

Novel Al complex as emitter in organic light emitting diodes

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In this study the new Al complex Aluminum bis(8-hydroxyquinoline) acetylacetonate (Alq₂Acac) was synthesized and its performance as electroluminescent and electron transporting layer for OLED was studied as compared to the Alq₃. Two time higher luminescence and efficiency compared to conventional Alq₃ was established, thus making the novel Al complex very promising for OLEDs.

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1. Introduction

Rapid advances in materials and manufacturing technology are making organic light-emitting diodes (OLEDs) the leading technology for a new generation full-color flat-panel display and solid state lighting applications. Since the pioneering work of Tang [1], reported efficient, low voltage electroluminescence in an organic thin film device with a novel heterojunction structure, Aluminum tris(8-hydroxyquinoline) (Alq₃) becomes one of the most widely used materials as an emitting layer for OLED due to its excellent stability and luminescent properties. Much efforts have been made to design and syntheses of many organic materials including novel metal-chelate complexes as emitting layers for improving the performance of OLEDs. By modifying the organic ligand in metal complex, changes in luminescent efficiency and stability can be achieved. In addition, blue or red shift of the emission can be achieved based on the type and the position of the substituent. Alq complex BAAlq (bis(2-methyl-8-quinolinyl)-4-phenyl-phenolate) was first introduced by Kodak group [2] as a blue-emitting material and mostly used as hole blocking layer [3] and as a blue emitter [4-6]. Many methyl-substituted derivatives nMeq₃Al [4, 7, 8], phenyl-substituted Alpq₃ [9], aluminum complexes such as Alq₂OR (OR=aryloxy or alkoxy ligand) [10], have been developed and have been demonstrated to be useful emissive materials or/and hole blocking/ electron transporting materials.

Ma et al. [11] have synthesized a new material dinuclear Aluminum 8-hydroxy-quinoline complex (DAAlq₃) with two time higher electron mobility than that in Alq₃.

Bingshe et al. reported about a mixed liquids 8-hydroxyquinoline aluminium complex (Alq₂A) with higher electron mobility and electroluminescent efficiency compared with Alq₃ [12].

In this paper the new Al complex Aluminum bis(8-hydroxyquinoline) acetylacetonate Alq₂Acac was synthesized and was investigated as electroluminescent and electron transporting layer for OLED.

2. Experimental

We investigated the electroluminescent devices with conventional structure: ITO/HTL/EL/M, where ITO is a transparent anode of In₂O₃:SnO₂, HTL - hole-transporting layer, EL - an emitting layer, and M - a metallic cathode of Al. Like HTL we used conventional TPD and developed by us composite film of N,N'-bis(3-methylphenyl)-N,N'-diphenyl-benzidine (TPD) incorporated in poly(N-vinylcarbazole) (PVK) matrix [13]. Devices with area 1 cm² were prepared on commercial polyethylene terephthalate (PET) substrates coated with ITO (40 Ω/sq). The HTL of PVK : TPD_x (x = 10 w% relatively PVK) composite films were obtained by spin-coating from 0.75% solutions in dichloroethane at 2000 rpm. The HTL of TPD, ELs (75 nm) of Alq₂Acac, and metal cathode (120 nm) were obtained by thermal evaporation in vacuum better than 10⁻⁴ Pa at rates 2-5 Å/s. PET substrate, PVK, TPD and Alq₃ were purchased from Aldrich. The Alq₂Acac (Fig. 1) was synthesized in the Department of the Applied Organic Chemistry at the Faculty of Chemistry in University of Sofia.

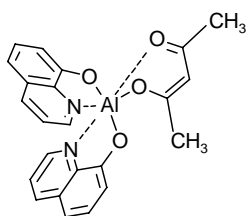


Fig. 1. Structure of Aluminum bis(8-hydroxyquinoline)acetylacetonate (Alq_2Acac).

All measurements were carried out with unpackaged devices at room temperature and ambient conditions. The photoluminescence spectrums (PL) were obtained on Spectrofluorimeter Perkin Elmer MPF 44. The morphology of the functional layers was studied with a scanning electron microscopy Philips 515. The current-voltage (I/V) curves were measured by programmable with Labview power supply. The luminescence (L) was measured in continuous DC mode and the light output was detected using a calibrated Hamamatsu silicon photodiode S2281-01. The luminous efficiency (η_L) was calculated by equation (1):

$$\eta_L = \frac{L}{I} \quad (1)$$

(where L is the luminance (in cd/m^2) and I is the current density (in A/m^2) and used for quantifying the properties of the OLEDs.

3. Results and discussion

The absorption and photoluminescence (PL) spectra of the studied complexes were presented on Fig. 2.

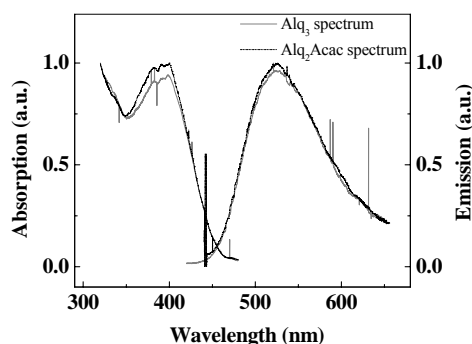


Fig. 2. Absorption and the fluorescent emission spectra of Alq_2Acac and Alq_3 .

Both complexes emit green light. The absorption and the fluorescent emission spectra of Alq_2Acac and Alq_3 are nearly identical. The light emission of Alq_3 and Alq_2Acac complexes is mostly attributed to the $\pi - \pi^*$ transition of

a quinolinolato ligand rather than an acetylacetonate ligand.

The current density-voltage characteristics of the studied devices are shown in Fig. 3 (a). The I/V curves of the devices with Alq_2Acac were located in lower voltage region compared to the devices with Alq_3 . The higher current density of the devices based on Alq_2Acac indicates that the electron transport of Alq_2Acac is better than that of Alq_3 . The luminance of the devices with Alq_2Acac is 2 times higher compared to the similar devices with Alq_3 (Fig. 3 (b)). The turn-on voltage of the devices with Alq_2Acac is lower compared to those with Alq_3 especially in the case with TPD hole transporting layer.

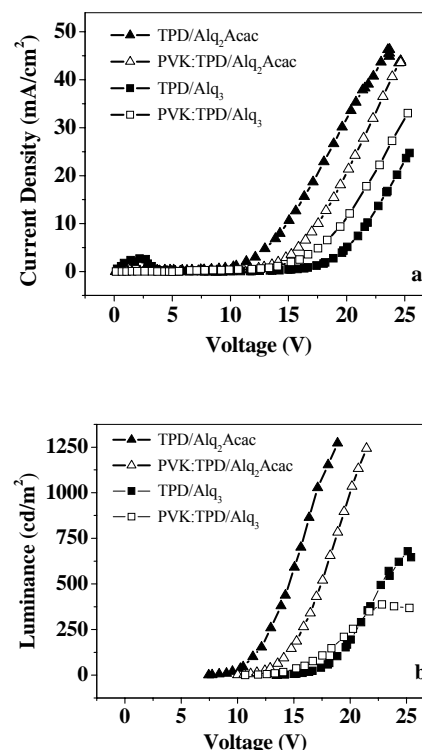


Fig. 3. I/V (3a) and L/V (3b) characteristics for devices with different HTL and EL.

It could be stressed that the efficiency of the devices with Alq_2Acac are nearly 50 % higher compared to those with Alq_3 with HTL of TPD and about 2 times higher with HTL of PVK:TPD (Fig.4). But as far as concerned to the stability of the devices, having in mind the changes of morphology in aging, better results could be expected with hole transporting layer with composite PVK:TPD.

Bingshe et. al. [12] reported about higher electron mobilities in Alq_2A than in Alq_3 , efficiency 4.35 cd/A for the device ITO/TNATA (10nm)/ NPD (50nm)/ Alq_2A (60nm)/LiF/Al and efficiency 2.49 cd/A for the similar device with EL of Alq_3 .

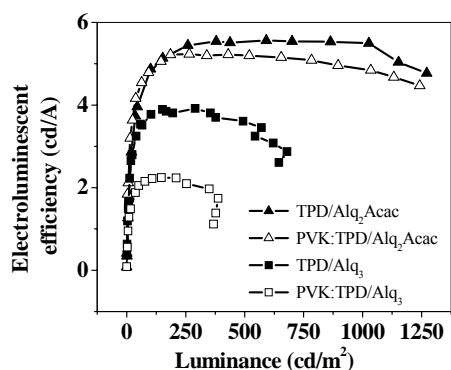


Fig. 4. Electroluminescent efficiency for devices with different HTL and EL.

Our results for the devices ITO/TPD (30nm)/Alq₂Acac or Alq₃ (75nm)/Al are 5.6 cd/A for Alq₂Acac and 3.9 cd/A for Alq₃. It is possible that the molecular structure of the novel metal-chelate complex Alq₂Acac led to subsequent increase of the device performance. Obviously the novel Al complex with mixed ligands poses better electroluminescent and electron transporting properties compared to the most used Alq₃.

SEM micrographs of the functional layers of the studied structures are presented on Figs. 5-7. The surface morphology of the developed by us HTL of composite films of PVK:TPD (Fig.5a) is very smooth and homogeneous, without any defects and cracks [13], thus creating a suitable conditions for the condensation of the next electroluminescent layers of Al complexes.

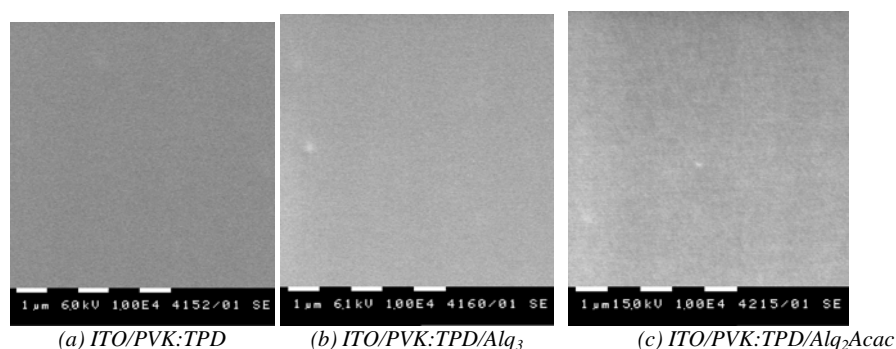


Fig. 5. SEM surfaces of OLED layers with composite HTL - as deposited.

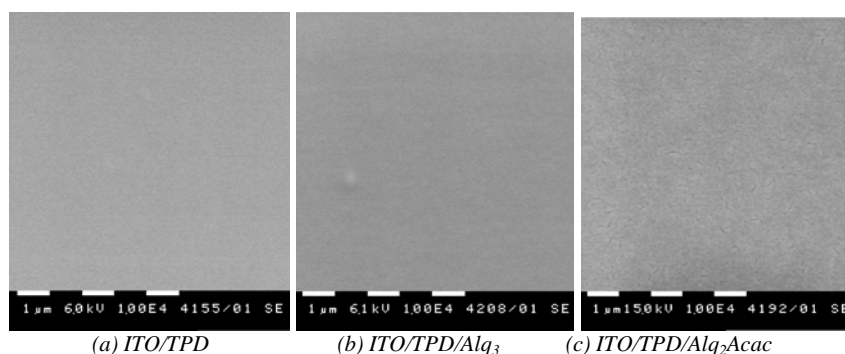


Fig. 6. SEM surfaces of OLED layers with HTL of TPD - as deposited.

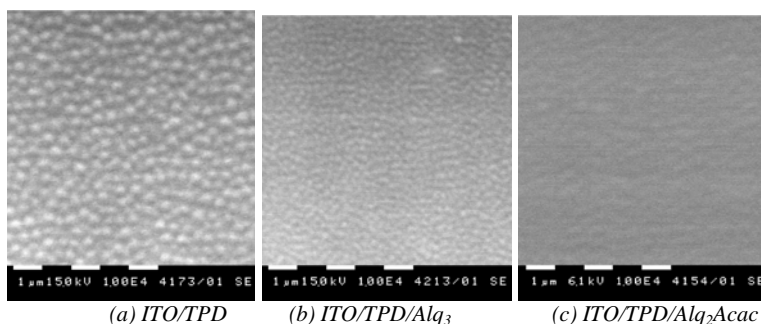


Fig. 7. SEM surfaces of OLED layers with HTL of TPD - after one day.

Both electroluminescent layers of Alq₃ (Fig.5b) and Alq₂Acac (Fig.5c) deposited on the composite films PVK:TPD show flat and amorphous surfaces which is a prerequisite for good performance of devices. The similar is the surface morphology of the vacuum as deposited TPD films (Fig.6a). In this case also the surfaces of both electroluminescent layers are very uniform and flat (Fig.6b,c).

We study the morphology of the functional layers of the devices after 1 day storage at ambient temperature. The strong recrystallization of the TPD layers was established (Fig.7a). The process of recrystallization has been started also in TPD/Alq₃ sample (Fig.7b), while the surface of the TPD/Alq₂Acac (Fig.7c) is still flat. The surface morphology of PVK:TPD, PVK:TPD/Alq₃ and PVK:TPD/Alq₂Acac layers does not show any changes after 1 day storage – better stability of devices with composite PVK:TPD hole transporting layer could be expected.

4. Conclusions

The novel complex Aluminum bis(8-hydroxyquinoline) acetylacetonate (Alq₂Acac) was synthesized and studied as electroluminescent and electron transporting layer for OLED. It was established that the devices with Alq₂Acac show lower turn-on voltage, 2 time higher luminance and more that 50 % higher efficiency compared to those with commercial Alq₃. The results obtained show that the change of one 8-hydroxyquinoline ligand with acetylacetonate ligand in the new complex improves substantially the performance of OLED. The higher electron mobility and luminescence efficiency made Alq₂Acac very promising material for OLED.

Acknowledgements

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