

# High efficiency green phosphorescent organic light-emitting diodes with a low roll-off at high brightness

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## ABSTRACT

Highly efficient green phosphorescent organic light-emitting diodes (PHOLEDs) with low efficiency roll-off at high brightness have been demonstrated with a novel iridium complex. The host material 1,3-bis(carbazol-9-yl)benzene (mCP) with high triplet energy is also used as the hole transporting layer to avoid carrier accumulation near the exciton formation interface and reduce exciton quenching. It provides a new approach for easily fabricating PHOLED with high triplet energy emitter. Moreover, the hole blocking layer is extended into the light emitting layer to form a co-host, realizing better control of the carrier balance and broader recombination zone. As a consequence, a maximum external quantum efficiency of 20.8% and current efficiency of 72.9 cd/A have been achieved, and maintain to 17.4% and 60.7 cd/A even at 10,000 cd/m<sup>2</sup>, respectively.

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## 1. Introduction

In the last few years, organic light-emitting diode (OLED) has shown its strong potential in the next generation of display and lighting applications. In particular, owing to the harvest of both singlet and triplet excitons for photon emission, iridium complex based phosphorescent organic light-emitting diodes (PHOLEDs) have boosted the internal quantum efficiency up to 100%, accelerating the mass production of OLEDs. However, the PHOLEDs suffer from a decrease of efficiency when the driving current density increases [1,2]. This roll-off phenomenon is mainly caused by triplet–triplet annihilation (TTA) [3] and triplet–polaron quenching (TPQ) [4], which limits the efficiency of

PHOLEDs at high brightness. To overcome the drawback, some solutions have been employed: (i) Avoiding carrier accumulation at the interface adjacent to light emitting layer (EML). For instance, Wang et al. [5] demonstrated that accumulated space charge at the exciton formation interface causes exciton quenching. In 2011, they further fabricated a simplified device using 4'-bis(carbazol-9-yl)biphenyl (CBP) as both light emitting host and hole transporting layer with low roll-off by eliminating 4,4'-N,N'-dicarbazole-biphenyl (NPB)/CBP heterojunction [6]; (ii) Balancing charge carriers in EML and broadening the recombination zone. Kim et al. [7] mixed 4,4',4''-tris(N-carbazolyl)triphenylamine (TCTA) and 1,3,5-tris(N-phenylbenzimidazole-2-yl)benzene (TPBi) as co-host to widen the recombination zone, achieving improved efficiency roll-off, which was attributed to low probability of exciton quenching. Recently, Chen et al. [8] mixed the hole transporting material TCTA and electron transporting material 1,3,5-tri(m-pyrid-3-yl-phenyl)benzene (TmPyPb) as

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co-host to fabricate a highly efficient iridium(III)bis(4,6-difluorophenyl)-pyridinato- $N,C^2$ )picolinate (Flrpic) based blue device. However, with relatively low triplet energy of 2.7 eV, TCTA is not a suitable host for many phosphorescent dyes with higher triplet energy such as deep blue emitters [9].

In this paper, we focus on a newly synthesized iridium based green phosphorescent emitter, iridium(III)bis(2-(4-trifluoromethylphenyl)pyridine)tetraphenylimidodiphosphate ( $\text{Ir}(\text{tfmppy})_2(\text{tpip})$ ), inset of Fig. 1a), which was first reported by Zheng group [10]. The incorporation of tetraphenylimidodiphosphate group into the molecule may enhance the electron mobility of the complex and reduce the TTA in the device due to the two electron transport units of P=O bond. However, the efficiency dropped from the peak value of 67.95 cd/A to 52.74 cd/A at 1000  $\text{cd/m}^2$ , which needs to be improved for high brightness application. In addition, an emission at 380 nm from 1,3-bis(carbazol-9-yl)benzene (mCP) host was still observable in the electroluminescence (EL) spectrum, indicating an incomplete energy transfer from mCP to the emitter  $\text{Ir}(\text{tfmppy})_2(\text{tpip})$ . To solve these issues, we tried to combine the two approaches mentioned above, using the high triplet energy (2.9 eV) host material mCP mixed with an electron transporting material TPBi as co-host, and utilizing mCP as the hole transporting layer (HTL) as well to remove the barrier between the HTL and EML. An external quantum efficiency (EQE) of 20.8% has been reached with a maximum current efficiency of 72.9 cd/A. The EQE and

current efficiency remain at 17.4% and 60.7 cd/A, respectively, at 10,000  $\text{cd/m}^2$ , showing a significantly reduced roll-off.

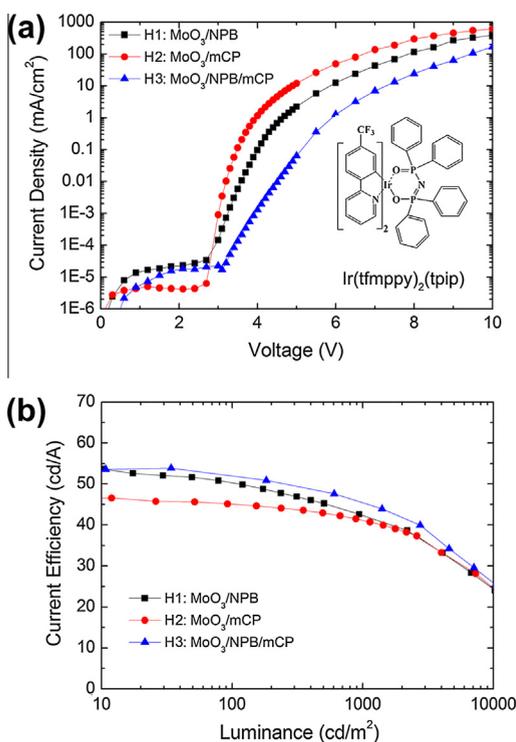
## 2. Experimental

Prior to evaporation, patterned indium tin oxide (ITO) substrates were cleaned in order by detergent, acetone and isopropyl alcohol, then dried by nitrogen. All devices in this work were fabricated by vacuum thermal evaporation onto ITO substrates under a base pressure of  $5 \times 10^{-6}$  Torr and the deposition rates were measured with quartz crystals. The  $\text{MoO}_3$  was evaporated from a tungsten boat with a deposition rate of 0.1  $\text{\AA/s}$ . The organic materials in quartz crucibles, except for the dopants, were evaporated at a rate of 0.5–1  $\text{\AA/s}$ . At the end, 100-nm-thick aluminum was deposited as the cathode. The current–voltage–luminance characteristics of the devices were measured using a computer controlled Keithley 2400 and Topcon BM-7A measurement system. All the measurements were carried out at room temperature under ambient atmosphere [11].

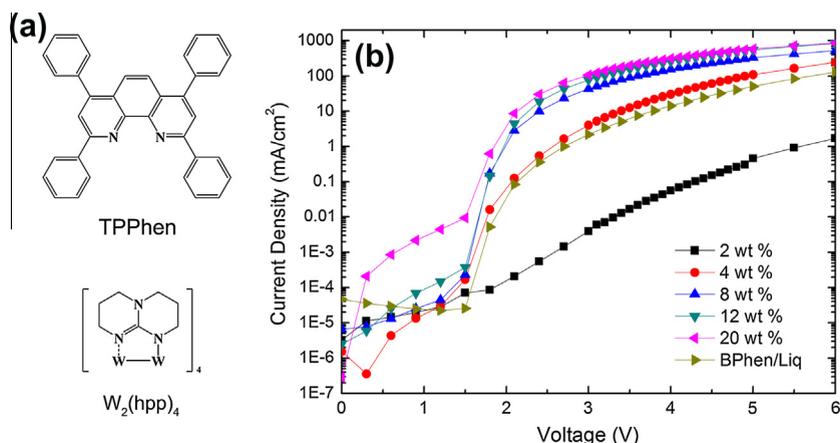
## 3. Results and discussion

As a common host for blue phosphorescent dyes, mCP has a high triplet energy and a very deep highest occupied molecular orbital (HOMO) level as well. It is very difficult to inject holes from ITO or normal hole injection layer to mCP. Therefore, mCP is usually not used as HTL. To study the feasibility of mCP as HTL, three devices were fabricated with a basic structure of ITO/ $\text{MoO}_3$  (1 nm)/HTL/mCP: $\text{Ir}(\text{tfmppy})_2(\text{tpip})$  (15 nm, 6 wt%)/4,7-diphenyl-1,10-phenanthroline (BPhen) (50 nm)/8-Hydroxyquinolinolito-lithium (Liq) (1 nm)/Al (100 nm), where  $\text{MoO}_3$  is the hole injection layer, which can modify the work function of ITO [12]. The HTL is as follows: H1, NPB (35 nm); H2, mCP (35 nm); H3, NPB (25 nm)/mCP (10 nm). NPB, a commonly used HTL material, is used for comparison with mCP.

Fig. 1 shows the current density and current efficiency curves of device H1–H3. With the help of  $\text{MoO}_3$ , holes can be easily injected from the ITO into either NPB or mCP. The HOMO levels of NPB and mCP are 5.4 eV and 5.9 eV, respectively, resulting in difficult hole injection from NPB to mCP. With this energy barrier, device H1 and H3 demonstrate lower current densities than H2. However, device H1 and H3 show completely different  $I$ – $V$  characteristics. The main difference is that in device H1, NPB HTL has direct contact with  $\text{Ir}(\text{tfmppy})_2(\text{tpip})$  doped mCP EML, whereas in device H3, an undoped mCP is inserted between NPB and EML. The current of device H1 is significantly higher than that of device H3, indicating that there may exist other channels for hole transporting. The  $\text{Ir}(\text{tfmppy})_2(\text{tpip})$ , whose HOMO of 5.4 eV is similar to that of NPB, may facilitate the hole transporting, which was observed on another phosphorescent emitter tris(2-phenylpyridine)iridium ( $\text{Ir}(\text{ppy})_3$ ) [13]. On the other hand, device H2 achieves the highest current, confirming that the mCP, with a high hole mobility of  $10^{-4} \text{ cm}^2/\text{V s}$  [14], can also be a HTL by inserting a thin layer of  $\text{MoO}_3$  at the ITO



**Fig. 1.** (a) Current density–voltage characteristics of H1–H3 and chemical structures (inset) of  $\text{Ir}(\text{tfmppy})_2(\text{tpip})$  used in this work. (b) Current efficiency–luminance characteristics of H1–H3.



**Fig. 2.** (a) Chemical structures of TPPhen and  $W_2(hpp)_4$ . (b) Current density–voltage characteristics of electron only devices with various n-type doping concentration. A device with BPhen as ETL and Liq as injection layer is set as a reference.

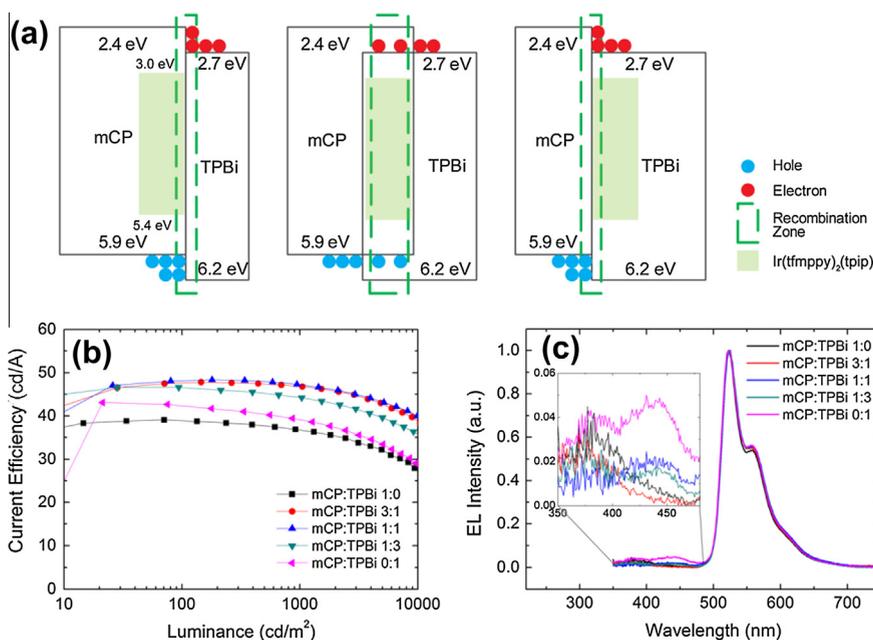
surface. However, despite the better roll-off performance by eliminating the accumulation of holes at the interface of NPB/EML [6,15], the current efficiency of  $MoO_3/mCP$  based device is the lowest as a consequence of excess injection of holes into light emitting zone.

To improve the electron transporting and get better hole–electron balance, an electron transporting material 2,4,7,9-tetraphenyl-1,10-phenanthroline (TPPhen) doped with a molecular n-dopant tetrakis(1,3,4,6,7,8-Hexahydro-2H-pyrimido[1,2-a]pyrimidinato) ditungsten (II) ( $W_2(hpp)_4$ ) were utilized with chemical structures shown in Fig. 2a. A set of electron only devices with ITO/BPhen (40 nm)/TPPhen: $W_2(hpp)_4$  (40 nm,  $x$  wt%)/Al (100 nm) were fabricated to optimize the doping concentration, where  $x$  was set to 2, 4, 8, 12, 20 wt%, respectively. Meanwhile, ITO/BPhen (80 nm)/Liq (1 nm) was as a reference. As illustrated in Fig. 2b, the current density of TPPhen: $W_2(hpp)_4$  based device is significantly enhanced compared to the reference device when the doping concentration is higher than 2 wt%. However, when the dopant concentration is further increased to 20%, the current does not increase too much, indicating a saturated electron current.

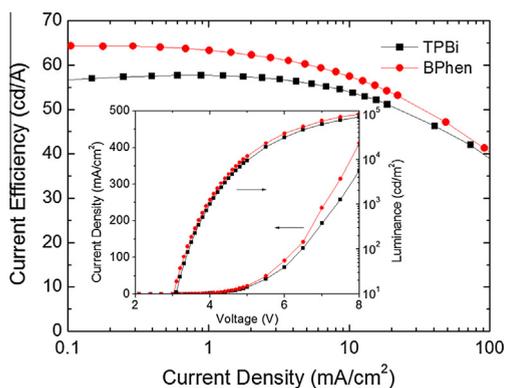
We adopt this novel electron transporting layer (ETL) with higher electron transporting ability in device structure to prove our assumption, and 10-nm-thick TPBi was as the hole blocking layer (HBL) to prevent possible energy transfer from EML to ETL. Furthermore, TPBi was mixed with mCP host to enhance electron injection into EML and broaden the recombination zone. The basic structure was ITO/ $MoO_3$  (1 nm)/mCP (35 nm)/mCP:TPBi:Ir(tfmppy)<sub>2</sub>(tpip) (15 nm)/TPBi (10 nm)/TPPhen: $W_2(hpp)_4$  (40 nm, 12 wt%)/Al (100 nm), where the ratio of mCP:TPBi was 1:0, 3:1, 1:1, 1:3, 0:1, respectively, and the concentration of Ir(tfmppy)<sub>2</sub>(tpip) in EML was set to 6 wt%. When the host is pure mCP or TPBi, the recombination zone is at the narrow interface between mCP and TPBi either at cathode side or anode side (Fig. 3a, left and right), resulting in strong TTA and TPQ processes and low efficiency as shown in Fig. 3b. However, when TPBi and mCP are mixed as a co-host, the efficiency increases dramatically, especially when the ratio is 1:1, a current efficiency of 47.2 cd/A is achieved

at 1000 cd/m<sup>2</sup>, a factor of 28.6% improvement compared to the device with pure mCP as host. More importantly, the current efficiency retains 39.7 cd/A at 10,000 cd/m<sup>2</sup>, and only 15.9% drop compared to that at 1000 cd/m<sup>2</sup>. The high efficiency and low efficiency roll-off can be mainly attributed to more balanced charge carriers and broader recombination zone. mCP is a hole transporting material, while TPBi is a dominantly electron transporting material. Holes transport from HTL to EML without any barrier and then slow down gradually at the presence of TPBi. The same happens for electrons as well. Therefore the recombination occurs in the whole emission layer instead of just mCP/TPBi interface. The recombination probability is significantly increased and the recombination zone is also broadened (Fig. 3a, middle).

In the EL spectrum of the device with pure mCP host shown in Fig. 3c, an apparent residual emission at 380 nm is observed, which is attributed to mCP host, [10] indicating an incomplete energy transfer from mCP to Ir(tfmppy)<sub>2</sub>(tpip). Due to the narrow recombination zone at the EML/TPBi heterojunction interface, there are not enough Ir(tfmppy)<sub>2</sub>(tpip) molecules in ground state close to mCP excitons, thus extra emission from host appears [16]. This phenomenon also exists in pristine TPBi host device. Another obvious TPBi induced emission appears besides the mCP emission, reflecting the poorest roll-off as shown in Fig. 3b. Increasing the doping ratio of phosphorescent dopant might suppress the emission of mCP and TPBi, but may bring serious self-quenching. Fortunately, with broadened recombination zone in co-host structure, more Ir(tfmppy)<sub>2</sub>(tpip) molecules will contribute to the light emission, i.e., more efficient energy transfer can be obtained. The spectra prove that the residual emission from hosts of co-host devices is relatively lower than that of single host devices, but still needs to be improved. As discussed above, this emitting system is most likely hole-abundant. To further optimize charge carrier balance and enhance the energy transfer in light emitting layer, we tried to increase the thickness of HTL to reduce the hole transporting into the EML, and the HBL was changed to improve the electron transporting as well. Thus we fabri-



**Fig. 3.** (a) Schematic energy diagrams of the devices with mCP, mCP:TPBi and TPBi hosts; (b) current efficiency–luminance characteristics and (c) normalized EL spectra (inset: a zoomed-in graph at short wavelength) of different ratio of mixed mCP:TPBi host with the device structure of ITO/MoO<sub>3</sub>(1 nm)/mCP (35 nm)/mCP:TPBi: Ir(tfmpy)<sub>2</sub>(tpip) (15 nm)/TPBi (10 nm)/TPPhen:W<sub>2</sub>(hpp)<sub>4</sub> (40 nm, 12 wt%)/Al (100 nm).

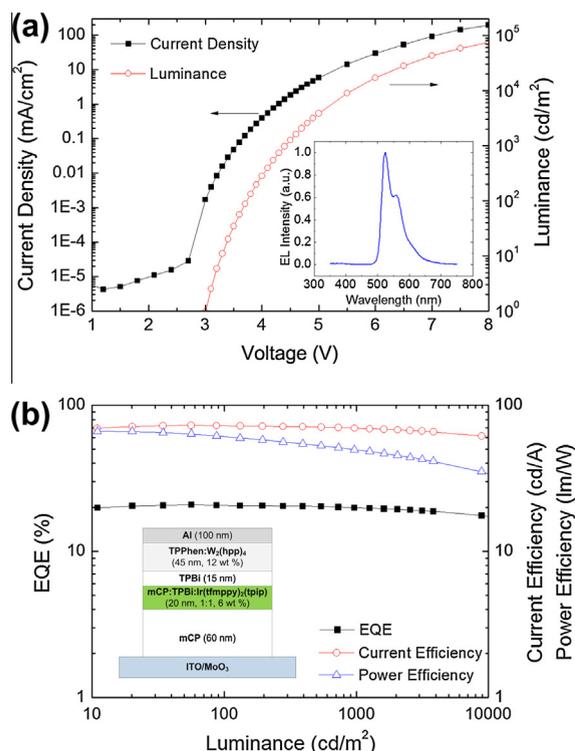


**Fig. 4.** Current efficiency–current density and current density–voltage–luminance characteristics (inset) of devices with TPBi and BPhen as HBL respectively. The basic device structure is ITO/MoO<sub>3</sub> (1 nm)/mCP (65 nm)/mCP:TPBi:Ir(tfmpy)<sub>2</sub>(tpip) (15 nm, 1:1, 6 wt%)/HBL (10 nm)/TPPhen:W<sub>2</sub>(hpp)<sub>4</sub> (50 nm, 12 wt%)/Al (100 nm).

cated devices with a structure of ITO/MoO<sub>3</sub>(1 nm)/mCP (65 nm)/mCP:TPBi:Ir(tfmpy)<sub>2</sub>(tpip) (15 nm, 1:1, 6 wt%)/HBL (10 nm)/TPPhen:W<sub>2</sub>(hpp)<sub>4</sub> (50 nm, 12 wt%)/Al (100 nm). Here, TPBi and BPhen were compared as different HBLs. The thickness of W<sub>2</sub>(hpp)<sub>4</sub> doped TPPhen was optimized from 40 to 50 nm to adjust the distance between emitters and the reflective electrode for better light outcoupling [17]. The thickness of HTL was increased from 35 to 65 nm to reduce the hole transporting a bit [18]. Fig. 4 illustrates the current efficiency–current density and current density–voltage–luminance characteristics (inset) of the devices. The maximum current efficiency

achieves 57.7 cd/A when TPBi is as the blocking layer, proving the improvement by optimizing the thicknesses of HTL and ETL. BPhen based device shows a slightly higher current density than TPBi based device, which is due to the higher electron mobility of BPhen ( $\sim 10^{-4}$  cm<sup>2</sup>/V s) [19] than TPBi ( $\sim 10^{-6}$  cm<sup>2</sup>/V s) [20]. However, with large lowest unoccupied molecular orbital (LUMO) gap between BPhen (3.2 eV) and EML (mCP 2.4 eV, TPBi 2.7 eV), electrons accumulate at the narrow interface, which is similar to NPB/mCP situation described above. Therefore, although higher current efficiency is obtained by BPhen based device, the current efficiency decreases a bit faster, especially at large current density because of high accumulated electron density induced TTA and TPQ processes.

Based on the above work for device optimization, we further developed a higher efficiency and less pronounced roll-off PHOLED with TPBi as the HBL. The device structure was ITO/MoO<sub>3</sub>(1 nm)/mCP (60 nm)/mCP:TPBi:Ir(tfmpy)<sub>2</sub>(tpip) (20 nm, 1:1, 6 wt%)/TPBi (15 nm)/TPPhen:W<sub>2</sub>(hpp)<sub>4</sub> (45 nm, 12 wt%)/Al (100 nm). The thickness of EML was optimized to 20 nm for wider recombination zone and 15-nm-thick HBL was used to suppress the possible triplet energy transfer from the EML to TPPhen [21]. Fig. 5a shows the current density–voltage–luminance characteristics. The inset EL spectrum shows a suppressed residual emission induced by mCP and TPBi, suggesting that a complete energy transfer is formed in the EML. It is shown in Fig. 5b that the maximum EQE, current efficiency and power efficiency of this device reach 20.8%, 72.9 cd/A and 66.3 lm/W, respectively. Furthermore, the EQE remains as high as 19.9% at 1000 cd/m<sup>2</sup> and 17.4% at 10,000 cd/m<sup>2</sup> with a very low roll-off of 12.6%. Due to the high EQE over a wide range of luminance, the current efficiency also reaches 69.8 cd/A



**Fig. 5.** (a) Current density–voltage–luminance characteristics and EL spectrum (inset) and (b) EQE, current efficiency and power efficiency versus luminance of optimized device, whose structure is shown the inset.

at 1000 cd/m<sup>2</sup> and 60.7 cd/A at 10,000 cd/m<sup>2</sup>, indicating a greatly improved device performance.

#### 4. Summary

In summary, we demonstrated a Ir(tfmppy)<sub>2</sub>(tpip) based device with high efficiency and low roll-off at high brightness. High triplet energy material mCP was used as both HTL and host for phosphorescent emitter, providing a new approach for easily fabricating PHOLED with high triplet energy emitter. It also eliminates the carrier accumulation at the interface adjacent to EML, which leads to a significant loss of efficiency with the increasing current

density. Meanwhile, by mixing TPBi with mCP as co-host, balanced charge carriers and broadened recombination zone are achieved, resulting in an enhanced efficiency and reduced efficiency roll-off.

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