

White Organic Light-Emitting Diodes Using Bis(2,4-dimethyl-8-quinolinolato)(triphenylsilanolato) Aluminum(III) as a New Hole-Blocking Layer

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The balanced white-emission of the organic light-emitting diodes (OLEDs), consisted of a deep blue *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-(1,1'-biphenyl)-4,4'-diamine (NPB) emitter and a new orange emitter made of the bis(2,4-dimethyl-8-quinolinolato)(triphenylsilanolato) aluminum(III) (24MeSAIq) doped with a red fluorescent 4-(dicyanomethylene)-2-*tert*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran (DCJTB) was tuned by varying a thickness of a DCJTB-doped 24MeSAIq material. For the white OLED with 10-nm-thick DCJTB (0.5%) doped 24MeSAIq, the maximum luminance of about 29,700 Cd/m² is obtained at 15 V. Also, Commission Internationale d'Eclairage (CIE) chromaticity coordinates of (0.32, 0.28) at about 100 Cd/m², which is very close to white light equi-energy point (0.33, 0.33), could be obtained.

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The use of white organic light-emitting diode (OLED) devices, in which discrete red, green, and blue (RGB) pixelation process can be accomplished without using a tedious and troublesome precision shadow mask, has recently become increasingly popular as one of the major methods to fabricate full-color display combined with RGB color filters, as a backlight of liquid crystal displays, and as solid-state lightings. White light-emission is obtained by mixing two complementary colors (e.g., bluish-green/red or deep blue/yellow) or three primary colors (red, green, and blue) from different light-emitting molecules and polymers. This can be done either using a multilayer structure with two or more emitting layers or doping an active host material with fluorescent dyes.^{1–8)}

In the white devices with multiple light emitting layers, a hole- or electron-blocking layer with an appropriate thickness is often inserted between emissive layers in order to control the amount of exciton formation in the each layer and to enhance a luminous efficiency. Problems of light output in white devices are the color-shifting with the increase of the bias voltage by the movement of carrier recombination zone over the light emitting layers and the mismatch of a luminance and luminous efficiency among sub pixels of the RGB colors as a function of life time. Therefore, the unchangeable color coordinates and the stable exciton recombination with respect to the bias voltage are essential to white OLEDs for stable performance characteristics. The incomplete energy transfer between the host and dopant molecules is needed to obtain light emission from both host and the dopant, and also, the complete energy transfer is usually used to employ a single-light emission from the dopant.^{2,6)} In addition, careful control of doping concentration is necessary to obtain a balanced white emission with Commission Internationale d'Eclairage (CIE) chromaticity coordinates of (0.33, 0.33).

To achieve a better luminance efficiency without affecting its bipolar transport property in the OLED devices, BAq among the bis(8-quinolinolato)(aryloxy) aluminum(III) (q₂AIOR) complexes, the bis(2-methyl-8-quinolinolato)(4-phenylphenolato) aluminum(III) (BAq) has been used as the

hole-blocking layer (HBL) in the phosphorescent OLED devices because of the longest operational lifetime ($T_{1/2}$) of 10,000 h at the initial brightness of 500 Cd/m².⁹⁾ However, in the fluorescent OLED devices, although BAq and SAq has ever been used as HBL in the single-layered emitting white OLEDs using the incomplete energy transfer between a host and a dopant, because of a low hole-blocking property due to a small difference between the ionization potential of that and of HTL, the white emission with the only real blue peak (about 445 nm) could not be easily fabricated with BAq or SAq alone, showing two peaks of a bluish-green and real blue color at a blue wavelength range.^{10–12)} Therefore, to fabricate a white OLED device with a high color purity using BAq or SAq as HBL, another deep blue emitter needs to be added to the white OLED. The primary objective of this study is to fabricate a white OLED device with a only real blue peak in a blue wavelength range, confining a recombination zone into HTL by employing the bis(2,4-dimethyl-8-quinolinolato)(triphenylsilanolato) aluminum(III) (24MeSAIq) material as stronger HBL material than BAq or SAq. The secondary objective is to study a two-layered emitting white OLED, consisted of an orange emitter of 24MeSAIq doped with a red fluorescent dopant of 4-(dicyanomethylene)-2-*tert*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran (DCJTB) which also works as the HBL and the deep blue emitter of *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-(1,1'-biphenyl)-4,4'-diamine (NPB).

24MeSAIq was synthesized by a homogeneous-phase reaction using aluminium *iso*-propoxide, 2,4-dimethyl-8-quinolinol ligand, and triphenylsilanol ligand with an isopropanol solvent at a reflux condition.¹³⁾ The substitution of methyl groups on the pyridyl ring of 8-quinolinolato ligand increases the band gap energy (E_g)¹⁴⁾ and the substitution of the bulky triphenylsilanolato ligand into q₂AIOR leads to weak intermolecular interactions. As reported through the UV–visible absorption spectrum and cyclic voltammogram of 24MeSAIq in the reference, the lowest unoccupied molecular orbital (LUMO) energy level and the highest occupied molecular orbital (HOMO) level of 24MeSAIq are found to be at around 2.94 and 6.14 eV, respectively, with the band gap energy (E_g) of 3.20 eV.¹³⁾

In a two-layered emissive white OLED device, its

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structure was composed of indium tin oxide (ITO) (120 nm)/2-TNATA (60 nm)/NPB (15 nm)/24MeSAIq:DCJTb (20 – x nm, 0.5%)/Alq₃ (35 + x nm) ($x = 0, 5, 10,$ and 15)/LiF (1 nm)/Al (100 nm), where ITO on glass (0.7 mm) has the sheet resistance of $\sim 10 \Omega/\text{square}$, 2-TNATA acts as the hole-injecting layer (HIL), NPB as the hole-transporting layer (HTL), 24MeSAIq as the hole-blocking layer (HBL) and a blue emitting layer, Alq₃ which emits a green-color as the electron-transporting layer (ETL), lithium fluoride (LiF) as the electron-injecting layer (EIL), and aluminum (Al) metal as the cathode. where DCJTb was mixed in the 24MeSAIq host as a red fluorescent dopant and its concentration was 0.5%. The thickness of the 24MeSAIq layer doped with DCJTb was increased from 5 to 20 nm to balance the injecting carriers in the white device while the corresponding Alq₃ ETL was decreased from 50 to 35 nm. Before loading the ITO glass into a deposition chamber, the ITO glass was cleaned with detergents and deionized water, and dried in the oven at the temperature of 120 °C for 2 h. Devices were fabricated by evaporating the organic materials and LiF at the rate of 0.05–0.2 nm/s onto the ITO glass substrate, sequentially at the pressure below 1×10^{-6} Torr. Finally, 100-nm-thick aluminum metal was deposited on the ITO glass with the organic materials at the rate of 0.1–2 nm/s without breaking vacuum. The emissive active area of the devices was $2 \times 2 \text{ mm}^2$.

Current–voltage characteristics were measured with a source-measure unit (236, Keithley Instrument). The intensities from the emission of OLEDs devices were measured by the photocurrent induced on the silicon photodiodes using a picoammeter (485, Keithley Instrument) The electroluminescent spectra of the as-fabricated devices were measured by optical emission spectroscopy (PCM-420, SC Tech.).

The deep blue emission portion composing of white emission was tuned by confining the recombination zone only into a neighbouring HTL, optimizing a thickness of HBL having the excellent hole-/exciton-blocking property. In electroluminescent (EL) spectra of two-component white OLED using bis(2-methyl-8-quinolinolato)(triphenylsiloxy) aluminum(III) (SAIq) having one methyl substituent on pyridyl ring as HBL, a recombination zone of blue emission is produced in HTL (about 450 nm) and HBL (about 480 nm), respectively,^{10,11} and even, is produced only in HBL (about 480 nm)¹² due to weak HBL property of SAIq.

In this study, we applied the enhanced HBL property of 24MeSAIq having two methyl substituent on pyridyl rings, to fabricate two-component white OLED device with only real blue peak (about 450 nm) in a blue wavelength range. Meanwhile, the balanced white light emission can be obtained by tuning the thickness ratio of the 24MeSAIq layer (20 – x nm) doped with DCJTb (0.5%) and the Alq₃ layer (35 + x nm). Figure 1 shows EL spectra at the luminance of 100 Cd/m² for the devices with two light-emitting zones composed of a NPB emitter and a 24MeSAIq emitter doped with DCJTb (0.5%) and the inset of Fig. 1 shows the schematic configuration of the device. As shown in Fig. 1, EL spectra of the device with the DCJTb (0.5%) doped 24MeSAIq emitter thickness of 20, 15, and 10 nm show two peaks with a deep blue and an orange color. For the 20-, 15-, and 10-nm-thick 24MeSAIq (DCJTb, 0.5%), the maximum intensities of blue peaks from the NPB layer were

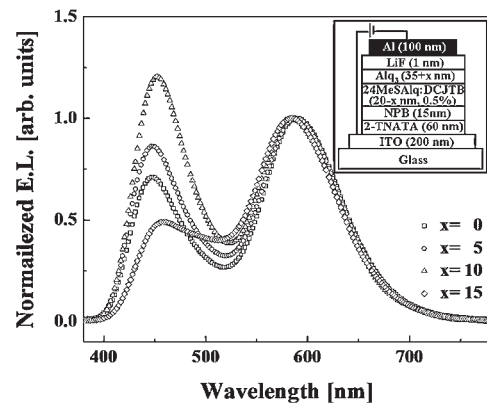


Fig. 1. EL spectra of the devices composed of glass/ITO (120 nm)/2-TNATA (60 nm)/NPB (15 nm)/24MeSAIq: DCJTb (20 – x nm, 0.5%)/Alq₃ (35 + x nm)/LiF (1 nm)/Al (100 nm) device at the luminance of 100 Cd/m² (open square; $x = 0$, open circle; $x = 5$, open triangle; $x = 10$, diamond; $x = 15$). The inset shows the schematic configuration of the white-emitting device.

found to be 447, 448, and 452 nm, respectively and orange peaks from the DCJTb (0.5%) doped 24MeSAIq to be 589, 588, and 585 nm, respectively. Therefore, the exciton recombination occurs both in the NPB layer and in the DCJTb (0.5%)-doped 24MeSAIq layer. Also, for the DCJTb (0.5%)-doped 24MeSAIq thickness doped with DCJTb (0.5%) of 20, 15, and 10 nm, the external quantum efficiency at the luminance of 100 Cd/m² was 1.46, 1.64, and 1.54%, respectively, and the turn-on voltage at the luminance of 0.1 Cd/m² was 4.2, 3.8, and 3.6 V, respectively. An orange emission from DCJTb indicates an incomplete energy transfer from 24MeSAIq to DCJTb and/or a direct trapping of charge carriers by DCJTb.³ Since the relative EL intensity of the NPB emitter with respect to that of the DCJTb emitter increases along with the decrease of the 24MeSAIq thickness doped with DCJTb (0.5%), it is possible to obtain a balanced white light by controlling the 24MeSAIq thickness doped with DCJTb. As the 24MeSAIq thickness doped with DCJTb (0.5%) decreases, the orange peak in EL shows a slight hypsochromic shift and the blue peak in EL shows slight bathochromic shift, and also, the turn-on voltage is decreased slightly, but the external quantum efficiency and power efficiency are increased. These photopic characteristics are expected to be due to strong hole-blocking properties of 24MeSAIq. Comparing with the device with the DCJTb (0.5%) doped-24MeSAIq thickness of 10 nm, the device with that of 5 nm showed a lower EL peak intensity in the blue EL spectrum portion while showing higher green EL spectrum portion. This is from the fact that the hole-blocking property of the 24MeSAIq layer is weakened. As the 24MeSAIq thickness is decreased, the more recombination would be expected in Alq₃ which emits green color.

Figure 2 shows the white EL spectra as a function of voltage for 10-nm-thick 24MeSAIq doped with DCJTb (0.5%) and the inset of Fig. 2 shows the CIE coordinates for corresponding EL spectra. As shown in Fig. 2, when the voltage was increased from 8 V (about 1 mA/cm² and 38 Cd/m²) to 13 V (about 100 mA/cm² and 3,360 Cd/m²), the maximum intensities of the EL spectra did not change nearly, resulting in the maximum EL peaks in the range from 448 to 451 nm for the deep blue color portion and the range

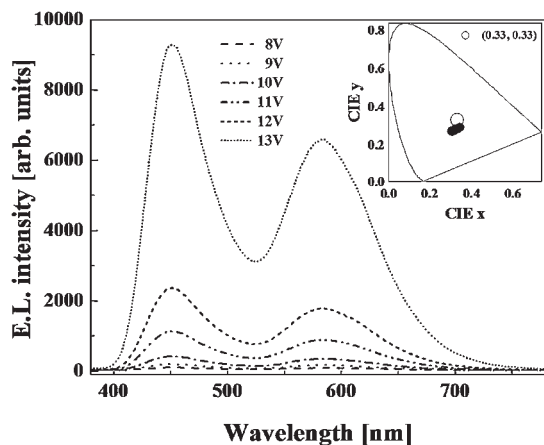


Fig. 2. EL spectra of the device composed of glass/ITO (120 nm)/2-TNATA (60 nm)/NPB (15 nm)/24MeSAIq:DCJTb (10 nm, 0.5%)/Alq₃ (45 nm)/LiF (1 nm)/Al (100 nm) as a function of the voltage. The inset shows the corresponding CIE chromaticity diagram with the coordinates of the spectra for the same device.

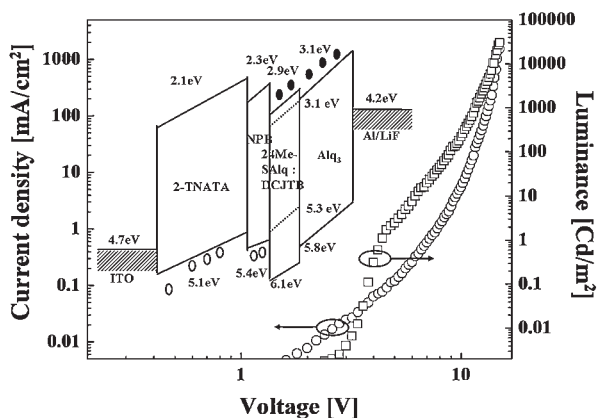


Fig. 3. The current–voltage (open circle) and luminance–voltage (open square) characteristics of the device composed of glass/ITO (120 nm)/2-TNATA (60 nm)/NPB (15 nm)/24MeSAIq:DCJTb (10 nm, 0.5%)/Alq₃ (45 nm)/LiF (1 nm)/Al (100 nm). The inset shows a schematic energy band diagram for the white light-emitting device.

between 583 and 584 nm for the orange color portion. The corresponding CIE chromaticity coordinates were in the range of (0.294–0.344, 0.288–0.261). The color shift with the increase of voltage is caused by the narrowing of the width of recombination zone in the DCJTb-doped 24MeSAIq layer with increasing current density or bias voltage.

Figure 3 shows the luminescent–voltage characteristics of the device with 10-nm-thick DCJTb (0.5%)-doped 24MeSAIq. The EL turn-on voltage at the luminance of 0.1 Cd/m² was 3.8 V and the maximum luminance was 29,700 Cd/m² at the voltage of 14.8 V and the current density of 1.57 A/cm². The luminous efficiency was 1.82 lm/W and the external quantum efficiency was 1.74% at the luminance of about 100 Cd/m² obtained at the current density of about 2 mA/cm² and the bias voltage of 8.4 V.

The inset of Fig. 3 shows a schematic energy diagram of the white OLED device with the NPB layer as the deep blue color emitter and the 24MeSAIq layer doped with DCJTb as the orange color emitter. Values of the LUMO and HOMO energy level of 24MeSAIq and other materials were quoted from the references.^{13,15,16} By using 24MeSAIq, the hole–

electron recombination in the HTL of NPB was enhanced by the HOMO energy level of 24MeSAIq (6.14 eV) relative to that of other q₂AlqOR such as BALq (5.88 eV) and SALq, as identified through the blue or white OLED devices investigated.^{12,13} In the case of LUMO energy levels, because of the similar LUMO energy level of 24MeSAIq (2.94 eV) and Alq₃ (3.1 eV), easy electron-transport from Alq₃ to 24MeSAIq is expected by hopping as shown in the inset of Fig. 3.

In summary, the white light-emitting device with the enhanced hole-blocking property was fabricated by mixing two complementary colors composed of an orange color emitter of 24MeSAIq doped with DCJTb (0.5%) and a deep blue color emitter of NPB. The blue light component of white light was obtained by confining the hole/exciton into the NPB emitter using 24MeSAIq as a strong HBL. Also, the orange-light component was obtained by the energy transfer from sky blue-emitting 24MeSAIq to the red dopant (DCJTb) or the direct trapping of charge carriers at DCJTb. Meanwhile, the white light-emitting device with 10-nm-thick 24MeSAIq doped with DCJTb (0.5%) shows the EL spectra with two peaks of around 450 nm and about 580 nm, resulting in white light emission with the CIE coordinates of (0.32, 0.28) at 100 Cd/m². The CIE coordinates was not nearly changed for the bias voltages investigated. However, the introduction of the 24MeSAIq as the HBL leads to an increase of the turn-on voltage. The device with the 10-nm-DCJTb (0.5%) doped 24MeSAIq layer as the hole-blocking material showed the turn-on voltage of about 3.8 V at the luminance of 0.1 Cd/m² and the maximum luminance of about 30,000 Cd/m² at the bias voltage of 14.8 V. The white color OLED investigated in this study should be beneficial to the development of maskless fabrication of full-color OLED displays if combined with the color filter technologies.

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