenyl (NPB:F_4-TCNQ). It is found that the hole injection from indium tin oxide (ITO) to CBP:MoO_3 is more efficient than that from ITO to NPB:F_4-TCNQ, although the CBP:MoO_3 is much less conductive than the NPB:F_4-TCNQ. In addition, the CBP:MoO_3 is helpful to block F_4-TCNQ from diffusing into the emissive zone and thereby relieve the exciton quenching induced by organic *p*-dopant. Thus, the improved hole injection structure of ITO/10 nm CBP:MoO_3/5 nm NPB:F_4-TCNQ/5 nm CBP:MoO_3 is provided to diminish the hole and exciton losses, greatly increasing the device performance than the other hole injection structures. The current research is believed beneficial for the development of OLEDs based on a *p-i-n* junction.

1. Introduction

During the past three decades, organic light emitting diodes (OLEDs) have gained enormous attention across the world [1–12], due to their appealing merits of being self-emissive, lightweight, and easily integrated with the flexible substrates. As of now, OLEDs have been widely recognized as one of the leading technologies to underlie the future markets of flat-panel displays and lighting. Whereas, in order to compete well with their counterpart inorganic LEDs, the architecture designs for making OLEDs more power-efficient are highly solicited.

The internal quantum efficiency and Ohmic loss are the two key factors to determine the power efficiencies of OLEDs. By using organometallic phosphorescent dyes or thermally activated delayed fluorescent materials, nearly 100% internal quantum efficiencies can be well achieved even at high luminance like 1000 cd/m^2, corresponding to 20–30% external quantum efficiencies for OLEDs without light outcoupling decoration [13–17]. The Ohmic loss dominates the working voltage of device required for giving certain luminance, including hole and electron losses. During the past two decades, the *p-i-n* architecture of OLEDs has been well developed, which can markedly reduce the Ohmic loss and thereby obtain low working voltage of device. The electrical doping of organic materials can bring two following benefits [18]. Firstly, the *p*-type doping of hole transport layer (HTL) or the *n*-type doping of electron transport layer (ETL) can increase the conductivity of organic material, thereby reducing transport loss and voltage drop across thin film. Secondly, the electrically doped organic materials are helpful to form Ohmic contacts with electrodes, thereby decreasing the injection losses for holes and electrons. More importantly, the *p-i-n* OLEDs have demonstrated long lifetimes at practical luminance [19,20], meeting the requirement of modern flat-panel display industry. Therefore, it is worth doing more deep investigations on the *p-i-n* OLEDs.

The thermodynamic limit (i.e., the minimum working voltage required for achieving given luminance) of OLEDs can be estimated by a generalized equation based on the blackbody radiation for solids not in equilibrium [21]. For example, the theoretical working voltage of green OLEDs necessary to reach luminance of 100 cd/m^2 reaches 1.95 V, ~0.45 V below the smallest ones obtained experimentally [22]. Moreover, at very high brightness (of 10,000 cd/m^2 and more) the working voltages with several volts above the physical limit are needed in the state-of-art OLEDs even for *p-i-n* junction [21]. Clearly, there is spacious room to improve the performance of current OLEDs via reducing the energy losses.

Scheme 1 depicts the energy losses resulting from the adoption of a single *p*-doped HTL. The energy loss of hole injection from top Al anode to *p*-doped HTL (Type I energy loss) can be decreased by using a *p*-doped HTL with lower-lying highest occupied molecular orbital (HOMO) level [23]. Nevertheless, the energy loss of hole injection from bottom indium tin oxide (ITO) anode to *p*-doped HTL has to be studied yet. The energy loss due to transport barrier from *p*-doped HTL to

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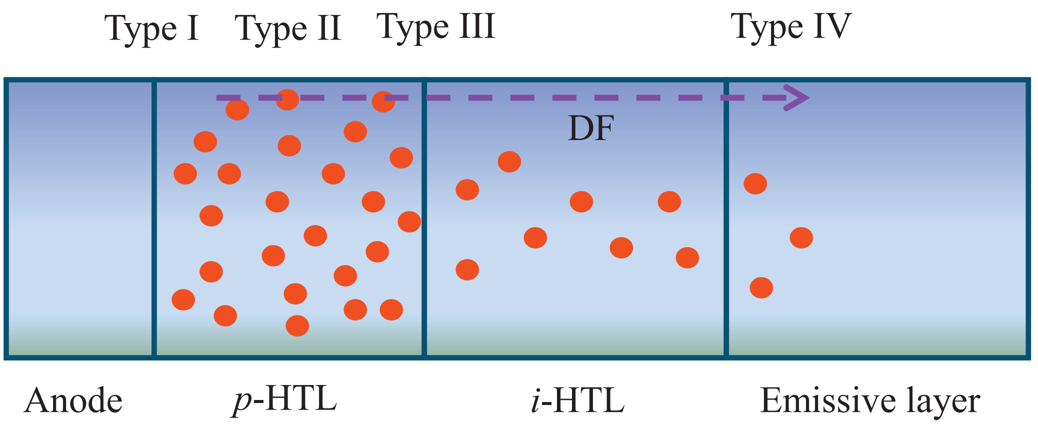

Scheme 1. The schematic diagram to illustrate four types of energy losses brought by a single *p*-doped HTL. The *p*- and *i*-HTL represent *p*-doped and intrinsic hole transport layers, respectively. The red circles denote *p*-dopants. The DF stands for the dopant diffusion. Type I is the hole loss incurred in the hole injection from anode to *p*-doped HTL; Type II is the hole loss incurred in the hole transport through the *p*-doped HTL; Type III is the hole loss due to transport barrier from *p*-doped HTL to *i*-HTL; Type IV is the exciton loss due to *p*-dopant diffusion-induced exciton quenching. Types I–III energy losses make up the Ohmic loss of hole current.

undoped HTL (Type III energy loss) may be alleviated by using a *p*-doped HTL with lower-lying HOMO level [24–27]. The energy loss of hole transport across *p*-doped HTL (Type II energy loss) can be reduced via applying higher-conductivity *p*-doped HTL with higher-lying HOMO level [18,25,28]. Although organic *p*-dopants, e.g., 4,4-bis[*N*-1-naphthyl-*N*-phenylamino]biphenyl (F_4-TCNQ), offer improved *p*-doping efficiency than inorganic ones [29,30], their tendency to penetrate into other layers of device will alter the optical and electrical properties of thin films, such as quenching some excitons in the emissive layer (Type IV energy loss) [31]. The chemical modification of organic *p*-dopant can lower the diffusion tendency but markedly reduce the *p*-doping effect at the same time [31]. The suppression of organic *p*-dopant diffusion via designing *p*-doped hole injection structure has not been explored so far.

Here, various *p*-doped hole injection structures have been constructed based on MoO_3 doped 4,4′-*N*,*N*′-dicarbazole-biphenyl (CBP:MoO_3) and F_4-TCNQ doped 4,4-bis[*N*-1-naphthyl-*N*-phenylamino]biphenyl (NPB:F_4-TCNQ). It is found that the combination of ITO/10 nm CBP:MoO_3/5 nm NPB:F_4-TCNQ/5 nm CBP:MoO_3 is an optimal design to reduce the four types of energy losses simultaneously and thereby improve the device performance.

2. Experimental details

The glass substrates coated with 100 nm thick ITO thin film were commercially available with a sheet resistance of 10 Ω per square. After cleaned in acetone, alcohol, and de-ionized water sequentially by an ultrasonic horn, the patterned ITO substrates were blown dry by a nitrogen gun and then treated in UV-ozone for 15 min before the usage. The tris(8-quinolinolato)aluminum (Alq3), CBP, NPB, F_4-TCNQ, and bathocuproine (BCP) with purities of > 99.5% were purchased from Jilin Optical and Electronic Materials Co., Ltd.; The Li_2CO_3 and MoO_3 with purities of > 99.99% were obtained from Sigma-Aldrich Company. All the materials were used as received. The weight ratios for *p*- and *n*-doping are used. All the electrically doped layers were made by the co-evaporation. The base pressure of the device fabrication by means of the thermal evaporation was 5.0×10^{-4} Pa.

In order to optimize the efficiency of hole injection from ITO to *p*-doped HTL, two hole-only devices were designed as follows:

HO-Device 1: ITO/16:1 NPB:F_4-TCNQ 20 nm/NPB 100 nm/MoO_3 10 nm/Al;

HO-Device 2: ITO/2:1 CBP:MoO_3 10 nm/16:1 NPB:F_4-TCNQ 10 nm/NPB 100 nm/MoO_3 10 nm/Al;

In the experiment, seven *p-i-n* OLEDs were fabricated as follows:

Device 1: ITO/16:1 NPB:F_4-TCNQ 20 nm/NPB 60 nm/Alq3 55 nm/4:1 BCP:Li_2CO_3 5 nm/Al;

Device 2: ITO/2:1 CBP:MoO_3 10 nm/16:1 NPB:F_4-TCNQ 10 nm/NPB 60 nm/Alq3 55 nm/4:1 BCP:Li_2CO_3 5 nm/Al;

Device 3: ITO/16:1 NPB:F_4-TCNQ 15 nm/2:1 CBP:MoO_3 5 nm/NPB 60 nm/Alq3 55 nm/4:1 BCP:Li_2CO_3 5 nm/Al;

Device 4: ITO/2:1 CBP:MoO_3 10 nm/16:1 NPB:F_4-TCNQ 10 nm/NPB 60 nm/Alq3 50 nm/4:1 BCP:Li_2CO_3 10 nm/Al;

Device 5: ITO/16:1 NPB:F_4-TCNQ 15 nm/2:1 CBP:MoO_3 5 nm/NPB 60 nm/Alq3 50 nm/4:1 BCP:Li_2CO_3 10 nm/Al;

Device 6: ITO/2:1 CBP:MoO_3 10 nm/16:1 NPB:F_4-TCNQ 5 nm/2:1 CBP:MoO_3 5 nm/NPB 60 nm/Alq3 50 nm/4:1 BCP:Li_2CO_3 10 nm/Al;

Device 7: ITO/2:1 CBP:MoO_3 20 nm/NPB 60 nm/Alq3 50 nm/4:1 BCP:Li_2CO_3 10 nm/Al;

Note that, device 6 was designed to use three hybrid-*p*-doped HTLs in attempt to reduce hole and exciton losses relative to all other devices. Each device was repeated four times to verify the reliability of its data.

The current density versus voltage (*J-V*) characteristics and luminance of the devices were measured using a programmable Keithley 2400 sourcemeter and an ST-86LA spot photometer, respectively, under the air condition.

3. Results and discussion

3.1. The improved hole injection from ITO to CBP:MoO_3 than to NPB:F_4-TCNQ

As shown in Fig. 1, HO-device 1 shows decreased *J-V* characteristics than HO-device 2, regardless of the higher conductivity of NPB:F_4-TCNQ than that of CBP:MoO_3 [26,30], indicating that the hole injection from ITO to CBP:MoO_3 is much more efficient than that from ITO to NPB:F_4-TCNQ, consistent with the past observation [23]. At a driving voltage of 3 V, the current density of device 2 is 527.3 mA/cm^2, greater than that (384.0 mA/cm^2) of device 1. *Note that*, the interface between *p*-doped CBP and NPB is thought an Ohmic contact for hole conduction, because the Fermi level alignment makes the offset of HOMO level at this *p*-doped interface ~ 0.2 eV [24–27].