Blue electroluminescent aluminum (III) tris[2-(2-hydroxyphenyl)-5-phenyl-1,3-oxazole] 

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Abstract 

Aluminum (III) tris[2-(2-hydroxyphenyl)-5-phenyl-1,3-oxazole] (Alppo3), has been synthesized as a new efficient blue electroluminescent (EL) material. Alppo3 provided good color purity, high luminance, and high efficiency of blue light-emission in an organic light-emitting device. The EL maximum wavelength is 420 nm and Commission Internationale de l’Eclairage coordinates are \( x = 0.16, y = 0.15 \) of blue color chromaticity. The luminance efficiency and the maximum luminance of Alppo3 device were 3 lm/W at 6.05 mA/cm\(^2\) (345 cd/m\(^2\)) and 13,900 cd/m\(^2\), respectively. 

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Keywords: Alppo3; Metal complex; Organic light-emitting device; Blue emission 

1. Introduction 

Organic light-emitting devices (OLEDs) are currently being pushed towards commercialization due to the potential for full color, thin flat-panel displays and light sources. To achieve full color displays, there are three primary colors required (red, green and blue). Among various emitting materials, however, current blue light-emitting materials exhibit only low efficiency compared with that of green or red ones [1–11]. In particular, the color purity requires improvement for blue OLEDs [12]. Generally, tris(8-hydroxy quinolinate) Al (II) (Alq3) is considered as one of the most excellent emitting materials for OLEDs. Its geometrical molecular structure can result in low photoluminescence (PL) quenching in condensed solid state and good stability against crystallization in amorphous thin films [13]. Therefore, in order to shift the luminance of Alq3 from green to blue region, as well as improving its efficiency, the 8-hydroxy quinoline ligand on Alq3 has been modified [14,15].

In this work, the aim is the development of a new emitting material for efficient blue OLEDs. Here, the blue electroluminescence (EL) of the aluminum (III) tris[2-(2-hydroxyphenyl)-5-phenyl-1,3-oxazole] (Alppo3) is reported. This material is synthesized based on following idea; generally, metal complexes such as Alq3, Znq2 show lower mobility for holes than electrons. Thus, a highly efficient blue OLED could be achieved if an emitting material could be provided with an electron trap. The injected holes would be efficiently recombined with trapped electrons in such an emitting material. Oxazole group is selected in this work, since the oxygen atom of oxazole group could act as an electron trap. In addition, to improve the amorphous state properties, phenyl group with a high rotational degree of freedom has been introduced at position 5 of the oxazole ring. 

2. Experimental 

2-Methoxybenzoic acid and 2-amino-1-phenylethanol were purchased from TCI and Aldrich Chemical Co., respectively. 1-Hydroxybenzotriazole (HBT) and Ethyldiisopropylamine were purchased from Nacalai tesque. Triphenylphosphine, hexachloroethane, triethylamine, and \( N,N' \)-dicyclohexylcarbodiimide (DCC) were purchased from Kanto Chemical Co. \(^1\)H-NMR spectra were measured by Varian FT-NMR GEMINI 2000 spectrometer to characterize the ligand.
2.1. Synthesis of 2-[(2-phenyl-2-hydroxyethyl)aminocarbonyl]ansiole

To CH₂Cl₂ (300 ml), o-anisic acid (8.2 g, 54 mmol), 1-hydroxybenzotriazole (HBT) (7.29 g, 54 mmol), ethyldiisopropylamine (10 ml, 54 mmol), 2-aminoo-1-phenylethanol (6.6 g, 48 mmol), and DCC (11.14 g, 54 mmol) were added at room temperature. The Na₂S₂O₃ (10 g) and saturated NaHCO₃ aqueous solution were added slowly to the mixture. The mixture was stirred for 2 h at room temperature. The mixture was filtered. The filtrate was washed with saturated NH₄Cl aqueous solution and K₂CO₃ aqueous solution. The solvent was evaporated and then purified by a column chromatographic method. Elemental analysis obtained from YANACO MT-5. The molecular weight of Alppo₃ powder was estimated using an ESI mass. Calcd. for Al₁C₄₅H₃₀N₃O₆: C, 73.46; H, 4.11; N, 5.71; Found: C, 72.98; H, 3.96; N, 5.65 for Alppo₃, m/z 736.20. 

2.2. Synthesis of 2-[(2-phenyl-2-oxoethyl)aminocarbonyl]ansiole

To a solution of 2-[(2-phenyl-2-hydroxyethyl)aminocarbonyl]ansiole (5.96 g, 22 mmol) in dichloromethane (200 ml), the Dess–Martin periodinane reagent [16] (10 g, 23.56 mmol) was added and then stirred for 70 min at room temperature. The Na₂S₂O₃ (10 g) and saturated NaHCO₃ aqueous solution were added slowly to the mixture. The mixture was stirred for 5 h at room temperature. The mixture was cooled to 0 °C. The N,N'-dicyclohexylurea was filtered out. The filtrate was washed with saturated NH₄Cl aqueous solution and K₂CO₃ aqueous solution. The solvent was evaporated and then purified by a chromatographic column using hexane/dichloromethane (1:40) as the eluant to obtain 2-[[(2-phenyl)-2-hydroxyethyl]aminocarbonyl]ansiole (colorless solid, 3.95 g, yield 93%). ¹H-NMR in CDCl₃ (δ, ppm): 8.44 (d, 1H), 7.98 (d, 1H), 7.40 (td, 2H), 7.0–7.2 (m, 2H), 4.02 (s, 3H).

2.3. Synthesis of 2-(5-phenyl-1,3-oxazolyl)ansiole

In dichloromethane (200 ml), triphenylphosphine (14.14 g, 54 mmol), hexachloroethane (12.76 g, 54 mmol), triethylamine (10.91 g, 107.8 mmol) and DCC (11.14 g, 54 mmol) were added at room temperature. The mixture was stirred for 2 h and then remained for 6 h under N₂ atmosphere. This mixture was separated using a column with eluent of CH₂Cl₂/hexane (volum ratio: 2/3) and then concentrated. Colorless solid, 3.95 g, yield 93%. ¹H-NMR in CDCl₃ (δ, ppm): 8.44 (d, 1H), 7.98 (d, 1H), 7.40 (td, 2H), 7.0–7.2 (m, 2H), 4.02 (s, 3H).

2.4. Synthesis of 2-hydroxyphenyl-5-phenyl-1,3-oxazole

In CH₂Cl₂ (100 ml), BBr₃ (1 mol solution in hexane, 44.7 ml, 44.7 mmol) and 2-[(5-phenyl-1,3-oxazolyl)ansiole (4.5 g, 17.9 mmol) were added at −78 °C. The mixture waswarmed to room temperature for 2 h and then remained for 2 h at room temperature. The Na₂S₂O₃ (10 g) and saturated NaHCO₃ aqueous solution were added slowly to the mixture. The mixture was stirred for 70 min at room temperature. The mixture was cooled to 0 °C. The N,N'-dicyclohexylurea was filtered out. The filtrate was washed with saturated NH₄Cl aqueous solution and K₂CO₃ aqueous solution. The solvent was evaporated and then purified by a chromatographic method. Elemental analysis obtained from YANACO MT-5. The molecular weight of Alppo₃ powder was estimated using an ESI mass. Calcd. for Al₁C₄₅H₃₀N₃O₆: C, 73.46; H, 4.11; N, 5.71; Found: C, 72.98; H, 3.96; N, 5.65 for Alppo₃, m/z 736.20. Tₘ 160 °C, m.p. 305 °C.

2.6. Fabrication of organic EL devices

The organic EL devices using Alppo₃ as an emitting layer were fabricated on an indium–tin oxide (ITO with a sheet resistance of 10 Ω/cm²) substrate. The organic layers and LiF were successively deposited onto ITO glass under 3 × 10⁻⁶ Torr. Aluminum cathode with a thickness of 150 nm was then deposited onto the LiF layer under 3 × 10⁻⁶ Torr. The deposition rate of organic layers and the metal cathode were 0.4 and 0.8 nm/s, respectively. 

3. Results and discussion

3.1. Characteristics of Alppo₃ OLEDs

Two types of OLEDs, device 1 and device 2, using Alppo₃ as an emissive layer have been characterized. The device structures are [ITO/TPD (50 nm)/Alppo₃ (50 nm)/LiF (1 nm)/Al] for device 1 and [ITO/TPD (50 nm)/Alppo₃ (45 nm)/PBD (5 nm)/LiF (1 nm)/Al] for device 2 (Fig. 1).

Fig. 2 shows the absorption and PL spectra of Alppo₃ in thin film state (45 nm), as well as the EL spectrum of the device 2. PL and EL spectra of device 1 are the same to the spectra of device 2.

The shapes of EL spectra of devices used in this study are independent of the driving voltage (from 3 to 16 V) or current.
density (over the range of 0.2–800 mA/cm²). The turn on voltage of devices is less than 3 V. The EL spectrum is similar to PL spectrum of the corresponding thin films. This reflects the fact that the EL spectrum originates from the Alppo₃ layer. The Commission Internationale de l’Eclairage coordinates are \( x = 0.16 \), \( y = 0.15 \). However, satisfactory performance from device 1 could not be achieved. The low EL performance of device 1 may be caused by the large electron-injection barrier and poor electron transport ability of Alppo₃ due to the existence of oxazole group. This causes the recombination of holes with electrons near the electrode. As a result, the recombination probability of carriers is reduced. The current density–voltage characteristics of two electron-only devices [Al (10 nm)/LiF (1 nm)/Alppo₃ or Alq₃ (70 nm)/LiF (1 nm)/Al], are presented in Fig. 3.

Fig. 1. Chemical structure of Alppo₃.

In an Alppo₃ device, the injection barrier for electrons is larger for about 125 meV than that of Alq₃. In fact, electron current is smaller for about one order in Alppo₃ device than Alq₃ device at about 14 V. The work functions of 50 nm thickness thin films on gold substrates, estimated by the vibrating capacitor Kelvin probe method (McAllister Technical Services, KP6500), were 4.87 eV for Alppo₃ and 4.77 eV for Alq₃. The electron affinity level was, estimated from optical absorption edge of 50 nm thickness thin films, 3 eV for Alppo₃ and 2.75 eV for Alq₃.

Fig. 2. Absorption, PL and EL spectra from Alppo₃ thin film.

Fig. 3. Electron current density–driving voltage characteristics of unipolar devices.

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Fig. 2. Absorption, PL and EL spectra from Alppo₃ thin film.

Fig. 3. Electron current density–driving voltage characteristics of unipolar devices.

Fig. 4. (a) Luminance–driving voltage and (b) luminance–current density characteristics.
In order to achieve efficient recombination of carriers in Alppo3 layer, 2-(4-biphenylyl)-5-(tert-butylphenyl)-1,2,3-oxadiazole (PBD), one of the most widely used hole-blocking materials, has been used with 5 nm thickness between Alppo3 and LiF/Al layer in device 2. This device shows a 7-fold increase in luminance at 12 V compared to device 1. The characteristics of device 1 and 2 are presented in Fig. 4.

3.2. Morphological stability of Alppo3

To investigate the effect of temperature on the morphological stability of Alppo3 film, thin films of Alppo3 and Alq3 were annealed at 200 °C for 2 h at a pressure of 1 × 10⁻³ Torr. Morphologies of the films before and after annealing were measured with an AFM using the topographical contact mode. Their AFM images are shown in Fig. 5.

The Alq3 film is rough with a RMS (root-mean-square-average) roughness of 4.53 nm. Annealing at 200 °C causes noticeable change in the surface roughness of the Alq3 film. The RMS roughness of Alq3 film reduces considerably to 2.18 nm. Furthermore, island-like features are also appeared.

However, in Alppo3 thin films, we could not find island-like features. The Alppo3 film is rough with a RMS roughness of 1.98 nm. Annealing at 200 °C causes no noticeable change in the surface roughness of the Alppo3 film. The RMS roughness of Alppo3 films reduces slightly to 1.71 nm. This morphological stability of the Alppo3 thin film is beneficial for improving the thermal durability of OLEDs.

4. Conclusion

Alppo3 has been synthesized as an efficient emitting material for a blue OLED. Alppo3 shows not only high Tg (160 °C), but also good color purity and high efficiency in OLEDs.

Our results reflect the fact that the EL efficiency and amorphous property or morphological stability of a practical material could be controlled at molecular level design by introducing a carrier trap and adjusting degree of freedom such as rotation or vibration within a molecule. However, the morphological control of a material by rotational degree of freedom may be more desirable than by vibrational one, since the energy loss via vibrational motions can cause the reduced quantum efficiency as well known in coordination complexes containing luminescent ligands [14].

Fig. 5. AFM images of (a) Alq3 and (b) Alppo3 thin films before (left) and after (right) annealing.
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