

Study of tris{2-(benzimidazol-2-yl) quinolinato} Aluminum

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Abstract: An emission material, tris(2-(benzimidazol-2-yl) quinolinato) Aluminum (**AIBIQ**) used for organic light emitting devices, has been synthesized. The decomposition temperature was observed at 436°C and no melting transition (T_m) of **AIBIQ** was observed up to 430°C. The emission spectrum of organic emitting device using **AIBIQ** as emitted layer exhibits a broad maximum at 596 nm. The color of the emitted light is in the orange region in the CIE coordinate of $x = 0.46$ $y = 0.46$.

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Keywords: Electroluminescence; orange light; device

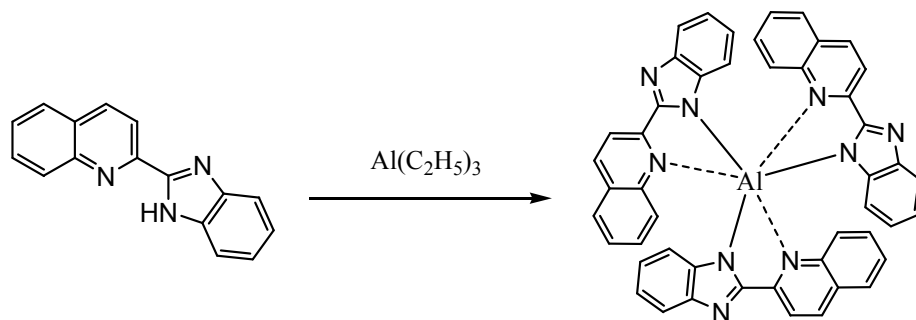
1. Introduction

Since an organic light emitting diode was reported by Tang and Vanslyke [1], LEDs based on organic or polymeric materials have generated considerable interest and enabled the development of low-cost, full-color, flat-panel displays along with other emissive products [2–5]. Luminescent chelate complexes have been shown to be particularly useful in electroluminescent (EL) displays because of their relatively high stability and volatility. The most well-known example of such chelate compounds is Alq_3 , not only a good emitter but also a highly efficient electron-transporting material, where q is the 8-hydroxyquinolinato ligand [6, 7]. Via the modification of the ligand of metal chelate compound, the emission color of a metal chelate compound may be tuned. Other properties, such as thermal stability and carrier mobility, may also be improved upon. In the present work, we report the synthesis and electroluminescent (EL) property of tris(2-(benzimidazol-2-yl) quinolinato) Aluminum (**AIBIQ**). The **AIBIQ** containing N,N-bidentate ligand instead of N,O-bidentate one such as

8-hydroxyquinoline [8]. Therefore, the thermal stability, an important character for the practical application in the electronic fields, of this metal complex is investigated by thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The organic emitting device using **AIBIQ** as emitting layer has been fabricated to study the electroluminescent property of this metal complex.

2. Experimental

The synthesis of the title compound was accomplished by following processes, as shown in Scheme 1. The triethylaluminum solution (25% w/w in hexane 1.37ml, 3×10^{-3} mole) was slowly added to 100 ml of THF solution containing benzimidazol-2-yl-quinoline [8] (2.45g, 10×10^{-3} mole) at 0°C under N_2 . After the resulting mixture was stirred at room temperature for 6 hours, 5 ml isopropyl alcohol was added to quench the reaction. The solvents were removed under vacuum condition at 5×10^{-3} Torr, and the residual solid was sublimed to purify the final product. Light green of



Scheme 1. Synthesis process for the AIBIQ complex.

AIBIQ was obtained in 75% yield. The formula of this compound has been determined by ^1H NMR and elemental analysis. The organic light emitting device, Fig. 1, using **AIBIQ** as the emitting and electron-transporting layer were fabricated on the transparent conductive indium-tin oxide (ITO) glass substrate. The organic layers and the cathode were sequentially deposited by conventional vacuum vapor deposition in the same chamber without breaking the vacuum under 3×10^{-6} Torr. In the present work, the N,N' -bis-(1-naphthyl)- N,N' -diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) was used as the hole-transport material (HTM), and tris (8-quinolinolato) aluminum (Alq_3) was employed as the electron-transporting material (ETM). The EL spectrum and the Commission Internationale de l'Eclairage (CIE) co-ordinates were measured by Pro-650 Spectroscanner (step size is 1.0 nm and bandpass is 4nm), the current-voltage (I-V) characteristic was measured by Keithley 2400 Source meter.

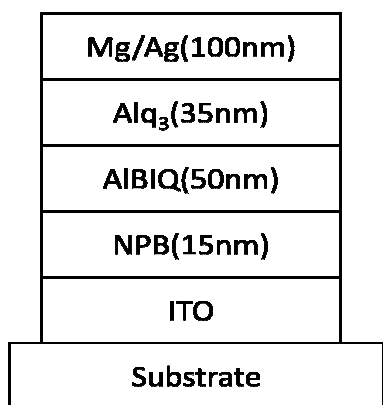


Fig. 1. The organic light emitting device (OLED) structure and molecular structures of **AIBIQ** and NPB.

Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer thermo-gravimeter (Pyris 1) under a dry nitrogen gas flow at the heating rate of $20^\circ\text{C}/\text{min}$. Glass transition temperature (T_g) and melting point (T_m) of materials were determined by differential scanning calorimetry of the Perkin-Elmer differential scanning calorimeter (DSC-7).

3. Results and discussion

Fig. 2 shows the TGA of **AIBIQ** that possesses a maximum rate of weight loss occurring at 501°C and no weight loss was observed at the temperature lower than 362°C . Above 600°C , there is about 16 wt % of residue composed of zinc ash. This aluminum complex is reasonably stable upon exposure to air and exhibited a very high thermal stability in nitrogen, which is attributed to the fact that the Al-N bond is highly

polarized [9, 10]. The melting temperature (T_m) of **AIBIQ** was not observed up to 436°C with DSC curve. The DSC and TGA results indicate that the **AIBIQ** possesses a very high thermal stability, which may serve as an advantage for the fabrication of organic light emitting device because the use of the materials with high thermal stability as the active emissive layer or carrier transporting layer may provide the device with greater longevity [11, 12].

The Photoluminescent (PL) spectra of the **AIBIQ** solutions and neat film, excited with 406 nm laser line, were illustrated in Figure 3. At low concentration, 5×10^{-5} M in DMSO, only one emission band is observed with maximum at 406 nm, corresponding to the relaxation of **AIBIQ** from the excited state of a single molecule into ground state. Besides the 460 nm band, a new emission band appeared while the concentration of **AIBIQ** increased from 5×10^{-5} to 1×10^{-3} M. This new emission band having a maximum at 470 nm is observed in the spectrum of the **AIBIQ** neat film. We have assigned this new emission band to the excimer and higher aggregates emission [13, 14] resulting from the relaxation of collision complex into the lower energy state.

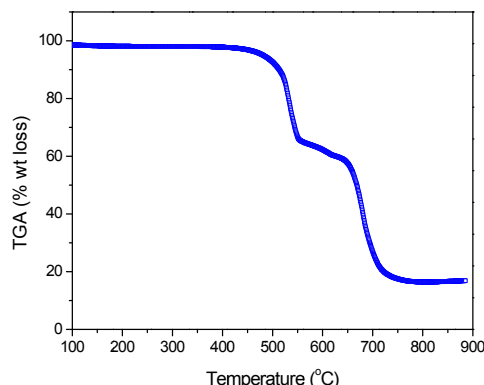


Fig. 2. TGA curve of **AIBIQ**.

The EL spectrum of organic light emitting device at the bias voltage of 12 V, Fig. 4, shows the broad emission band in the 500-700 nm region with the maximum at 570 nm. The emission is almost fixed in the orange region in the CIE coordinate of $x = 0.46$ $y = 0.46$. For the small molecular organic materials, to develop the new type of material with red emission is very important because this kind of material is very seldom prepared so far, and it is very important for the fabrication of full color display panels. The change of the spectral wavelength may be achieved also by general conception of search and design of modified materials for wide band emission consists in substitution of the backside groups by electron

acceptors like halogens etc. and different kind of donors [15, 16].

At the same time important role here may play electron-vibration interactions determining the spectral broadening of the emission lines. So the future strategy of the materials design may be in this way also.

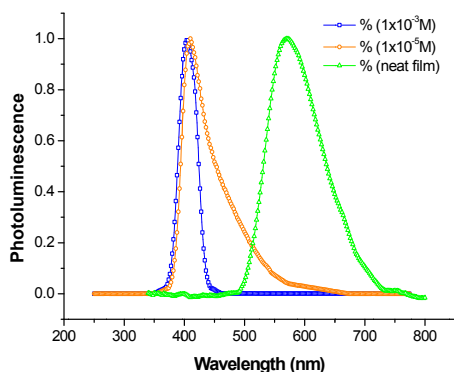


Fig. 3. Photoluminescent spectra of the AIBIQ in solutions and neat film.

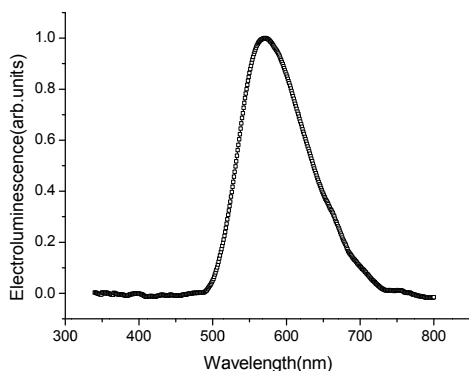


Fig. 4. EL spectrum of OLED fabricated in this work

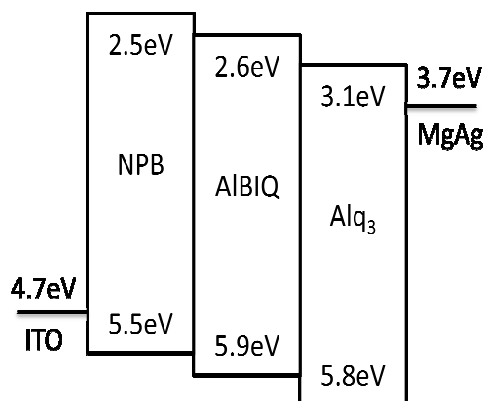


Fig. 5. Energy level diagram of OLED materials, ITO, and Mg-Ag alloy.

Figure 5 shows the energy level diagram of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the different organic materials and the work function of cathode and anode. The LUMO energy of AIBIQ is 2.6eV determined from the HOMO energy (5.9eV) obtained from the cyclic voltammetry (CV) method and the optical band gap estimated from the absorption onset. Comparing the energy level of AIBIQ with NPB, it is clear that the AIBIQ has the much higher hole injection barrier than that of NPB; in fact, it is impossible for the hole injection from ITO into AIBIQ without the assistance of NPB or some other kind of HTLs. This diagram also pointed out that the Alq₃ has the lower electron injection barrier than that of AIBIQ, so the electron injection from the MgAg into AIBIQ will be enhanced and confines the recombination zone at the interface between NPB and AIBIQ. Fig. 6 shows current-voltage and luminance-voltage characteristics of this device having a low turn on voltage of about 5.5V for current and luminance. This device shows a brightness of 1580 cdm⁻² at the driving voltage of 12V with current density of 196 mA/cm², decaying to 60 cdm⁻² in 120 hours.

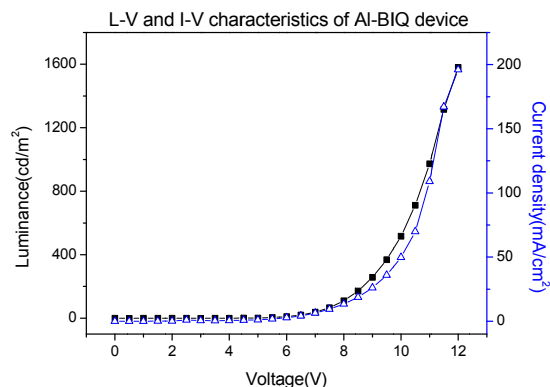


Fig. 6. Current-voltage and luminance-voltage characteristics of OLED fabricated in this work.

4. Conclusion

A novel metal complex, tris (2-(benzimidazol-2-yl) quinolinato) Aluminum (AIBIQ), was successfully prepared by the reaction of benzimidazol-2-yl-quinoline and triethylaluminum. Because of its high thermal stability and excellent electrical characteristics, AIBIQ and its related compound suggest a possible application for the use of orange-light of the organic light emitting devices.

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