Journal of Luminescence 129 (2009) 1192–1195

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Synthesis and electroluminescent property of dinuclear aluminum 8-hydroxyquinoline complex

Guang Wang [a,*], Yi He [b], Li Yang [a], Bin Qi [a]

[a] Faculty of Chemistry, Northeast Normal University, Changchun 130024, PR China
[b] College of Chemistry, Jilin University, Changchun 130022, PR China

ARTICLE INFO

Article history:
Received 27 September 2008
Received in revised form
21 May 2009
Accepted 27 May 2009
Available online 6 June 2009

Keywords:
Electroluminescence
OLED
Dinuclear aluminum 8-hydroxyquinoline
Alq_3

ABSTRACT

A new structural dinuclear aluminum 8-hydroxyquinoline complex ($DAlq_3$) with two aluminum chelate-center was designed and synthesized. It was assessed as light-emitting material in organic light-emitting device (OLED). The green light emission was observed in films and OLEDs. $DAlq_3$ has better electron mobility and also shows a higher electroluminescence (EL) efficiency than that of aluminum 8-hydroxyquinoline (Alq_3).

1. Introduction

Organic-metal complexes have been studied in the past few years due to excellent electrical and optical properties. Especially, the use in light-emitting diodes has shown to be a field of potential application [1–5]. Aluminum 8-hydroxyquinoline (Alq_3) is a typical representative with high emitting efficiency and excellent electron-transporting ability [1]. Much work has been done to modify 8-hydroxyquinoline to fabricate new aluminum complexes for getting better properties. Introduction of benzene ring at 5-position or 3-, 4-position of 8-hydroxyquinoline causes bathochromic shift of the emission of the complex [6,7]. Many papers reported that different alkyl substitution at the 2-, 4-, 5- or 7-position of 8-hydroxyquinoline do not cause much change in the emission color or the efficiency of the complex [8–13]. If the carbon atom of 4- or 5-position in 8-hydroxyquinoline ring was substituted by nitrogen atom, the emitting color of complexes shifts to blue or red range, respectively [14,15]. The pentacoordination aluminum 8-hydroxyquinoline complexes, Alq_2L, can emit blue light, where q is "2-methyl-8-hydroxyquinoline" and L is phenolato ligand or hydroxyl [16–18]. Although these complexes exhibit high photoluminescence (PL) efficiency and color-tunability, their molecules tend to form aggregation in film, which leads to exciton quenching and low-emitting efficiency. Big size of molecule is anticipated to reduce molecular aggregation and increase the emitting efficiency. However, to the best of our knowledge, there is no report about the relationship of the LED efficiency and molecule size of Alq_3.

In this paper, we report the design and synthesis of a dinuclear aluminum 8-hydroxyquinoline complex ($DAlq_3$), and its emission (photoluminescence and electroluminescence (EL)) characteristics in solution and in the solid state. We also compare its electron mobility and EL performance to that of the Alq_3. The molecular structures of $DAlq_3$ and Alq_3 are shown in Scheme 1.

2. Experiment

^1H NMR spectra were recorded on a Varian 400 MHz spectrometer. The element analysis was carried out on Elementar Analysensysteme Gmbh Varioel. UV and PL spectra were measured with a Varian Cray50 and Perkin-Elmer Ls50B Luminescence Spectrometer, respectively. A Agilent 8114 A 100 V/2 A pulse generator and Agilent Model 54815 A digital oscilloscope were used to carry out the transient EL experiments

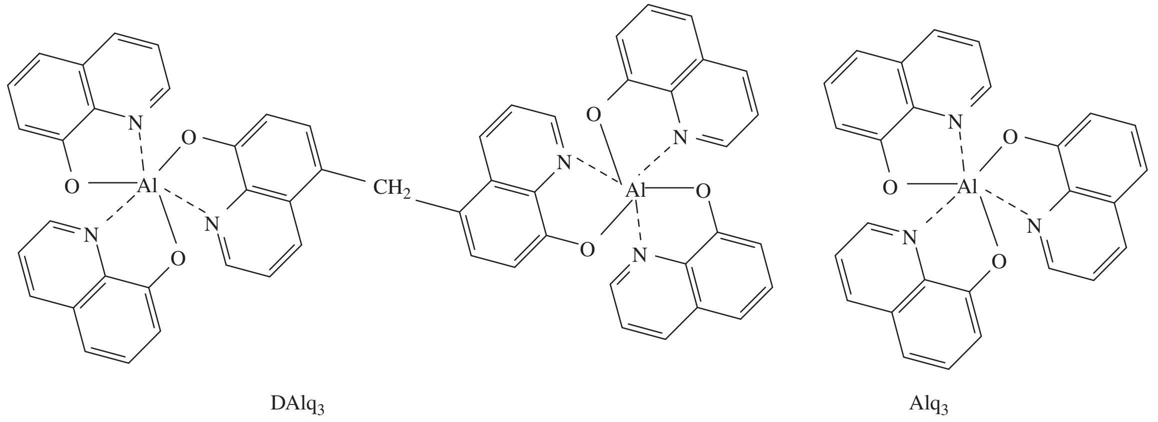
2.1. Synthesis

The 5,5′-methylene-bis-8-hydroxyquinoline a mixture of 8-hydroxyquinoline (29 g, 0.2 mol), formaldehyde (9 mL, 37% aqueous solution) and concentrated hydrochloric acid (85 mL) was heated to reflux for 90 min. After cooled to room temperature, the yellow precipitate was collected and redissolved in water, the mixture was neutralized with diluent ammonia to pH = 7,

---

[*] Corresponding author. Tel.: +86+431+85099544; fax: +86+431+85098768.
E-mail address: wangg923@nenu.edu.cn (G. Wang).

0022-2313/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2009.05.018



Scheme 1. Molecular structures of $DAlq_3$ and Alq_3.

the precipitate reappeared and was collected by filtration. The crude product was purified by recrystallization from DMF, white solid, yield, 10.1 g (33.4%). Mp 216–217 °C. ^1H NMR (δ, DMSO): 4.68 (s, 2H), 6.94–7.10 (m, 4H), 7.53–7.57 (d, 2H), 8.43–8.50 (d, 2H), 8.85–8.90 (s, 2H), 9.67 (s, 2H).

$DAlq_3$ a solution of 5,5′-methylene-bis-8-hydroxyquinolinol (1.51 g, 5 mmol) in 40 mL purified DMF was added dropwise into a stirring benzene (40 ml) solution of triethylaluminum (1.14 g, 10 mmol) under a nitrogen atmosphere at room temperature. The reaction mixture was stirred for 2 h and a pale yellow solid appeared. The precipitate was a diethyl aluminum compound [18]. Afterwards, a benzene solution (35 mL) of 8-hydroxyquinoline (2.9 g, 20 mmol) was added into the above mixture and the reactor was continuously stirred for 24 h. The product was collected by filtration and washed with benzene for twice. The crude product was then purified by the train sublimation method. Elemental analysis ($C_{55}H_{36}N_6O_6Al_2$): calculated: C. 70.97; H. 3.87; N. 9.03. Found: C. 71.02; H. 3.78; N. 9.09. $DAlq_3$ can dissolve in polar solvent such as $CHCl_3$, CH_2Cl_2 and THF.

Alq_3 was synthesized according to reported method [12] and purified by the train sublimation.

2.2. Preparation of organic light-emitting device (OLED) and complex films

N,N′-di(naphthalene-1-yl)-*N,N′*-diphenyl-benzidine (NPB) was used as a hole-transporting material to fabricate double-layer electroluminescent devices. Electroluminescent devices have a structure of ITO/NPB (80 nm)/$DAlq_3$ or Alq_3 (80 nm)/Mg:Ag (100 nm). The fabrication procedure is as follows: first, NPB was vapor deposited onto ITO-coated glass substrate at a deposition rate of 3–4 nm s^{-1} at 1×10^{-4} Pa, then a layer of $DAlq_3$ or Alq_3 was vapor deposited on the NPB. Finally, last Mg/Ag alloy was vacuum deposited onto the organic layer at 1×10^{-5} Pa.

The complex films for absorption and photoluminescence spectra measurement were fabricated by vapor deposition onto quartz plates.

3. Results and discussion

3.1. Electron mobility of complexes

Transient EL is common method to measure mobility of organic (JAP-89(7), 3711 (2001)). For the transient EL experiment, an Agilent 8114 A 100 V/2 A programmable pulse generator was used to apply rectangular voltage pulse to the devices. The repetition rate of the pulse was 1 kHz, and the pulse length was 5 μs. The time-dependent EL signals were detected by the 50 Ω input resistance of a digital oscilloscope (Agilent Model 54825 A, 500 MHz/2 Gs/s) together with a photomultiplier (time resolution ≅0.65 ns) located directly on top of the emitting devices.

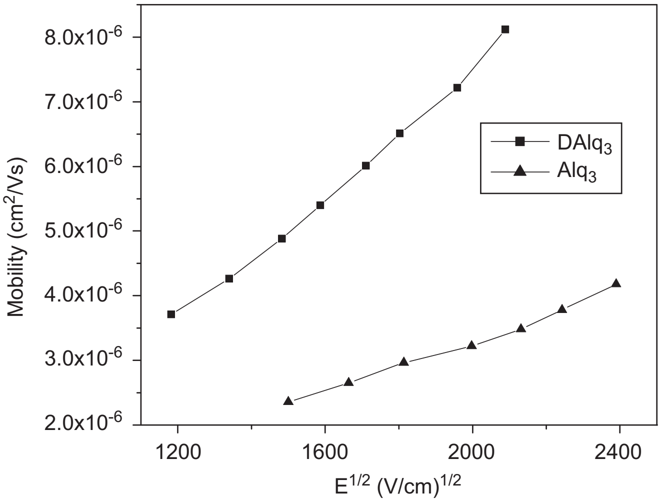


Fig. 1. Electron mobility of complexes as a function of the square root of the bias field.

Generally, the charge carrier mobility μ is given by $\mu = L/(t_d F)$ with $F = V/d$, where F is the electric field, L the thickness of the active material, V the applied voltage, t_d is the delay time. For the case of NPB/$DAlq_3$ double device, because the entire electric field almost drops across the $DAlq_3$ layer, as described in steady-state characteristics, under this condition, d may be considered to be the thickness of the $DAlq_3$ layer. Thus, the electron mobility in $DAlq_3$ can be determined and is in the range 3.71×10^{-6} and $8.11\times10^{-6}\,cm^2/V\,s$ at electric fields ranging between 1182.0 and 2089.1 $V/cm^{1/2}$. Fig. 1 shows the electron mobility of the $DAlq_3$ as a function of the square root of the bias field. It can be seen that the electron mobility in $DAlq_3$ shows an increase with the square root of the electric field. This kind of field-dependent mobility is typical in EL organic materials [19].

Fig. 1 shows the electron mobility of $DAlq_3$ and Alq_3 as a function of the square root of the bias field. It can be seen that at the same square root of the electric field, the electron mobility of $DAlq_3$ is as two times as that of Alq_3, which indicates that the