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A very high efficiency electrophosphorescent device doped with short triplet lifetime phosphor using multi-recombination zones

Dongfang Yang[1,2], Liangliang Han[1,2], Wenlian Li[1,3], Bei Chu[1,3], Zisheng Su[1,2], Dongyu Zhang[1,2], Tianle Li[1,2], Guang Zhang[1,2] and Jianzhuo Zhu[1,2]

[1] Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 3888-Dong Nanhu Road, Changchun 130033, People's Republic of China
[2] Graduate School of the Chinese Academy of Sciences, Beijing 100039, People's Republic of China

E-mail: wllioel@yahoo.com.cn and beichu@163.com

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Abstract
We have demonstrated a high-efficiency electrophosphorescent device doped with bis(2-phenyl-benzoimidazole) iridium (III) acetylacetonate with a triplet lifetime in the range of nanoseconds. Then the doped mixed host was sandwiched by two doped single-host layers. Multi-recombination zones were formed in the emission layer. Such a structure could increase the proportion of recombined carriers to injected carriers and extend the recombination zone. As a result, a maximum external quantum efficiency of 18.6% was attained due to the presence of multi-recombination zones. The mechanism of improving the electroluminescence performance was also discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Organic light-emitting devices (OLEDs) have attracted considerable attention in recent years due to their applications in full-colour displays and solid-state lighting [1–3]. In particular, substantial efforts have been devoted to the development of efficient phosphorescent (PH) OLEDs, because they can harvest both singlet and triplet excitons to achieve a maximum internal quantum efficiency of 100% which could be affected by the carrier injection efficiency, the exciton formation efficiency and the exciton radiative efficiency [4]. Nevertheless, some factors prevent the device from attaining a high quantum efficiency, which can be divided into two sorts. One is the low ratio of the number of excitons to the number of injected carriers (carrier utilization efficiency), and the other is the presence of quenching processes of non-radiative triplet excitons, such as triplet–triplet quenching and triplet–charge carrier quenching processes [5–7]. It is worth noting that the triplet quenching processes play major roles in decreasing the electrophosphorescence efficiency even within the low current density reported by Kalinowski and Stampor [5]. Hence triplet quenching can also influence the peak efficiency of PHOLEDs.

Increasing the carrier injection efficiency and enhancing the proportion of recombined carriers can improve the ratio of the carrier utilization efficiency; meanwhile, designing device structures with a broad recombination zone and using materials with a short triplet lifetime can reduce the quenching processes to obtain highly effective PHOLEDs [7–9]. Various efforts have been made to enhance the performance of these PHOLEDs. Leo's group used a double emitting layer (EML) configuration to improve the efficiency significantly [10]. The carrier could inject into the middle of the EML without any obstacle, and the carrier which recombined in the undoped

[3] Author to whom any correspondence should be addressed.

regions could be considerably reduced. Lee's group obtained a high efficiency for the PHOLED using a mixed-host strategy to widen the recombination zone [11]. Despite these encouraging results, further optimization of the device structure will be considered based on combining both increasing carrier utilization efficiency and decreasing the quenching processes.

Our previous work showed that a phosphor, bis(2-phenylbenzoimidazole) iridium (III) acetylacetonate (IrPi), has short triplet excited state lifetimes of ∼4 ns and ∼52 ns in the film and in the solution, respectively, which are markedly shorter than that of a conventional green phosphor, fac-tris(2-phenylpyridine) iridium ($Ir(ppy)_3$) doped 4,4′-*N*,*N*′-dicarbazole-biphenyl film (713 ns) [9]. It is shown that the devices not only have reduced efficiencies roll-off, but have also offered high efficiencies.

In this paper, we have fabricated a multi-recombination zone device with this short triplet lifetime IrPi phosphor. In this device, carrier utilization efficiency and the quenching processes were comprehensively considered. Finally, a very high maximum external quantum efficiency (EQE) of 18.6% was obtained.

2. Experimental section

The PHOLEDs were fabricated using pre-cleaned indium tin oxide (ITO) glass (25 Ω/sq) by thermal evaporation at a base pressure of 3×10^{-4} Pa, followed by a LiF buffer and an Al cathode layers in the same vacuum run. The deposition rates and thicknesses of all the layers were monitored *in situ* using an oscillating quartz monitor. The evaporating rates of organic layers, LiF layer and Al cathode were kept at 1–2 Å s^{-1}, 0.1 Å s^{-1}, 10 Å s^{-1}, respectively. The electroluminescence (EL) spectra of these devices were measured by a Hitachi F-4500 fluorescence spectrophotometer. All measurements were carried out at room temperature under ambient conditions.

For comparison, three OLEDs with structures of ITO/2-TNATA (10 nm)/NPB (15 nm)/TCTA (10 nm)/EML (30 nm)/TPBI (30 nm)/LiF (0.5 nm)/Al (120 nm) were fabricated. The EMLs in the three devices are shown as follows:

(A) [6 wt% IrPi doped TCTA] (15 nm)/[6 wt% IrPi doped TPBI] (15 nm),
(B) [6 wt% IrPi doped MH] (30 nm),
(C) [6 wt% IrPi doped TCTA] (10 nm)/[6 wt% IrPi doped MH] (10 nm)/[6 wt% IrPi doped TPBI] (10 nm).

Here, MH denotes a mixed host of TCTA : TPBI (1 : 1). 2-TNATA, NPB, TCTA and TPBI are, respectively, 4, 4′, 4″-tris[2-naphthyl(phenyl)amino]triphenylamine, 4, 4′-bis[*N*-(1-napthyl)-*N*-phenylamino]-biphenyl, 4, 4′, 4″-tris(*N*-carbazolyl)triphenylamine and 1,3,5-tris(*N*-phenylbenzimidazole-2-yl)benzene, which function as the hole injecting layer (HIL), the first hole-transporting layer (HTL), the second HTL/electron blocking layer (EBL) and the hole blocking layer (HBL)/electron transport layer (ETL). The energies of the highest occupied molecule orbital (HOMO) and the lowest unoccupied molecule orbital (LUMO) of the IrPi are 4.9 and 2.5 eV, and these values of the other organic materials are cited from the literature [8, 12].

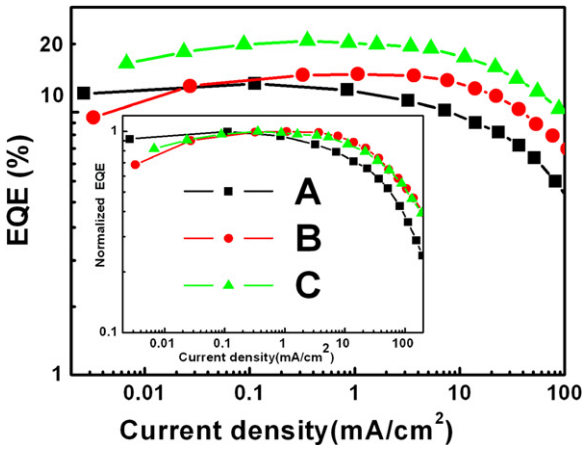

Figure 1. EQE as a function of current density of devices A, B and C (inset: the normalized EQE of devices A, B and C as a function of current density).

3. Results and discussion

Figure 1 depicts EQE as a function of current density of devices A, B and C. It can be seen that device C exhibits a maximum EQE of 18.6% while devices A and B offer only 12.5% and 13.9%, respectively. Normalized EQEs of devices A, B and C are shown in the inset of figure 1. This indicates that the proportion of the efficiency reduction in device C is smaller than that in device A by 11% and 25%, when the current density is 10 mA cm^{-2} and 100 mA cm^{-2}, respectively, and the proportion of efficiency reduction in device C is almost similar to that in device B.

To elucidate the improving mechanism of device C on performance, we compare carrier transporting and recombination processes in device C with those in devices A and B. Figure 2 indicates the schematic energy level diagrams of the three devices. For device A, there is no carrier injection barrier at TCTA/[TCTA : IrPi] and [TPBI : IrPi]/TPBI interfaces, so almost all the carriers could easily inject into the EML. At the same time, the [TCTA : IrPi]/[TPBI : IrPi] interface possesses a barrier of about 0.5 eV to holes from TCTA to TPBI and a barrier of about 0.5 eV to electrons from TPBI to TCTA (see figure 2(*a*)). The energy barriers combined with the low hole mobility in TPBI and the low electron mobility in TCTA improve the EL efficiency by forcing the recombination to occur at the interface as revealed by He *et al* [10]. However, a large number of carriers and excitons accumulate at the interface and consequently generate quenching processes at a low current density.

Figure 2(*b*) shows the energy diagram of device B. The EML, which is a mixed host of hole-transporting TCTA and electron-transporting TPBI, supports a bipolar transport [3, 13]. Thus, carrier recombination could occur over an extended region in the EML, which is broader than that of device A, and then, quenching processes could substantially reduce and efficiency would increase. Nevertheless, because of the barrier for holes from TCTA to TPBI and the barrier for electrons from TPBI to TCTA, some holes and electrons are blocked by mixed layers at the interfaces of TCTA/[MH : IrPi] and [MH : IrPi]/TPBI, i.e. HTL/EML and

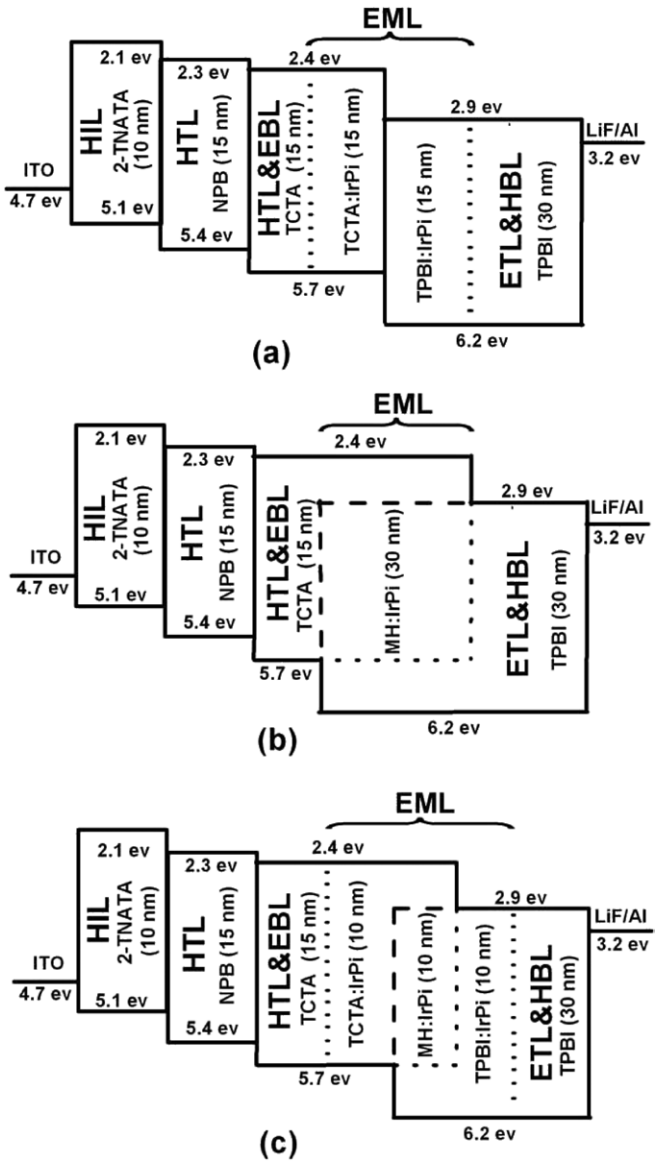

Figure 2. Energy level diagrams of devices A (*a*), B (*b*) and C (*c*), respectively.

EML/ETL, respectively. These carriers failing to inject to the EML could not contribute to the formation of excitons and EL emission.

For device C, the EML consists of three sub-EMLs: [TCTA : IrPi] layer, [MH : IrPi] layer and [TPBI : IrPi] layer. At the interfaces of HTL/EML and EML/ETL, i.e. TCTA/[TCTA : IrPi] and [TPBI : IrPi]/TPBI, the carrier injection barrier no longer exists, and hence the carriers could penetrate through the interfaces and enter the EML without any obstacle (as shown in figure 2(*c*)). Compared with device B, the ratio of the number of carriers injected into the EML to the number of carriers injected into the device increases. Furthermore, for the bipolar transporting [MH : IrPi] layer sandwiched between the [TCTA : IrPi] and the [TPBI : IrPi] layers, the interfaces of [TCTA : IrPi]/[MH : IrPi] and [MH : IrPi]/[TPBI : IrPi] present blurry boundaries. And the blurry interfaces allow continuous carrier transport [13]. Hence some carriers could provide a homogeneous distribution in the MH layer. Meanwhile, due to the carrier barrier between TCTA and TPBI and the low hole mobility in TPBI as well as low electron mobility in TCTA, the other carriers would partially pile up and recombine at these two interfaces [14]. Then, three recombination zones form: the [MH : IrPi] layer, and two interfaces of [TCTA : IrPi]/[MH : IrPi] and [MH : IrPi]/[TPBI : IrPi]. The recombination zone of device C, much wider than that of device A, could decrease in the quenching processes. And this result is proved by the normalized EQE curve (as shown in the inset of figure 1). Moreover, the presence of high charge carrier density and multiple recombination zones could increase the carrier recombination probability as shown by previous studies [2, 14]. 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. Hence the peak EQE of device C is higher than that of devices A and B by 6.1% and 4.7%, respectively.

To further validate the above conjecture, a 0.5 nm red emitting 4-(dicyanomethylene)-2-(t-butyl)6-methyl-4Hpyran (DCJTB) layer, with HOMO of 5.11 eV and LUMO of 3.03 eV, was inserted into three positions of devices A, B and C and their recombination zones and exciton distributions were compared. The three positions are denoted as P1, P2 and P3, apart from the HTL/EML interfaces by 5 nm, 15 nm and 25 nm, respectively (referred to as devices A^{P1}, A^{P2}, A^{P3}, B^{P1}, B^{P2}, B^{P3}, C^{P1}, C^{P2} and C^{P3}). The experiments were used to detect the exciton density in each EML via the relative EL intensity of the red DCJTB emission to the green IrPi emission. The EL emission spectra of the aforementioned three devices at 5 V are displayed in figure 3.

At the P1 position, device C^{P1} emits a stronger red DCJTB emission than that of devices A^{P1} and B^{P1}, which indicates that the exciton density is higher and the recombination zone is wider than that of devices A and B. It testifies to the fact that the mixed layer could partially block holes; some excitons form and pile up at the interface of [TCTA : IrPi]/[MH : IrPi]. Such an interface was 10 nm away from the interface of TCTA/[TCTA : IrPi]. Then, the excitons would diffuse to the two sides of the interface. In the meantime, the result also suggests that some holes will be blocked by the MH layer and stay in the HTL in device B, which are ineffective to radiative recombination.

The same phenomenon was also observed at the P3 position. The device C^{P3} emits a stronger red DCJTB emission than that of devices A^{P3} and B^{P3}. Excitons form and accumulate at the interface of [MH : IrPi]/[TPBI : IrPi]. Such an interface was 20 nm away from the interface of TCTA/[TCTA : IrPi]. Finally, the excitons diffuse to the two sides of the interface. Meanwhile, this implies that some electrons are blocked by the MH layer and stay in the ETL in device B.

At the P2 position, only the DCJTB red emission is observed from device A^{P2}. Thus, we can speculate

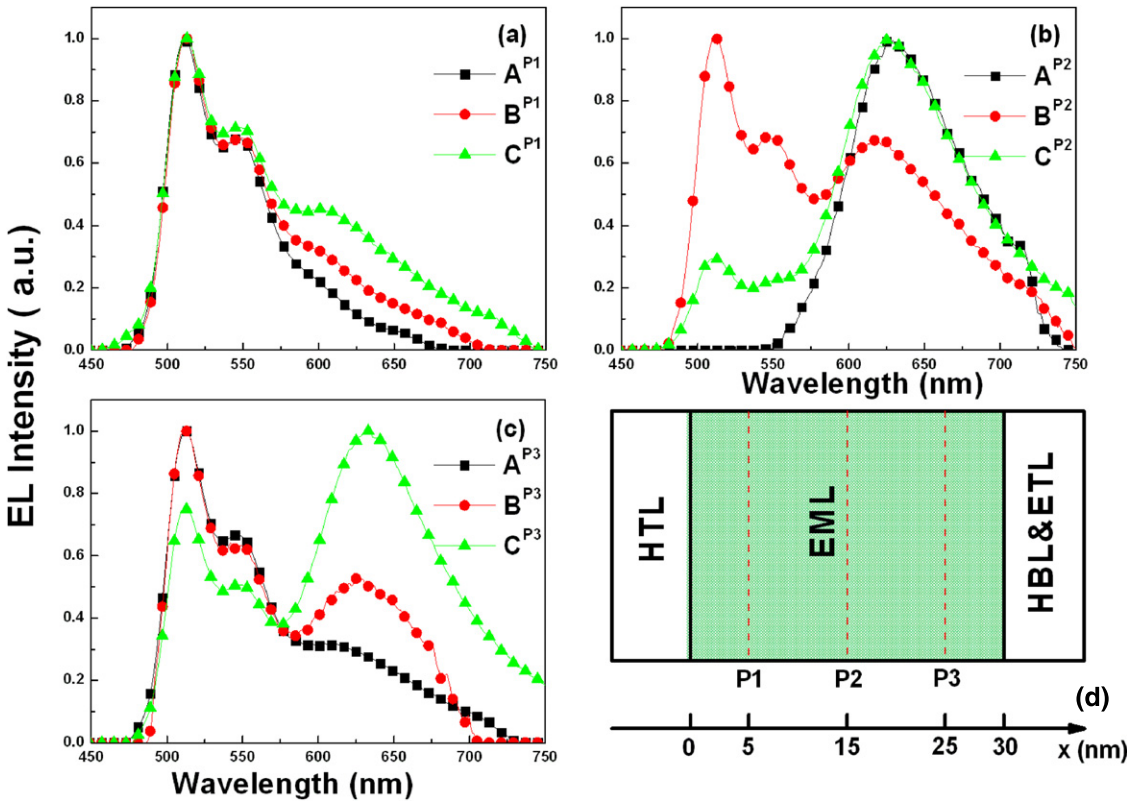

Figure 3. Normalized EL spectra of devices A^{P1}, B^{P1}, C^{P1}, A^{P2}, B^{P2}, C^{P2}, A^{P3}, B^{P3} and C^{P3} at 5 V. The DCJTB layer inserted, respectively, in three EMLs at P1 position (*a*), P2 position (*b*), P3 position (*c*) and the schematic diagram of the positions of DCJTB in the EML (*d*).

that almost all excitons are formed near the interface of [TCTA : IrPi]/[TPBI : IrPi] in device A^{P2}. It can be seen that the sharp peak of the EL spectrum of device C^{P2} is between those of devices A^{P2} and B^{P2}. From the above three positions, and taking the carrier transport properties of TCTA and TPBI into account, excitons form in the MH layer as well as on the two sides of the interfaces of [TCTA : IrPi]/[MH : IrPi] and [MH : IrPi]/[TPBI : IrPi], and this structure can adjust the distribution of carriers and excitons.

In addition, similar structure devices (referred to as devices A_2, B_2 and C_2) were also made with $Ir(ppy)_3$ instead of the IrPi dopant. It is worth mentioning that the peak EQE of device C_2 is lower than that of device B_2, but higher than that of device A_2 (as shown in figure 4). The different trend between devices C and C_2 can be attributed to the different triplet lifetimes of IrPi and $Ir(ppy)_3$. Carrier accumulation can bring two effects: enhancing the probability of carrier recombination and increasing the exciton quenching, simultaneously. The performance of the device depends on the competition between recombination and quenching.

Generally speaking, the quenching processes of long triplet lifetime materials are more serious and more sensitive to exciton density than that of short triplet lifetime materials [7, 9]. As mentioned above, the carrier concentrations of devices C_2 are high at the interfaces of [doped TCTA]/[doped MH] and [doped MH]/[doped TPBI] in the EML. High carrier concentration could increase exciton recombination probability, but it will instead bring the quenching processes at low current density due to the long lifetime of $Ir(ppy)_3$.

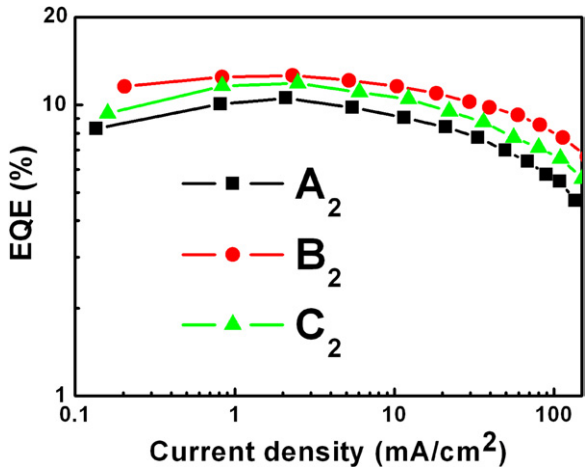

Figure 4. EQE as a function of current density of devices A_2, B_2 and C_2.

Contrarily, there is no carrier accumulation in the B_2, so device C_2 is less effective than device B_2.

4. Conclusions

In summary, we designed a new device structure with a doped mixed-host layer sandwiched by doped TCTA and doped TPBI layers. Multi-recombination zones formed, and a maximum EQE of 18.6% was achieved. Due to the reduction in carrier loss, the structure increases the recombination probability and decreases the quenching processes. Moreover, adjusted carrier

distribution based on material with a short triplet lifetime in EML can increase the efficiency. On the basis of this result we expect that the development of a short triplet lifetime phosphor with other colour emissions will be important. In the future, we will study the operating lifetime of the phosphors with a short triplet lifetime.

Acknowledgments

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