$C_{60}/N,N'$ -bis(1-naphthyl)- N,N' -diphenyl-1,1'-biphenyl-4,4'-diamine:MoO₃ as the interconnection layer for high efficient tandem blue fluorescent organic light-emitting diodes

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The high efficient tandem blue fluorescent organic light emitting diodes (OLEDs) with the transparent interconnection layer (ICL) of fullerence (C_{60})/Molybdenum oxide (MoO₃)-doped N,N' -bis(1-naphthyl)- N,N' -diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) were presented. A stack consisting of 0.5 nm of LiF and 1 nm of Ca, which is located from C_{60} to adjacent electron transporting layer is used as an electron injection layer. The experiment results indicate that the luminance of the tandem device is basically equal to that of the traditional single-unit device, but the current density of the tandem device is much less than that of the single-unit device under a same luminance. The current efficiency and the maximal power efficiency of tandem device with LiF/Ca/ C_{60} /NPB:MoO₃/MoO₃-based interconnection layer have been approximately enhanced by 250% and 126%, respectively. In addition, we also analyze that the mechanism of the efficiency enhancement is ascribed to the effective charge separation and transport of the ICL in tandem OLEDs. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4811551>]

White organic light emitting devices (WOLEDs) have drawn much attention due to their applications as the back-light for liquid crystal displays and the solid-state lightings.¹ Apparently, blue light emitting plays a key role for the white light devices, which is still confronted with some problems such as low efficiency and short lifetime compared with other colors-emitting.^{2,3} Tandem organic light emitting devices (OLEDs) have received considerable attention recently because of their high current efficiency and long lifetime.⁴⁻⁶ Tandem OLED generally consists of two or more emissive units. Thus, in principle, the electroluminescence (EL) intensity of the tandem device can linearly increase with the number of emissive units.

Understandingly, the interconnection layer (ICL) plays a critical role to the performance of tandem OLEDs. The interconnection layer must also have a high optical transmission and a low electrical resistance to minimize power loss. It is obvious that a key controlling factor in the performance of tandem OLEDs is an efficient interconnection layer for both the transport of the charge carriers and the output of the photons. Up to now, some kinds of ICLs in tandem OLEDs have been tried, such as 1,3,5-tri(phenyl-2-benzimidazole) benzene(Bphen):Li/ N,N' -bis(1-naphthyl)- N,N' -diphenyl-1,1'-biphenyl-4,4'-diamine (NPB):FeCl₃⁴ and Bphen:Li/MoO₃.⁶ These ICLs can work well for the tandem OLEDs with two EL units, in which current efficiency can be obtained by the two units, but the driving voltage of the tandem OLEDs increases gradually along with incremental number of the stack EL units; therefore, the power efficiency of this kind of devices could not be increased in real applications.

Recently, we demonstrated the blue OLEDs consisting of two blue EL units by using C_{60} /NPB:MoO₃ as a

transparent ICL. In this ICL, the lowest unoccupied molecular orbital (LUMO) level of C_{60} is very deep, which makes it difficult for electrons to be injected into the LUMO of adjacent electron transporting layer (ETL). To resolve this problem, we have used a stack ultra thin layers consisting of alkali halide LiF and metal Ca as the electron injection layer (EIL) to assist electron injection from ICL into ETL. The metal oxide MoO₃ layer on the top of the ICL serves as a hole injection layer (HIL) in the top unit.^{7,8} We applied this combination of C_{60} /NPB:MoO₃ as ICL and LiF/Ca as EIL to fabricate the tandem fluorescent blue OLEDs, which resulted in the improvement of the device's current efficiency and power efficiency.

Figure 1 shows the structure diagrams of a single-unit device (Device A) and two tandem devices (Device B and Device C). Moreover, other two tandem devices (Device M and Device N) with the typical ICLs of Bphen:Li/MoO₃⁶ and Bphen:Li/NPB:MoO₃⁴ have also been fabricated simultaneously for detailed comparison between these devices. All tandem devices have the same two EL units except different ICLs. For all devices, the p-bis(p-N, N-diphenyl-amino-styryl) benzene (DSA-ph) doped 2-methyl-9,10-di (2-naphthyl) anthracene (MADN) and Bphen were used as blue emitting layer and ETL, respectively. The substrate is an indium-tin-oxide (ITO) coated glass with a sheet resistance of about 20 Ω /sq. The ITO surface was 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 of the M. Braun glove box. All layers were deposited by thermal evaporation in a high vacuum system with a base pressure of less than 5×10^{-4} Pa without breaking the vacuum. The electroluminescent characteristics of all devices are measured by using a Keithley source measurement unit (Keithley 2400 and Keithley 485) and the PR 650 spectra scan spectrometer. All the measurements are carried

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FIG. 1. The structure diagrams of a single-unit device (device A) and two tandem devices (device B and device C).

out in ambient atmosphere at room temperature except for the lifetime tests.

Figure 2 depicts the J - V - L characteristics of the devices A, B, C, M, and N, respectively. It can be clearly seen that the performance of tandem devices B, C, M, and N shows higher operation voltage to achieve the same value of current density and luminance as compared with that of the device A. Under the same luminance, the operation voltages of the devices B and C are lower than those of the devices M and N, which indicates that the charge could be effectively separated and transported by the ICL adopted in devices B and C comparing to those of the device M and N. The device B with LiF/C₆₀/NPB:MoO₃/MoO₃-based ICL exhibits an operation voltage of 17 V at 1000 cd/m², which is three times higher than that of device A (5 V) at the same luminance. However, the incorporation of a very thin (1 nm) Ca interlayer at the interface between the LiF and C₆₀ layer in the ICL (device C) significantly reduced the operation voltage to 11 V at 1000 cd/m², which indicated that the insertion of a thin metal Ca layer effectively enhances the electron injection properties of the LiF/Ca/C₆₀/NPB:MoO₃/MoO₃-based ICL. As shown in Figure 3, the luminances of three devices (C, M, and N) are all greater than those of the devices A and B at same current density. As the promising one, the current efficiency of the device C attains 33.8 cd/A at current density of 72.9 mA/cm², which is nearly 2.5 times higher than that of

the single-unit device A (13.5 cd/A) at 68.9 mA/cm² and similar to the maximum current efficiencies of conventional tandem devices M and N. This result reveals that LiF/Ca/C₆₀/NPB:MoO₃/MoO₃ is functioned as an effective ICL.

One of the most important parameters in real device applications is power efficiency. Figure 4 shows the relationship between power efficiency and current density for these devices. It can be obviously seen that device C with a maximal power efficiency of 9.7 lm/W was obtained, which is about 1.24, 1.26, and 1.35 times higher than those of device N (7.8 lm/W), device A (7.7 lm/W), and device M (7.2 lm/W), respectively. Although efficiency roll-off of device C has appeared, the power efficiency of device C still attains 9 lm/W and 7 lm/W at 100 cd/m² and 1000 cd/m², respectively. This result shows that the introducing of LiF/Ca/C₆₀/NPB:MoO₃/MoO₃-based ICL could effectively reduce the operation voltage for tandem devices at a certain luminance and apparently promotes the enhancement in power efficiency, which is superior to the reported works previously.⁴

Figure 5 depicts the accelerated lifetime decay curves for devices A, C, M, and N. The half-lifetime under the brightness of 5000 cd/m² is about 2.6, 11.9, 11.5, and 11.8 hours for devices A, C, M, and N, respectively. We attribute the obvious improvement in tandem devices' reliability to the efficient electroluminescence under relatively low current density at a certain luminance. Because the organic semiconductor materials

FIG. 2. The current density-voltage-luminance (J - V - L) characteristics for devices A, B, C, M, and N.

FIG. 3. The current efficiency-current density-luminance characteristics for devices A, B, C, M, and N.

FIG. 4. The power efficiency-current density characteristics for devices A, B, C, M, and N.

would become unstable to withstand the Joule's heat caused by the high current density flowing through the device. Moreover, the device C also shows a little bit longer half-lifetime than that of the devices M and N.

An excellent ICL with effective charge transport ability of tandem OLEDs is generally very important. By effective doping method, the Fermi level within the MoO_3 -doped NPB is close to the highest occupied molecular orbital (HOMO) level of NPB. If the C_{60} and NPB: MoO_3 contacted each other, a common Fermi level throughout both layers is required by the equilibrium, which is close to the HOMO level of NPB: MoO_3 . Therefore, under the external electric field, the electrons may tunnel through from HOMO level of NPB: MoO_3 to LUMO level of C_{60} . Then these electrons will immediately be driven away from the interface and injected into emission layer by the external electric field. From the energy level diagram (inset of Figure 6), it is difficult for electrons to be injected from C_{60} to Bphen because they need to overcome a high barrier (1.6 eV). After the thin Ca layer was inserted between LiF and semiconductor material C_{60} , there would be the Schottky contact formed at the interface of Ca/C_{60} , and Figure 6 shows the obvious rectification characteristic in device D. In the forward bias of the case,

FIG. 5. The accelerated operation lifetime tests for devices A, C, M, and N. We fixed the initial luminance at 5000 cd/m^2 , and supplied constant voltages to different devices under the temperature of 303 K in glove box.

FIG. 6. Current density-voltage characteristics of the ICL-only devices and energy level diagram for LiF/Ca/ C_{60} /NPB: MoO_3 / MoO_3 -based interconnection layer (inset). D: ITO/Bphen(50)/LiF(0.5)/Ca(1)/ C_{60} (15)/NPB: MoO_3 (15)/ MoO_3 (3)/NPB(50)/Al, E: ITO/Bphen(50)/LiF(0.5)/Al(1)/ C_{60} (15)/NPB: MoO_3 (15)/ MoO_3 (3)/NPB(50)/Al, F: ITO/Bphen(50)/LiF(0.5)/ C_{60} (15)/NPB: MoO_3 (15)/ MoO_3 (3)/NPB(50)/Al. The numbers in parentheses are thickness (nm).

the Fermi level will up-shift and be close to the LUMO level of C_{60} , which reduces the energy barrier between C_{60} and Ca and facilitates the electron injection from C_{60} to Bphen. Therefore, the stack consisting of metal Ca and LiF was used as the EIL to assist the electron injection from ICL to Bphen. The holes left in the HOMO level of the NPB: MoO_3 are injected into the emitting layer (EML) of its own emitting unit in the same way.^{7,9} From Figure 6, it can be found that the current density of the device D shows a higher current density than that of other ICL-only devices in the whole range of driving voltage. This result demonstrated that LiF/Ca/ C_{60} /NPB: MoO_3 / MoO_3 exhibits an effective charge transport ability as an ICL.

Figure 7 shows the transmittance of C_{60} (15 nm)/NPB: MoO_3 (15 nm) as the ICL. This ICL is transparent in the visible region from 400 to 800 nm, which is essential to achieve an efficient tandem OLED.¹⁰ The EL spectra of device A and device C are obtained at various viewing angles. It could be easily found that the relative intensity of the spectrum shoulder peak around 500 nm in device C is

FIG. 7. Transmittance spectrum of C_{60} /NPB: MoO_3 thin film. Inset: EL spectra of device C at different viewing angles and device A at viewing angles of 0° .

decreased by increasing the viewing angle comparing with that of the device A, because of optical interference and weak microcavity effect between two emission layers from each stacked unit.^{8,11} Although this optical interference and weak microcavity effect has happened in device C, its current efficiency is nearly 2.5 times higher than that of the single-unit device A.

In summary, we demonstrated the high efficiency blue fluorescent tandem OLEDs consisting of C₆₀/NPB:MoO₃ as an ICL and LiF/Ca as an EIL. Despite a feeble optical interference has emerged, the tandem OLED shows a high current efficiency of 33.8 cd/A and a power efficiency of 9.7 lm/W. The remarkable enhancement in both current efficiency and power efficiency has been attributed to the effective charge separation and transport of ICL with high optical transmittance and excellent electron injection ability of LiF/Ca in tandem OLEDs. We note that the introduction of effective ICL is important to realize high performance tandem OLEDs.

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