CHAPTER 4

SINGLE LAYER Alq₃-BASED OLED

4.1 Introduction

In this chapter, an elementary study will be conducted on the fabrication process and characterization of Alq₃ based organic light emitting diode (OLED). Fig. 4.1 shows the molecular structure of Alq₃. Alq₃ is a green emissive material which is a small molecule of an organic group. Due to their thermal stability, Alq₃ is widely deposited using a thermal evaporation technique in OLED fabrication [El-Nahass et al., 2010; C. B. Lee et al., 2004; T. H. Lee et al., 2009; Rajeswaran et al., 2009]. In this case, an evaporation rate plays an importance role to control the surface morphology of the thin film and enhance the luminescence efficiency of the Alq₃-based OLED [C. B. Lee, et al., 2004]. Additionally, the thermal evaporation method allows the thin film of Alq₃ to be either emissive [Cester et al.; T. H. Lee, et al., 2009; H. Mu et al., 2007; Haichuan Mu et al.] or electron transporting layer [Reyes et al., 2002; C. Zhang et al., 2008] in a multilayer structure OLED. However, Alq₃ can also be deposited using a solution process such as spin coating method due to their high solubility in a common organic solvent such as chloroform [Omar et al., 2009]. Moreover, this technique is proven to be the easiest and cheapest way to fabricate OLED [Balaganesan et al., 2003; Coya et al.; Mao et al., 2011].

This chapter focuses in the investigation on the optical, photoluminescence and performance of Alq₃ based single layer OLED prepared by a spin coating technique.
The samples were prepared and characterized in an ambient air environment in order to utilize a robust method of fabricating an OLED device. Based on this study, the improvement in performance of OLED can clearly be seen as described in the next chapter when the dopant molecule is introduced.

![Figure 4.1: Molecular structure of Alq3 used in this work](image)

4.2 Experimental

Thin film of Alq3 was prepared by the spin coating method as described in Chapter 3. Clean glass was used as a substrate. The single layer OLED was constructed as ITO/PEDOT:PSS/Alq3/Al where ITO and PEDOT:PSS acts as a bulk anode layer, Alq3 acts as an emissive layer and Al acts as a metal cathode. The thickness of PEDOT:PSS and Alq3 layers measured are 20±6 nm and 83±5 nm, respectively. All measurements were performed at room temperature and the sample was not encapsulated. Fig. 4.2 shows the schematic structure of an OLED used in this study.

Structural properties of the thin film were analyzed by FTIR (Perkin Elmer) and XRD (Siemens). Optical absorption and photoluminescence characteristics of the thin film were obtained from UV-Vis-NIR (Jasco-V50) and luminescence spectrometer (Perkin Elmer LS 50B), respectively. The thickness of the thin film device was measured by KLA Surface profilometer (P-6). Current density-voltage-luminance (J-V-
characteristics of the device were measured using chroma meter CS-200 (Konica Minolta) powered by a source measure unit (Keithley 2400). Impedance measurements were carried out by using a Solatron 1260 Impedance analyzer. The amplitude of AC signal was 20 mV and the measurement frequency was set in the range of $10^{-1}$ Hz to $10^{-5}$ Hz. All characterizations of the device performance were performed at room temperature without encapsulation.

**Figure 4.2:** Schematic structure of a single layer Alq$_3$ based OLED fabricated in this work

### 4.3 Structural Study

Transmittance spectrum from FTIR measurement of Alq$_3$ in thin film form is shown in Fig. 4.3. As expected, the finger print of hydroxyl quinolate group is observed at wavenumber of 1460 and 1500 cm$^{-1}$. The peak at 1460 and 1500 cm$^{-1}$ corresponds to a CC/CN stretching + CH bending vibration associated with both the pyridyl and phenyl groups in Alq$_3$ [Muhammad et al., 2010]. At a higher wavenumber region, two IR transmittance peaks are observed centered at 1606 and 1578 cm$^{-1}$ which can be assigned to a CC stretching vibration involving the quinoline group of ligands [Koay et al., 2009]. At a lower band, another two vibrations centered at 1385 and 1328 cm$^{-1}$
associated to CC/CN stretching and CH bending of the quinoline fragments of Alq₃ are observed. The three bands which are assigned to a CH/CCN bending and CN stretching vibrations are located at the end of this spectral range with transmittance peak of 1282, 1230 and 1115 cm⁻¹.

![FTIR transmittance spectrum of Alq₃ thin film](image.png)

**Figure 4.3:** FTIR transmittance spectrum of Alq₃ thin film

Fig 4.4 shows the XRD pattern of Alq₃ thin film measured using 2θ method. A broad XRD peak was observed at 2θ=24° which corresponds to the disorder molecular structure of amorphous organic materials [Chauhan et al., 2010]. This indicates that the Alq₃ is formed as an amorphous thin film when prepared using solution process technique. This result is consistent with the reported literatures [Chauhan, et al., 2010; El-Nahass, et al., 2010; J. Zhang et al., 2004]. It is important to form an amorphous emissive thin film in order to produce a large Stoke’s shift device. In contrast, the thin film may form a crystalline thin film if it is fabricated using a vapor deposition method [Rajeswaran, et al., 2009]. The peak observed spread along the spectrum are not significant and cannot be judged as crystalline peaks.
4.4 Optical and Photoluminescence Study

Fig. 4.5 shows the normalized absorption spectrum of Alq3 thin film. The thin film shows broad absorption peak in the visible region centered at around 392 nm with a shoulder peak around 340 nm. A narrow absorption peak also can be seen in the ultraviolet (UV) range at 288 nm. The absorption band in the UV range is referred as the Soret (B) band (288 nm) and in the visible range it is referred as the Q band (392 nm). The electronic transition that involved absorption in the UV and visible range for the organic semiconductor are $\sigma \rightarrow \sigma^*$, $n \rightarrow \pi$ and $\pi \rightarrow \pi^*$ as reported by Kumar et. al. [R. Kumar et al., 2008]. The $\pi \rightarrow \pi^*$ is referred as the transition between bonding and antibonding molecular orbital of the quinolinate ligand [J. Zhang & Frenking, 2004]. In the high energy of absorption band at 288 nm, the electronic transition involved is $\pi \rightarrow d$ and in the region of 210–275 nm, the $d \rightarrow \pi^*$ transition takes place [Farag, 2007]. On the other hand, for the low energy band (Q-band), the absorption is attributed to the $\pi \rightarrow \pi^*$
excitation between bonding and anti-bonding molecular orbitals of the materials [Barberis et al., 2006; J. Zhang & Frenking, 2004].

Figure 4.5: Normalized UV-Vis absorption spectra of Alq₃ thin film

Optical absorption spectrum can be used to determine the optical energy gap, $E_g$ of the organic semiconductor materials. The absorption coefficient ($\alpha$) was calculated using the formula $\alpha = 2.303A/d$ where, $A$ is the absorbance of the thin film and $d$ is the thickness. Thus the optical energy gap of the films was determined by applying the Tauc relationship [Tauc, 1968] :

$$a_0(E - E_g)^n$$

where, $a_0$ is an energy-independent constant. The value of $n$ obtained, determines the type of the absorption transition where $n=1/2$ and 2 for direct and indirect transition, respectively. If the Alq₃ is considered to have a direct band transition type [Muhammad, et al., 2010], then $n=1/2$. Eq. 4.1 becomes;

$$a_0(E - E_g)^{1/2}$$

(4.2)
From Eq. 4.2, graphs of $(ahv)^2$ against $E$ were plotted, as shown in Fig 4.6. Extrapolation of the plot at $(ahv)^2 = 0$ gives the optical energy gap, $E_g$. From Fig 4.6, the presence of a direct allowed transition Alq3 thin film was obtained with energy gaps of $2.80 \pm 0.02$ eV. This result is similarly reported in ref. [El-Nahass, et al., 2010; Muhammad et al.]. The typical energy band diagram of Alq3 is illustrated in Fig. 4.7 where HOMO and LUMO level are at 5.8 and 3.0 eV, respectively [Muhammad, et al., 2010].

![Figure 4.6: Tauc plot of Alq3 thin film](image-url)
It is essential to study the luminescence properties of the materials in order to fabricate good OLED devices. For that purpose, photoluminescence (PL) was performed to the samples. From the absorption results, the absorption edges are used to excite the materials in PL experiment. The 388 nm optical excitation energy was chosen to excite the thin film because the value is near to the maximum absorption of Alq$_3$. The normalized PL spectrum of the Alq$_3$ in thin film form is shown in Fig. 4.8. The Alq$_3$ exhibits broad PL spectrum centered at 512 nm, which corresponds to green light emission that is also reported in [Koay, et al., 2009; S. Kumar et al., 2005; Xu et al., 2006]. The film shows significant red-shift behavior from the absorption spectra which follow Franck-Condon transitions where the emission energy is lesser than the excitation energy [S. B. Lee et al., 1997].
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4.5 Electroluminescence Study

Performance of Alq\textsubscript{3} based OLED was investigated by fabricating a single layer OLED with the configuration of ITO /PEDOT:PSS/Alq\textsubscript{3}/Al where ITO/PEDOT:PSS and Al were acting as an anode and a cathode, respectively. Fig. 4.9 shows the current density-voltage-luminance (J-V-L) characteristic of the Alq\textsubscript{3} based OLED. The turn on voltage of the device, where $L=1\text{cd/m}^2$ is obtained around 15 V. However, the critical voltage is not observed in the range of the applied voltage. It suggests that the device can be operated at higher voltage i.e. more than 20 V. Alq\textsubscript{3} has a high glass transition ($T_g$) of 175°C [Naito et al., 1993] which leads to better thermal stability. Better thermal stability can prevent Joule heating in an OLED operation. The maximum current density and luminance of the device are $7.3\pm0.2\ \text{A/m}^2$ and $8\pm1\ \text{cd/m}^2$, respectively. The performance of the Alq\textsubscript{3} single layer OLED is comparatively lower than that published results [C. B. Lee, et al., 2004; Uddin et al., 2006] which is probably due to the poor environment in which the device is prepared and characterized. This matter can be solved by preparing the OLED device in a glove box [Castro et al.] and the device

Figure 4.8: Normalized photoluminescence spectra of Alq\textsubscript{3} thin film
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should also be tested under vacuum [Caria et al., 2006] or in encapsulated condition [Jung et al., 2011]. However, in order to establish a robust method, the fabrication of the OLED is performed in a clean room environment and the device was tested in an ambient air environment without encapsulation.

Injection process is one of the importance mechanisms in an electroluminescence process. As mentioned in Chapter 2, an injection of charge carrier from an electrode into an organic thin film in an OLED system can be explained either through Richardson-Schottky (RS) or Fowler-Nordheim (FN) model. However, FN-tunneling theory always been used because it is easier to understand in which the Columbic effects is ignored. In this model, only charge tunneling is considered. Besides, in FN theory, the charge carrier needs to gain a sufficient electric field in order to overcome the energy barrier height, $\Phi$, before passes through the metal-organic interface. The data from $J$-$V$ plot in Fig.4.9 has been manipulated, so that FN plot can be determined. Fig. 4.10 shows a FN plot of the single layer Alq$_3$ OLED. The FN tunneling injection of carriers can also be described mathematically by equation (4.3) and simplified by (4.4)

$$J \propto F^2 \exp\left(-\frac{K}{F}\right), \text{ where } K = \frac{8\pi(2m^h)^{1/2} \phi^{3/2}}{3qh} \tag{4.3}$$

$$\ln\left(\frac{J}{F^2}\right) \propto -K \cdot \frac{1}{F} \tag{4.4}$$

where $F$ is an electric field ($F=V/d$, $d$ is thickness of the organic thin film) and $K$ is the gradient obtained from $\ln(J/F^2)$ vs $1/F$ plot. From the equations above, an effective barrier height, $\Phi$ of the Alq$_3$ OLED obtained is 0.88±0.05 eV. This finding is similar as reported previously [Lane et al., 2007].
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![Graph of Current density-voltage-luminance (J-V-L) relationship of the Alq₃ based OLED](image)

**Figure 4.9:** Current density-voltage-luminance (J-V-L) relationship of the Alq₃ based OLED

![Graph of F-N plot of the Alq₃-OLED](image)

**Figure 4.10:** F-N plot of the Alq₃-OLED

Transportation mechanism of an OLED device can be investigated by changing the linear scale of a current-voltage characteristic into a logarithm scale, where the current, \( J \) and voltage, \( V \) can be related a power law equation, \( J \sim V^m \). The \( m \) value
represents a differential resistance of three different regions of carrier transportation in OLED device which are Ohmic, space-charge-limited current (SCLC) and trap charge limited current (TCLC). Fig. 4.11 shows such a plot for the Alq3-OLED investigated. At low applied voltage (Ohmic), the device gives the \( m \) value of 1.9. This value increases up to 4.7 when the voltage supplies increase from 8 to 10 V. Increases in the applied voltage cause an increase in transportation of carrier in organic thin film and thus lead in high current density. This condition is so called SCLC where the charge carrier accumulates in the organic layer to create excitons (electron-hole pair). After a certain time, the accumulated carrier creates an internal electric field which prevents more injection of carrier from the respective electrodes. Due to Coulombic interaction, the excitons, was then, recombined and released energy in the form of emission of light. As the applied voltage increases further, the SCLC effects became negligible and the abundant charge carriers filled up the natural traps within the organic layer. High carrier transportation caused the \( m \) value to increase rapidly to 9.1. This phenomenon is so called TCLC. The nature traps in an organic semiconductor usually come from impurities.

![Log J-Log V plot of the Alq3 based OLED](image)

**Figure 4.11:** Log J-Log V plot of the Alq3 based OLED
Current efficiency of the device can be directly calculated as the ratio of luminance over current density (L/J). Dependency of the current efficiency with the drive voltage of the Alq$_3$ OLED can be seen in Fig 4.12. The current efficiency is slowly reduced with the increase in the applied voltage. It is expected that the current efficiency will drastically drops in high voltage due to the Joule heating. At the maximum luminance at the highest brightness of luminance of 8±1 cd/m$^2$, the current efficiency of the OLED device was calculated to be 1.1±0.2 cd/A.

A constructive study for Alq$_3$ based OLED has been publish by Cai et al. [Cai et al., 2011]. The OLED device was constructed as multilayer structure of ITO/PEDOT:PSS/NPD/ Alq$_3$/Bhen/LiF/Al, where NPD is N,N’-diphenyl- N,N’-bis(1-naphthylphenyl)-1,1’-biphenyl-4,4’-diamine acting as hole injection layer, Bhen is N,N’-diphenyl- N,N’-bis(1-naphthylphenyl)-1,1’-biphenyl-4,4’-diamine acting as electron injection layer and LiF was lithium fluoride acting as low work function metal cathode. An existence of these three layers make the OLED structure differ as compare
to the single layer OLED system fabricated in present work. From this report, the maximum brightness and current efficiency of the Alq$_3$ based OLED are $\sim$14 000 cd/m$^2$ and 4.37 cd/A, respectively. The turn on voltage was around 8 V. These results are absolutely better than the device performance obtained from this work. Even though both OLED devices used Alq$_3$ as the emissive material, there are a few differences that should taking in to consideration to explain the big difference in performance between those devices. Firstly, the additional layers of NPD, Pbhen and LiF in the OLED structure are result in an efficient charge carrier injection and accumulation into emissive layer of OLED. Hence, probability of exciton to be formed and recombined is higher, thus enhance the brightness, current efficiency and even the turn on voltage. Secondly, the devices were fabricated in glove box with inner gas flow inside which reduce a degradation effect from oxidation process, and as a comparison, the OLED device in this study was fabricated in ambient air environment and the chances to be degraded is higher. Thus, the performance of the device is poor and it is postulated that the performance could be higher if the devices are fabricated inside the glove box.

4.6 Impedance Study

The impedance properties of the Alq$_3$ OLED device is represented as a Cole-Cole plot in Fig. 4.13. The plot is measured corresponds to the amount of voltage applied across the device. Both the real and imaginary parts are frequency dependence. The area of the semicircle of the plot observed is reduced as the voltage applied is increased. A clearer figure at a larger scale of the OLED device operated at 5 V is shown in Fig. 4.13. The reduction of the semicircle area indicates that the conductivity of the device increases as the voltage applied increases. It can also be interpreted as sufficient charge carrier in organic layer is transported. Similar observation is also reported in references [Balaganesan, et al., 2003]. It is noted that the conductivity is
inversely proportional to impedance. Thus, the total impedance measured is plotted to clarify this relation. Fig. 4.14 shows the plot of the total impedance corresponding to applied voltage. As expected, the impedance value is reduced significantly when a higher voltage is applied.

**Figure 4.13:** Impedance Cole-Cole plots for Alq₃ OLED with different driven voltage.

The insert show the plot at low impedance range.

**Figure 4.14:** $|Z|$ versus frequency for Alq₃ OLED with different driven voltage
Based on the impedance spectra, the equivalent circuit for the OLED device can be constructed as combination of parallel resistance \((R_p)\) and capacitance \((C_p)\) network in series with a resistance \((R_s)\) as shown in Fig. 4.15. For that purpose, the spectra were analyzed using a complex impedance formula:

\[
|Z| = Z' + iZ'' = \left[ R_s + \frac{R_p}{1 + (\omega R_p C_p)^2} \right] - i \left[ \frac{C_p}{1 + (\omega R_p C_p)^2} \right]
\]

where \(Z'\) and \(Z''\) are absolute impedance, real and imaginary part of the impedance, respectively. The simulated results for the device are presented as a solid line in Fig. 4.16. From the simulated results, the value of \(R_s\), \(R_p\) and \(C_p\) is tabulated in Table 4.1. From the value of \(R_p\), an effective conductivity \((\sigma_{eff})\) is calculated and also listed in Table 4.1. The impedance parameters \((R_s, R_p\) and \(C_p)\) are associated with the intrinsic properties of the OLED device [Chen et al., 2010]. \(R_s\) represents an external resistance between the electrodes and the organic layer. \(R_p\) and \(C_p\) are associated with the resistance of the organic layer and the geometric capacitance of the material, respectively. The value of \(R_p\) reduces significantly with the magnitude of \(10^2\) when 5V of voltage is applied compared to the device without biasing. Consequently, the value of \(\sigma_{eff}\) also increases since the conductivity is inversely proportional to the resistance. This result can be explained by injection and accumulation of charge carrier. As the voltage is increased, the carrier injection and transportation are enhanced which lead to higher concentration of charge carrier. As a result, resistance value of the organic layer drops significantly. However, the reduction in the value of \(C_p\) is very low, approximately \(5\times10^{-9}\) F, and seems rather constant. This is because the geometric capacitance is an intrinsic property of the organic materials and it depends on the type of materials, an effective thickness and the area of the device. A typical thickness and a size of an active area of the device is ~80 nm and ~2.6\times10^{-5} m^2, respectively, and the permittivity of vacuum is 8.85\times10^{-12} F/m. The permittivity constant, \(k\), is calculated to
be ~3.5 which is approximately the same with the reported value of $k \approx 3.0$ for an organic molecule [Chauhan, et al., 2010].

![Equivalent circuit of Alq₃ OLED](image)

**Figure 4.15:** Equivalent circuit of Alq₃ OLED

![Simulated of impedance data for Alq₃ device at different voltage](image)

**Figure 4.16:** Simulated of impedance data for Alq₃ device at different voltage. The insert shows the simulated result at low impedance range.
Table 4.1: Impedance parameter used to simulate the measured impedance plot of Fig. 4.16

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>$R_s$ (Ω)</th>
<th>$R_p$ (Ω)</th>
<th>$C_p$ (nF)</th>
<th>$\sigma_{\text{eff}}$ ($\Omega^{-1}$ m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>25</td>
<td>4.7×10$^3$</td>
<td>10</td>
<td>6.553×10$^{-9}$</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>6.8×10$^4$</td>
<td>10</td>
<td>4.529×10$^{-8}$</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>7.3×10$^3$</td>
<td>10</td>
<td>4.219×10$^{-7}$</td>
</tr>
</tbody>
</table>

Fig. 4.17 (a) shows the overlapping plots of the real and imaginary impedance of the device under the influence of three applied voltages. The overlapping point is referred as the resonance frequency, $\omega_p$ [Chauhan, et al., 2010]. It is observed that the value of the $\omega_p$ of the Alq$_3$ OLED is shifted towards higher frequency which is related to the reduction of the relaxation time, $\tau$. The relation between $\omega_p$ and $\tau$ obeys Debye equation; $\omega_p \times \tau = 1$. The variation of the relaxation time is then shown in Fig. 4.16(b) at three different applied biases. This result shows that as the voltage increases, the time for the charge carriers hopping from one molecule to another becomes shorter. This relaxation time is also known as effective lifetime of a charge carrier [Bisquert, 2001]. Shorter lifetime may result in an increase in the carrier mobility which can be related to the diffusion coefficient of the organic layer [Garcia-Belmonte et al., 2008]. Thus this method can be used to understand the relation between the applied biases to the carrier mobility of the organic material. In an organic solar cell application, the effective lifetime is related to the capture rate of exciton in the recombination region [Mora-Seró et al., 2008].
Figure 4.17: (a) Frequency dependent real (circle) and imaginary (square box) part of the impedance of Alq$_3$ device. (b) Bias voltage dependence of the peak frequency and dielectric relaxation time.
4.7 Summary

The basic study of Alq$_3$ based OLED has been discussed by focusing on the robust preparation and structural, optical and electrical characterization methods. The FTIR result shows that the corresponding elements of Alq$_3$ are retained in the thin film form. The XRD pattern shows the amorphous structure of the Alq$_3$ thin film prepared by the spin-coating technique. The optical absorption and PL results show the large Stoke’s shift which corresponds to the disorder structure of the amorphous thin film. The device shows the maximum luminescence and current efficiency of 8±1 cd/m$^2$ and 1.1±0.2 cd/A, respectively. The effective barrier height obtained from the F-N plot is 0.88±0.05 eV. From the impedance results, the conductivity of charge carrier increases, when the voltage applied is increased. These results show that the structural and optical properties of the Alq$_3$ thin film are not affected by the robust preparation condition. However, the performance of the device is slightly poor. These indicate that a controlled condition is essential in order to fabricate a high performance device. However, in this work, the robust method is intentionally used in order to investigate the possibility of fabricating practical Alq$_3$ OLED in an uncontrolled environment. In the next chapter of this dissertation, some modification to the methods of preparing the device is introduced such that the performance of the Alq$_3$ based OLED is significantly improved.
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