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A simple method for preparing novel green emitting Al-tris(8-hydroxyquinoline) complex and blue-green emitting Mg- tris(8-hydroxyquinoline) complex

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Abstract

Two novel photo luminescent complexes in which the amino group of the ligand coordinates to the metal (III) ions for the first time, have been blended through the simple chemical synthesis in the presence of NaOH. These complexes were characterized by X-ray analysis, PL spectra and FT-IR spectroscopy. X-ray crystallographic studies of the complexes reveal that complex 1 and 2 are amorphous one-dimensional chain, which further assembles into a three-dimensional network via the interchain π–π^* stacking interaction and strong hydrogen bonds, The extensively strong hydrogen bonds in complex 1 and 2 leads to the formation of three-dimensional framework. Photoluminescence properties of the compounds 1 and 2 have been examined in solid state at room temperature. These compounds have been found to exhibit blue-green photoluminescence and may be good candidates for photoactive materials.In this paper, we have reported the effect of salicylic acid on mixed organic Alq_3 and Mgq_2 chelates prepared by a simple chemical reaction. When salicylic acid is added to Al-Quinolate, photoluminescence spectrum shows only a broad band emission at 510 nm under excitation 385nm. When Salicylic acid is added to Mg-Quinolate, photoluminescence spectrum shows different emission shifted to 490nm (Blue-Green) .The excitation spectra is very broad and is observed at 385 nm.

Keywords:

Alq_3 and Mgq_2 chelates, Photoluminescence, Organic phosphor

1.0 INTRODUCTION

The probable electroluminescence from organic and polymeric materials has suggested considerable interest since the pioneering studies by Tang and Vanslyke [1], Adachi et al [2] and Burroughs et al [3]. Alq_3 is highly efficient electron transport material amongst the various organic molecules. It also gives intense emission resulting in wide-ranging application in OLED design. Even if traditionally Alq_3 is known to be a good electron transport material, recently hole transport properties have as well been studied [4-5]. Alq_3 is a green emitter with PL peak wavelength in the range of 500 - 525 nm. In the molecules, the quinoline's function as bidentate ligands and bind to aluminium atom through both nitrogen and oxygen atom, and the coordination numbers are 6.

The best green emitting material for use in organic EL devices has been tris 8- hydroxyquinoline–Al complex (Alq_3). Even though, Alq_3 has low fluorescence efficiency, it has excellent properties as an emitting material, highly stable film formation, high carrier (electron) transport, and good heat resistance [6-9].

Materials and characterization

All reagents were purchased commercially and used without further purification. FT-IR spectrum (400–4000 cm^{-1}) was recorded from Bruker FT-IR spectrophotometer. Solid state emission spectra of the compounds were recorded using Hitachi 4000 spectrophotometer. RGB co-ordinates were also carried out to know the proportion of the three primary colors.

1.1 Experimental

The corresponding salt mostly nitrate in desired amount was dissolved in double distilled water. Salicylic Acid (20%) was dissolved in Methanol in another beaker and Quinoline (80%) in minimum Acetic Acid in the third one. Separate solution of NaOH was prepared by dissolving NaOH pellets in double distilled water in the fourth beaker. Solution of Quinoline (80%) was added to Salicylic Acid (20%) solution and then NaOH solution was added to the mixed solutions and finally nitrate solution was added to it. The solution of NaOH is needed to maintain basicity in the solution (i.e. pH >7). Precipitate obtained was then filtered with the help of filter paper. The filtrate was dried under the lamp for several hours to drive away the moisture and used for photoluminescence measurements. Photoluminescence measurements were made on Hitachi 4000 spectrophotometer.

1.1.1 Complex 1: Alq₃ doped with Salicylic Acid

i. X-Ray Diffraction

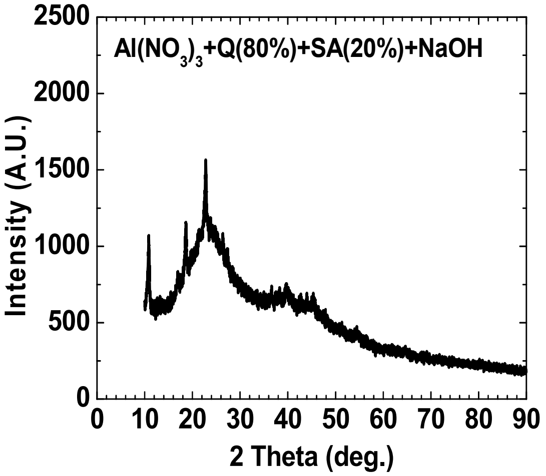

Fig. 1 X-Ray Diffraction of Alq$_3$ doped with Salicylic Acid.

Fig. 1 shows that there are much weaker diffraction peaks indicating lower crystallite or orientation. In addition, its higher volume fraction of insulating side chains may also contribute to its low field-effect mobility. However, too much crystallite causes brittleness. The crystallite parts give sharp narrow diffraction peaks and the amorphous component gives a very broad peak. The ratio between these intensities can be used to calculate the amount of crystallite in the material. No JCPDS data is found to match with the prepared chelate. So, a completely different compound is formed.

ii. Photoluminescence spectra

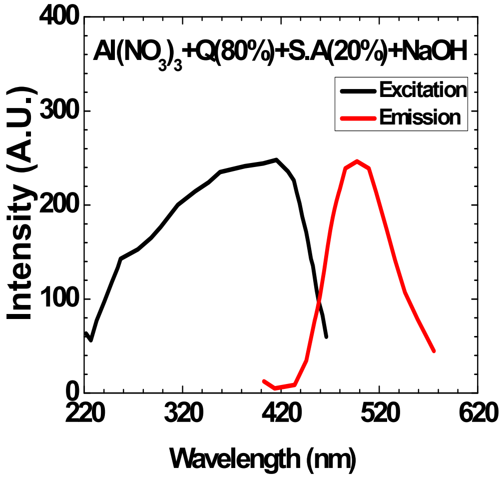

Fig. 2 Photoluminescence spectra of Alq$_3$ doped with Salicylic acid

The investigation of the photoluminescence excitation (PLE) spectra show any excitation photon energy, in the spectral range extending from the electronic transition band, contributes to the photoluminescence. This behaviour is due to fast non - radiative relaxation, with subsequent radiative recombination to the ground state. This means that fast energy transfer prices are at work among the various orbital states with final relaxation to the LUMO states. The excitation and photoluminescence (PL) spectra in the spectral range from 200 - 600 nm of Al-Quinolate doped with Salicylic Acid powder form is as shown in Fig. 2.

The excitation spectra of Al-Quinolate doped with salicylic acid, which is a yellow precipitate powder, shows two peaks at 385 nm. When the powder is excited at 385 nm, it emits intense green light of wavelength 510 nm. Mixing salicylic acid makes the excitation broad compared to pure Alq$_3$ with the tail extending in blue region.

iii. Infra- red Spectra

From IR spectra, as shown in fig.3, it was found that the following organic groups are observed:

i. Peaks at 1581.29, and 1469.73 cm^{-1} show the presence of asymmetric vibration of CO, bending of NH$_2$, symmetric and asymmetric bending of NH$_3$ and asymmetric bending of CH$_3$ respectively indicating the presence of aromatic ring.

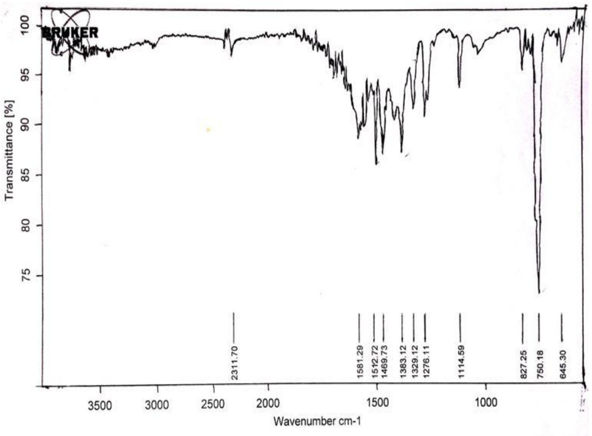

Fig. 3 FTIR of Al$(NO_3)_3$+ Q(80%) +S.A(20%) +NaOH

ii. Absorption peak is also observed at 1276 cm^{-1} showing vibrational C-O bond indicating its presence.

iii. Highly intensified specific peak at 750 cm^{-1} is observed showing the aromatic substitution.

1.1.2 Complex 2: Mgq$_2$ doped with SA

i. X-Ray Diffraction

Fig. 4 above shows XRD pattern of the complex. Weaker diffraction peaks indicating lower crystallinity or orientation are seen. In addition, its higher volume fraction of insulating side chains may also contribute to its low field-effect mobility. However, too much crystallinity causes brittleness. The crystallinity parts give sharp narrow diffraction peaks and the amorphous component gives a very broad peak. The ratio between these intensities can be used to calculate the amount of crystallinity in the material. No JCPDS data is found to match with the prepared chelate. So, a completely different compound is formed. XRD peaks are observed at different angles, which indicate the crystalline nature of the complex formed. The 100% line was observed at 2 Theta = 29.5°.

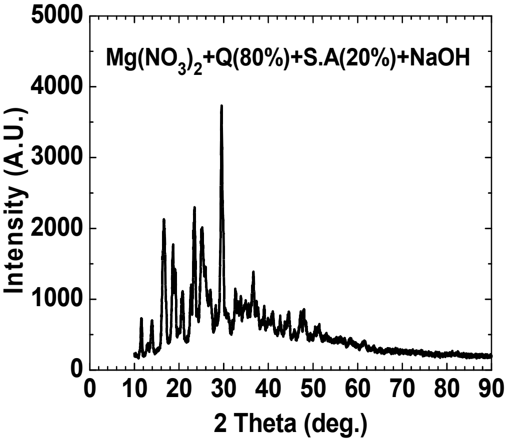

Fig. 4 X-Ray Diffraction of Mgq$_2$ doped with Salicylic Acid.

XRD **Table 1. peaks at different angles:**

S.No.	2 Theta (deg.)	Intensity (A.U.)
1	29.5	3723.33
2	23.36	2187.5
3	16.48	1955.83
4	25.02	1895
5	18.62	1746.67

ii. Photoluminescence spectra

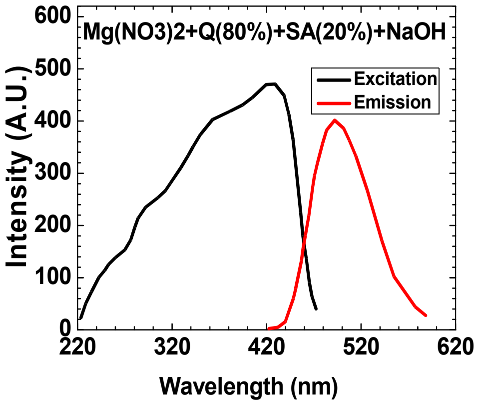

Fig. 5 Photoluminescence spectra of Mgq$_2$ doped with Salicylic acid

Fig. 5 shows the photoluminescence spectra of Magnesium Quinolate (80%) when doped with Salicylic acid (20%). Intense photoluminescence is observed for Mg-chelate. The emission is different and shifted to 490nm (Blue-Green). The excitation spectrum is very broad and observed at 385 nm.

iii. Infra- red Spectra

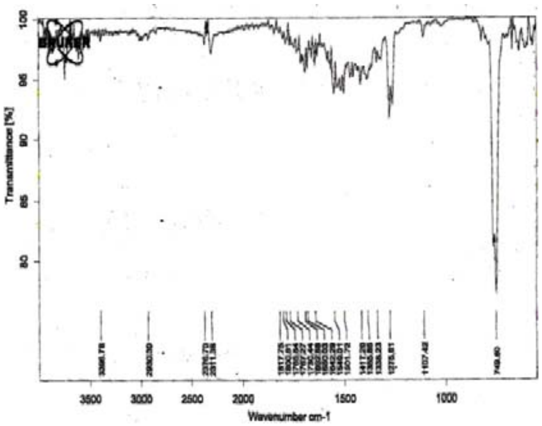

Fig. 6 FTIR of Mg(NO3)2+Q(80%)+S.A(20%)+NaOH

There are two specific peaks observed in the IR spectra.

i. The peak at 1275.81 cm^{-1} shows vibrational C-O bond which is an acidic group.

ii. A specific intensified peak at 749.80 cm^{-1} shows aromatic substitution.

The IR peaks obtained may be due to the crystalline nature of the complex formed.

2.0 CONCLUSION

It is found that the Alq_3 chelate doped with Salicylic acid is amorphous, whereas Mgq_2 chelate doped with Salicylic acid is crystalline in nature. The results also indicate that a change in the cation (i.e. if instead of Al, Mg is used) shifts the emission wavelength spectra towards left by 20 nm but the intensity increases. Hence, it can be concluded that both the emission and excitation from metal chelates might be very useful in display and lighting applications.

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