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Significant improvement of OLED efficiency and stability by doping both HTL and ETL with different dopant in heterojunction of polymer/small-molecules*

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This paper reports that the polymer/organic heterojunction doped light-emitting diodes using a novel poly-TPD as hole transport material and doping both hole transport layer and emitter layer with the highly fluorescent rubrene and DCJTB has been successfully fabricated. The basic structure of the heterostructure is PTPD/Alq_3. When hole transport layer and electron transport layer are doped simultaneously with different dopant, the electroluminescence quantum efficiencies are about 3 times greater than that of the undoped device. Compared with undoped device and conventional TPD/Alq_3 diode, the stability of the doping device is significantly improved. The process of emission for doped device may include carrier trapping as well as Förster energy transfer.

Keywords: heterojunction, doping, organic electroluminescence, stability

PACC: 4270J, 7280L, 7360

1. Introduction

In the last decade, organic light emitting diodes (OLED) have attracted great attention in both fundamental research and device fabrication because of their potential application to display components.[1−6] Recently, tremendous progress in conjugated polymers has been made, and polymer-OLED technology is expected to show great impact on the future of general lighting application and flat-panel displays.[7−13] There are, however, many problems to be solved for OLEDs such as the device stability and efficiency. One of the methods to improve their stability is to apply polymer materials to device.[8−10] In addition, doping of fluorescent dyes into the charge transport/emitting layer now has been shown to be most effective in improving the device stability and efficiency.[14,15]

TPD (Triphenylamines derivatives) are often used as the hole transport materials in OLED.[16] All TPD are small molecules, whose thermal stability are lower than that of polymer. In order to enhance the thermal stability of TPD for hole transport materials and device durability, we have synthesized the novel electroluminescent poly-TPD (PTPD) with charge transporting properties in our previous work.[17] It is found that all PTPD have better thermal property than TPD, due to the remarkable higher glass transition temperature (T_g). Consequently, the device stability is obviously improved. We adopt a doping method and expect for further enhancement of the device stability. Doping is rarely employed in heterojunction in literature. In our work, we further expand the possible doping methods. Both the EML and HTL are doped in polymer/organic heterojunction where the same dopant is used.[18] In this study, we dope both layers simultaneously by using different dopants. We select PTPD as the hole transport layer (HTL), Tris-(8-hydroxyquinoline) aluminium (Alq_3) as an emitter layer (EML) and electron transport layer (ETL), the high fluorescent 5, 6, 11, 12-tetraphenylnapthacene (rubrene) and 4-(dicyanomethylene) -2-t-butyl-6 -(1,1,7,7-tetramethyljulolidyl-9enyl)-4H-pyran (DCJTB) as a guest dopant in the device. A comparison with doped device and undoped device is given. In this paper, the emission mechanism of the doping device is included.

2. Experimental section

The chemical structures of PTPD and dopant are shown in Fig.1.

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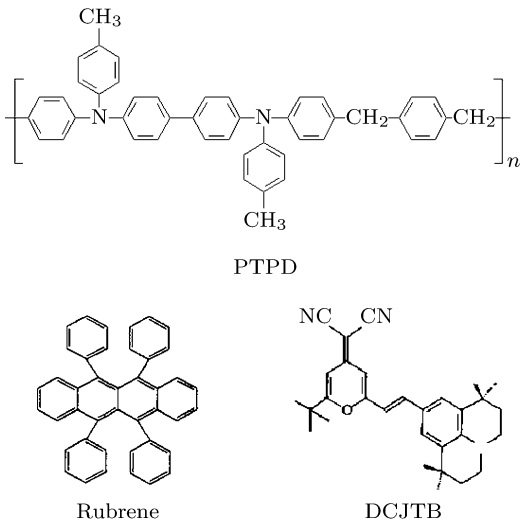


Fig.1. The chemical structure of PTPD and dopant

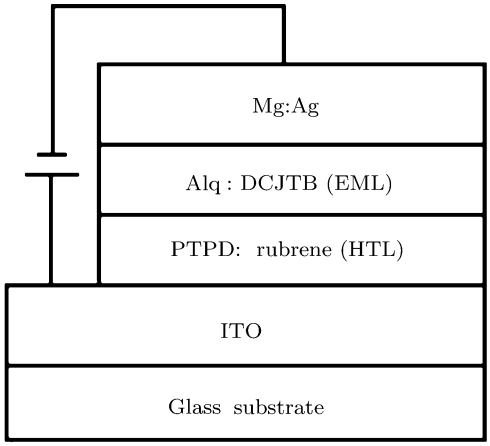


Fig.2. The structure of the device A.

According to the method of Ref.[16], PTPD was synthesized in our lab. The other chemical materials used for this work were commercial purchased. We fabricated four different device structures as follows:

Device A: ITO/PTPD: Rubrene/Alq_3: DCJTB /Mg:Ag

Device B: ITO/PTPD: Rubrene /Alq_3 /Mg:Ag

Device C: ITO/PTPD /Alq_3: DCJTB /Mg:Ag

Device D: ITO/PTPD /Alq_3 /Mg:Ag

Here, PTPD: rubrene and Alq_3: DCJTB indicated PTPD and Alq_3 doped with rubrene and DCJTB, respectively.

Fabrication of device set Device A as example: After the solvent treatment ultrasonically and oxygen plasma ashing of an indium-tin-oxide (ITO) ($10\,\Omega/\square$)film coated on glass substrate, PTPD ($M_w = 2.7 \times 10^5$) mixed with rubrene by a given concentration was solved in tetrahydrofuran (THF) and spin-coated (3000 rpm, 20 s) onto ITO glass substrates. After the film was dried under nitrogen flow at a moderate temperature, DCJTB was co-evaporated with Alq_3 on HTL in a vacuum of 6.1×10^{-3} Pa at a rate of 0.2–0.4 nm/s. The device was completed by the co-evaporation of a 150 nm thick Mg:Ag(10:1) cathode. The device A structure was shown in Fig.2. The other devices were fabricated with the same method and condition as described above. In this experiment, we set the dopant concentration at 5 wt% with respect to the host molecules. The thickness of the HTL and EML was typically 50 nm, measured by a Sloan DEKTAK II surface profilometer. All the devices were immediately characterized in room ambient and temperature without encapsulation.

Electroluminescence (EL) and UV–Vis spectra were measured with a spectrofluorometer (Hitachi P-4010), a multichannel spectrometer (Otsuka Electronics MCPD7000), and a spectrophotometer (Hitachi U-4100), respectively. The highest molecular orbital (HOMO) of the organic film was determined by an analysis based on Riken Keiki AC-1 under ambient atmosphere. The band-gap energy of the material was obtained from absorption spectrum and the value of the lowest unoccupied molecular orbital (LUMO) was estimated with the band-gap energy and HOMO level. Luminance–current density–voltage–characteristic are recorded simultaneously with the measurement of the EL spectra by attaching the spectrometer to a programmable Keithley 2400 power source. All measurements were carried out at room temperature under ambient atmosphere.

3. Results and discussion

Energy band diagram of doping device is shown in Fig.3.

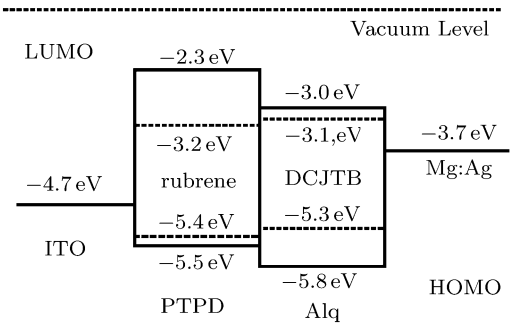


Fig.3. Energy band diagram of doping device.

In EL process, the dopant can act as a trap for either holes or electrons. When the current goes through the device, one of the carriers (hole or electron) is trapped and eventually recombines with the opposite carrier, then forms the dopant bound exciton. This carrier trapping process is very common and can occur in parallel with energy transfer in a given device. The only requirement for efficient carrier trapping is either the case that the dopant must have a HOMO energy higher than the HOMO of host it is doped into, or the case that a LUMO energy is lower than that of the host material.[19] As shown in Fig.3, the HOMO energy of Rubrene or DCJTB is higher than the HOMO of PTPD or Alq_3; and the LUMO energy of Rubrene or DCJTB is lower than that of the PTPD or Alq_3. Consequently, Rubrene or DCJTB can act as a trap for holes or electrons in the PTPD/Alq_3 diode.

Förster exciton transfer theory has been popularly invoked[19] to explain dopant-assisted emission in a host transport material. One characteristic parameter of the theory is the Förster radius (R_0). It is a measure of the distance over which an exciton on a host molecule can be transferred to a dopant molecule and is given by[20,21]

$$R_0^6 \propto \int_0^\infty F_{\mathrm{M}}(\tilde{v})\varepsilon_{\mathrm{Q}}(\tilde{v})\frac{\mathrm{d}(\tilde{v})}{\tilde{v}^4}$$

where $F_{\mathrm{M}}(\tilde{v})$ is the normalized host emission spectrum, $\varepsilon_{\mathrm{Q}}(\tilde{v})$ is the dopant absorption spectrum. For a given dopant concentration, the larger the R_0, the more efficient is the transfer of excitons from host to dopant. The product term $F_{\mathrm{M}}(\tilde{v})\varepsilon_{\mathrm{Q}}(\tilde{v})$ inside the integral reflects the amount of the overlap between the host emission and the dopant UV–Vis absorption spectra. The EL emission spectra of PTPD and Alq_3, together with the UV–Vis absorption spectrum of Rubrene and DCJTB are given in Fig.4. Clearly, the spectral overlap of Rubrene or DCJTB with PTPD or Alq_3 is excellent. Consequently, transferring energy from an HTL or ETL bound exciton to rubrene or DCJTB molecules can be a very efficient process.

The luminance (L)–current–density (J–V)–characteristics of devices (A–D) are summarized in Fig.5. Among the four types of devices measured, the turn-on voltage of the undoped device (Device D) is the lowest. This is because dopant molecules give rise to traps which inevitably lead to reduced charge carrier mobility.[22] A larger increase of the turn-on voltage is obtained with dopant placed in Alq_3 (Device C) than in PTPD (Device B). This is due to the reason the electron mobility is at least 100 times lower[23] than hole mobility. Hence a much larger portion of the voltage is sustained in Alq_3. The largest turn-on voltage is measured in Device A with dopant in both PTPD and Alq_3 .The luminance current efficiencies (η) of the various devices can be obtained from the L–V dependence in Fig.5. For Devices B and C, η is about the same at 0.42 cd/A (with a measured peak power efficiency of 0.24 lm/W). Because of the different spectral response, it is better to compare the quantum efficiencies. The quantum efficiency of the doped Devices A at 2.3% is about 3 times larger than that of the undoped device at 0.74%. This result is in good agreement with the literature Ref.[24] where TPD is used as the HTL. The quantum efficiency of the double doped devices with different dopants is the highest in all devices. We observed that the doping of the HTL and ETL with different dopants considerably improved the quantum efficiency of device.

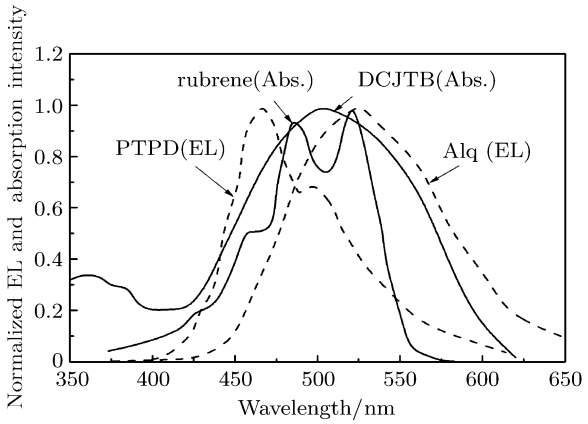


Fig.4. Normalized spectra of PTPD (EL), Alq_3 (EL), DCJTB (Absorption) and rubrene (Absorption).

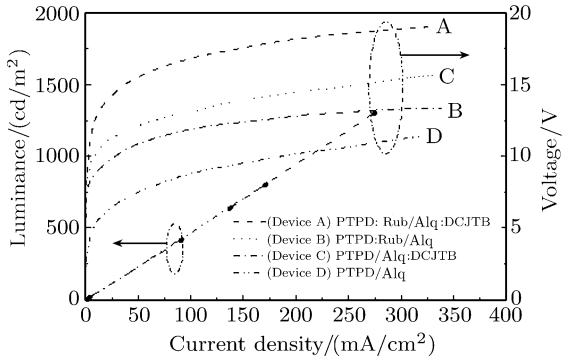


Fig.5. The luminance (L)–current density (J–V) characteristics of devices.

Figure 6 shows initial luminance decay with time for the four devices and a referenced TPD/Alq_3 device. The vertical axis shows normalized luminance, which is luminance divided by the individual initial luminance. The half decay time of the initial luminance ($T_{1/2}$) indicates the devices stability. It is obvious that a) the stability of the double doped devices with different dopant is the highest in all devices, b) the stability of the doped devices is significantly higher than that of the undoped device, c) the durability of the four devices with PTPD as HTL is higher than that of the referenced device with TPD as HTL. The reasons are that a) PTPD has better thermal stability than TPD,[15] b) doping can lead to significant enhancements in the stability of the OLED, and prevent crystallization of the glassy HTL or ETL materials,[18] c) doping double layers in particular should lead to further overall stability of the film' morphology.[25]

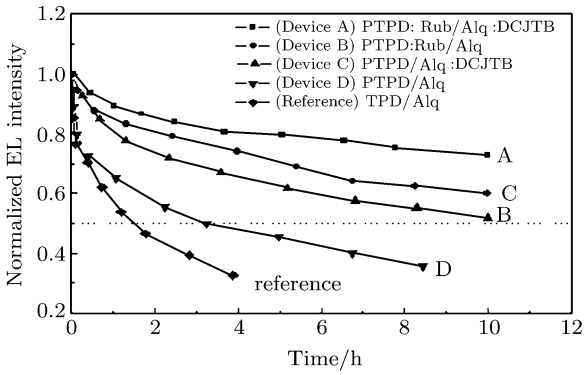


Fig.6. Comparison of the degradation trends of the four devices and a referenced typical TPD/Alq_3 device. (not encapsulated).

Here, we discuss the process of emission for doped device. The EL spectra of four devices are shown in Fig.7. In the undoped device D, the EL spectrum is composed of only intrinsic Alq_3 (Fig.4∼D), so, the holes and the electrons recombine primarily inside Alq_3. In device B with the rubrene-doped PTPD layer, the EL spectrum is composed primarily of the intrinsic rubrene and the small component of PTPD, suggests that the carrier recombination and EL emission occur inside the rubrene-doped PTPD layer. In this device, following the energy transfer mechanism, the majority of PTPD exciton's energy is transferred to the rubrene molecule and makes it become rubrene exciton. Rubrene exciton, together with the exciton formed by carrier trapping mechanism, composes the rubrene molecule emission. The minority of PTPD excitons transits directly to the ground state, forms PTPD emission. In device C, with the DCJTB-doped Alq_3 layer, the EL spectrum consists mostly of the intrinsic DCJTB, with the similar consideration that the carrier recombination and EL emission occurred inside the DCJTB. In device A with doping both hole transport and emitter layers with rubrene and DCJTB, the EL peak is composed primarily of the intrinsic DCJTB and the small component of rubrene. Holes and electrons are trapped by rubrene and DCJTB molecules respectively. The carrier recombination occurs at the interface of rubrene and DCJTB. Successive creation of the excitons and Förster energy transfer from PTPD to a rubrene molecule as well as Alq_3 to a DCJTB molecule occur. In any case, both carrier trapping and Förster energy transfer result in the DCJTB and rubrene emission. Thus, based on these EL spectra, the process of emission for doped device may include carrier trapping as well as Förster energy transfer.

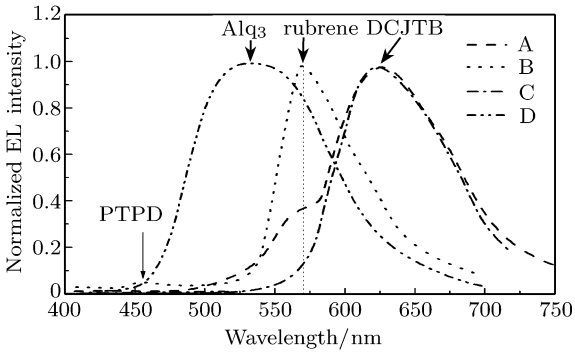


Fig.7. EL emission spectra of the four devices.

4. Conclusions

We have successfully fabricated polymer/organic heterostructure doped light-emitting diodes using a novel poly-TPD as hole transport material and doping both hole transport layer and emitter layer with the highly fluorescent rubrene and DCJTB. The basic structure of the diodes is PTPD/Alq_3. When hole transport and emitter layers are doped simultaneously with different dopant, the EL quantum efficiencies at 2.3% are about 3 times greater than that of the undoped device at 0.74%. Compared with undoped device and conventional TPD/Alq_3 diode, the doped device stability is significantly improved. Based on their EL spectra, the process of emission for doped device may include carrier trapping as well as Förster energy transfer.

It impressively shows the promising potential of these devices if it can be further extended to optimized structure devices and controlled doping.

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