Improving working lifetime and efficiency of phosphor doped organic light-emitting diodes

Yunfei Li,[1] Yuying Hao,[1,2,*] Wenlian Li,[3] Shuqing Yuan[1], Huihui Liu[2], Yanxia Cui,[1] Hua Wang,[2] Bingshe Xu,[2] and Wei Huang[4]

[1]College of Physics and Optoelectronics, Taiyuan University of Technology, Taiyuan 030024, China
[2]Key Laboratory of Interface Science and Engineering in Advanced Materials of Taiyuan University of Technology, Taiyuan 030024, China
3Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Science, Changchun 130033, China
[4]Key Laboratory for Organic Electronics & Information Displays (KLOEID) and Institute of Advanced Materials, Nanjing University of Posts and Telecommunications (NUPT), Nanjing 210046, China
[*]haoyuyinghyy@sina.com

Abstract: Long working lifetime and high efficient phosphorescent organic light-emitting diode (PHOLED) in which mixed host composed of wide-band-gap based 4, 7-diphenyl-1, 10-phenanthroline (Bphen) and (4,4'-bis(carbazol-9-yl)-biphenyl) (CBP) was demonstrated. The PHOLED with structure of ITO / MoO_3 / CBP:MoO_3 (15v%, 30 nm) / CBP(10 nm) / ([50v%:50v% CBP:Bphen]: 6v% $Ir(ppy)_3$)(30 nm) / Bphen (40 nm) / LiF (1 nm) / Al offers a peak power efficiency of 41.6 lm/W (a peak current efficiency of 39.8 cd/A)) at a low driving voltage of 3 V which increases by 55% and 27% compared to that of corresponding single-host (SH) and double emitting layer (DML) devices, respectively. Especially very long work lifetime (3530 hs) at an initial luminance of 500 cd/m^2 of the mixed hosted device is exhibited, rising by about 4.1 and 2.46 times relative to that of corresponding SH and DML devices. High efficiency and longer working lifetime was attributed to the absence of heterojunction and balanced charge carrier transport characteristics in the mixed host based OLED structure. The more detail mechanism was also presented.

OCIS codes: (230.3670) Light-emitting diode; (160.4890) Organic materials; (160.4760) Optical properties; (310.6870) Thin films, other properties.

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1. Introduction

In recent years, phosphorescent organic light-emitting diodes (PHOLEDs) have attracted great attention due to their potential to achieve nearly unity internal quantum efficiency [1, 2]. Some revealed results have demonstrated significantly improved efficiency by various device optimization techniques [3–7]. Such techniques, however, are always along with the complex heterojunction (HJ) structure for balancing the carrier injection/transport and limiting the long lived triplet exciton in intended recombination zone. Though the HJ interface itself is crucial for achieving high electroluminescent (EL) performance, the abrupt HJ with the high local field could limit the device reliability and result in high driving voltage. The accumulated charges in HJ interface are prone to form chemically unstable cationic species which would accelerate the formation of non-radiative trap centers and thus the device degradation [8, 9]. Moreover, the high working voltage of the HJ-OLED could lead to high Joule heating, which would deteriorate the organic materials [10, 11]. In order to extend the working lifetime, the

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uniform or graded mixed-host (MH) structure has been introduced to eliminate the sharp HJ interface [11, 12]. Such MH-OLEDs could, however, not control effectively the carrier transport, resulting in a higher carrier leakage and thus lower efficiency [12, 13]. Recently, the certain graded MH-PHOLEDs have exhibited high EL efficiency [14, 15]. But such a graded MH structure would induce complexity of the device fabrication processes, which is undesirable for industrial manufacture. Besides several uniformly mixed host PHOLEDs have been demonstrated [16–21]. High efficient PHOLEDs based on uniformly mixed hosts seem to need the exciton blocking layers (EBLs) on both sides of the emission layer (EML) because such a EBL could confine the triplet excitons within EML, but the structure with EBL would lead to multi-HJ interface easily degrading OLED thus its working lifetime. Therefore there is also an efficiency–lifetime tradeoff in PHOLEDs with a uniform MH structure. The improvement of both efficiency and working lifetime in uniform MH-OLEDs is still expected by rational design of the device structure. The enhanced efficiency and prolonged working lifetime were obtained in green MH-PHOLEDs by suitable combination of the exciton blocking/electron transport materials with co-host compositions [21, 22]. The white OLED with 40% higher efficiency and about 40 times longer lifetime than the conventional bilayer heterostructure were reported by a new strategy of double blue emitting layers (using a dye-doped electron-transporting blue host to cover the uniformly MH blue-emitting layer) combined with a uniformly MH yellow-emitting layer [23].

In light of above publications in the present demonstration we design a new uniform MH-PHOLED structure which is markedly different with above reported PHOLEDs. Usually, the mixed host is composed of hole-transport-type host (HTH) and electron-transport-type host (ETH), such as 4, 4′, 4”-tris (N-carbazolyl) triphenylamine (TCTA) and 1, 3, 5-tris(N-phenylbenzimidazole-2-yl) benzene (TPBI) [19–22]. Not only do these host materials need high triplet energy, but also HTH requires shallower HOMO level for hole injection and ETH must behave deep LUMO energy for electron injection. The fact that simultaneously such requirements are satisfied is highly difficult to reach so that finding such a suitable host is still a challenge. In this manuscript mixed host is composed of wide-band-gap based 4, 7-Diphenyl-1,10-Phenanthroline (Bphen) and 4,4’-bis (carbazol-9-yl)-biphenyl (CBP). We find that Bphen presents a electron mobility of ~10^{-4} $cm^2/V{\cdot}s$ [24] while CBP behaves hole and electron mobility of 2×10^{-3} $cm^2/V{\cdot}s$ and 3×10^{-4} $cm^2/V{\cdot}s$ [25], respectively, i.e., it mainly provides hole transport. If stable Bphen is blended with CBP by a feasible ratio, almost equivalent electron- and hole-transport ability in whole MH (CBP:Bphen) zone, i.e., real bipolar carrier transport could be realized. Thus if tris(2-phenylpyridine) iridium ($Ir(ppy)_3$) doped such a mixed host will be used the triplet excitons could be uniformly distributed in the mixed host. Furthermore, in this new structure on both sides of EML there present CBP doped MoO_3 as hole transport layer (HTL) and Bphen as electron transport layer (ETL), in which there are not again HJ interface and special EBL. Nevertheless in the case of the absence of sharp HJ interfaces and special EBL there still presents controllable and balanced carrier injection, transport and recombination in such real bipolar host so that the improving working lifetime and efficiency were demonstrated. As a result a peak power efficiency of 41.6 lm/W (peak current efficiency of 39.8 cd/A) at a low driving voltage of 3 V and a power efficiency of 32.1 lm/W (36.8 cd/A) at 1000 cd/m^2 were respectively extracted, which is similar to the results of reported MH-PHOLED based on $Ir(ppy)_3$ doped TCTA:TPBI [19, 22]. But for our demonstration especially long work lifetime, 3530 hs was achieved at the initial luminance of 500 cd/m^2 and the extrapolated work lifetime was 1765 hs at the initial luminance of 1000 cd/m^2 according to the scalable law of Coulombic degradation [26], which increases by ~3.5 times compared with that of MH-PHOLED based on $Ir(ppy)_3$ doped TCTA:TPBI [22]. As a result of using our mixed hosted OLED the high efficiency and extending working lifetime can be meanwhile harvested. Such PHOLEDs with highly simplified layered structures will possess large significance for industrial applications.

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2. Experimental

All materials used were purchased without further purification and were deposited on the precleaned ITO coated glass with a sheet resistance of 10 Ω/sq at a base pressure of 5×10^{-4} Pa. The growth rates and thicknesses of the films were monitored by quartz crystal monitors, which have been cross calibrated with ellipsometry measurements to ensure accuracy. The deposition rate was controlled by a calibrated quartz crystal oscillator and maintained at rates of 0.1 nm/s for the organic materials, 0.01 nm/s for MoO_3 and LiF as well as 0.5 nm/s for Al, respectively. The devices with doped layer were fabricated by co-evaporating hosts and dopants loaded in the separate heating sources. To eliminate possible run-to-run difference, all devices were fabricated under identical experimental conditions and each device was reproduced for multiple times. In this paper, all doping concentrations were given by volume percentage (v%), here v denotes volume. The luminance-current-voltage (L-C-V) characteristics and EL spectra of the devices were determined using KEITHLEY 2400 and SpectraScan PR 655 under ambient conditions. Then, the working lifetimes of the devices with encapsulation were measured by an OEL-life-meter made in Beijing Obodi photoelectric technology Co. at room temperature.

3. Result and discussions

In order to choose a feasible ratio between Bphen and CBP for obtaining a real bipolar host, the J-V curves of single hole devices with structure of ITO / MoO_3 (0.5 nm) / x v% Bphen:CBP (40 nm) / NPB (10 nm) / Al and single electron devices with structure of ITO / CBP(10 nm) / x v% Bphen:CBP (40 nm) / LiF (0.5 nm) / Al, here x = 25, 50 and 75, respectively, were determined, as shown in Fig. 1. From Fig. 1 it can be seen that device with 50 v% Bphen in the mixed host displays a balanced electron and hole transport characteristic.

Thus 50 v% [Bphen:CBP] based PHOLED with structure of ITO / MoO_3 / CBP:MoO_3 (15 v%, 30 nm) / CBP(10 nm) / ([50 v% CBP:Bphen]: 6 v% $Ir(ppy)_3$ (30 nm) / Bphen (40 nm) / LiF (1 nm)/Al was fabricated, as shown in Fig. 2, which hereafter is referred to as Device-A. Here, MoO_3, [CBP:MoO_3], CBP and Bphen denote anode buffer, hole transporter, MoO_3 blocking which prevents from the diffusion of p-dopant MoO_3 from HTL into the EML, as well electron transporting layer, respectively.

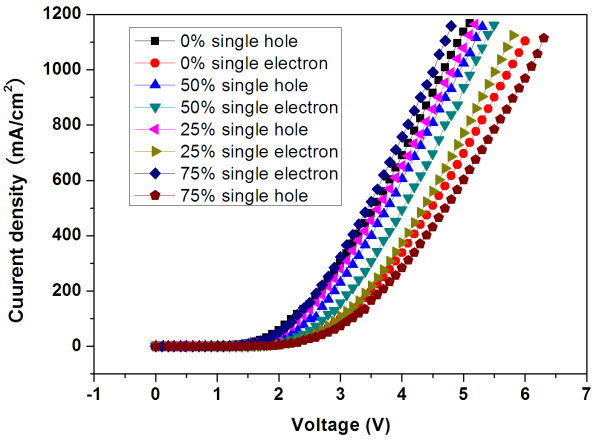

Fig. 1. J-V curves of single carrier devices with changed ratio CBP:Bphen mixed host.

For comparison the reference devices: Device-B and C were also respectively constructed in which only EML structure is different with that of Device-A. For Device-B there are double EMLs with Bphen and CBP as hosts, respectively and for Device-C there is a single EML with only CBP as host, as indicated in Fig. 2. From Fig. 2(A) it is noticed that the HJ interfaces for

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Device-A were completely eliminated so that the injected holes and electrons arising from ITO anode and Al cathode respectively could be freely transported into the mixed-hosted EML, that is, there almost does not exist barriers for the transporting processes.

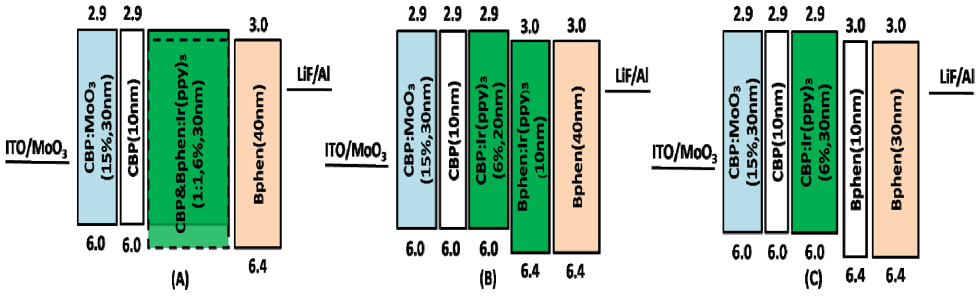

Fig. 2. The schematic structure diagrams for new structure Device-A and references Device-B and C.

Figure 3 describes EL spectra of Devices-A, B and C at a current density of 100 mA/cm^2. It is clear that all EL emission peaks are located at 512 nm that exclusively originates from the triplet excited state of $Ir(ppy)_3$ phosphor, which is an important indication of efficient confinement of triplet excitons within EML for the three devices.

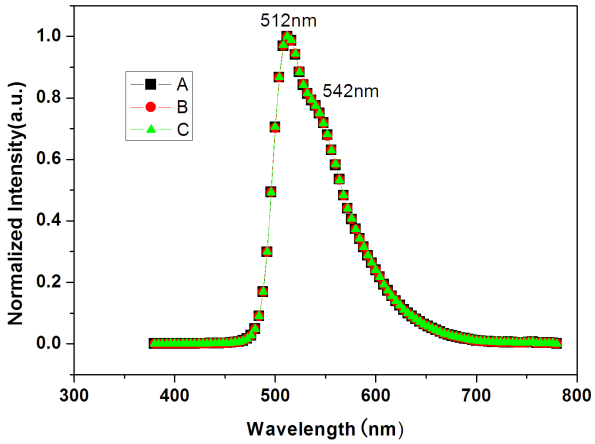

Fig. 3. Normalized EL spectra of Devices-A, B and C at 100 mA/cm^2. The peak emission at 512 nm and shoulder peak emission at 542 nm for $Ir(ppy)_3$ are indicated.

Figure 4 shows the dependence of current density and luminance on voltage (J-L-V) of Devices-A, B and C. For Device-A, the driving voltage is significantly lowered and the luminance is distinctly enhanced compared with Device-B and -C, which is attributed to the dramatically improved electron injection/transport properties. That is, balanced hole and electron injection/transport for carrier recombination in Device-A are indeed realized due to use of the mixed host which leads to elimination of HJ interfaces.

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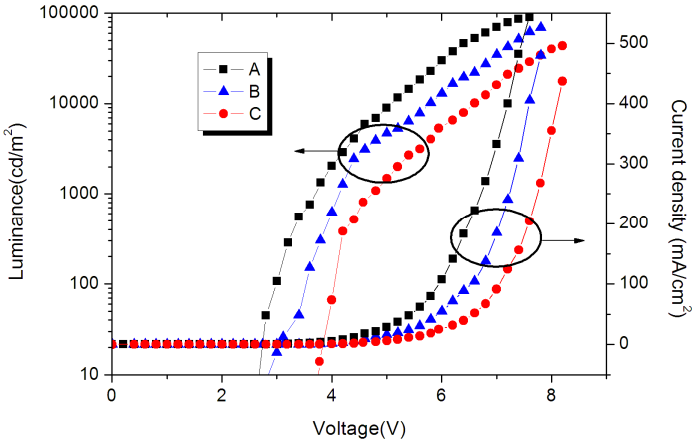

Fig. 4. Current density-luminance-voltage (J-L-V) characteristics of Devices-A, B and C, the maximum luminance is indicated for Device-A: 89561 cd/m^2 at 7.6 V; Device-B: 68738 cd/m^2 at 7.8 V; Device-C: 43520 cd/m^2 at 8.2 V.

Figure 5 compares the current/power efficiency and external quantum efficiency (EQE) of Device-A, B and C. It is noted that Device-A exhibits a peak power efficiency of 41.6 lm/W (39.8 cd/A) at 3.0 V, which is enhanced by 55.2% (46.9%) and 27.2% (22.5%) in comparison to Device-C and Device-B, respectively. The EQE of Device-A reaches 16.0% at 100 cd/m^2, which is 48% and 22% higher than that of Device-C and Device-B (See Table 1). The fact that the improvement in efficiency for Device-A is highly significant for application on display and lighting technology.

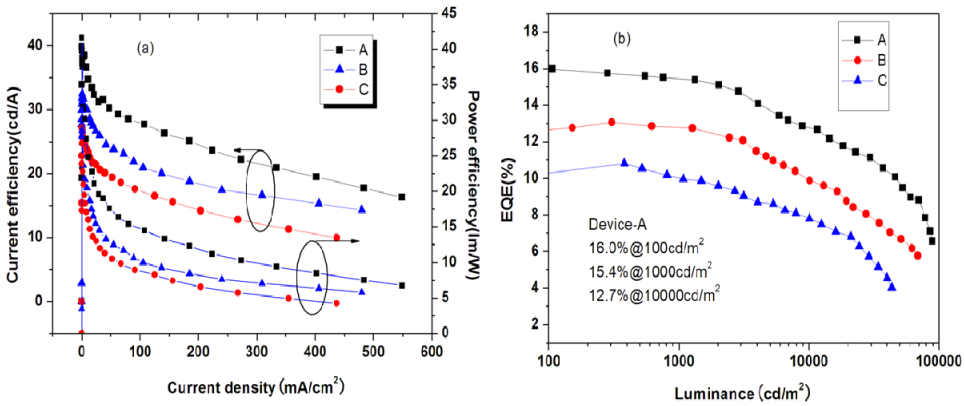

Fig. 5. (a) Current efficiency and power efficiency as well as (b) EQE of Devices-A, B and C.

Table 1. Performance and working lifetime of Devices-A, B and C.

Device	Maximum power efficiency (lm/W)	Maximum current efficiency (cd/A)	EQE @100cd/m^2 (%)	EQE @1000cd/m^2 (%)	Working lifetime (h)
A	41.6@3.0V	39.8@3.0V	16.0	15.4	3674
B	32.7@3.1V	32.5@3.1V	13.1	12.8	1469
C	26.8@3.6 V	27.1@3.6 V	10.8	10.1	835

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It is well known that CBP is generally used as host material for PHOLEDs, has a higher mobility for hole than for electron. $Ir(ppy)_3$ is also a well-known hole-transport-type emitter [25]. Thus, $Ir(ppy)_3$ doped CBP is not an actual bipolar host because CBP behaves better transporting property for hole than for electron. Therefore, the recombination zone of Device-C with only CBP host is positioned at a shallow region of the EML/ETL interface. In this region, surplus hole would be accumulated at EML/ETL-interface, so that high density excitons result in triplet-triplet (T-T) and triplet-polaron (T-P) annihilation [2, 25]. For Device-B double EMLs could broaden recombination zone and then reduced the T-T and T-P annihilation but the carrier recombination still occurred in narrow zones on both sides of D-EML interface, the excessive exciton concentration on the side of ($CBP:Ir(ppy)_3$) at D-EML interface is especially serious due to presence of the high hole injection barrier at $CBP:Ir(ppy)_3$/$Bphen:Ir(ppy)_3$ interface and the inferior hole transport of Bphen. As a result the T-T and T-P annihilation is still inevitable for Device-B. Furthermore, the fact that electrons could be into CBP has also taken place due to the use of thinner CBP emission layer than Device-C. In contrast, elimination of the abrupt HJ at CBP/Bphen interface for Device -A would result in uniform distribution of two carriers in whole EML region, which could effectively avoid the accumulation of excitons and charge carriers at the interfaces. Such an advantage should be attributed to the introduction of electron-transporting Bphen in the mixed host so that its bipolar transporting is realized, thus balanced recombination between hole and electron in the mixed host appears.

Figure 6 shows the working lifetimes for Device-A, B and C with encapsulation, which were measured under constant current with an initial brightness of 500 cd/m^2. The operational lifetime is referred to as the time that the luminance was decreased to half of the initial value. Device-A offers a longest lifetime of 3674 hs among the three device, which increases by 4.1 and 2.5 times comparing to Device-C and Device-B, respectively (see Table 1). The main reason responsible for the significantly improved lifetime of Device-A is considered as bellow. Firstly, the above described balanced bipolar transport property of the mixed host and complete elimination of HJ interface effectively prevent from excessive hole accumulation. Secondly, the unique structural design of Device-A reduces the driving voltage and limits effectively the leakage currents which otherwise results in the undesirable heat effect. In addition, the broadened EML region alleviated photochemical reaction and hence weakens the degradation of the device performance.

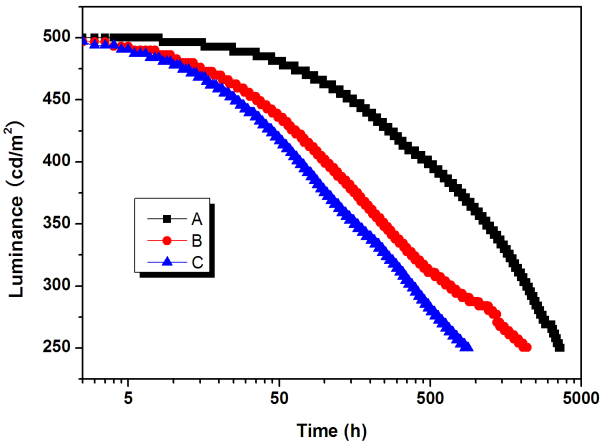

Fig. 6. The working lifetime of Devices-A, B and C under constant current density with an initial brightness of 500 cd/m^2 at room temperature.

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4. Conclusions

High efficient and long working lifetime PHOLED based on 50 v% Bphen:CBP host with 6 v% $Ir(ppy)_3$ dopant has been demonstrated. Especially a large increase in working lifetime comparing to corresponding SH- and DML-devices has been achieved. Harvest of such an excellent EL performance is due to balanced charge injection and transport as well as elimination of HJ interface which is main degradation factor of OLED. The achievement of high efficient and long working lifetime can be expected by reasonable construction design and material selection, which are considerably important for improving OLED performance.

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