Influence of doping concentration on the dominant injection and transport mechanisms of electrons within Alq$_3$ doped NPB films

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ABSTRACT

In this work, we separately investigated the dependence of electron injection and transport processes on the doping concentration by comparing the current density-voltage (J–V) characteristics of a series of electron-only devices with tris(8-hydroxyquinoline) aluminum (Alq$_3$) doped into N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'-diphenyl-4,4'-diamine (NPB) as transport layer. Here, Alq$_3$ molecules function as electron injection sensitive centers. Experimental results revealed that 0.2 wt% is the optimal doping concentration to facilitate electron injection from hole-block layer into host molecules. With increasing doping concentration, more and more electrons inject directly onto Alq$_3$ molecules while the average distance of Alq$_3$ molecules decreases gradually, thus which accelerate electron hopping between Alq$_3$ molecules. With the help of electroluminescent (EL) spectra, recombination centers of the 0.2 wt% and 0.6 wt% doped EL devices were probed to shift toward cathode and anode, respectively. These results suggested that electron hopping between Alq$_3$ molecules becomes the dominant electron transport mechanism when the doping concentration is higher than 0.6 wt%.

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1. Introduction

Since the first demonstration of efficient organic light-emitting devices (OLEDs) reported by C. W. Tang and co-workers in 1987, the optimization of device structure and the investigation on electroluminescent (EL) mechanisms have attracted great interest throughout the world [1–4]. After >20 years of intense research and development, the efficiencies and brightness of green and red EL devices have basically satisfied the requirements of application [5–8]. However, blue emitting materials possess relatively high energy gaps [9–12], which are generally accompanied by relatively low-lying highest occupied molecular orbital (HOMO) levels or relatively high-lying lowest unoccupied molecular orbital (LUMO) levels, thus the high hole or electron injection barrier [13,14]. Therefore, most blue EL devices possess unbalanced carrier injections and low current density, thus the low recombination probability and brightness. Furthermore, most blue emitting materials transport only holes or electrons, thus causing the very narrow recombination zone and the severe exciton quenching, which is in fact the main reason for the notorious EL efficiency roll-off [15,16].

Previously, we have demonstrated an efficient device design strategy in facilitating the injection of electrons from hole block layer (HBL) into light-emitting layer (EML) by doping tris(8-hydroxyquinoline) aluminum (Alq$_3$) into N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'-diphenyl-4,4'-diamine (NPB) as electron injection sensitizer [17,18]. The presence of Alq$_3$ molecules within EML not only facilitates the injection of electrons from HBL into EML but also stays the transport of holes within EML, thus causing the improved carriers' balance and the wider recombination zone. As a result, bright blue and white electroluminescence with significant enhanced efficiency and suppressed efficiency roll-off was obtained. More interestingly, the doping concentration of Alq$_3$ significantly influenced the injection, transport and distribution of carriers, thus determining the EL spectrum [17]. Based on experimental results, EL processes of these devices were discussed and energy band bending was suggested to interpret the enhanced electron injection. However, the detailed EL mechanisms of these devices, especially the effect of doping concentration on electron injection and transport processes, are not fully understood.

In this work, we investigated in detailed the conversion of dominant injection and transport mechanisms of electrons with the increasing doping concentration. To separately investigate the influence of doping concentration on the injection and transport processes of electrons, two types of electron-only devices with Alq$_3$ doped NPB films as transport layers were designed and fabricated. Experimental results confirmed that Alq$_3$ molecules function as electron injection sensitive centers. To make clear the influence of doping concentration on the recombination center, a series of devices were fabricated by inserting 0.2 nm 4-(Dicyanomethylene)-2-tert-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) film into EML as sensitive layer. With the help of EL spectra, recombination centers of 0.2 wt% and 0.6 wt% doped EL

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devices were probed to shift toward cathode and anode, respectively. This result demonstrated the conversion of dominant electron transport mechanisms from electron transfer between NPB molecules to electron hopping between Alq_3 molecules with increasing doping concentration. In addition, 0.2 wt% was determined to be the optimal doping concentration for Alq_3 molecules to facilitate the injection of electrons from HBL onto NPB molecules, while 0.6 wt% was suggested to be the crucial concentration for the conversion of dominant electron transport mechanisms.

2. Experimental

All the organic materials used in this study were obtained commercially and used as received without further purification. The devices used in this investigation were fabricated by thermal evaporation in vacuum onto ITO coated glass substrates with the sheet resistance of 15 Ω/sq., while the low-pressure oxygen plasma treatment of ITO substrates was performed in a special chamber with the pressure of 10 Pa. Most of the organic layers were deposited with the rate of 0.05 nm/s under high vacuum ($\leq 3 \times 10^{-5}$ Pa), while the 0.2 nm inserted DCJTB layer were deposited with the rate of 0.002 nm/s. The doped layer of each device was prepared by co-evaporating Alq_3 and NPB from two individual sources, and the doping concentration was determined by controlling the evaporation rate of Alq_3. LiF and Al were evaporated in another vacuum chamber ($\leq 8.0 \times 10^{-5}$ Pa) with the rates of 0.01 and 1 nm/s, respectively, without being exposed to the atmosphere. The thickness of these deposited layers and the evaporation rate of individual materials were monitored in vacuum with quartz crystal monitors. The shape of the cathode was defined using a shadow mask during the deposition of Al. The active area of these devices as defined by the overlapping area of the cathode and the anode is 10 mm^2. After fabrication, all the devices were measured immediately in air at room temperature without encapsulation. Current density-voltage characteristics were measured by using a Keithley source measurement unit (Keithley 2400 and Keithley 2000). The EL spectra were measured with a Hitachi F–7000 fluorescence spectrophotometer.

3. Results and discussion

To elucidate the detailed sensitization processes of electron injection in the devices based on Alq_3 doped NPB films, it is necessary to investigate the influence of doping concentration on the injection and transport processes of electrons. As shown in Fig. 1, we designed two types of electron-only devices with the structures of ITO/BCP(20 nm)/NPB(35 nm)/Alq_3(x wt%): NPB(5 nm)/BCP (20 nm)/LiF (1 nm)/Al(100 nm) (type I) and ITO/BCP(20 nm)/Alq_3(y wt%): NPB(50 nm)/NPB (10 nm)/BCP(20 nm)/LiF (1 nm)/Al(100 nm) (type II), respectively. Where anode is ITO (indium-tin-oxide) without low-pressure oxygen plasma treatment, cathode is LiF/Al. BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) functions as hole

blocker and electron transporter at anode and cathode sides, respectively. Therefore, only electrons are expected to transport in these devices [19,20]. In type I devices, only 5 nm NPB film near the electron transport layer was doped with Alq_3 in order to depress the influence of electron transport discrepancy on electron current; therefore, these devices exhibit the influence of doping concentration on electron injection characteristic. On the other hand, 10 nm neat NPB layer was deposited upon the 50 nm Alq_3 doped NPB layer in type II devices in order to ensure the uniform electron injection; therefore, these devices exhibit the influence of doping concentration on electron transport characteristic.

Nine type I devices with x equal to 0, 0.1, 0.2, 0.4, 0.6 0.8, 1.0, 1.5 and 2.0, respectively, were fabricated and compared. Current density-voltage (J-V) characteristics of these devices were measured and shown in Fig. 2. In this case, electron injection dependence on doping concentration is very complicated. With increasing doping concentration, electron injection increases firstly and then decreases to the lowest point at 0.4 wt%. Interestingly, electron injection increases gradually again when the doping concentration is higher than 0.6 wt%. On the other hand, nine type II devices with y equal to 0, 0.1, 0.2, 0.4, 0.6 0.8, 1.0, 1.5 and 2.0, respectively, were fabricated and compared. With increasing doping concentration, as shown in Fig. 3, electron transport in Alq_3 doped NPB layer decreases firstly and then increases gradually when the doping concentration is higher than 0.6 wt%. That is to say, 0.6 wt% is the crucial concentration for both injection and transport of electrons in Alq_3 doped NPB layer. In addition, it is worth to note that the increase of electron current tends to saturation when the doping concentration of Alq_3 is higher than 0.8 wt%. To ensure the validity of these data, we repeated these experiments twice and similar results were obtained each time. These results demonstrate the significant influence of doping concentration on the injection and transport processes of electrons, and the detailed mechanisms will be discussed separately in follow.

To interpret the significant dependence of electron injection and transport on the doping concentration of Alq_3, the detailed injection and transport processes of electrons in these electron-only devices were discussed based on theory and experimental results. As shown in Fig. 4, electrons inject firstly from aluminum cathode into the doped layer via BCP layer, which functions as electron injection layer. Theoretically speaking, some electrons will be trapped directly by Alq_3 molecules (process 1) because the LUMO level of Alq_3 is 0.8 eV lower than that of NPB, which decreases the necessary field or voltage [21]. In a previous paper, electron transfer from the LUMO level of BCP to that of NPB (process 2) has been experimentally demonstrated to be possible [17]. In this case, the accumulation of electrons within BCP
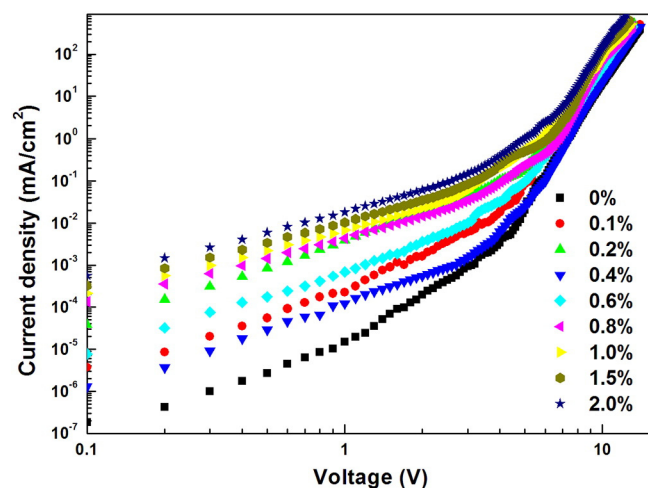

Al 100 nm	Al 100 nm
LiF 1 nm	LiF 1 nm
BCP 20 nm	BCP 20 nm
Alq$_3$:NPB 5 nm	NPB 10 nm
NPB 35 nm	Alq$_3$:NPB 50 nm
BCP 20 nm	BCP 20 nm
ITO	ITO
I	II

Fig. 1. Structures of the devices used in this work.

Fig. 2. Current density-voltage characteristics of type I devices with different doping concentrations of Alq_3.