



Solution-processed small molecule thin films and their light-emitting devices

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ABSTRACT

Thin films of N,N'-bis-(3-Naphthyl)-N,N'-biphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB), tris-(8-hydroxyquinoline)-aluminum (Alq₃) and their blends prepared by spin-coating process were investigated. Experimental results revealed that the NPB films prepared by spin-coating process have smoother surface than that of Alq₃, which was attributed to their different molecular structures. Organic light-emitting devices (OLEDs) with emitting layer prepared by spin-coating the blends of NPB and Alq₃ exhibited a maximum luminance and a current efficiency over 10,000 cd/m² and 3.8 cd/A respectively, and when 10-(2-benzothiazolyl)-2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H,11H-[1]benzopyrano[6,7,8-ij]quinolizin-11-one was doped in, a current efficiency of 8 cd/A can be obtained. Comparative device performance to the vapor-deposited OLEDs suggested that solution-process could be an alternative route for the fabrication of OLEDs based on Alq₃.

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1. Introduction

In recent years, much effort has been paid on the study of organic light-emitting devices (OLEDs) based on both small molecules and conjugated polymers for their promising applications in solid state light sources and flat-panel displays [1]. Although there are more similarities than differences between small molecular organics and polymers in both their electronic and optical properties, there is a definite difference between the two in the method used for fabricating the devices: vapor phase deposition for the OLEDs based on small molecules and solution-process for those based on polymers. Compared to polymers, small molecules can be synthesized and purified easily, but their vapor-deposition process increases the cost of devices and limits their applications. So the development of small molecule OLEDs fabricated via solution-process is of great importance to remedy their disadvantages.

Usually, small molecules are blended into a miscible polymer so that they can be prepared by solution-based deposition [2–4]. However, these kinds of polymers are hard to find due to the differences in entropy and enthalpy between polymers and small molecules. Therefore, phase separation may occur either after some time of operation or immediately after the spin-coating process. Recently, several groups have reported small molecule OLEDs prepared by spin-coating small molecule solutions with well designed and synthesized small molecules, such as binuclear gallium complexes and aluminum chelates, efficient phosphorescent or fluorescent small molecule OLEDs were fabricated [5–8]; multilayer small molecule OLEDs were also produced by photo-

crosslinking [9,10] or the mold transfer process [11]. Although all of these OLEDs showed excellent performance, additional procedures during the spin-coating process increase the fabrication complexity, and the solution-process of widely used fluorescent organic materials with simple structure is rarely reported.

In this paper, we demonstrated small molecule OLEDs with a simple structure built by spin-coating process. N, N'-bis-(3-Naphthyl)-N, N'-biphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB) and tris-(8-hydroxyquinoline)-aluminum (Alq₃) were used because of their wide use and low cost. It was found that the film-formability of NPB in the spin-coating process was better than that of Alq₃, and the phase of the spin-coated thin films of small molecules were different from that of polymers due to their different molecular sizes. Small molecule OLEDs, fabricated by spin-coating the blends of NPB and Alq₃ as the emitting layer (EML), exhibited the maximum luminance and current efficiency over 10000 cd/m² and 3.8 cd/A respectively. After 10-(2-benzothiazolyl)-2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H,11H-[1]benzopyrano[6,7,8-ij]quinolizin-11-one (C545T) was doped into the blend of NPB and Alq₃ as EML, the current efficiency increased to 8 cd/A. These results show that small molecule OLEDs based on Alq₃ with simple structure could be fabricated by spin-coating process with excellent performance.

2. Experiments

2.1. Film deposition method and morphology characterization

The structures of NPB and Alq₃ are shown in Fig. 1. All the materials were purchased from Luminescence Technology Corp (Taiwan) and used without any further purification. Thin films of NPB, Alq₃, and

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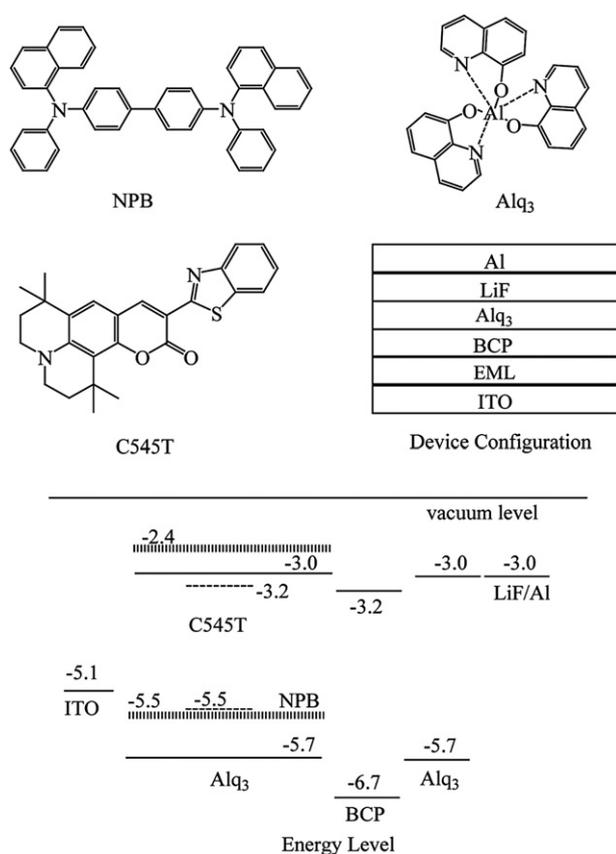


Fig. 1. Chemical structures of small molecules and the device configuration.

their blends were spun over the pre-cleaned glass substrates coated by Indium tin oxide (ITO) from chloroform solutions at a concentration of 10 mg/ml and a speed of 2000 rpm. Three kinds of annealing conditions were used: (1) at 80 °C in vacuum for 30 min, (2) at 80 °C in air for 30 min, and (3) at room temperature in air for 30 min. The morphology of the spin-coated thin films was measured by atomic force microscopy (AFM) (model SOLVER P47 from NT-MDT, Moscow, working at semi-contact mode).

2.2. Device fabrication and characterization

The small molecule OLEDs were fabricated on the patterned, pre-cleaned ITO-coated glass substrates. The configuration of the devices in this work was shown in Fig. 1. The emitting layer was co-host of NPB and Alq₃ at different weight ratios or the co-host doped with C545T. To begin with, EML materials were first dissolved in chloroform at a concentration of 10 mg/ml and then spin-coated in air at a speed of 2000 rpm, followed by annealing at 80 °C in vacuum for 30 min. The film thickness was measured by ellipsometry. 9-dimethyl-4,7-diaryloxy-1,10-phenanthroline (BCP), Alq₃, LiF and Al were vacuum-deposited in sequence at speeds of 0.1 nm/s, 0.2 nm/s, 0.01 nm/s, and 0.3 nm/s with the thicknesses of 10 nm, 30 nm, 0.5 nm, and 80 nm, respectively. Thicknesses of the deposited layers and the evaporation speed of the individual materials were monitored by quartz oscillator. Current-voltage-luminance (*J-V-L*) curves were performed on Keithley 2602 and electroluminescent (EL) spectrum on PR650.

3. Results and discussion

3.1. Characteristics of spin-coated thin films

AFM images of the spin-coated films of NPB, Alq₃, and their blends are presented in Fig. 2. With the increase of NPB, thin films become

more uniform, and the size of grains in the films decreases. Table 1 shows root mean square (RMS) of the films of the blends at different NPB to Alq₃ weight ratios annealed in different conditions. We found that RMS of the spin-coated films decreased with the increase of NPB portion in the blends. These results suggest that NPB is better than Alq₃ in forming excellent thin films.

A possible explanation to this phenomenon may lie in the difference between their molecular structures. As depicted in Fig. 1, NPB is a linear molecule very much like a flexible segment of a polymer. In addition, the two hooks-like amino substitutes at both ends of the molecule could strengthen intermolecular force by physical bond. When randomly dispersed in the solvent matrix, the intermolecular hook-like groups will tangle physically and form physical bonds. Therefore, thin film phase could form very well on ITO glass substrates via spin-coating. In contrast, the globular configuration of Alq₃ (also shown in Fig. 1) [12] was not as suitable for spin-coating because of its weak intermolecular force that may only include the Van Der Waals force since there is no physical bond between them. As a result, the surface of films of Alq₃ is rougher than that of NPB.

The smaller molecular size of small molecules also led to different film phases from that of polymers. The polymers exhibit fibrous-like structures with a special orientation [13]. In Fig. 2, however, all AFM images exhibit granular-like structures randomly distributed in the films. It is believed that the intermolecular force and the centrifugal force collaborate with each other during the spin-coating procedure [14]. Compared to polymers, small molecules have far smaller molecular size and so the intermolecular force is not as strong as the centrifugal force during spin-coating. As a result, small molecule films exhibit little or no orientation.

It is also interesting to note that RMS of the thin films showed dependence on the annealing conditions. Films annealed in vacuum are smoother than those under normal pressure. This might be attributed to the different evaporation rate of the residual solvent in the spin-coated films. To give a comprehensive understanding on this point, the morphology of the spin-coated films comprising only NPB or Alq₃ annealed at room temperature in air (shown in Fig. 3) was measured for comparison to those annealed in vacuum at 80 °C. The RMS are 0.8 nm and 1.1 nm for films of NPB and Alq₃ respectively, which is larger than that of the films annealed in vacuum at 80 °C (shown in Table 1). This can be explained as follows: as the T_g of Alq₃ is high (175 °C), it will make no change on the physical properties of the Alq₃ using either annealing conditions. So the main reason to the large discrepancy in the RMS of these two annealing conditions should be the different solvent evaporation rates under the two annealing conditions. The relatively low solvent evaporation rate will induce larger crystals or aggregates in the films [15,16].

3.2. Device characteristics

To investigate the performance of these spin-coated thin films, a series of small molecule OLEDs was fabricated with the blending films of NPB and Alq₃ serving as EML at different NPB to Alq₃ ratios by weight. The structure was shown in Fig. 1. The weight ratios are 0:1, 1:2, 1:1, 2:1, and 85:15, denoted as Device A, B, C, D, and E, respectively. BCP served as hole-blocking layer (HBL) and Alq₃ as electron-transporting layer (ETL).

As can be seen from Fig. 1, no hole-transport layers were used in the devices and holes were directly injected into the EML to form NPB⁺, the cation of NPB. The electrons were injected into ETL and transported into the EML to form Alq₃⁻, the anion of Alq₃ through the HBL. And then, in EML close to the interface between the EML and the HBL, NPB⁺ and Alq₃⁻ recombined to form the Alq₃^{*} excitons of Alq₃, which decays radiatively [17,18]. To confirm that no emission was emitted from the ETL of Alq₃, we compared EL spectrum of Device E and F. The structure of F was:

ITO/ NPB: Alq₃ (50 nm)/BCP (10 nm)/Alq₃ (2 nm)/Rubrene (1 nm)/Alq₃ (27 nm)/LiF (0.5 nm)/Al (80 nm)

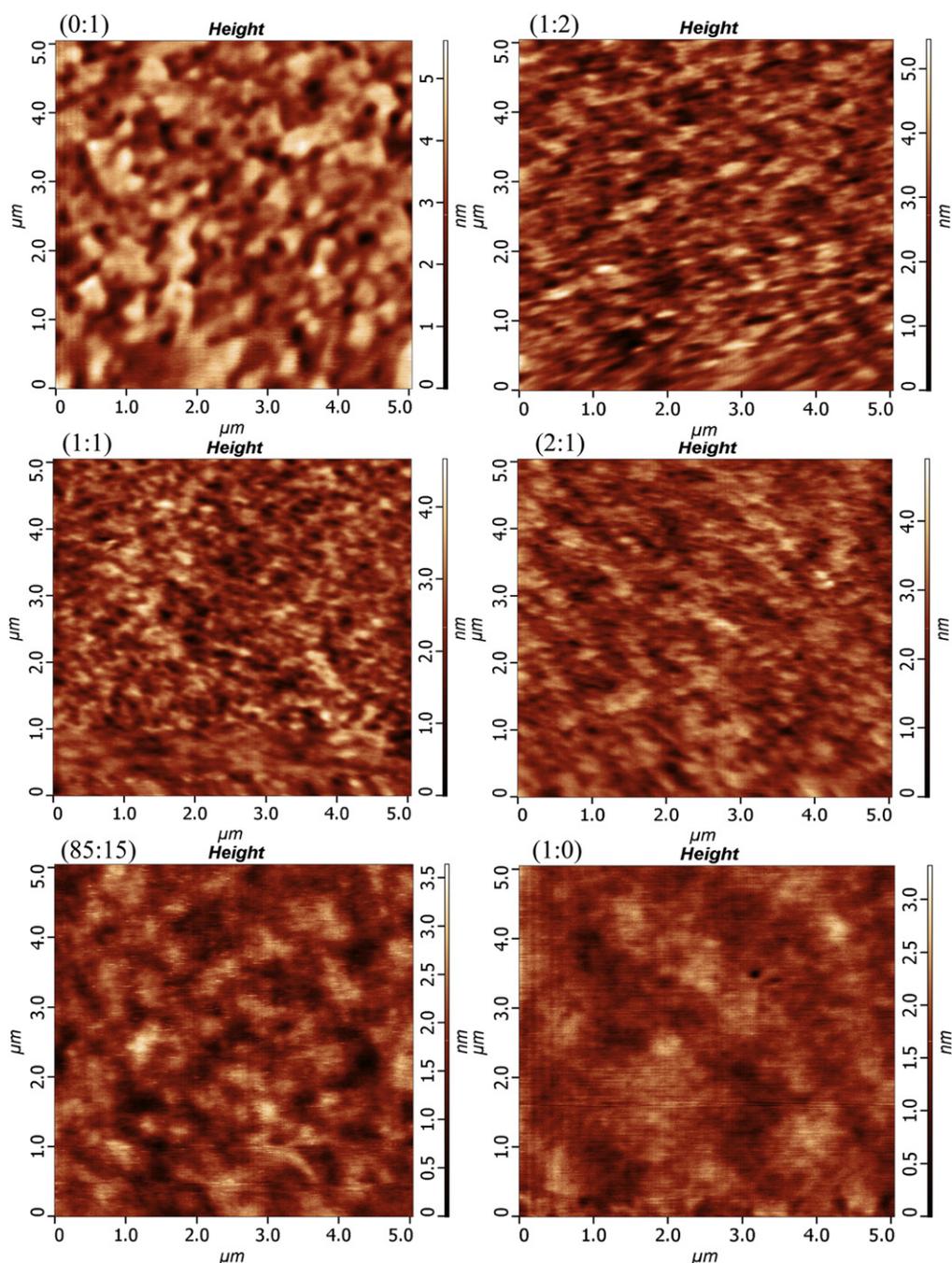


Fig. 2. AFM images of thin films of blends of NPB and Alq₃ at different NPB to Alq₃ weight ratios annealed in vacuum at 80 °C for 30 min.

In this structure, rubrene was used as sensing layer to probe whether the Alq₃ layer can emit light. We chose rubrene as the sensing layer because it emits a yellow color at 560 nm which is easily

Table 1

RMS of thin films of the blends with different ratios annealed at different annealing conditions.

Annealing conditions	NPB to Alq ₃ weight ratios					
	0:1	1:2	1:1	2:1	85:15	1:0
Vacuum ^a	0.77 nm	0.74 nm	0.60 nm	0.52 nm	0.42 nm	0.31 nm
Normal pressure ^b	0.91 nm	0.87 nm	0.80 nm	0.75 nm	0.68 nm	0.34 nm

^a Annealed at 80 °C in vacuum for 30 min.

^b Annealed at 80 °C under normal pressure for 30 min.

distinguishable from the Alq₃ emission. In Fig. 4 it was found that the spectra of Device E and F were nearly identical, and no emission at 560 nm in Device F was detected, which suggests that excitons are confined and only radiatively decay in the mixed-host layer.

The *J*–*V*–*L* curves (a) and the efficiency versus current density curves (b) of Device A to E are shown in Fig. 5. The currents increased while increasing NPB portions in the blends, but the turn-on voltage decreased. For example, the turn-on voltage decreased from 8 V in Device A to 5.3 V in Device E. This reduction of the turn-on voltage is due to the increased conductivity when the blend has more NPB, which is in turn because the carrier mobility of NPB is higher than that of Alq₃ [19,20]. The increase of NPB also leads to a balance of holes and electrons and thus results in higher current efficiency and luminance. For example, they increase from 0.8 cd/A and 800 cd/m² in Device A to 3.8 cd/A and 10,000 cd/m² in Device E, respectively.

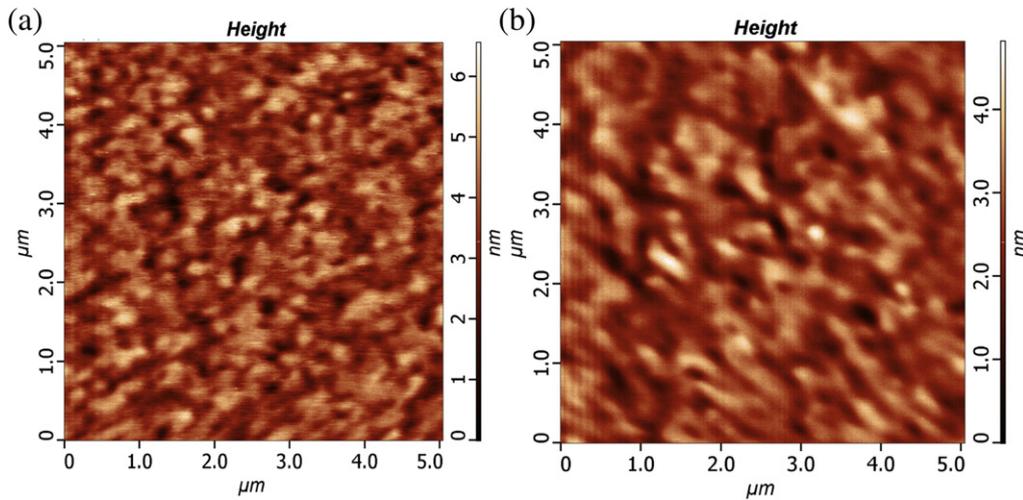


Fig. 3. AFM morphology of thin films of pure Alq₃ (a) and NPB (b) annealed at room temperature in air for 30 min.

To further investigate the solution-processed EML OLEDs based on Alq₃, a green dopant C545T was doped into the co-host comprising NPB and Alq₃. C545T is a highly efficient dopant which is usually used in the OLEDs to improve the device performance [21–23]. The weight ratio of NPB to Alq₃ in the co-host was fixed at 85:15, and the dope profile of C545T in the co-host were 0.2%, 0.4%, 0.6%, 0.8%, and 1%. The characteristic of the doped devices is shown in Fig. 6. It's easy to conclude that the current efficiency increases dramatically comparing to the undoped devices. The highest efficiency can reach to 8 cd/A when the dope profile is 0.8% which is comparable to the vapor-deposited OLEDs based on C545T [24].

In previous reports, small molecule OLEDs based on Alq₃ were all fabricated by vapor depositions [25–28]. But our research indicates that they could be produced by spin-coating process like the polymer light-emitting devices. Our research also demonstrates an alternative way that could avoid the complexity of co-evaporating process in vacuum deposition for small molecule OLEDs. As for the devices in this paper, other layers following the EML, such as HBL and ETL, were still deposited by thermal evaporation, so simplifying the HBL and the ETL of the devices and/or how to fabricate the devices with all layers fabricated by solution-process will be focused on in future studies.

4. Conclusion

In conclusion, spin-coated thin films of NPB and Alq₃ and their blends were investigated. It was suggested that the film-formability of small molecules in solution-process could be affected by molecular

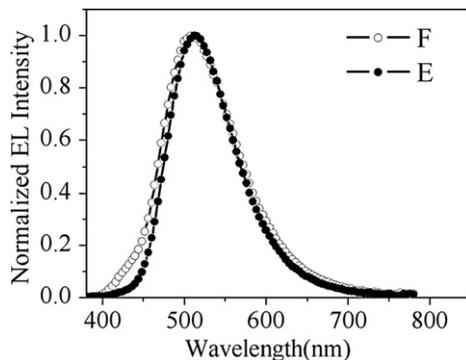


Fig. 4. Comparison of EL spectra of Device E (solid circle) and Device F (open circle). E: ITO/NPB: Alq₃ (50 nm)/BCP (10 nm)/Alq₃ (30 nm)/LiF (0.5 nm)/Al (80 nm). F: ITO/NPB: Alq₃ (50 nm)/BCP (10 nm)/Alq₃ (2 nm)/Rubrene (1 nm)/Alq₃ (27 nm)/LiF (0.5 nm)/Al (80 nm); all with the weight ratio of NPB to Alq₃ fixed at 85:15.

structures and the annealing conditions. Devices with blends of NPB and Alq₃ as EML were also fabricated by solution-process. The maximum luminance and current efficiency achieved were over 10,000 cd/m² and 3.8 cd/A. The current efficiency even reached to 8 cd/A when C545T was doped into the EML. Excellent device performance indicates that solution-process is an alternative way to prepare small molecule OLEDs based on Alq₃, which is expected to reduce the fabrication cost and to avoid the complex fabrication procedures especially for multi-doped OLEDs in the future.

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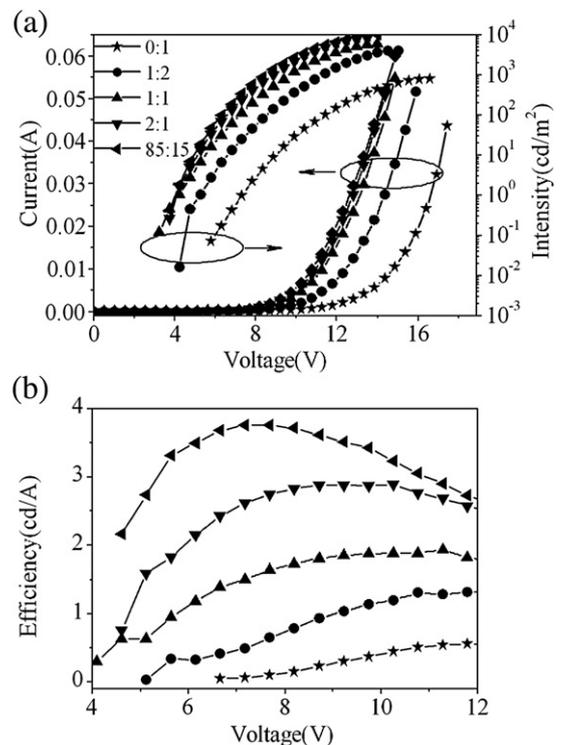


Fig. 5. (a) Current density–voltage, luminance–voltage, and (b) efficiency–voltage characteristics of the devices at different NPB to Alq₃ weight ratios with the structure ITO/NPB: Alq₃/BCP/Alq₃/LiF/Al.

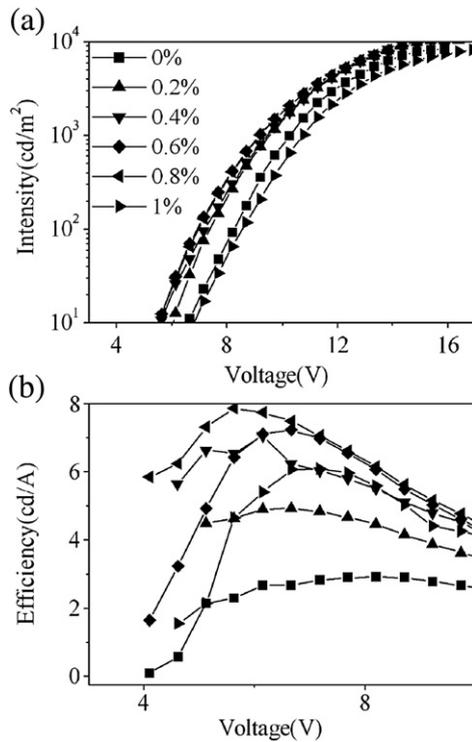


Fig. 6. (a) Luminance–voltage and (b) efficiency–voltage characteristics of devices at different C545T doping profile with NPB to Alq₃ weight ratio fixed at 85:15.

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