Fluorescent White OLEDs with a High Color-rendering Index Using a Silicon-Cored Anthracene Derivative as a Blue Host

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Abstract

Fluorescent white organic light-emitting diodes showing high color-rendering indices (CRIs) of up to 81 was demonstrated, with a silicon-cored anthracene derivative (PATSPA) doped with DPAVBi utilized as the deep-blue host and dye materials, and the commercial dyes rubrene and DCM2 utilized as the orange- and red-light-emitting dyes. The devices, consisting of three emissive layers, showed bright-white-light emission, but the ratio of the blue peak to the orange and red peaks changed with the current density and the thickness of the blue emissive layer. A high CRI was achieved with the use of a deep-blue emitter doped in a novel host and by optimizing the blue-layer thickness. The device with a blue-layer thickness of 10 nm showed the Commission Internationale de l'Eclairage (CIE) color coordinate of (0.33, 0.35), a high CRI of 81, and a moderate external quantum efficiency of 2% at a current density of 2.5 mA/cm^2.

Keywords: white-light-emitting diodes, high color-rendering index, fluorescence, anthracene derivative

1. Introduction

Since Tang et al. demonstrated the first efficient organic light-emitting diodes (OLEDs), they have attracted great attention due to both the great scientific interest in them and their many potential applications, such as full-color displays, flexible display devices, and light sources [1-8]. Generally, there are two types of electroluminescence: fluorescence and phosphorescence. Phosphorescence-based OLEDs are currently the subject of intense study because their internal quantum efficiency can reach 100%, theoretically [9-11]. They usually have a shorter lifetime than the fluorescent OLEDs, however, and the lifetime of blue phosphorescent OLEDs is particularly low. Even though their efficiency is low, all the colors (from red to blue) of fluorescence-based OLEDs have been developed over the past decades in terms of stability, efficiency, and color purity [12-14], owing to their high stability. Moreover, white OLEDs (WOLEDs) composed of two or three fluorescent dye colors have advantages in achieving a high color-rendering index (CRI) and high stability for display or lighting applications. It is difficult to fabricate WOLEDs that possess a high CRI by using phosphorescent-emitting materials because there are few proper deep-blue phosphorescent dopant and host materials [15]. From this viewpoint, fluorescence-based WOLEDs have merits as a white-light source compared with phosphorescence-based WOLEDs: a longer lifetime and a high CRI.

WOLEDs for lighting applications require a high CRI as well as efficiency. Many WOLEDs showing high efficiency and stable chromaticity coordinates based on fluorescent OLEDs have been reported, but they hardly achieved a high CRI of above 80 [16, 17]. Therefore, the emission peak wavelength of the red, green, and blue dyes and the color purity of the device are the key factors for achieving a high CRI.

In this work, trichromatic white-light-emitting diodes showing high CRIs were demonstrated with the use of deep-blue-, orange-, and red-light-emitting fluorescent dyes. A silicon-cored anthracene derivative was also adopted as the blue host material, showing the excellent performance of the blue OLED, as described in these authors' previous

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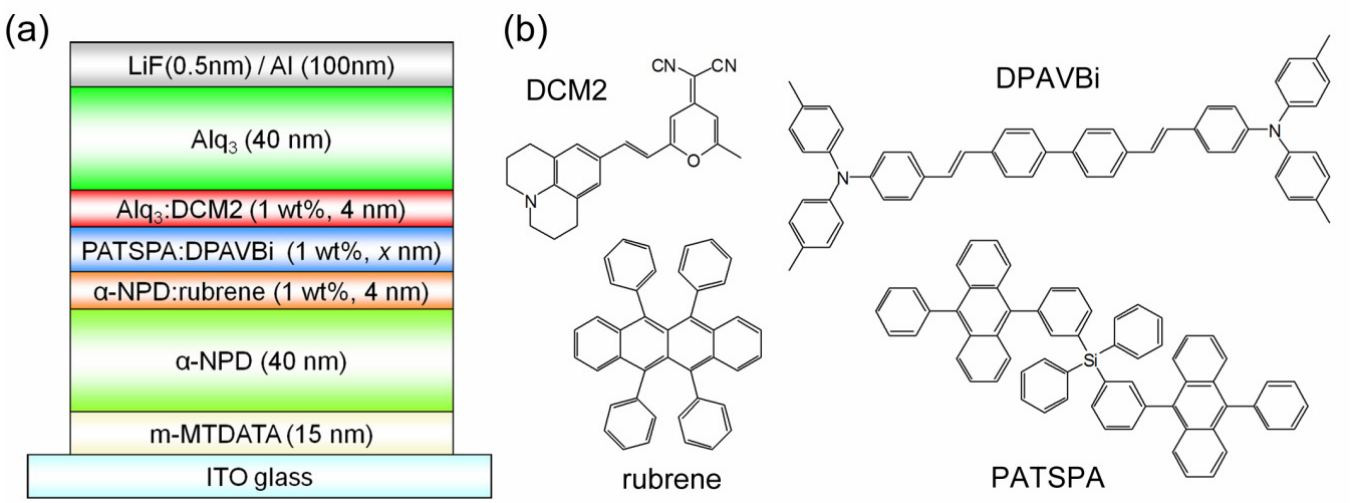

Fig. 1. (a) The device structure of the trichromatic white-light-emitting diodes based on a novel blue host and the widely used red, orange, and blue dyes. (b) Their chemical structures.

report [12], and achieving high efficiency and saturated blue color in the white-light-emitting device. The white OLEDs exhibited high CRIs of 81, with color coordinates of (0.33, 0.35) and a maximum external quantum efficiency (EQE) of 2%.

2. Experiment

Fig. 1(a) shows the device structure of the bottom-emission WOLEDs that were studied in this work. Patterned indium-tin-oxide (ITO) substrates were cleaned with isopropyl alcohol, acetone, and methanol and were rinsed with deionized water. After drying in a vacuum oven at 120°C, they were treated in UV-ozone for 5 min before depositing organic layers. 15 nm 4,4′,4″-tris[3-methylphenyl (phenyl)amino]triphenylamine (m-MTDATA) was successively evaporated as the hole injection layer (HIL), 40 nm 4,4′-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (α-NPD) as the hole transport layer (HTL), 40 nm tris(8-hydroxyquinoline)aluminum (Alq_3) as the electron transport layer (ETL), and LiF (0.5 nm) and Al (100 nm) as the cathodes on top of the ITO glass substrates under the pressure of 3×10^{-6} Torr. The light-emitting layers were orange-, blue-, and red-light-emitting ones, which are α-NPD doped with 5,6,11,12-tetraphenylnaphthacene (rubrene) (1 wt%; 4 nm), bis[3-(10-phenylanthracen-9-yl)phenyl] diphenylsilane (PATSPA) doped with 4,4'-bis[2-[4-(N,N-ditolylamino)-phenyl-1-yl]-vinyl-1-yl]-1,1'-biphenyl (DPAVBi) (1 wt%; 8, 10, or 12 nm), and Alq_3 doped with 4-(dicyanomethylene)-2-methyl-6-julolidyl-9-enyl-4H-pyran (DCM2) (1 wt%; 4 nm). The chemical structures of the organic conjugated molecules (three dopants and the PATSPA host) are shown in Fig. 1(b). The thickness of the film was monitored using a quartz crystal sensor, keeping the deposition rate at 1 Å/s for organic materials and 4–6 Å/s for Al.

The electrical characteristics of devices, such as the current-voltage-luminance (I-V-L) characteristics and the electroluminescence (EL) spectra, were measured at room temperature using a Keithley 236 source-measure unit and a Keithley 2000 multimeter equipped with a photomultiplier tube (PMT), through an ARC 275 monochromator. The external quantum efficiency (EQE) and power efficiency (PE) of the WOLEDs were calculated from the EL spectra and intensity, which were measured using a calibrated Si photodiode placed at an angle normal to the device's surface, assuming that the device was a Lambertian source. The CRIs were calculated using the procedure defined by CIE [18]. The highest-occupied-molecular-orbital (HOMO) energy levels of all the materials that were used in this work were measured using Riken Keiki AC-2 (750H), and the lowest-unoccupied-molecular-orbital (LUMO) energy levels were calculated from each material's optical band gap.

3. Results and Discussion

The light-emitting layers of the WOLEDs consist of α-NPD:rubrene for the orange-light-emitting layer, PATSPA:DPAVBi for the blue-light-emitting layer, and Alq_3:DCM2

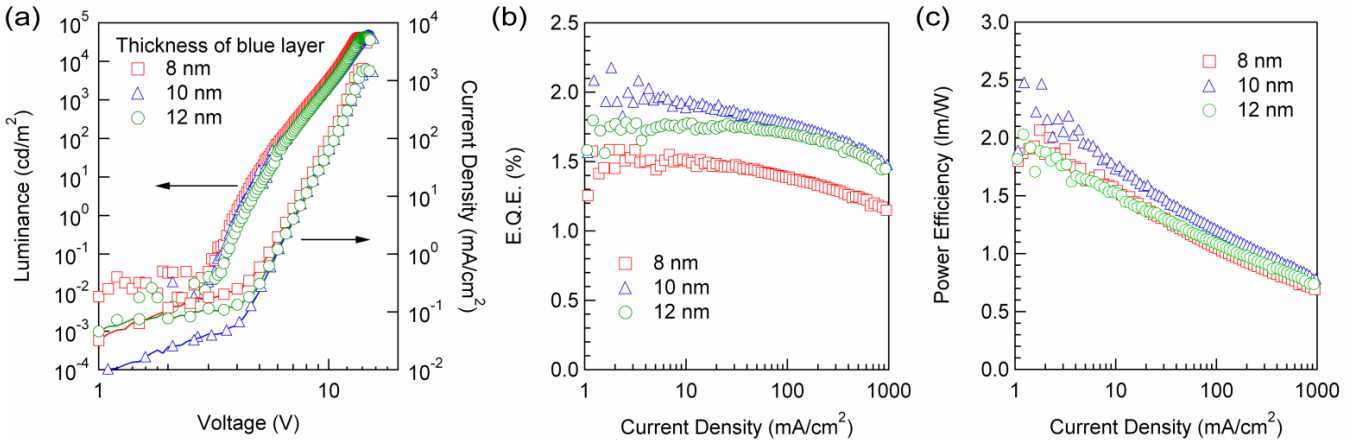

Fig. 2. The device characteristics of WOLEDs after varying the thickness of the blue-light-emitting layer into 8, 10, and 12 nm in terms of (a) luminance-voltage and current-voltage, (b) external quantum efficiency, and (c) power efficiency as a function of the current density.

for the red-light-emitting layer. Every dye was doped in a host with a weight ratio of 1%. PATSPA is a silicon-cored anthracene derivative for the blue fluorescent host, which possesses a high glass transition temperature (T_g) of 148°C, as reported by Lyu et al. [12]. Enhanced stability of the devices can thus be expected. The HOMO and LUMO energy levels of PATSPA were determined to be -5.91 and -2.89 eV, respectively. The blue layer was placed between the red and orange layers so that excitons can be formed mainly on the blue layer. Red or orange color emission may originate from both direct exciton recombination and the Föster energy transfer from the blue layer.

Three devices were fabricated in the same structure, with the thickness of the blue-emitting layer varied into 8, 10, and 12 nm to find out the optimum thickness for higher device performances. The current-voltage-luminance properties of the three devices are plotted in Fig. 2(a). The device with a thicker layer showed slightly higher voltages at a fixed current density or luminance, but they were almost similar because of the small difference in thickness (2-4 nm). The turn-on voltage of the devices was 3-3.3 V, depending on the device thickness, and the luminance of all the devices exhibited a maximum value of above 40,000 cd/m^2. As can be seen in Fig. 2(b) and 2(c), the device using 10 nm of the blue-light-emitting layer showed the highest efficiencies of 2.2% in EQE and 2.5l m/W in PE, which may be the optimized thickness of the blue-light-emitting layer in this device structure.

Fig. 3 shows the normalized EL spectra of each device, measured at the driving current densities of 25, 50, and 150 mA/cm^2. The main EL peak of DPAVBi doped in PATSPA is located at 458 nm, with a vibronic peak of around 485 nm, which corresponds to the previous results of blue OLEDs [12]. Rubrene and DCM2 exhibited their EL peaks at 555 and 596 nm, respectively. The ratio of blue to red and orange in EL intensity was increased when the current density in all the devices increased, but the shift in the EL intensity ratio of each peak was significantly reduced in the device with a thicker blue layer. In detail, the relative EL intensity of the blue color increases, and that of the orange or red color decreases gradually, as the thickness of the blue layer is increased from 8 to 12 nm. There exists a high injection barrier from the rubrene-doped α-NPD (HOMO: -5.5 eV) to PATSPA (HOMO: -5.91 eV), resulting in the recombination of the excitons at this interface in a very low current density. In addition, anthracene-based PATSPA is a dominant hole-carrier material, and Alq_3 is an electron-dominant material. Therefore, another exciton recombination zone can exist at this interface. When the driving current density was increased, the excitons recombined mainly in the blue-light-emitting area. As a result, the blue emission increased, with an expanded exciton recombination area in the PATSPA:DPAVBi layer when the thicker blue layer was used.

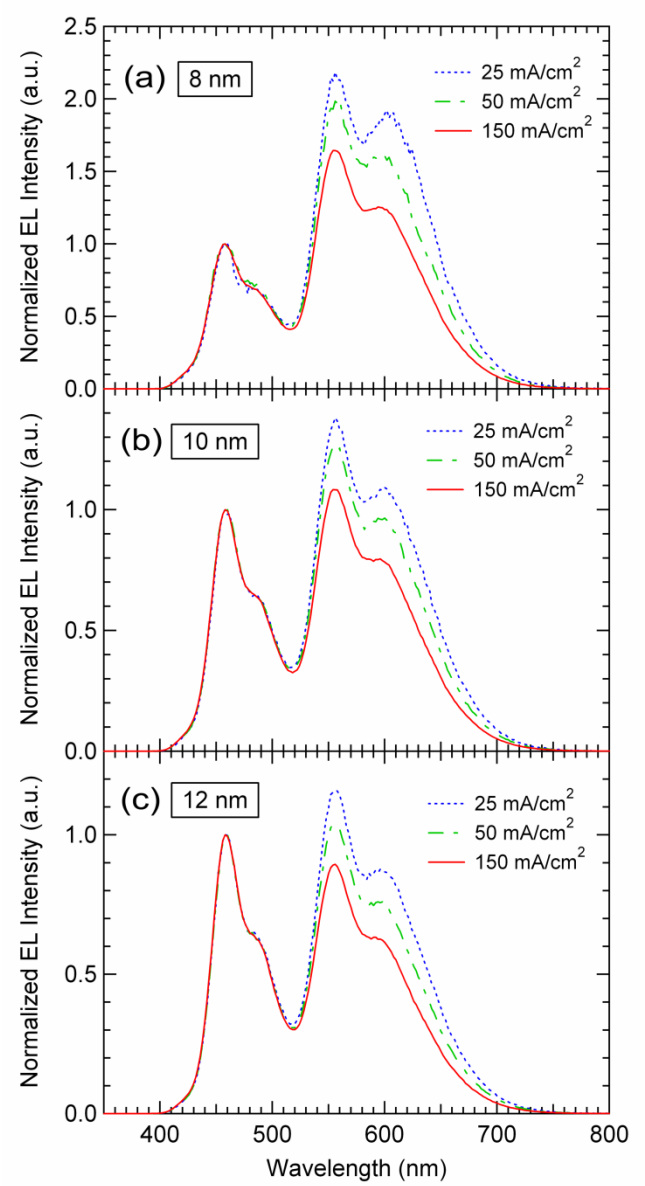

Fig. 3. Normalized EL spectra of the three devices measured at various current densities of 25, 50, and 150 mA/cm^2.

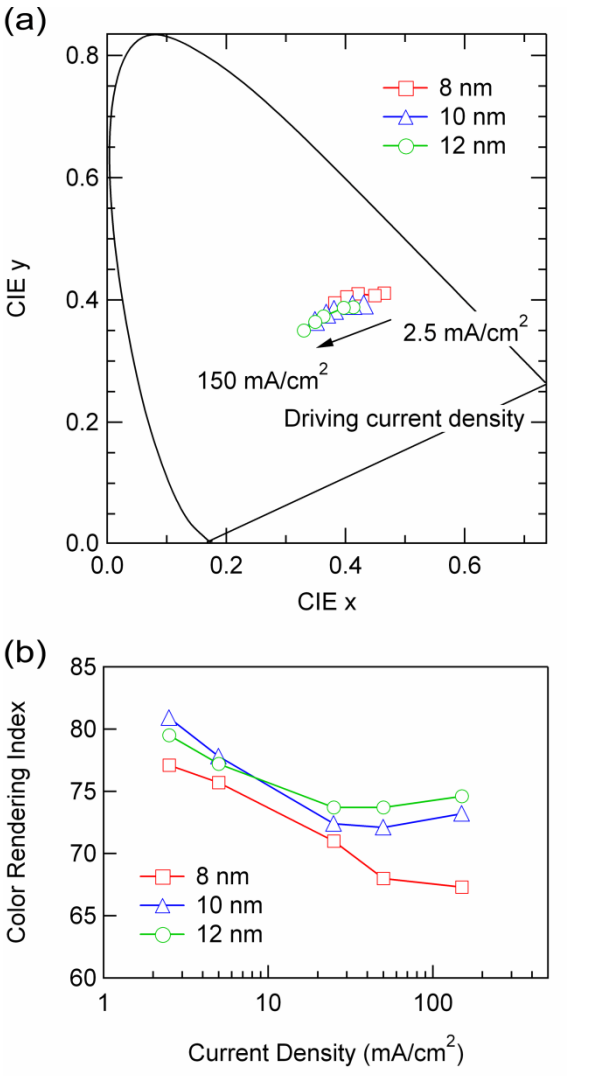

Fig. 4. (a) The CIE coordinates and (b) color-rendering indices of WOLEDs along with various driving current densities.

The Commission Internationale de L'Eclairage (CIE) chromaticity coordinates of the devices are shown in Fig. 4(a). At a very low current density of 2.5 mA/cm^2, all the devices showed reddish-white colors with the color coordinates of (0.47, 0.41), (0.43, 0.39), and (0.41, 0.39) for the device with an 8-, 10-, and 12-nm blue layer, respectively. Then they were close to the ideal CIE chromaticity coordinates for a pure white color (0.33, 0.33) when the driving current density was increased to 150 mA/cm^2, which were (0.38, 0.40), (0.35, 0.37), and (0.33, 0.35) for each device. The color coordinates changed much when a thin (8-nm) blue layer was used, but as the thickness of the blue layer was increased to 12 nm, the device showed less color shifting along with the current density. It can be supposed from these results that the exciton recombination zone was mostly located within the PATSPA:DPAVBi layer, as described in the previous paragraph.

The color-rendering indices were also calculated from the EL spectra of the three devices, along with the driving voltages, which are plotted in Fig. 4(b). All the devices showed a high CRI of above 75 at low current densities (<5 mA/cm^2), and the device with a 10-nm blue layer showed a high CRI of 81. At that time, the color temperature was 3006 K.

4. Conclusion

In summary, trichromatic WOLEDs were fabricated using deep-blue-, orange-, and deep-red-light-emitting fluorescent dyes that adopted the silicon-cored anthracene derivative (PATSPA) as the blue host material. By optimizing the blue-layer thickness, high CRIs of up to 81 were achieved. Although the efficiency of the devices was not high, it is believed that the WOLEDs exhibiting a high CRI are valuable for applications such as solid-state lighting.

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