A Novel Asymmetric Complex for Organic Electroluminescence

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As a promising technology for flat panel display, organic electroluminescence (EL) has attracted more and more attention since 1987.¹ Many emitting materials, including low-weight molecules and polymers, have been designed and utilized in fabricating organic light-emitting diodes (OLEDs).^{2–9} In order to achieve a device with good performance, the organic thin film should be amorphous and uniform. Among the organic EL emitting materials, tris(8-hydroxyquinoline) aluminium (Alq₃) has been one of the most popular and effective molecules with its excellent thermal stability and good performance forming amorphous films.

Because of the commercial prospects and the easy preparation of Alq₃, enormous research about Alq₃ and its devices has been carried out.^{10–12} Two geometric isomers of Alq₃ have been found, one possessing C₃ symmetry called 'facial' and the other possessing C₁ symmetry called 'meridianal'. In fact, only the meridianal isomer can be characterized in the solid phase.¹³ It is reasonable to think that the asymmetric isomer is more competent in forming uniform films. Our quantum chemistry calculation of these two isomers also indicated that the C₃ symmetry isomer is more unstable and tends to lose its ligands more easily. However, even the C₁ symmetry isomer may have some uncertain defect, which would result in crystallization of its thin film and a failure of the devices.¹⁴ Some incompatibilities with the hole transport materials also exist in many emitting complexes that would lead to phase separation. These facts demonstrate that Alq₃ and many other complexes used in organic EL probably have not attained the full performance for form-stable, uniform amorphous thin films.

The ideal emitting materials should possess good thermal stability and high purity. The glass transition temperature (T_g) is a key parameter for determining the stability of the amorphous materials. A high T_{g} could minimize the probability of crystallization in amorphous thin films, especially under the condition of high temperature. The T_g of Alq₃ is about 175 °C,¹⁵ far below its decomposing temperature. Therefore, Alq₃ in a sense could not reach the expected stability in amorphous films. We consider it possible to design asymmetric compounds to further improve the thermal performance and the ability to form amorphous films. Up to date, the asymmetric compounds for organic EL remain rare⁶ except for some terbium and europium complexes.¹⁶ We report here a new asymmetric aluminium complex (salicylidene-o-aminophenolato) (8-quinolinoato) aluminium (Al(Saph-q)), which has two kinds of ligands: 8-hydroxyquinoline (q) and salicylidene-o-aminophenol (Saph). The molecular structure of Al(Saph-q) is shown in Fig. 1. This complex is expected to serve as a lightemitting material in OLEDs. It is worth noting that Al(Saph-q) can readily form a stable amorphous

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Fig. 1. Molecular structure of Al(Saph-q)

glass with a high T_g of 226 °C. This thermal property of Al(Saph-q) was determined by differential scanning calorimetry (DSC).

The salicylidene-o-aminophenol ligand with a salen structure was utilized in our molecule, which has always been considered to be unstable.² However, when this structure was located at the centre of a molecule and surrounded by rigid aromatic rings, it seemed remarkably stable due to the coordination structure. Since the number of the coordination atoms of Al(Saph-q) is only five, less than that of Alq₃, the sterical block of the molecule could be decreased, thus further stabilizing the ligands. The previous asymmetric compound with а phenolato ligand, bis(2-methyl-quinolinolato)(phenolato)aluminium,⁶ was reported to be less stable than Alq₃. It is reasonable to think that the introduction of a tridentate ligand (Saph) will lead to obtaining a highly stable complex.

In our experiment, it was found that when heated Al(Saph-q), unlike Alq₃, tended to melt, even under a 1×10^{-3} Pa vacuum, and yield a bulk glass solid when the fusioned material was cooled very slowly. It was thought that the asymmetric structure could increase the interaction between the molecules and result in enhanced cohesion of this material. Therefore, Al(Saph-q) was inclined to melt rather than to sublime. This indicated the excellent ability of Al(Saph-q) to form amorphous glass, which would facilitate forming amorphous film without crystallization. In order to verify the amorphism of its films, thin films of Al(Saph-q) on quartz glass were prepared by vacuum vapour deposition, and the Xray diffraction (XRD) image was measured (Fig. 2). No crystallization signal was found in the image. An atomic force microscope (AFM) was utilized to observe the surfaces of the films. The AFM image of the surface morphology showed that the rootmean-square of the roughness (Rms, the standard deviation of the height value) was only about 1.3



Fig. 2. X-ray diffraction patterns of Al(Saph-q) thin film

Table 1. The film stability comparison of Al(Saph-q) with other light-emitting materials

| Emitting materials | Original Rms | Rms after 24 hours | Change ratio (%) |
|-----------------------|-----------------|--------------------|---------------------|
| Al(Saph-q) | 1.3 | 1.2 | -7.7 |
| Alq ₃ | 5.8 | 7.4 | 27 |
| Gaq3 | 8.8 | 12.3 | 40 |
| Znq ₂ | 5.3 | 85.7 | 1617 |

nm. This showed an excellent ability of this compound to form a uniform thin film. However, it was more important to research the stability of the amorphous films, especially the stability comparison with other emitting materials. So several conventional emitting materials were prepared and their thin films were obtained using the same process. Tris(8-hydroxyquinoline) gallium (Gag₃) and 8-hydroxyquinoline zinc (Znq₂) are popular emitting materials used in organic EL. It has been reported that the solid film of Gaq₃ could yield a very strong photoluminescence (PL) and an EL device with Znq_2 could harvest a higher brightness even than Alq_3 .¹⁷ The results of the comparison of film stability of Al(Saph-q) with other conventional emitting materials are listed in Table 1. In this experiment, AFM images of fresh films and films after storage for 24 hours were measured. Gaq₃ is analogous to Alq₃ with two isomers. It is worth noting that Znq_2 , possessing distinct C_2 symmetry, showed the worst performance. The normalized PL and absorption spectra of the film of Al(Saph-q) (Fig. 3) were also measured. That there is almost no overlap between the PL and the absorption spectra indicates almost no self-absorption in this material.

EL devices were fabricated by a conventional vacuum vapour deposition method under a 2×10^{-3}



Fig. 3. PL, EL and absorption spectra of Al(Saph-q); (a) absorption spectrum; (b) PL spectrum; (c) EL spectrum

Pa vacuum at room temperature. N,N'-diphenyl-N,N'-di(m-methylphenyl)benzidine (TPD) was used as the hole transport layer material. Two types of devices were prepared: ITO/TPD(60 nm)/Al $(Saph-q)(40 \text{ nm})/Alq_3(30 \text{ nm})/MgAg(10:1)(A)$ and ITO/TPD: Al(Saph-q) (40:1 weight)(60 nm)/ $Alg_{3}(40 \text{ nm})/MgAg(10:1)(B)$. The active area of each cell was about 40 mm². The devices emitted bright yellow light with considerable stability. It was found that Al(Saph-q) possessed excellent compatibility with TPD and there was a strong energy transfer from TPD to Al(Saph-q). The maximum brightness of device A was up to 2000 cd/m^2 and that of device B was up to 2500 cd/m^2 with the maximum wavelength of the EL emission both at around 573 nm, and the maximum luminous efficiencies up to 1.5 lm/W(A) and 1.8 lm/W(B), respectively.

In summary, a new emitting material based on a tridentate ligand with a high glass transition temperature was obtained. This material has some unique characteristics that will be conducive to forming high quality amorphous films. The potential application of such a novel complex as a thermally stable emitting material for OLEDs has also been demonstrated.

EXPERIMENTAL

Al(Saph-q) was synthesized through a reaction in the ethanol solution of q, Saph and AlCl₃. First, a solution of 8-hydroxyquinoline (0.05 M) and piperidine (0.05 M) in 100 ml ethanol was added to a solution of AlCl₃ · $6H_2O$ (0.5 M) in 10 ml ethanol

very slowly with intensive stirring. Then, a solution of salicylidene-o-aminophenol (0.01 M) and piperidine (0.02 M) in 500 ml ethanol was introduced slowly. The mixture was stirred for about 1 hour and cooled to room temperature and kept in the dark for about 10 hours. A yellow precipitate was formed when an equivalent amount of water was poured into the solution. The product was collected by filtration and washed with ethanol rapidly, then dried under an infrared lamp. The obtained product power showed strong yellow fluorescence under an ultraviolet lamp. The materials were further purified by an improved train sublimation method. The salicylidene-o-aminophenol ligand was obtained by heating the mixture of 2-aminophenol in ethanol solution and the following recrystallization. The molecular structure of Al(Saph-q) was supported by high-resolution mass spectrum (MS), nuclear magnetic resonance (NMR) and element analyses. High-resolution MS found: 382.08793, calc. for C22H15O3N2Al: 382.08981; element analysis found: C, 68.85; H, 3.83; N, 7.17, calc. for Al(Saphq): C, 69.11; H, 3.93; N, 7.33.

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