

Improved efficiency of blue phosphorescence organic light-emitting diodes with irregular stepwise-doping emitting layers

Editor's Choice

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We demonstrate highly efficient blue phosphorescence organic light-emitting diodes (PHOLED) with irregular stepwise-doping emitting layers (EMLs). High efficiency is realized by inserting a high-doping EML between two relatively low-doping EMLs. Peak luminous efficiency and power efficiency of 19.2 cd A⁻¹ and 18.0 lm W⁻¹ are achieved, while those of a

continuous stepwise-doping device are 9.8 cd A⁻¹ and 8.6 lm W⁻¹. The dramatic efficiency enhancement is mainly attributed to the high hole–electron recombination probability and suppressed triplet excitons quenching by fine tuning the doping concentrations in the EMLs.

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1 Introduction Phosphorescence organic light-emitting diodes (PHOLED) can facilitate low-power consumption full-color display and solid-state lighting applications because they possess an internal quantum efficiency of 100% in theory [1–4]. Compared to red and green PHOLED, high-efficiency blue PHOLED is more difficult to realize, since it requires a host material with large triplet energy (TE) to confine the triplet excitons on phosphorescence emitters [5]. Moreover, the neighboring hole- and electron-transporting materials should have higher TE than that of the blue phosphor [6] to prevent the triplet exciton quenching. However, these kinds of materials are rare and hard to design [7, 8]. Based on a conventional blue phosphorescent dopant and their host materials, a common approach of improving the performance is to optimize the emitting layer (EML), such as introduction of a mixed-host architecture [9, 10], double hosts [11], and stepwise EML [12–16], and so on.

Compared to the conventional organic light-emitting diode (OLED), stepwise-doping EML allows for better control of charge transport and recombination, which can be classified as two kinds of EML. One type of stepwise-doping

EML consists of graded bipolar transport hosts and constant concentration of dopant. Chwang et al. [12] reported a stepwise graded bipolar transport emissive layer with 4,4'-bis[*N*-(1-naphthyl)-*N*-phenyl-amino]biphenyl (NPB) and tris-(8-hydroxyquinoline)aluminum (Alq₃) as hosts and 1% 2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H,11H-10-(2-benzothiazolyl)quinolizino-[9,9a,1gh]coumarin (C545T) as the dopant. The power efficiency was 1.6 times larger than that of a uniformly mixed device. Erickson and Holmes [13] reported a single-layer green PHOLED based on a graded-composition EML by mixing both hole- and electron-transporting host materials (HTMs and ETMs, respectively). The graded EML consists of nearly 100% HTM on the anode side and nearly 100% ETM on the cathode side. A peak external quantum efficiency of 19.3 ± 0.4% was realized at a luminance of 600 cd m⁻². The other type of stepwise-doping EML is comprised of a dopant with graded concentration in a host material. The emitter has either hole-transporting or electron-transporting property, which is usually opposite to the host material. Lei et al. [14] reported the first stepwise doping blue PHOLED by doping bis[(4,6-difluorophenyl)-

pyridinato-N,C2'](picolinate)Ir(III) (FIrpic) in *N,N'*-dicarbazolyl-1,4-dimethene-benzene (DCB) with varied concentrations of 5, 10, 20, and 45% in each step. The device showed a peak luminous efficiency of 15.4 cd A⁻¹, which is almost 80% higher than that of the conventional FIrpic-based PHOLED. However, the shoulder at 500 nm of the electroluminescence (EL) spectrum was enhanced and became the main emission peak in the graded doped device. The bathochrome issue of the EL spectrum is caused by a shift of the recombination zone far away from the reflective cathode. Recently, Lee [15] has investigated the charge-trapping effects in PHOLED by changing the doping concentration of emitter in EML. In the device based on the (4,4'-*N,N'*-dicarbazole)biphenyl (CBP):FIrpic host-guest system, the performance was not influenced by three different stepwise-doping profiles (2–6–10%, 10–6–2%, 10–6–10% with direction from HTL to ETL), indicating that there is little hole and electron trapping effect in the device. The result is contradictory to the reports published previously [14, 16]. In order to get a better understanding and further improve the performance of blue phosphorescent OLED, we have performed a detailed investigation on the effects of stepwise-doping profile.

In this work, an irregular stepwise-doping EML architecture is presented that permits the realization of both high luminous efficiency and power efficiency. The layer composition is formed by inserting a high-doping EML between two relatively low-doping EMLs. This irregular stepwise-doping profile allows for high hole–electron recombination probability and suppressed triplet exciton quenching in EML.

2 Experimental The hole-transporting material 4,4',4''-tri(*N*-carbazolyl)triphenylamine (TCTA) has a triplet excited state of 2.85 eV [17], which is well above that of the blue phosphorescent emitter FIrpic (2.62 eV) [17].



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Therefore, it is chosen as the host of FIrpic. 4,7-diphenyl-1,10-phenanthroline (BPhen) can be doped by cesium carbonate (Cs₂CO₃), improving electron injection from the cathode. The basic PHOLED configuration is ITO/EHI608(40 nm)/NPB(10 nm)/TCTA:FIrpic(30 nm)/BPhen(10 nm)/BPhen: Cs₂CO₃(5%, 20 nm)/Al(150 nm), where EHI608 is the hole-injection layer (HIL), and 5% Cs₂CO₃-doped BPhen works as an electron-injection layer (EIL). NPB is HTL and an electron-blocking layer (EBL), while undoped BPhen works as ETL and a hole-blocking layer (HBL). In the standard device A, doping concentration through the whole EML is uniform (10%), while the EML of stepwise-doping device B and device C are divided by five 6-nm thick regions. For device B, a doping profile of 0–5–10–15–20% has been processed, while in device C is 0–5–10–20–15% with lower doping ratio at ETL/EML interface. The total thicknesses of EML and the total amount of FIrpic in all devices are identical. EML structures of devices A, B, and C are schematically shown in Fig. 1.

The devices were fabricated by the following processes. First, ITO-coated glass substrates were cleaned successively using deionized water, acetone, and isopropanol in an ultrasonic bath, and then dried in a drying cabinet followed by pretreatment with oxygen plasma. Then, the organic films of EHI608, NPB, TCTA:FIrpic, BPhen, and BPhen:Cs₂CO₃ were deposited by thermal evaporation under a base vacuum of about 10⁻⁶ Torr. Finally, Al metal was evaporated in another vacuum chamber without breaking the vacuum. The thicknesses of the films were determined by quartz thickness monitors. The active area of the EL device, defined by the overlap of the ITO and the cathode electrode, was 3 mm × 3 mm. The performances of the devices were measured with a computer-controlled system using a Photo Research PR650 spectrophotometer and a Keithley 2400 Source Meter.

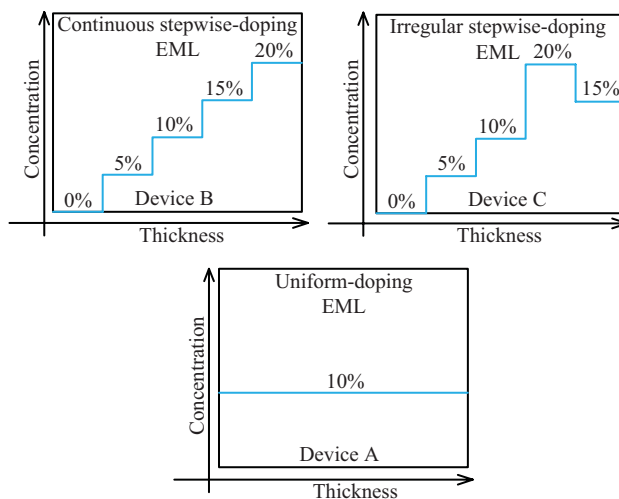


Figure 1 (online color at: www.pss-a.com) The EML structures of devices: uniform-doping EML of device A, continuous stepwise-doping EML of device B, and irregular stepwise-doping EML of device C.

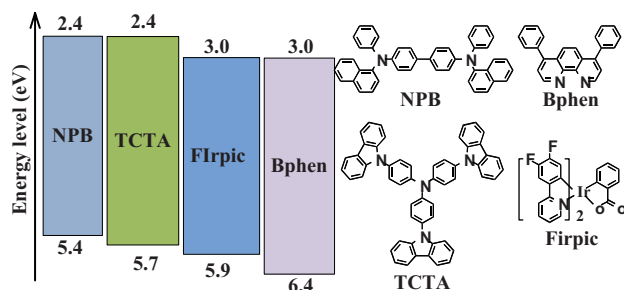


Figure 2 (online color at: www.pss-a.com) Energy level diagram and chemical structures of materials used in PHOLEDs.

3 Results and discussion Figure 2 depicts the energy-level diagram of the materials used in the experiments. The hole transport from NPB to TCTA is favorable, since highest occupied molecular orbitals (HOMO) difference between NPB (HOMO: 5.4 eV) [17] and TCTA (HOMO: 5.7 eV) [17] is only 0.3 eV. Though the HOMO level difference between TCTA and FIrpic (HOMO: 5.9 eV) [17] is small (0.2 eV), the hole drift mobility is reduced by increasing FIrpic doping concentration, due to the energetic disorder [18]. On the other hand, the electron transporting direct from BPhen to TCTA is unlikely due to large lowest unoccupied molecular orbitals (LUMO) mismatch (0.6 eV) [17]. FIrpic (LUMO: 3.0 eV) [17] has an electron-transport property [14], however, it acts as a deep trap for electrons in TCTA host because of the large LUMO difference [16]. Unless the dopant concentration is high enough that the electrons can hop via FIrpic sites, electrons at FIrpic sites are almost immobile. Moreover, since the LUMO levels of BPhen and FIrpic are almost aligned, electrons can be easily injected from BPhen to EML at high FIrpic doping ratio.

Figure 3 shows the current density–driving voltage (J – V) and luminous efficiency–current density characteristics of uniform-doping devices with various dopant concentrations. Devices at low doping ratio (5%, 10%) exhibit almost identical current density. Due to the small HOMO offset

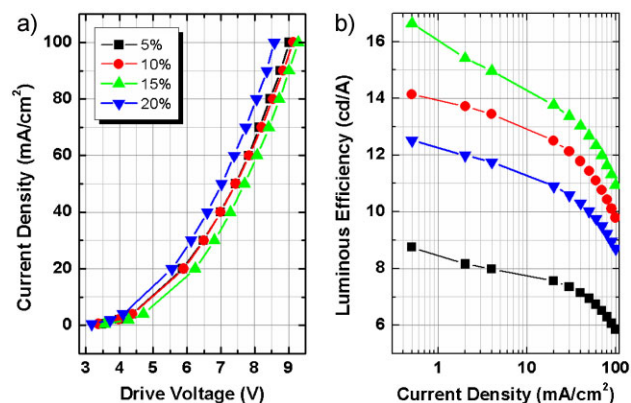


Figure 3 (online color at: www.pss-a.com) The J – V (a) and luminous efficiency–current density (b) characteristics of uniform-doping devices.

(0.3 eV) between NPB and TCTA and little energy disorder in EML at a low doping ratio, hole transport from NPB to TCTA is favorable. Increasing the FIrpic ratio on the premise of a low doping ratio leads to more electrons being trapped at the LUMO level of FIrpic to directly form more triplet excitons, resulting in enhanced luminous efficiency. As FIrpic doping ratio increases to 15%, the distance between FIrpic molecules becomes shorter, leading to enhanced electron transport in EML by a hopping mechanism. However, hole transport is significantly reduced because of the huge energy disorder at high doping ratio, leading to the lowest current density. This leads to much better charge balance in EML, resulting in the highest luminous efficiency at 15% doping ratio. In devices at 20% doping ratio, hole transport in EML is impeded further, while electrons can transport directly from BPhen to FIrpic and hop via FIrpic molecules more easily owing to their shorter distances. Therefore, the largest current density at 20% doping ratio is attributed to the significantly enhanced electron transport, while the seriously reduced luminous efficiency suffers from poor charge balance and triplet–triplet annihilation. The charge trapping at low doping ratio and hopping at high doping ratio are consistent with the report by Chin et al. [19].

Since an increase of FIrpic doping ratio causes deteriorated hole transport and enhanced electron transport, the recombination zone in EML deviates from the cathode side at high concentration. According to the optical interference principle [20], the intensity of EL spectra at long wavelength (>472 nm) will be enhanced with doping ratio. However, it is reduced for device at 20% doping ratio, as shown in Fig. 4. Given that FIrpic and Bphen have almost aligned LUMO level and electron transport is strengthened at high doping ratio, a large number of electrons can transport and store at NPB/EML interface. The accumulated electrons in the EML may create an additional electric field [21], which can lead to strong field-induced quenching near the NPB/EML interface.

Figure 5 shows the current density–luminance–driving voltage (J – L – V) characteristic and the dependence of the

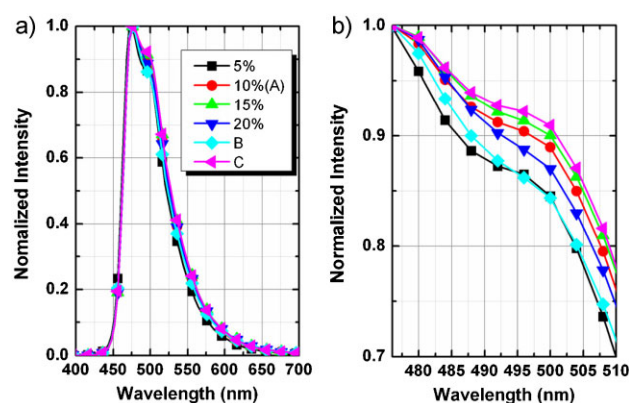


Figure 4 (online color at: www.pss-a.com) The normalized EL spectra of uniform-doping and stepwise-doping devices (a) and the enlarged drawing at wavelength from 472 to 510 nm.

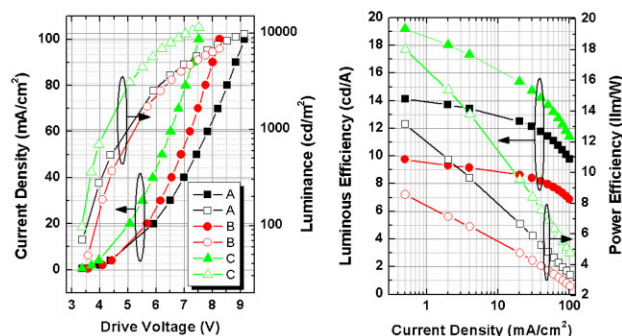


Figure 5 (online color at: www.pss-a.com) The J - L - V (a) and luminous efficiency–power efficiency–current density characteristics (b) of devices A, B and C.

luminous efficiency and power efficiency on current density. Device B shows reduced driving voltage and decreased luminance, while device C exhibits reduced driving voltage and increased luminance. In device B with the stepwise-doping profile (0–5–10–15–20%), hole and electron transport are pronounced at the NPB/TCTA interface and TCTA:20%Flrpic/BPhen interface, respectively. As the Flrpic doping ratio increasing from the anode to the cathode side, the hole transport is impaired while the electron transport is improved according to the analysis of uniform-doping devices. Hence, the number of holes and electrons to recombine at the interior of EML is reduced, leading to diluted triplet excitons that result in lower efficiencies. In addition, device B shows reduced intensity of EL spectra at long wavelength as shown in Fig. 4, indicating the recombination zone shifts closer to the cathode. The triplet excitons might diffuse to the adjacent ETL and are quenched by lower TE BPhen (2.4 eV) [22] because of a long diffusion length of the triplet exciton [3, 23]. Therefore, the stepwise-doping profile (0–5–10–15–20%) gives rise to low concentration of the triplet excitons and stronger triplet exciton quenching, resulting in a reduced peak luminous efficiency of 9.8 cd A^{-1} and power efficiency of 8.6 lm W^{-1} , compared to device A with a peak luminous efficiency of 14.1 cd A^{-1} and power efficiency of 13.1 lm W^{-1} .

In device C, the positions of the 15% doping ratio layer and the 20% doping ratio layer are interchanged to form an irregular stepwise-doping profile (0–5–10–20–15%). According to the analysis of uniform-doping devices, electrons can transport from BPhen to the 15% doping ratio layer by a hopping mechanism, though the electron-transport ability in the 15% doping ratio layer is poorer than that in the 20% doping ratio layer. Since the 20% doping EML possesses not only a hole-blocking property but also an electron-transporting property, a large number of holes and electrons will recombine to form excitons at the 10%/20% interface. Compared to device B, the relative intensity of shoulder peak (see Fig. 4) at long wavelength is more pronounced, indicating the recombination zone is far from the cathode side. This leads to a suppressed possibility of triplet exciton quenching by BPhen layer. It is also found that

the dominated maximum peak still locates at 472 nm in device C, which demonstrates the EL color of blue stepwise doped PHOLED is not altered to a large extent. Therefore, the stepwise doping profile (0–5–10–20–15%) enhances the hole–electron recombination probability in EML and reduces the possibility of triplet excitons quenching, leading to dramatically enhanced peak luminous efficiency of 19.2 cd A^{-1} and power efficiency of 18.0 lm W^{-1} . It is expected that the luminance efficiency and the stability of device C can be further improved by using HTL and ETL with higher TE, and a more stable blue phosphorescent emitter. Moreover, the device C exhibits the Commission Internationale de L’Eclairage (CIE) coordinates of (0.18, 0.39), which can collocate with an orange phosphorescence emitter to fabricate high-efficiency white OLED for lighting applications.

4 Conclusions In conclusion, we have investigated the effect of a stepwise-doping profile in EML on the device performance, and developed a blue PHOLED with improved efficiency by optimizing the stepwise-doping EML. A peak luminous efficiency of 19.2 cd A^{-1} and a power efficiency of 18.0 lm W^{-1} have been achieved by the irregular stepwise-doping profile of 0–5–10–20–15% in EML, which are about 95.9 and 109.3% higher than those of continuous stepwise-doping device with the same amount of Flrpic. Our results provide a valuable way to improve charge-carrier balance and control the recombination zone in EML, which are the key points for high-efficiency OLEDs.

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