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# Exciplex emission and Auger process assistant green organic electrophosphorescence devices with very low doped level of iridium complex

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**Abstract**
We demonstrate efficient and simple structure phosphorescence organic light-emitting diodes, in which 4, 4′, 4″-tris[3-methyl-pheny(phenyl)-amino]triphenyl -amine (m-MTDATA) and 4,7-diphenyl-1,10-phenanthroline (Bphen) are used as hole transport and electron transport layers, respectively, accompanied by 3 wt% *fac*-tris(2-phenylpyridine) iridium doped in 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)-benzene (Ir : TPBi) as the emitting layer. As a result, a 29 lm $W^{-1}$ peak power efficiency and 2.2 V turn-on voltage are achieved, respectively. The achievement of excellent electroluminescence (EL) properties was attributed to the contribution of exciplex formation at the interface of m-MTDATA/Ir : TPBi and the Auger-type two-step process of charge carrier injection. The competition between the interfacial exciplex and Ir-complex emissions in the EL processes was also discussed.

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

## 1. Introduction

Heavy metal complex based phosphorescent (PH) materials have been extensively used to fabricate highly efficient electroluminescent (EL) devices since the pioneering work of Forrest and coworkers in organic light-emitting diodes (OLEDs) [1, 2]. The PHOLEDs based on phosphor materials can significantly improve the EL performances because their strong spin–orbital coupling induces an efficient intersystem crossing from the singlet to the triplet excited state, which enables them to utilize both the excited states, and therefore, the internal quantum efficiency can theoretically approach 100% [3, 4]. However, the turn-on voltage (luminance of 1 cd $m^{-2}$ was detected) of PHOLEDs is relatively high, at about 1–2 V, compared with that of fluorescent OLEDs due to the need for dispersing the phosphorescent molecules in a high energy gap matrix [4, 5]. To obtain high power efficiency and low driving voltages, a low charge injection barrier at the interfaces of the metal/organic layer is needed, that is, an ohmic contact between the metal electrode and the carrier transporter would be crucial. In recent years, the p-doping hole-transporting layer (HTL) and n-doping electron- transporting layer (ETL) for enhancing carrier injection and lowering drive voltages in OLEDs have attracted considerable attention [6–8]. Although adoption of p-doping and n-doping carrier-transporting layers in the device may enhance carrier injection and lower the drive voltages, beyond all doubt, such p-i-n structure based devices would make the fabrication technique burdensome.

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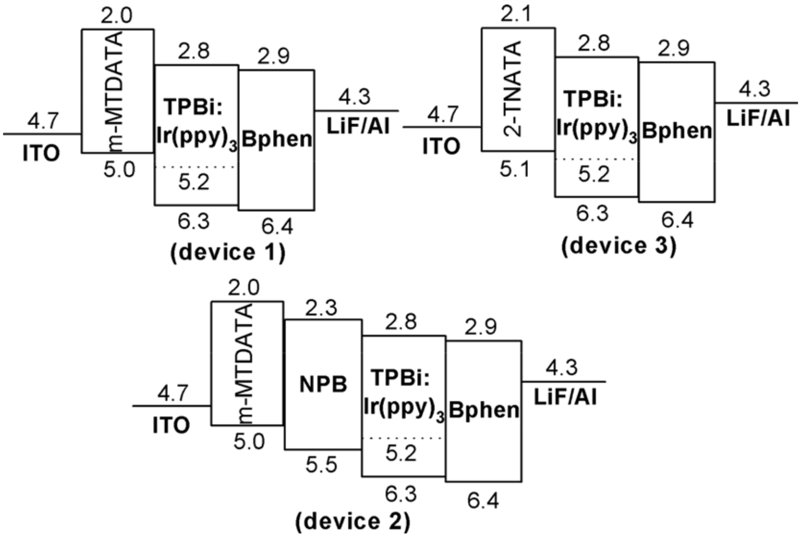

**Figure 1.** The HOMO and LUMO energy level diagram of the OLEDs fabricated in this work.

## 2. Experimental

Thus we design and fabricate a simple architecture device using high carrier mobility 4′,4″-tris[3-methyl-pheny(phenyl)-amino]triphenyl-amine (m-MTDATA) and 1,3,5-tris (*N*-phenylbenzimidazol–2-yl)-benzene (TPBi) as the HTL and host of green emitter *fac*-tris(2-phenylpyridine) iridium ($Ir(ppy)_3$), respectively. Exciplex easily formed at the interface of m-MTDATA/TPBi due to larger band-edge offsets of the two species [9], so they can act, respectively, as the electron-donor and acceptor. In this work we demonstrated in more detail a PHOLED device in which $Ir(ppy)_3$ doped TPBi acted as the emission layer (EML) and m-MTDATA and 4,7-diphenyl-1,10-phenanthroline (Bphen) as HTL and ETL, respectively. That is, m-MTDATA and Bphen layers are, respectively, laid adjacent to the ITO anode and the complex cathode LiF/Al. Since at the interface of ITO and m-MTDATA layers an ohmic contact appears to be formed [10, 11], the electric field energy would be less consumed at this contact interface. Furthermore, the well-known host material, hole-dominated transporting 4,4′-bis(9-carbazolyl)-2,2′-biphenyl (CBP) was substituted with electron-dominated transporting TPBi which has an electron mobility of $\sim 10^{-5}\,cm^2\,V^{-1}\,s^{-1}$ [12]. In terms of the presence of the almost identical carrier mobility ($\sim 10^{-4}\,cm^2\,V^{-1}\,s^{-1}$) [10, 11] between m-MTDATA and Bphen, and the special electron transport feature of TPBi, a good charge balance is maintained. As a result, the optimized device with a structure of ITO/m-MTDATA(30 nm)/TPBi : $Ir(ppy)_3$(3 wt%, 30 nm)/Bphen(10 nm)/LiF(1 nm)/Al(120 nm) offers a peak power efficiency of 29 $lm\,W^{-1}$ and only a turn-on bias voltage of 2.2 V. The high power efficiency is almost the same as that of the traditional multilayer device based on 7 wt% $Ir(ppy)_3$ doped CBP as the emitter.

Three series devices with $x = 1$–7 wt% $Ir(ppy)_3$ were fabricated as follows:

- *Series* 1: ITO/m-MTDATA (30 nm)/TPBi : $Ir(ppy)_3$ ($x$ wt%, 30 nm)/Bphen (10 nm)/LiF(1 nm)/Al(120 nm); here m-MTDATA works as the hole-injection (HI)/HTL. It is noticed that in these devices the traditional HTL, 4,4′-bis[*N*-(1-napthyl)-*N*–phenyl-amino]-biphenyl (NPB), and general hole/exciton-blocking layer, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), were no longer used, respectively. This device is in fact a simple three layer structure in which $Ir(ppy)_3$ doped TPBi was sandwiched between m-MTDATA and Bphen layers.
- *Series* 2: ITO/m-MTDATA (10 nm)/NPB (20 nm)/TPBi : $Ir(ppy)_3$ ($x$ wt%, 30 nm)/Bphen (10 nm)/LiF(1 nm)/Al(120 nm).
- *Series* 3: ITO/2-TNATA (30 nm)/TPBi : $Ir(ppy)_3$ ($x$ wt%, 30 nm)/Bphen (10 nm)/LiF(1 nm)/Al(120 nm); here 2-TNATA denotes that 4,4′4″–tris[2-naphthyl(phenyl)-amino]triphenylamine is used to replace m-MTDATA in series 1.

The above three structure devices which have 3 wt% $Ir(ppy)_3$ will be, respectively, called devices 1, 2 and 3, hereafter. Figure 1 shows the energy level diagram of the OLEDs fabricated in this work, where the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy data are cited from previous literature [9, 13, 14]. Detailed processes of fabrication and measurement for OLEDs have been described in our previous paper [13].

## 3. Results and discussions

Figure 2 shows the effect of the $Ir(ppy)_3$ concentration on the turn-on voltage of the above-mentioned devices; we observe that device 1 shows a maximum luminance of 9000 $cd\,m^{-2}$ and the lowest turn-on bias of 2.2 V, which is even lower than the optical energy gap of $Ir(ppy)_3$ (2.4 eV).

Figure 3 and its inset depict current density–power efficiency–current efficiency characteristics of devices 1, 2 and 3, respectively. It can be seen that the devices with 3 and 7 wt% $Ir(ppy)_3$ present almost identical power efficiency, at around 29 $lm\,W^{-1}$, but different current efficiency at 23.8 $cd\,A^{-1}$ and 28.1 $cd\,A^{-1}$, respectively. It is interesting that either power or

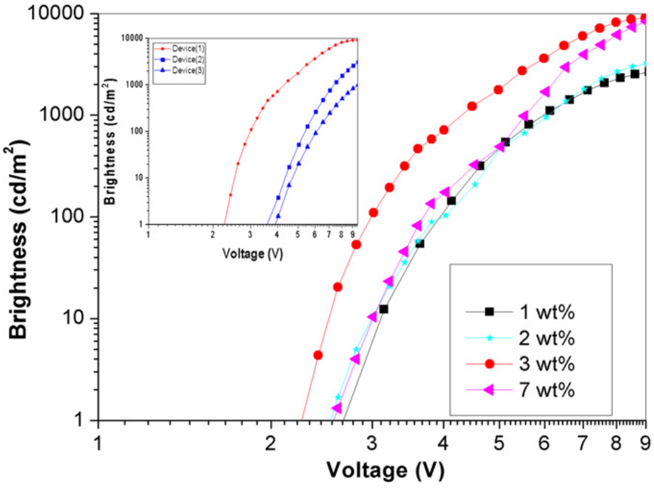

**Figure 2.** Brightness ($B$)–voltage ($V$) characteristics of series 1 with different Ir(ppy)$_3$ contents. Inset: the $B$–$V$ characteristics of devices 1, 2 and 3, respectively.

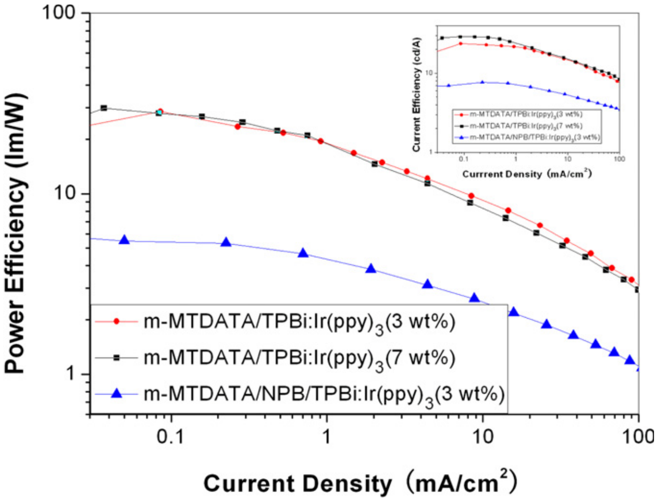

**Figure 3.** Current density–power efficiency characteristics of the series 1 device in which the Ir(ppy)$_3$ concentrations are 3 and 7 wt%, and ITO/m-MTDATA(10 nm)/NPB(20 nm)/TPBi : Ir(ppy)$_3$ (3 wt%, 30 nm)/Bphen (10 nm)/LiF(1 nm)/Al(120 nm), respectively. Inset: current density–current efficiency characteristics of the above three devices.

current efficiency of the NPB containing device is the lowest one, indicating that the inserted NPB between m-MTDATA and EML plays a decreasing role for the EL intensity. This finding can be understood as follows.

Firstly, from the structure of device 1, we note that the interface of m-MTDATA and TPBi easily offers exciplex emission [9] under electrical excitation. This is attributed to a larger difference between the ionization potential (IP) (5.0 eV) of m-MTDATA and electron affinity (EA) (2.8 eV) of TPBi [15] and easy exciplex -formation of m-MTDATA [16]. Figure 4($a$) shows exciplex EL emission from the interface of m-MTDATA/TPBi, but the 2-NTATA/TPBi-interface only emits a blue band from the 2-NTATA monomer, which would be due to lower exciplex-forming ability of 2-NTATA over m-MTDATA [9]. As Ir(ppy)$_3$ was doped into TPBi (known as Ir-TPBi), the m-MTDATA/Ir-TPBi based device provides green EL which comes mainly from the Ir(ppy)$_3$ dopant although the EL band overlapped with a longer wavelength at 540 nm. The 540 nm shoulder band appears to originate from the exciplex of the m-MTDATA/Ir-TPBi-interface. In other words, exciplex emission at the interface of m-MTDATA/Ir-TPBi also contributes to the EL intensity of device 1. Both the EL spectra of devices 2 and 3 comprise two sub-bands, i.e. other blue bands lie at 425 and 450 nm (see figure 4($b$)), present besides the green sub-band of Ir(ppy)$_3$, the former and latter result from NPB and 2-NTATA monomer components, respectively. This implies that NPB and 2-NTATA have lower exciplex formation probability than m-MTDATA, because NPB has larger IP (5.7 eV) and 2-NTATA has larger additional spatial blocks [9] than m-MTDATA, respectively. Thus in low Ir(ppy)$_3$ doped devices 2 and 3, the monomer emissions would compete with that of Ir(ppy)$_3$, so that the Ir(ppy)$_3$ emission obviously failed. It is concluded that the EL intensity of devices 1, 2 and 3 is closely related to exciplex formation between HTL and TPBi. To compare the effect of the Ir(ppy)$_3$ content in TPBi on the exciplex formation, the EL spectra of 1, 3 and 7 wt% Ir(ppy)$_3$ doped TPBi in the series 1 device are indicated in figure 4($c$). We note that the EL spectra of both 1 and 3 wt% Ir(ppy)$_3$ containing devices comprise a shoulder peak at 540 nm while the 7 wt% one does not offer such a shoulder peak, indicating that exciplex emission was quenched by the Ir(ppy)$_3$ emitter in the last device. This proves that EL emission of 3 wt% Ir(ppy)$_3$ doped device 1 covers the contribution of exciplex emission.

Figure 4($d$) shows schematic level diagrams and excited processes corresponding to (1) pure exciplex emission from the interface of m-MTDATA/TPBi and (2) overlapping emission of Ir(ppy)$_3$ and exciplex emission of m-MTDATA/Ir-TPBi, respectively. The exciplex emission at around 540 nm corresponding to an energy of 2.3 eV, whose energy level is still higher than that of the turn-on voltage in device 1, reveals that another favourable mechanism would be existing for achieving such a low turn-on bias voltage except for the contribution of the interfacial exciplex emission formed between m-MTDATA/TPBi. Moreover, the EL spectra of device 1 at different biases are identical under 2.4–12 V (not shown here). These phenomena make us speculate that the Auger-type two-step injection mechanism [17] is possibly present in the EL process; in other words, EL emission from Ir(ppy)$_3$ appears to pass through two-step processes as indicated in figure 5. That is, the exciplex excited state acts as an interim energy level, i.e. plays a role of a stepping stone in Auger processes. Accumulation of charges of both signs at the interface of m-TDATA/Ir-TPBi (3 wt%) under electrical excitation of 2.2 V may be transferred to the exciplex excited state, followed by the triplet ($T_1$) energy level (2.43 eV) of Ir(ppy)$_3$ effectively by Auger recombination. Finally the energy on $T_1$ that experiences a fast radiative decay is relaxed to the ground state and emits green light at 510 nm. More detailed dynamic processes are still underway and the result will be published elsewhere.

## 4. Summary

In conclusion, a Ir(ppy)$_3$ based PHOLED device with a low turn-on bias of 2.2 V and a peak power efficiency of 29 lm W$^{-1}$

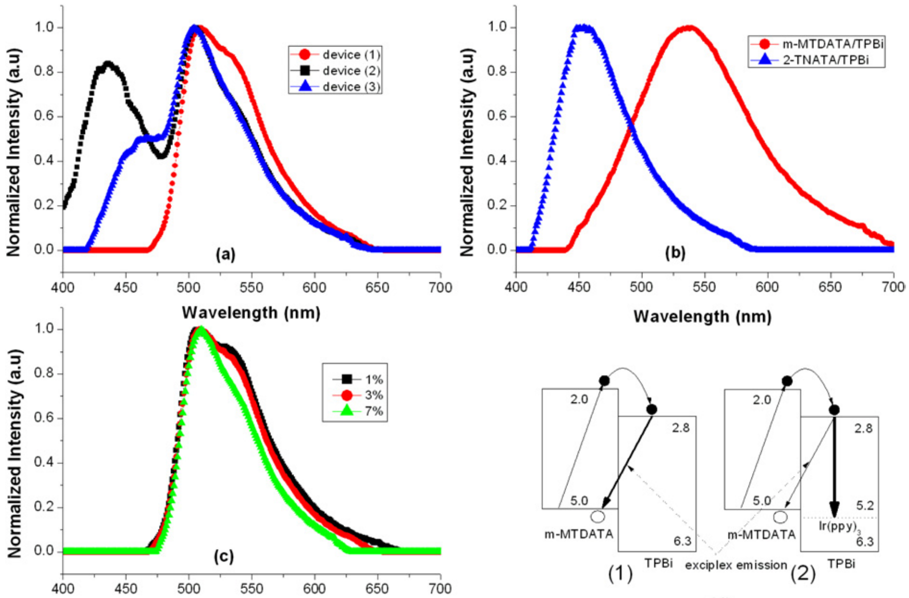

**Figure 4.** (*a*) The EL spectrum of devices 1, 2 and 3 at 8 V, respectively. (*b*) The EL spectrum of ITO/m-MTDATA (30 nm)/TPBi (30 nm)/Bphen (10 nm)/LiF (1 nm)/Al (100 nm) and ITO/2-TNATA (30 nm)/TPBi (30 nm)/Bphen (10 nm)/LiF (1 nm)/Al (100 nm) at 12 V, respectively. (*c*) The EL spectra of ITO/m-MTDATA/1 wt%, 3 wt% and 7 wt% Ir(ppy)$_3$ doped in TPBi/LiF/Al, respectively. (*d*) The proposal energy diagram of (1) exciplex formation of device with m-MTDATA/TPBi and (2) m-MTDATA/ Ir(ppy)$_3$ doped in TPBi.

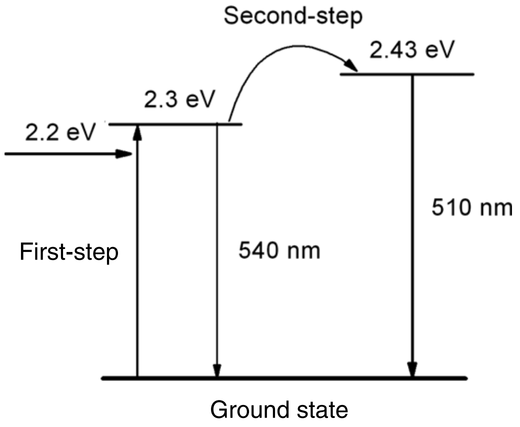

**Figure 5.** The proposal Auger recombination process worked in device 1 under electrical excitation.

was demonstrated. The excellent EL performance can be attributed mainly to the following: (1) using high carrier mobility based HTL and ETL materials as well as a high electron transporting host; (2) the exciplex formed at the HTL/host-interface and Auger processes contribute to the low turn-on bias voltage. Because the device is composed of simple three-organic layers and only 3 wt% green Ir-complex dopant, it is expected that this OLED structure is useful in developing highly efficient OLEDs with a simple fabrication process and effective cost. Further improvement in the performance of this device is still continuing.

## Acknowledgment

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