The effect of EWG and EDG on the HOMO and LUMO of Alq₃.

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Abstract Tris-(8-hydroxyquinoline) aluminium (Alq₃) is used as both the emission and electron transporting layer in organic light emitting diodes. One way to tune the emissive colour of Alq₃ is to introduce electron-withdrawing or electron-donating groups (EWG and EDG) onto the hydroxyquinoline ligands. These groups will have an effect on the energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital. In this study Alq₃ powders were synthesized with an EDG (-CH₃) substituted at position 5 and 7 ((5,7-dimethyl-8-hydroxyquinoline) aluminium) and EWG (-Cl) at position 5 ((5-chloro-8-hydroxyquinoline) aluminium). Optical absorption and cyclic voltammetry measurements were done on the samples. The optical band gap was determined from these measurements. The band gap does not vary with more than 0.2 eV from the theoretical value of Alq₃.

1. Introduction

Organic materials such as small molecules and polymers have unique properties that open up new approaches for the fabrication of plastic electronic devices rather than conventional inorganic materials, such as Si and Ge devices. Organic light emitting diodes (OLEDs) are a promising energy alternative for the future and are therefore one of the most interesting organic devices. It can be used for potential low cost lighting as well as flexible devices. The first step in the fabrication of these devices is the selection of the emissive layer, which forms the heart of the OLED device and generates the desired photons when a current is applied. In the preparation of OLEDs, emissive layers are needed that fit in the band diagram to fulfil the energy requirements to generate photons [1]. The optical band gap (E_g) is a necessary parameter to be considered. The value of E_g defines the fundamental light absorption edge. Light with enough energy can promote electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Therefore tuning the optical band gap into the desired value for applications is of great importance.

In OLED devices the matching of the HOMO and LUMO energy levels of the emissive materials with the work functions of the electrodes as well as their optical, chemical and electrical stabilities are of utmost importance. The electronic energy levels (HOMOs and LUMOs) of the materials determine the OLED device structure and selection of electrodes and charge transfer materials [2].

By introducing substituents to the Alq₃ molecule, the optical properties of the material will change, because these substituents take part in the formation of the HOMO and LUMO levels [3]. An accurate way of determining the HOMO and LUMO levels of these new materials is needed in order to see if

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they are suitable replacements for the emissive layer in OLED devices. Generally the ionization potential (I_p) of the organic molecules is measured by ultraviolet photoelectron spectroscopy (UPS), while the electron affinity (E_a) is determined from the difference of the ionization potential and the optical band gap, from optical absorption spectra [2]. But this is not a direct measurement technique to determine the position of the HOMO and LUMO energy levels.

The electrochemical processes are similar to the charge injection and transport in the OLED devices. Cyclic Voltammetry (CV) has therefore been recognized as an easy and effective approach to evaluate the position of both the HOMO and LUMO energy levels and the optical band gap of the organic materials. It has also been used to determine the reversibility, reproducibility and stability of organic films on the electrodes [2].

In this paper CV measurements were done on Alq$_3$, as well as Alq$_3$ substituted with chloride in the 5 position (5Cl-Alq$_3$) or methyl groups in the 5 and 7 positions (5,7Me-Alq$_3$) in dichloromethane (DCM). Optical absorption was also done on these 3 samples in DCM. The I_p, E_a (HOMO and LUMO energy levels) and E_g were determined from the CV and absorption measurements.

2. Experimental details

The HOMO and LUMO energy levels of the emissive layers in OLEDs can be estimated by cyclic voltammetry. CV gives direct information of the reduction and oxidation potentials of the materials. The oxidation process corresponds to the removal of electrons from the HOMO energy level and the reduction process corresponds to electron addition in the LUMO energy level of the materials [2]. The current will arise from the transfer of electrons between the energy level of the working electrode and the molecular energy levels of the materials under study.

The onset potentials of oxidation and reduction of a material can be correlated to the ionization potential (I_p) and electron affinity (E_a) according to the empirical relationship proposed by Bredas et al [4] on the basis of a detailed comparison between valence effective Hamiltonian calculations and experimental electrochemical measurements. The correlation can be expressed as:

$$I_p = -\left(E_{ox} + 4.4\right) eV \qquad (1)$$

$$E_a = -\left(E_{red} + 4.4\right) eV \qquad (2)$$

$$\text{and } E_g = I_p - E_a \qquad (3)$$

where E_{ox} and E_{red} are the onset potentials of oxidation and reduction, respectively, while E_g is the optical band gap of the material. The 4.4 eV constant in the relation between Ip, Ea and the redox potentials arises from the difference in gas-phase ionization potentials and electrochemical oxidation potentials of solid films and the solid-state polarization energy [5]. The onset potentials are determined from the intersection of the two tangents drawn at the rising current and baseline charging current of the CV traces.

Cyclic voltammograms of the samples were recorded with a PARSTAT 2273 model potentiostat utilising a three-electrode electrochemical cell at a constant scan rate of 100 mV/s. The samples were dissolved in DCM (0.5 mM) and 0.2M of [^{n}Bu$_4$N][B(C$_6$F$_5$)$_4$] was used as the electrolyte because this solvent-electrolyte combination is known to minimize substrate-solvent and substrate-electrolyte interactions after generating charged species during oxidation or reduction [6], [7]. Glassy carbon (3.14 mm^2) was used as the working electrode and Pt was used as both the auxiliary and pseudo reference electrode. Free ferrocene with redox potential for the FcH/FcH$^+$ coupled assigned as 0.00 V was used as internal reference standard. The experiment was done in a glove box under Ar atmosphere at 25 °C.

Optical absorption spectroscopy was used to determine the optical band gap of the three Alq_3 derivatives. The E_g of the samples were estimated from the optical absorption edge and using the Tauc relation [8]:

$$\alpha h\nu = \left(h\nu - E_g \right)^n \tag{4}$$

where α is the absorbance, E_g is the band gap corresponding to a particular absorption of photon energy at $h\nu$ and n is 1/2 for allowed direct, 3/2 for forbidden direct, 2 for allowed indirect and 3 for forbidden indirect transitions in the materials [2]. The direct band gap were obtained from extrapolation of the straight line portion of their $(\alpha h\nu)^2$ versus $h\nu$ plots to $\alpha = 0$.

The absorption spectra of the samples were recorded with a Perkin Elmer Lambda 950 UV-VIS spectrophotometer. The optical absorption spectroscopy studies of the samples were carried out in DCM solutions so that they can be directly compared to the results obtained from the CV measurements.

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 (purchased from Sigma Aldrich and used without further purification)) (1.36 mmol) was slowly added to a water solution (20 ml) of aluminium 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 one week of drying at room temperature. Yield: 0.228 g (87 % based on Al).
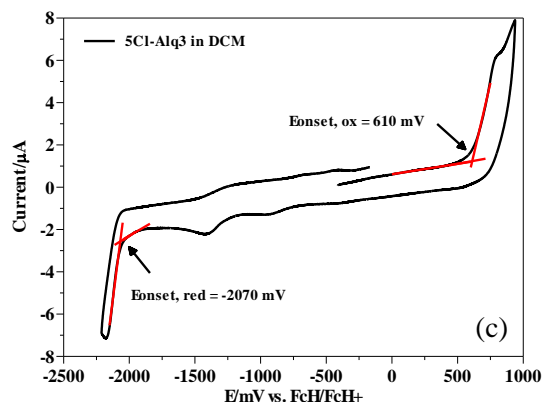
3. Results and discussion
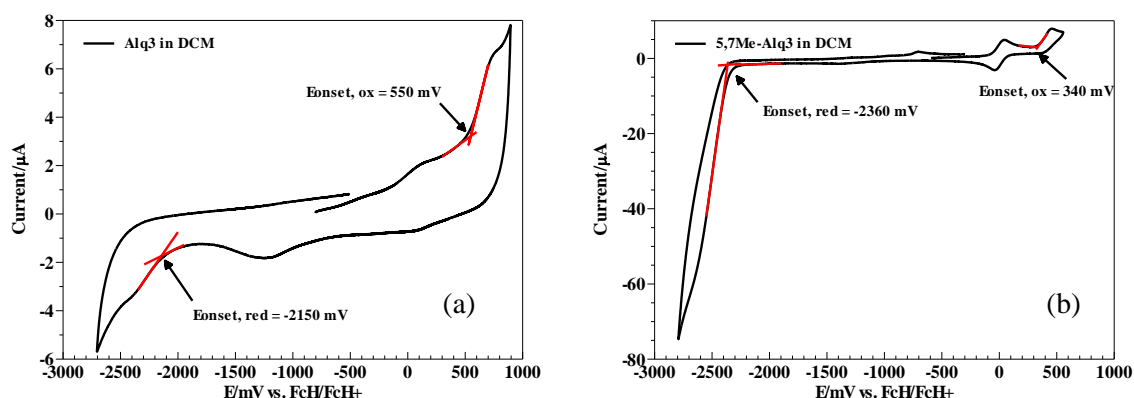
Figure 1: Cyclic voltammograms of (a) Alq$_3$ (b) 5,7Me-Alq$_3$ and (c) 5Cl-Alq$_3$ in DCM.

Figure 1 shows the cyclic voltammograms for the 3 synthesized samples. The onset potentials for oxidation of the samples were observed at 550, 340 and 610 mV, while reduction potentials were -2150, -2630 and -2070 mV for Alq$_3$, 5,7Me-Alq$_3$ and 5Cl-Alq$_3$ respectively. The electronic band gaps for the samples were determined using equation 3 and are listed in table 1.
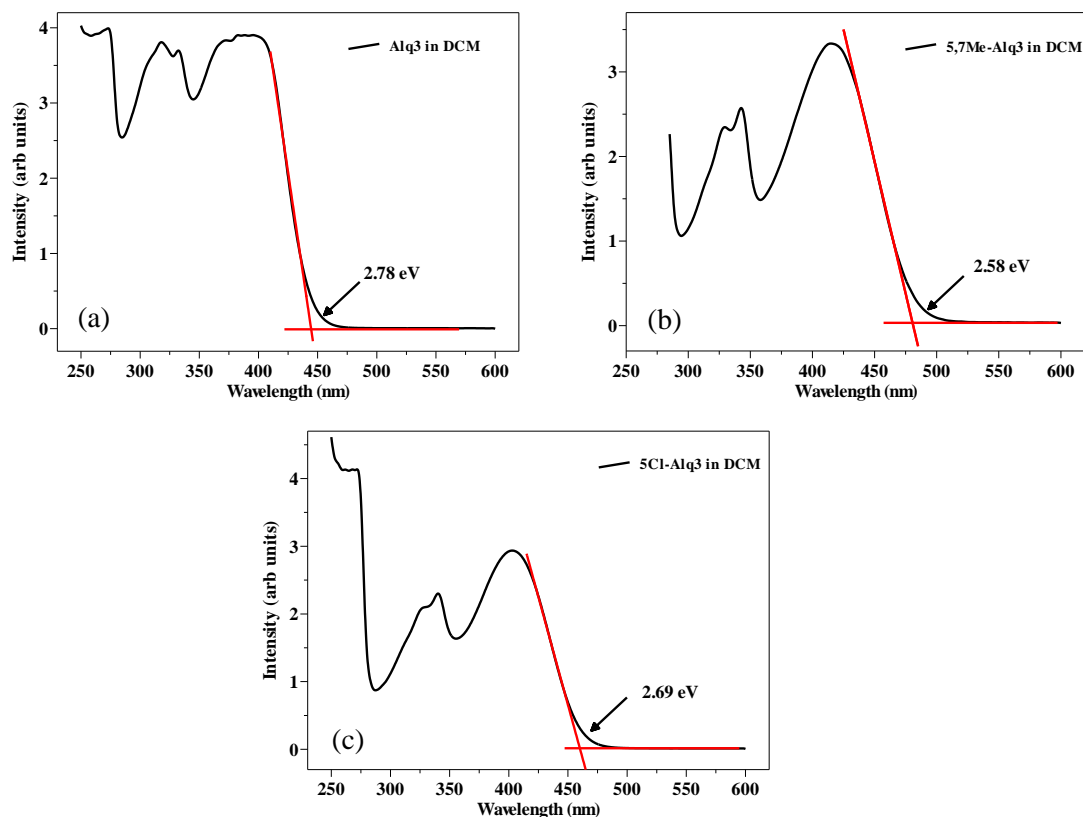

Figure 2: The absorption spectra of (a) Alq$_3$ (b) 5,7Me-Alq$_3$ and (c) 5Cl-Alq$_3$ in DCM. The energy gap is determined from the absorption edges.

Figure 2 shows the absorption spectra for the three Alq_3 samples dissolved in DCM. The spectrum of Alq_3 is dominated by an intense absorption band at ~380 nm. In addition to this intense band, there are 2 weak absorption bands at ~320 and ~330 nm. The broad band at 380 nm is reported to be a ligand centered electronic transitions [9]. The two bands at 320 and 330 nm are assigned to the vibronic progression due to the ring deformation mode of an electronic transition at 346 nm [9]. The same bands are observed for the 5,7Me-Alq_3 and 5Cl-Alq_3 samples, but are red shifted. The corrected base line of the absorption spectra is drawn horizontally. In order to determine the absorption edge a straight line was fitted to the right hand side of the maximum peak (located at ~380 nm for Alq_3) and its intersection with the corrected baseline was determined [10]. In the case of Alq_3, the intersection was found to be at ~445 nm, which corresponds to an optical gap of 2.78 eV. For 5,7Me-Alq_3 and 5Cl-Alq_3 the band gap is 2.58 and 2.69 eV respectively.
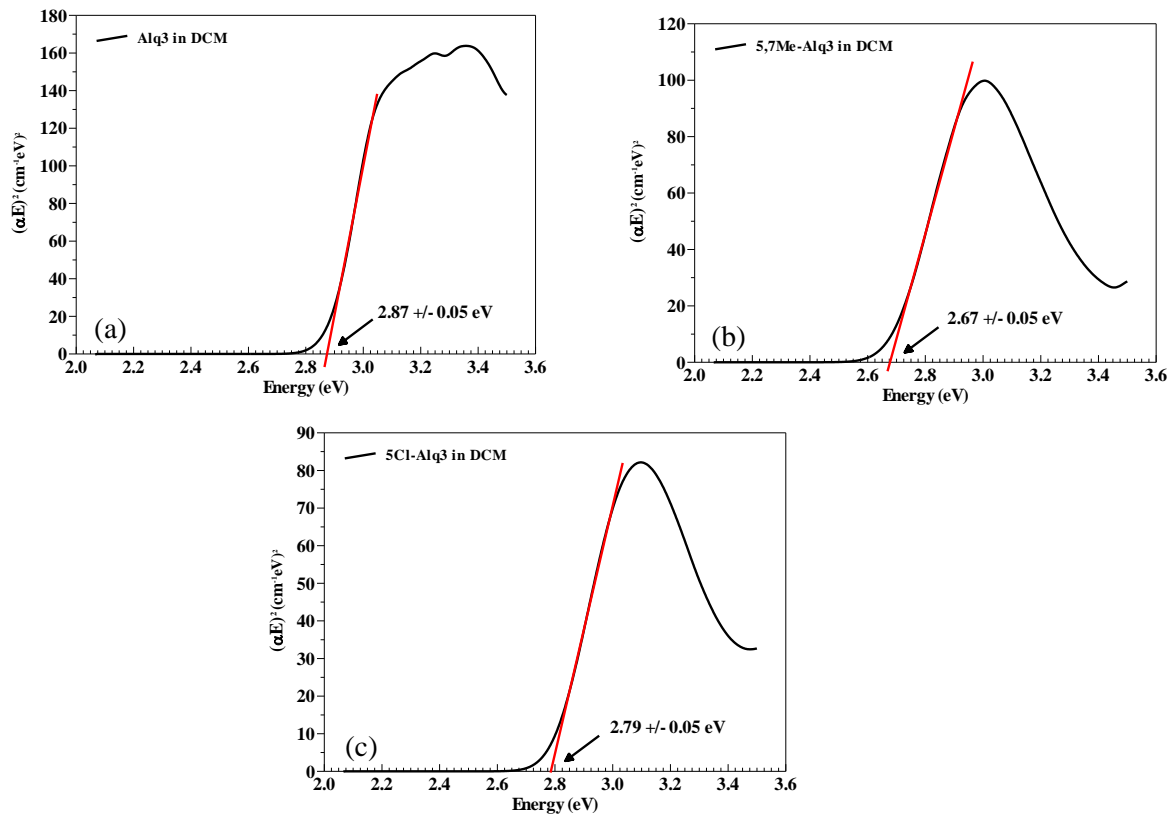

Figure 3: Plot of $(\alpha E)^2$ versus photon energy (E) for (a) Alq_3 (b) 5,7Me-Alq_3 and (c) 5Cl-Alq_3 in DCM.

The direct allowed band gap was determined for the three samples and the plots are shown in figure 3. The obtained values are recorded in table 1.

Table 1: Comparison of the optical band gap of the three samples obtained from CV and optical absorption measurements.

	CV	Absorption edge	Tauc
Alq_3	2.70 eV	2.78 eV	2.87 eV
5,7Me-Alq_3	2.70 eV	2.58 eV	2.67 eV
5Cl- Alq_3	2.68 eV	2.69 eV	2.79 eV

Table 1 summarizes the results obtained for the optical band gap of Alq_3, 5,7Me-Alq_3 and 5Cl-Alq_3 respectively, by using CV and optical absorption measurements. The theoretical value of the optical band gap of solid state Alq_3 is 2.80 eV [11]. The value obtained from CV measurements is 0.1 eV lower, while the values obtained from the optical absorption are 0.02 eV lower and 0.07 eV higher respectively. These values differ from the theoretical value because the band gap was determined from a DCM solution and it is known that solvents play a role on the value of the band gap [12]. The band gap obtained from the CV measurements should be more meaningful [2] as it corresponds directly to an electron being excited from the HOMO to the LUMO level. The EWG and EDG do not have a big influence on the band gap and it does not vary by more than 0.2 eV from the theoretical value of Alq_3. It is therefore suitable to use in OLED devices with the same device architecture as that of Alq_3 devices. This, however, explains the red shift that was observed in the absorption spectra.

4. Conclusion:

Alq_3 molecules with Cl and methyl substituents were successfully synthesized. The absorption spectra of Alq_3 show a broad band at 380 nm and two weak bands at 320 and 330 nm. The main peak of 5Cl-Alq_3 and 5,7Me- Alq_3 is red shifted. The optical band gap for the three samples were determined from the CV and optical absorption measurements and was found to vary by no more than 0.2 eV from the theoretical value of Alq_3. Samples with EWG and EDG are thus suitable to use as the emissive layer in OLED devices.

5. References
[1]   Shafiee A, Salleh M M and Yahaya M 2011 *Sains Malaysiana* **40** 173.
[2]   Misra A, Kumar P, Srivastava R, Dhawan S K, Kamalasanan M N and Chandra S 2005 **43** *Indian J. Pure Ap. Phy.* 921 .
[3]   Shi Y W, Shi M M, Haung J C, Chen H Z, Wang M, Liu X D, Ma Y G, Xu H and Yang B 2006 *Chem. Commun.* 1941.
[4]   Bradas J L, Silbey R, Boudreux D X and Chance R R 1983 *J. Am. Chem. Soc.* **105** 6555.
[5]   Yang C J and Jenekhe S A 1995 *Macromolecules* **28** 1180.
[6]   Kemp K C, Fourie E, Conradie J and Swarts J C 2008 *Organomet.* **27** 353.
[7]   Cook M J, Chambrier I, White G F, Fourie E and Swarts J C 2009 *Dalton Trans.* 1136.
[8]   Tauc J, Grigorovici R and Vancu A 1966 *Phys. Status Sol.* **15** 627.
[9]   Ravi Kishore V V N, Aziz A, Narasimhan K L, Periasamy N, Meenakshi P S and Wategaonkar S 2002 *Synth. Met.* **126** 199.
[10]   Schlaf R, Schroeder P G, Nelson M W, Parkinson B A, Merritt C D, Crisafulli L A Murata H and Kafafi Z H 2000 *Surf. Sci.* **450** 142.
[11]   Dalasinski P, Lukasiak Z, Wojdyla M, Rebarz M and Bala W 2006 *Opt. Mater.* **28** 98
[12]   Su B, Xhang M, Shao Y and Girault H H 2006 *J. Phys. Chem.* **110** 21460.