

# White organic light-emitting diodes from three emitter layers

M.S. Kim, J.T. Lim, C.H. Jeong, J.H. Lee, G.Y. Yeom \*

Department of Advanced Materials Science and Engineering, SungKyunKwan University, Suwon, Gyeonggi-Do, 440-746, South Korea

Available online 6 September 2006

## Abstract

Three-wavelength white organic light-emitting diodes (WOLEDs) were fabricated using two doped layers, which were obtained by separating the recombination zones into three emitter layers. A sky blue emission originated from the 4,4'-bis(2,2'-diphenylethen-1-yl)biphenyl (DPVBi) layer. A green emission originated from a tris(8-quinolinolato)aluminum (III) (Alq<sub>3</sub>) host doped with a green fluorescent 10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H,5H,11H-[1]benzopyrano [6,7,8-ij]-quinolizin-11-one (C545T) dye. An orange emission was obtained from the *N,N'*-bis(1-naphthyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) host doped with a red fluorescent dye, 4-(dicyanomethylene)-2-*tert*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB). A white light resulted from the partial excitations of these three emitter layers by controlling the layer thickness and concentration of the fluorescent dyes in each emissive layer simultaneously. The electroluminescent spectrum of the device was not sensitive to the driving voltage of the device. The white light device showed a maximum luminance of approximately 53,000 cd/m<sup>2</sup>. The external quantum and power efficiency at a luminance of approximately 100 cd/m<sup>2</sup> were 2.62% and 3.04 lm/W, respectively.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** WOLED; White emission; Three wavelength; Energy transfer; Doping

## 1. Introduction

Over the last decade, extensive research into organic light-emitting diodes (OLEDs) has been made with the aim of improving the out-coupling efficiency and brightness as a way of implementing efficient blue, green, and red OLEDs in passive and active matrix displays. Small-capacity information OLED displays have already been commercialized by Samsung SDI, Philips, TDK, Sanyo, and Pioneer. Recently, the application of white organic light-emitting diode (WOLED) devices has become increasingly popular as one of the major methods of fabricating a full-color display when combined with RGB color filters, for use as a flat panel display backlight, and for general solid-state lighting applications [1]. In WOLED devices, a discrete red, green, and blue (RGB) pixelation process can be accomplished without the need for a tedious and troublesome precision shadow mask.

White light emission can be obtained by mixing two complementary colors (e.g., red/bluish green, blue/orange, or green/magenta) or the three primary colors (red, green, and blue) from small molecules and/or polymers [1–7]. In order to obtain a

white emission from an OLED, an excitation of more than one molecular species is essential because the luminescence of a single organic molecule does not span the entire visible spectrum.

White light emission is mainly achieved by modifying the spectral characteristics in OLEDs. First, the doping method [2] using a luminescent dye can be used to allow energy transfer from the host to the dopant, or to allow carrier trapping directly at a dopant site [3]. This method has been used to obtain a white emission from small-molecular-weight OLEDs originating from two or three different layers [1,3–7]. Second, the spatial tuning of the exciton recombination zone can be controlled using a carrier-blocking layer that preferentially blocks one type of carrier between the hole-transporting layer (HTL) and electron-transporting layer (ETL). Controlling the thickness of this blocking layer enables exciton formation in both the HTL and ETL. Simultaneous emission from these two layers can be achieved if the layers are themselves emissive or contain lumophore dopants, leading to the appropriate color balance. Third, white light emission can be induced by confining each exciton of RGB into a different well for organic multiple quantum-well structures (MQWs), in which the injected carriers are distributed in different light-emitting wells [8]. In addition, the formation of both excimers (among homolayers) and

\* Corresponding author. Tel.: +82 31 299 6562.

E-mail address: [gyyeom@skku.edu](mailto:gyyeom@skku.edu) (G.Y. Yeom).

exciplex (among heterolayers) can give rise to white emission due to the complicated intermolecular interactions between the donor and acceptor [1]. Both methods are widely used in tuning white emission.

The following four problems need to be solved before white OLEDs can be used: one is color shifting with increasing bias voltage due to the movement of the carrier recombination zone over the light-emitting layers. Another is mismatch of the luminance and luminous efficiency among the subpixels of the RGB colors as a function of the lifetime. Third is the need to achieve a stable green light among the RGB colors via cascade energy transfer between the multilayers [9]. The fourth is improvement in the luminous efficiency. Hence, unchangeable color coordinates and stable exciton recombination with respect to the bias voltage in the emitting layers are essential for realizing white OLEDs with stable performance characteristics.

In this study, three-layered emitting WOLEDs with three wavelengths were fabricated by separating the exciton recombination zone into three emitter layers, generating a sky blue, green, and red color. One of the aims in this study was to achieve WOLEDs with stable performance characteristics without affecting its bipolar transporting property to obtain almost unchangeable color coordinates in white emission. The other was to fabricate a balanced white light with Commission Internationale d'Eclairage (CIE) chromaticity coordinates of (0.33, 0.33), by controlling the exciton energy transfer among the multilayers, emitting three different colors consisting of sky blue, green, and orange.

## 2. Experimental

Fig. 1a shows the schematic configuration of the WOLEDs fabricated in this study, and Fig. 1b shows the molecular structures of the chromophores in the devices. The multilayered WOLED with three different emissive layers was composed of glass/tin-doped indium oxide (ITO) (150 nm)/2-TNATA (35 nm)/NPB (10 nm)/NPB: DCJTJTB (5.0 nm, 0.2%)/DPVBi (12 nm)/Alq<sub>3</sub>: C545T (x nm, 0.2%)/Alq<sub>3</sub> (45 nm)/Li (1.0 nm)/Al (100 nm) (x=2.5, 2.0, 1.5, and 1.0, respectively). The ITO (anode) coated on glass (0.7 mm) has a sheet resistance of about 10 Ω/sq. 2-TNATA and NPB act as a hole-injecting layer (HIL) and the HTL, respectively. NPB doped with DCJTJTB (red fluorescent dye), DPVBi, and Alq<sub>3</sub> doped with C545T (green fluorescent dye) are emissive layers that emit red, blue, and green, respectively. Alq<sub>3</sub>, lithium (Li) and aluminum (Al) function as the ETL, an electron-injecting layer, and a cathode, respectively. Before loading the ITO coating on glass was cleaned with detergents and deionized water, and dried in an oven at 120 °C for 2 h. The devices were fabricated by evaporating both the organic materials and metal at a rate of 0.05–0.2 nm/s onto the ITO coated on glass substrate, sequentially at a pressure  $<1 \times 10^{-6}$  Torr. Doping in each emitting layer was carried out simultaneously by co-evaporating the host and dopant. The emissive active area of the devices was  $2 \times 2 \text{ mm}^2$ .

The current–voltage–luminance characteristics were measured using a source-measure unit (2400, Keithley Instrument

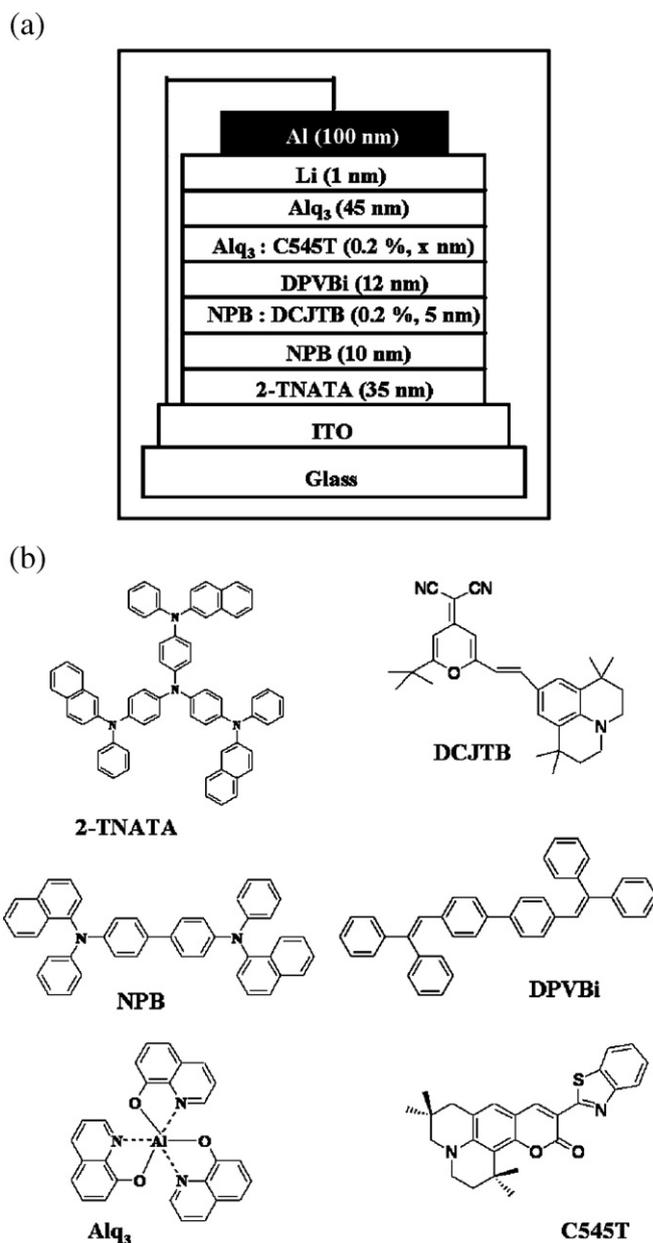


Fig. 1. (a) Schematic device configuration. (b) Molecular structures.

Inc.). The intensity of the emission of the OLED devices was determined by measuring the photocurrent induced on the silicon photodiodes using a picoammeter (485, Keithley Instrument Inc.). The electroluminescent (EL) spectra of the as-fabricated devices were measured by optical emission spectroscopy (PCM-420, SC Tech. Inc.).

## 3. Results and discussions

The WOLEDs investigated in this study were composed of a glass/ITO (120 nm)/2-TNATA (35 nm)/NPB (10 nm)/NPB: DCJTJTB (5.0 nm, 0.2%)/DPVBi (12 nm)/Alq<sub>3</sub>: C545T (x nm, 0.2%)/Alq<sub>3</sub> (45 nm)/Li (1.0 nm)/Al (100 nm) device. Table 1 also shows the photometric properties, level of C545T doping, and thickness of the C545T-doped Alq<sub>3</sub>. Devices 1, 2, 3, and 4

Table 1

Doping level (%), thickness ( $t$ ) of the C545T-doped Alq<sub>3</sub> and the current density ( $J$ ), power efficiency ( $\eta_{\text{PL}}$ ), external quantum efficiency ( $\eta_{\text{ext}}$ ), CIE coordinates, and maximum brightness ( $L_{\text{max}}$ ) of OLEDs

	Device 1	Device 2	Device 3	Device 4
Doping level of C545T (wt.%)	0.2	0.2	0.2	0.2
Thickness of C545T-doped Alq <sub>3</sub> (nm)	2.5	2.0	1.5	1.0
$J$ (mA/cm <sup>2</sup> ) <sup>a</sup>	1.35	1.19	1.42	1.38
$\eta_{\text{PL}}$ (lm/W) <sup>a</sup>	2.82	3.04	2.38	2.12
$\eta_{\text{ext}}$ (%) <sup>a</sup>	2.17	2.62	2.08	1.77
CIE coordinates <sup>a</sup>	0.35, 0.38	0.44, 0.41	0.35, 0.39	0.34, 0.37
$L_{\text{max}}$ (cd/m <sup>2</sup> )	56,600	53,300	50,000	42,800

<sup>a</sup> At 1.00 cd/m<sup>2</sup>.

have a layer thickness of C545T-doped Alq<sub>3</sub> of 2.5, 2.0, 1.5, and 1.0 nm, respectively, as shown in Table 1.

In OLEDs, the luminous efficiency can generally be improved by the doped system in the OLEDs. The emission spectra of DCM-series (for example: DCJTb, DCM2 [10], etc.) doped devices are generally red-shifted from yellow to deep red with increasing dopant concentration in the organic solid due to a solid-state solvation effect (SSSE) [10]. However, in the case of doping Alq<sub>3</sub> with DCM2, the external quantum efficiency ( $\eta_{\text{ext}}$ ) and power efficiency ( $\eta_{\text{PE}}$ ) decreased with increasing dopant concentration (>0.5%) or increasing doped layer thickness (>10 nm), due to concentration quenching and hole trapping processes. As a result, the current decreased as a result of the consequent reduction in the hole mobility of this layer [11]. In addition, a shoulder at the long-wavelength edge of emission spectrum begins to grow in the C545T-doped Alq<sub>3</sub> at concentration >1.0%, ultimately resulting in an undesirable hue shift and a lowering of the luminance efficiency caused by concentration quenching [12]. In this study, a doped system was introduced to improve the luminous efficiency in WOLEDs. As shown in the device configuration in Fig. 1a, each host of NPB and Alq<sub>3</sub> were doped with 0.2% DCJTb, as a red dye, and 0.2% C545T, as a green dye. In addition, the doped layer thickness of the green and orange emitters was optimized within a thickness of <5.0 nm.

In order to tune to a balanced white emission, the EL characteristics at a luminance of 100 cd/m<sup>2</sup> was measured as a function of the thickness of the C545T-doped Alq<sub>3</sub> layer between 2.5 nm and 1.0 nm (Fig. 2). The EL spectra of Devices 1–4 were composed of a bluish green portion with a maximum peak ( $\lambda_{\text{max}}$ ) between 491 and 514 nm, and an orange portion with a  $\lambda_{\text{max}}$  between 554 and 567 nm, which originated from emission of three light-emitting layers. The bluish green portion consisting of the EL spectra originated from both the DPVBi (approximately 480 nm) and the Alq<sub>3</sub> layers doped with C545T (approximately 515 nm). The orange portion was generated from the NPB layer doped with DCJTb (approximately 550 nm). The  $\lambda_{\text{max}}$  of the bluish green components in Devices 2–4 showed wavelengths of 514, 508, and 502, respectively, and the  $\lambda_{\text{max}}$  of the orange components showed wavelengths of 555, 557, and 557 nm, respectively. Therefore, the  $\lambda_{\text{max}}$  of bluish green components were hypsochromic-shifted with decreasing thickness of the C545T-doped Alq<sub>3</sub> layer in Devices 2–4, while the  $\lambda_{\text{max}}$  of

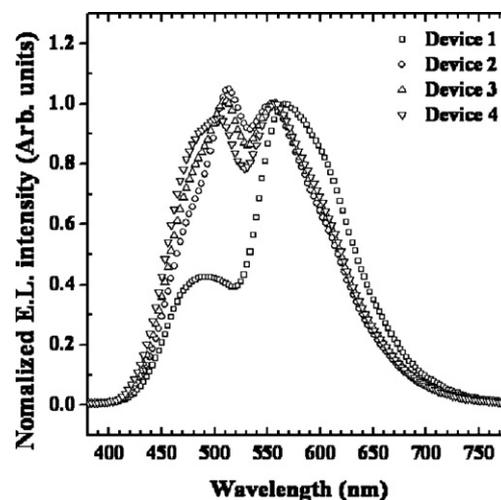


Fig. 2. Electroluminescent spectra of the devices composed of glass/ITO (120 nm)/2-TNATA (35 nm)/NPB (10 nm)/NPB: DCJTb (5.0 nm, 0.2%)/DPVBi (12 nm)/Alq<sub>3</sub>: C545T ( $x$  nm, 0.2%)/Alq<sub>3</sub> (45 nm)/Li (1.0 nm)/Al (100 nm) ( $x=2.5, 2.0, 1.5,$  and  $1.0$ , respectively) at the luminance of 100 cd/m<sup>2</sup> (square, Device 1; circle, Device 2; triangle, Device 3; down triangle, Device 4).

the orange components did not shift significantly. The hypsochromic shift of the bluish green component was attributed to an increase in the sky blue intensity compared with the orange intensity, as a result of a reduction of Foster energy transfer from green emission to red emission [6]. In addition, the peak width of bluish green component became slightly wider than that of the orange component with decreasing C545T-doped Alq<sub>3</sub> layer thickness.

White emission was achieved in Devices 2–4 when the thickness of the C545T-doped Alq<sub>3</sub> layer was <2.0 nm. The corresponding Commission Internationale d'Eclairage (CIE)

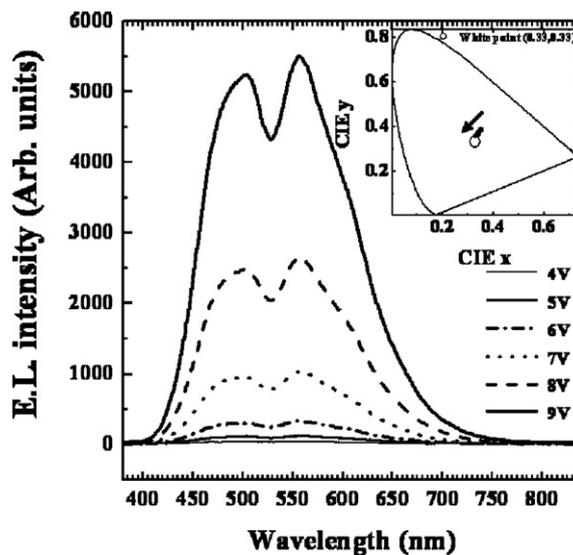


Fig. 3. Normalized electroluminescent spectra of the device composed of glass/ITO (120 nm)/2-TNATA (35 nm)/NPB (10 nm)/NPB: DCJTb (5 nm, 0.2%)/DPVBi (12 nm)/Alq<sub>3</sub>: C545T (1.0 nm, 0.2%)/Alq<sub>3</sub> (45 nm)/Li (1.0 nm)/Al (100 nm) as a function of the voltage (4 to 11 V). The inset shows the corresponding CIE chromaticity diagram with the coordinates of spectra for the same device. The white point is the Commission Internationale d'Eclairage chromaticity coordinates of (0.33, 0.33) (4 to 11 V).

chromaticity coordinates for Devices 2–4 were (0.44, 0.41), (0.35, 0.39), and (0.34, 0.37), respectively. Therefore, among the WOLEDs investigated, Device 4 was the closest to the white point of (0.33, 0.33).

In the case of Device 1, which had a 2.5-nm-thick C545T-doped Alq<sub>3</sub> layer, the EL intensity of the orange component was higher than that of the bluish green component. As the thickness of the C545T-doped Alq<sub>3</sub> increased, the EL intensity increased due to an increase in exciton energy transfer from the green layer to the orange layer. This exciton energy transfer from the green layer to the orange layer is believed to have originated from the incomplete energy transfer processes causing more emission from the orange layer as a result of long-range energy transfer from the green layer through the 12-nm-thick DPVBi to the orange layer [6].

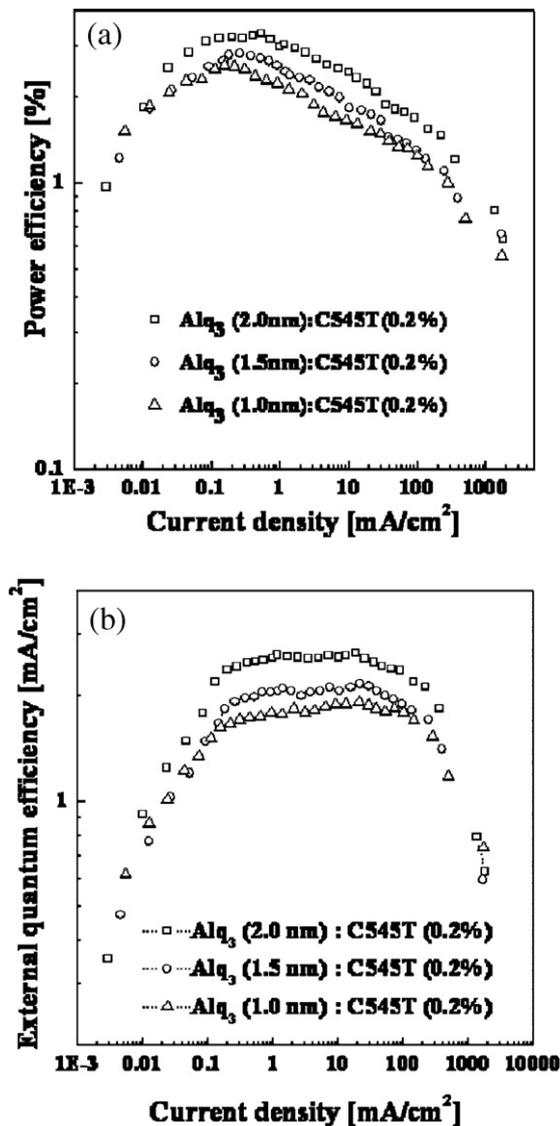


Fig. 4. (a) The power efficiency–current density characteristics of the device were composed of glass/ITO (120 nm)/2-TNATA (35 nm)/NPB (10 nm)/NPB:DCJTB (5 nm, 0.2%)/DPVBi (12 nm)/Alq<sub>3</sub>: C545T (*x* nm, 0.2%)/Alq<sub>3</sub> (45 nm)/Li (1.0 nm)/Al (100 nm) (square, *x*=2.0, circle, *x*=1.5, and triangle, *x*=1.0). (b) The external quantum efficiency–current density characteristics of the same device.

Fig. 3 shows the white EL spectra as a function of the voltage for Device 4 having a 1.0-nm-thick C545T-doped Alq<sub>3</sub> layer (0.2%), and the inset of Fig. 3 shows the CIE coordinates for corresponding EL spectrum. As shown in the inset of Fig. 3, as the voltage increased from 4 (0.32 cd/m<sup>2</sup>) to 11 V (about 1000 cd/m<sup>2</sup>), the corresponding CIE chromaticity coordinates of the EL spectra showed only a slight blue shift within the range of 0.33–0.35 and 0.36–0.39. This slight blue shift in the CIE coordinates was caused by movement of the recombination zone due to the current density or bias voltage applied to the DCJTB-doped NPB (orange), DPVBi (sky blue), and the C545T-doped Alq<sub>3</sub> (green) layers.

Table 1 shows the brightness (L) of Devices 1–4. The maximum values ( $L_{\max}$ ) were 53,300, 50,000, and 43,800 cd/m<sup>2</sup> for Devices 2, 3, and 4, respectively. In addition, the turn-on voltages at a luminance of 0.1 cd/m<sup>2</sup> were 3.6, 3.6, and 3.8 V for Devices 2–4, respectively.

Fig. 4a and b show the power efficiency ( $\eta_{\text{PE}}$ )–current density ( $J$ ) and external quantum efficiency ( $\eta_{\text{ext}}$ )–current density ( $J$ ) characteristics, for Devices 2–4, respectively. Device 2 showed the highest  $\eta_{\text{PE}}$  of 3.32 lm/W at 0.54 mA/cm<sup>2</sup>. The  $\eta_{\text{PE}}$  values of the white emission at an  $L$  of approximately 100 cd/m<sup>2</sup> for Devices 2–4 were 3.04, 2.76, and 2.12 lm/W, respectively. Device 4 showed a lower  $\eta_{\text{PE}}$  of 2.12 lm/W at an  $L$  of 100 cd/m<sup>2</sup> than that of Devices 2 and 3. However, Device 2 actually had the highest  $\eta_{\text{ext}}$  of 2.62% at approximately 100 cd/m<sup>2</sup>. In addition, the values of  $\eta_{\text{ext}}$  in white emission for Devices 2–4 were 2.62%, 2.08%, and 1.77%, respectively. Therefore, the luminous efficiency, that is, both  $\eta_{\text{PE}}$  and  $\eta_{\text{ext}}$  of Device 2, was the highest of Devices 2–4, even though Device 4 showed an emission closest to the white light emission point of (0.33, 0.33). The differences in the  $\eta_{\text{ext}}$  obtained in these devices are closely related to the photopic response function of the human eye i.e., the response is maximal at a wavelength of 550 nm, and rapidly decreased with decreasing wavelength. Its value at the DPVBi peak of 480 nm was only 14% of its maximum at 550 nm.

#### 4. Conclusions

Hetero-multilayered WOLEDs with two doped layers, which were obtained spatially by separating each recombination zone in the three emitter layers, were successfully fabricated. Very bright WOLEDs with a maximum luminance exceeding 50,000 cd/m<sup>2</sup> and a high external quantum efficiency,  $\eta_{\text{ext}}$ , of up to 2.65% was obtained. The white light originated from the partial excitation of the three emitter species with simultaneous emission achieved by controlling the layer thickness and concentration of each fluorescent dye in the emissive layers. The EL spectra of the white light-emitting device were not sensitive to the driving voltage investigated in this study, covering the three RGB peaks in the visible range. The color coordinates of the doped devices were well within the white range with increasing bias. The white device has a maximum luminance of approximately 53,300 cd/m<sup>2</sup>. At a luminance of approximately 100 cd/m<sup>2</sup>, the external quantum and power efficiencies were 2.62% and 3.04 lm/W, respectively. The WOLED examined in this study should be beneficial to the

development of the maskless fabrication of full-color OLED displays when combined with color filter technologies.

### Acknowledgements

This work was supported by the National Research Laboratory Program (NRL) of the Ministry of Science and Technology and by the Ministry of Commerce, Industry and Energy (MOCIE).

### References

- [1] B.W. D'Andrade, S.R. Forrest, *Adv. Mater.* 16 (2004) 1685.
- [2] C.W. Tang, S.A. Van Slyke, C.H. Chen, *J. Appl. Phys.* 65 (1989) 3610.
- [3] J. Kido, W. Ikeda, M. Kimura, K. Nagai, *Jpn. J. Appl. Phys., Part 2* 35 (1996) L394.
- [4] J. Kido, M. Kimura, K. Nagai, *Science* 267 (1995) 1332.
- [5] R.H. Jordan, A. Dodabalapur, M. Strukelj, T.M. Miller, *Appl. Phys. Lett.* 68 (1996) 1192.
- [6] R.S. Deshpande, V. Bulovic, S.R. Forrest, *Appl. Phys. Lett.* 75 (1999) 888.
- [7] C.W. Ko, Y.T. Tao, *Appl. Phys. Lett.* 79 (2001) 4234.
- [8] Z.Y. Zie, Y.Q. Li, J. Feng, J.S. Huang, Y. Wang, C.N. Li, S.Y. Liu, J.C. Shen, *Synth. Met.* 106 (1999) 71.
- [9] M. Berggren, A. Dodabalapur, R.E. Slusher, Z. Bao, *Nature* 389 (1997) 466.
- [10] V. Bulovic, A. Shoustikov, M.A. Baldo, E. Bose, V.G. Kozlov, M.E. Thompson, S.R. Forrest, *Chem. Phys. Lett.* 287 (1998) 455.
- [11] K.O. Cheon, J. Shinar, *Appl. Phys. Lett.* 81 (2002) 1738.
- [12] C.H. Chen, C.W. Tang, *Appl. Phys. Lett.* 79 (2001) 3711.