Efficient blue fluorescence tandem organic light emitting device with a novel intermediate connector*

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A novel intermediate connector (IC) was formed which was composed of aluminum (Al, 3 nm)/1,4,5,8,9,11-hexaazatriphenylene-hexacarbonitrile (HAT-CN). The 3-nm-thick Al in the IC is certified to efficiently generate intrinsic charge carriers, and the HAT-CN is proved to work as the holes injection layer (HIL) for the corresponding electroluminescent (EL) unit simultaneously. This simply IC comprehensively takes advantage of the features of the HAT-CN so as to stack two single EL units without introducing extra material. In addition to a significant enhancement in luminance and current efficiency, a current efficiency (*CE*) of 10.2 cd/A and a luminance of 2 042 cd/m^2 under the current density 20 mA/cm^2 of this tandem organic light emitting device (TOLED) are yielded, which are notably almost the sum of that of the two single-unit devices.
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The efficient and small molecule organic light emitting device (OLED) have obtained great development in the last three decades, since it was reported for the first time by Tang and VanSlyke in 1987[1]. Owing to the advantages of high brightness, long lifetime and low power consumption, the OLEDs are currently being widespread researched and commercial interested on the applications in next-generation flat-panel displays and solid-state-lighting sources[2,3]. For conventional OLED, the luminance is driven by current density. And a high current density is needed in order to achieve high brightness for application. However, the operational lifetime of an OLED will be decreased with an increasing current density[4]. A commonly used method to overcome this problem is using tandem OLED (TOLED) which consists of stacked two or multiple electroluminescent (EL) units connected in series via intermediate connector (IC)[5-7]. The IC commonly works as an internal electrode, to generate intrinsic charge carriers and to facilitate opposite carriers (electrons and holes) injection into the adjacent EL units.

Generally, the IC is a heterojunction typically formed by organic-organic semiconductor, organic semiconductor-metal and organic semiconductor-metal oxide[8-10]. To improve the performance of an organic semiconductor used in the IC, an electrical doped organic semiconductor layer is typically adopted. The n-type dopants in the doped organic layer are typically alkali metal, alkali metal compounds, alkaline earth metals or alkaline earth metal compounds, such as Li[11], Mg[12], Cs_2CO_3[13] and CsN_3[14]. The p-type dopants are usually $FeCl_3$[15], F4-TCNQ[16].

In most cases, a joined IC means one or multiple materials introduced in the device, which lead to an increase in the fabrication process and cost. Little work has been tried to stack the EL units without introducing extra material, which would be realizing a decrease in complexity of fabrication process and cost. In our work, two different blue fluorescence EL devices were stacked while the thickness of cathode Al of the first EL unit device is decreased to 3 nm. The current efficiency (*CE*) is enhanced to 10.2 cd/A for this tandem device, which is almost the sum of the two single-unit devices. A novel IC is used that is composed of the Al (3 nm)/ 1,4,5,8,9,11-hexaazatriphenylene-hexacarbonitrile (HAT-CN). The Al in the IC is certified to generate intrinsic charge carriers, and the HAT-CN can facilitate holes injection into the second EL unit simultaneously.

The configurations of devices used in our work are shown in Tab.1, which were deposited on patterned ITO-coated glass substrates with a sheet resistance of 15 Ω/sq. The ITO-coated glass substrates were routinely cleaned in an ultrasonic bath for each 20 min with distilled water, ethyl alcohol and acetone. Then they were treated by O_2 plasma under conditions of 1.3×10^{-2} Pa at 75 W for 20 min. All these layers, including the cathode and the IC layer Al, were grown onto the substrates in

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sequence by thermal evaporation in the vacuum chamber at the base pressure less than 3×10^{-4} Pa. The evaporation rates were kept at 0.1 nm/s for LiF and also Al in the IC layer, 0.1 nm/s for the organic layers and 1.0 nm/s for the Al cathode. The current density-voltage-luminance (*J*-*V*-*L*) characteristics of the devices were measured with a luminance meter (DLM-1000S) by using direct current (DC) voltage bias with Keithley2400. The EL spectra of the emission were measured by OPT-2000 instruments in the dark. All measurements were carried out at room temperature under ambient conditions without device encapsulation. All the materials used in our experiments were purchased by commercially without further sublimation purification.

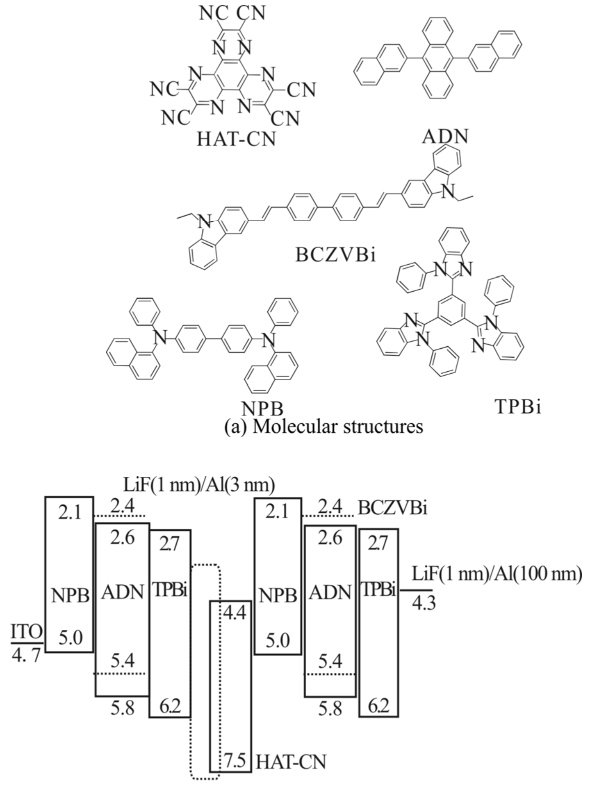
Tab.1 Layer structures of the OLED devices

Device	Layer structures
Device A	ITO/NPB(60 nm)/ADN: BCzVBi(6 wt%, 35 nm)/TPBi(20 nm)/LiF(1 nm)/Al(100 nm)
Device B	ITO/HAT-CN(20 nm)/NPB(60 nm)/ADN: BCzVBi(6 wt%, 35 nm)/TPBi(20 nm)/LiF(1 nm)/Al(100 nm)
Tandem device C	ITO/NPB (60 nm)/ADN: BCzVBi (6 wt%, 35 nm)/TPBi (20 nm)/LiF (1 nm)/Al (3 nm)/ HAT-CN (20 nm)/NPB (60 nm)/ADN: BCzVBi (6 wt%, 35 nm)/TPBi (20 nm)/LiF (1 nm)/Al (100 nm)
Tandem device D	ITO/NPB (60 nm)/ADN: BCzVBi (6 wt%, 35 nm)/TPBi (20 nm)/LiF (1 nm)/HAT-CN (20 nm)/NPB (60 nm)/ADN: BCzVBi (6 wt%, 35 nm)/TPBi (20 nm)/LiF (1 nm)/Al (100 nm)

The molecular structures and the energy level diagrams of the materials used in this work are shown in Fig.1. The HAT-CN was adopted as holes injection layer (HIL) in the single-unit device B. All devices were fabricated with ADN used as the emitting layer doping the blue dopant of 4,4′-bis(9-ethyl-3-carbazovinylene)-1,1′-biphenyl (BCzVBi). The current efficiency-voltage (*J*-*V*) and luminance-current density (*L*-*J*) characteristics of the devices A, B and the tandem device C are shown in Fig.2. The typical performance parameters, including turn-on voltage (V_{on}), *CE*, power efficiency (*PE*) and Commission International de l'Eclairage (CIE) coordinates (*x*, *y*) are summarized in Tab.2. The device B exhibits a better turn-on voltage than device A, which shows the similar performance with correlative references when the HAT-CN was used as HIL[17].

Under an operational current density of 20 mA/cm^2, the devices A, B and the tandem device C require a driving voltage of 7.3 V, 7.0 V and 13.4 V corresponding to the luminance of 956 cd/m^2, 1 117 cd/m^2 and 2 042 cd/m^2, and the *CE* of 4.7, 5.3, and 10.2 cd/A, respectively. Clearly, the driving voltage, the luminance and the *CE* of the tandem device C are all increased to about the sum of those of the single-unit devices A and B, which means that the tandem device C shows the features of a tandem device.

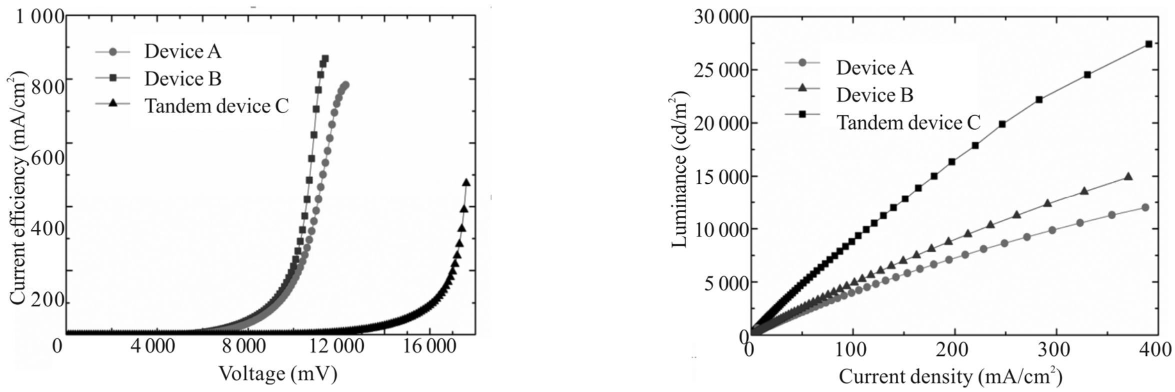
The EL spectra at 20 mA/cm^2 of the devices A, B and the tandem device C are shown in Fig.3, which have not apparently different with each other. The *CE*-*L*-*PE* curves of the devices A, B and the tandem device C are shown in Fig.4. It can be found that the *PE* of the tandem device C is just half of the sum of those of devices A and B. And we notice in Tab.2 and Fig.4 that the *CE* of the tandem device C is appreciably greater than double of that of the device A, which almost equal to the sum of those of the devices A and B. That means the HAT-CN in the IC can simultaneously take effect as an HIL for the second EL unit in the tandem device C. In addition, the HAT-CN are recognized as the n-type organic semiconductor material without absorption in the visible range[17]. That means this IC would be a favorable way to realize a tandem device.



(a) Molecular structures

(b) Energy level diagrams, where the part in the dot border rectangle worked as the IC in the tandem device C

Fig.1 The molecular structures and the energy level diagrams of the materials



(a) *J-V* characteristics (b) *L-J* characteristics

Fig.2 *J-V-L* characteristics of the devices A, B and the tandem device C

Tab.2 EL characteristics of the devices

Device	V_{on} (V) at 1 cd·m^{-2}	Maximum *CE* (cd/A)	*CE*(cd/A) at 20 mA/cm^2	Maximum *L* (cd/m^2)	*L* (cd/m^2) at 20 mA/cm^2	Maximum *PE* (lm/W)	*PE* (lm/W) at 20 mA/cm^2	*CIE* (*x*, *y*) at 20 mA/cm^2
Device A	3.6	5.0	4.7	15 261	956	1.6	1.4	(0.17, 0.22)
Device B	3.5	5.6	5.4	17 974	1 117	2.1	1.9	(0.17, 0.22)
Tandem device C	7.3	10.9	10.2	27 417	2 042	2.0	1.8	(0.17, 0.22)
Tandem device D	10.4	5.2	5.0	298	102	-	-	(0.17, 0.22)

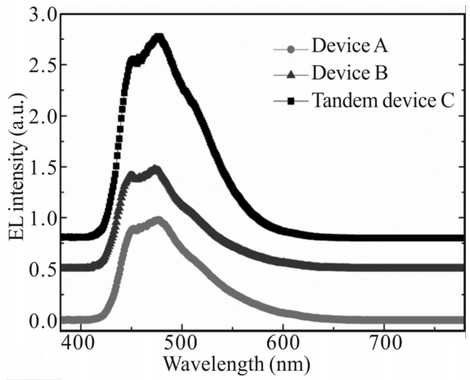


Fig.3 EL spectra at 20 mA/cm^2 of the devices A, B and the tandem device C

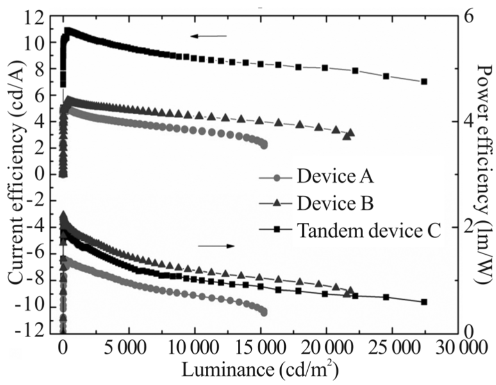


Fig.4 *CE-L-PE* characteristics of the devices A, B and the tandem device C

As for the IC work mechanism in the tandem device C, the organic-organic semiconductor heterojunction or organic semiconductor-metal heterojunction both can be worked as an IC as we mentioned in the part of introduction. Considering that the HAT-CN is a strong electron acceptor which can be used as an effective holes injection material, there are two heterojunctions of Al/HAT-CN and HAT-CN/NPB in the tandem device C, which both probably be worked as IC to generate intrinsic charge carriers. To figure out this query in the tandem device C, the tandem device D was designed without the 3-nm-thick Al layer, which has the only potential IC of the HAT-CN/NPB. The configuration and the EL characteristic parameters of the tandem device D are also shown in Tabs.1 and 2, respectively. The *L-V* characteristics of the tandem devices C and D are shown in Fig.5. Apparently, the performance of the tandem device D is terribly bad, the turn-on voltage of the tandem device D is 10.4 V, and the luminance os only 109 cd/m^2 under the operational current density of 20 mA/cm^2, corresponding the driving voltage of 17.4 V. That indicates the n-p heterjunction junction of HAT-CN/NPB is not an effective IC in the tandem device D in our work, it would be the same effect in the tandem device C. Therefore, the Al/HAT-CN should be the virtual IC of the tandem device C, of which the Al (3 nm) is worked to generate intrinsic charge carriers. This conclusion is different from the heterojunction formed by organic-organic semiconductor[18,19].

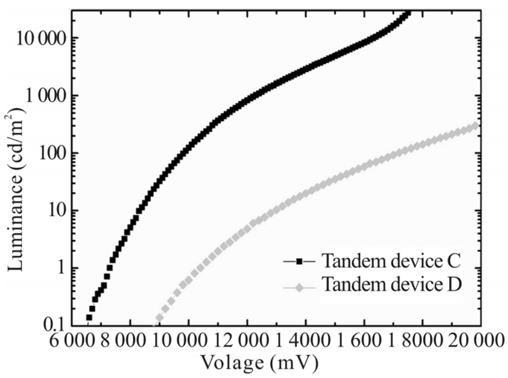


Fig.5 *L-V* characteristics of the tandem devices C and D

In summary, the tandem device C stacked by two EL single-unit devices is demonstrated, of which a novel IC as Al(3 nm)/HAT-CN is formed. The Al in the IC is certified to efficiently generate intrinsic charge carriers, and the HAT-CN simultaneously facilitates as an HIL for the corresponding EL unit. Under the current density of 20 mA/cm^2, The *CE* and the luminance are enhanced to 10.2 cd/A and 2 042 cd/m^2 for this tandem device, respectively, which is notably almost the sum of those of these two single-unit devices.

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