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

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Received 31 July 2004; in final form 25 August 2004
Available online 25 September 2004

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 substitutent. 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 (Tg = 175 °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-1H,5H,11H-benzo[7]pyrano[6,7-ij]quinolizin-11-one, C-545T [3]) or red [such as 4-(dicyanomethylene)-2-t-butyl-6-(1,1,7,7-tetramethyljulolidylid-9-eny)-4H-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, O3)aluminum, or mer-Al(Saq)3, for solution process [8]. Its physical and
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 derivates 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 C176/C0 3.1/C0 6.0 eV, respectively. 1H NMR was recorded by a Varian Unity-300 MHz spectrometer. The d-solvent and the internal standard are trimethylsilian (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–Kα as source, respectively. The crystallization and surface morphorology 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.

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 ppm (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.

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Fig. 1. TGA spectrum of mer-Al(Saq)₃ and its chemical structure.
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 (C₁ 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/□)/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 luminescent yield are 7.4 V and 0.54 cd/A @ 20 mA/cm², respectively. In comparison of those fabricated by solu-
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 $^1$H 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.

Acknowledgements

The authors thank Mr. Chung-Kuang Chou, Department of Materials Science and Engineering, National Chiao Tung University, Taiwan for AFM measurement. This work was supported by the MOE Program for Promoting Academic Excellence of Universities under the grant number 91-E-FA04-2-4-B and the National Science Council of Taiwan, Republic of China under the grant numbers NSC 92-2215-E-009-045 and NSC 92-2623-7-009-006.

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