

Blue Organic Light-Emitting Diodes Fabricated by Using an Enhanced Hole-Blocking Property

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Blue-emitting organic light-emitting diodes (OLEDs) have fabricated by using a hole-blocking layer, bis(2,4-dimethyl-8-quinolinolato)(triphenylsilanolato)aluminum (III) (24MeSAlq). The device of glass/ITO/2-TNATA (60 nm)/NPB (15 nm)/24MeSAlq (20 nm)/Alq₃ (45 nm)/LiF (1 nm)/Al (100 nm) was fabricated by applying a principle confining an exciton recombination zone into a hole-transporting layer, resulting in a maximum electroluminescent peak at 446 nm originating from a 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]-biphenyl (NPB) emissive layer. Among q₂AlOR-type aluminum derivatives (q = 8-quinolinolato ligand; Al = aluminum; OR = aryloxy or siloxy ligand), 24MeSAlq with a highest occupied molecular orbital (HOMO) energy level of 6.14 eV exhibits excellent hole-blocking properties compared to bis(2-methyl-8-quinolinolato)(4-phenylphenolato)aluminum (III) (BALq) with a HOMO energy level of 5.88 eV, and it generates deep-blue light efficiently from the NPB layer.

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I. INTRODUCTION

In order to commercialize an organic light-emitting diode (OLED) display, for competitiveness with other display technologies, full color OLED materials need to be developed. Several concepts have been tried to fabricate full-color OLED display, such as the selective deposition technique forming micro-patterned RGB (red, green, and blue) subpixels by using accurate shadow masks, the down-conversion of blue emission by color changing media (CCM) [1], splitting white emission through color filters [2,3], and stacked heterostructures with separate RGB cells [4]. The light output of a blue OLED has to be improved, particularly in terms of luminous efficiency, luminance, and color purity, for full-color applications because it is much more difficult to produce a blue emission due to its intrinsic characteristic of a wide band gap. Although many blue OLED materials [5,6] have been reported until now for full-color OLEDs, only a limited number of materials are known to be applicable in term of a luminance, efficiency, and lifetime [7,8].

Since Tang and VanSlyke reported an efficient double-layered OLED utilizing tris(8-quinolinolato) aluminum (III) (Alq₃) [9], blue OLED organic light-emitting diodes (OLEDs) using many aluminum complexes based on quinoline ligands, such as q₂AlOR (q = 8-quinolinolato

ligand, OR = aryloxy ligand, and Al = aluminum) [10–12] and q₂AlOAlq₂ derivatives [13], have been developed and have been demonstrated to be useful emissive materials and/or hole-blocking/electron-transporting materials. Kwong *et al.* [14] reported on the operating stability and luminous efficiency of an orange-red electrophosphorescent device with a variety of hole and exciton blocking materials of q₂AlOR-type complexes. Especially, among these complexes, the device using BALq as an excellent hole blocker had a maximum efficiency of 17.6 Cd/A with a projected operational lifetime of 15, 000 h normalized to 100 Cd/m².

In this paper, as a hole-blocking material, the application of bis(2,4-dimethylquinolinolato) (triphenylsilanolato)aluminum (III) (24MeSAlq) is reported. The hole-blocking properties of 24MeSAlq in the fabricated blue OLEDs will be discussed through electroluminescent spectra and current density - voltage - luminance characteristics in addition to its electrochemical property induced by using a cyclic voltammogram.

II. EXPERIMENTS

Cyclic voltammetric measurements: Experiments on cyclic voltammetry were carried out in a three-electrode compartment cell with a total volume of electrolyte solution (0.1 M tetra(n-butyl)ammonium perchlorate [(n-BU)₄NClO₄] in acetonitrile) of 20 ml. All potentials were measured against a Ag/AgCl (sat. KCl) electrode (0.197

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Table 1. Optical properties of blue OLEDs with the structure of glass/ITO/2-TNATA (60 nm)/NPB (15 nm)/HBL ((20 - x) nm)/Alq₃ ((35 + x) nm)/LiF (1 nm)/Al (100 nm).

| Device | Thickness of HBL/Alq ₃ [nm] | EL λ_{max}^c [nm] | η_L at 100 Cd/m ² [lm/W] | η_{ext} at 100 Cd/m ² [%] | L_{max} [Cd/m ²] | V at 100 Cd/m ² [V] |
|--------|--|---------------------------|--|---|--------------------------------|--------------------------------|
| A | 20/35 ^a | 448 | 1.16 | 1.64 | 18,850 at 14.6 V | 7.4 |
| B | 15/40 ^a | 450 | 1.04 | 1.32 | 14,900 at 14.4 V | 7.3 |
| C | 10/45 ^a | 452 | 1.24 | 1.38 | 20,290 at 13.8 V | 6.8 |
| D | 5/50 ^a | 453 | 1.16 | 1.18 | 15,910 at 14.0 V | 6.6 |
| E | 10/45 ^b | 514 | - | - | - | - |

^a24MeSAIq and ^bBAIq complex as HBL material; ^cmaximum EL peaks at a luminance of 100 Cd/m².

V versus NHE) as the reference electrode, a platinum wire as a counter electrode, and an indium tin oxide film having the effective area of 12 mm² as a working electrode, on which a 100 nm thin film of sample was deposited by using thermal evaporation. The measurements were performed using a potentiostat (CHI660B, CH Instruments, Ltd.) under an argon atmosphere. From these onset potentials of the oxidation and the reduction of cyclic voltammograms, the electrochemical energy levels (E^{HOMO} and E^{LUMO}) and the electrochemical band gap (E_g^{CHEM}) could be calculated. According to above electrochemical data, the highest occupied molecular orbital (HOMO) level, the lowest unoccupied molecular orbital (LUMO) energy level, and the band gap of 24MeSAIq were found to be at around 6.14, 2.94 and 3.20 eV, respectively. Also, E^{HOMO} , E^{LUMO} and E_g^{CHEM} of BAIq were 5.88, 2.91 and 2.97 eV, respectively. These E_g^{CHEM} values agree with the optical band gap (E_g) of the ultraviolet-visible (UV) spectrum.

Fabrication of OLEDs: Blue OLED devices with the structure of glass/ITO (about 10 Ω/\square)/2-TNATA (60 nm)/NPB (15 nm)/24MeSAIq or BAIq (20 - x nm)/Alq₃ (35 + x nm) (x = 0, 5, 10 and 15)/LiF (1 nm)/Al were fabricated by using vacuum deposition, in which the 24MeSAIq or BAIq materials were used as a hole-blocking layer (HBL)/an electron-transporting layer (ETL), the 4,4',4''-tris[2-naphthylphenyl-1-phenylamino]triphenylamine (2-TNATA) as a hole-injecting layer (HIL), the 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]-biphenyl (NPB) as a hole-transporting layer (HTL), the tris[8-hydroxyquinolinonato]aluminum (III) (Alq₃) as an ETL, and lithium fluoride (LiF) as an electron-injecting layer (EIL). Before loading it into a deposition chamber, the ITO substrate was cleaned with detergents and deionized water and dried in an oven at a temperature of 120 °C for 2 hours. Devices were fabricated by evaporating organic layers at the rate of 0.05 ~ 0.2 nm $\text{\AA}/s$ onto the ITO substrate sequentially at a pressure below 1×10^{-6} Torr. Finally, onto the EIL layer, a 100-nm-thick aluminum metal was deposited at a rate of 0.1 ~ 2 nm/s as a cathode. The emissive active area of all devices was 2×2 mm².

Current - voltage characteristics were measured with a source-measure unit (236, Keithley Instruments, Inc.).

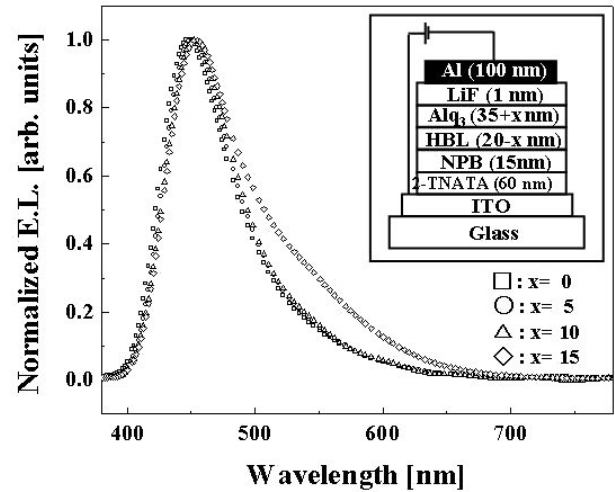


Fig. 1. EL spectra of devices composed of glass/ITO (120 nm)/2-TNATA (60 nm)/NPB (15 nm)/24MeSAIq (20 - x nm)/Alq₃ (35 + x nm)/LiF (1 nm)/Al (100 nm) at a luminance of 100 Cd/m² (open squares; x = 0, open circles; x = 5, open triangles; x = 10, open diamonds; x = 20). The inset shows a schematic configuration of the blue-emitting device.

The intensities from the blue emission of the devices were measured by using a picoammeter (485, Keithley Instruments, Inc.) to measure the photocurrent induced on the silicon photodiodes. The electroluminescent spectra of the as-fabricated blue devices were measured by using optical emission spectroscopy (PCM-420, SC Tech. Inc.).

III. RESULTS AND DISCUSSION

A blue emission can be tuned by confining an exciton recombination zone only into a neighboring HTL layer by optimizing the thickness of the HBL layer. Figure 1 shows the EL spectra for the device with various thicknesses of 24MeSAIq (20 - x nm)/Alq₃ (35 + x nm) [x = 0 (device A), 5 (device B), 10 (device C) and 15 (device D)] at a luminance of about 100 Cd/m². Also, Table 1 presents the optical properties of the devices fabricated using 24MeSAIq and BAIq (device E) as the HBL. The

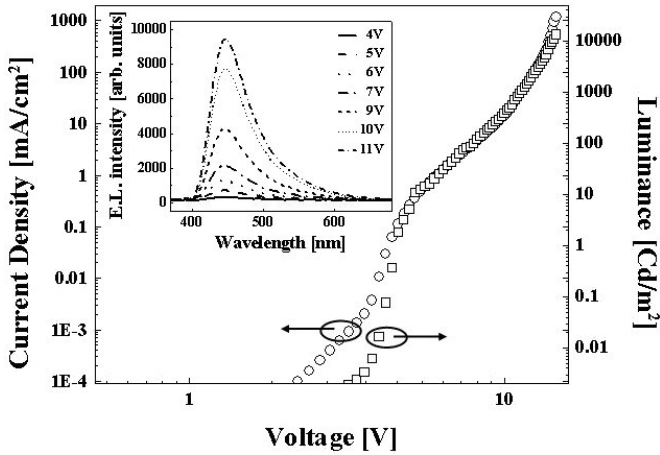


Fig. 2. Current density - voltage - luminance characteristics of the blue device with the ITO/2-TNATA (60 nm)/NPB (15 nm)/24MeSAIq (20 nm)/Alq₃ (35 nm)/LiF (1 nm)/Al (100 nm) structure. The inset shows the EL spectra obtained as a function of bias voltage for the same device.

higher E^{HOMO} of 24MeSAIq (6.14 eV) as compared to BAIq (5.88 eV) improves the hole/exciton-blocking property and efficiently confines the recombination zone into the HTL layer to function as the emissive layer, as shown in the maximum EL peak of Table 1. When the thickness of the 24MeSAIq in the device is varied, the devices with the thickness of 20, 15 and 10 nm exhibit the maximum intensity of the corresponding EL spectra at deep-blue colors of 448, 450 and 452 nm, respectively. With decreasing film thickness of the HBL (24MeSAIq), the turn-on voltage decreases, and the EL spectra show a slight bathochromic shift. For the device with 5-nm-thick 24MeSAIq (device D), the EL spectra show shoulder peaks at the green range of about 520 nm. This is attributed to exciton recombination in the Alq₃ layer as the thickness of 24MeSAIq decreases and the hole-blocking property gradually weakens in the device. By using more than 10-nm-thick 24MeSAIq, the exciton recombination was nearly restricted to neighboring NPB layer, as shown in Figure 1. Also, the device shows a real blue emission with a 68-nm FWHM (the full width at half-maximum). In addition, it was estimated that the exciton recombination did not formed in either the HBL of 24MeSAIq (PL_{max} : 461 nm) [15] or the HIL layer of 2-TNATA (PL_{max} : 480 nm) [16] due to the fact that the PL spectra of 2-TNATA and 24MeSAIq could not be moved to a wavelength with an energy higher than its EL spectrum.

The inset of Figure 2 shows blue EL spectra for bias voltages from 5 V to 12 V for the blue device (Device A) with a 20-nm-thick 24MeSAIq and a 35-nm-thick Alq₃ layer. As the figure shown, the increase in the voltage from 5 V (about 1 mA/cm² and 17 Cd/m²) to 12 V (about 100 mA/cm² and 3,160 Cd/m²) did not change the maximum peak of the EL spectra significantly resulting in the maximum EL intensities remaining be-

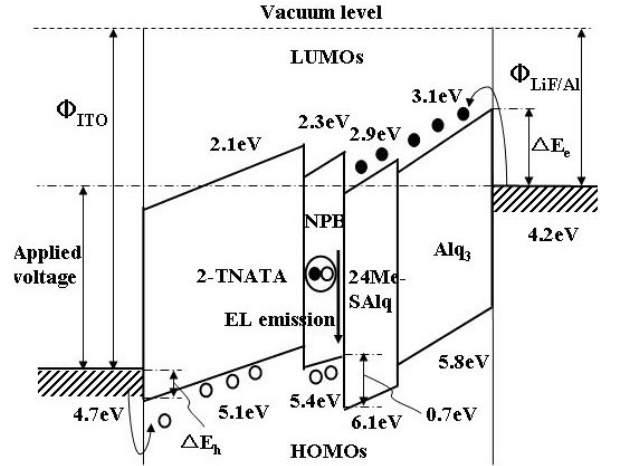


Fig. 3. Schematic energy band diagram of the blue OLED with 24MeSAIq as a hole-blocking layer.

tween 450 nm to 453 nm. The corresponding shift of the CIE (Commission Internationale de L'Eclairage) chromaticity coordinates was in the range of (0.163 ~ 0.167, 0.128 ~ 0.135). This is largely attributed to the strong hole-blocking property of the 24MeSAIq material. Figure 2 shows the current density - voltage - luminance characteristics of the blue OLED device having 10-nm-thick 24MeSAIq as the HBL. The onset voltage of the device with 10-nm-thick 24MeSAIq is 3.8 V at about 1 Cd/m². This device shows an external quantum efficiency of about 1.38 % and a power efficiency of 1.24 lm/W at a luminance of about 100 Cd/m² at a bias voltage of 6.8 V and current density of 3.50 mA/cm². The maximum luminance was 20,290 Cd/m² at a voltage of 13.8 V and a current density of 1.39 A/cm².

Figure 3 presents a schematic energy diagram of the blue device with 24MeSAIq as the hole-blocking layer. The LUMO and the HOMO levels of 24MeSAIq are values calculated from the electrochemical data measured by using cyclic voltammetry. Also, the energies of the other materials were obtained from Refs. 16-18. As we can expect from the electrochemical-energy band data, the hole-electron recombination was enhanced by the difference of E^{HOMO} between 24MeSAIq (6.14 eV) and NPB (5.40 eV). E^{HOMO} is as high as about 0.26 eV relative to that of BAIq (5.88 eV). However, due to the insignificant differences of E^{LUMO} between the HBL of 24MeSAIq (2.94 eV)/BAIq (2.91 eV) and NPB, the electron-transporting properties of the HBL through the Alq₃ electron-transporting layer (3.1 eV) starting from aluminum cathode was estimated to have a similar contribution.

IV. CONCLUSIONS

In summary, the blue device with the ITO/2-TNATA (60 nm)/α-NPD (15 nm)/24MeSAIq (20 nm)/Alq₃ (35

nm)/LiF (1 nm)/Al (100 nm) structure, which efficiently confines the exciton recombination in the HTL, shows a maximum intensity at a real blue color wavelength of 448 nm. However, in the case of the device having the same structures except for BAq as HBL instead of 24MeSAq, a green color with a broad EL wavelength of 512 nm was obtained. These differences are from the more efficient blocking property of excitons/holes in the OLED because E^{HOMO} of 24MeSAq is higher than that of BAq. Also, the higher E^{HOMO} possibly prevents diffusion of holes/excitons from the HTL, not only to the HBL but also to the ETL. This HBL property of the fabricated 24MeSAq device could be understood by using a high-energy barrier between the HBL and the HTL. The OLED device containing the 10-nm-thick 24MeSAq showed a maximum luminance of 20,290 Cd/m² at a bias voltage of 13.8 V and a current density of 1.39 A/cm².

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