Synthesis and study of Alq$_3$, Naq and Liq for OLEDs

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Abstract

Pure Alq$_3$, Naq and Liq complexes were synthesized by simple chemical reaction method at room temperature. These complexes were characterized by X-ray diffraction (XRD), photoluminescence (PL) and Fourier transform infrared (FTIR). The crystalline nature of the synthesized complexes is revealed by X-ray diffraction analysis, while Fourier transform infrared spectroscopy verifies the molecular structure. It also confirms the completion of quinoline ring formation and presence of quinoline structure in the metal complex. PL spectra revealed that in Alq$_3$, the emission depends on the basiciting agent and its concentration. With NH$_4$OH the emission is observed in green region for any concentration around 510 nm. The emission position and intensity however is function of concentration of NaOH as basiciting agent. For lower concentration the emission is observed at 510 nm similar to the reported emission in literature. Intense emission in blue region is obtained when NaOH is used in high concentration. Naq and Liq complexes exhibit intense luminescence in blue green region with the excitation peaking around 385 nm. Thus, the synthesized organic phosphors are the promising candidates for green- and blue-emitting OLEDs, PLLCD and solid-state lighting applications.
   Keywords:
       Quinolates, Organic phosphors, Photoluminescence

1.0 INTRODUCTION

Organic light-emitting materials have been attracting the attention of researchers from industry and academic institutions owing to their applications in organic light-emitting diodes (OLEDs) [1], stimulating interest in next-generation displays and lighting technologies [2]. Of the several organic molecules quinoline based materials are of particular interest owing to easy preparation, stable film formation, good heat resistance and high carrier transport ability. Tang and coworkers fabricated Alq$_3$-based multilayer thin film electroluminescent devices in 1987 [4-6]. Alq$_3$ proceeds to be the starting material amongst the class of low molecular weight materials for OLEDs. Properties like relative stability, simple synthesis, good electron transportation ability and light emitting properties results in the extensive applications of Alq$_3$ in OLED design and flat panel display. Alkali based quinolates are of

the metal centre decreases the number of quinoline ligands might decrease the formation of non-radiative products.

These new Mqx might be more stable than the traditional Alq$_3$.

1.1.1 Experimental

Synthesis of Alq$_3$ as well as alkali quinolates were carried by simple co-precipitation technique.

interest as electron transport layer because of the properties comparable to that of LiF/Al layer. Of the three alkali quinolates, Lithium 8-hydroxyquinolinate (Liq) is of current interest [7-8]. It is used as host material in emission layers [8] and also as interface materials for the electron-transporting and electron-injecting layers in devices [9-12]. The crystal structure of complexes containing lithium are known to vary co-ordination numbers in the range of 2 to 8, [13-14], with smaller numbers more common. The complexes are usually composed of dimers, trimers, tetramers, and hexamers. The sodium as well as postassium quinolates has got also similar properties and structure. This paper reports the synthesis and photoluminescence of these quinolates. Although Alq$_3$ is widely used in OLED devices, other metal quinolates (Mqx) might have better optical and electrical properties. Changing from a 3+ ion to a 1+ ion as

1.1.2 Synthesis of Alq$_3$

   Appropriate amount of Tris(8-hydroxyquinoline) procurred from Loba Chemie, India was dissolved in minimum amount of acetic acid. Solution of Al(NO$_3$)$_3$.4H$_2$O is prepared separately by dissolving Al(NO$_3$)$_3$ in 3:1 ratio with respect to Tris (8-hydroxyquinoline) in double distilled water. Both the solutions were reacted by mixing the solutions with each other. During the whole reaction the pH of the solution is maintained around 10. This is done by adding either 0.1M solution of NaOH or NH$_4$OH. Green precipitate is obtained

after the reaction which is then filtered off using Whatmann 42 filter paper. The filtrate was washed with absolute alcohol for several times. The filtrate was dried under the lamp for several hours after washing with absolute alcohol for several times to drive away the moisture. Several samples with varying concentration of NaOH and NH₄OH were prepared.

1.1.3 Synthesis of Mq (M = Li, Na, K)

Synthesis of Mq is carried out in similar fashion as described earlier except appropriate alkali hydroxide is used instead of $Al(NO_3)_3.4H_2O$ in stoichiometric proportion.

Photoluminescence studies were carried on Hitachi F-4000 Spectrofluorometer with the excitation slit 1.5 nm and the emission slit 1.5 nm. XRD analysis was carried on Righaku machine and the FTIR spectra was taken on Bruker machine.

1.2 Results and discussion:

Figure. 1 shows the XRD of the synthesized metal quinolates. The XRD pattern in all the three cases is similar to that of parent moiety 8-Hydroxyquinoline (ICDD file No.(14-0954). The relative intensities are changed due to inclusion of metal ions in the moiety. The XRD pattern for Alq₃(fig. 1c matches with that reported in ICDD database (File No.26-1550). The other two are not reported in the database.

1.2.2 Infra red spectra

FTIR spectroscopy permits the absorption in different regions to be identified, so as to establish the structural relationship between them. IR indicates the functional groups present in the compound.

In the IR spectrum, Naq (fig.2b) exhibited absorption at 1101.18 cm⁻¹ (*m*) which corresponds to the presence of quinoline C–O bonds. The C–H stretching mode meant for the phenyl ring was relatively weak and was observed at about 3601.70 cm⁻¹. The peaks at 1644.41 cm⁻¹ (*s*) are attributed to $\nu C=N$ stretching, and the peak at 1459.11 cm⁻¹ is assigned to $\nu s(-C=N-C=C-)$.The peak at 1564.57 cm⁻¹ (*s*) is assigned to C=C stretching vibrations of the aryl rings while the peak at 794.58 cm⁻¹ and 751.08 cm⁻¹ are assigned to the $\nu C-H$ of aryl rings.
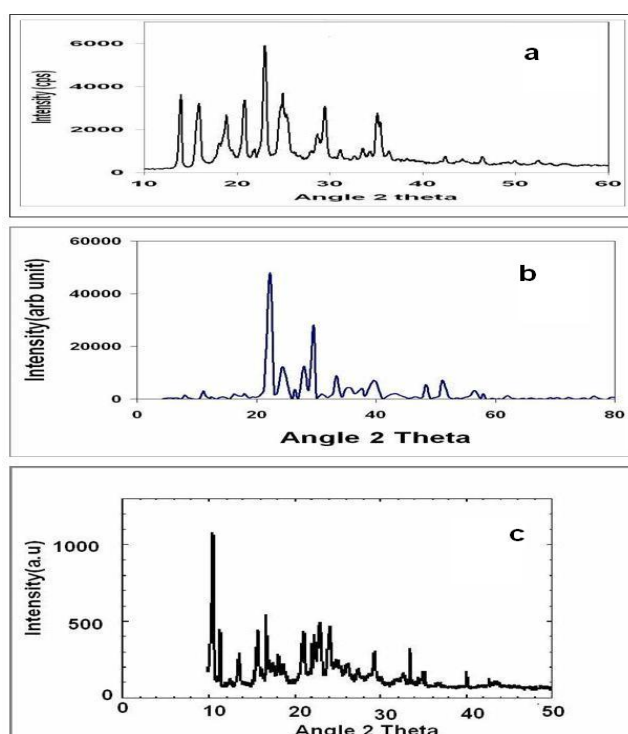

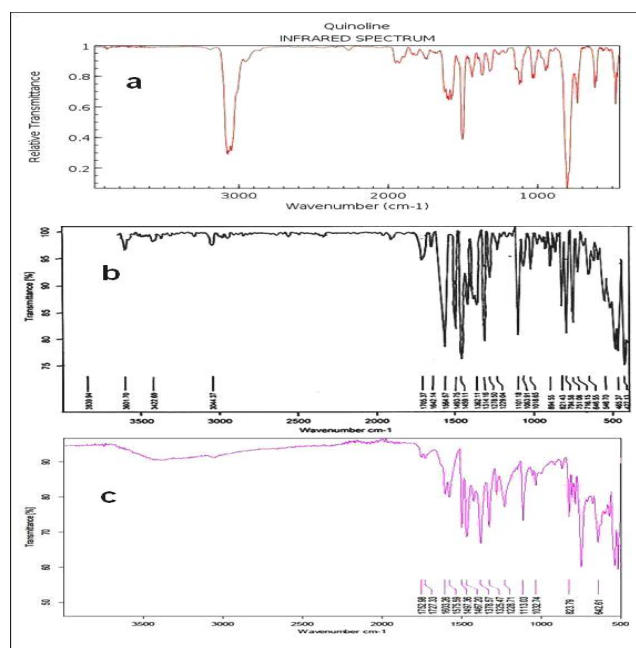**Fig. 1: XRD of various quinolates a)Liq b)Naq c)Alq₃**

Fig. 2: FTIR spectra of various quinolates a) 8Hq b)Naq c) Alq₃

The strong carboxylic acid peak at 1705.37 cm⁻¹ (*s*) is almost reduced. Another two peaks at 1362.11 cm⁻¹ and 1314.11 cm⁻¹ can be considered to the symmetric stretching of carboxyl (CO_2), whereas the peak at 1065.11 cm⁻¹ (*m*) may be judged as the stretching of carboxyl (CO). The peak at 821.43 cm⁻¹ can be attributed to the stretching of

the δ band of carboxyl CO_2. The characteristic peaks of quinolic rings ranges from 600 cm^{-1} - 800 cm^{-1} showed the presence of quinolic rings. The two peaks below 500 cm^{-1} around 465 cm^{-1} and 427 cm^{-1} may arise due to the presence of Na (chemical element). Therefore the complex formation took place successfully and verified at last the structure to be Naq. Similar IR spectrum was observed for Liq (not shown).

In the IR spectrum, Alq_3 (fig. 2c) exhibited absorption at 1103.03 cm^{-1} (*m*) and 1032.74 cm^{-1}, corresponding to the existence of quinoline C–O bonds. The peaks at 1603.26 cm^{-1} (*s*) are attributed to νC=N stretching and the peak at 1467.20 cm^{-1} is assigned to νs(–C=N–C=C–). The peaks at 1575.59 cm^{-1} (*s*) is assigned to C=C stretching vibrations of the aryl rings and the peak at 823.79 cm^{-1} is attributed to the νC–H of aryl rings. The strong carboxylic acid peak at 1727.33 cm^{-1} (*s*) is little bit diminished and two peaks developed at 1603.26 cm^{-1} (*s*) is assigned to the asymmetric stretching of carboxyl (CO_2). Another two peaks at 1378.57 cm^{-1} (*w*) and 1325.47 cm^{-1} (*m*) can be regarded due to the symmetric stretching of carboxyl (CO_2), while the peak at 1032.74 cm^{-1} (*m*) can be considered as the stretching of carboxyl (CO). The peak at 823.79 cm^{-1} (*m*) can be assigned to the stretching of the δ band of carboxyl CO_2. The characterstic peaks of quinolic rings from 600 cm^{-1} - 800 cm^{-1} showed the existence of quinolic rings. The two peaks near 500 cm^{-1} may arise due to the presence of Al (chemical element). Consequently, the complex formation took place successfully and verified at last the structure to be Alq_3.

1.1.4 Photoluminescence spectra

Figure. 3 exhibits the photoluminescence spectra of Alq_3 synthesized under different conditions. The sample synthesized using NH_4OH as basiciting agent shows typical emission around 510 nm (fig. 3a) with excitation peaking at 385 nm (fig. 3b). The prominent PL emission peak observed at 510 nm in green region of the spectrum from the green emission of yellowish-green Alq_3 powder is attributable to α- phase of meridional isomer of Alq_3 [15-16]. The sample synthesized with NaOH as basiciting agent shows different emissions as a function of NaOH concentration. For lower concentration the emission is observed around 510 nm with excitation at 385 nm. This is similar to what is observed earlier with NH_4OH as basiciting agent. The intensity of emission is lower as compared to the sample synthesized with NH_4OH. However, the sample synthesized with higher concentration of NaOH shows different emission. The emission is blue shifted and is observed around 467 nm (fig. 3c).The excitation is also blue shifted and observed around 350 nm (fig. 3d) with a shoulder around 385 nm. The intensity is very high compared to other samples. Such blue shifted emission is observed from Alq_3 in δ phase. Such phase is obtained by vaccum sublimation of Alq_3 powder and is well

reported in literature. Washing this sample increases further the emission intensity by three times (fig. 3e) as compared to the unwashed sample.
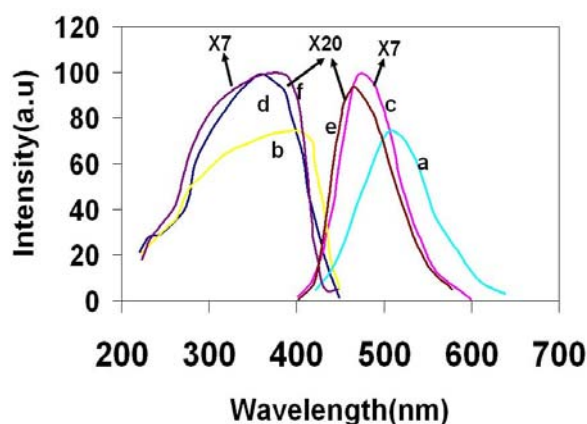

Fig. 3: Photoluminescence spectra of various Alq₃ samples; emission a,e,c corresponding excitation b,d,f.

Figure. 4 shows the photoluminescence spectra for Mq (M = Li, Na). Intense Blue emission for Liq is observed at 467 nm (fig. 4a). The excitation is broad covering the wavelength range 300-420 nm with the peak around 385 nm (fig. 4b). Similar less intense emission is observed for Naq (fig. 4c). The intensity of emission is nearly three times less as compared to the
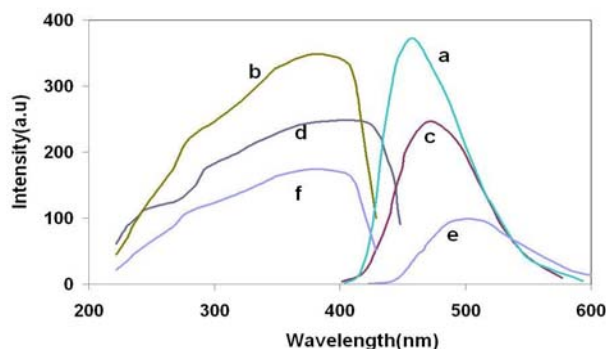

Fig. 4 Photoluminescence spectra of various quinolates: Emission a)Liq c)Naq e)Alq3; Excitation b) Liq d)Naq f)Alq3

emission intensity of Liq. If the intensity of emission is compared with Alq_3 (fig. 4c) then emission intensity of Mq (M = Li, Na) is much greater than Alq_3 and is nearly 10 times greater in case of Liq and 3 times in case of Naq. Thus, emission efficiency of alkali quinolates is much greater than Alq_3. Since, the electron injection efficiency of Liq is much higher as compared to Alq_3, this material will serve as a efficient blue emitter in case of OLED. The excitation is broad and peaking around 385 nm with the edge droping beyond 420 nm. This would serve the purpose

as efficient phosphor for converting UV light to Blue light and will be useful for PCLED applications.

2.0 CONCLUSION

Metal complexes such as Aluminium-8-hydroxyquinoline, Naq and Liq were synthesized by simple chemical synthesis. These phosphors were characterized by XRD analysis, photoluminescence measurements and FTIR analysis. In Alq_3, the emission depends on the basiciting agent and its concentration. With NH_4OH the emission is observed in green region for any concentration around 510 nm. The emission position and intensity however, is function of concentration of NaOH as basiciting agent. For lower concentration the emission is observed at 510 nm similar to the reported emission in literature. Intense emission in blue region is obtained when NaOH is used in high concentration. Naq and Liq complexes exhibit intense luminescence in blue green region with the excitation peaking around 385 nm. Thus, the synthesized organic phosphors are the promising candidates for green- and blue-emitting OLEDs, PLLCD and solid-state lighting applications.

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