A High Thermal Stable Light-Emitting Complex Based on a Tridentate Ligand

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A new complex with a tridentate ligand, (salicylidene-*o*-aminophenolato)(8-quinolinoato)aluminum (Al(Saph-q)), bearing a high glass transition temperature of 226 °C, shows a strong potential as a stable light-emitting material for organic electroluminescence.

As a promising technology for flat panel display, organic electroluminescene (EL) has attracted more and more attentions since 1987.[1] Many organic materials including low-weight molecules and polymers have been utilized to fabricate organic light-emitting diodes (OLEDs).[2–8] In order to obtain the high performance OLEDs, organic materials are required to have good thermal stability and the ability to form amorphous thin films. For these reasons tris(8-hydroxyquinoline) aluminum (Alq_3),[1] with a high glass transition temperature (*T*g) of 175 °C,[9] has become one of the most widely used emitting materials.

We report here a new complex, (salicylidene-*o*-aminophenolato)(8-quinolinoato)aluminum (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 Figure 1 (inset). This complex was expected to serve as a light-emitting material in OLEDs. By introducing a tridentate ligand, Al(Saph-q) possesses a lower symmetry compared with Alq_3. It is considered that low symmetry will be conducive to the formation of uniform amorphous thin film. Additionally, salicylidene-*o*-aminophenol has three chelate atoms to form complex with the central metal, thus, its coordination ability is stronger than 8-quinolinoline. It is reasonable to think that the introduction of a tridentate ligand will lead to obtaining high stable complex.

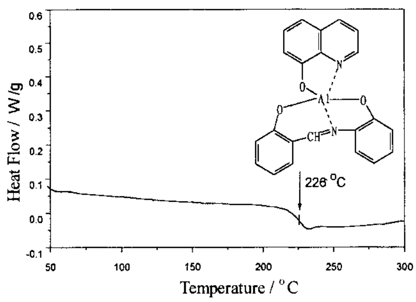

Figure 1. The molecular structure and DSC chart of (Al(Saph-q)).

A previous effort of introducing tridentate ligands has been made by Hamada.[10] A structure of salicylidene-leucine was designed, however, the solid complex could not be isolated from the reaction solution and, then, no further result was reported. In order to obtain effective solid emitting material and to improve the stability of the compounds, q and a different salen structure have been introduced in our complex. It is expected that the complex with aromatic ligand is more stable than that with alicyclic one.

Al(Saph-q) was synthesized through the reaction of the two kinds of ligands, q and Saph, with $AlCl_3$ in ethanol solution (Figure 2). After the reaction was completed, the reaction mixture was mixed with equivalent water and filtered, washed with ethanol quickly and then dried under an infrared lamp. The product was a yellow powder with strong yellow photoluminescence (PL). The molecular structure was supported by high-resolution mass spectrum (HRMS), nuclear magnetic resonance (NMR) analysis and elemental analysis. (HRMS *m/z*; M^+ found: 382.08793. Calcd. for $C_{22}H_{15}O_3N_2Al$: 382.08981. Element analysis; found: C, 68.85; H, 3.83; N, 7.17%. Calcd. for Al(Saph-q): C, 69.11 ; H, 3.93; N, 7.33%.)

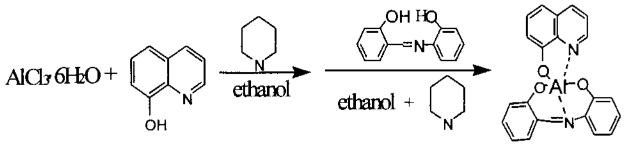

Figure 2. The schematic diagram of preparation of Al(Saph-q).

The thermal property of Al(Saph-q) was determined by differential scanning calorimetry (DSC). The DSC chart is shown in Figure 1. The DSC chart shows a well defined *T*g of 226 °C, which demonstrates that Al(Saph-q) possesses good thermal stability. In order to verify its ability to form amorphous thin films, Al(Saph-q) was heated under a vacuum of 1×10^{-3} Pa. It was found that when heated, Al(Saph-q) is inclined to form sticky liquid, and when cooled to room temperature, Al(Saph-q) is apt to form bulk glass solid. This characteristic is very different from major conventional emitting materials utilized in OLEDs, possibly due to its lower symmetry and high thermal stability. The film of Al(Saph-q) on indium-tin-oxide(ITO)-coated glass which had been prepared through vacuum vapor deposition was detected by an atomic force microscope (AFM). The AFM image of the surface morphology and its roughness analysis are shown in Figure 3. The root-mean-square of the roughness (Rms, the standard deviation of the height value) is only about 1.3 nm. The normalized photoluminescence (PL) and absorption spectra (Figure 4) of the film of Al(Saph-q) on quartz glass were also measured. The fact that there is almost no overlap between the PL and the absorption spectra indicates no self-absorption in this material.

In order to investigate the EL property of Al(Saph-q), the OLEDs have been fabricated using conventional vacuum vapor deposition under a 2×10^{-3} Pa vacuum at room temperature with *N,N*'-diphenyl-*N,N*'-di(*m*-tolyl)benzidine (TPD) as the hole transport layer (HTL) and Alq_3 as electron transport layer (ETL), respectively. The device structure was ITO/TPD(60 nm)/ Al(Saph-q)(40 nm)/Alq_3(30 nm)/MgAg(10:1). The normalized EL spectrum is also shown in Figure 4. It has been confirmed that the EL emission comes from Al(Saph-q), since the PL and EL spectra of Al(Saph-q) possess the similar shape and almost the same maximum wavelength. The maximum

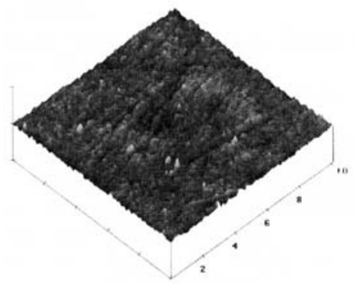

	Image Statistics	
Img.	Z range	26.892 nm
Img.	Mean	0.007 nm
Img.	Ram Mean	0.007 nm
Img.	Rms(Rq)	1.303 nm
Img.	Ra	1.008 nm

Figure 3. The AFM image and its roughness analysis of the film of Al(Saph-q).

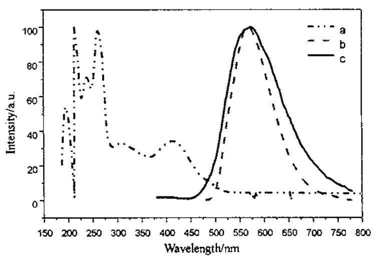

Figure 4. PL,EL and absorption spectra of Al(Saph-q).
a) absorption spectrum; b) PL spectrum; c) EL spectrum.

wavelength of the EL emission is located around 573 nm and the maximum brightness up to over 2500 cd/m^2 with the maximum efficiency up to 1.8 lm/W. It is expected that the application of Al(Saph-q) in the fabrication of OLEDs will be conducive to the improvement of the device stability. And, in fact, it has been demonstrated that the half-life time of the device with Al(Saph-q) as the light-emitting layer was considerably increased compared with the device with Alq_3 as the light-emitting layer.

In summary, an amorphous emitting material based on a tridentate ligand with high Tg was obtained. The unique characteristics of Al(Saph-q) enable it to be a fine candidate for the light-emitting material in the fabrication of high stable OLEDs. The introduction of a tridentate ligand in the complex structure opens a new route for exploring new materials for organic EL.

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