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RESEARCH ARTICLE

A simple unilateral homogenous PhOLEDs with enhanced efficiency and reduced efficiency roll-off

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Abstract In this paper, highly efficient phosphorescent organic lighting emitting diodes (PhOELDs) with low efficiency roll-off are demonstrated by using a unilateral homogenous device structure with wide band-gap material 4, 4', 4″-tri(N-carbazolyl)-triphenylamine (TCTA) as hole transporting layer and emitting layer (EML). The optimized blue device exhibits a high power efficiency of 40 lm/W, external quantum efficiency of 19.2% and current efficiency of 37.7 cd/A. More importantly, the device exhibits a low efficiency roll-off at 1000 cd/m^2. In addition, the white homogenous PhOLEDs only exhibits the efficiency roll-off 5.6% and 17.5%, corresponding to the brightness of 1000 and 5000 cd/m^2 respectively. These interesting results demonstrate that the simple unilateral homogenous device structure is a promising way to enhance the device efficiency and reduce the efficiency roll-off.

Keywords enhance efficiency, efficiency roll-off, unilateral homogenous structures

1 Introduction

Organic light emitting diodes (OLEDs) have been studied extensively since the first invention of small organic molecules system by Tang and VanSlyke [1]. Compared to fluorescent counterpart, phosphorescent OLED can utilize both singlet and triplet excitons, the internal quantum efficiency of the device can reach to 100%. During the past decades, green [2–4] and red [5,6] phosphorescent electroluminescent devices with high efficiencies, long lifetimes, and proper CIE coordinates have been well developed. However, blue phosphorescent devices are still the bottleneck for the high CIE coordinates (y-coordinate value < 0.30), high power efficiency and low efficiency roll-off. To solve the problems, a variety of methods have been proposed. Such as, syntheses of new electron transport materials with high electron mobility [7], designing bipolar blue host materials to balance the hole and electron [8,9]. For phosphorescent device structure, the efficiency can also be improved by tuning the excitons recombination zone, the energy-transfer and excitons diffusion between the neighbor layers through changing layer thickness or adding different carrier injecting layers. Recently, Kido et al. had designed a new device structure with suitable host and electron transport material, the external quantum efficiency (EQE) up to 20% was harvested [10,11]. Lee et al. reported a novel device with two hosts *N*,*N*′-dicarbazolyl-3,5-benzene (mCP) and 2,2'-bis[5-phenyl-2-1,3,4-xadazolyl]biphenyl (OXD), the current efficiency of the OLED improved about 30.8% and 141.4% compared to OLEDs with only mCP or OXD as the emitting layer (EML), respectively [12]. Zhang et al. reported a dual electron-transport layer (D-ETL) blue phosphorescent organic lighting emitting diode (PhOELD), by sandwiching a new material between the emission layer (EML) and electron transport layer (ETL), which showed much better chromaticity, higher power efficiency (improved about 30%) [13]. However, there are still many bottlenecks, such as high efficiency roll-off and complex production processes. To further overcome the problem, the homogenous devices with only a single organic material have been executed. Cai et al. demonstrated an efficient sky blue phosphorescent p–i–n homojunction organic light-emitting device with a low-driving-voltage of 3.9 V at 1000 cd/m^2, by doping FIrpic into the bipolar host material 4,6-bis[3-(carbazol-9-yl) phenyl] pyrimidine (46DCzPPm) as the EML [14]. Tsuji et al. used new ambipolar material bis(carbazolyl)benzodifuran (CZBDF) to fabricate simple homojunction device, which presented the same results as heterojunction devices

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[15]. Wang et al. also reported the high-performance of green, orange, and red top-emitting organic light-emitting diodes (TOLEDs) with homogenous device structure, which even showed higher than the multi-layer heterojunction bottom-emitting devices using the same emitting layers [16]. Compared to the multilayered counterpart, homogenous device structure made the fabrication processes simplified, reduced structural heterogeneities, and formed rather stable electroluminescence (EL) spectra. All of these advantages suggest that homogenous device structure possesses great potential for practical application in future.

Noteworthy, the homogenous phosphorescent device with enhanced efficiency and reduced efficiency roll-off is still rather rare and needs further research. Here, we report a unilateral homogenous phosphorescent device structure based on 4, 4', 4″-tri(N-carbazolyl)-triphenylamine (TCTA). In this device configuration, the unilateral homogenous devices is using TCTA as bifunctional material simultaneously, which could efficiently reduce the hole inject barrier. TCTA acted as both hole transporting materials and host of EML, which could reduce the hole transport barrier at the interface of the EML/hole transport layer (HTL). TmPyPB was used as ETL to facilitate the injection of electron and restriction of excitons and hole. The iridium(III)bis((4,6-difluorophenyl)-pyridinate-N,C$^{2'}$)picolinate (FIrpic) and $(fbi)_2Ir(acac)$ (fbi = 2-(9,9-diethyl-9H-fluoren-2-yl-1H-benzoimidazole) were used as the dopant for blue, orange and white OLED. The carriers recombination zone was effectively broadened and the triplet-triplet annihilation which arose from the high concentration of the triplets [17–19] was suppressed in the unilateral homogenous structure. As we expected, the performance of blue, orange and white phosphorescent OLEDs based on TCTA as the host were greatly improved.

2 Experiments

In this paper, all the devices are fabricated by vacuum deposition. The indium tin oxide (ITO) substrate with a sheet resistance of 20 Ω/square was cleaned with the cleaner and deionized water under the ultrasound for 15 min respectively. Then the ITO was dried in an oven for 3 hours. Finally, the ITO was treated with UV-ozone for 5 min. At last, the substrate was loaded into a vacuum deposition chamber. The EL devices were fabricated by successive deposition of organic materials and electron materials onto the ITO-coated glass substrate at high vacuum (10^{-6} Torr) with a rate of 1.0–1.2 Å/s. The EL spectrum, luminance, CIE coordinates and the current density-voltage-luminance-efficiency characteristics of the devices are measured with a rapid scan system using a Photo Research PR655 spectrophotometer and a Keithley 2400 digital source. All the data of EL characteristics are measured at room temperature under an ambient atmosphere.

3 Results and discussion

3.1 Energy transfer between host and guest from spectrum analysis

Figure 1 shows the photophysical properties of host and dopant. It exhibits the absorption spectrum of FIrpic and $(fbi)_2Ir(acac)$, and photoluminescence spectra of pure TCTA and codoped TCTA. FIrpic exhibits two typical absorption peaks locating at 280 and 380 nm. And orange shows the absorption at the two at 346 and 438 nm. Meanwhile, TCTA exhibits a main PL peak at 384 nm. There is a good spectral overlap between the PL spectra of TCTA and the absorption spectra of FIrpic and $(fbi)_2Ir(acac)$, which indicates the efficiently energy transfer from TCTA to FIrpic. Furthermore, the triplet energy of the TCTA, FIrpic and $(fbi)_2Ir(acac)$ are 2.80, 2.65 and 2.22 eV, respectively. It also ensured the triplet energy efficient transitions from TCTA to FIrpic and $(fbi)_2Ir(acac)$. Therefore, a complete energy-transfer process from TCTA to FIrpic or $(fbi)_2Ir(acac)$ is capable.

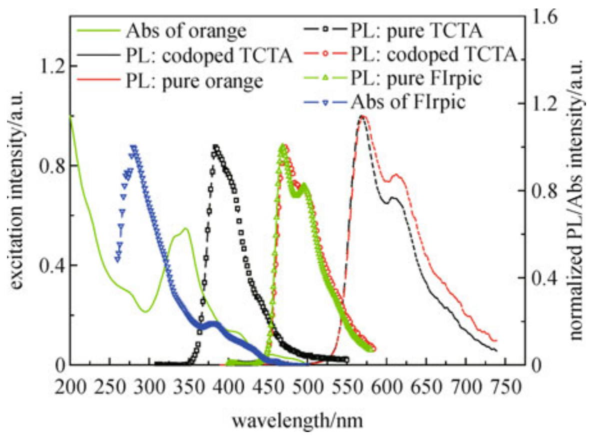

Fig. 1 Absorption (Abs) spectra of FIrpic and orange ($(fbi)_2Ir$ (acac)), photoluminescence (PL) spectra of pure TCTA, FIrpic and orange doped TCTA and FIrpic

3.2 High efficiency unilateral homogenous device

As we all know, the mobility of the electron transport materials affected the device efficiency greatly [20]. So the excellent material of 3,3'-[5'-[3-(3-pyridinyl)phenyl][1,1':3',1''-terphenyl]-3,3''-diyl]bispyridine (TmPyPB) was selected as the ETL in order to get optimized device structure. In this paper, the unilateral homogenous device (device 1) was fabricated to improve the device efficiency with the device structure of ITO/MoO_3 (10 nm)/TCTA (60 nm)/TCTA:FIrpic (12%, 20 nm)/TmPyPB (40 nm)/LiF

(1 nm)/Al (150 nm). And the control device (device 2) with N,N'-bis(naphthalen-1-yl)-N,N'-bis(pheny) benzidine (NPB) (40 nm) instead of TCTA was used as the HTL. The homogenous architecture could potentially improve the efficiency [16] and reduce the efficiency roll-off. The device structure and energy levels of the homogenous structure were shown in Fig. 2.

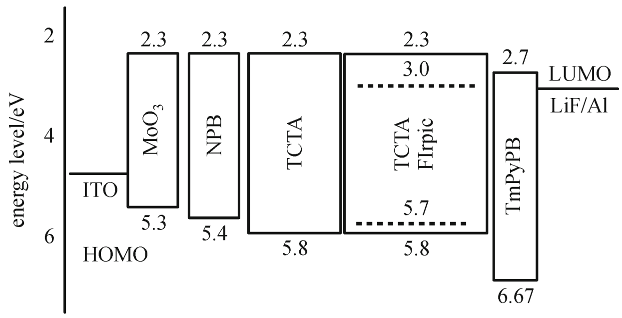

Fig. 2 Structure and energy levels of unilateral homogenous device (device 1) and control device (device 2). ITO: indium tin oxide; HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital

Figure 3(a) shows the current density-voltage-brightness (*J-V-B*) curves, it could be found the driving voltage of the homogenous device is lower than the control device, as the driving voltages of the two devices are 4.8 and 5.6 V at 1000 cd/m^2, respectively. Comparison in the turn-on voltage (the voltage at 1 cd/m^2) of the two devices, device 2 (3.0 V) is higher than the homogenous device 1, which shows the brightness of 10 cd/m^2 at 3 V. The reduction of operational voltage may be originated from the less organic/organic interface. As shown in Fig. 3(b), it could be found the maximum luminescence efficiency (LE) of homogenous device (device 1) reach to 37.7 cd/A, whereas the control device (device 2) shows the maximum efficiency only 28.4 cd/A. Moreover, the efficiencies of homogenous device are higher than the control device at the range of brightness studied. Especially, at ultrahigh brightness of 10000 cd/m^2, the efficiency (19.1 cd/A) still remain over twice than the control device (7.8 cd/A). The detailed device performances at different brightness are listed in Table 1. It is concluded that the homogenous device exhibits improved efficiency and reduced efficiency roll-off in current efficiency, which is desired for phosphorescent emission. For example, at the luminance of 1000 cd/m^2, the current efficiency of device 1 is still as high as 34.2 cd/A, which is 90.3% of the maximum efficiency, but for control device the efficiency rolled off higher than 15.8% at this high brightness. Furthermore, at ultrahigh brightness of 5000 cd/m^2, the current efficiency of unilateral homogenous device is still keeping 72% of the maximum value, but for control device there only about 54% of its maximum. In addition, from the EL curves (inset of Fig. 3), it can be found all the devices with two peaks at 470 and 496 nm, which is a typical FIrpic EL characteristic peak. One can note that the height of the peak at 496 nm decreases slightly in the devices 2, and it is clearly evidence that the recombination zone shift toward the ETL side from devices 2 to 1 [21].

The homogenous device exhibits better performance than the control device. These improvements could be attributed to the following reasons: 1) the employ of unilateral homogenous structure could reduce the injection barrier and drive voltage, which caused by multilayer interface [17]. 2) Utilizing TCTA as the HTL and EML could effectively transport hole and limit excitons in the EML, and exploring TmPyPB as ETL with higher triplet (2.8 eV) and HOMO (6.67 eV) [22] could effectively limit hole and exciton within the EML, meanwhile, block the tripled energy transfer from TCTA to ETL. 3) The

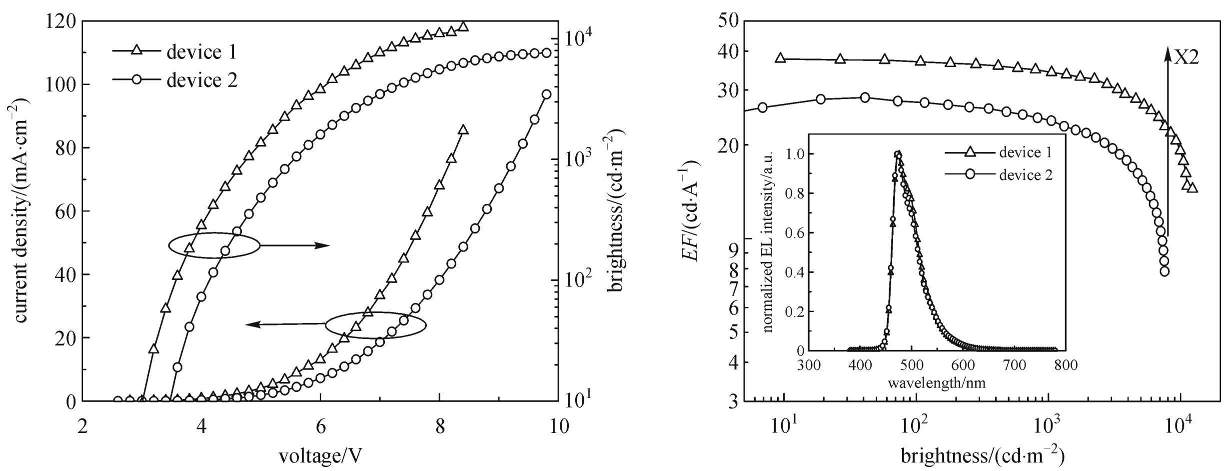

Fig. 3 (a) *J-V-B* curves of devices 1 and 2; (b) current efficiency of unilateral homogenous device (device 1) and control device (device 2) at different brightness. Inset: EL spectra of unilateral homogenous device (device 1) and control device (device 2)

Table 1 EL performance of blue and white PhOLEDs at different conditions

	$V^{a)}$	EQE^{max}	LE^{max}	$LE^{1000\ cd/m^2}$	$LE^{5000\ cd/m^2}$	$LE^{10000\ cd/m^2}$
blue/TCTA	2.8/6.5	19.1	37.7	34.2	27.1	19.1
blue/NPB	3.0/7.1	14.5	28.4	23.9	15.4	7.8[a)]
white/TCTA	3.0/9.7	15.9	40.8	38.7	34.0	30.3
white/NPB	3.1/7.0	15.1	35.8	32.8	25.1	13.1

Note: a) Measured operating voltages, presented in the order of values at 1 cd/m^2 and 20 mA/m^2

homogenous device structure could broaden the excitons recombination zone. As shown in Fig. 4, it could be found that the unilateral homogenous device efficiency continuously increases until thicknesses of EML reaching 25 nm, and the efficiency reduces with further increasing the doped layer. As we all know, high triplet concentration results in triplet-triplet annihilation. In the homogenous device, broader recombination zone of 25 nm (control device only 12 nm) benefits the triplet energy transfer from TCTA to guest and reduces triplet-triplet annihilation. Thus it could get the higher efficiency and lower efficiency roll-off.

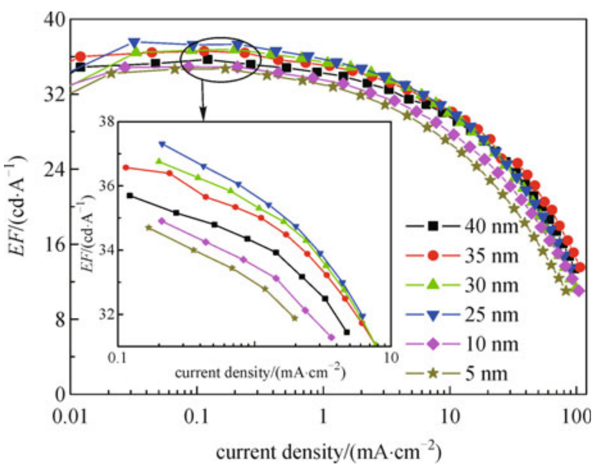

Fig. 4 Thickness of excition recombination zone in homogenous device

To further confirm the better performances of unilateral homogenous devices structure, we fabricated the white PhOLED with this new device structure (device 3). The device 3 with structure of ITO/MoO_3 (10 nm)/TCTA (60 nm)/TCTA:FIrpic:$(fbi)_2Ir(acac)$ (7%, 0.5%, 20 nm)/ TmPyPB (40 nm)/LiF (1 nm)/Al (150 nm). And the control device (device 4) with NPB (40 nm) instead of TCTA was used as HTL. It is noteworthy that the white PhOLED with unilateral homogenous structure also exhibits the excellent performance. All the characters of devices were shown in Fig. 5 and Table 1.

As shown in Fig. 5, the white device with unilateral homogenous structure exhibits the current efficiency of 40.8 cd/A at 100 cd/m^2, 38.7 cd/A at 1000 cd/m^2 and 34.0 at 5000 cd/m^2. While for control device, the current

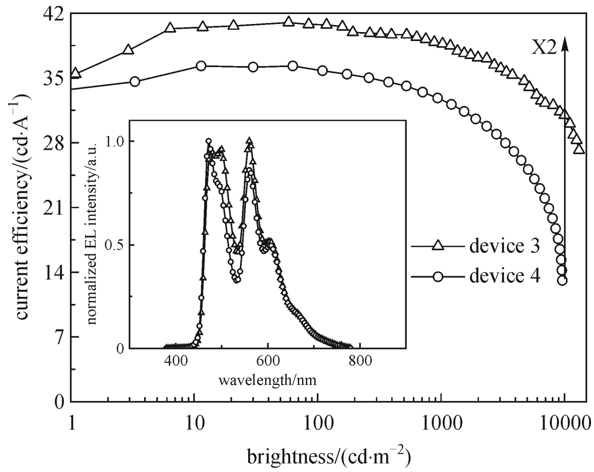

Fig. 5 Current efficiencies of white PhOLED with homogenous and control structures. Inset: EL spectra of different device structures

efficiency is only 35.8, 32.8, 25.1 cd/A at same condition (Table 1). In addition, the unilateral homogenous structure device shows a reduced roll-off in efficiency. For example, the homogenous device exhibits the efficiency roll-off only 5.6% and 17.5%, respectively, when the brightness at the 1000 and 5000 cd/m^2. While the corresponding value are 9.6% and 30.9% for the control device. Especially, at ultrahigh brightness of 10000 cd/m^2, the efficiency of homogenous device still remains more than twice of the control device exhibiting the value of 30.3 cd/A, but for control device only of 13.1 cd/A. More importantly, at the brightness of 10000 cd/m^2, device 4 shows the efficiency roll-off of 63.9%, which is nearly three times than the unilateral homogenous device, only of 26.1%. The improved efficiency and reduced efficiency roll-off could be attributed to the better charge balance and widen the excitons recombination region.

4 Conclusions

In summary, we have demonstrated a simplified high efficiency unilateral homogenous device structure. By optimizing the device structure, balanced charge transfer and broaden recombination zone are achieved in the simple homogenous structure. The blue, orange and white PhOLEDs exhibit improved devices efficiency and reduced efficiency roll-off. More importantly, the simple unilateral homogenous device structure can be used as an effective strategy to developing efficient PhOLEDs with enhanced efficiency and reduced efficiency roll-off behavior.

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