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Non-doped-type white organic light-emitting diodes for lighting purpose

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ABSTRACT

We demonstrate a non-doped white organic light-emitting diode (WOLED) in which the blue-, green- and red-emissions are generated from 4,4′-bis(2,2′-diphenylvinyl)-1,1′-biphenyl, tris(8-hydroxyquinoline)aluminum (Alq) and 4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyl-julolidyl 9-enyl)-4*H*-pyran (DCJTB), which is used as an ultrathin layer. The DCJTB ultrathin layer plays the chromaticity tuning role in optimizing the white spectral band by modulating the location of the DCJTB ultrathin layer in the green emissive Alq layer. The optimized WOLED gives the Commission Internationale de l'Eclairage-1931 *xy* coordinates of (0.319, 0.335), a color rendering index of 91.2 at 10 V, a maximum brightness of 21010 cd/m^2 at 12 V and a maximum current efficiency of 5.17 cd/A at 6.6 V. The electroluminescence mechanism of the white device is also discussed.

1. Introduction

During the past decade, white organic light-emitting diodes (WOLEDs) have attracted more and more attention because of their applications to full color displays, backlights for liquid-crystal displays, even next generation of paper-thin lighting sources, etc.[1–4] To obtain white emission from a WOLED, two complementary colors or three primary colors from organic active layers are required. But for application of solid state lighting, the white emission should satisfy special specifications, such as color rendering index (CRI) higher than 80 and color stability; in addition, its correlated color temperature (CCT) must lie between 2500 and 6000 K [5]. The CRI of a white light source is a measure of the color shift that an object undergoes when illuminated by the light source as compared with the color of the same object when illuminated by a reference source of comparable color temperature. To obtain high CRI, the emission spectra of WOLEDs must be broad enough to cover the entire visible spectral region. Thus, WOLEDs based on two complementary colors, such as blue and yellow, would not be suitable for lighting purpose. In general, the doping technique is usually utilized in obtaining white emission that comes from small molecule and polymer devices with high efficiency and brightness. During the doping process people must accurately control the evaporation rates of two or more materials simultaneously, and it remains technologically difficult to warrant this. So the non-doped technique was developed to fabricate WOLEDs [6–8]. The co-evaporation process is avoided in the non-doped technique, so the fabrication process can be controlled more accurately. The simple device structures and excellent reproducibility make them well-suited to low-cost lighting applications and beneficial to industrialization.

In this work, we demonstrate a non-doped WOLED for lighting purpose. 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-hydroxy-quinoline)aluminum (Alq) and red-emitting ultrathin layer of 4-(dicyanomethylene)-2-t-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB). The DCJTB ultrathin layer is embedded into the Alq green-emitting layer and its location is tuned for obtaining good white emission. Thus we obtained a WOLED that shows Commission Internationale de l'Eclairage-1931(CIE) coordinates of (0.319, 0.335), a CCT of 6145 K, a CRI of 91.2 at 10 V, a maximum brightness of 21010 cd/m^2 at 12 V and a maximum current efficiency of 5.17 cd/A at 6.6 V.

2. Experimental details

Fig. 1 shows the chemical structures of organic materials used in this work, the structure and the energy level diagram of the WOLEDs. The devices have structures of indium tin oxide (ITO)/NPB (55 nm)/DPVBi (5 nm)/Alq (*x* nm)/DCJTB (0.05 nm)/Alq (12-*x* nm)/Bphen (10 nm)/Alq (35 nm)/LiF (0.5 nm)/Al (200 nm), where x=0, 3, 5, 7, 10, or 12, and the corresponding devices are named as devices A, B, C, D, E, and F, respectively. *N*, *N*′-diphenyl-N, *N*′-bis(1-naphthyl)(1,1′-benzidine)-4, 4′-diamine (NPB) is used as the hole-transporting layer; DPVBi acts as the blue-emitting layer; the DCJTB and the Alq between DPVBi and 4, 7-diphenyl-1,10-phenanthroline (Bphen) are selected as the red-emitting

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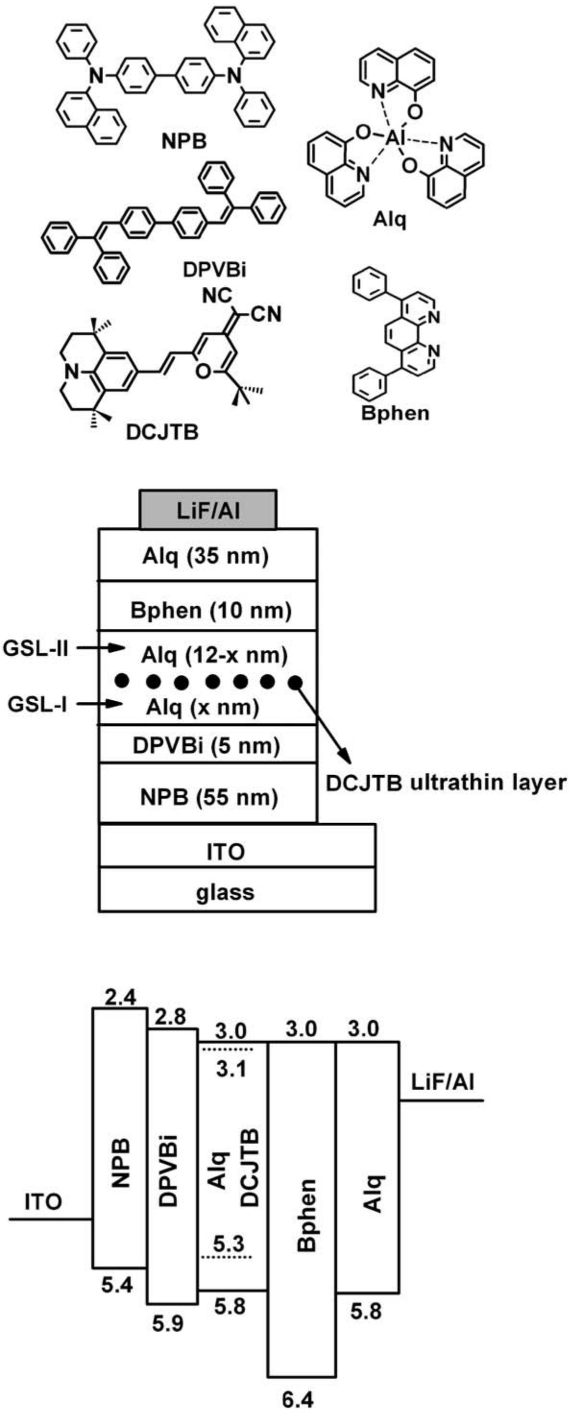

Fig. 1. The chemical structure of organic materials, the device structure of the WOLEDs and the schematic energy band diagram of the WOLEDs.

material and the green-emitting material, respectively; Bphen acts as the hole blocking layer; Alq next to LiF acts as the electron transporting layer (ETL); LiF acts as an electron injecting layer and Al as the cathode. The thickness of 0.05 nm DCJTB means that the DCJTB layer is about 5% the coverage of a monolayer by assuming that the average size of DCJTB molecule in one dimension is about 1 nm [9]. Indeed, such an ultrathin layer is more or less equivalent to the doping process (i.e. the DCJTB molecule are dispersed in the previous Alq layer) and the amount of DCJTB molecule should be carefully controlled in order to avoid quenching effect and to warrant a reproducible process. The ITO-coated substrates were routinely cleaned by ultrasonic treatment in solvents and then cleaned by exposure to a UV-ozone ambient. All organic layers were deposited in succession without breaking vacuum (3×10^{-4} Pa). Thermal deposition rates for organic materials, LiF, and Al were ~1, ~1, and ~10 Å/s, respectively. EL spectra were measured with an OPT-2000 spectrophotometer. The brightness–current density–voltage characteristics were measured with a Keithley model 2400 power supply combined with a ST-900*M* spot photometer and were recorded simultaneously with measurements.

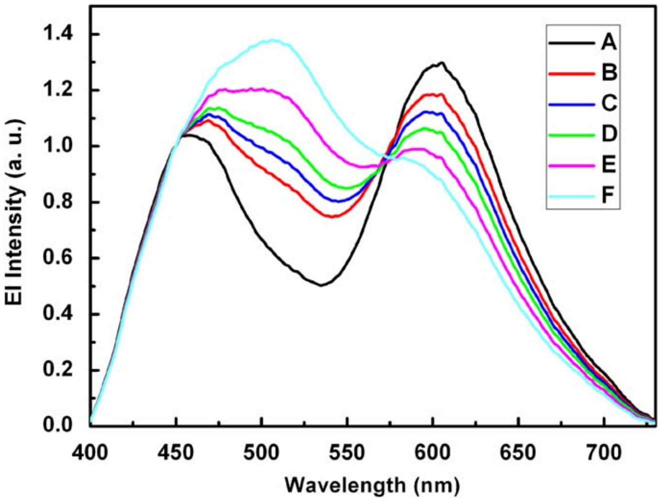

Fig. 2. Normalized EL spectra of devices A, B, C, D, E and F under the applied voltage of 9 V (normalized to 450 nm).

3. Results and discussion

Fig. 2 depicts the EL spectra of the WOLEDs at a bias of 9 V. The emissions from DPVBi, Alq and DCJTB are observed. From the energy levels of the WOLEDs shown in Fig. 1, the emissions from the DPVBi, Alq and DCJTB are predictable. Due to levels alignment of materials as indicated in Fig. 1 the excitons would form at NPB/DPVBi, DPVBi/Alq and Alq/Bphen interfaces. It might be conceivable that the excitons would not form at the Alq/Bphen interface since Alq is well-known as a good electron transporting material and a bad hole-transporting material, so the hole density at the Alq/Bphen interface would be rather low or negligible. In most OLEDs, however, hole is the majority carrier; the hole density may even be higher than the electron density in Alq [10,11]. Therefore, a large amount of holes would pile up and the excitons would form at the Alq/Bphen interface. The DCJTB excitons would form through trapping or energy transfer from Alq excitons. So the blue emission from DPVBi, the green emission from Alq and the red emission from DCJTB are observed. Though the WOLEDs with different x have the same blue-, green- and red-emitting layer thicknesses, the white emitting spectra are largely different. From the spectra of WOLEDs with $x=0$ and $x=12$, we note that Alq molecules between DPVBi and DCJTB (called the green sublayer-I (GSL-I), hereafter) emit much stronger green light than the Alq molecules between DCJTB and Bphen (called the green sublayer-II (GSL-II), hereafter). From the energy levels of the WOLEDs in Fig. 1, it is seen that the DCJTB behaves as a deep hole trap but a shallow electron in Alq. When the holes flow from DPVBi to Bphen layers, most of them would be trapped by DCJTB molecules and only a few can reach Bphen layer. Therefore the Alq molecules in GSL-I contribute a much stronger green emission than Alq molecules in GSL-II. As a result, when the DCJTB ultrathin

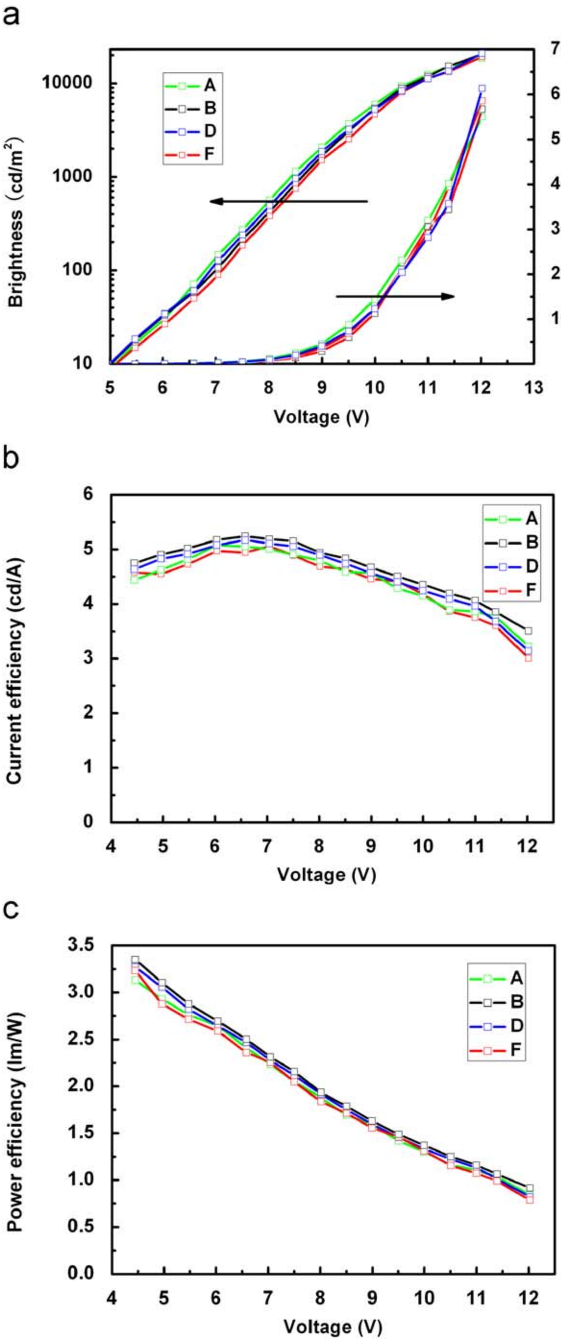

Fig. 3. (a) The brightness–current density–voltage characteristic of the devices A, B, D and F; (b) the current efficiency–voltage characteristic of the devices A, B, D and F; and (c) the power efficiency–voltage characteristic of the devices A, B, D and F.

layer is shifted from DPVBi to Bphen layers, the green emission intensity would increase largely in contrast to the blue emission intensity. On the other hand, the holes trapped by DCJTB molecules would decrease since they are consumed by the increased Alq molecules in GSL-I, leading to a decrease in the red-emission intensity relative to the blue emission intensity. The brightness–current density–voltage, current efficiency–voltage and power efficiency–voltage characteristics of devices A, B, D and F are shown in Fig. 3(a–c), respectively. The EL characteristics of the devices A, B, D and F are summarized in Table 1. Device D shows a CRI of 91.1 and the CIE coordinates of (0.328, 0.343) at 9 V, which is closest to the equi-energy white point (0.333, 0.333).

Table 1
CIE coordinates, CCT, and CRI of the WOLEDs at 9 V and the maximum efficiency of the devices A, B, D and F. The CRIs are calculated from the EL spectra of the WOLEDs through the method described in Ref. [12].

	CIE coordinates	CCT	CRI	Maximum efficiency
Device A	(0.369, 0.312)	3747 K	79.6	5.07 cd/A @ 6.0 V
Device B	(0.346, 0.333)	4876 K	88.3	5.24 cd/A @ 6.6 V
Device D	(0.328, 0.341)	5708 K	91.1	5.17 cd/A @ 6.6 V
Device F	(0.300, 0.363)	6846 K	82.5	5.06 cd/A @ 7.0 V

Table 2
CIE coordinates, color temperatures and CRI of the device D at different applied biases.

Applied bias	CIE coordinates	CCT	CRI
7V	(0.342, 0.352)	5112 K	90.5
9V	(0.328, 0.341)	5708 K	91.1
10V	(0.319, 0.335)	6145 K	91.2
12V	(0.305, 0.322)	6989 K	91.3

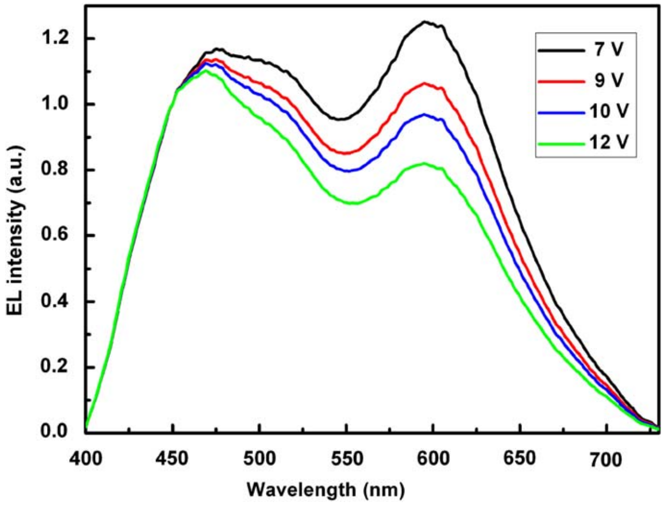

Fig. 4. The normalized EL spectra of device D at different voltages (normalized to 450 nm).

According to Table 1, among the WOLEDs we studied in this work, the device D emit the best white light, though it is not the one with the highest efficiency. The EL details of device D are listed in Table 2. We can see that the CIE coordinates are all within the white region, and all the CRIs exceed 90. The color quality meets the technology specification of the lighting application. A maximum brightness of 21010 cd/m^2 at 12 V, a peak current efficiency of 5.17 cd/A at 6.6 V and a maximum power efficiency of 3.27 l m/W at 3.3 V are attained. Fig. 4 shows the normalized EL spectra of device D at different bias voltages. The spectra cover the 400 – 700 nm region. The red and green emission intensities decrease relative to the blue emission intensity as the bias voltage increases. It is suggested that this phenomenon is due to shifting of the recombination zone towards the anode side as the driving voltage increases [13,14].

4. Conclusions

In summary, a lighting object-based non-doped-type WOLED was demonstrated. A maximum brightness of 21010 cd/m^2 and a current efficiency of 5.17 cd/A were observed as well the CIE coordinates shift slightly under the biases from 7 to 12 V. A CRI of 91.2 and the corresponding CCT of 6145 K were obtained as well, which are presumed to be attributed to the simultaneous exciton formation in the blue-, green- and red-emission layers. And the EL color was modulated by shifting the location of DCJTB ultrathin layer in the green emissive Alq layer. Although the properties of the WOLED should be further improved for commercial applications, this device configuration provides a new route in designing WOLEDs based on illumination applications.

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