Highly efficient blue fluorescent OLEDs with doped double emitting layers based on p–n heterojunctions*

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We fabricate a kind of novel efficient blue fluorescent organic light emitting device (OLED) based on p–n heterojunctions composed of hole transporting layer (HTL) N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine (NPB) and electron transporting layer (ETL) 4,7-diphnenyl-1,10-phenanthroline (BPhen), into which a new blue material, DNCA (a derivation of N^6, N^6, N^{12}, N^{12}-tetrap-tolylchrysene-6,12-diamine), is partially doped simultaneously, and double emitting layers are configured. With a turn-on voltage of 2.6 V at 1 cd/m^2, this type of OLED presents a maximum luminance efficiency ($\eta_{\max}$) of 8.83 cd/A at 5.818 mA/cm^2 and a maximum luminance of over 40000 cd/m^2. Meanwhile, the Commission Internationale De L'Eclairage (CIE) coordinates of this device change slightly from (0.13, 0.27) to (0.13, 0.23) as the driving voltage increases from 3 V to 11 V. This improvement in the electroluminescent characteristics is attributed mainly to the ideal p–n heterojunction which can confine and distribute excitons evenly on two sides of the heterojunction interface so as to improve the carrier combination rate and expand the light-emitting region.

Keywords: heterojunction, organic light-emitting diodes, exciplex emission, double emitting layers

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1. Introduction

Organic light emitting devices (OLEDs) have been regarded as a promising technology for lighting and display applications due to their high efficiency, easy processing, and excellent visual effects. With the development of materials and structural research, the efficiency and maximum brightness of OLEDs has been improved enormously.[1−3] Even though highly efficient red and green OLEDs have been demonstrated, the efficiency of blue OLEDs has been quite limited and further improvement is needed to fulfill the demands of solid-state lighting and full-colour display applications.[4,5] Blue electrophosphorescent devices with both singlet and triplet excitons contributing to light emission could obtain nearly 100% internal quantum efficiency in theory. However, there are few host materials with a high enough triplet-excited-state energy to realize exothermic energy transfer.[6] Furthermore, high turn-on voltage, quick efficiency roll-off and short lifetimes impede the development of blue electrophosphorescent OLEDs,[7] whereas blue electrofluorescent OLEDs could avoid these drawbacks. Hence, the study of blue electrofluorescent OLEDs is still important, especially for lighting applications and full colour displays.

The wide carrier recombination zone and efficient exciton confinement in the emitting layers were usually key to the design of highly efficient OLEDs. The mixed host emissive layer was utilized to confine excitons in the emission layer by adjusting carrier transport.[8,9] Meanwhile, using double emission

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layers (DELs) was also an effective approach to enhance the utilization of excitons, which could expand the carrier recombination zone.[10−14] For mixed host devices, the doping ratio is difficult to accurately control by vacuum deposition with three co-evaporation sources. The traditional devices with a double-emission-layer, a hole transporting layer (HTL), an electron transporting layer (ETL), a hole-transporting host (HT-HOST), and an electron-transporting host (ET-HOST) were different materially. The barriers of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) between the HT-HOST and ET-HOST are small, and not high enough to form an ideal p–n heterojunction between the HTL and ETL to confine excitons. The emission zones of these devices would always be close to the electrode and could shift to the electrode with an increase in bias voltage, which might result in electrode-induced quenching. Additionally, the different materials of the transport layer and host could result in a carrier injection barrier, which would not be beneficial to exciton distribution. So it is necessary to choose two different high barrier hosts to form the ideal p–n heterojunction to study the exciton distribution and electroluminescent mechanism.

In this study, we report on a high efficiency blue fluorescent OLED based on a p–n heterojunction between the carrier transport layers. This device is doped with a novel blue fluorescent material, DNCA (a derivation of N^6, N^6, N^{12}, N^{12}-tetrap-tolylchrysene-6, 12-diamine). N, N'-bis (naphthalen-1-yl)-N, N'-bis(phenyl)-benzidine (NPB) is used as the HTL and HT-HOST, and 4, 7-diphnenyl-1, 10-phenanthroline (BPhen) with a high HOMO is used as the ETL and ET-HOST. The reason we chose NPB and Bphen is that their carrier transport rates are of the same order of magnitude,[15,16] which is suitable for the formation of an ideal p–n heterojunction between the carrier transport layers. Due to the effective confinement and radiation of excitons on both sides of the p–n interface, this double emission layer blue OLED should show remarkably improved efficiency compared with that with a single emission layer (SEL) located at the hole-transport or electron-transport layer.

2. Experiments

Four different blue OLEDs were fabricated in this paper to study the effect of the p–n heterojunction. Their configurations are shown in Fig. 1.

All of the devices were prepared by thermal evaporation of organic layers onto pre-cleaned indium tin oxide (ITO)-coated glass substrates in an ultrahigh vacuum system at a base pressure of 8×10^{-5} Pa. The evaporation rate was 0.05 nm/s for the pure organic layers, and the evaporation rate for the doped layer was determined by its weight doping ratio. LiF and Al were evaporated onto the organic layer as the cathode with rates of 0.01 nm/s and 0.3 nm/s, respectively. The current density–voltage–brightness (J–V–B) characteristics and EL spectra of the blue OLEDs were measured using a Keithley 2400 source and a PR650 scan spectrometer. Photoluminescence (PL) and absorption (Abs) spectra of the organic materials were measured with a Hitachi F-4500 fluorescence spectrophotometer and a Hitachi U-4100 UV–Vis-NIR spectrophotometer. All the measurements were carried out under ambient atmosphere.

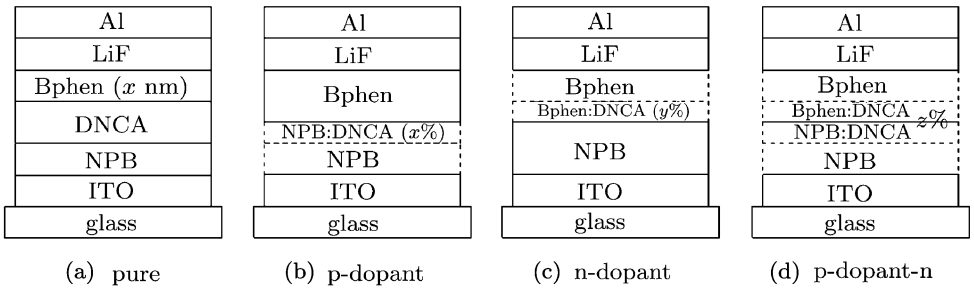


Fig. 1. Schematic structures of the blue OLEDs. (a) Device A: ITO/NPB (40 nm)/DNCA (30 nm)/Bphen (x nm)/LiF (0.8 nm)/Al (120 nm), (x = 20, 30, 40, 60 nm); (b) Device B (p-dopant): ITO/NPB (30 nm)/NPB: DNCA (20 nm)/Bphen (50 nm)/LiF (0.8 nm)/Al (120 nm); (c) Device C (n-dopant): ITO/NPB (50 nm)/Bphen: DNCA (20 nm)/Bphen (30 nm)/LiF (0.8 nm)/Al (120 nm); (d) device D (p-dopant-n): ITO/NPB (30 nm)/NPB: DNCA (20 nm)/Bphen: DNCA (20 nm)/Bphen (30 nm)/LiF (0.8 nm)/Al (120 nm).

3. Results and discussion

To study the EL characteristics of the DNCA, we fabricated Device A with different Bphen layer thicknesses. A new shoulder emission peak appears with the increasing thickness of the Bphen layer, as depicted in Fig. 2. With the increase in thickness, the carrier recombination zone in EML moves to the interface between EML and ETL gradually, which results in a shoulder emission peak of the EL spectrum at about 500 nm, owing to exciplex emission.[17,18] This exciplex emission can affect the emission of the other three kinds of p–n heterojunction devices. To clarify the doping relationship between the host and guest, which could produce the effect on the distribution of excitons on both sides of the p–n heterojunction, we fabricated devices B and C by doping DNCA in the HTL-HOST (p-dopant) and ETL-HOST (n-dopant), respectively.

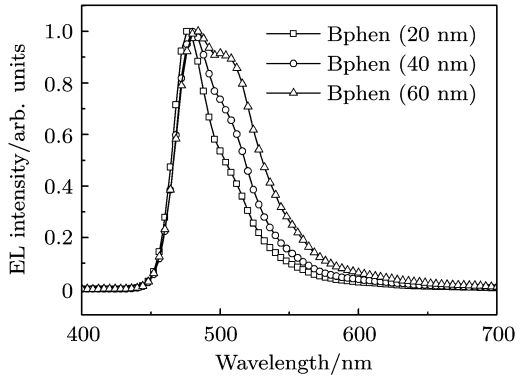


Fig. 2. The EL spectra of Device A with different thicknesses of Bphen at a voltage of 5 V.

Figure 3 shows the curves of J–V–B (inset) and current efficiency versus current density of p-dopant device separately with doping ratios of 3%, 6%, and 9%. From the inset in Fig. 3, we can easily find that current densities of devices with 6% and 9% doping concentration are higher than those with 3%, because the high doping concentration can improve the chance for the electron to be directly injected from Bphen to DNCA, other than to NPB. However, the obvious luminance enhancement could not be found at the same current density, which resulted in the decrease in current efficiency due to the quenching of the high doping concentration.[19] Although the device with low doping ratio cannot accommodate more electrons to be injected from ETL, it has a higher efficiency than the others when the current density exceeds 50 mA/cm^2. From this evidence, we can conclude that the radiative emission by the energy transfer route should be more than that of carrier trapping, and the doping concentration could affect exciton distribution and the recombination zone that exists in the p-dopant device.

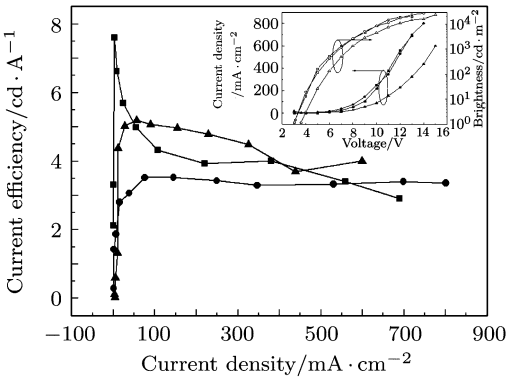


Fig. 3. Current efficiency versus current density of Device B with different doping ratios of 3% (triangles), 6% (circles), and 9% (squares). The inset shows the dependences of current density and brightness on voltage.

Figure 4 shows the EL characteristics of n-dopant devices with different doping concentrations. The inset in Fig. 4 indicates the different B–V–J curves in the sequence of these devices. DNCA favours hole transport, while an injection barrier of about 0.2 eV between the LUMOs of DNCA and Bphen is unfavourable for electron injection and transport with increasing doping ratio (see Fig. 5), and this is responsible for the decrease in current density with the increase in doping concentration. It is obvious that the device with high doping ratio could impede electron transport in the ETL-HOST, which results in a low current density. Although the maximum current efficiencies of these three devices are similar, the current efficiency of the device with 9% doping concentration decreases quickly due to the effect of concentration quenching. Moreover, with doping concentration increasing from 3%, 6%, to 9%, the CIE coordinates of these devices vary from (0.14, 0.24), (0.14, 0.30) to (0.14, 0.33) at 5 V, while the CIE coordinates of the pure device are (0.14, 0.30) at 5 V. We suppose that electrons transported from the LUMO of Bphen can recombine with the holes transported from the HOMO of DNCA in the emission zone, thereby resulting in an exciplex emission, which has been mentioned above and depicted in Fig. 5(a). This colour shift results from the fact that the dopants with high doping ratio in EML can accept more direct injections of holes, which will lead to more recombinations of electrons transported from Bphen and holes transported from DNCA, with the optimal doping concentration of DNCA being 3%. This low optimal doping concentration also supports the view that the emission is

attributed to host–guest energy transfer rather than direct recombination on the dopant. Therefore, a relatively low optimal concentration is essential for high efficiency and stable colour coordinates in n-dopant devices.

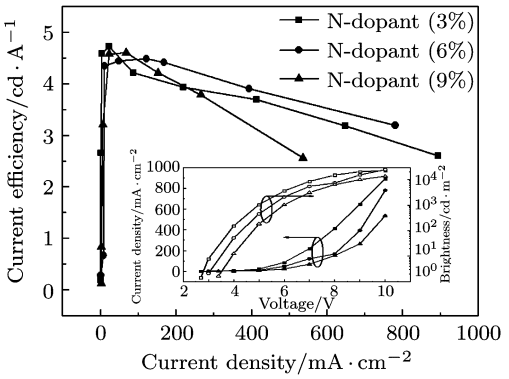


Fig. 4. Current efficiency versus current density of Device C with different doping ratios. The inset shows the dependences of current density and brightness on voltage.

On the basis of these experiments, we study the effect of the doping ratio on the EL performances of p-dopant and n-dopant blue devices. Both types of device could present a perfect EL performance under a relatively low doping concentration. As shown in Fig. 5(b), the absorption spectrum of DNCA overlaps partially with the PL spectrum of NPB and mostly with that of Bphen, which indicates that the Förster energy transfer from NPB and Bphen to DNCA should occur separately for mono-doped devices. In order to further improve the performance of OLED, it is feasible to dope the novel blue emitters in the HTL-HOST and ETL-HOST simultaneously by expanding the recombination zone (integrating the two light emissions in each EML) for excitons to enhance the efficiency of the blue OLED.

In order to study the effect of doping DNCA on both sides of the p–n interface with different concentrations, we fabricate D-type devices with doping ratios of 3%, 6%, and 9% to compare the EL characteristics with those of the B- and C-type devices. As shown in the inset in Fig. 6, the current density apparently augments with the doping concentration at the same driving voltage, which is consistent with the fact that the high concentration of dopants admits more direct carrier injections, thereby facilitating hole transport. However, there is no obvious improvement in current efficiency, but a decrease in the maximum of luminance with doping ratio is detected. It is presumed that more holes transport to the p–n heterojunction by DNCA, resulting in the exciplex emission, the shift of emission zone from heterojunction to Bphen and the perturbation to exciton equilibrium distribution. This is proved by the red-shift of CIE colour coordinates from (0.13, 0.25), (0.13, 0.30) to (0.13, 0.32) with an increase in doping concentration from 3%, 6%, to 9% of the D-type devices. We can see from Fig. 7 that Device D with a 3% doping concentration has a higher efficiency of 8.83 cd/A, compared with those of Device B (5.19 cd/A) and Device C (4.73 cd/A). Meanwhile, the maximum luminance of 40040 cd/m^2 for Device D is significantly improved, which is superior to those of Device B (23990 cd/m^2) and Device C (23290 cd/m^2). From these results, we can see that the blue OLED with double emitting layers based on the novel p–n heterojunction does confine the excitons in each EML effectively and keep excitons distributed on both sides of the p–n heterojunction evenly. This implies

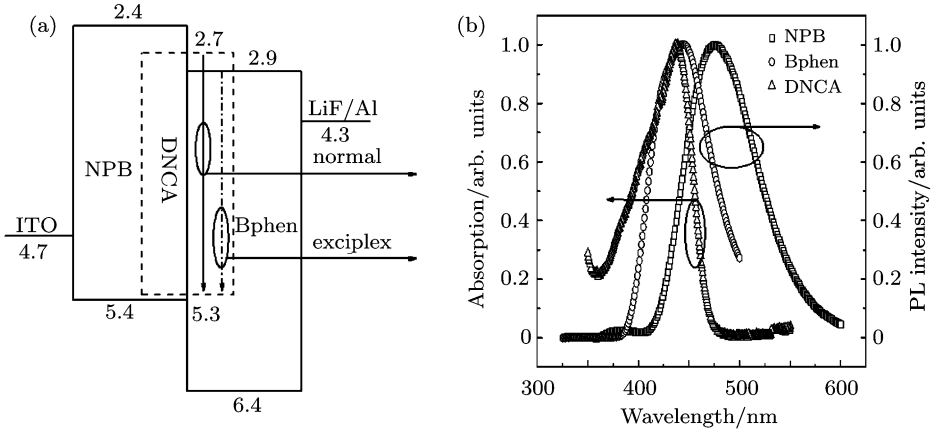


Fig. 5. (a) Schematic of the energy levels of the OLEDs and the formation of exciplex emission. (b) The absorption spectra of the DNCA and PL spectra of NPB and Bphen.

that the carrier recombination zone can be expanded accordingly, so the two routes of radiative emission from both EMLs could be utilized efficiently by energy transfer to enhance OLED EL performance.

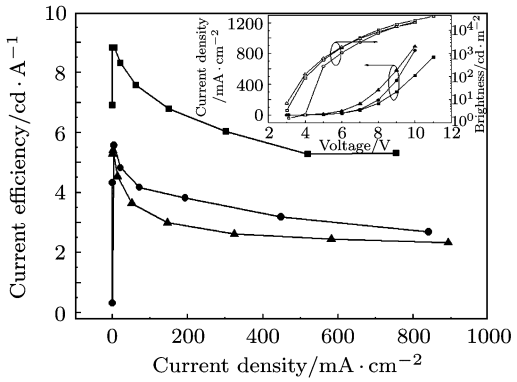


Fig. 6. The current efficiency versus current density characteristics of Device D with a doping concentration of 3% (squares), 6% (circles), and 9% (triangles). The inset shows the dependences of current density and brightness on voltage.

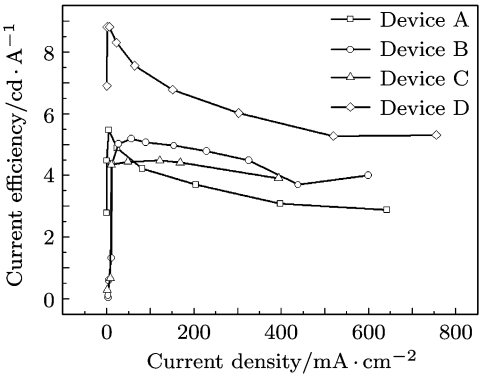


Fig. 7. The current efficiency–current density curves of the devices with different structures.

4. Summary

High-efficiency blue fluorescent OLEDs based on p–n heterojunctions are demonstrated by partially doping both NPB and Bphen with DNCA simultaneously, in which the recombination of excitons distributed in the two EMLs can be utilized effectively. This type of device, with a turn-on voltage of 2.6 V at 1 cd/m^2, presents a peak current efficiency ($\eta_{\max}$) of 8.83 cd · A^{-1} and a maximum luminance of over 40000 cd/m^2, which could be attributed to the effective p–n heterojunction confining and distributing excitons evenly on the two sides of the interface, thereby resulting in an improvement in the carrier combination rate and the expansion the light-emitting region.

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