Optimization for tandem organic light-emitting diodes based on Firpic*

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A series of single-unit and tandem blue phosphorescent organic light-emitting diodes (OLEDs) were prepared by adjusting the concentration of dopant based on the structure of ITO/NPB/EL unit/Alq_3/Cs_2CO_3/Al. The results show that tandem device with doping concentration of 10 wt% has appropriate energy transfer, which achieves the best performance with a maximum current efficiency of 3.4 cd·A^{-1}. Further study found that current efficiency and power efficiency of the tandem OLED adding BCP as hole blocking layer (HBL) can achieve 7.85 cd·A^{-1} and 0.72 lm·W^{-1}, respectively. It is 2.88 times and 1.57 times larger than those of sing-unit devices, and green peak is restrained effectively.
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Tandem organic light-emitting diode (TOLED) has advantages of high brightness, long lifespan, stable chroma[1-9] and so on, making it as a promising novel device structure. Compared with red and green light devices, blue light devices have a lower performance because of scarce materials and shorter lifespan. Wu[10] proposed two new charge generation layers (CGLs) based on LiF/Bphen/Ir(ppz)$_3$/Ir(ppz)$_3$:MoO_x/MoO_x and LiF/Ir(ppz)$_3$/Bphen/MoO_x, respectively, and the current efficiency of these tandem devices are more than twice as much as that of single-unit devices under the same density. Lei[11] used a conductive polymer/metal oxide heterostructure to prepare and optimize the charge generation layer of PEDOT:PSS/ZnO. The results showed that charges can be generated at the PEDOT:PSS/ZnO interface, and it is found that the connection interface has a significant effect on performance. Deng[12] prepared and studied a novel organic light-emitting diode (OLED) based on Cs_2CO_3/Al/MoO_3 as charge generation layer, and the electrical characteristics and normalized EL spectrum showed that this structure of Cs_2CO_3/Al/MoO_3 can be well used for charge generation and transmission. As a typical dopant for emission layer, bis(4,6-difluorophenylpyridinato-N,C2)picolinatoiridium (Firpic) has been widely applied in OLED. Firpic is a common iridium complex as phosphorescent materials. Singlet and triplet excitons can be back to ground state due to the spin orbit interaction, which generates from metal-ion 5d (a transition metal-ion). It breaks the maximum internal quantum efficiency (*IQE*) of fluorescent material which is 25% and reaches 100% theoretically. Therefore, the performance of OLED can be profoundly affected by phosphorescent materials. 1,3,5-Tris(1-phenyl-1H-benzimidazol-2-yl)ben-zene (TPBi), and bromocresol purple (BCP) can be used as hole blocking layer (HBL), but BCP is usually used as HBL with low cost. BCP is widely applied in OLED because the highest occupied molecular orbital (*HOMO*) of BCP is 6.5 eV, which can block exciton and holes[13]. In this paper, to study the impacts on tandem phosphorescent devices, BCP and Firpic are used as HBL and dopant, respectively.

The EL spectrum of Firpic researched in our lab is shown in Fig.1. The structures of BCP and Firpic are shown in Fig.2.

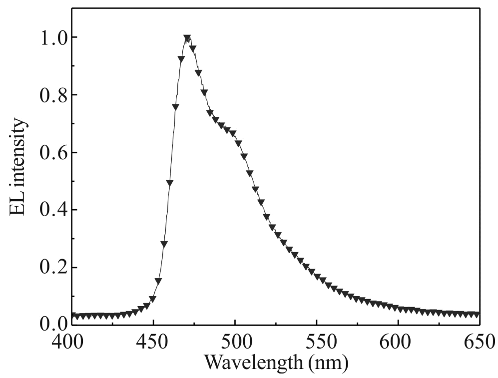

Fig.1 Typical EL spectrum of Firpic

The thickness of indium-tin oxide (ITO) substrate used in this experiment is about 200 nm. The transmittance is above 84%, and the sheet resistance is about 7 Ω/□. The glass substrate was treated by conventional cleaning

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operation to remove oil stain and dust on its surface with acetone, anhydrous ethanol, and deionized water. And the all substrates were ultrasonically cleaned. In order to obtain a higher surface cleanliness and ITO work function, oxygen plasma was used to treat the pre-cleaned substrate. During the processing, the O_2 flow rate is maintained at 800 mL/min. The power of ultrasonic cleaner is 80—100 W, and the processing time is 8 min. The ITO glass substrates were immediately placed into vacuum chamber of the evaporation coater. Single-unit and tandem OLED devices were prepared by vacuum thermal evaporation under the high vacuum condition (~10^{-5} Pa). The deposition rates are kept at 0.1 nm/s for organic materials, at 0.02 nm/s for Al as buffer layer, at 0.3 nm/s as cathode, and at 0.02 nm/s for Cs_2CO_3. Blue EL units were all doped with TPBi and Firpic simultaneously.

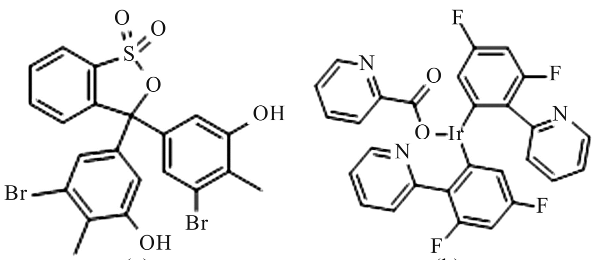


Fig.2 Structures of (a) BCP and (b) Firpic

The thickness was monitored by a calibrated quartz thickness monitor. And then its performance parameters were measured under the normal atmosphere. The normalized EL spectra were measured by using the PR670 Spectrum Scan spectrometer. The luminance-voltage and current-voltage characteristics were measured simultaneously by a programmable Keithley2450 voltage current source.

Fig.3 shows the structures of single-unit T1 and tandem T2 with changing doping concentration *x*. The feasibility of CGL has been proven in previous work[14]. To find the optimal value for performance, *x* changes from 5 to 15, and the interval is 5. From Fig.4(a) and 4(b), because of various concentration of Firpic, it is discovered that the turn-on voltage of T1 is about 11 V, lower than that of T2 which is about 19 V. The turn-on voltage of T2 isn't beyond the twice of that of T1, because Cs_2CO_3/Al can improve the performance of CGL[15] and increase the current density. So it makes the carriers injected into the two emission layers increase. The maximum brightness of T1 and group T2 are 600 cd·m^{-2} and 1 250 cd·m^{-2}, respectively. It is equivalent to connect two same EL units.

Fig.4(c) and (d) show the current and power efficiencies of T1 and T2. It can be speculated that the energy transfer between TPBi and Firpic is insufficient due to the low doping concentration of *x*=5. The efficiency of devices prepared with *x*=15 is degraded due to the increase of quenching. It can be learned from Fig.4(c) and (d) that the device prepared with *x*=10 achieves the maximum current and power efficiencies in T2 simultaneously, which are 3.4 cd·A^{-1} and 0.40 lm·W^{-1}, respectively. It is 26% more efficient than the single-unit device T1, whose current and power efficiencies are 2.7 cd·A^{-1} and 0.48 lm·W^{-1} under the same current density. It is proved that energy transfer between TPBi and Firpic is insufficient at a low concentration (*x*) for dopant leading to the decrease of current efficiency.

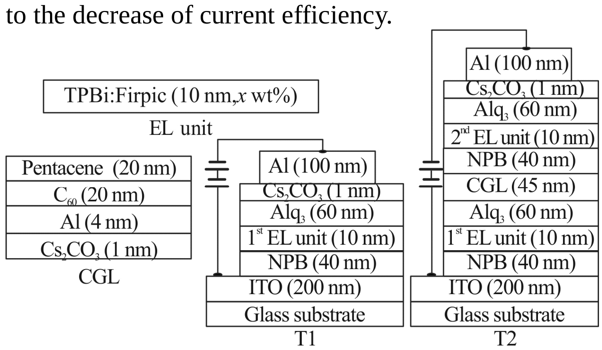
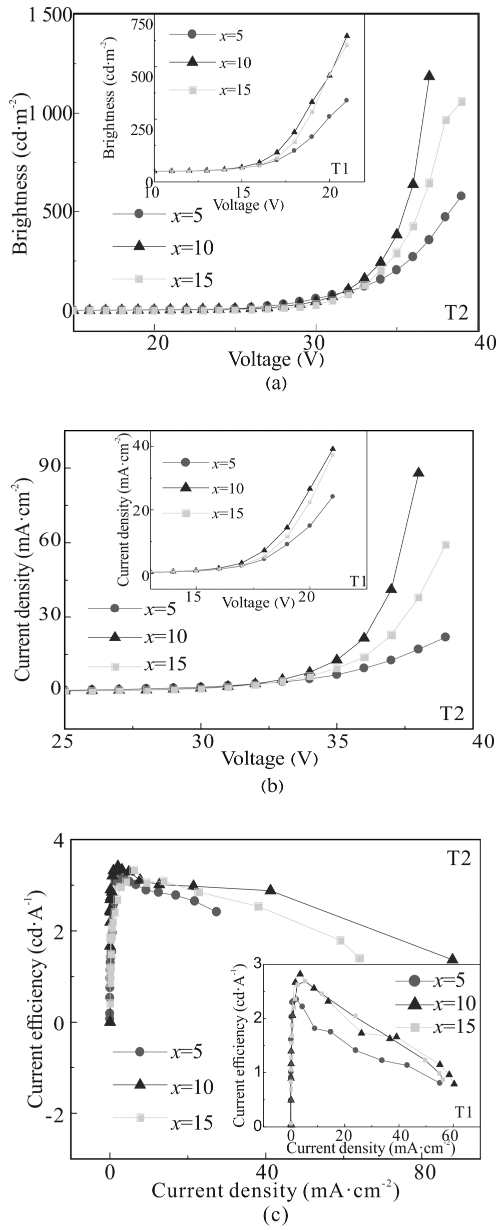


Fig.3 Structures of single-unit T1 and tandem T2



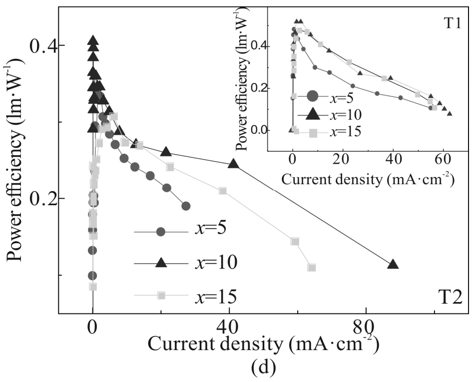


Fig.4 EL performances of the single-unit (inset) and tandem OLEDs: (a) The brightness-voltage characteristics; (b) The current density-voltage characteristics; (c) The current efficiency; (d) The power efficiency

The characteristics curves of power efficiency for group T1 and T2 in Fig.4(d) are similar to those in Fig.4(c). But, compared with single-unit devices, the power efficiency of tandem devices is slightly decreased. The reason is the over twice operating voltage for double-unit device than that of single-unit device, the imbalanced carriers injection and increase of internal resistance. Therefore, it is planned to optimize carrier injection for devices in later work.

In order to study the balance of carrier injection, BCP is added to the device structure as HBL. And a series of devices were designed and prepared. The structures are shown in Fig.5, where there is no BCP layer in T2, single BCP layer in T3, and double BCP layers in T4.

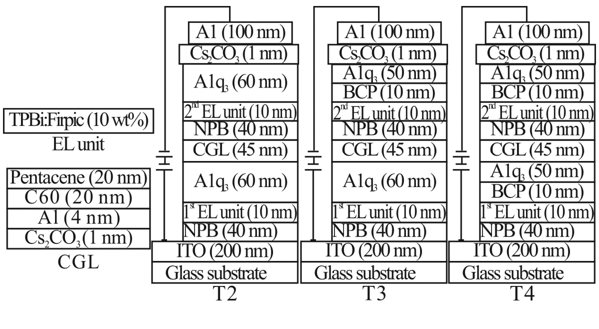


Fig.5 Structures of tandem OLEDs with no BCP (T2), single BCP (T3) and double BCP (T4)

The brightness-voltage characteristics and the current density-voltage characteristics for three tandem OLEDs are shown in Fig.6. It can be seen from Fig.6 that the brightness of device T3 adding a HBL between electron transport layer and emission layer is higher while the current density of T3 is lower compared with those of device T2 at the same voltage. The brightness of device T4 with two HBLs becomes larger while the current density of T4 is smaller compared with those of device T3 at the same voltage. The recombination probability between electrons and holes increases after BCP is added. But the leakage current of the device decreases. Generally, the performance of the device is improved.

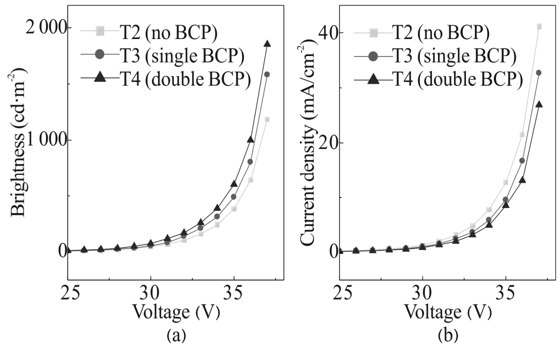


Fig.6 (a) The brightness-voltage characteristics and (b) the current density-voltage characteristics for tandem OLEDs

From Fig.7, the current efficiency and power efficiency of T3 are greatly improved compared with those of T2. The performance of device T4 is greatly improved. At a current density of 5 mA·cm^{-2}, the current efficiency and power efficiency for all devices are shown as Tab.1.

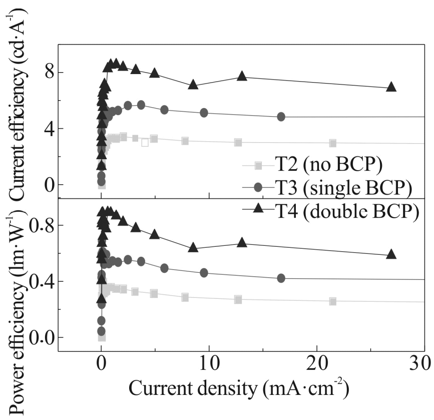


Fig.7 EL performances of three tandem OLEDs

Tab.1 Efficiency for devices fabricated with *x*=10 at current density of 5 mA/cm^2

Device	Current efficiency (cd·A^{-1})	Power efficiency (lm·W^{-1})
T1	2.72	0.46
T2	3.29	0.31
T3	5.52	0.51
T4	7.85	0.72

The reason for the improvement in performance is due to the fact that the current density curves of the devices adding BCP tend to increase with the increase of voltage, which leads to the decrease of leakage current. And the HBL effectively blocks the transport and diffusion of holes so that holes and electrons can be effectively recombined in emission layers, which increases the probability of exciton recombination. The current efficiency and power efficiency of device T4 are respectively increased to 2.88 times and 1.57 times than those of device T1.

For further explanation, from the energy level diagram as shown in Fig.8, the energy levels for these materials are borrowed from Ref.[2]. It can be seen that when holes inject into the emission layer from the anode, holes are easily blocked on the emission layer due to the high *HOMO* level of BCP[16]. Thereby it further increases the intensity of blue light emission.

$$\eta_p = \frac{\pi \times \eta_c}{V \times \rho}, \quad (1)$$

where V is the operating voltage, η_p, η_c and ρ stand for power efficiency, current efficiency and current density, respectively. From Eq.(1), since the current efficiency is proportional to the brightness, and it is inversely proportional to the current density. As the hole blocking layer BCP is added, the leakage current of the device is reduced, and the current efficiency is increased. Power efficiency is inversely proportional to the operating voltage. From Fig.6(a), the operating voltage is slightly reduced after the HBL is added. Therefore, the power efficiency is higher than before.

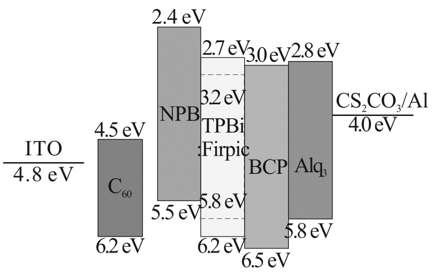


Fig.8 Energy level diagram of devices

Fig.9 shows that the main emission peak of the blue light is at 440 nm for T2, and the green emission shoulder peak is at 560 nm. When a layer of BCP as HBL is added, the green shoulder peak at 560 nm in the spectrum is significantly reduced for T3. When two layers of BCP as HBL are added, the peak at 560 nm disappears. From this, we can infer that holes are injected into Alq_3 due to T2 without hole blocking layer. So a green shoulder peak disappears in the spectrum as BCP is added. It is known from Fig.1 that the main emission peak of Firpic is at about 470 nm. Obviously, the electroluminescence peak of Firpic in this paper with a slight blue shift indicates that micro-cavity effect still occurs in the tandem OLEDs[16].

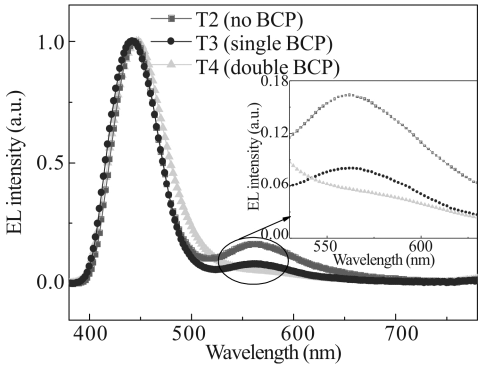


Fig.9 Normalized EL spectra of all tandem devices at 35 V

In summary, EL unit was prepared by mixing 5 wt%, 10 wt% and 15 wt% of Firpic with TPBi, and the effect of dopant concentration on performance is researched. The results show that lower and higher doping concentration lead to the insufficient energy transfer and quenching, respectively. Device achieves the best emission performance when the emission layer is doped with 10 wt% of Firpic. As for tandem device, the current efficiency is improved while the power efficiency is decreased compared with those of single-unit device. To research the imbalanced injection of carriers, BCP is made as HBL to prepared a series of devices. The final results show that the current efficiency and power efficiency of tandem OLED with a layer of HBL are increased to 5.52 cd·A^{-1} and 0.51 lm·W^{-1}, and those of the tandem OLED with two HBLs are increased to 2.88 and 1.57 times than those of single-unit device. Research content indicates that the suitable concentration of dopant is important for performance, and the high *HOMO* energy level of BCP can effectively balance the carrier injection to make the efficiency enhanced. In addition, developing better modified electrode materials, fabricating efficient transport layer materials, optimizing the thickness of EL unit and designing CGL with strong charge generation ability are feasible to improve the current efficiency and power efficiency of tandem OLEDs.

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