High efficiency green phosphorescent top-emitting organic light-emitting diode with ultrathin non-doped emissive layer

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Ultrathin non-doped emissive layer (EML) has been employed in green phosphorescent top-emitting organic light-emitting diodes (TOLEDs) to take full advantages of the cavity standing wave condition in a microcavity structure. Much higher out-coupling efficiency has been observed compared to conventional doped EML with relatively wide emission zone. A further investigation on dual ultrathin non-doped EMLs separated by a special bi-layer structure demonstrates better charge carrier balance and improved efficiency. The resulting device exhibits a high efficiency of 125.0 cd/A at a luminance of 1000 cd/m² and maintains to 110.9 cd/A at 10,000 cd/m².

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1. Introduction

Phosphorescent top-emitting organic light-emitting diodes (TOLEDs) have been the subject of intense research due to their many significant advantages for flat panel displays, such as high efficiency, high pixel resolution and large aperture ratio [1,2]. It is well known that a reasonable emissive layer (EML) structure is critical to phosphorescent OLEDs (PHOLEDs) performance. During the last three decades, various EML structures have been realized, including conventional non-doped EML [3], host-guest [4], double-host [5], co-host [6], crossfading-host [7] and ultrathin structure [8]. In general, these EML structures can be categorized into host-guest doped EML and non-doped EML. Actually, most of highly efficient monochrome and white OLEDs have been realized based on host-guest doped EML structure, whereas non-doped EML-based devices most often exhibit low efficiencies due to triplet-triplet annihilation [9]. Realistically, the doping technology may suffer from the poor reproducibility for mass production processes since it is difficult to precisely control the deposition rate and dopant concentration during multi-source evaporation process [10], and usually the efficiency of PHOLEDs strongly depends on the doping concentration of the dye. In order to simplify the device structure and fabrication process, an alternative ultrathin EML structure with non-doped phosphorescent dye has been introduced and received an increasing attention. For example, Divayana et al. [8,11] reported OLEDs with a repeating ultrathin non-doped EML structure, which can avoid co-evaporation and simplify the fabrication process. Nevertheless, the external quantum efficiency (EQE) dropped fast with current density due to an additional triplet-polaron annihilation (TPA) in sequential doping as the current passed through the phosphorescent dyes. Liu et al. [12] improved the performances of non-doped PHOLEDs by introducing a simple triplet double-quantum-well structure. Recently, highly efficient and simple monochrome blue, green,
orange, and red bottom-emitting OLEDs (BOLEDs) based on ultrathin non-doped EMLs have been reported as well [13]. The even simpler structure and the high efficiency indicate the feasibility of ultrathin non-doped EML-based OLEDs.

However, there are surprisingly few reports on TOLEDs based on ultrathin non-doped EML structure. It is generally known that the emission of TOLED is not only determined by the cavity of the device, but also strongly dependent on the position of the emitter layer within the two reflectors [2]. The EML can be positioned either at the maximum (antinode) or the minimum (node) field strength of the standing wave, resulting in enhanced or suppressed emission, respectively [14]. Additionally, even with the same location of EML, the different EML profiles with various recombination zones and recombination efficiencies might also have a great influence on TOLEDs.

Therefore, in this research, green phosphorescent TOLEDs based on single ultrathin non-doped EML and doped EML are fabricated respectively to elucidate the different influence of cavity standing wave effect. Furthermore, by introducing dual ultrathin non-doped EMLs and comparing two kinds of bi-layer separate structures, the reasons for different recombination efficiencies are discussed in detail. The resulting best device achieves a high current efficiency of 125.0 cd/A at a luminance of 1000 cd/m² and maintains to 110.9 cd/A at a luminance of 10,000 cd/m².

2. Experimental section

To fabricate TOLEDs, a patterned 150-nm-thick aluminum (Al) film was first deposited on pre-cleaned glass substrates through a shadow mask, and then the samples were loaded into a vacuum thermal evaporator at a base pressure of $5 \times 10^{-6}$ Torr for organic film deposition. The deposition rates were monitored in-situ with quartz crystals. And the typical deposition rate for the transport organic materials, ultrathin phosphorescent dye, and sliver (Ag) are 1–2, 0.02–0.05, and 2–3 Å/s, respectively. The overlap between Al anode and Ag cathode is $3 \times 3$ mm as the active emissive area of the devices.

The basic device structure with different emission layer profiles is shown in Fig. 1, including host–guest doping EML, single ultrathin EML, and double ultrathin EMLs. Here, 1,3-bis(carbazol-9-yl)benzene (mCP) is used as hole transport layer (HTL), which is used as light emitting host as well. For electron transport layer (ETL), we use 4,7-diphényl-1,10-phenanthroline (Bphen) and 1,3,5-tris(N-phenyl-benzimidazol-2-yl)benzene (TPBi), and the latter is also a light emitting host material with predominant electron transport property. The phosphorescent dopant in this study is iridi-um(III)bis(2-(4-trifluoromethylphenyl)pyridine)tetraphenylimidodiphosphinate ($\text{Ir}(\text{tpfmpy})_2$ (tpip)), which was introduced by Zheng group [15].

Doped EML profile refers to the 6 wt.% $\text{Ir}(\text{tpfmpy})_2$ (tpip) co-evaporated with mCP as emissive layer, while 0.5-nm-thick $\text{Ir}(\text{tpfmpy})_2$ (tpip) is as EML for single ultrathin profile and two 0.5-nm-thick $\text{Ir}(\text{tpfmpy})_2$ (tpip) layers separated by a bi-layer structure as double ultrathin EMLs profile. A 3-nm-thick MoO$_3$ layer and a bi-layer structure 8-hydroxyquinoline lithium (Liq) (1 nm)/aluminum (Al) (1 nm) are utilized as hole and electron injection layer, respectively. To extract additional light from the devices and achieve both appropriate reflectivity and low absorption of the top contact [16] for major emission wavelength of $\text{Ir}(\text{tpfmpy})_2$ (tpip), an 80-nm-thick mCP layer deposited on the silver (Ag) is used as capping layer (CPL).

A computer controlled system with Keithley 2400 Source Meter and Topcon BM-7A Luminance Colorimeter is used to measure the current density–voltage–luminance characteristics of the devices. The spectral radiant intensity is measured with a calibrated Labsphere CDS 610 spectrometer.

3. Results and discussion

According to the previous reports [6,15], promising BOLED performances have been achieved based on phosphorescent dopant $\text{Ir}(\text{tpfmpy})_2$ (tpip) with conventional host–guest EML system. It will be very interesting to see how far it will go with ultrathin EML and TOLED structures. Firstly, four bottom emission devices with ultrathin non-doped EML were fabricated by varying EML thickness to obtain the optimum thickness. The basic structure is: ITO/MoO$_3$ (3 nm)/mCP (55 nm)/$\text{Ir}(\text{tpfmpy})_2$ (tpip) (x nm)/TPBi (10 nm)/Bphen (45 nm)/Liq (1 nm)/Al (100 nm), where x varied from 0.1, 0.5, 1.0, to 2.0 nm. Additionally, the device using the doped EML with mCP:$\text{Ir}(\text{tpfmpy})_2$ (tpip) (6 wt.%) was also fabricated for comparison.

Fig. 2(a) shows the normalized emission spectra of the devices. As the thickness of $\text{Ir}(\text{tpfmpy})_2$ (tpip) EML increases, the emission peak shifts from 520 (0.1 nm EML) to 528 nm (2 nm EML). And it can be seen from Fig. 2(b) that the current density does not vary much, while significant differences are observed in the current efficiency characteristics. The highest current efficiency is obtained when the thickness of $\text{Ir}(\text{tpfmpy})_2$ (tpip) is increased from 0.1 to 0.5 nm, which results from more recombination sites and more effective carrier trapping. In addition, the efficiency of the device with 0.5-nm-thick EML is very close to that of the doped one. However, the efficiency drops with a further increase of the EML thickness. This may be due to emitter molecular aggregation at high thickness [17], which is in consistent with aforementioned spectrum redshift.

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Fig. 1. Schematic diagram of top-emitting devices with different EML profiles.
With optimized ultrathin EML thickness of 0.5 nm, further investigation was conducted by comparing ultrathin EML and doped EML in both bottom and top OLED to observe the influence of cavity standing wave effect on device performance. Detail device structures are:

**Device T1 (doped EML):** Al/MoO3 (3 nm)/mCP (40 nm)/mCP:Ir(tfmppy)2(tpip) (6 wt.%, 15 nm)/TPBi (10 nm)/Bphen (45 nm)/Liq (1 nm)/Al (1 nm)/Ag (22 nm)/mCP (80 nm).

**Device T2 (ultrathin EML):** Al/MoO3 (3 nm)/mCP (55 nm)/Ir(tfmppy)2(tpip) (0.5 nm)/TPBi (10 nm)/Bphen (45 nm)/Liq (1 nm)/Al (1 nm)/Ag (22 nm)/mCP (80 nm).

Two controlled BOLEDs (referred as device B1 and B2) with the similar layer structures were also fabricated respectively, except that the reflective Al anode was replaced by transparent indium tin oxide (ITO), and the semi-transparent Ag cathode was replaced by a reflective Al electrode.

As shown in Fig. 3(a), the TOLEDs show much lower current densities than BOLEDs, which may be attributed to the poorer hole injection efficiency from Al (4.3 eV) anode to mCP (5.9 eV) compared with from ITO (4.7 eV) anode to mCP (5.9 eV) in the presence of a 3-nm-thick MoO3 hole injection layer. However, the two BOLEDs with doped EML and ultrathin EML show comparable electrical properties, so do the two TOLEDs, which suggests that the charge injection and transport in either BOLEDs or TOLEDs are similar for different EML structures. This implies that the differences observed in efficiencies of BOLEDs or TOLEDs may be mainly related to the recombination efficiency and microcavity effect. The efficiencies of the four devices are shown in Fig. 3(b). As it can be seen, the top emitting device T1 with doped EML exhibits a current efficiency of 85.7 cd/A at 1000 cd/m², around 2.0 times as high as 43.0 cd/A achieved by corresponding bottom emission device B1. In contrast, the efficiency value of the ultrathin non-doped EML-based top emitting device T2 is found to be 108.5 cd/A at 1000 cd/m², up to 2.7 times as high as 40.0 cd/A obtained by non-cavity device B2. It has been well known that the position of the emission layer within the optical microcavity structure has a great influence on the emission intensity out of the device [14]. This influence is mainly caused by the standing wave of the electromagnetic field as mentioned above. By restricting the emission zone at the antinode of the ultrathin EML-based TOLED, a larger efficiency enhancement is achieved, resulting from a strong standing-wave electric field formed by the interference of the incident and reflected lights inside TOLED. On the other hand, relatively poor enhancement is obtained if the active region is broader.

To further investigate the influence of standing wave effect, a set of simulation was conducted by finite-difference time-domain (FDTD) method [18], where the modeled structure is glass/Al (100 nm)/organic layer (110 nm)/Ag (22 nm)/organic layer (80 nm) with the dipole located at between 45 and 60 nm from the reflective Al electrode, while the cavity length is fixed at 110 nm to meet the resonant condition. To match the random orientation and emission behavior of evaporated small molecules, we set three independent orthogonal dipoles and averaged the light intensities in air. Additionally, the actual radiated power is highly dependent on the surrounding materials, since the reflections from the structures will interfere with the fields from the dipole, changing the actual radiated power. Therefore, we get the power emitted from the dipole source by measuring the power flowing out of a small box of monitors surrounding the source. By utilizing the box of monitor technique, Purcell effect was taken in consideration in the FDTD simulation. The fraction of the power transmitted into the air was obtained by integrating the far field intensity over all viewing angles, which were calculated by FDTD simulation. The out-coupling efficiency is defined by the ratio of the power transmitted into the air to the total radiated power of a
dipole source, as depicted in Fig. 4. It can be seen that the out-coupling efficiency increases initially with the increase of the distance between dipole and reflective electrode. After reaching a maximum at 55 nm, the out-coupling efficiency drops with a further increase of distance, indicating that the location (55 nm) is at the first antinode in this optical cavity. This antinode position is in good agreement with the result calculated by Fabry–Pérot resonance equation [19], which thus confirmed the accuracy of FDTD simulation. The results of the pure optical out-coupling efficiency simulation reveal two important suggestions. First, if an ultra-narrow emission zone is restricted exactly at the antinode, the microcavity device could achieve the best out-coupling efficiency. Secondly, if a relatively broad emission zone (usually more than 10 nm) is placed near the antinode, the out-coupling efficiency of this device will be averaged, and poorer than that of the device based on an ultra-narrow emission zone located at the antinode.

The results of this simulation are in good agreement with the experimental results mentioned above, where top-emitting device T2 with ultrathin EML has an up to 2.7 times enhancement in current efficiency compared to bottom-emitting device B2, while device T1 has a normal 2.0 times improvement compared to device B1 with doped EML.

Although the single ultrathin EML-based top-emitting device showed rather high relative efficiency enhancement, it still has potential to improve recombination efficiency. The most efficient way to get high recombination efficiency in PHOLEDs is to balance holes and electrons in the EML, while the main emission mechanism in the above-mentioned device T2 would be carrier trapping [20]. Therefore, a strategy for carrier control is proposed to further improve efficiency by introducing dual ultrathin non-doped EMLs separated by a bi-layer structure. The device structure is Al/MoO3 (3 nm)/mCP (50 nm)/Ir(tfmppy)2(tpip) (0.5 nm)/separate layer/Ir(tfmppy)2(tpip) (0.5 nm)/TPBi (10 nm)/Bphen (45 nm)/Liq (1 nm)/Al (1 nm)/Ag (22 nm)/mCP (80 nm), in which a bi-layer separate structure exchanges the layer sequence, i.e., mCP (2.5 nm)/TPBi (2.5 nm), which makes the ultrathin Ir(tfmppy)2(tpip) like “doping” in both mCP and TPBi host, so does the second ultrathin EML. This structure is similar to dual “co-host” systems with thin thickness and is beneficial for carrier balance. For comparison, the device T4 with the similar layer structure was also fabricated, except that the separate structure exchanges the layer sequence, i.e., mCP (2.5 nm)/TPBi (2.5 nm), which makes the ultrathin Ir(tfmppy)2(tpip) like “doping” in a single host, either mCP or TPBi.

Fig. 5(a) depicts the J–V characteristics, which shows very little difference among devices with a single ultrathin EML and dual ultrathin EMLs, indicating that the separate structures do not affect J–V characteristic of the dual ultrathin EMLs-based devices. Nevertheless, the device T3 with dual “co-host” system greatly improve the efficiency. It is shown in Fig. 5(b) that the maximum current efficiency of device T3 reaches 126.3 cd/A at 328 cd/m2, and maintains to 125.0 cd/A at 1000 cd/m2, which is superior to the current efficiency of 108 cd/A at 1000 cd/A for device T2. On the other hand, unfortunately, after exchanging the separate structure layer sequence, instead, the device T4 shows a current efficiency with a significant decrease of 7.4% at 1000 cd/A, compared with device T2.

As it is known, both energy transfer and carrier trapping usually contribute to emission process in host–guest system [21]. The bi-layer separate structure for device T3 is so thin that the holes and electrons can easily tunnel through corresponding TPBi and mCP layer, respectively. Therefore, a fraction of excitons will form in the separate layer structure interface (TPBi (2.5 nm)/mCP (2.5 nm)), followed by energy transfer to the dopant. Additionally, a certain fraction of charges (including a portion of carriers tunneling through the separate layers) will transport directly to the dopant sites and be trapped to form excitons. Furthermore, the excitons will be well confined within the ultrathin EMLs due to the surrounding wide band gap and the high triplet energy materials mCP and TPBi. It is because both of the above mechanisms existed simultaneously in the device T3 that the dual ultrathin EMLs surrounded by two hosts of mCP and TPBi can effectively trap tunneled carriers to form excitons and harvest excitons formed in the bi-layer separate structure, as illustrated in Fig. 6. However, as for device T4, although there are double ultrathin EMLs located between transport layers and separate layers, the recombination zone still

**Fig. 4.** Calculated out-coupling efficiency as a function of different dipole locations at the wavelength of 526 nm.

**Fig. 5.** J–V and CE–L characteristics of the device T2, T3 and T4.
might be at the middle interface of bi-layer separate structure, i.e. mCP (2.5 nm)/TPBi (2.5 nm), rather than the locations of ultrathin EML. And here, 2.5 nm is sufficient to suppress Förster-type energy transfer because the typical Förster radius for Ir complexes is less than 2 nm [22]. Hence, the primary emission mechanism in device T4 might be solely Dexter energy transfer. On the contrary, the carrier trapping is suggested to be the major channel of dopant excitation in the device T2, since its recombination zone is only located at ultrathin EML surrounding by two hosts of mCP and TPBi.

4. Summary

It has been successfully demonstrated that a single ultrathin EML-based TOLED with intentionally satisfying microcavity resonance and standing wave antinode conditions shows a greater relative efficiency enhancement, compared with a conventional doped EML-based TOLED. By investigating emission characteristics of the devices based on single ultrathin EML and dual ultrathin EMLs with two different separate structures, three different emission processes are elucidated in great detail. Remarkably, a mCP (2.5 nm)/TPBi (2.5 nm) bi-layer separate structure is applied in device to get more balanced charges and increase the recombination efficiency, resulting in a maximum current efficiency of 126.3 cd/A at 328 cd/m². 

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