

## Blue-shifted photoluminescence of Alq<sub>3</sub> dispersed in PMMA

J G MAHAKHODE<sup>1</sup>, S J DHOBLE<sup>2,\*</sup>, C P JOSHI<sup>3</sup> and S V MOHARIL<sup>2</sup>

<sup>1</sup>D.B. Science College, Gondia, Maharashtra, India

<sup>2</sup>Department of Physics, R.T.M. Nagpur University, Nagpur 440 010, India

<sup>3</sup>Physics Department, Shri Ramdeobaba K. N. Engineering College, Nagpur 440 013, India

MS received 30 May 2010; revised 3 July 2010

**Abstract.** Alq<sub>3</sub> is known to emit bright green light under UV excitation. Blue shift of the emission was reported in recent literature. This was ascribed to the presence of various isomers/crystallographic modifications obtained through train sublimation. Here a blue shift was reported for Alq<sub>3</sub> dispersed in PMMA. No isomers/phases, which were responsible for blue-shift, separated and yet the emission maxima shift to shorter wavelengths as the concentration of Alq<sub>3</sub> in PMMA decreases. The results were interpreted on the basis of cross relaxation between interacting Alq<sub>3</sub> molecules.

**Keywords.** Organometallic compounds; chemical synthesis; luminescence.

### 1. Introduction

Since the first demonstration of an organic light-emitting diode (OLED) based on Alq<sub>3</sub> (Tang and Van Slyke 1987), the interest in this material is ever increasing. Properties such as stability, easy synthesis, good electron transport and intense emission result in extensive application of Alq<sub>3</sub> in OLED design. Although traditionally Alq<sub>3</sub> is known to be a good electron transport material, hole transport properties have also been studied recently (Fong and So 2006). Alq<sub>3</sub> is a green emitter with PL peak wavelength in the range of 500 nm. In the molecules, the quinoline function as bidentate ligands and bind to aluminium atom through both nitrogen and oxygen atoms, and the coordination numbers are 6. The optical transition responsible for photoluminescence in Alq<sub>3</sub> is centered on the organic ligand. The light emission of Alq<sub>3</sub> originates from the ligand's electronic  $\pi-\pi^*$  transition from the highest occupied molecular orbital (HOMO), lying mainly on the phenoxide ring, to the lowest unoccupied molecular orbital (LUMO), located on the pyridyl ring. The luminescent property of Alq<sub>3</sub>-type Mq<sub>3</sub> (M = Al, Ga, In) is related to the metal–nitrogen bond (Nan Li *et al* 2006). On the basis of *ab initio* calculations, the co-existence in the thin film of two geometrical isomers, meridional-Alq<sub>3</sub> and facial-Alq<sub>3</sub>, is stated by Curioni *et al* (1998a). According to these studies, the facial isomer is less stable in energy than the meridional (Curioni *et al* 1998b). Along with the well-known three crystalline phases of Alq<sub>3</sub>; alpha, beta and gamma (Brinkmann *et al* 2000), the existence of delta phase showing blue-shifted luminescence was

reported (Braun *et al* 2001). Subsequent results proved that the phase consists of facial Alq<sub>3</sub> molecules, whereas all other phases contain only meridional isomers (Cölle *et al* 2003). Many research efforts have been devoted to shift the luminescence of Alq<sub>3</sub> to the blue region, either through doping or by modification of the ligand, to obtain novel emissive materials. It was found that the emission of an oxo-bridged complex, Qal–O–AlQ, is blue shifted about 40 nm from that of Alq<sub>3</sub> (Van Slyke 1992). As the covalent nature of the metal–nitrogen bond is decreased, the emission shifts to shorter wavelengths (Chen and Shi 1998). Montes *et al* (2004) studied blue shift by modifying the 5-position of ligand by electron-withdrawing or electron-donating groups. Electron-rich modifiers resulted in blue shift, and blue shift has also been observed in various modifications of Alq<sub>3</sub>. Muccini *et al* (2004) separated and studied PL of facial isomer, which emits bright blue light. Thangaraju *et al* (2006) reported PL of both facial and meridional isomers of Alq<sub>3</sub> in the form of thin films deposited on glass and silica substrates and found that they possess different lifetimes. The delta phase was also separated by embedding Alq<sub>3</sub> in silica matrix (Levichkova *et al* 2006) and blue-shifted emission was observed. Nan Li *et al* (2006) also observed blue shifted PL of Alq<sub>3</sub> in silica SBA-15. Huang *et al* (2005) investigated in detail the PL and PLE spectra of the Alq<sub>3</sub> molecules embedded in the nanovoids of porous anodized alumina membrane. An obvious PL spectral blue-shift is observed and is considered to be due to the confinement of nanovoids in nanopore walls, which prevents Alq<sub>3</sub> molecules from aggregation and thus weakens intermolecular interaction.

It is thus seen that blue shift in Alq<sub>3</sub> emission is observed by modification of ligands, separation of crystallographic phases/isomers or by quantum confine-

\*Author for correspondence (sjdhoble@rediffmail.com)

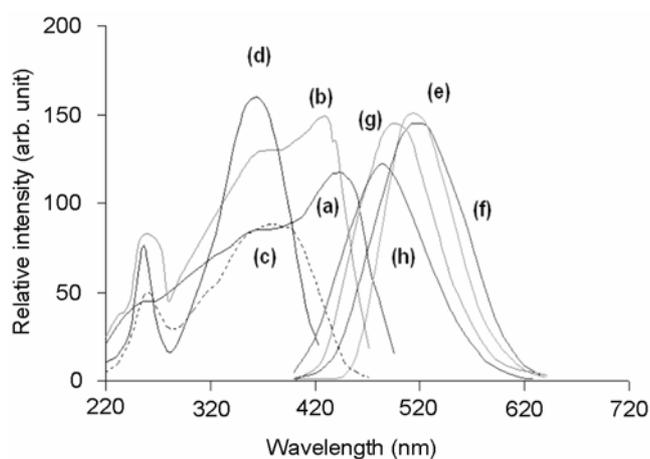
ment. In this paper, we report a continuous blue shift with the concentration of  $\text{Alq}_3$  in PMMA matrix. The shift is attributed to cross relaxation.

## 2. Experimental

8-Hydroxyquinoline (Merck, 5 g) was dissolved in a mixture of 25 ml double distilled water and 25 ml of acetic acid. It was vigorously stirred until an orange transparent solution was obtained.  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (LOBA Chem., 4.3069 g) was dissolved in double distilled water, and stirred until a clear solution was obtained. These two solutions were mixed and the resulting suspension was stirred for 10 min. A solution of ammonium hydroxide (precipitating agent) was added to this mixture, drop by drop with continuous stirring. A yellow-green precipitate was filtered out. The obtained precipitate was washed 8–10 times with double distilled water and dried. For making PMMA films containing  $\text{Alq}_3$ , typically 1 g of PMMA was taken and dissolved in 20 ml of chloroform. To this thick solution, a solution of 1 g  $\text{Alq}_3$  and 10 ml chloroform was added. The entire mixture was stirred well, spread on a polished metal plate and kept as is for several hours for evaporation to dryness. A uniform film of thickness 10–20 microns was obtained. Films of different concentrations were similarly made by varying the amount of  $\text{Alq}_3$ . X-ray diffraction (XRD) patterns were recorded on Philips PANalytical X'pert Pro diffractometer. Photoluminescence spectra were recorded on Hitachi F-4000 spectrofluorimeter with spectral slit width of 1.5 nm.

## 3. Results and discussion

XRD pattern of synthesized  $\text{Alq}_3$  revealed that it was in a crystalline state which is admixture of various phases. This is consistent with the previous observations that



**Figure 1.** Excitation (a–d) and emission (e–h) spectra of  $\text{Alq}_3$  in PMMA. (a) and (e)  $\text{Alq}_3$ :PMMA 1:1, (b) and (f) 10% of  $\text{Alq}_3$  in PMMA, (c) and (g) 1% of  $\text{Alq}_3$  in PMMA, (d) and (h) 0.1% of  $\text{Alq}_3$  in PMMA.

various phases are separated only after procedures like train sublimation, etc., are employed. Figure 1(e–h) shows emission spectra for PMMA films containing  $\text{Alq}_3$  in various concentrations. The emission from high-concentration films (weight ratio 1:1) is similar to that of the powder. A broad band around 520 nm in the green region of the spectrum is observed. With decreasing concentration of  $\text{Alq}_3$ , the maximum shifts to shorter wavelengths. For 0.1 weight percent  $\text{Alq}_3$ , the emission maximum is located around 484 nm. A similar shift was observed in excitation spectra as well (figure 1a–d). Spectra for  $\text{Alq}_3$  powder consist of distinct maxima around 243 and 435 nm with several shoulders around 310, 365, 385 and 413 nm. PMMA film containing equal (by weight) amount of  $\text{Alq}_3$  also exhibits a similar spectrum. With decreasing the concentration, the longer wavelength bands disappear and they are replaced by bands at shorter wavelengths that appeared as shoulders in the excitation spectrum for powder. For 0.1 weight percent  $\text{Alq}_3$ , the excitation maximum is obtained at wavelengths as short as 365 nm.

Blue shifts in both the emission and excitation spectra are observed with the decreasing concentration of  $\text{Alq}_3$ . In earlier works (Cölle *et al* 2003a; Levichkova *et al* 2006; Thangaraju *et al* 2006), such a shift was assigned to the formation of specific phase/isomer of  $\text{Alq}_3$ . Colle and co-workers (Cölle *et al* 2003b) obtained the new crystalline phase of  $\text{Alq}_3$ , i.e.  $\delta$ -phase of  $\text{Alq}_3$ , by thermal sublimation in a horizontal glass at high temperature (410°C). Its optical properties have been tentatively discussed in terms of the isomerism of the  $\text{Alq}_3$  molecule. As compared to the  $\alpha$ -phase, the  $\delta$ -phase of  $\text{Alq}_3$  shows the strong blue-shifted PL. Levichkova *et al* (2006) concluded that a blue shift of the PL maximum corresponded to isolated  $\text{Alq}_3$  molecules in a  $\text{SiO}_2$  matrix. They further reported that formation of facial isomer from meridional isomer of  $\text{Alq}_3$  molecule is responsible for blue emission. Blue shift can also be obtained by modification of ligands (Chen and Shi 1998). It might be tempting to interpret the blue shift as an evidence for formation of a particular phase/isomer. In the present study, neither annealing nor sublimation at high temperature was performed. Hence structure of  $\text{Alq}_3$  molecule remains the same in blended thin film as that in  $\text{Alq}_3$  powder, and yet a blue shift of 37 nm is observed for blended thin films. The observed blue shift of emission may be attributed to cross relaxation. The concentration dependence of the emission colour reminds us the luminescence of  $\text{Tb}^{3+}$  (Blasse 1988). At low concentrations, the luminescence is blue due to the  $^5D_4 \rightarrow ^7F_6$  transition. For higher concentrations, this emission is quenched due to cross relaxation and the green emission arising from the  $^5D_4 \rightarrow ^7F_5$  transition becomes dominant. We propose that similar cross relaxation is responsible for the concentration dependence of  $\text{Alq}_3$  emission. Optical absorption studies of Brinkman *et al* (2000) reveal several energy levels for various phases of  $\text{Alq}_3$ . At low concentrations,  $\text{Alq}_3$  molecules are more or

less isolated and one observes emission from higher states. With increasing concentrations, Alq<sub>3</sub> molecules come closer and can interact. Auzel *et al* (2006) reported that blue-shift phenomena in Alq<sub>3</sub> films are not exclusive of samples treated thermally, but rather they belong to the same amorphous films irrespective of any thermal treatment following their evaporation at RT. Indeed, the blue shift seems to be related to the intrinsic properties of the Alq<sub>3</sub> molecule and its aggregation states, rather than to Rayleigh scattering (RS) effects on the crystallites of the same films. Tris(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>) has been diluted into various sol-gel matrices, and a strong blue shift with respect to the well-known emission band of amorphous thin films has been observed, due to the absence of interactions among molecules that are isolated in the microscopic pores of glasses. Recently, Baldacchini *et al* (2009) found that annealed tris(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>) films in various atmospheres display an abrupt variation of the intensity, peak wavelength and line width of the photoluminescence band between 150 and 180°C, which hint at phase transition phenomena. Baldacchini *et al* (2009) reported that the blue shift was wrongly attributed to a mixing of facial and meridional isomers. The presence or absence of different molecular packing play a basic role for the optical properties of the Alq<sub>3</sub> molecule, as it was already suggested in a different context (Brinkmann *et al* 2000). Consequently, more and more Alq<sub>3</sub> molecules reach lower excited states by cross relaxation. The states themselves may be lowered due to molecular interactions. Hence, the emission is obtained at longer wavelengths corresponding to these lower excited states. For Alq<sub>3</sub> powder, emission is obtained around 517 nm which corresponds to the lowest excited state.

#### 4. Conclusions

It is thus shown that blue shift can be obtained simply by lowering the concentration of Alq<sub>3</sub> which can be

explained by the phenomenon of energy transfer by cross relaxation. Blue shift thus cannot always be taken as evidence of formation of delta phase or ligand modification.

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