



Electrochemical synthesis of Organic Light Emitting Diode(OLED) and characterizations by X-ray Diffraction and supportive techniques

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Received on: 29-Jan-2016 Accepted and Published on: 6-Mar-2016

ABSTRACT

A facile and sustainable electrochemical approach towards the synthesis of tris-(8-hydroxyquinoline)aluminum(III) (Alq3) using 8-Hydroxy quinoline as a ligand is presented. The synthesis has been done at three different conditions (a) 0.015M of 8-Hydroxy quinolin in 50% methanol, at pH 7 for 24 hours (b) 0.0303M of 8-Hydroxy quinolin in 40% methanol at pH 1 for 48 hours (c) 0.0317M of 8-Hydroxy quinolin in 50% methanol at pH 2 for 24 hours. The potential was applied 1.5 V and 12.0 V respectively. Simple room temperature electrolysis method has been employed, where Al wire as well as Al foil was used as a sacrificial anode for Al³⁺ ion source and platinum wire as a cathode. Tris-(8-hydroxyquinoline) aluminum (III) (Alq3) was synthesized for the first time by direct dissolution of Al³⁺ into the solution of 8-Hydroxy quinoline from Al electrode in the electrochemical cell. The structural characterizations have been done by using Single X-ray diffraction and Powder X-ray diffraction (XRD) and TGA techniques. Complexes of Aluminum with 8-Hydroxyquinoline have a wide applications to material science as organic light emitting diode (OLED).

Keywords: tris-(8-hydroxyquinoline) aluminum(III), OLED, Al wire, platinum wire

INTRODUCTION

Tris (8-hydroxyquinoline) aluminum (Alq3) is one of the most commonly used materials in organic light emitting diodes (OLEDs). It serves as an electron transporting and/or green light emitting material. Due to its importance in OLED applications, the properties of Alq3 have been extensively studied from various visual angles.^{1,2} Its physicochemical properties are still under active investigation.

The molecule consists of three chelating oxyquinoline ligands, occurring in the facial (fac) and meridional (mer) isomers. Among the two structural isomers, fac-Alq3 is particularly desirable for its blue-shifted fluorescence and a high quantum yield. However, fac-Alq3 has been a difficult species to capture for its relatively short lifetime in solution.^{3,4}

In this paper we have presented a electrochemical synthesis of

the single isomers of mer-Alq3 that will be advance development of the next-generation Alq3-based multicolor OLEDs and lasers.

The electrochemical technique represents one of the simplest and most direct methods of carrying out oxidation or reduction reactions, since the removal or addition of electrons can be achieved without the addition of external agents. The synthesis involves the oxidation or reduction of solute species at inert electrodes to yield either direct products, or intermediate species, which subsequently decompose to give the product. For example if electric current is applied between copper and platinum electrode, copper gets oxidized and cupric ions enter the reaction medium. Therefore if the reaction medium contains ligands capable of chelating with copper, MOF can be formed either at the electrode surface or by the slow evaporation of the solution.

EXPERIMENTAL

Analytical grade (A.R.) 8-Hydroxy quinoline is used as a ligand. Al wire and Al foil were used as Anode and Pt (99.99% pure) wire was used as Cathode. A.R grade methanol was used as a solvent.

Al was taken as the working electrode and platinum was taken as the counter electrode. The electrodes were dipped in a 50% methanol solution of 8-Hydroxy quinoline of known molarity[(a) 0.015M of 8-Hydroxy quinolin, pH7, (b). 0.00317M of 8-Hydroxy quinolin, pH 2(c) 0.0303M of 8-hydroxy quinolin in

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Cite as: *Int. Res. Adv.*, 2016, 3(1), 5-8.

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40% methanol. The same experiment were performed with Al foil taking as a working electrode. The first two set up the potential was applied for 24 hours and for set up (c) for 48 hours at room temperature. Here, pH was controlled by using sulphuric acid.

Potential was applied for a fixed time interval using a potentiostat (Potentiostat Wenking Model POS 73). All reactions were carried at potential 12 V. and 1.5 V respectively. The white powder was obtained at the surface of platinum electrode and also by slow evaporation of solution.

CHARACTERIZATION

Powder X-ray Diffraction

Room-temperature X-ray powder diffraction data were collected with a Bruker D8 Advance diffractometer using Ni-filtered Cu-K α radiation. Data were collected with a step size of 0.05° and a count time of 1s per step over the range 2° <2 θ <60°.

Single Crystal X-ray Diffraction

Single crystal diffraction studies were carried out on a Bruker AXS SMART Apex CCD diffractometer with a Mo K α (0.71073Å) sealed tube at 28°C. The software SADABS was used for absorption correction and SHELXTL for space group and structure determination and refinements. Metal centers were located first and then remaining atoms were deduced from subsequent difference Fourier map. Hydrogen atoms were located using geometrical constraints. All atoms except H were refined anisotropically. The least-squares refinement cycles on F^2 was performed until the model converged.

Thermal analysis

TG analysis was carried out using Perkin-Elmer TGA7 and DTA7 system on well ground samples in flowing nitrogen atmosphere with a heating rate of 10°C/min. These studies were carried out to analyze the thermal stability of the obtained products and to ascertain the temperature at which the evolution of the organic moiety occurred.

Vibrational Spectroscopy

Fourier Transformed Infra Red spectra were recorded on a Nicolet 5DX spectrophotometer with pressed KBr pellets in the range 4000 to 400cm⁻¹.

RESULTS AND DISCUSSIONS

The white crystalline powder (complex of Al with 8-Hydroxyquinolin) of Alq3 obtained for set (b) 0.00317M of 8-Hydroxyquinolin in 50% methanol, at 12V, pH 2, for 24 hours, voltage applied across the Al & Pt electrodes was characterized by PXRD and FTIR. The figure 1 shows the powder x-ray diffraction (PXRD) pattern of pure 8-Hydroxyquinolin.^{7,8}

The figure 2 shows the powder x-ray diffraction of formed complex of Al with 8- Hydroxyquinolin . The above two PXRD patterns clearly show the different peaks.The Figure 3 shows the matched PXRD of synthesized in two conditions as given in experimental sections.^{9,10}

Following is the matched PXRD pattern of Alq3 with 8-hydroxyl quinolin. Here the black colour pattern is of 8- hydroxyl quinolin, red colour pattern is of Alq3 when Al hanger was used

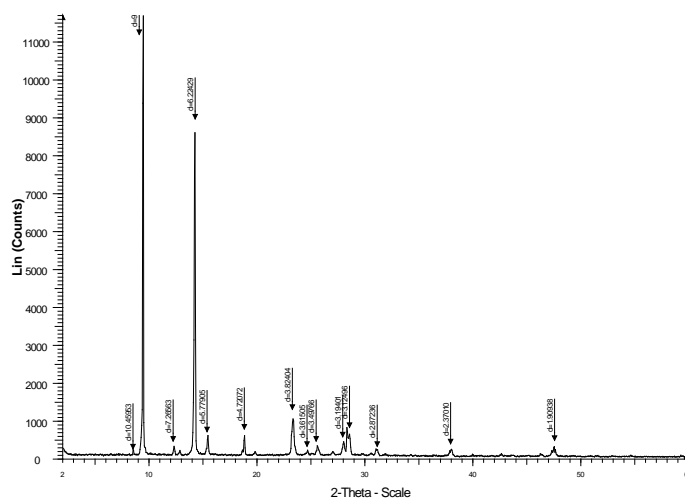


Figure 1. PXRD pattern of 8- Hydroxyquinolin

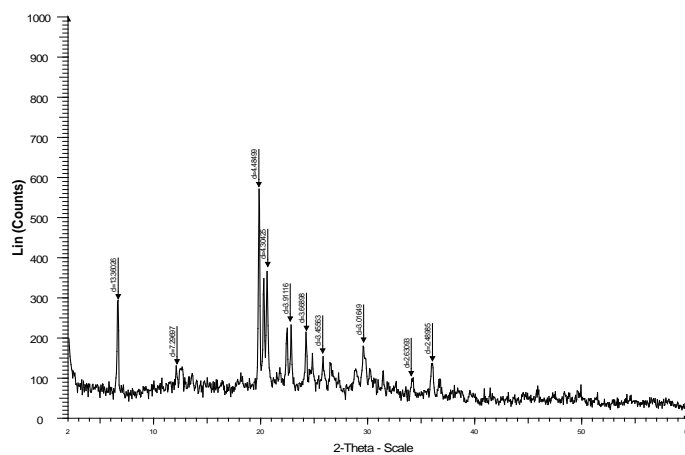


Figure 2. PXRD pattern of Alq3 when Al hanger wire is used as Anode.

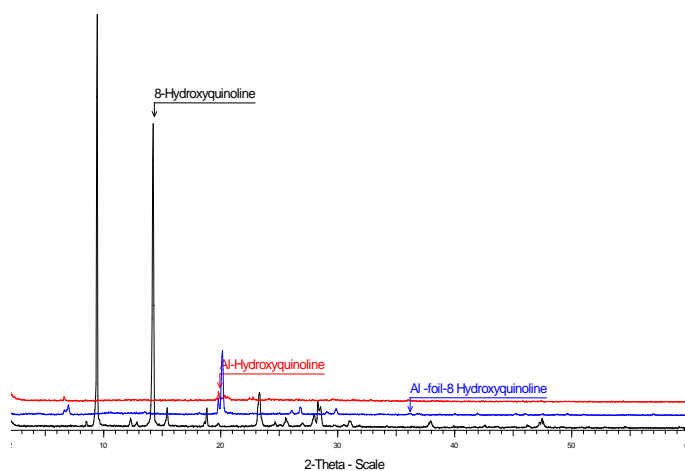


Figure 3. Matched PXRD pattern

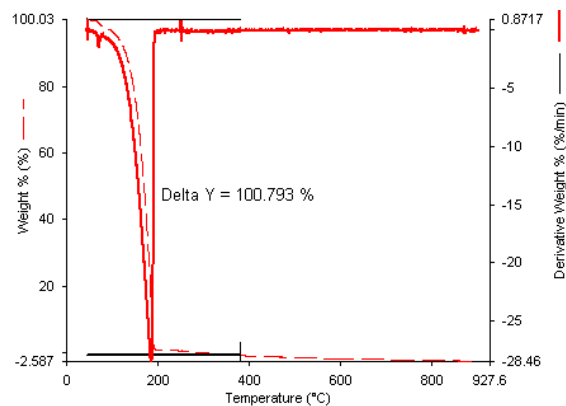


Figure 4. TGA of 8-hydroxyquinolin in derivative form

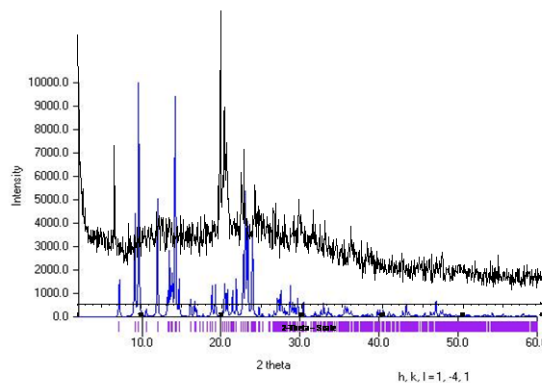


Figure 7. Matched PXRD pattern of Alq3 with PXRD of ja993608k cif reference [5]

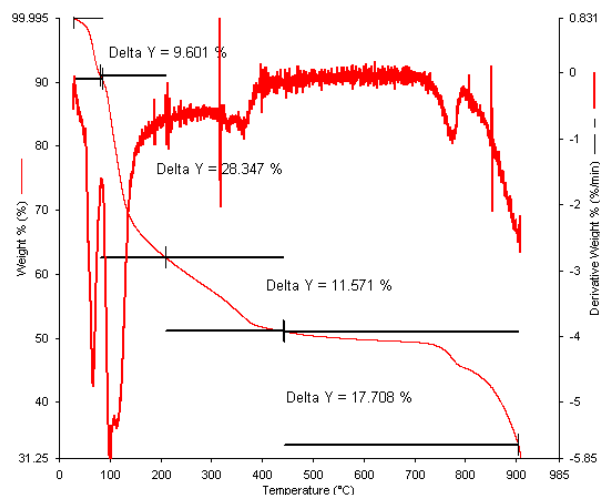


Figure 5. TGA of Alq3 in derivative form

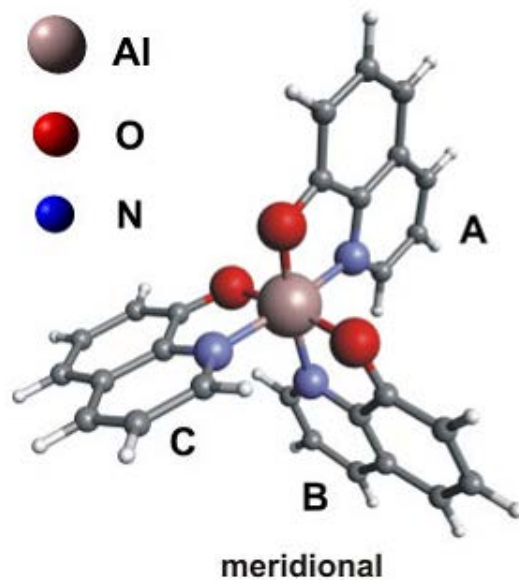


Figure 8. The structure of mer Alq3

The 9.6 01% mass loses in first step , 28.347% mass loss in second step ,11.571% mass loss in third step and 17.708% mass lose in fourth step .

This matched PXRD pattern shows that the formed compound is the meridional form of Alq3. The structure of meridional Alq3 is shown in figure 8.

The structure of meridional Alq₃ has been obtained by opening the cif ja993608k in Diamond software which is reported in the literature.

CONCLUSIONS

It was observed that with the increase in external potential, the rate of oxidation of metal increased. The complexation rate increased, with the formation of powder precipitate. But at an optimum applied potential, controlled oxidation of metal electrode took place, resulting in the formation of soluble metal – ligand complex. On standing and slow evaporation at room temperature, fine crystals of the complex were obtained. The solvated metal ions form the starting point for solid formation. Subsequently the ligand molecules attach themselves to the central metal ion,

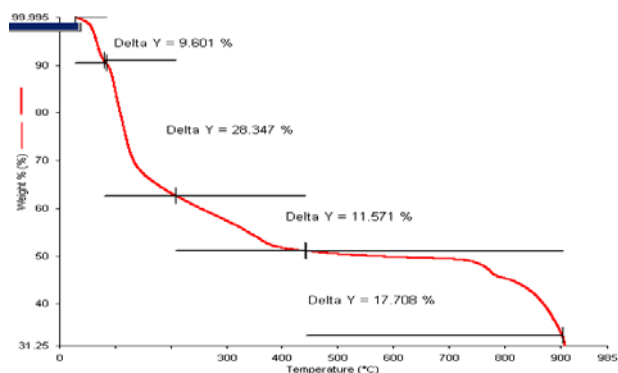


Figure 6. TGA of Alq3 in normalized form

and blue is of Alq3 when Al foil was used as working electrode. The blue colour and red colour patterns are superimposing into each other showing same compound. But they are not superimposable with 8-hydroxyquinolin. The intensity of blue patterns is higher than that of red means in case of Al foil formed Alq3 is more crystalline.

Figures 4, 5 and 6 show the decomposition of 8- hydroxyl quinolin and Alq3 on increasing the temperature as a function of time. The derivative curve of pure 8-hydroxyl quinolin reveals that complete degradation in one step. But Alq3 decomposes in four step with increasing temperature.

forming a template for crystal growth. Dehydration on slow evaporation leads to the formation of the solid.

Complexes of Aluminum with 8-Hydroxyquinoline have a wide applications to material science as light emitting diode and in luminescence.⁶

ACKNOWLEDGMENT

Authors thanks to Professor A. Ramanan, Department of Chemistry, Indian Institute of Technology Delhi for providing guidance and also thank to Indian Institute of Technology for providing facility for SXRD, PXRD and TGA analysis. The Author also thank to CSIR for providing fund for this work.

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SUPPLEMENTARY MATERIAL

Pdf file of figures is available as supplementary file and can be downloaded from article site.