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Bright electroluminescent devices with tunable spectra obtained by strictly controlling the doping concentration of electron injection sensitizer

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ABSTRACT

In this paper, we report an efficient strategy to design bright blue and blue–green electroluminescent (EL) devices by slightly doping tris(8-hydroxyquinoline) aluminum (Alq_3) into N,N′-diphenyl-N,N′-bis(1-naphthyl)-1,1′-diphenyl-4,4′-diamine (NPB) as the light-emitting layer (EML). Bright EL devices with tunable spectra were obtained by strictly controlling the doping concentration of Alq_3. With increasing current density, EL efficiencies of these devices increase first and then decrease gradually after reaching the maximum. Analyzing the current density–voltage ($J-V$) characteristics of hole-only and electron-only devices, we found the presence of Alq_3 molecules in EML not only facilitates the injection of electrons from hole block layer (HBL) into EML but also stays the transport of holes in EML, thus causing significant enhancement of EL efficiency and brightness due to improved carriers balance and broadening of recombination zone. More interestingly, the doping concentration of Alq_3 strongly influences the injection and transport processes of electrons, thus determining the distribution of holes and electrons on NPB and Alq_3 molecules.

1. Introduction

Organic light-emitting devices (OLEDs) have attracted great interest throughout the world owing to their potential application in the next generation of full-color flat panel displays [1–3]. For commercial application, the three primary colors of blue, green, and red are basically required. On the other hand, many research groups have paid their attention to the development of blue–green, yellow, and orange electroluminescence (EL), which can be utilized to compose white EL by mixing two or three of them together with certain proportions [4–8]. In the past years, green, red, yellow, and orange EL devices have been improved significantly; consequently, their efficiencies and brightness basically satisfy the requirement of application. However, blue and blue–green EL devices have remained the most challenging of the primary emissive colours in terms of efficiency and brightness [9–12].

Firstly, the relative low luminescent efficiencies of blue materials are believed to be the main factor responsible for the inferior performances of corresponding EL devices [9,10]. In the past years, several groups have devoted to the design and synthesis of novel materials, and certain progress has been obtained [13–16]. Secondly, blue materials have relatively high energy gaps, which are generally accompanied by low-lying highest occupied molecular orbital (HOMO) levels or high-lying lowest unoccupied molecular orbital (LUMO) levels [11,12]. As a result, most blue EL devices possess relatively high hole injection or electron injection barrier [15,16]. Also, unbalanced carrier injections result in low EL efficiency and brightness. In addition, most blue materials transport only holes or only electrons, which results in narrow recombination zone, thus causing the undesired roll-off of EL efficiency due to exciton quenching [17,18].

Dye doping is an efficient method to improve the performance of OLEDs because it can prevent concentration quenching of the dyes' emission, avoid crystallization of the dye molecules as well as improve the injections of electrons and holes [19–22]. Therefore, OLEDs fabricated by the dye doping method generally show higher efficiency, excellent stability, and even good spectral purity [23,24]. However, the high energy gaps of blue materials make it difficult to choose proper host materials for device fabrication because a good host material is required to possess wider energy gap in order to include the HOMO and LUMO levels of guest material within those of it [16,25–27]. Consequently, blue materials will trap holes or only electrons only if they are doped into certain host materials. Furthermore, the high exciton energy of blue materials not only causes inefficient energy transfer from host to blue materials but also makes it easy to lose energy by

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back transfer to host material or transfer to the material in adjacent layer [27–30].

In this work, we report an efficient strategy to design bright blue and blue–green EL devices by slightly doping tris (8-hydroxyquinoline) aluminum (Alq_3) into N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'-diphenyl-4,4'-diamine (NPB) as hole transport and light-emitting layer (HTL/EML). When the doping concentration of Alq_3 is less than 1%, NPB acts as a blue-emitting and hole transport material, while Alq_3 in EML functions as an electron injection sensitizer and green-emitting material. Interestingly, not only EL efficiency but also EL spectrum strongly depends on the doping concentration of Alq_3. With the help of energy levels and spectra, EL mechanisms and processes of these devices were investigated. Experimental results reveal the presence of Alq_3 molecules in EML not only facilitates the injection of electrons from hole block and electron transport layer (HBL/ETL) into EML but also stays the transport of holes in EML. Furthermore, we also discovered that the doping concentration of Alq_3 significantly influences the injection of electrons from HBL into EML and the transport of electrons in EML.

2. Experimental

Indium–tin-oxide (ITO) coated glass with a sheet resistance of 15 Ω/sq was used as the anode substrate. Prior to film deposition, patterned ITO substrates were cleaned with detergent, rinsed in de-ionized water, dried in an oven, and finally treated with oxygen plasma for 10 min at a pressure of 10 Pa. All the organic layers were deposited at the rate of 0.1 nm/s under high vacuum ($\leq 3\times10^{-5}$ Pa). The doped layer of each device was prepared by co-evaporating Alq_3 and NPB from two individual sources, and the doping concentrations were strictly controlled by modulating the evaporation rates of Alq_3. LiF and Al were evaporated in another vacuum chamber ($\leq 8.0\times10^{-5}$ Pa) at the rates of 0.01 and 1 nm/s, respectively, without being exposed to the atmosphere. The thickness of each layer and the evaporation rate of individual materials were monitored in vacuum with quartz crystal monitors. A shadow mask was used to define the cathode and to make ten 10 mm^2 devices on each substrate. The films of NPB and Alq_3 used for the measurement of absorbance and PL spectra were prepared by thermal evaporation in vacuum onto quartz substrates. Current density–brightness–voltage characteristics were measured using a programmable Keithley source measurement unit (Keithley 2400 and Keithley 2000) with a calibrated silicon photodiode. Photoluminescence (PL) and EL spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. The absorbance spectrum was measured using a TU 1901 UV–vis spectrophotometer.

3. Results and discussion

3.1. Dependence of EL spectrum and efficiency on doping concentration of Alq_3

Since the first demonstration of efficient OLED [1], NPB has been widely used as a hole transport material due to its excellent hole transport ability and thermal stability. Few groups have used it as an emitting material for its poor electron transport ability and high-lying LUMO level [27,31], although it can provide deep blue PL. In this work, the typical electron transport material Alq_3, which is also an excellent green material, was selected as the electron injection sensitizer. By doping Alq_3 into NPB, four devices having the structure ITO/Alq_3(x%):NPB(50 nm)/BCP(30 nm)/Alq_3(30 nm)/LiF(1 nm)/Al(100 nm) were fabricated by strictly controlling x to be 0.2, 0.4, 0.6, and 0.8. ITO substrates treated with low-pressure oxygen plasma were selected as the anodes, Alq_3 doped NPB layers were designed as HTL/EML, BCP, which is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, as the HBL/ETL, Alq_3 was selected as the ETL, and LiF/Al as the cathode. For comparison, a similar device with neat NPB layer was fabricated as the reference device. Fig. 1 shows the proposed energy level diagram of these device structures, with the thickness of each layer [31,32]. After low-pressure oxygen plasma treatment, the work function of ITO anode was increased from 4.7 to 5.1 eV [33], which facilitates the injection of holes.

As shown in Fig. 2, current density decreases monotonously with increasing doping concentration, except that the 0.6% doped device shows higher current density than that of the 0.4% doped device. Fig. 3 shows the EL spectra of these devices operating at 10 mA/cm^2. Deep blue emission centered at about 435 nm was observed in the reference device, which indicates the pure NPB emission [31]. For the doped devices, green emission was also observed besides the blue emission of NPB. We have measured the PL spectrum of Alq_3 thin film, which is centered at 515 nm. Therefore, the green emission observed in the doped devices can

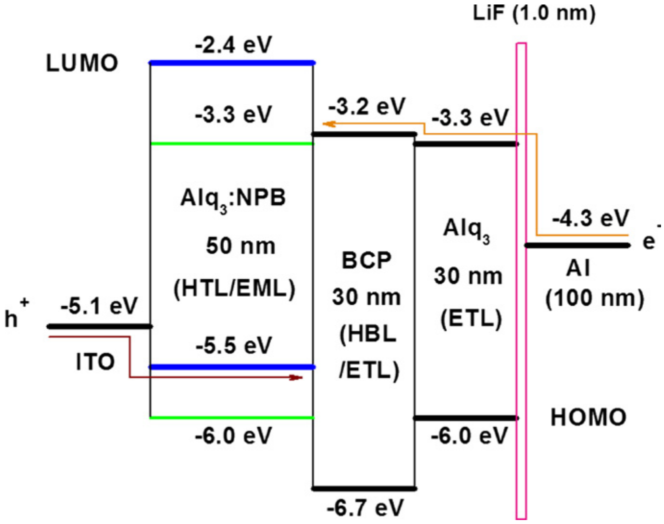

Fig. 1. Proposed energy level diagram of the OLEDs used in this study. The blue and green lines within EML represent the energy levels of NPB and Alq_3, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

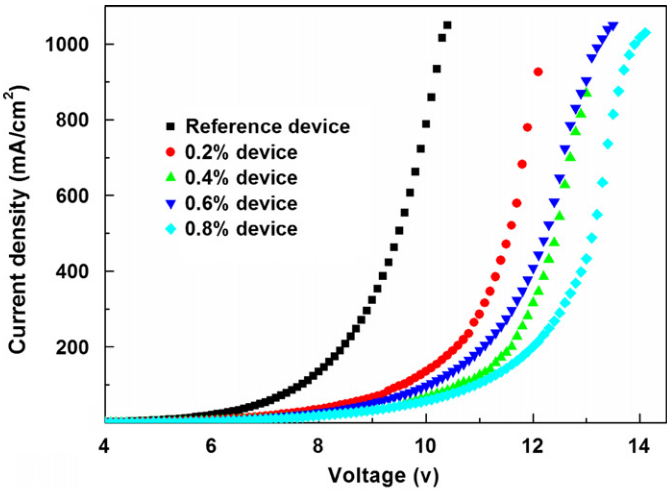

Fig. 2. Current density–voltage ($J-V$) characteristics of these devices with different concentrations of Alq_3.