

Lighting object-based nondoped-type white organic light-emitting diode with *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-(1,1'-benzidine)-4,4'-diamine as the chromaticity-tuning layer

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We demonstrate a nondoped white organic light-emitting diode in which the blue, green, and red emissions are generated from 4,4'-bis(2,2'-diphenylvinyl)-1,1'-biphenyl, tris(8-hydroxyquinoline)aluminum, and a submonolayer of 4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyl-julolidyl-9-enyl)-4*H*-pyran layers, respectively. A thin layer of *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-(1,1'-benzidine)-4,4'-diamine (NPB), which differed from the traditional hole-transporting layer, was introduced into the device. The thickness of this thin NPB layer was changed to tune the chromaticity and optimize the white color quality. The white device with a 3 nm chromaticity-tuning NPB layer gives the Commission Internationale de l'Eclairage-1931 *xy* coordinate of (0.327, 0.336), a color rendering index of 90.2, a maximum luminance of 19,096 cd/m², and a maximum current efficiency of 4.12 cd/A. The electroluminescence mechanism of the white device was also discussed. © 2007 Optical Society of America

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White organic light-emitting diodes (WOLEDs) are attractive because of their applications to full color displays, backlight for liquid-crystal displays, paper-like thin lighting, etc. [1–4]. White light emission can be achieved by mixing two complementary colors or three primary colors. But for lighting, the white emission is required to satisfy special specifications, such as color rendering indexes (CRIs) higher than 80 and color stability; in addition its correlated color temperature (CCT) must be between 2500 and 6000 K [5]. Thus, broadband spectra covering the entire visible spectral region would be needed. Although the coevaporation-based doping technique is usually used for device fabrication, accurate control of the coevaporation ratio is very difficult. So the nondoped technique was developed to fabricate WOLEDs [6–8]. Also, to balance the red, green, and blue emissions of the WOLED, an effective method is also highly required.

In this Letter, we show the characteristics of a newly designed nondoped WOLED device for lighting. Its electroluminescence (EL) is generated from blue-emitting layer of 4,4'-bis(2,2'-diphenylvinyl)-1,1'-biphenyl (DPVBi), green-emitting layer of tris(8-hydroxyquinoline)aluminum (Alq₃), and red-emitting submonolayer of 4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyl-julolidyl-9-enyl)-4*H*-pyran (DCJTB). A thin layer of *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-(1,1'-benzidine)-4,4'-diamine (NPB) layer (called thin-NPB, hereafter) was inserted between the Alq₃ and DPVBi layers, and its

layer thickness was varied to find good white color emission. From the device, we obtained the Commission Internationale de l'Eclairage (CIE)-1931 *xy* coordinate of (0.327, 0.336), a CCT of 5804 K, a CRI of 90.2, a maximum luminance of 19,096 cd/m² at 12 V, and a maximum current efficiency of 4.12 cd/A at 6.5 V.

The OLED device has a structure of indium tin oxide (ITO)/NPB (*d* nm)/Alq₃[I] (2 nm)/thin-NPB (*a* nm)/DPVBi (6.5 nm)/DCJTB (0.03 nm)/Alq₃[II] (38.5 nm)/LiF (0.5 nm)/Al (200 nm), where the NPB layer thickness *d* and thin-NPB layer thickness *a* were varied, keeping their total thickness constant, i.e., *d*+*a*=63 nm. This device is called the WOLED, hereafter. Detailed processes of fabrication and measurement for OLEDs were described in our previous paper [9].

Figure 1(a) shows the normalized EL spectra of the WOLED devices with 2, 2.5, and 3 nm thick thin-NPB, which were measured at 8 V. The emission peak in the blue region shifts to shorter wavelengths when thin-NPB layer thickness *a* is increased from *a*=2 nm to *a*=3 nm, while the emission intensity in the 500–540 nm region decreases. The inset of Fig. 1(a) shows the EL spectra of (blue) DPVBi, (green) Alq₃, and (red) DCJTB, which were obtained from three OLEDs with the structures (1) ITO/NPB (60 nm)/DPVBi (20 nm)/Alq₃ (40 nm)/LiF (0.5 nm)/Al, (2) ITO/NPB (60 nm)/Alq₃ (60 nm)/LiF (0.5 nm)/Al, and (3) ITO/NPB (60 nm)/DCJTB (0.03 nm)/

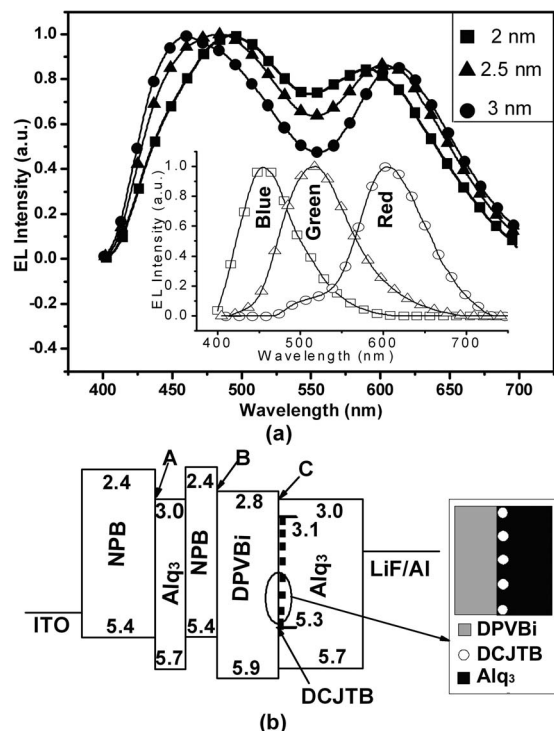


Fig. 1. (a) EL spectra of WOLED device with different thin-NPB layer thickness under the applied voltage of 8 V. The corresponding CIE-1931 xy coordinates are (0.329, 0.368), (0.323, 0.315), and (0.321, 0.290) when the thickness of the thin-NPB is 2, 2.5, and 3 nm, respectively. With increased bias, the CIE-1931 xy coordinates of the device with a 3 nm thin-NPB layer are located nearest to the coordinates (0.333, 0.333). Inset, EL spectra from DPVBi (\square), Alq₃ (\triangle), and DCJTb (\circ), which were obtained with different OLEDs (see text). (b) Schematic level diagram of the WOLED device (eV). A, B, and C denote the interfaces.

Alq₃ (60 nm)/LiF (0.5 nm)/Al, respectively. The first two OLEDs emit EL from only the emitting layer, but the DCJTb device emits EL from not only the DCJTb layer but also from the Alq₃ electron-transport layer. The EL band peaks of DPVBi, Alq₃, and DCJTb are observed at about 450, 515, and 605 nm, respectively. Taking into account the inset of Fig. 1(a), it is suggested that the EL of the WOLED is caused by the DPVBi, Alq₃, and DCJTb layers, although the overlapping of the DPVBi and Alq₃ emission bands makes it difficult to find the Alq₃ emission peak at 515 nm, giving a peak shift to about 500 nm. It is observed that the Alq₃ emission intensity decreases when the thin-NPB layer thickness is increased from $a=2$ nm to $a=3$ nm. This indicates that the green emission arises not from the electron transport Alq₃[II] layer but from the 2 nm thick Alq₃[I] layer. On the other hand, it is observed that the DPVBi emission intensity increases as the thin-NPB layer thickness is increased, and the red emission band shifts to longer wavelengths, 605 nm at $a=3$ nm. This shift is due to less overlapping with the Alq₃ emission band, which decreases with increased thin-NPB layer thickness. The observed spectral change is understood from the schematic energy level diagram of the WOLED device shown in Fig. 1(b), as mentioned below. The

thickness of 0.03 nm means that the DCJTb layer is about 3% the coverage of a monolayer, assuming that the average size of a DCJTb molecule in one dimension is about 1 nm [10]. Therefore the DCJTb layer is drawn as the line of circles in Fig. 1(b). We note that at interface B the band offsets of the highest occupied molecular orbital levels and the lowest unoccupied molecular orbital levels are 0.5 and 0.4 eV, respectively; i.e., the hole-injection barrier at the interface is larger than the electron-injection barrier. But the holes would still dominantly overcome the barrier and then enter the DPVBi layer, rather than the electron's injecting into the thin-NPB layer, because of the larger mobility of holes compared with electrons. However, when the thin-NPB layer is thin enough, some of the electrons can transport through it to the Alq₃[I] layer; thus excitons can also be formed in the Alq₃[I] layer. The holes are almost uniformly distributed over the whole NPB and Alq₃[I] layer region of 65 nm thickness because of the high hole mobility, while the distribution of electrons in the same layers is not uniform and depends on the distance from interface B because of the low electron mobility. The electron density decreases with increasing distance from interface B. From this suggestion, we can understand why the Alq₃[I] EL intensity decreases with increasing distance (i.e., increasing thin-NPB layer thickness).

Figure 2 shows the EL spectra of the WOLED device with 3 nm thick thin-NPB layer, which was measured with increasing bias voltage from 8 to 12 V. The EL spectra obviously vary with the increase in voltage: the blue emission from DPVBi first increases under biases from 8 to 10 V and then decreases as the bias increases from 10 to 12 V; the green emission from Alq₃[I] increases at the biases from 8 to 12 V, in contrast to the red emission from DCJTb. Such a color variety in a multilayer device under changing biases could typically be attributed to the recombination zone shift toward the anode as the voltage increases [11,12]. With the increase of the bias, the electron mobility is strongly enhanced by the increas-

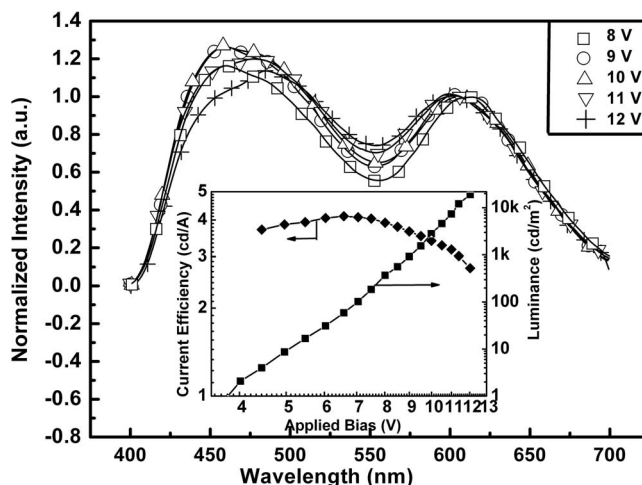


Fig. 2. EL spectra of the WOLED device with a 3 nm thick thin-NPB layer, which was applied at 8 V. Inset, luminance-efficiency-voltage characteristics.

ing electric field. As a result, the recombination is first centralized in the red emitting layer next to interface C (Fig. 1) at lower biases, then it extends gradually to the subsequent layers, i.e., the blue and then green emission layers. It is noticed that, compared with the emission from DCJTB, the emission from DPVBi gradually decreases as the bias increases from 10 to 12 V, which seems to be opposite to the theory mentioned above; this phenomenon can be understood as follows. The region at which excitons piled up in the DPVBi layer next to interface B becomes narrower and narrower as the bias increases, and the excitons with high density may lead to singlet-singlet annihilations [13].

On the other hand, to further improve EL efficiency, a device with a structure of ITO/NPB (60 nm)/Alq₃[I] (2 nm)/thin-NPB (3 nm)/DPVBi (6.5 nm)/DCJTB (0.03 nm)/BCP (8 nm)/Alq₃[II] (40.5 nm)/LiF (0.5 nm)/Al (200 nm), in which 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) acts as a hole-blocking layer was also constructed. However, we found that the DCJTB emission peak shifted from 605 to 575 nm. As a submonolayer of DCJTB was inserted between the DPVBi and BCP layers, BCP appears to be a quasi host in the BCP-based device. This can be regarded as a quasi-doped system of DCJTB in the BCP layer. For the BCP-free device, the quasi host is Alq₃. Because of the dielectric relaxation of the different quasi-host materials (Alq₃ or BCP), the shift in the spectrum resulted [6,14].

Table 1 summarizes the CIE-1931 *xy* coordinates, CCT, and CRI values at various bias voltages in the same WOLED used in Fig. 2. This shows that the CIE-1931 *xy* coordinates shift slightly as bias voltage is increased from 8 to 12 V. The inset of Fig. 2 plots the luminance-efficiency-voltage characteristics of the WOLED device with a 3 nm thick thin NPB layer. A maximum luminance of 19,096 cd/m² was obtained

at 12 V, and a maximum current efficiency of 4.12 cd/A was obtained at 6.5 V. The turn-on voltage is about 4.5 V. A good white OLED performance was obtained at 12 V (see Table 1), for example, CIE-1931 *xy* coordinates of (0.327, 0.336). This is due to well-proportioned and balanced distribution of excitons among the red, green, and blue-emission layers.

In summary, a nondoped white OLED device for lighting was demonstrated. A maximum luminance of 19,096 cd/m² and a current efficiency of 4.12 cd/A were observed, as well a slight shift in the CIE-1931 *xy* coordinates under biases from 8 to 12 V. A CRI of 90.2 and the corresponding CCT of 5804 K were obtained as well, which was attributed to simultaneous exciton formation in the three emission layers. The EL colors were modulated by a thin NPB layer, i.e., a chromaticity-tuning layer. It is expected that the newly designed device structure is useful for white OLEDs for lighting.

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Table 1. CIE-1931 *xy* Coordinates, CCT, and CRI of the WOLED Device with a 3 nm Thin-NPB Layer

Applied Bias (V)	CIE Coordinates		CCT (K)	CRI
	x	y		
8	0.321	0.290	6014	80.9
9	0.315	0.299	6673	84.8
10	0.313	0.302	6714	85.8
11	0.318	0.320	6305	88.3
12	0.327	0.336	5804	90.2