

P-168: Investigation of High-Efficiency Electrophosphorescent Organic Light-emitting Diodes with Double-Emission Layers

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Abstract

Highly efficient electrophosphorescent organic light-emitting diodes (PHOLEDs) with double-emission layers by doping both hole- and electron-transport hosts with green dye bis(2-phenylpyridine)iridium(III)acetylacetonate [(ppy)₂Ir(acac)] have been fabricated and investigated. In particular, the dependence of performance characteristics on the thickness and doping concentration of the double-emission layers is studied. By fine tuning these two parameters a peak luminous efficiency of 77cd/A, corresponding to 20.5% external quantum efficiency (EQE), is achieved at a current density of 0.053mA/cm² from the optimized device. Even at 1000cd/m², it still shows very high luminous efficiency of 71cd/A, with a power efficiency of 40lm/W. A shifting exciton formation zone with the driving current as well as triplet-triplet annihilation can explain the efficiency profile observed experimentally.

1. Introduction

Double-emission layer (D-EML) structure with doping of both the hole-transport and electron-transport emission layers with dyes has been well investigated and utilized in fluorescence-based organic light-emitting diodes (OLEDs). It can lead to enhancement of luminous efficiency as well as device lifetime [1-5]. However, the same concept has not been employed in phosphorescent OLEDs (PHOLEDs) until the first demonstration of high-efficiency devices introduced by Zhou *et al* in 2002, wherein the improved performance was mainly attributed to reduced losses of triplet excitons to the adjacent undoped regions [6]. A further work done by the same group demonstrated a high-efficiency and low-voltage PHOLED showing external quantum efficiency (EQE) of 19.3% at 100cd/m² by incorporating D-EMLs into the *p-i-n* structure [7]. Clearly the concept of D-EMLs does work for phosphorescent dyes as well. However, few reports on D-EMLs in PHOLEDs have been published so far [8]. A detailed investigation is needed to supply more insight on this particular structure.

We performed a detailed study of high-efficiency PHOLEDs with D-EML structure. D-EML here is comprised of hole-transport host 4,4',4''-tris(N-carbazolyl)-triphenylamine (TCTA) and electron-transport host 3-phenyl-4-(1'-naphthyl)-5-phenyl-1,2,4-triazole (TAZ), both doped with the green phosphorescent dye bis(2-phenylpyridine) iridium(III) acetylacetonate [(ppy)₂Ir(acac)]. In fact, over 19% EQE has already been reported with individual TCTA and TAZ host doped with *fac* tris(2-phenylpyridine)iridium [Ir(ppy)₃] or (ppy)₂Ir(acac) with or without the help of additional exciton blocking layers [9, 10]. Therefore it is anticipated that a limit approaching EQE (20%) will be more easily implemented for D-EMLs device. As expected a peak luminous efficiency of 77cd/A, corresponding to 20.5 % EQE, is achieved at a current density of 0.053mA/cm² from our optimized device. Particularly, dependence of performance, such as current density (*J*)-voltage (*V*)-luminance (*L*) and efficiency

characteristics, on the thickness and doping concentration of two emission layers is discussed in detail. A shifting exciton formation zone with the driving current as well as triplet-triplet annihilation [11] may account for the efficiency profile observed experimentally.

2. Experiment

The PHOLEDs were prepared by thermal evaporation of organic layers onto clean indium-tin oxide (ITO)-coated (75nm) glass substrates in a high vacuum chamber with a base pressure lower than 10⁻⁴ Pa. The sheet resistance of the ITO layer was 25Ω/□. It was treated by CF₄-plasma at a pressure of 20Pa for 10 sec to enhance hole injection ability prior to organic thin film deposition [12]. A 73-nm-thick film of N,N'-Bis(3-methylphenyl)-N,N'-bis(phenyl)-benzidine (TPD) served as the hole-transport layer (HTL). Next, a (X+Y)-nm-thick D-EMLs consisting of TCTA and TAZ doped with (ppy)₂Ir(acac) at various concentrations (Z₁ or Z₂ by weight) was prepared. A 40-nm-thick layer of tris-(8-hydroxyquinoline) aluminum (Alq₃) was used as electron-transport layer (ETL) followed by efficient LiF (1nm)/Al (150nm) bi-layer cathode. Device area was 2×2 mm². The evaporation rate was typically 1-2 Å/s, 0.2-0.3 Å/s and 3-4 Å/s for organic materials, LiF and Al, respectively. A quartz crystal monitor was used for determining the thickness of films *in situ*. The doping layer was achieved by co-evaporation from two separate heated sources at desired deposition rates. D-EMLs parameters, including thickness and doping concentration, are listed in Table 1.

Table 1. Thickness and doping concentration in D-EMLs of all devices fabricated in this work

		TCTA: (ppy) ₂ Ir(acac) X nm / Z ₁ %wt	TAZ: (ppy) ₂ Ir(acac) Y nm / Z ₂ %wt
Series I	A	5.5 / 13%	25.5 / 7%
	B	9 / 13%	18 / 7%
	C	13 / 13%	11 / 7%
Series II	D	9 / 11%	18 / 8%
	E	9 / 13%	18 / 7%
	F	9 / 16%	18 / 5%
Series III	G	7 / 16%	22 / 5%
	H	7 / 13%	22 / 7%
	I	9 / 13%	18 / 7%

The *J-V-L* characteristics were recorded simultaneously with a semiconductor parameter analyzer (HP4145B) and a large diameter (25mm) silicon photodiode mounted 2mm above the measured device. The edge emission from the substrate was not captured due to the use of black paste on edge. The EQE was measured at the same time under the assumption of Lambertian emission profile. The electroluminescent (EL) spectral characterization and the luminance calibration of the photodiode were carefully performed with a PhotoResearch PR650 spectrometer.

We also characterized the photoluminescence (PL) transient decays of four different thin films. They were 13%-(ppy)₂Ir(acac): TCTA (50nm); 7%-(ppy)₂Ir(acac): TAZ(50nm); 13%-(ppy)₂Ir(acac): TCTA (15nm)/7%-(ppy)₂Ir(acac): TAZ (35nm) bi-layer; and neat (ppy)₂Ir(acac) (50nm), which were all prepared on quartz substrates by high vacuum thermal evaporation. The excitation laser has a wavelength of 355nm and a pulse width of 3ns at a repetition rate of 10Hz. PL signals was recorded by reverse-biased photodiode combined with a digital oscilloscope.

3. Results and Discussion

As shown in Fig. 1, the room temperature transient phosphorescent lifetime of 13%-(ppy)₂Ir(acac) in TCTA, 7%-(ppy)₂Ir(acac) in TAZ and 13%-and 7%-(ppy)₂Ir(acac) in TCTA/TAZ bi-layer are comparable and characterized to be 200ns ± 25ns, longer than that of neat (ppy)₂Ir(acac) film in which “self-quenching” may increase the probability for nonradiative decay [11]. As the phosphorescence efficiency is approximately proportional to its lifetime, therefore the comparable phosphorescence lifetime of (ppy)₂Ir(acac) in TAZ and TCTA/TAZ bi-layer support a prediction that using D-EMLs structure would result in a similar maximum EQE of (19 ± 0.5)% [10] or even higher.

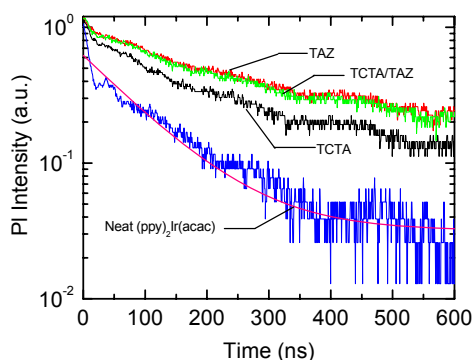


Figure 1. PL transient spectra of 13%-(ppy)₂Ir(acac): TCTA (50nm); 7%-(ppy)₂Ir(acac): TAZ(50nm); 13%-(ppy)₂Ir(acac): TCTA (15nm)/7%-(ppy)₂Ir(acac): TAZ (35nm) bi-layer; and neat (ppy)₂Ir(acac) (50nm); pink line is a guide to eyes.

The first series of devices were fabricated and denoted as devices A, B, and C with corresponding parameters as summarized in Table 1. Their EL performances were compared in order to see how they were influenced by the thickness of the D-EMLs. Fig. 2.a and 2.b show the J - V - L characteristics of these three devices. It can be seen that device C shows higher current density over the whole voltage range than device B. Device A is the lowest. Referring to the schematic energy level diagram shown in Fig. 3, TAZ host does function as a hole blocking layer as well due to its deeper highest occupied molecular orbital (HOMO) as compared to TCTA. Difference in J - V curves can be explained by the predominantly electron-transporting TAZ layer which blocks hole transport within the device. Thus the thinnest TAZ will incur a less hole blocking thus the highest current density. One may argue that hole transport should be assisted by phosphorescent dopants within the D-EMLs through hopping process. However, the same total amount of dopants in D-EMLs (~2.41nm in thickness) is inconsistent with such large difference in current e.g., between device A and C. Actually the doping concentration influences the

resulted J - V characteristics very little, as being discussed in the following context.

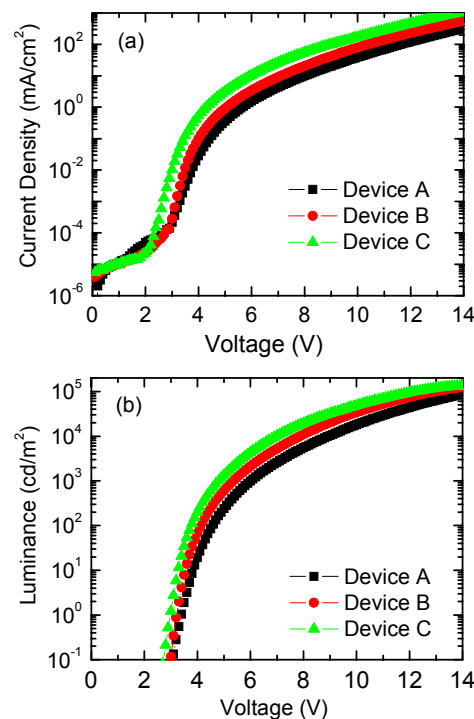


Figure 2. (a) J - V and (b) L - V curves of devices A, B, and C.

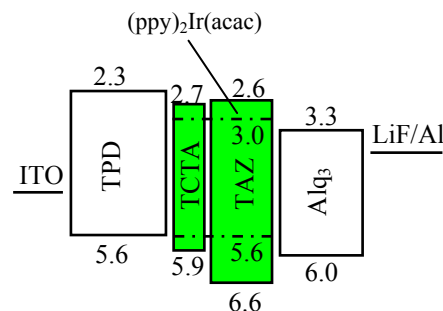


Figure 3. Schematic energy level diagram of PHOLED with D-EMLs structure, LUMO and HOMO values are cited from literatures.

Device C also exhibits the lowest operating voltage (defined as the driving voltage to achieve luminance of 100cd/m²) among the three devices. However, its EQE is much poorer than those of A and B over the entire current range, as depicted in Fig. 4. Additionally, device A and B show comparable EQE profile with thicker TAZ host. Therefore, we believe that hole blocking of TAZ play a crucial role to confine the excitons formed at the interface on both sides of the D-EML. At least 18nm TAZ is required to obtain high efficiency.

The second series of devices were fabricated and compared to study the dependence on the doping profile. Device parameters of D, E, and F are listed in Table 1. Fig. 5.a and 5.b show the J - V - L characteristics of these devices. As expected, the doping profile doesn't much influence the J - V curves when the thickness is constant. The voltages required to reach 20mA/cm²

are all within 7.8-7.9V and that needed for 1000cd/m² are within 5.3-5.4V.

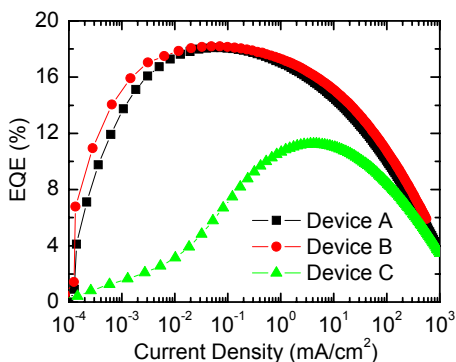


Figure 4. External quantum efficiency (EQE) comparisons of devices A, B, and C.

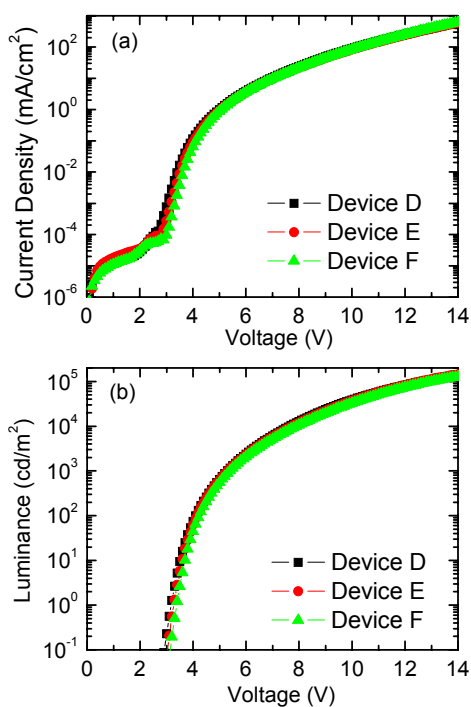


Figure 5. (a) *J-V* and (b) *L-V* curves of devices D, E, and F.

Although they show similar *J-V-L* curves, the EQE profile over the whole current density are quite different. As shown in Fig. 6, the respective maximum EQE of devices D, E, and F are at 0.32mA/cm², 0.09mA/cm², and 0.015mA/cm². This tendency can be correlated with the decreasing of (ppy)₂Ir(acac) concentration in TAZ host from devices D to F. If the dominant exciton formation region occurs within TAZ side at lower current driving (e.g., ≤ 0.5mA/cm²), less dopants in TAZ will result in efficiency saturation at lower current density. We also note that the peak EQE of device E and F are both 18.6%, higher than that of device D (17.4%). The reduced peak EQE of device D can be ascribed to its higher (ppy)₂Ir(acac) concentration in TAZ host thus triplet-triplet annihilation quenching the light emission partially. Therefore, the optimized concentration in TAZ should not be

higher than 7% (by weight) in our case to reduce “self-quenching” [11]. We further infer that the main exciton formation zone would shift gradually to TCTA side with increasing current density. This will result in EQE profile at higher current density range (e.g., ≥ 10mA/cm²) being dominated by the TCTA side. From Fig. 6, we can see that EQE profile of device D and E at higher current density range are quite similar, while better than that of device F. Again, triplet-triplet annihilation due to its higher (ppy)₂Ir(acac) concentration at TCTA side may account for the reduced efficiency observed. To avoid this, the doping concentration in TCTA should not be higher than 13%. Based on the above analysis, we shall use concentrations of 13% in TCTA and 7% in TAZ. The thickness will further be adjusted to optimize device performance.

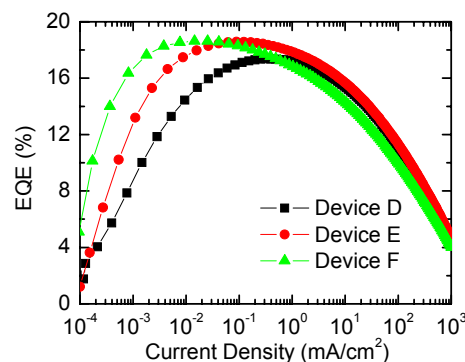


Figure 6. EQE comparisons of devices D, E, and F.

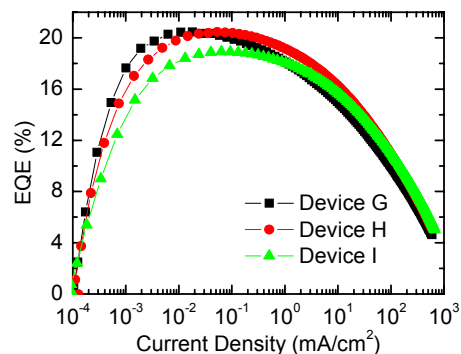


Figure 7. EQE comparisons of devices G, H, and I.

The next series of devices were denoted as G, H, and I with parameters listed in Table 1. Fig. 7 shows the EQE comparisons of the three devices. With thicker TAZ for device G and H, the maximum EQE of 20.5% is truly obtained. Again, the maximum EQE of device G is achieved at 0.018mA/cm² lower than those of devices H (0.053mA/cm²) and I (0.063mA/cm²). This observation is consistent with our argument that less dopants causes efficiency saturation at lower current density. Additionally, at higher current density range, devices H and I show similar EQE profiles which are better than that of device G. This further supports our previous inference that the main exciton formation zone is shifting to TCTA side at higher current density and triplet-triplet annihilation quenching partial light emission. Fig. 8 depicts the power efficiency characteristic of these devices. The respective

maximum power efficiency of devices G, H and I are 65lm/W, 65lm/W and 62lm/W. At 1000 cd/m², the power efficiencies are 36lm/W, 40lm/W and 40lm/W, respectively. Clearly the overall performance of device H is the best among the three devices, which is also the best optimized device in this work.

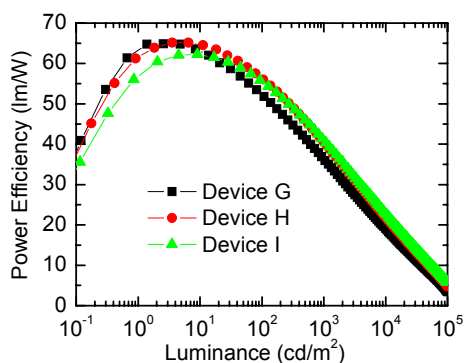


Figure 8. Power efficiencies of devices G, H, and I.

Fig. 9 gives the J - V comparisons of devices G, H, and I. Because of the thinner TAZ used in device I, it shows higher current density over the whole driving voltage than the other two which is consistent with the previous discussion.

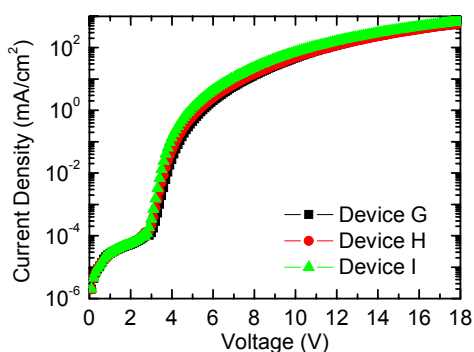


Figure 9. J - V curves of devices G, H, and I.

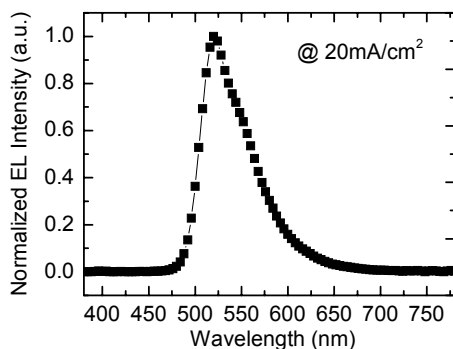


Figure 10. Normalized EL spectrum of device H at the current density of 20mA/cm².

It is worth mentioning that three devices in each series were fabricated in the same run. Among all three series of devices, devices B, E, and I are actually the same. Although they were fabricated in different runs, their EL performances are almost identical indicating negligible extraneous errors. All of the performance comparisons are reproducible. Another point should be mentioned is that the EL spectra of all devices are identical purely from (ppy)₂Ir(acac) emission without any contribution from adjacent TPD or Alq₃ (see example spectrum in Fig. 10). They do not change with driving current.

4. Conclusion

In summary, we have investigated the influence of thickness configuration as well as doping profile on the EL performance of PHOLEDs with D-EMLs comprising of (ppy)₂Ir(acac): TCTA and (ppy)₂Ir(acac): TAZ. The thickness of TAZ host much affects the performance characteristics, such as J - V - L and the maximum EQE. In contrast, the (ppy)₂Ir(acac) doping concentration does not influence the J - V curves but the EQE profile. This observation can be correlated with a shift of exciton formation region with the current density and explained by triplet-triplet annihilation on two sides. By fine tuning the thickness and doping concentration, a peak luminous efficiency of 77cd/A, corresponding to 20.5% EQE, is achieved. Even at 1000cd/m², it show a very high luminous efficiency of 71cd/A and a power efficiency of 40lm/W.

5. Acknowledgement

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6. References

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