Effect of NaCl doped into Bphen layer on the performance of tandem organic light-emitting diodes*

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To improve the performance of tandem organic light-emitting diodes (OLEDs), we study the novel NaCl as n-type dopant in Bphen:NaCl layer. By analyzing their relevant energy levels and carrier transporting characteristics, we discuss the mechanisms of the effective charge generation layer (CGL) of Bphen:NaCl (6 wt%)/MoO_3. In addition, we use the Bphen:NaCl (20 wt%) layer as the electron injection layer (EIL) combining the CGL to further improve the performance of tandem device. For this tandem device, the maximal current efficiency of 9.32 cd/A and the maximal power efficiency of 1.93 lm/W are obtained, which are enhanced approximately by 2.1 and 1.1 times compared with those of the single-emissive-unit device respectively. We attribute this improvement to the increase of electron injection ability by introducing of Bphen:NaCl layer. Moreover, the CGL is almost completely transparent in the visible light region, which is also important to achieve an efficient tandem OLEDs.

Keywords: tandem OLEDs, NaCl doping, charge generation layer

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1. Introduction

Tandem organic light-emitting diodes (OLEDs) have received much attention due to their significantly improved current and quantum efficiencies at low current densities, and good stabilities compared with those of single-emissive-unit OLEDs containing one electroluminescence (EL) unit.[1–9] Tandem OLEDs generally consist of two or multiple EL units through charge generation layer (CGL). The operational mechanism of the CGL in tandem OLEDs is that the electrons and holes generated in CGL are transported and injected into the adjacent EL units. Obviously, the CGL plays a critical role in charge generation, transport, and injection processes.

A variety of CGLs have been developed for the applications of tandem OLEDs. Extensive efforts have been made to explore highly efficient CGL such as n-doped organic/metal or metal oxide,[1–3] n-doped organic/organic,[6] n-doped organic/p-doped organic,[7] and undoped cases.[8] Therefore, exploring more n-type dopants is especially important for improving the performance of the CGL. Up to now, some of n-type dopants used for the CGL in the tandem OLEDs have been tried, such as Li,[9] $CsCO_3$,[10] CsN_2,[11] Rb_2CO_3,[12] and $LiCO_3$.[13]

The novel NaCl n-type dopant has not been reported in the tandem OLEDs so far. In this paper, we mainly investigate the effect of the NaCl as n-type dopant in Bphen:NaCl layer on the performance of tandem OLEDs. The tandem OLEDs consisting of two green EL units are fabricated based on Bphen:NaCl/MoO_3 as CGL. The mechanisms of the CGL are discussed by analyzing their relevant energy levels with respect to those of the neighboring organic layer. Moreover, to further improve the performance of the tandem device, the Bphen:NaCl is used as electron injection layer (EIL) to increase the injection and transport of electrons.

2. Experiment

Figure 1 shows the structure diagrams of a single-emissive-unit device (Device A) and two tandem devices (Devices B and C). All of the devices each were fabricated on an ITO substrate with a sheet resistance of 20 Ω/sq. The ITO surface had been cleaned by using ultrasonication in acetone and isopropyl for 15 min before it was loaded into the BOC Edwards Auto-500 type thermal evaporation system inside the M. Braun glove-box. All layers were deposited by thermal evaporation in a high vacuum system with a base pressure of less than 2×10^{-4} Pa. The EL characteristics of all devices are measured by Keithley 2400 sourcemeter, Keithley 485 picoammeter, and the PR 650 spectra scan spectrometer. The Femi level (E_f) of the NaCl doped into Bphen film was

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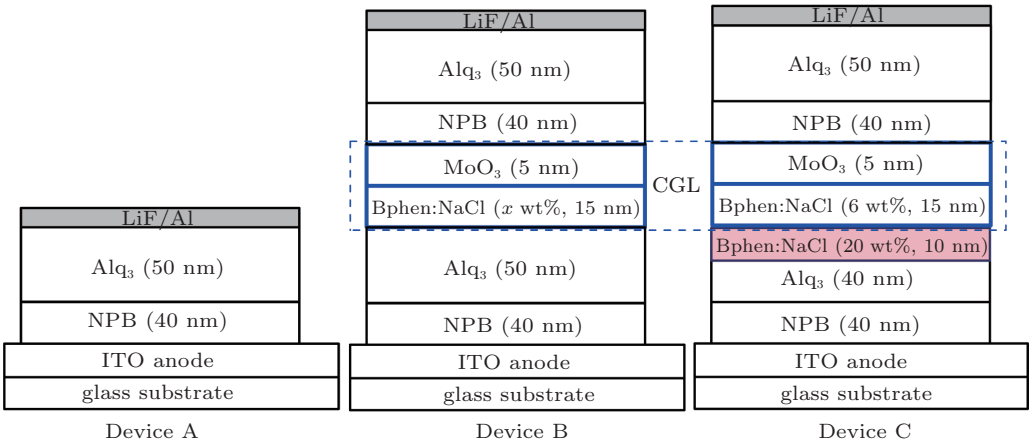


Fig. 1. (color online) Structure diagrams of a single-emissive-unit device A, tandem devices B ($x = 6$, 10, 20, and 30), and tandem device C.

measured by KP020 Kelvin probe. The active area of all devices was 3 nm×3 mm. All measurements were carried out at room temperature in ambient atmosphere without any protective coatings.

3. Results and discussion

Figure 2 shows the current efficiency–current density–power efficiency characteristics of devices A, B, and C. It can be seen that the tandem device B with 6-wt% NaCl-doped Bphen shows the higher current efficiency, which is enhanced approximately by 1.9 times compared to that of the device A. Thus the Bphen:NaCl (6 wt%)/MoO_3 as CGL shows the better charge generation and injection characteristics, which further improves the carrier recombination in the adjacent emission units. Previous reports revealed that MoO_3 can pronouncedly modify the energy level alignment, and be beneficial to the charge separation at MoO_3/NPB interface and electron injection at Bphen:Mg/MoO_3 interface from MoO_3 into suitable molecular energy level of adjacent emission units.[14] Also shown in Fig. 2 is that the current efficiency of tandem device B could not be further improved by increasing the NaCl-doped concentration to 10 wt%, nor 20 wt% nor 30 wt%. The reason is that the electrons cannot be effectively injected from the conduction band of MoO_3 into molecular energy levels of adjacent emission units.

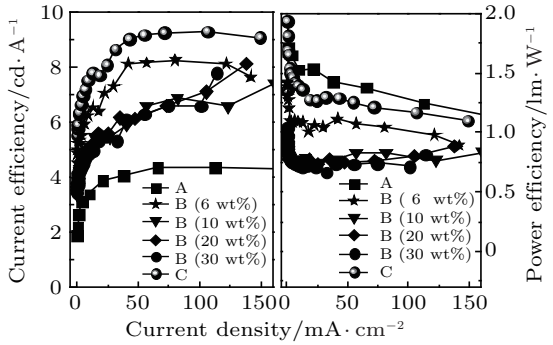


Fig. 2. Current efficiency–current density–power efficiency characteristics for devices A, device B ($x = 6$, 10, 20, and 30), and device C.

Next, we further examine the values of E_f of the NaCl doped into Bphen films, which are measured by Kelvin probe. Figure 3 shows the schematic energy level diagrams of Bphen:NaCl layers with various NaCl-doped concentrations, in which the positions of E_f, lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) are depicted. The ΔE which represents the energy separation between the LUMO edge and E_f decreases due to the effect of NaCl serving as n-type dopants. The inset of Fig. 3 shows the schematic energy level diagrams of the Alq3/Bphen:NaCl/MoO_3 interfaces. E_f is aligned across the interfaces in a thermodynamic equilibrium state. Thus the Bphen:NaCl interlayer between the Alq_3 and MoO_3 provides a better energy level matching due to the higher barrier at Alq3/MoO_3 interface. Therefore, electrons will be easily transferred from the conduction band of MoO_3 to the LUMO level of Alq_3 by the decrease of ΔE. By comparing different NaCl-doped concentrations, it can be seen that Bphen:NaCl (6 wt%) sample shows the minimum ΔE, which can effectively reduce the electron injection barrier from MoO_3 to Alq_3 and then enhance the efficiency of tandem device.

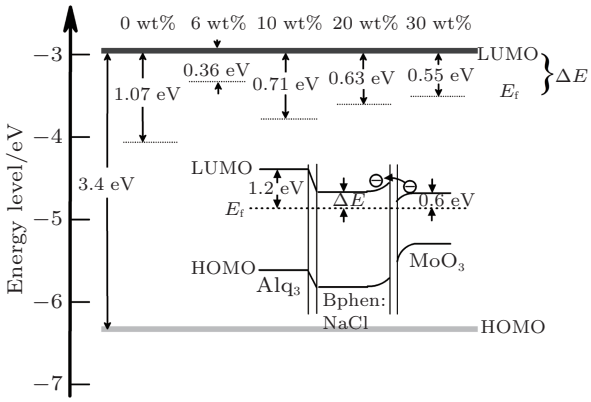


Fig. 3. Schematic energy level diagrams of LUMO, HOMO, and E_f with different NaCl-doped concentrations in Bphen:NaCl films. Inset: schematic energy level diagrams of the Alq3/Bphen:NaCl/MoO_3 interfaces.

To further clarify the effect of NaCl-doped layer on the EL performance of device, the electron-only device with the structure of ITO/Bphen (80 nm)/Bphen:NaCl (y wt%, 10 nm)/Al (Device D) is designed. As shown in Fig. 4, the Bphen:NaCl (20 wt%) layer exhibits the highest current density under the same voltage in the electron-only devices. This indicates that Bphen:NaCl (20 wt%) layer serving as EIL will be beneficial to the electron transport from CGL to adjacent emission unit. Therefore, the device C is fabricated to improve the performance of tandem device. As shown in Fig. 2, it can be obviously seen that device C with a maximal current efficiency of 9.32 cd/A and a maximal power efficiency of 1.93 lm/W are obtained, which are enhanced approximately by 2.1 and 1.1 times compared with those of the device A respectively. This result demonstrates that Bphen:NaCl (20 wt%) layer can further increase electron injection from CGL to under emission unit, and thus it improves the current efficiency for tandem device.

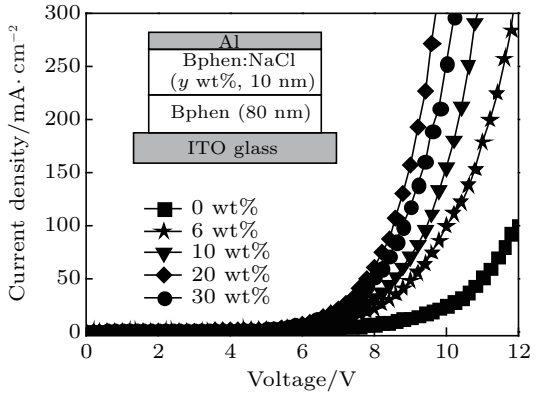


Fig. 4. Current density–voltage characteristics for electron-only device D ($y = 0$, 6, 10, 20, and 30) with different NaCl doping concentrations.

An excellent CGL with effective charge transport ability is very important for tandem OLEDs. By effective doping method, the E_f level within the NaCl-doped Bphen is close to the lowest unoccupied molecular orbital level of Bphen as shown in Fig. 3. Based on these electron injection schemes, two CGL-only devices are constructed, including Device E: ITO/Bphen (40 nm)/Bphen:NaCl (20 wt%, 10 nm)/Bphen:NaCl (6 wt%, 15 nm)/MoO_3 (5 nm)/NPB (50 nm)/Al, and Device F:ITO/Bphen (50 nm)/Bphen:NaCl (6 wt%, 15 nm)/MoO_3 (5 nm)/NPB (50 nm)/Al. According to the reported literature,[14] the interface of MoO_3/NPB has a better energy level matching. Under an applied bias, electrons can be effectively transferred from the HOMO level of NPB to the conduction band of MoO_3. The holes in the HOMO level of the NPB are left and injected into the emitting layer of its own emitting unit. From the energy level diagram (inset of Fig. 5), the electrons can be easily injected into the LUMO of Bphen:NaCl (6 wt%) due to small injection barrier at the Bphen:NaCl (6 wt%)/MoO_3 interface. Then, it is difficult for electrons to be injected from Bphen:NaCl (6 wt%) into Bphen because of the higher barrier (1.01 eV) between the Bphen and Bphen:NaCl (6 wt%). Consequently, as the EIL, the Bphen:NaCl (20 wt%, 10 nm) layer can effectively reduce injection barrier at Bphen/Bphen:NaCl interface. In addition, it can be known that the Bphen:NaCl (20 wt%) shows better conductive characteristic than that of Bphen:NaCl (6 wt%) in Fig. 4, which further improves the electronic transport from CGL to under emission unit. From Fig. 5, it can be found that the current density of the device E shows a higher current density than that of device F in the whole range of driving voltage. This result demonstrates that Bphen:NaCl (20 wt%, 10 nm)/Bphen:NaCl (6 wt%, 15 nm)/MoO_3 (5 nm) exhibits an effective charge transport ability.

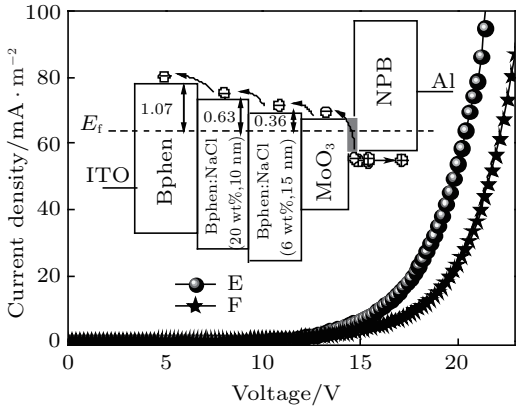


Fig. 5. Current density–voltage characteristics of the CGL-only Devices E and F. Inset: energy level diagram for Bphen:NaCl (20 wt%, 10 nm)/ Bphen:NaCl (6 wt%, 15 nm)/MoO_3 (5 nm).

To further demonstrate the advantages of Bphen:NaCl (20 wt%) layer serving as EIL, two tandem devices with blue emission unit and orange emission unit are fabricated. The configurations of the devices are shown as follows: Device M: ITO/NPB (50 nm)/MADN:DSA-ph (3 wt%, 30 nm)/Bphen (20 nm)/Bphen:NaCl (20 wt%, 10 nm)/Bphen:NaCl (6 wt%, 15 nm)/MoO_3 (5 nm)/NPB (50 nm)/Alq_3:rubrene (1 wt%, 30 nm)/Bphen (30 nm)/LiF (0.8 nm)/Al; Device N: ITO/NPB (50 nm)/MADN:DSA-ph (3 wt%, 30 nm)/Bphen (30 nm)/Bphen:NaCl (6 wt%, 15 nm)/MoO_3 (5 nm)/NPB (50 nm)/Alq_3:rubrene (1 wt%, 30 nm)/Bphen (30 nm)/LiF (0.8 nm)/Al. As shown in Fig. 6, the EL spectra of device M and device N are obtained at 100 cd/cm^2. It can be easily found that the relative intensity of the spectral shoulder peaks around 468 nm and 500 nm for the device M is increasing compared with that of the device N, because the introducing of Bphen:NaCl (20 wt%, 10 nm) layer could inject more electrons into blue emission unit underneath, which enhances the emitting intensity of blue emission unit. In addition, the inset shows a transmittance of Bphen:NaCl (6 wt%, 15 nm)/MoO_3 (5 nm) as the CGL. This CGL is almost completely transparent in the visible region from 380 nm

to 800 nm, which is also essential to achieve the efficient tandem OLEDs.[15]

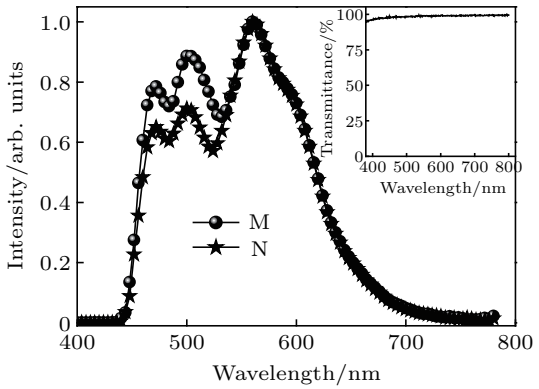


Fig. 6. EL spectra of device M and N at a luminance of 100 cd/cm^2. Inset shows the transmittance spectrum of Bphen:NaCl (6 wt%, 15 nm)/MoO_3 (5 nm) thin film.

4. Conclusion

In this paper, we systematically investigate the effect of the NaCl serving as n-type dopant in Bphen:NaCl layer on the performance of tandem OLEDs. The E_f level with 6-wt% NaCl-doped Bphen is close to the LUMO level of Bphen, which reduces the electrons injection barrier at the Bphen:NaCl (6 wt%)/MoO_3 interface. Meanwhile, the Bphen:NaCl (20 wt%) layer is used as an EIL to further improve electron injection and transport into emission unit underneath. For the tandem device including both the CGL and the EIL, a maximal current efficiency of 9.32 cd/A and the maximal power efficiency of 1.93 lm/W are obtained, which are enhanced approximately by 2.1 and 1.1 times compared with those of the single-emissive-unit device, respectively. The CGL is almost completely transparent in the visible region, which is also essential to achieve an efficient tandem OLEDs. According to the spectra of two tandem devices with blue emission unit and orange emission unit, it can be found that the characteristics of tandem device are further improved by the introducing of Bphen:NaCl (20 wt%, 10 nm) as the EIL due to the enhancement of electron injection from CGL to blue emission unit. Therefore, we note that the introductions of effective CGL and EIL with Bphen:NaCl is important to realize high performance of tandem OLEDs.

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