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Green Phosphorescent Organic Light-Emitting Diode Based on Interlayer Emitting Layer Blend of Hole- and Electron-Transporting Materials as a Co-Host of the Three Emitting Layers

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Highly efficient green phosphorescent organic light-emitting diodes (PHOLEDs) are achieved by using a three emitting layers structure in which the interlayer composes a blend of a hole- and an electron-transporting materials as the co-host. Both the efficiency and operational lifetime of the devices are improved with such a three emitting layers structure. The optimized device shows a maximum current efficiency and luminance of 65.8 cd/A and 127435 cd/m^2, respectively, which are nearly two folds over the conventional structure device. The three emitting layers structure improves the charge carriers injection and transport balance and confinement in the emitting layers, which lead to increasing charge carriers recombination probability and decreasing exciton annihilation by the hole transporting and electron transporting materials. Such factors are critical to improve the efficiency and operational lifetime of the green PHOLEDs.

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Organic light-emitting diodes (OLEDs) have attracted a lot of attention due to their advantages in both next-generation displays and for solid-state lighting applications.[1–3] Phosphorescent organic light-emitting diodes (PHOLEDs) are an effective way to achieve high efficiency because of their potential for achieving unity internal quantum efficiency (IQE) through harvesting both singlet and triplet exciton.[1] Green PHOLEDs with almost 100% IQE have been reported.[3,4] Nevertheless, these green-emitting phosphorescent OLEDs are still unable to achieve the desired high efficiency combined with high operational stability. A variety of methods have been suggested to improve the performance of PHOLEDs through device engineering such as double emissive layer (EML), tandem structure, multiple quantum well (MQW) structure. However, the efficiency of the PHOLEDs, especially at high luminance, is quite limited because of a severe roll-off resulted from the triplet-triplet annihilation (TTA) or triplet-polaron annihilation (TPA) in the EML,[5,6] which is generally caused by space charge accumulation in a narrow exciton recombination region. Generally, the carriers piling up would ionize the nearby molecules and degrade the organic material. Since the width of this region is usually very narrow (about 10 nm), the generated photons and heat induce a strong photochemical reaction within the small region and reduce the device lifetime. A high triplet excited state bipolar host material may be an alternative since the utilization of the bipolar hosts could extend the exciton distribution, thus avoiding the problem of space charge accumulation. However, it is hard to synthesize the host materials like this that simultaneously satisfies all the requirements.

Blending different hole-transporting and electron-transporting host materials instead of a single bipolar host material have been demonstrated to be an effective approach to get high-efficiency PHOLEDs with reduced efficiency roll-off.[7–9] For example, a combination of hole transporting host material 4,4′,4″-tris(*N*-carbazolyl)triphenylamine (TCTA) with an electron-transporting host 1,3,5-tri(*m*-pyrid-3-yl-phenyl)benzene(TmPyPb) as co-host has been adopted to realize high efficiency blue PHOLEDs and the efficiency roll-off at high luminance is greatly improved.[10] However, in these devices, operational stability has not been discussed.

In this paper, we use a three emitting layers structure to simultaneously overcome the high efficiency and long operational stability issues of PHOLEDs. In the three emitting layers device, the interlayer emission layer (EM2) consists a blend of a hole-transporting material (4,4′-N,N′-dicarbazole)biphenyl (CBP) and an electron-transporting material 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBi) to act as the co-host, while both the emission layers EM1 and EM3 adopt CBP as the host that connected with the hole transporting layer and the hole-blocking layer (HBL), respectively. Both the efficiency and operational lifetime of the devices are improved with such a three EMLs structure. The optimized device shows a maximum current efficiency and a operational lifetime of 65.8 cd/A and 39384 h, respectively, which are dramatically improved compared with the device with a single CBP host and the device with a uniform CBP:TPBi co-host. The enhancement is attributed to broadened charge carrier recombination zone and increased charge carrier recombination probability in the EMLs. Such factors are critical to improve the efficiency and operational lifetime of the green PHOLEDs.

Device configuration used in this experiment is indium tin oxide(ITO,150 nm)/4,4′4″-tris[2-naphthyl(phenyl)-amino] triphenylamine(2-TNATA, 35 nm)/4,4′-bis[*N*-(1-naphthyl)-*N*-phenyl-amino]biphenyl (NPB, 20 nm)/EML(35 nm)/biphenoxy-bi(8-hydroxy-3-methylquinoline) aluminum (Balq, 25 nm)/tris-(8-hydroxyquinolinato) aluminum(Alq3, 15 nm)/LiF(1 nm)/Al(100 nm). Here, 2-TNATA, NPB, Balq, Alq3, and LiF were employed as the hole injection layer (HIL), hole transporting layer (HTL), hole blocking layer (HBL), electron transporting layer (ETL), and electron injection layer (EIL), respectively. Balq was employed as the HBL due to it can efficiently improve the PHOLED operational lifetime than TPBi as reported previously.[11] Three devices were fabricated, as shown in Fig. 1. Device A uses CBP as a host for the EML, and device B uses CPB:TPBi (ratio was optimized and fixed at 3:1) as a mixed host for the EML, while Device C uses a CBP:TPBI co-host for the interlayer emissive layer (EM2), which is sandwiched between EM1 and EM3 with CPB as the single host. A green light-emitting material tris(2-phenylpyrimidine) irdirum (PI3) (structure was shown in the inset of Figure 2) was doped in the host as the EML. The doping concentration of PI3 was fixed at 8% in every EML. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of PI3 were measured using cyclic voltammetry (CV), and others materials are obtained from Refs. 12–16 All organic materials were supplied from Xi'an Ruilian Modern Electronic Chemicals Co.Ltd. The devices were encapsulated together with an oxygen and moisture absorbing desiccant sheet using a glass lid and a UV curable epoxy resin inside a nitrogen-filled glove box after cathode formation. Current density–voltage–luminance characteristics of the devices were measured with Keithley 2400 and Photo Research Spectra Scan PR670 photometer and the active area of each device was 3 × 3 mm^2.

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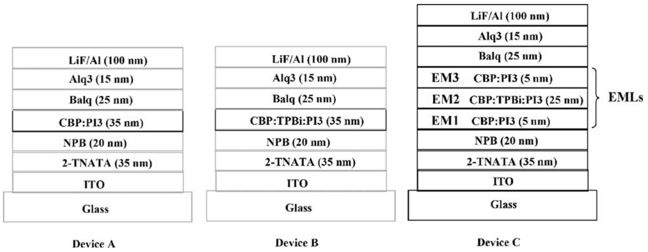

Figure 1. Device configurations of standard and three emitting layers in this study.

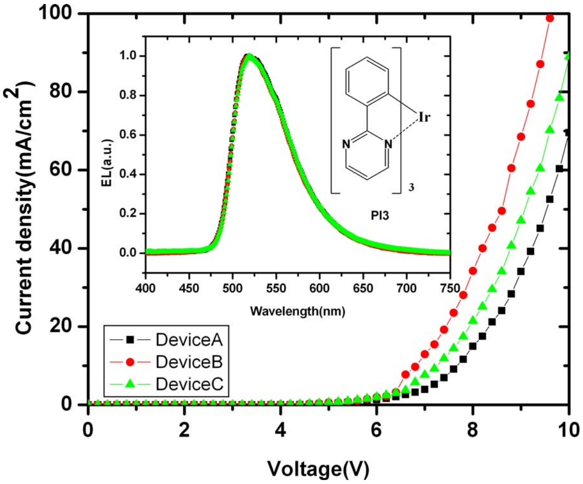

Figure 2. Current density-voltage characteristics of the devices and the inset are the EL spectra of the PHOLEDs and the molecular structure of the emitter PI3.

Figure 2 shows the current density (*J*)–Voltage (*V*) characteristics of the devices. Comparing Devices A and B, Device B shows a higher current density at the same driving voltage. The high current density in Device B is mostly due to the EML which consists a mix of CBP and TPBi as the bipolar transporting host. In a mixed host EML, space charges of electrons and holes recombine to produce double-carrier current which is significantly higher than the single-carrier current.[17] Compared with Device B, Devices C is a potential quantum well structure, so charges can be trapped inside the EML, leading to a lower current density as similar to device A.

The three devices present the same EL spectrum with a peak located at 520 nm, which is attributed to the emission of PI3. However, the three devices show different luminescence-current density curves, as shown in Fig. 3. The maximum luminescence of Devices A, B, and C reach up to 60785 cd/m^2, 86976 cd/m^2 and 127435 cd/m^2, respectively. Moreover, Device C displays the highest luminescence at a given current density.

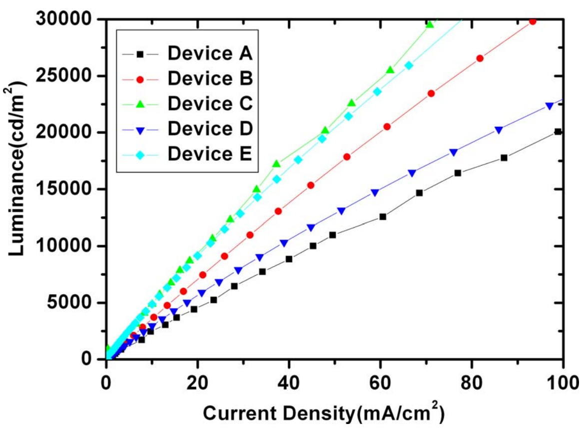

Figure 3. Current density – luminance characteristics of PHOLEDs.

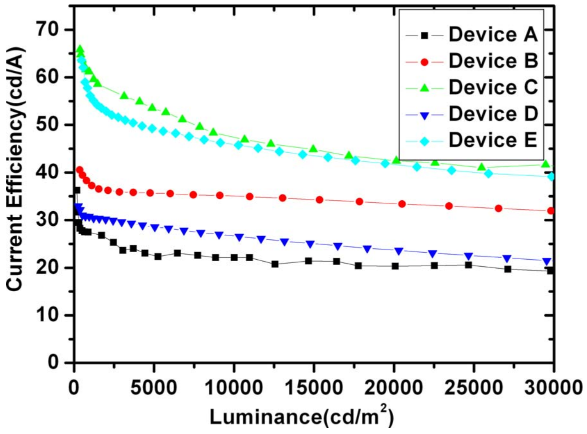

Figure 4. Luminance-current efficiency characteristics of PHOLEDs.

Figure 4 shows the current efficiency-luminescence characteristics of the PHOLEDs. Device A shows a maximum current efficiency of 36.3 cd/A, corresponding to a power efficiency of 22 lm/W. By using the mixed host structure, the maximum current efficiency of Device B reaches up to 40.5 cd/A, corresponding to a power efficiency of 30.1 lm/W. The more significantly improvement in power efficiency of Device B results from the reduced driving voltage, as shown in Fig. 2. More importantly, the utilization of blending host structure significantly improves the efficiency roll-off at high luminance (Figure 4). But device B does not realization the goal of substantially efficiency increase. On contrast, the maximum current efficiency of Device C reaches up to 65.8 cd/A, which is about 1.8 and 1.6-times higher than that of Devices A and B, respectively. Similarly, the power efficiency of Device C is also boosted to 45.1 lm/W. Although Device C presents a rapid efficiency roll-off, the current efficiency of Device C is higher than that of Devices A and B in the whole luminescence region.

Figure 5 describes the operational lifetime of the PHOLEDs. The lifetime of the devices were monitored with an initial luminance of 3000 cd/m^2 under constant currents at room temperature. Using a lifetime acceleration factor of 1.6th power,[18] the lifetime at an initial luminance of 3000 cd m^{-2} is estimated to be 17132 h for Device A. The operational stability of Devices B and C are significant improved compared with Device A. The half-lifetime of Device C at an initial luminance of 3000 cd m^{-2} is estimated to reach up to 27937 h, which

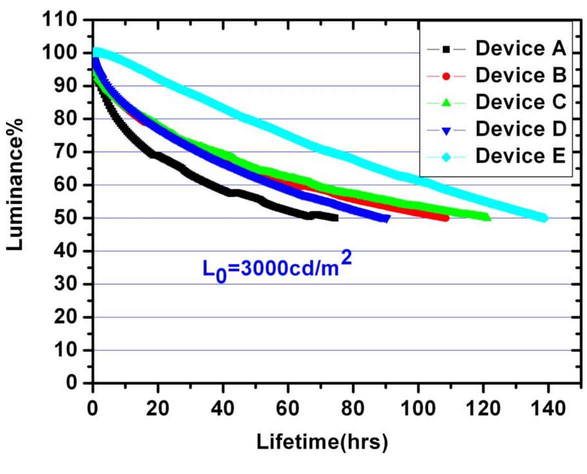

Figure 5. Lifetime characteristics of fabricated green PHOLEDs at a luminance of 3000cd/m^2.

Table I. EL data of PHOLEDs device A B C D and E.

Device	Maximum Luminance Efficiency(cd/A)	Maximum Luminance(cd/m^2)	Lifetime@100cd/m^2 (h)	CIE(x, y)[a]
Device A	36.3	60785	17132	0.31,0.60
Device B	40.5	86976	25028	0.31,0.61
Device C	65.8	127435	27937	0.31,0.62
Device D	32.9	57820	20826	0.33,0.61
Device E	63.6	106381	32047	0.33,0.61

[a] Commission Internationale de L'Eclairage coordinates.

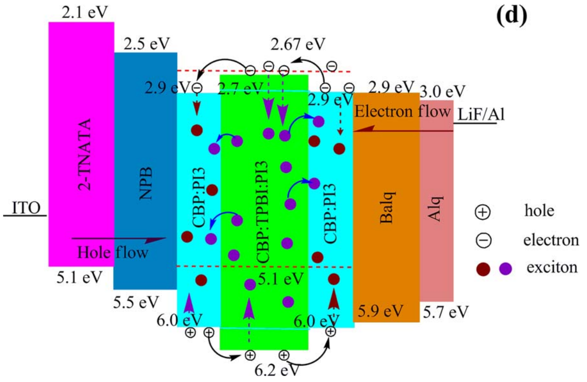

Figure 6. Schematic device structures and principle diagrams of the devices in this study. The HOMO and lowest unoccupied molecular orbital levels are obtained from Refs. 12–16.

is 1.6 times to that of Device A. The improved operational stability of Device C is attributed to broadened charge carrier recombination zone and wide exiton distribution, which eliminates charge carrier pilled up in the EML and hence decreases the luminescence decay of the device.

The high current efficiency in Device C can be explained by the efficient exciton confinement in EMLs because of the utilization of the three EMLs structure. The operation mechanisms of Device C are illustrated in Figure 6. By blending hole-transporting CBP and electron-transporting TPBi with an optimized ratio of 3:1 forms a bipolar transporting host for the interlayer EM2. Such a bipolar transporting host results in improved balance of hole and electron injection and transport in the EML, which increases charge carrier recombination opportunity and hence improves the efficiency of the device. In Device C, the main emitting region would occur at EM2 because of the bipolar property. Comparing Devices B and C, the exciton in EM2 of Device C can be dispersed into the adjacent EM1 and EM3, making exciton recompose in the three EMLs, which avoid excess exciton accumulation at the interface of NPB/EMLs and EMLs/Balq. As a result, TTA and TPA can be effectively restrained, which enhances the device efficiency and lifetime. However, the exciton density in the 25 nm thick EM2 is much higher than that in the 35 nm thick EML in Device B, as demonstrated by the higher EL efficiency of Device C, which lead to more severe efficiency roll-off in Device C than Device B. On the other hand, the carriers of Device B are blocked at the interfaces of HTL/mixed host EML and mixed host EML/ETL, respectively. These carriers failing to inject to the EML could not contribute to the formation of exciton and EL emission. For device C, at the interfaces of HTL/mixed host EM2 and mixed host EM2/ETL, implant 5 nm ultrathin EM1 and EM3, could effective use excess hole and electron blocked at mixed host EM2, therefore, such a carrier distribution not only restrains the quenching processes, but also increases the recombination probability. Taking the above arguments into account, we can conclude that device C offers the merits of devices A and B; also the multiple recombination zones further increase the performance of device C combining both increasing carrier utilization efficiency and decreasing the quenching processes.[19] In order to demonstrate its general applicability for OLEDs, we fabricated device D and E based on Ir(ppy)3 as emitter material. Device D structure was the same as device A and device E structure was the same as device C. Results show that the three emitting layers structure device efficiency was higher for about 1.9 times than the convention device. The detailed EL data of the devices are summarized in Table I.

In summary, we have demonstrated a three EMLs PHOLEDs structure based on bipolar mixed-host interlayer EML which can confine charges and excitons inside all EMLs enhanced the luminance efficiency of green PHOLEDs by almost two times. The device maximum current efficiency of 65.8 cd/A, maximum luminance of 127435 cd/m^2, and operational stability. This device design strategy represents a pathway toward high efficacy operational stability OLEDs and should be applicable to other phosphorescent emitters as well as OLED display and white lighting applications.

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