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The effect of electron donating and withdrawing groups on the morphology and optical properties of Alq_3

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ABSTRACT

By adding electron donating (EDG) and withdrawing groups (EWG) to the Tris-(8-hydroxyquinoline) aluminum (Alq_3) molecule, the emission color can be tuned. In this study the effect of EDG and EWG on the morphology and optical properties of Alq_3 were investigated. Alq_3 powders was synthesized with an EDG ($-CH_3$) substituted at positions 5 and 7 ((5,7-dimethyl-8-hydroxyquinoline) aluminum) and EWG (–Cl) at position 5 ((5-chloro-8-hydroxyquinoline) aluminum). A broad absorption band at ~380 nm was observed for Alq_3. The bands of the substituted samples were red-shifted. The un-substituted Alq_3 showed a high intensity emission peak at 500 nm. The –Cl and $-CH_3$ samples showed a red-shift of 33 and 56 nm respectively. The morphology of the samples was studied using a scanning electron microscope. The photo degradation of the samples was also investigated and the dimethyl sample shows the least degradation to the UV irradiation over the 24 h of continuous irradiation.

1. Introduction

Tang and VanSlyke developed the first efficient multi-layered organic light emitting diode (OLED) in 1987 [1]. They used tris-(8-hydroxyquinoline) aluminum (Alq_3) as both the electron transporting and emitting layer. Since then substantial progress has been made in the field, leading to more and more commercial OLED products (screens for cell phones, mp3 players and cameras). Alq_3 is still used in these devices due to its high fluorescent efficiency, relatively good electron mobility and thermal stability [2]. It has been widely reported [3–5] that the emission color of Alq_3 can be chemically tuned. The emission of Alq_3 originates from the ligand's electronic π–π^* transitions. This is from the highest occupied molecular orbital (HOMO) that is mainly situated on the phenoxide ring to the lowest unoccupied molecular orbital (LUMO) situated on the pyridyl ring [2]. The highest electron density of the HOMO of Alq3 is located on the C-5, C-7 and C-8 positions of the phenoxide oxygen and for the LUMO on the C-2 and C-4 positions of pyridyl nitrogen [2]. It is predicted that electron donating group (EDG) and electron withdrawing group (EWG) at these positions can lead to either a blue-shift or red-shift of the absorption and emission spectra.

In this study the effect of EDG and EWG on the morphology and optical properties were investigated. Alq_3 powders were synthesized with an EDG ($-CH_3$) substituted at position 5 and 7 ((5,7-dimethyl-8-hydroxyquinoline) aluminum (**5,7Me-Alq_3**)) and EWG (–Cl) at position 5 ((5-chloro-8-hydroxyquinoline) aluminum (**5Cl-Alq_3**)).

2. Experimental

2.1. Synthesis

A methanol solution (20 ml) of the preferred 8-hydroxyquinoline (8-hydroxyquinoline, 5-chloro-8-hydroxyquinoline or 5,7-dimethyl-8-hydroxyquinoline (purchase from Sigma Aldrich and used without further purification)) (1.36 mmol) was slowly added to a water solution (20 ml) of aluminum trichloride (0.1 g, 0.45 mmol) with stirring at room temperature. Stirring was continued overnight and a yellow precipitate was filtered out and washed with cold methanol to remove excess 8-hydroxyquinoline. The filtrate was recrystalized in a water/methanol mixture (10%:90%) by slow evaporation at room temperature. Yellow crystalline powder was obtained after 1 week of drying at room temperature. Yield: 0.228 g (87% based on In). Fig. 1 shows the molecular structure of the metal complexes synthesized with the EWG and EDG.

2.2. Characterization

The excitation and emission photoluminescence (PL) data were collected with a Cary Eclipse fluorescence spectrophotometer equipped with a Xenon flash lamp. The absorption spectra were collected by a Perkin Elmer Lambda 950 UV–vis spectrophotometer.

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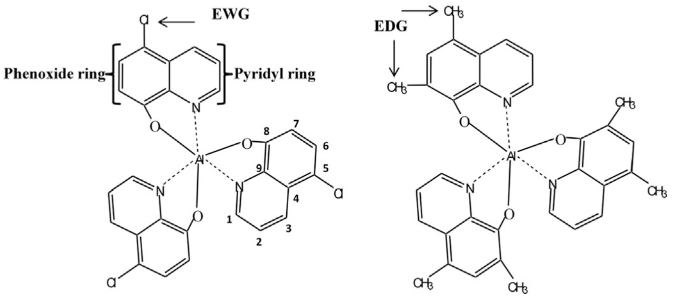

Fig. 1. The two metal complexes that were synthesized with the EWG (5Cl-Alq_3) and EDG (5,7Me-Alq_3).

To study the photon degradation the sample was irradiated with an 8 W Matelec UV lamp for 24 h. The emission data was collected every 20 s by a HR4000CG-UV–NIR Ocean Optics spectrometer. The morphology of the samples was determined by scanning electron microscopy (SEM) using a Shimadzu SSX550 microscope.

3. Results and discussion

3.1. Optical properties

Fig. 2(a) shows the absorption spectra for the three Alq_3 samples dissolved in ethanol. The spectrum of **Alq_3** is dominated by an intense absorption band at 383 nm. In addition to this intense band, there are two weak absorption bands at 317 and 332 nm. The broad band at 383 nm is reported to be a ligand centered electronic transitions [6]. The band at 383 nm has multiple electronic origins and is a superposition of two or more electronic transitions. Burrows et al. [7] calculated the three lowest-energy transitions of the meridional isomer and found it to be at wavelengths of 377, 369 and 362 nm. The absorption maximum for Alq_3 in solution is at 383 nm, which is close to the average of 372 nm for the three bands. The absorption band is broad enough (FWHM=80 nm), so it is not expected that these nearly degenerate energy transitions will be resolved at room temperature. The three lowest-energy electronic transitions are effectively donor–acceptor transitions, from a phenoxide donor to a pyridyl acceptor. The two bands at 317 and 332 nm are assigned to the vibronic progression due to the ring deformation mode of an electronic transition at 346 nm [6]. The main bands of **5,7Me-Alq_3** and **5Cl-Alq_3** are both red-shifted by 27 and 11 nm respectively.

Fig. 2(b) shows the solid state emission spectra of the three Alq3 derivatives. All the samples were excited at a wavelength of 345 nm. This wavelength correlates to a higher energy electronic transition (S_4 and above) [6,8]. The **Alq_3** sample has an emission peak at 500 nm with a FWHM of 80 nm. The emission spectrum is red-shifted by ~0.4 eV from the excitation spectra. This can be interpreted as the Franck–Condon (or Stokes) shift, which results from large conformational energy changes upon optical excitation. The broadness of the peak can also be attributed to these conformational changes, due to strong exciton–phonon coupling [7]. Alq_3 is known to be a singlet emitter [9]. The emission is due to the relaxation of an excited electron from the S_1 to S_0 level. The small peak at 400 nm corresponds to the emission of 8-hydroxyquinoline. This is an indication that a small amount of unreacted 8-hydroxyquinoline is still present in the powder samples.

The **5,7Me-Alq_3** sample shows a red-shift of ~56 nm to 556 nm. Singh et al. [10] found a similar shift in 5,7-dimethyl-8-hydroxyquinoline zinc to 560 nm. The shift is due to the decrease in the band gap of the material. Qin et al. [4] reported that electron donating groups and groups capable of extended π conjugation at the 5-position of the phenoxide ring should lead to higher HOMO levels and smaller HOMO–LUMO gaps, thus resulting in a red-shift.

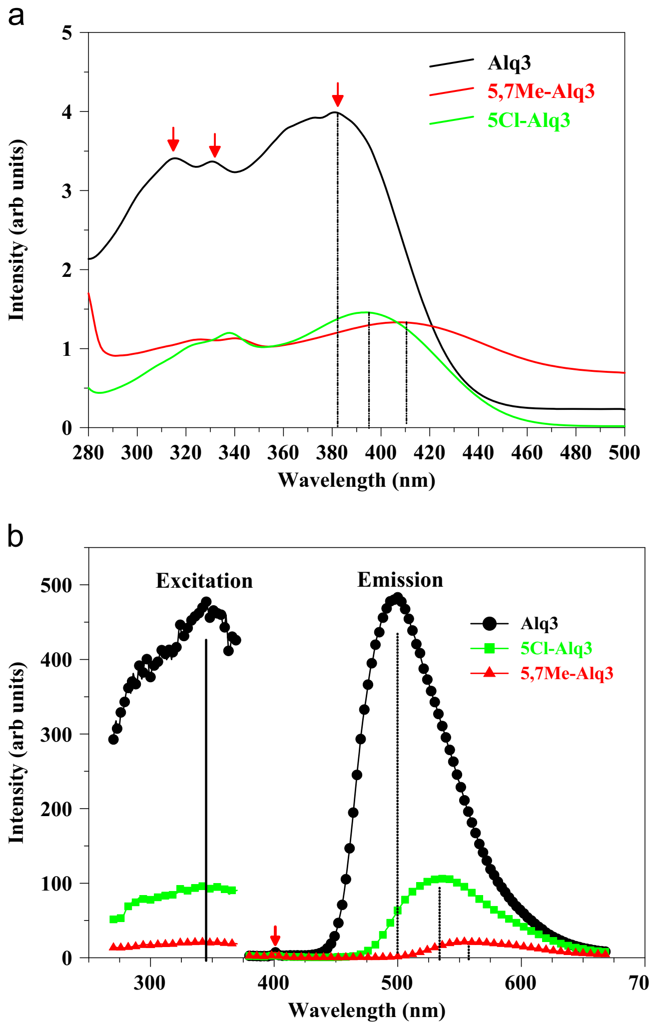

Fig. 2. (a) The absorption and (b) the excitation (left side of graph) and emission spectra (right side of graph) of the various Alq_3 derivatives. The solid black line indicates the excitation maximum and the dashed black lines indicate the emission maxima.

In the case of **5Cl-Alq_3** a red shift of ~33 nm to 533 nm was observed. The highest electron density of Alq_3's HOMO is located at the C-5, C-7 and C-8 positions of the phenoxide oxygen. It is predicted that an electron-withdrawing group at these positions will lead to a blue-shift in the absorption and emission spectra. However this prediction is not suitable in the case of **5Cl-Alq_3**. Shi et al. [5] found that in the case of 5F-Alq_3 the lone electron pair on the F atom and the high electron density at the C-5 position will cause the F group to take part in forming the HOMO of Alq_3 through a conjugation effect, giving rise to the higher HOMO energy level of 5F-Alq_3. The higher HOMO level will lead to a narrowed HOMO–LUMO gap and a red-shift of the emission peaks.

The above explanation also applies to the red-shift observed in the absorption spectra of **5,7Me-Alq_3** and **5Cl-Alq_3**.

There was a significant decrease in the absorption and PL intensity of **5,7Me-Alq_3** and **5Cl-Alq_3** compared to that of **Alq_3**. Sapochak et al. suggested that the stronger coupling of the metal–ligand stretching coordinating to the electronic transition in Alq_3 may provide additional paths for non-radiative decay [11]. The decrease in the absorption and PL intensity is therefore reasonable because the conjugated

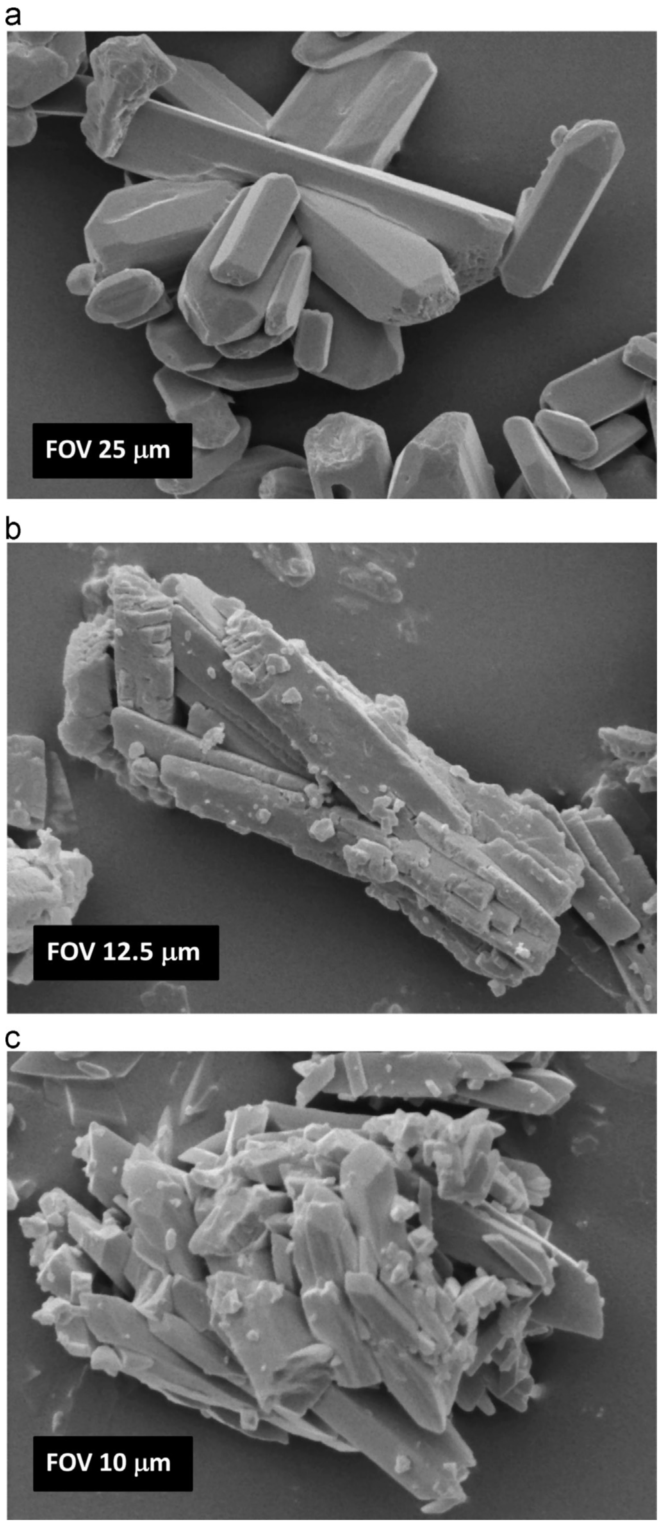

Fig. 3. SEM images of (a) **Alq$_3$** – FOV 25 µm (b) **5Cl-Alq$_3$** – FOV 12.5 µm and (c) **5,7Me-Alq$_3$** – FOV 10 µm.

effect makes the coupling of the metal–ligand stronger which will lead to an increase in the energy loss in the excited state vibration [5].

Fig. 3 shows the SEM images of the different Alq$_3$ derivatives (the images were slightly enhanced with photo-editing software). The **Alq$_3$** sample image, Fig. 3(a), shows smooth, big rod like crystals with lengths between 4 and 16 µm and widths between 2 and 3 µm. The **5Cl-Alq$_3$** sample, Fig. 3(b), formed agglomerated rods, encrusted with semi-spherical particles. The lengths and widths of these rods ranged from 1 to 1.5 µm. Similarly, agglomerated rod-like structures encrusted with semi-spherical particles were observed for the **5,7Me-Alq$_3$** samples, Fig. 3(c). These rods have varying lengths generally shorter than the rods of Fig. 3(a and b). It therefore shows that adding EWD and EDG into the Alq$_3$ clearly has an effect on the morphology of the samples.

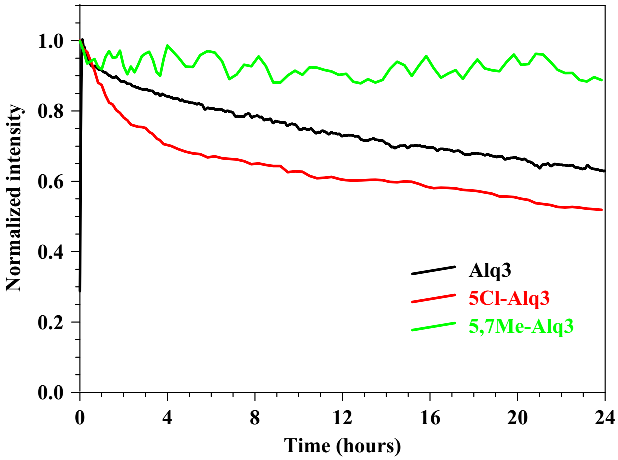

Fig. 4. Normalized photo degradation spectra of the three Alq$_3$ compounds under UV exposure ($\lambda = 385$ nm).

Fig. 4 shows the normalized photo degradation curves for the three Alq$_3$ samples. The spectra were obtained over a period of 24 h of continuous photon irradiation. A decrease of 35% of the PL intensity is observed for the **Alq$_3$** sample and a decrease of 50% for the **5Cl-Alq$_3$** sample. In the case of the **5Cl-Alq$_3$** sample the PL intensity decreases rapidly at the beginning and reaches one half of its original intensity after 4 h and then the rate of decrease slowed down for longer exposure times. The samples were fully exposed to oxygen and moisture in the open air, which are known to destroy the molecular structure at the C-7 position [7,12–14]. In the case of **5,7Me-Alq$_3$** there was no decrease in the PL intensity. It is believed that the methyl group at position 7 protects the phenoxide ring from O and OH groups to form CåO, C3O3H and OåC3O3H bonds.

4. Conclusion

Alq$_3$ with CH$_3$ as EDG and Cl as EWG were successfully synthesized. The **Alq$_3$** has a main absorption band at 383 nm which is assigned to ligand centered electronic transitions. Two weak bands at 317 and 332 nm are assigned to vibronic progressions. The absorption spectra of **5,7Me-Alq$_3$** and **5Cl-Alq$_3$** are red-shifted by 27 and 11 nm respectively. The emission peak of **Alq$_3$** is at 500 nm with a FWHM of 80 nm. The emission is due to the relaxation of an excited electron from the S$_1$ to S$_0$ level. The emission peak of **5,7Me-Alq$_3$** is red-shifted by 56 nm and that of **5Cl-Alq$_3$** by 33 nm. The PL intensity of both the samples decreased significantly due to prolonged photon irradiation. The SEM micrographs showed rods like structures for all the samples. In the case of **Alq$_3$** the big smooth rods formed, but for the other two samples the rods are agglomerated and encrusted with smaller particles, and vary much more in size. The **Alq$_3$** and **5Cl-Alq$_3$** samples' luminescence intensity decreased under UV exposure. This decrease is attributed to oxygen and moisture induced destruction of the molecule. The **5,7Me-Alq$_3$** sample showed relatively slow rate of degradation and this might be due to the methyl group protecting the carbon bond at position 7.

Acknowledgments

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