Improved lifetime of an OLED using aluminum (III) tris (8-hydroxyquinolate)

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Abstract

Improved lifetime with enhanced efficiency of an Alq3 based OLED was realized by the co-evaporation of hexamethylbenzene (HMB). Two different solvated crystalline systems of Alq3, Alq3(C7H8)1/2, Alq3(C2H5OH), were synthesized to investigate the effect of optically inactive materials on the emission properties of Alq3. Clathrate solvents perturb the excited electronic states of Alq3 so that the incorporated materials in OLEDs should be chemically and optically inactive to control polymorphs. HMB acts as a carrier blocker for both electrons and holes. However, Alq3 may be stabilized from Joule heat if the Joule heat is efficiently consumed as the vibrational/rotational energy of HMB. Consequently, the self-quenching and the crystallization of Alq3 are effectively suppressed by the HMB, resulting in prolonged operating time and enhanced efficiency for Alq3-OLEDs.

Keywords: Alq3; Organic EL; Lifetime; Hexamethylbenzene

1. Introduction

Luminescent organic metal complexes are a fascinating class of materials science due to their promising potential over a wide range of applications such as organic light-emitting devices (OLEDs), lasers, transistors and fluorescent sensors for the highly specific probes. In particular, great progress has been achieved in the development of OLEDs with low power consumption, excellent emissive quality, and wide viewing angle.

Alq3 is frequently used in OLEDs as the emissive or electron transporting layer. Its geometrical molecular structure provides low photoluminescence (PL) quenching and good stability for its crystallization in the amorphous thin film. Its stability in thermally deposited thin films has been attributed to the existence of two isomers, meridinal (mer) and facial (fac) [1–4]. However, the facial isomer was not found in X-ray diffraction and IR spectroscopy analyses of Alq3 [5,6]. These results seem to indicate that the amorphous phase in thin films is attributed to polymorphs composed only of mer-Alq3. Very recently, it has been reported that â-Alq3 might be composed of fac isomers [7]. Therefore, there is now some disagreement about the amorphous structure based on the isomeric mixture of Alq3 in thin films.

On the other hand, the existence of polymorphs causes an unexpected performance change in practical devices. In fact, during device operation, the morphological change of the organic layers caused by high current density resulting from Joule heating can limit the durability and shorten the lifetime of OLEDs [8–12].

In this work, the goal is to improve the lifetime of Alq3 based OLEDs without losing efficiency. First, we synthesized two different solvated systems using toluene (C7H8) and ethanol (C2H5OH), Alq3(C7H8)1/2 and Alq3(C2H5OH). These two systems show how an optically inactive material co-evaporated with Alq3 can affect the performance of an OLED.

2. Experimental

2.1. General

UV absorption spectra were recorded on a JASCO V-570 spectrometer. PL and EL spectra were recorded on a JASCO FP-6500 spectrometer. Samples were excited by 365 nm UV
light; the bandwidth of the light source was 3 nm. For the PL measurements of crystalline phases, an isolated single crystal was mounted on a quartz plate. The luminance–voltage–current (L–V–J) characteristics were measured using a Topcon BM-8 luminance meter and related circuits. In single crystal X-ray analysis, all measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation at 50 kV and 40 mA. The first sweep of data used ω scans from 130.0 to 190.0° in 5.0° step at χ = 45.0° and ϕ = 0.0°; the second sweep was performed using ω scans from 0.0 to 160.0° in 5.0° step at χ = 45.0° and ϕ = 180.0°. The data were collected at 23 ± 1 °C to the maximum 2θ value of 55°. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. The non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically. The structure was solved by direct method (SIR92) and expanded using Fourier techniques (DIRDIF99) for all crystalline systems.

2.2. Single crystal X-ray analysis of Alq3(C7H8)1/2

A yellow platelet crystal of Al1C34N3O3Al1H26, having approximate dimensions of 0.02 × 0.15 × 0.10 mm³, was mounted on a glass fiber. A total of 44 oscillation images were collected. The exposure rate was 6.7 (s/deg). Of the 19849 collected reflections, 9017 were unique (Rint = 0.039); equivalent reflections were merged. The final cycle of full-matrix least-squares refinement on F was based on 2363 observed reflections (I > 3.00σ(I)) and 406 variable parameters.

2.3. Single crystal X-ray analysis of Alq3(C2H5OH)

A yellow platelet crystal of Al1C27N3O3H18, having approximate dimensions of 0.10 × 0.20 × 0.20 mm³, was mounted on a glass fiber. A total of 15 oscillation images were collected. The exposure rate was 10.0 (s/deg). Of the 6586 collected reflections, 4141 were unique (Rint = 0.039); equivalent reflections were merged. The final cycle of full-matrix least-squares refinement on F was based on 2486 observed reflections (I > 3.00σ(I)) and 406 variable parameters.

2.4. Fabrication of organic EL devices

The OLEDs were fabricated on an indium-tin oxide (ITO) with a sheet resistance of 10 Ω/cm² substrate. The thickness of the emissive layer was 60 nm. The organic layers and LiF (0.5 nm) were successively deposited onto ITO glass under 2 × 10⁻⁶ Torr; then an aluminum cathode with a thickness of 150 nm was deposited onto the LiF layer under 3 × 10⁻⁴ Torr. The emitting area was 2 × 2 mm². N, N’-diphenyl-N, N’-bis-(3-methyl-phenyl)-[1,1’-biphenyl]-4,4’-diamine (TPD) was used as a hole-transport layer with 60 nm thickness. The deposition rate of Alq3, TPD and the metal cathode were 3 and 8 Å/s, respectively. Hexamethylbenzene (HMB) was deposited at the 0.5 Å/s for device 2, 1.0 Å/s for device 3.

3. Results and discussion

3.1. Crystal structure analysis

The crystalline systems synthesized in this work consist of mer-Alq3 isomers. Their cell parameters are summarized in Table 1 (CCDC 209267 and 209268). Alq3(C7H8)1/2. This system has a monoclinic space group P21/n. Disordered toluene molecules at a statistical inversion center are occluded in a host lattice of Alq3 molecules. The molecular packing in this crystal results in short distances of 3.5 Å between neighboring symmetrically related quinoxaline ligands along the B/B’ [202] and C/C’ [201] directions. The C/C’ links show a periodic stacking along the [100] direction via C/C’S π–π contacts. A 2D array is formed by these π–π contacts as presented in Fig. 1a. Therefore, the incorporated solvents will perturb the electronic state of Alq3 even though they are optically inactive.

Alq3(C2H5OH). This system also crystallizes in the monoclinic space group P21/n. In this crystal, Alq3 molecules are arranged with short intermolecular π–π contacts (< 3.5 Å) between symmetrically related quinoxaline ligands along the B/B’ [102] and C/C’ [101] directions. The periodic π–π links are winding up along the [001] direction; these molecular packing structures are shown in Fig. 1b. The oxygen of an ethanol can perturb the intermolecular π–π contacts due to its lone pair electron. The distance between the oxygen of ethanol and the C ligand is less than 3.8 Å. In addition, C2H5OH has rotational and vibrational degrees of freedom. Its degrees of freedom randomly perturb the electronic states of Alq3 even in a well-defined crystalline system.

| Table 1 | Crystal data for Alq3(C7H8)1/2 and Alq3(C2H5OH) |
|---------|---------------------------------------------|
| Empirical formula | C43N6O6Al1H18 | C27N3O3Al1H26 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | P21/n (no. 14) | P21/n (no. 14) |
| a (Å) | 10.737 | 11.198 |
| b (Å) | 13.761 | 13.198 |
| c (Å) | 16.849 | 16.756 |
| α (deg) | 97.632 | 94.331 |
| β (deg) | 97.632 | 94.331 |
| γ (deg) | 97.632 | 94.331 |
| V (Å³) | 2467.3 | 2469.2 |
| Z | 4 | 4 |
| F(000) | 1152 | 209267 |
| Agreement indices | R1 = 0.044, Rw = 0.066 | R1 = 0.078, Rw = 0.15 |
3.2. PL spectra of crystalline Alq$_3$-systems

Fig. 2 presents the room-temperature PL spectra of several crystalline Alq$_3$ systems. The overall shape and peak position of Alq$_3$ in the PL spectrum are critically affected by the molecular packing structure. The substantially large full width at half-maximum (FWHM) was observed in the α-Alq$_3$ and Alq$_3$ (C$_2$H$_5$OH) with respect to the β-Alq$_3$. In contrast, Alq$_3$(C$_7$H$_8$)$_{1/2}$ shows slightly reduced FWHM.

To get some physical insight into the different PL spectra in solvated systems, we performed geometry optimization and molecular orbital calculations using a Gaussian 98W package at 6-31++(d,p) level. For this calculation, we expected it to provide useful physical insights into the optical properties of these crystalline systems. The geometry of β-Alq$_3$ was prepared by a train sublimation method. The calculated results show two sets of three closely spaced molecular orbitals. These calculated molecular orbital surfaces and the energy differences between the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) are shown in Figs. 3 and 4, respectively.

In the β-Alq$_3$ structure, the HOMOs and the LUMOs of Alq$_3$ largely preserve the electronic structure of the individual ligands. These localized orbitals, however, are slightly disrupted by the clathrated solvents. We can see the increased energy difference between the HOMO and LUMO in Alq$_3$(C$_7$H$_8$)$_{1/2}$ compared with that of β-Alq$_3$. In addition, two other transitions are expected to contribute to the PL spectra, caused by the two different π–π stacking types, Q/Q' along the [001] direction and Q/S/Q' along [100] direction. There are two possible orientations for the methyl group in toluene. In Alq$_3$(C$_7$H$_8$)$_{1/2}$ I, the HOMO and LUMO sets are well localized on the individual ligands. The surface of the LUMO and the LUMO + 1, however, are extended to another ligand in Alq$_3$(C$_7$H$_8$)$_{1/2}$ II, with reversed orientation of toluene compared with Alq$_3$(C$_7$H$_8$)$_{1/2}$ I. Consequently, the optical properties of the Alq$_3$(C$_7$H$_8$)$_{1/2}$ crystal system are dependent on the orientation of the methyl group as observed in PL spectrum: blue shifted peak position and shoulder at about 490, 515 nm, respectively.

In the Alq$_3$(C$_2$H$_5$OH) system, the hydroxyl group with lone pair electrons in ethanol perturbs the π electronic states of Alq$_3$. In addition, its degree of freedom allows the π electronic states of Alq$_3$ to be randomly perturbed. Therefore, the line broadening and red shifted peak position of PL spectrum occur in this system. The geometry of the hydroxyl group in Alq$_3$(C$_2$H$_5$OH) II is rotated 60° from that in Alq$_3$(C$_2$H$_5$OH) I. In both systems, upper excited states are extended to other ligands, as shown in Fig. 3.

From the above results, toluene derivatives were selected to control the emission spectrum of Alq$_3$, because they are chemically and optically stable. However, alcohol derivatives could act as an electron trap and also coordinate with the Alq$_3$. 

![Fig. 1. Molecular packing structure of (a) Alq$_3$(C$_7$H$_8$)$_{1/2}$ and (b) Alq$_3$(C$_2$H$_5$OH) with π–π overlaps between neighboring molecules. Clathrated solvents are shown in a quadrangle. H atoms are omitted for clarity.](image1)

![Fig. 2. The PL spectra of single crystal samples for the α-Alq$_3$, β-Alq$_3$, Alq$_3$(C$_7$H$_8$)$_{1/2}$, and Alq$_3$(C$_2$H$_5$OH).](image2)
3.3. Electroluminescence (EL) control and prolonged lifetime of Alq₃ based OLED

For emission control of the OLED, the incorporated materials should be chemically and optically inactive. These requirements are demonstrated in this section. Fig. 5 describes the EL spectra from three types of Alq₃ based OLEDs.

At first, phenanthroline (Phen) was co-evaporated with Alq₃ so that its hole blocking ability would enhance the recombination probability of carriers in the Alq₃ layer. Phen’s derivative is used as a useful hole blocking material;
2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine, BCP) [13,14]. In addition, energy transfer or exciplex between Phen and Alq₃ could be possible, along with the perturbation of the electronic states of Alq₃, which could result in a blue shifted EL spectrum. The operation time for this device, however, was too short to measure any EL characteristics except the EL spectrum at D.C. 7 V. One plausible reason for this is the crystallization of Phen. The planar molecular structure of Phen enables it to crystallize in evaporated thin film. Since organic thin films prepared by thermal evaporation are glassy and amorphous, crystallization is considered to be one of the dominant degradation mechanisms. Another reason is its chemical reactivity. Because of its high current density, Phen can be coordinated to Alq₃ by Joule heating during operation of the device. Chemical reaction of the excited states can remove emissive species from the device. Even worse, such reaction products can act as a quenching center for excitons formed on nearby unaffected sites. These are limitations on durability and shorten the lifetime of OLEDs.

Next, HMB was co-evaporated with crystalline Alq₃ since HMB is chemically and optically inactive. The UV absorption and PL spectra of the co-evaporated thin film are shown in Fig. 6. The EL spectra of the OLEDs were omitted since they were quite similar to the PL spectra of corresponding thin films.

![Fig. 4](image_url)  
**Fig. 4.** The energy differences between the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) for Alq₃(C₇H₈)₁/₂ I, Alq₃(C₇H₈)₁/₂ II, β-Alq₃, Alq₃(C₂H₅OH) I, and Alq₃(C₂H₅OH) II.

![Fig. 5](image_url)  
**Fig. 5.** EL spectra from three types of Alq₃ based OLEDs: HMB is hexamethylbenzene and Phen is phenanthroline. HMB and Phen were evaporated with 1 Å/s rate, while Alq₃ was 3 Å/s rate.

![Fig. 6](image_url)  
**Fig. 6.** UV absorption and PL spectra of thin film, co-evaporated HMB with Alq₃; the evaporation rate was 1 Å/s for HMB and 3 Å/s for Alq₃. Crystalline Alq₃ was prepared by a train sublimation method for 72 h at 10⁻³ Torr.
Co-evaporated HMB prevents the closed molecular packing of Alq3 so that the Alq3 shows a relatively small Stokes shift in the thin film state. In this device, the HMB may act as a carrier blocker for both electrons and holes. In addition, Alq3 is stabilized from Joule heat if the Joule heat is efficiently consumed as the vibrational/rotational energy of HMB. Consequently, the self-quenching and the crystallization of Alq3 are effectively suppressed by the HMB. These effects were observed as the prolonged operating time and enhanced efficiency of OLED (Fig. 7).

![Graphs showing OLED operating times](image)

**Fig. 7.** OLED operating times of about 200 cd/m² (left) and 1000 cd/m² (right). The emissive layers were Alq3 for device 1 and Alq3/HMB for device 2 and device 3. The evaporation rate of Alq3 was 3 Å/s for all devices. HMB was deposited with the rate of 0.3 ± 0.2 Å/s for device 2 and 0.7 ± 0.2 Å/s for device 3.

![Graphs showing I–V–L characteristics](image)

**Fig. 8.** $I–V–L$ characteristics of OLEDs: (a) current density–voltage, (b) luminance–voltage and (c) luminous efficiency–voltage.
The measurements of $J-V-L$ characteristics and operation time were performed in air (19.8% oxygen) at room temperature without any protection of devices. For device 3, the turn-on voltage was shifted toward a higher voltage compared with that of device 2, as shown in Fig. 8. This shift reflects the way in which HMB acts as a barrier for carrier flow in a device. On the other hand, the devices are stabilized by HMB as shown by the character of the operation time.

4. Conclusion

We have investigated the effect of molecular packing structure, as well as clathrate solvents, on the light emission of Alq$_3$ in various solvated crystalline systems. The clathrate solvents perturb the LUMO set of Alq$_3$ although the electronic energy difference between the Alq$_3$ and clathrate solvent is large. Especially important, the large rotational degree of freedom of the OH group in the Alq$_3$(C$_2$H$_5$OH) crystal system creates a broader PL spectrum than that of the Alq$_3$(C$_7$H$_8$)$_{1/2}$ structure. From single crystalline systems with clathrate solvent, we can see that a lone pair electron perturbs the LUMO sets of Alq$_3$. In addition, clathrate solvents with a lone pair electron can cause the decomposition of Alq$_3$. Therefore, to control the poly-morphology of Alq$_3$ or other emitting materials, any co-evaporated materials should be inactive chemically and optically. HMB prolongs operation time without efficiency loss for Alq$_3$-based OLEDs. Co-evaporated HMB prevents the closed molecular packing of Alq$_3$ so that the Alq$_3$ shows a relatively small Stokes shift in the thin film state. In this device, HMB may act as a carrier blocker for both electrons and holes. In addition, Alq$_3$ is stabilized by Joule heat if the Joule heat is efficiently consumed as the vibrational/rotational energy of HMB. Consequently, the self-quenching and the crystallization of Alq$_3$ are effectively suppressed by the HMB. These effects were observed as the prolonged operating time and enhanced efficiency of the OLED.

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