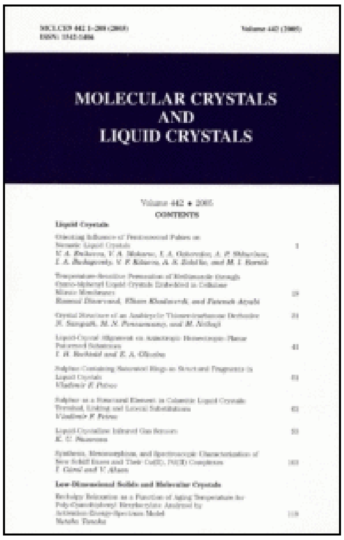
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Selective Synthesis of Facial and Meridianal Isomers of Alq_3

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Alq_3 was synthesized by mixing 8-quinolinol and $Al(OH)_3$ at about 95°C. The reaction time of 24 h leads to formation of α-phase Alq_3 which is formed by meridianal Alq_3, while the reaction time of 100 h leads to γ-Alq_3 which is formed by facial Alq_3. Unlike the conventional method, γ-Alq_3 was obtained without heating α-Alq_3 at about 400°C. The γ and α phases were determined by X-ray diffraction, and confirmed by photoluminescence spectra with vibronic structure. Organic light emitting diode (OLED) fabricated using mer-Alq_3 shows higher green Alq_3 electroluminescence and longer lifetime than OLED fabricated using fac-Alq_3.

Keywords γ-Alq_3; electroluminescence; facial; meridianal Alq_3; organic light emitting diode; photoluminescence

1. Introduction

Organic molecule tris(8-hydroxyquinoline) aluminum (Alq_3) is widely used in organic light emitting diodes (OLEDs) as electron transport material and green emitting material. The Alq_3 molecule has two isomers, one is facial and the other is meridianal (called fac- and mer-isomers, hereafter) [1–5]. The mer-isomer gives rise to green emission, while the fac-isomer gives blue emission [2,3].

Alq_3 has been synthesized by reaction of either AlO(OH), $AlCl_3$, $Al(NO_3)_3 9H_2O$, or $Al_3\ (SO_4)_3 nH_2O$ with 8-hydroxyquinolinol, which provides the mer-isomer as a major product [5]. The synthesized Alq_3 is obtained as a form of powder. The powder consists of a very large number of randomly oriented micro-size crystals or particles. Four crystalline phases (α, β, γ, and δ) have been characterized so far [3,4,6]. The γ- and δ-Alq_3 are formed by molecules of fac-isomer, while the α- and β-Alq_3 are formed by molecules of mer-isomer [2,3,7–9].

To obtain blue emission from Alq_3, it is necessary to make γ- or δ-Alq_3. The γ-Alq_3 is currently prepared by heating α-Alq_3 or $Al_3(C_6H_5Cl)_{1/2}$ under a nitrogen atmosphere at temperature between 390 and 420°C [7] or by thermal annealing of α-Alq_3 at 407 C and at 30 Mpa for 10 s [3,4]. The temperature and pressure control, however, is critical to obtain γ- or δ-phase crystal efficiently. Therefore this method is neither easy nor convenient.

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The present paper reports new synthesis method of α-Alq_3 (i.e., mer-isomer) and an easy method to obtain γ-Alq_3 (i.e., fac-isomer) without heating at high temperature like 400°C. We describe the physical and spectroscopic properties of the synthesized Alq_3 powders to confirm the formation of γ- and α-Alq_3. The synthesized Alq_3 powders dissolved in solution are also studied. Additionally we show electroluminescence (EL) characteristics of OLED devices fabricated using the synthesized γ- and α-Alq_3 powders.

2. Experimental Procedures

Alq_3 was synthesized by mixing 8-quinolinol and $Al(OH)_3$ in distilled water at about 95 C, where $Al(OH)_3$ was prepared by applying spark discharge to Al metal in distilled water. In a typical synthesis, 39.0 g (0.5 mol) of $Al(OH)_3$ was dropped gradually into 800 ml of water containing 145.2 g (1 mol) of 8-quinolinol. When the mixing ratio of 8-quinolinol to $Al(OH)_3$ was 3:1 as theoretically expected, we obtained formation of needle-shape 8-quinolinol crystal but we could not obtain Al-quinoline compound. Therefore ratio of 2:1 was finally chosen. The reaction time of 24 h leads to formation of yellow-color Alq_3 powder (called 08 powder, hereafter), while the reaction time of 100 h leads to white-color Alq_3 powder (called 07 powder). The obtained powders were dried at 110°C. The impurity contamination of synthesized powders was checked by HPLC (High Performance Liquid Chromatography) method. Appreciable contamination was not found for the two powders. Sublimation for purification was performed for the 08 powder in a horizontal glass tube at 2×10^{-2} mmHg and 330°C for 12 h. For comparison with our products, we also studied the optical properties of other Alq_3 powders which were purchased from Shin-Nittetsu (called SNT, hereafter) and Aldrich chemical companies.

The particle sizes of powder were measured with a Horiba LA-920 laser scattering particle size distribution analyzer. The 07 powder consists of micro-particles with various sizes from 1 μm to 20 μm, the majority size is about 5 μm, while the 08 powder consists of particles with sizes distributed from 1 μm to 100 μm, the majority size is about 25 μm. X-ray powder diffractions were obtained with a Rigaku-Denki RINT2500VHF X-ray diffractometer using Cu K_α radiation. Data were collected at room temperature in a 2θ range of 5–48°.

Optical absorption spectra were measured with a Shimadzu UV-3100PC spectrophotometer. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured at various temperatures between 10 K and 300 K with a Spex Fluorolog-3 fluorophotometer. The excitation source was a 450 W Xe-lamp. Filters were used to avoid the half and second harmonics of the excitation light.

PL quantum efficiency was measured with a Hamamatsu Photonics absolute internal QE measurement system which consists of Xe-lamp, monochromater, integrated sphere, and photonic multichannel spectral analyzer PMA-2. This measurement was done under 350 nm excitation. PL lifetimes were measured with a Hamamatsu Photonics streak camera under excitation with 266 nm fourth harmonic of Nd:YAG laser of 5 ns pulse width.

OLED devices with Alq_3 emitting layer were fabricated by thermal evaporation at 310°C and 2×10^{-5} Pa. The device structure is ITO/α-NPD(50 nm)/Alq_3(30 nm)/LiF(0.5 nm)/Al(100 nm), where parenthesis means the layer thickness. The 07, 08, and sublimed 08 Alq_3 powders were used in the fabrication. The EL characteristics of OLEDs were measured with a Konica-Minolta Spectroradiometer CS-1000A.

3. Experimental Results and Discussion

3.1. *X-Ray Patterns and PL Spectra of Powders*

Figure 1 shows the X-ray powder diffraction (XRD) patterns of the 07 and 08 Alq_3 powders. We compared these patterns with the XRD patterns of α-, β-, γ-, and δ-Alq_3 [1,4,7,8,10,11] and with a calculated XRD pattern for γ-phase [11]. The 07 powder exhibits quite similar XRD pattern to γ-Alq_3, while the 08 powder exhibits similar pattern to α-phase Alq_3.

Figure 2 shows the PL spectra of the 07, 08, and sublimed 08 powders at room temperature (290 K) and 12 K. The 08 powder exhibits the PL peak at 508 nm, while the 07 powder exhibits a blue shift to 498 nm at 290 K. The blue shift is clearly observed in the PL spectra at 12 K. This shift is understood as follows. The HOMO-LUMO band gap is 0.3 eV higher in fac-isomer than in mer-isomer [18], leading to blue shift for fac-isomer. The 07 powder contains γ-Alq_3 microcrystals, while the 08 powder contains α-Alq_3 microcrystals. Both γ- and δ-Alq_3 are formed by fac-isomer, while the α-Alq_3 is formed by mer-isomer [2,3,7,8]. Therefore the 07 powder shows blue-shifted PL spectrum with respect to the 08 powder.

Vibronic progression is observed in the low-energy side of the PL band for the two powders. The onset of emission appears at 420 nm for the 07 powder, and the peaks of the vibronic components appear at about 426.5, 438.5, 450, 464, 474, 484, 491 nm (PL band peak position). We suggest from the XRD measurment that this vibronic structure is due to γ-Alq_3.

The 08 powder has PL onset at about 448 nm, and vibronic components at about 455, 469, 480, 492, and 503 nm (PL band peak position). Brinkmann et al observed PL onset at 452.5 nm and vibronic components at about 456, 467, 479, 491, and 502 nm (PL band peak) for α-Alq_3 at 4.2 K [7]. These are quite similar to the vibronic structure observed for the 08 powder, indicating that the 08 powder consists of particles with α-phase. This is consistent with the result of XRD.

The PL quantum efficiency was estimated to be 26 and 32% for the 07 and 08 powders, respectively. Muccini et al. obtained the PL efficiency of 20 ± 3 and 32 ± 2% for fac- and mer-isomers solved in $CHCl_3$ solution, respectively [2]. Lower

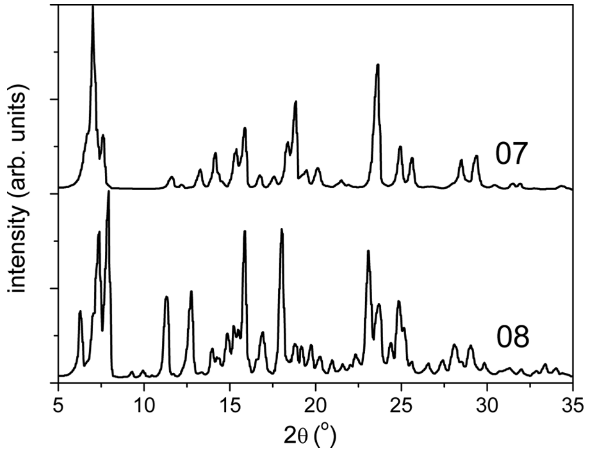

Figure 1. X-ray diffractograms of the 07 and 08 Alq_3 powders.

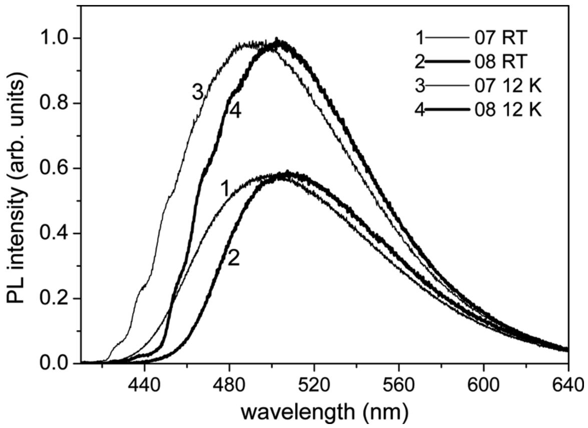

Figure 2. PL spectra of the 07 and 08 Alq$_3$ powders excited at 350 nm at 290 and 12 K.

PL efficiency for the fac-isomer than for the mer-isomer is consistent with our PL efficiency result because the 07 powder is formed by fac-isomer and the 08 powder is formed by mer-isomer.

The PL lifetime was estimated to be 13.1, 13.5, and 19.6 ns for the 07, 08, and sublimed 08 powder, respectively. These values are close to previous results obtained from evaporated neat films (e.g., 16 ns [12], 22 ns [13], 12 ns [14], 18 ns [15]). Longer PL lifetime of 19.6 ns and higher quantum efficiency of 45% were obtained for the sublimed 08 powder. This is reasonable because purification has been achieved by the sublimation for the 08 powder.

Using the PL quantum efficiency and lifetime measured from the 07 and sublimed 08 powders, the radiative lifetime of the green emitting S_1 state is estimated to be 50.4 and 43.5 ns for fac- and mer-Alq$_3$, respectively. It was found that the electric-dipole transition probability in the transition from the S_1 state to the S_0 ground state is lower for fac-Alq$_3$ than for mer-Alq$_3$.

3.2. *Absorption and PL Spectra in Liquid*

Absorption and PL spectra of the 07 and 08 powders were measured in various solvents, e.g., acetonitrile (CH_3CN), dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), and toluene ($C_6H_5CH_3$). Figure 3 shows the absorption, PL, and PLE spectra in case of actonitrile solvent. Same spectra were also obtained for the SNT powder (Fig. 3). Intense absorption bands with peaks at 384 and 257.2 nm are observed for the three samples, in addition to weak vibronic progressional componets at 331, 317, and 305 nm, which are due to quinoline molecule. The PL emission band has a peak at 522 nm. Similar spectra were obtained for the other solvents, but the PL band peak is a slightly different among different solvents, e.g., 520, 517, and 519 nm for the dichloromethane, chloroform, and toluene, respectively. Such a difference is due to the solvation effect [16,17]. The PLE spectra of the 07 and SNT powders in the solvent are the same as the PLE of Figure 3, and they are also quite similar to the absorption spectra.

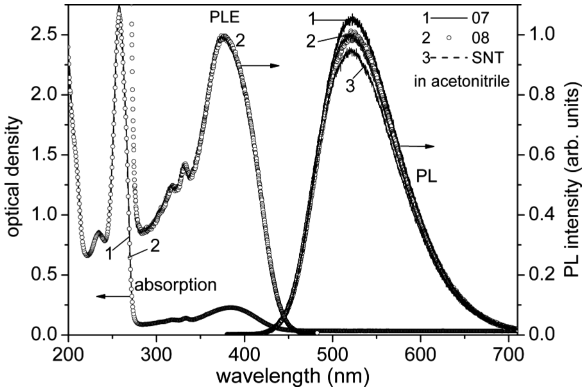

Figure 3. Absorption and PL spectra of the 07, 08, and SNT Alq_3 powders in acetonitrile solvent at 290 K, and PLE spectrum for 550 nm emission in the 08 powder in acetonitrile. The PL was obtained by excitation at 330 nm. The concentration of Alq3 is 0.056 g/l.

Unusual behavior was observed in case of toluene. The PL band peak appears at 507 and 518 nm immediately after dropping the 07 and 08 powders into toluene solution, respectively (Fig. 4). Its position never shifts for the 08 powder as time is passing, while PL peak shifts to longer wavelength gradually for the 07 powder, e.g., 511 nm after 27 min for the 07 powder, and takes a stable peak position at 518 nm after 20 h, which is the same wavelength as the 08 powder (Fig. 4). The different behavior between the 07 and 08 powders is understood as follows.

The dipole moment is estimated to be higher for fac-Alq_3 than for mer-Alq_3, i.e., 4.1 and 7.1 D [18], 4.4. and 7.9 D [19], or 5.3 and 7.9 D [20] for mer- and fac-Alq_3, respectively. On the other hand, the moment of toluene is 0.36 D. Therefore, the fac-isomer is less soluble in toluene than the mer-isomer because of higher dipole moment, which leads to aggregation by dipole-dipole interaction. The 07 powder contains molecules of fac-Alq_3 as mentioned above. As a result, it takes a time to be melted completely in toluene.

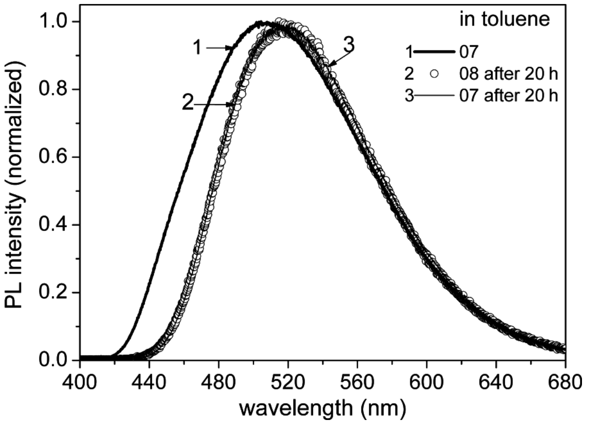

Figure 4. PL spectra of the 07 Alq_3 powders, at room temperature, immediately after solving in toluene (curve 1) and of the 08 and 07 powders after 20 h (curves 2 and 3).

The large peak shift of PL band from 507 nm to 518 nm observed for the 07 sample indicates that the fac-Alq_3 is not stable in toluene solvent and converted to mer-Alq_3 although it takes a time to complete the conversion This is consistent with a theoretical calculation that the mer-isomer is to be about 5 kcal/mol more stable than the fac-isomer [20].

We found that the PL bands of the 07 and 08 powders never change the positions into dichloromethane, chloroform, and acetonitrile solvents as time is passing. This means that these powders are more soluble in these solvents than in toluene. This is understood from dipole moments for the dichloromethane, chloroform, and acetonitrile (1.14, 1.15, and 3.44 D, respectively) which are much higher than for toluene (0.36 D).

3.3. *Solution ^{13}C and ^{1}H NMR Spectra*

The ^{13}C NMR Spectra were obtained for the 07 and 08 powders dissolved in $CDCl_3$ solvent in a spectral range of 108–160 ppm. The spectrum for the 07 sample is shown in upper figure of Figure 5, The spectrum was the same as the spectrum for the 08 sample. These spectra are identical with the spectra obtained by Kaji *et al.* [3],

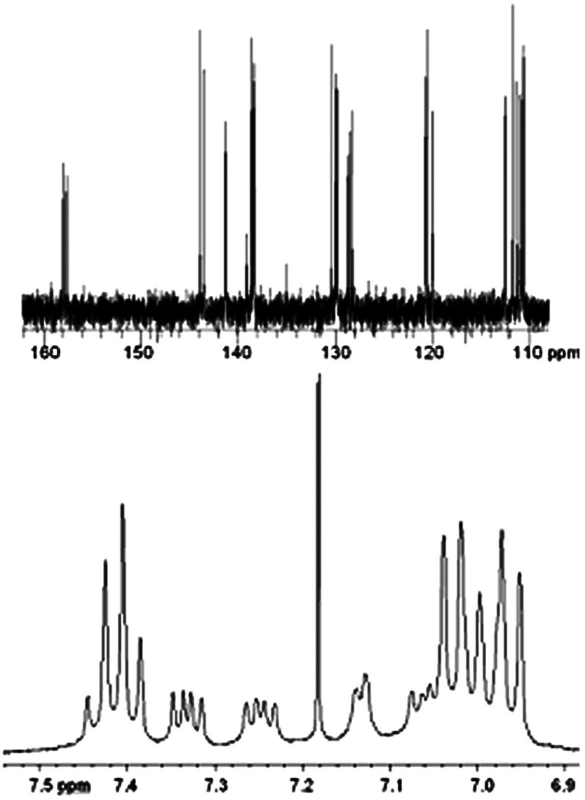

Figure 5. ^{13}C NMR spectrum (upper figure) of the 07 Alq_3 powder solved in $CDCl_3$ solvent and ^{1}H NMR spectrum (lower) at 6.88–7.54 ppm for 08 Alq_3 powder in $CDCl_3$ solvent.

who also reported that γ- and δ-Alq_3 powders become mer-isomer on dissolving them into $CDCl_3$ solution.

Lower figure of Figure 5 shows a part of ^1H NMR spectrum for the 08 powder dissolved in $CDCl_3$ solvent. Same spectrum was obtained for the 07 powder dissolved in $CDCl_3$ solvent. Our spectra are also identical to the ^1H NMR spectra obtained in $CDCl_3$ by Kaji *et al.* [3] and Utz *et al.* [21].

Our ^{13}C and ^1H NMR spectra confirm that neither Alq_3-derivative nor impurity-combined Alq_3 is formed in the 07 and 08 powders, but pure Alq_3 molecules are formed by the present synthesis method. The NMR also indicates that (1) fac-Alq_3 is converted to mer-Alq_3 in $CDCl_3$, and (2) mer-Alq_3 is stable in $CDCl_3$. Taking into account the PL results of the 07 and 08 powders dissolved in various solvents, it is concluded that fac-isomer is not present in any solvent even if the original powder contain fac-isomer.

3.4. *OLED Devices*

Figure 6 shows the layer structure of the OLED (ITO/α-NPD(50 nm)/ Alq_3(35 nm)/ LiF/Al), together with the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) energies for α-NPD and Alq_3, which were obtained from [22]. The Alq_3 emitting layer was fabricated using the 07, 08, and sublimed 08 Alq_3 powders, their OLEDs are called Devices 07, 08, and 08S, respectively.

The EL spectra are shown in Figure 7. Same green Alq_3 emission band with a peak at about 538 nm is obtained from the three devices. Since the gap of the LUMO energy between α-NPD and Alq_3 is high (0.8 eV, see Fig. 6), electrons from the Alq_3 layer are not injected into the α-NPD layer. Therefore EL from the hole-transporting α-NPD layer was not observed even at high bias voltages like 8.6 V. On the other hand, holes are easily injected into the Alq_3 layer because of small HOMO energy gap (0.4 eV, see Fig. 6) between α-NPD and Alq_3, leading to only EL emission from Alq_3.

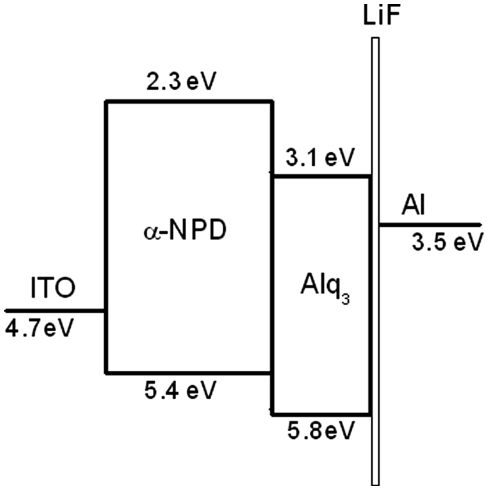

Figure 6. Schematic energy level diagram of the OLED device and its layer structure.

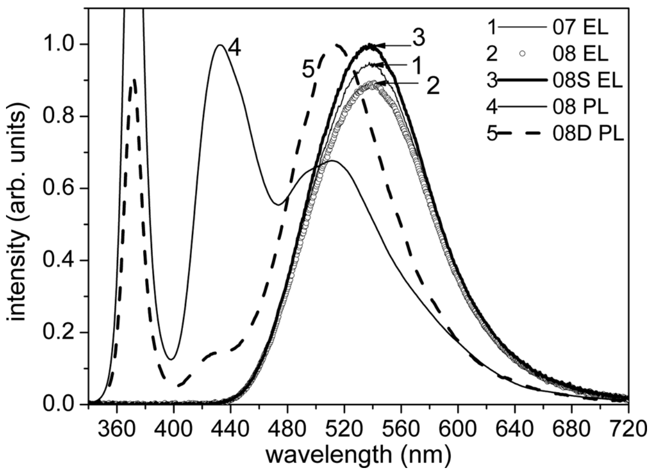

Figure 7. EL spectra of OLEDs with emitting layers fabricated using the 07, non-sublimed 08, and sublimed 08 (indicated 08S) Alq_3 powders, measured at 8.5 V, and PL spectra of active and damaged OLED 08 devices which were excited at 370 nm (curves 4 and 5, respectively). The damaged OLED 08 is named as 08D. A sharp line at 370 nm is due to LED used for photo-excitation.

Curve 4 of Figure 7 shows PL spectrum from the Device 08, which was irradiated with 370 nm LED light through the ITO layer of the device. The hole transporting layer α-NPD gives a PL peak at about 433 nm, while the Alq_3 layer gives a green emission with a peak at about 512 nm. Devices 07 and 08S show the same EL and PL spectra as Devices 08. This means that Alq_3 is converted to mer-isomer during the thermal evaporation even if the powder containing fac-Alq_3 was used in the device fabrication. This is consistent with result of theoretical computation that mer-isomer is more stable than fac-isomer in gas phase and the gas phase is principally composed by mer-isomer [19]. The Alq_3 EL peak is red-shifted relative to the PL peak. Such a peak shift has been also observed in OLED devices with TPD/Alq_3 [23,24].

Nanjundaswamy *et al.* observed the EL peak at about 528 nm from OLED of ITO/α-NPD(70 nm)/Alq_3(50 nm)/Al [25]. Bulovic *et al.* obtained an EL peak at about 530, 537, and 543 nm from OLED of ITO/α-NPD(50 nm)/Alq_3(x = 20, 35, and 50 nm)/Mg:Ag, respectively [24]. The EL peak shifts to low energy with increasing the Alq_3 layer thickness x. The peak wavelength at x = 35 nm is close to that of our OLED with x = 30 nm. These results indicate that the EL peak wavelength depends on layer thickness of α-NPD and Alq_3.

When high current density of more than 200 mA/cm^2 was applied to Device 08, this device was damaged and no EL was emitted. Curve 5 of Figure 7 is the PL spectrum from the damaged Device 08, which was excited with the 370 nm LED. The 512 nm Alq_3 emission and the 433 nm α-NPD emission are still observed. Unlike the active Device 08, however, the 433 nm emission is much weaker than the 512 nm emission. This is understood as follows.

Application of high current density gives rise to destruction of the interface between the Alq_3 and α-NPD layers, followed by diffusion of Alq_3 molecules into the α-NPD layer. When α-NPD is photo-excited, the excited energy is transferred

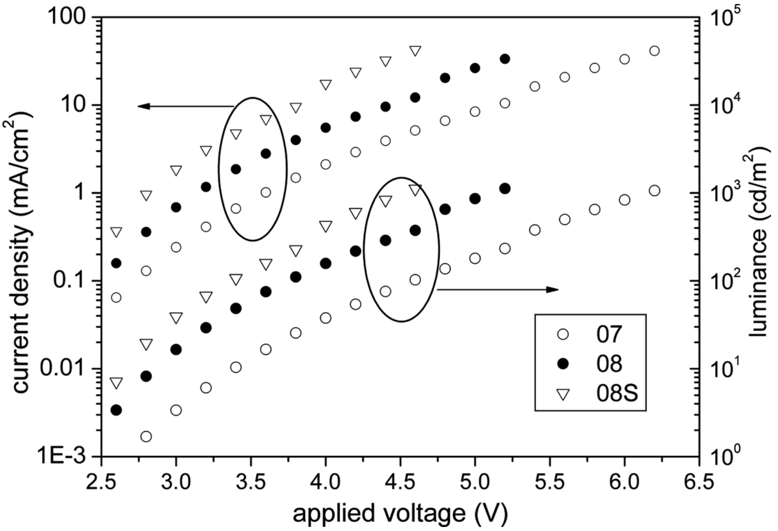

Figure 8. Current density and luminance plotted against applied voltage for OLEDs with emitting layers fabricated using the 07, non-sublimed 08, and sublimed 08 (indicated 08S) Alq_3 powders.

to neighboring Alq_3. As a result, emission from α-NPD becomes weak, while emission from Alq_3 is enhanced. Same result was obtained for Device 07. It is noted that the same 512 nm Alq_3 PL band was obtained for the active and damaged devices. From these results, we confirm presence of green-emitting mer-isomer in Device 07 although fac-Alq_3 powder was used for the device fabrication.

The current density in the V-I-L curve is much higher for the Device 08S than for the others (Fig. 8). The lowest current density was obtained for the Device 07. The highest luminance is obtained from the sublimed 08 powder, while the lowest one from the 07 powder. Figure 9 plots the EL intensities of three OLEDs against the operation time, which were measured at a current density of 25 mA/cm^2. The OLED lifetime becomes short on going from Device 08S to Device 08 to Device 07. Therefore it is suggested that, for fabrication of OLEDs with high luminance and long operation lifetime, Alq_3 powder containing γ-phase is not suitable and the sublimed powder is desirable.

4. Summary

Alq_3 was synthesized by mixing 8-quinolinol and $Al(OH)_3$ (mixing ratio is 2:1) in distilled water at about 95°C. The reaction time of 24 h leads to formation of α-Alq_3 which is formed by mer-Alq_3 molecules, while the reaction time of 100 h leads to γ-Alq_3 which is formed by fac-Alq_3 molecules. Unlike the conventional method, γ-Alq_3 was obtained without heating α-phase Alq_3 at about 400°C. The crystalline phases were determined by X-ray diffraction, and confirmed by PL spectra with vibronic structure. Presence of mer-isomer was confirmed by the ^{13}C and ^{1}H NMR measurement that was performed in $CDCl_3$ solution. The radiative lifetime of the singlet S_1 state of mer-Alq_3 was determined as 43.5 ns using the PL quantum

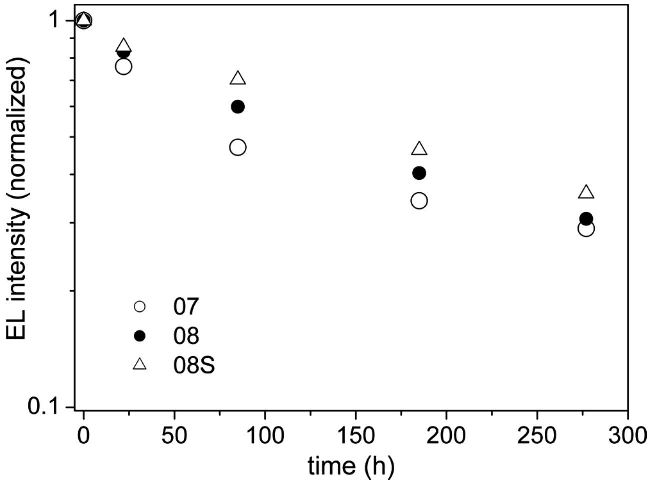

Figure 9. EL densities at current density of 25 mA/cm^2, which are plotted against applied operation time for OLEDs with emitting layers fabricated using the 07, 08, and sublimed 08 (indicated 08S) Alq$_3$ powders.

efficiency and PL lifetime. Same lifetime was obtained for the two isomers. The optical characteristics of these Alq$_3$ materials in solution are investigated. Unlike α-Alq$_3$, γ-Alq$_3$ shows poor solubility in toluene. On the other hand, both α-Alq$_3$ and γ-Alq$_3$ are quickly soluble in dichloromethane, chloroform, and acetonitrile solvents. This is explained by difference of dipole moment among α-Alq$_3$, γ-Alq$_3$, and solvents. It is concluded that fac-isomer is not present in any solvent and it is converted to mer-isomer. The OLED fabricated using sublimed α-Alq$_3$ shows higher green EL intensity of Alq$_3$ and longer OLED lifetime than the OLED fabricated using γ-Alq$_3$.

Acknowledgments

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