

The study of the sublimable six-coordinated aluminum quinolate with sulfonamide substituents

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Abstract

A sublimationable blue-green host materials based on tris(8-hydroxyquinolato)aluminum, meridional tris(5-*N*-ethylanilinesulfonamide-8-quinolato) aluminum, *mer*-Al(Saq)₃, was investigated and characterized by thermogravimetric analysis (TGA) and ¹H nuclear magnetic resonance (NMR). Via molecular engineering, the sublimation enthalpy of *mer*-Al(Saq)₃ can be adjusted by introducing the *N*-ethylanilinesulfonamide substituent. Its electroluminescence (EL) was also characterized by the device architecture of glass/ITO (200 nm)/CuPc (15 nm)/NPB (60 nm)/*mer*-Al(Saq)₃ (55 nm)/LiF (1 nm)/Al (200 nm). It shows a blue-green spectrum with blue-green of 1931 CIE_{x,y}(0.25, 0.39). Our experiments revealed that the Al–N bond order might not be the major issue in sublimation process.

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1. Introduction

For the development of the organic light-emitting devices (OLEDs), tris(8-quinolinolato)aluminum (Alq₃) was synthesized for the first time in 1956 [1]. After discovering the first high-efficient OLEDs by Tang in 1987 [2], Alq₃ is still the most widely used electron-transporting and host emitting material to date. This is because Alq₃ is not only thermally and morphologically stable ($T_g = 175^\circ\text{C}$) during sublimating process but also easily synthesized and purified. Due to its molecular shape, exciplex formation can also be suppressed. However, due to the limitation of its band-gap, Alq₃ can only sensitize green (such as 10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-benzo-[*l*]pyrano[6,7,8-*ij*]quinolizin-11-one, C-545T [3]) or red [such as 4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-

4*H*-pyran, DCJTB] dopants. Therefore, the wider band-gap Alq₃ derivatives are highly potential to be applied as blue host materials or other applications such as color tuning.

According to the semiempirical approach of Zerner International Neglect of Differential Overlap (ZINDO) theory [4], filled π orbitals of Alq₃ are localized in the phenoxide of the quinolate ligand, while the unfilled π^* orbitals are in the pyridyl side. Therefore, reducing electron density from the phenol ring at C5 and C7, or increasing electron density to the pyridine ring at C2 and C4 will cause Alq₃ based materials to widen their energy of the transition (blue-shift) [5]. This modification of molecular design may weaken the metal-nitrogen bond order in Alq₃ based complexes [6] and cause their thermal instability during sublimation process [7].

In our previous study, we have successfully introduced sulfonamide groups at the C5 in Alq₃ based complex as blue-green host, i.e., meridional tris(5-*N*-ethylanilinesulfonamide-8-quinolato-N₁, O₈)aluminum, or *mer*-Al(Saq)₃, for solution process [8]. Its physical and

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chemical properties were also demonstrated. The average bond length between the Al and N for *mer*-Al(Saq)₃ and Alq₃ are 2.050 Å [9] and 2.049 Å [10], respectively, in XRD analysis. It showed that the strong e-withdrawing group of the sulfonamide substitute does not affect the bond order of the Al–N bond. Although the theoretical calculations can reasonably predict and explain the feature of the modifications, but they still lack the practical experiments to calibrate their deviation. In this Letter, we will report one of sublimable Alq₃ derivatives with the sulfonamide substituent, *mer*-Al(Saq)₃ and its physical characteristics.

2. Experimental

All of the materials used in this research were commercially available. *mer*-Al(Saq)₃ was prepared as shown in previous work [8]. Its T_g/T_m and HOMO/LUMO were measured as 143/192.5°C and –3.1/–6.0 eV, respectively. ¹H NMR was recorded by a Varian Unity-300 MHz spectrometer. The *d*-solvent and the internal standard are trimethylsilylan (TMS) and CDCl₃, respectively. The thermal properties of *mer*-Al(Saq)₃ was determined from thermogravimetric analysis (TGA) at 10°C/min heating rate. Photoluminescence (PL) was carried out by Acton Research Spectra Pro-150. The thin film morphology and X-ray diffraction (XRD) were measured by the atomic force microscopy (AFM) of Digital Instruments Dimension 3100 and PHILIPS X'Pert Pro (MRD) with Cu–K_α as source, respectively. The Al(Saq)₃ layer was sublimated at the constant pressure (1.4×10^{-5} Torr) and temperature (285 °C). The emitting area of the device was 3×3 mm². Its voltage–current–luminance characteristics and EL spectra were measured by using a PR-650 opti-

cal power meter and a Keithley 2400 digital source meter under atmosphere environment after encapsulation.

3. Results and discussion

TGA was used to evaluate the feasibility of sublimating *mer*-Al(Saq)₃. As shown in Fig. 1, the weight lost of *mer*-Al(Saq)₃ at 5.0 wt% was located at 372 °C, and the charcoal yield is 40.0 wt%. The behavior of weight lost was initiated from 317.2 °C in this analysis and lower than that of Alq₃ [11]. This result suggested that *mer*-Al(Saq)₃ can be sublimated under specific conditions at 280 °C and 1.4×10^{-5} Torr. The species of *mer*-Al(Saq)₃ collected before and after sublimation were further characterized by ¹H NMR and shown in Fig. 2. The protons on the *N*-ethyl groups were detected at 1.00–1.09 ppm (–CH₃) and 3.42–3.75 ppm (–CH₂–) in the high field. All of the aromatic protons were shifted to 6.89–7.39, 8.13–8.26 (the quinolato and the phenyl rings) and 8.51–8.74 ppm (the quinolato rings) in down field. It is shown in Fig. 2a and b that these curves are almost identical, indicating that *mer*-Al(Saq)₃ can be sublimated without decomposition. Identical results before and after sublimation were also indicated in both elemental analysis and optical characteristics.

The crystallization and surface morphology of sublimated *mer*-Al(Saq)₃ films were characterized by using XRD and AFM. Their results were shown in Fig. 3. A pin-hole free surface with 1.658 nm mean roughness and 2.082 nm rms roughness could be observed. These sublimated *mer*-Al(Saq)₃ films were annealed at 60, 140, and 170 °C, respectively, before proceeding XRD analysis. Their corresponding spectra were also shown in Fig. 3. Amorphous-feature could clearly be observed

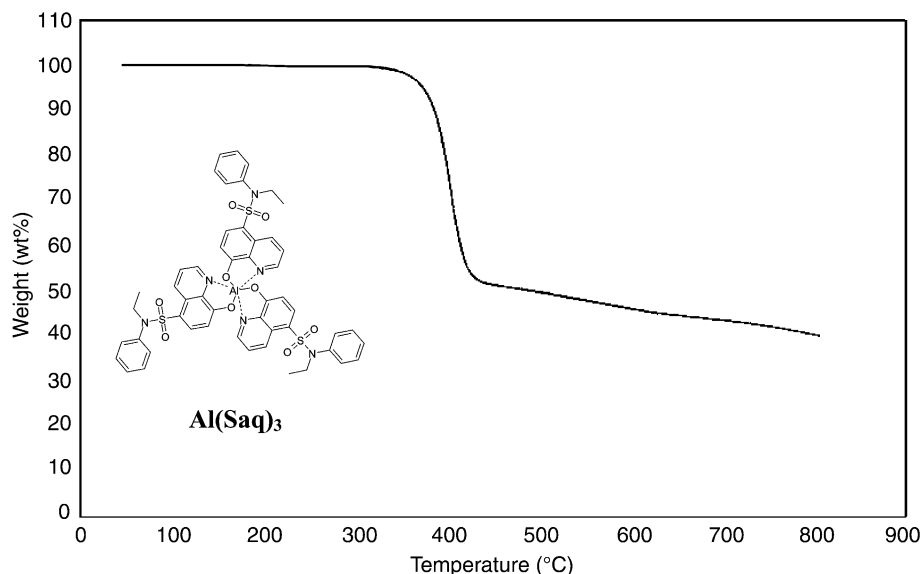


Fig. 1. TGA spectrum of *mer*-Al(Saq)₃ and its chemical structure.

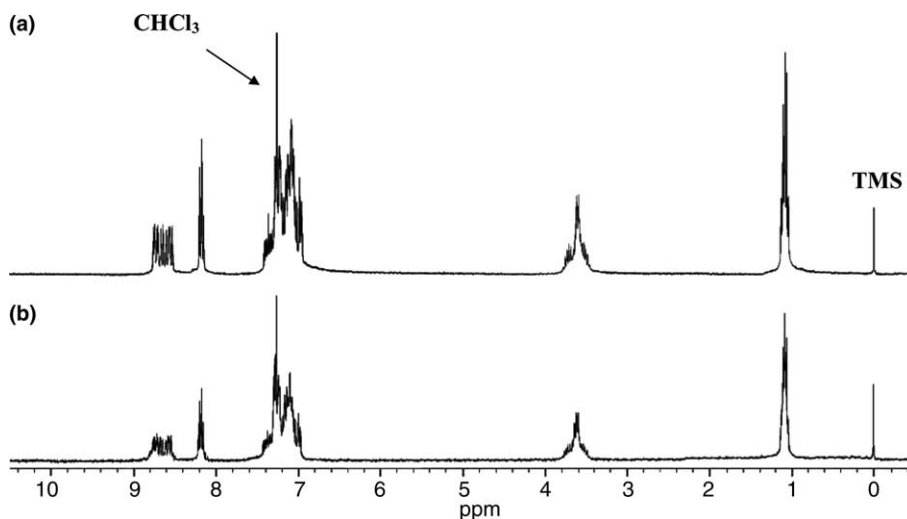


Fig. 2. ^1H NMR spectrum of *mer*-Al(Saq) $_3$ before sublimation (a) and after sublimation (b).

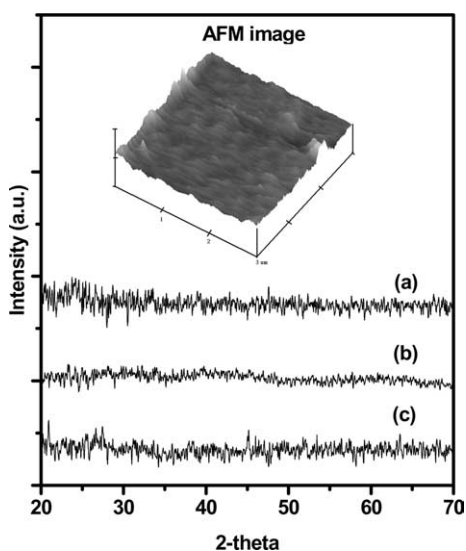


Fig. 3. XRD spectra of sublimated *mer*-Al(Saq) $_3$ films annealed at: (a) 60 °C, (b) 140 °C, (c) 170 °C for 48 h.

from these spectra, indicating that no crystalline was generated during annealing process. It could be due to the globular shape and the poor symmetric structure (C_1 symmetry) of *mer*-Al(Saq) $_3$ that the intermolecular packing was fully suppressed [12]. Even when the annealing temperature went over its T_g point (143 °C) to 170 °C.

For the electroluminescence (EL) characterization, the device architecture ITO (20 ohm/ \square)/CuPc (15 nm)/NPB (60 nm)/*mer*-Al(Saq) $_3$ (55 nm)/LiF (1 nm)/Al (200 nm) and the energy diagram of HOMO–LUMO were illustrated in Fig. 4. CuPc and NPB were used as the hole-injection layer (HIL) and the hole-transporting layer (HTL) to reduce the barrier of holes to transport from the anode to the emitting layer. The current–voltage–brightness (I – V – B) and the luminescent spectra are shown in Fig. 5. The turn-on voltage and the luminous yield are 7.4 V and 0.54 cd/A @ 20 mA/cm 2 , respectively. In comparison of those fabricated by solu-

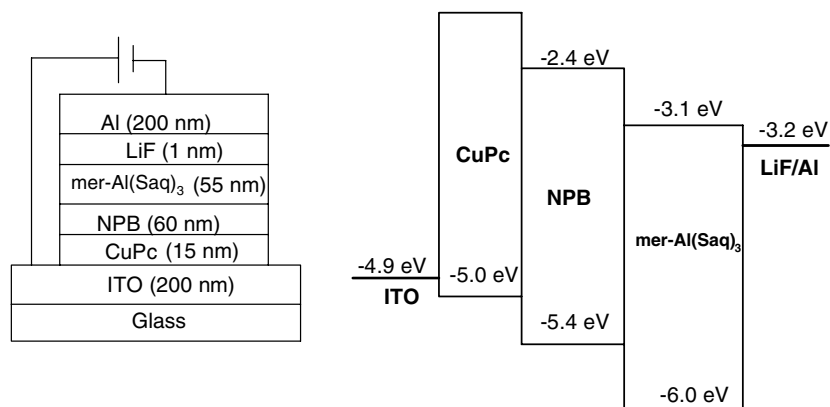


Fig. 4. The device architecture and the energy diagram.

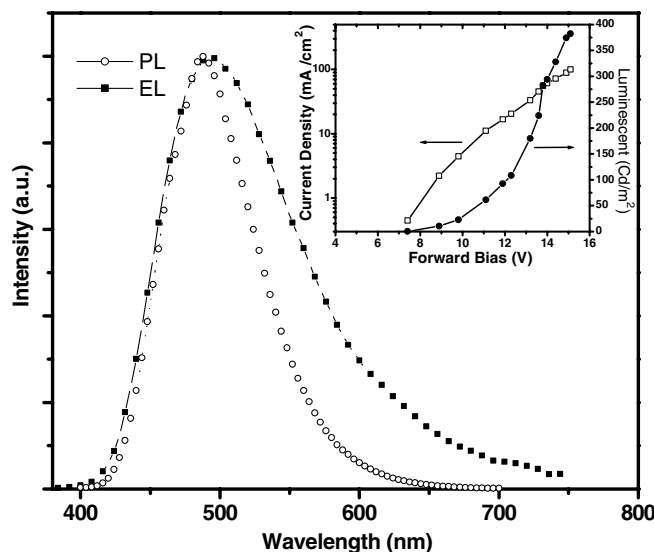


Fig. 5. EL properties of the sublimated *mer*-Al(Saq)₃ device.

tion process, the turn-on voltage and efficiency were increased due to the excitons could be confined within the emitting layer in multi-layer architecture. But the blue-green emitter still has a lower efficiency because its larger band-gap, which may form a barrier of injecting holes from the anode side into HOMO of *mer*-Al(Saq)₃. Therefore, the excitons concentrated on the interface of HOMO/NPB of *mer*-Al(Saq)₃ and cause the quenching effect. In Fig. 5, the EL chromaticity showed as the 1931 CIE coordinates was (0.25, 0.39) and its emission appeared at 496 nm. For comparison, the full width at half maximum (FWHM) of the EL spectrum shown as 116 nm was wider than that of the PL spectrum shown as 78 nm. It could be observed that a shoulder emission appeared at the longer wavelength in EL spectrum. This phenomenon could be contributed by the excitons accumulated at the interface of NPB and HOMO of *mer*-Al(Saq)₃ in which the exciplex was formed and radiated itself energy [13].

In summary, we have successfully demonstrated the feasibility of *mer*-Al(Saq)₃ in sublimation process by thermal analysis and ¹H NMR. We also found that the Al–N bond order may not be the major issue in sublimation process. In our point of view, the sublimation enthalpy [14], molecular polarity [15], and molecular weight should be considered in this kind of six-coordinated aluminum complex.

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