

White top-emitting organic light-emitting diodes using one-emissive layer of the DCJTB doped DPVBi layer

M.S. Kim^a, C.H. Jeong^a, J.T. Lim^a, G.Y. Yeom^{a,b,*}

^a Department of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, Gyonggi-Do, 440-746, Republic of Korea

^b The National Program for Tera-level Devices, Hawolgok-dong, Sungbuk-gu, Seoul, 136-791, Republic of Korea

Available online 23 August 2007

Abstract

White top-emitting organic light-emitting diodes (TEOLEDs) composed of one doped emissive layer which emits two-wavelength light though the radiative recombination were fabricated. As the emissive layer, 4,4-bis(2,2-diphenylethen-1-yl)biphenyl (DPVBi) was used as the host material and 4-(dicyanomethylene)-2-*tert*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) was added as the dopant material. By optimizing the DCJTB concentration (1.2%) and the thickness of the DPVBi layer (30 nm), the intensity ratio of the two wavelengths could be adjusted for balanced white light emission. By using the device composed of glass/Ag (100 nm)/ITO (90 nm)/2-TNATA (60 nm)/NPB (15 nm)/DPVBi:DCJTB (1.2%, 30 nm)/Alq₃ (20 nm)/Li (1.0 nm)/Al (2.0 nm)/Ag (20 nm)/ITO (63 nm)/SiO₂ (42 nm), the Commission Internationale d'Éclairage (CIE) chromaticity coordinate of (0.32, 0.34) close to the ideal white color CIE coordinate could be obtained at 100 cd/m².

© 2007 Elsevier B.V. All rights reserved.

Keywords: WOLED; Two-wavelength light; Microcavity; Refractive index matching

1. Introduction

Since Tang and Vanslyke developed high efficiency organic light-emitting diodes (OLEDs) using tris-(8-hydroxyquinoline) aluminium (Alq₃), the OLED devices have been actively investigated as one of the next generation flat panel display devices owing to the advantages such as low driving voltage, high emission efficiency, self-emission, etc. [1]. In addition, these days, white organic light-emitting diodes (WOLED) are also intensively studied as the application to liquid crystal display (LCD) backlight, full color active matrix OLED panel, room lightening, etc. To obtain white light emission, a light-emitting material composed of two/three monochromatic light-emitting layers, a material composed of one/two emitting layers doped with dopants for multi-wavelength emission in the each layer, etc. are generally used to have the balanced color relation

for white light emission. Some of the problems in the application of these WOLEDs to flat panel displays are the change of Commission Internationale d'Éclairage (CIE) chromaticity coordinate with the change of operating current density and the change of CIE coordinate due to the difference in the lifetime of the each light-emitting material [2,3].

For the large area active matrix OLED (AMOLED), because of the difficulty in the fabrication of large area shadow mask, the use of WOLED is being considered and, for large area LCD backlight, due to the difficulty in the current control of the WOLED devices, the use of AMOLED instead of passive matrix OLED (PMOLED) is also considered. In addition, in the application of WOLED devices to LCD backlight, AMOLED, etc. the top-emitting OLED (TEOLED) structure tends to show superior light output efficiency compared to the conventional bottom-emitting OLED (BEOLED) structure because of the higher aperture ratio especially when a thin film transistor (TFT) substrate based on amorphous silicon is used for the operation of the OLED devices. Also, to reduce the CIE color coordinate change due to the differences in the lifetime of each emissive layer during the operation of the devices, a TEOLED device

* Corresponding author. Department of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, Gyonggi-Do, 440-746, Republic of Korea. Tel.: +82 31 290 7395; fax: +82 31 290 7410.

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

composed of one emissive layer emitting two-wavelength light is preferred.

Therefore, in this study, a TEOLED device composed of one emissive layer emitting two-wavelength light has been studied and the effects of material parameters such as anode indium tin oxide (ITO) thickness, the emissive layer thickness and dopant concentration, and multilayer capping layer on the variation of emitting wavelength, relative emission intensity of the two-wavelengths, and the light output efficiency were investigated to obtain a balanced white light emission.

2. Experimental

The white TEOLED structure used in this study is glass/Ag (100 nm)/ITO (x nm)/2-TNATA (60 nm)/NPB (15 nm)/DPVBi:DCJTB ($y\%$, $30-z$ nm)/Alq₃ ($20+z$ nm)/Li (1.0 nm)/Al (2.0 nm)/Ag (20 nm)/refractive index matching capping layer and its schematic diagram of the device is shown in Fig. 1(a). Fig. 1(b) shows the molecular structure of the organic materials and, among these materials, 2-TNATA was used for a hole injection layer (HIL), NPB for hole transporting layer (HTL),

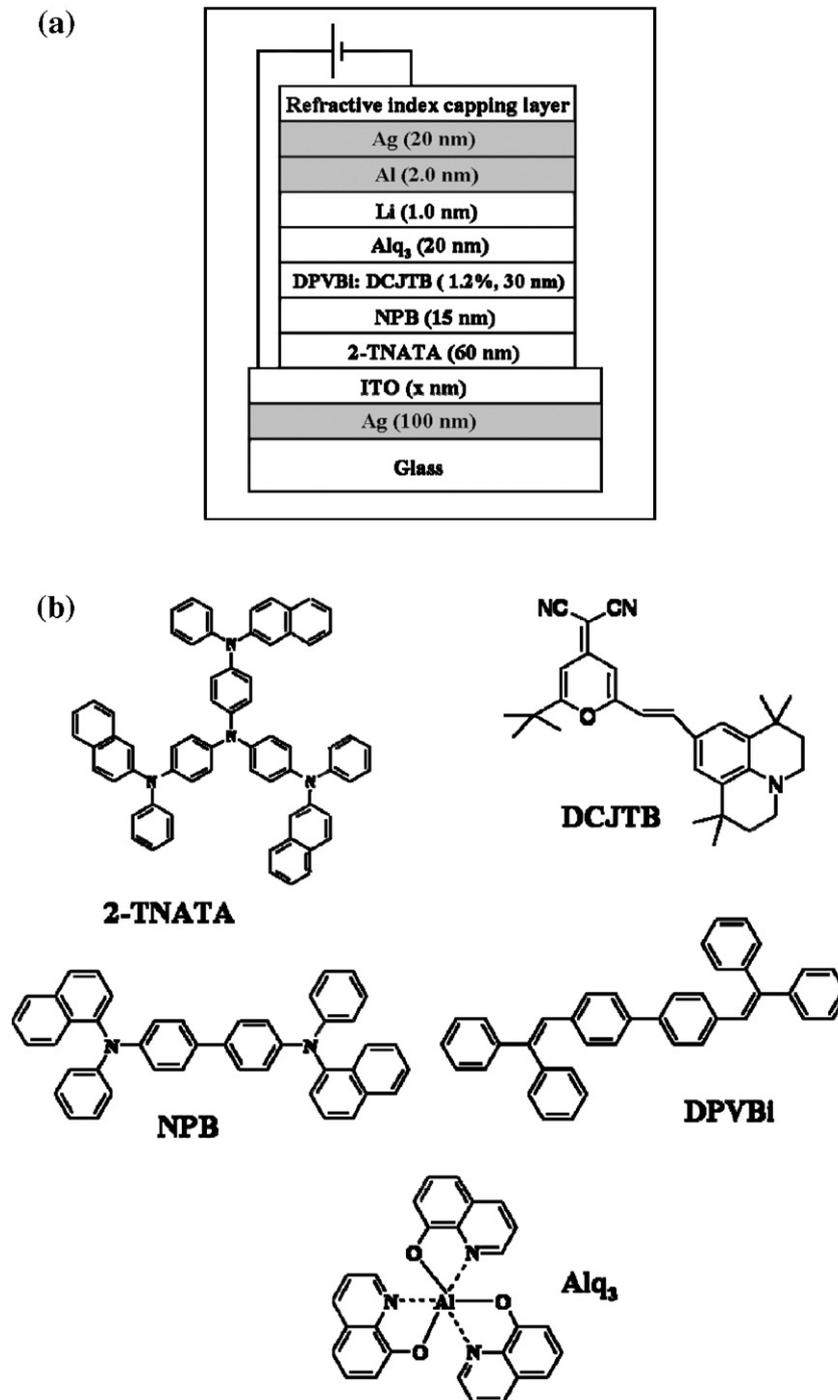


Fig. 1. (a) Schematic diagram of the TEOLED device configuration. (b) Molecular structures of the organic materials in the device.

DPVBi for blue host, DCJTb for red dopant to DPVBi, Alq₃ for electron transporting layer (ETL), Li for electron injecting layer (EIL), and Al/Ag for cathode metal. In this structure, for the emission layer, red dopant DCJTb was doped in blue host DPVBi to obtain two-wavelength based white color emission. To obtain balanced two-wavelength emission from the emission layer by varying the microcavity length (L) of the device, the thickness of anode ITO was varied from 50 nm to 110 nm while keeping the thickness of the remaining organic materials at 110 nm. Also, to change the intensity ratio of the two balanced wavelengths, the thickness and dopant concentration of DCJTb doped DPVBi were varied while keeping the thickness of DPVBi:DCJTb/Alq₃ at 50 nm. Finally, the effect of different refractive index matching capping layer such as Alq₃, ITO, and ITO/SiO₂ on the balanced white light emission and light output efficiency was investigated.

As the sample, 0.7 mm thick glass substrate was cleaned with acetone, alcohol, and deionized water in sequence and, on the cleaned glass substrate, 100 nm thick Ag was deposited by e-beam evaporation followed by anode ITO deposition by DC magnetron sputtering at 2.6 nm/s of deposition rate with 400 W of DC power. The Ag/ITO deposited glass substrate was annealed at 350 °C for 3 min in a furnace at the nitrogen atmosphere. The sheet resistance of the annealed Ag/ITO deposited glass substrate was 30 Ω/square. The organic materials and Li were deposited in a thermal evaporator with the deposition rate of 0.05–0.2 nm/s at the pressure of 1×10^{-6} Torr in sequence. The Al and Ag layer composing the cathode metal were also deposited in the evaporator at 0.5 nm/s without breaking vacuum. The emitting area of the device was 1.6×1.6 mm².

The spectrum of the fabricated white TEOLED was observed by optical emission spectroscopy (OES; PCM-420, SC Tech. Inc.) and the CIE chromaticity coordinates were estimated using a chroma meter (CS100, Minolta Camera Co., Ltd.) The current (I)–voltage (V) characteristics of the devices were measured by a source-measure unit (236, Keithley Instrument Inc.) and the electroluminescence (EL) was measured by a silicon photodiode and a picoammeter (485, Keithley Instrument Inc.).

3. Results and discussions

The two-wavelength TEOLED device shown in Fig. 1(a) has a microcavity structure having a Fabry–Perot filter in the device, where, two mirrors having partial reflectivity are located in parallel with an optical distance of L [4–6]. In this filter, when a light is incident to the filter, only the light with certain wavelengths (λ_{\max}) satisfying the following relationship can be extracted out of the filter.

$$\frac{2L}{\lambda_{\max}} + \frac{\Phi}{2\pi} = m \quad (m = \text{integer}).$$

In our devices, as the mirrors, the bottom reflector is Ag/ITO (anode) and the top reflector is Li/Al/Ag (cathode) and L is the calibrated optical distance between the reflective anode and the semitransparent cathode. Also, Φ is the phase shift between anode and cathode. By changing the optical distance of the

device, the wavelengths emitting from the TEOLED are changed [7,8] and, for the same material thickness, the optical distance is larger for the material with a higher refractive index (refractive index: $n_{\text{ITO}} = 1.9\text{--}2.2$, $n_{\text{organic}} = 1.6\text{--}1.7$). Therefore, the thickness of anode ITO was varied to obtain complementary color relation for the white light emission and the change of the light output spectra was observed. The results are shown in Fig. 2 for the anode ITO thickness range from 50 nm to 110 nm. The device structure was composed of glass/Ag (100 nm)/ITO (x nm)/2-TNATA (60 nm)/NPB (15 nm)/DPVBi:DCJTb (30 nm, 0.1%)/Alq₃ (20 nm)/Li (1.0 nm)/Al (2.0 nm)/Ag (20 nm). As shown in Fig. 2, the variation of the ITO thickness changed λ_{\max} of the emitted spectrum by observing λ_{\max} at 507 nm and 555 nm for 110 nm thick ITO, λ_{\max} at 477 nm and 545 nm for 90 nm thick ITO, λ_{\max} at 452 nm for 70 nm thick ITO, and λ_{\max} at 430 nm and 742 nm for 50 nm thick ITO. Among these anode ITO thickness, a complementary color relation such as blue/yellow, cyan/red, green/magenta, etc. for white light emission could be obtained for 90 nm thick ITO by showing sky blue (477 nm)/orange (545 nm) colors. However, as shown in the figure, the intensity of the orange color wavelength portion was not high enough to form a balanced white light. Therefore, to increase the intensity of the orange wavelength portion, the dopant concentration of red dye DCJTb in DPVBi and the thickness of the emission layer were varied while keeping the total thickness of DPVBi:DCJTb and Alq₃ at 50 nm.

Fig. 3(a) shows the effect of DCJTb dopant concentration in the DPVBi on the change of the EL spectrum for 90 nm thick ITO thickness in the TEOLED device shown in Fig. 2. Therefore, the device was composed of glass/Ag (100 nm)/ITO (90 nm)/2-TNATA (60 nm)/NPB (15 nm)/DPVBi:DCJTb (30 nm, $x\%$)/Alq₃ (20 nm)/Li (1.0 nm)/Al (2.0 nm)/Ag (20 nm) ($x=0.8, 0.6, 0.4, \text{ and } 0.2$). As shown in the figure,

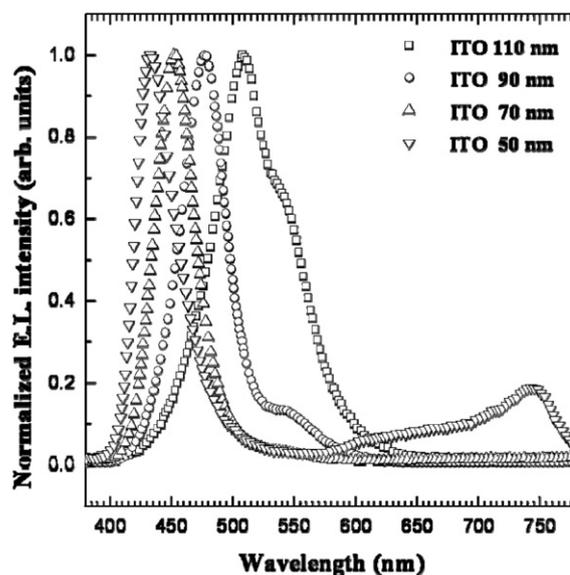


Fig. 2. Normalized electroluminescent spectra of the devices composed of glass/Ag (100 nm)/ITO (x nm)/2-TNATA (60 nm)/NPB (15 nm)/DPVBi:DCJTb (30 nm, 0.1%)/Alq₃ (20 nm)/Li (1.0 nm)/Al (2.0 nm)/Ag (20 nm). ($x=50, 70, 90, 110$ respectively) device at the luminance of 100 cd/m².

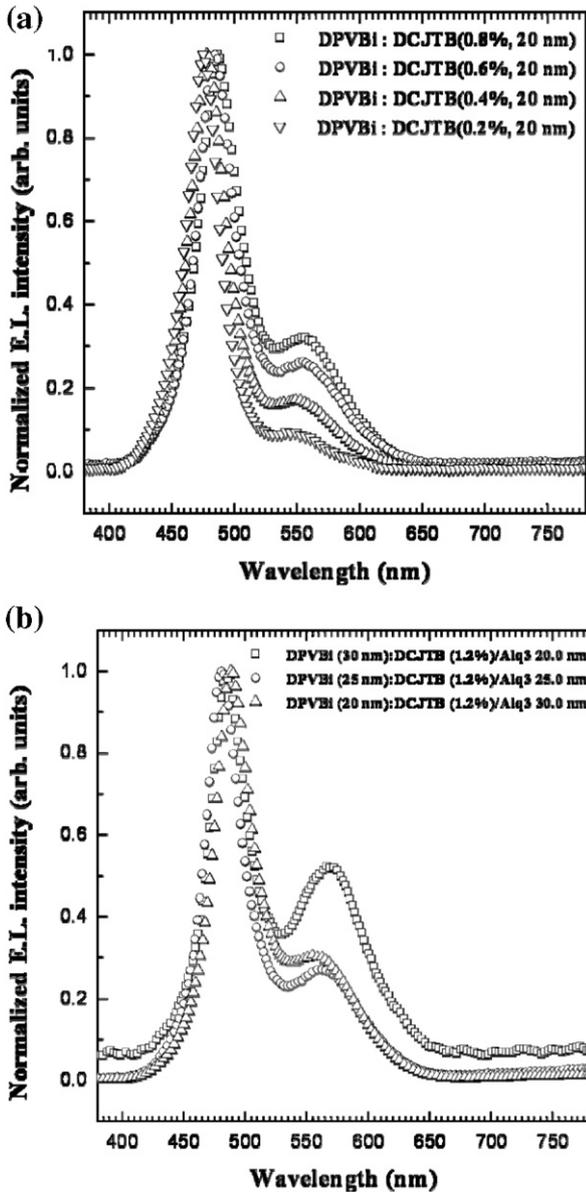


Fig. 3. (a) Normalized EL spectra of the devices composed of glass/Ag (100 nm)/ITO (90 nm)/2-TNATA (60 nm)/NPB (15 nm)/DPVBi:DCJTb (30 nm, x%)/Alq₃ (20 nm)/Li (1.0 nm)/Al (2.0 nm)/Ag (20 nm) (x=0.8, 0.6, 0.4, and 0.2). (b) Normalized EL spectra of the devices composed of glass/Ag (100 nm)/ITO (90 nm)/2-TNATA (60 nm)/NPB (15 nm)/DPVBi:DCJTb (x nm, 1.2%)/Alq₃ (50-x nm)/Li (1.0 nm)/Al (2.0 nm)/Ag (20 nm) (x=30, 25, and 20).

the increase of dopant concentration from 0.2% to 0.8% increased the EL peak intensity of orange color about 3 times compared to the peak intensity of the sky blue color even though the peak wavelength was moved towards longer wavelength slightly. The increase of the orange color wavelength with the increase of the red dopant concentration is known to be from the solid-state salivation effect (SSSE) occurring for DCM-series material such as DCJTb, DCM2, etc. [9]. Fig. 3(b) shows the effect of 1.2% DCJTb doped DPVBi thickness from 20 nm to 30 nm on the relative intensity of the EL spectrum. Here, 1.2% DCJTb was used to obtain more optimal orange spectrum (0.8%:553 nm, 1.2%:562 nm) balanced with the blue spectrum

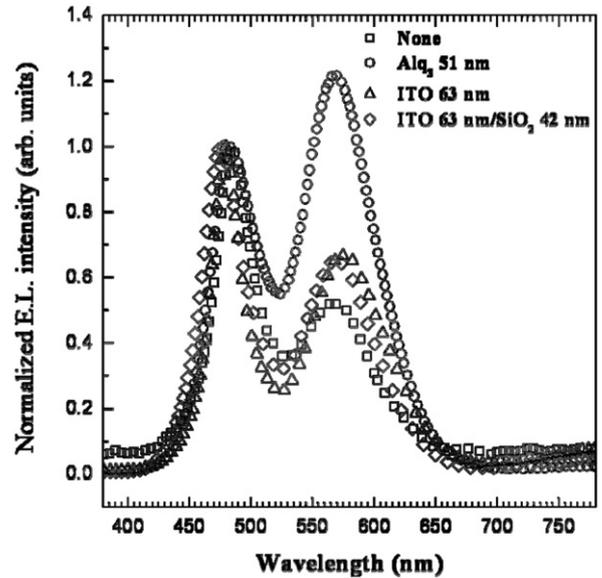


Fig. 4. Normalized EL spectra of the devices composed of glass/Ag (100 nm)/ITO (90 nm)/2-TNATA (60 nm)/NPB (15 nm)/DPVBi:DCJTb (30 nm, 1.2%)/Alq₃ (20 nm)/Li (1.0 nm)/Al (2.0 nm)/Ag (20 nm)/refractive index matching layer.

(477 nm) of DPVBi for white light emission. The total thickness of DPVBi:DCJTb/Alq₃ was maintained at 50 nm to limit the change of the spectrum only to the thickness of the emissive layer. As shown in the figure, the increase of the emissive layer increased the relative intensity of orange color peak compared to the intensity of sky blue color possibly by the enhanced recombination at the dopant sites. Therefore, for the experimental conditions, an EL spectrum closer to white light could be obtained when 1.2% DCJTb doped DPVBi layer thickness was 30 nm and Alq₃ thickness was 20 nm.

To increase the light intensity from the above optimized TEOLED device, a capping layer for refractive index matching was deposited on the cathode metal layer and the effect of different refractive index matching materials on the EL spectrum of the emitted light and its EL intensity was investigated for the device composed of glass/Ag (100 nm)/ITO (90 nm)/2-TNATA (60 nm)/NPB (15 nm)/DPVBi:DCJTb (30 nm, 1.2%)/Alq₃ (20 nm)/Li (1.0 nm)/Al (2.0 nm)/Ag (20 nm). The results are shown in Fig. 4 and Table 1 for the refractive index matching materials of Alq₃ (51 nm), ITO (63 nm), and ITO (63 nm)/SiO₂ (42 nm). In Table 1, the power efficiency and the corresponding CIE coordinate in addition to the emitted EL intensity are also shown for different refractive index materials. In

Table 1
Optical characteristic of white TEOLED with different refractive index matching layers (refractive index matching layer, refractive index, power efficiency (η_{PL}), CIE coordinates, and maximum brightness (L_{max}))

Capping layer	Alq ₃ (51 nm)	ITO (63 nm)	ITO (63 nm)/SiO ₂ (42 nm)
Refractive index	1.6	1.95	1.95/1.46
η_{PL} (lm/W) ^a	1.2	1.1	1.4
CIE coordinates ^a	0.34, 0.36	0.35, 0.32	0.32, 0.34
L_{max} (cd/m ²)	12,700	11,500	14,500

^a At 1.00 cd/m².

general, due to the differences in the refractive index between the cathode metal of the TEOLED device and air, some of light emitted inside of the TEOLED device cannot be extracted through the semitransparent cathode metal by Snell's law. That is, when the light passes through from a medium with a refractive index of n_1 to a medium with a refractive index of n_2 , if n_2 is larger than n_1 , the light is reflected backward but, if n_2 is smaller than n_1 , the light is reflected forward. Therefore, by depositing a material having the refractive index between the refractive index of the cathode material and the air, the extraction efficiency can be improved [10,11]. As shown in Table 1, the refractive index of Alq₃ is 1.6, that of ITO is 1.95, and that of ITO/SiO₂ is 1.95/1.46 and the extracted EL intensity was the highest for the combination of ITO/SiO₂. Also, because of the huge differences in the refractive index between the air and semitransparent cathode metal, the use of ITO showed higher EL intensity compared to Alq₃. Especially, the highest EL intensity for the combination of ITO/SiO₂ is believed to be related to the smoother transition of refractive index from the semitransparent cathode metal to the air. From the highest extracted EL intensity of the combination of ITO/SiO₂, the use of ITO/SiO₂ also showed the highest power efficiency. In addition, possibly due to the differences in the reflectivity of the light between the cathode metal and air for different wavelengths, the extracted EL intensity of the orange color relative to that of the sky blue color was increased further by depositing the refractive index materials on the cathode metal as shown in Fig. 4. Among the capping materials, Alq₃ showed the highest orange spectrum intensity, however, with Alq₃, the white light balancing cannot be obtained because the intensity of orange spectrum portion was higher than that of the blue spectrum portion. The use of ITO/SiO₂ as the capping layer showed the better balancing of emission intensities between blue spectrum portion and orange spectrum portion. Due to the change of the relative intensity ratios by using different refractive index materials, the CIE coordinates were also varied depending on the refractive index material. As shown in Table 1, for the TEOLED device composed of glass/Ag (100 nm)/ITO (90 nm)/2-TNATA (60 nm)/NPB (15 nm)/DPVBi:DCJTb (30 nm, 1.2%)/Alq₃ (20 nm)/Li (1.0 nm)/Al (2.0 nm)/Ag (20 nm)/refractive index matching layer, the use of ITO (63 nm)/SiO₂ (42 nm) as the refractive index matching material showed the CIE coordinate of (0.32, 0.34) which is very close to the (0.33, 0.33) of white point in addition to the highest EL intensity of 14,500 cd/m² at the operating voltage of 12.8 V.

4. Conclusions

In this study, white TEOLEDs composed of glass/Ag (100 nm)/ITO (x nm)/2-TNATA (60 nm)/NPB (15 nm)/DPVBi:DCJTb ($y\%$, $30-z$ nm)/Alq₃ ($20+z$ nm)/Li (1.0 nm)/Al (2.0 nm)/Ag (20 nm)/refractive index matching layer which have one doped emissive layer emitting two-wavelength light were fabricated and the effect of material parameters on the optical properties of the fabricated TEOLEDs was investigated. By varying the microcavity length of TEOLEDs through the variation of the anode ITO thickness and, by optimizing the dopant DCJTb concentration and the thickness of the emissive DPVBi layer, an EL spectrum composed of two complementary wavelengths close to white light could be obtained. Also, by the deposition of a refractive index matching layer composed of ITO (63 nm)/SiO₂ (42 nm), a higher EL intensity could be obtained. For the TEOLED device composed of glass/Ag (100 nm)/ITO (90 nm)/2-TNATA (60 nm)/NPB (15 nm)/DPVBi:DCJTb (1.2%, 30 nm)/Alq₃ (20 nm)/Li (1.0 nm)/Al (2.0 nm)/Ag (20 nm)/ITO(63 nm)/SiO₂ (42 nm), the maximum EL intensity of 14,500 cd/m² at 12.8 V could be obtained with CIE chromaticity coordinate of (0.32, 0.34) close to ideal white color CIE coordinate of (0.33, 0.33) at 100 cd/m².

References

- [1] C.W. Tang, S.A. Vanslyke, *Appl. Phys. Lett.* 51 (1987) 913.
- [2] B.W. D'Andrade, S.R. Forrest, *Adv. Mater.* 16 (2004) 1585.
- [3] J. Kido, W. Ikeda, M. Kimura, K. Nagai, *Jpn. J. Appl. Phys., Part 2* 35 (1996) L394.
- [4] S.F. Hsu, C.C. Lee, S.W. Hwang, C.H. Chen, *Appl. Phys. Lett.* 86 (2005) 253508.
- [5] A. Dodabalapur, L.J. Rothberg, R.H. Jordan, T.M. Miller, R.E. Slusser, J.M. Phillips, *J. Appl. Phys.* 80 (1996) 6954.
- [6] F. Jean, J.Y. Mulot, B. Geffroy, C. Denis, P. Cambon, *Appl. Phys. Lett.* 81 (2002) 1717.
- [7] A. Dodabalapur, L.J. Rothberg, T.M. Miller, E.W. Kwock, *Appl. Phys. Lett.* 64 (1994) 2486.
- [8] Shih Feng Hsu, Chung-Chun Lee, Andrew T. Hu, C.H. Chen, *Curr. Appl. Phys.* 4 (2004) 663.
- [9] K.O. Cheon, J. Shinar, *Appl. Phys. Lett.* 81 (2002) 1738.
- [10] M.H. Lu, M.S. Weaver, T.X. Zhou, M. Rothman, R.C. Kwong, M. Hack, J.J. Brown, *Appl. Phys. Lett.* 81 (2002) 3921.
- [11] T. Tsutsumi, M. Yahiro, H. Yokogawa, K. Kawano, M. Yokoyama, *Adv. Mater.* 13 (2001) 1149.