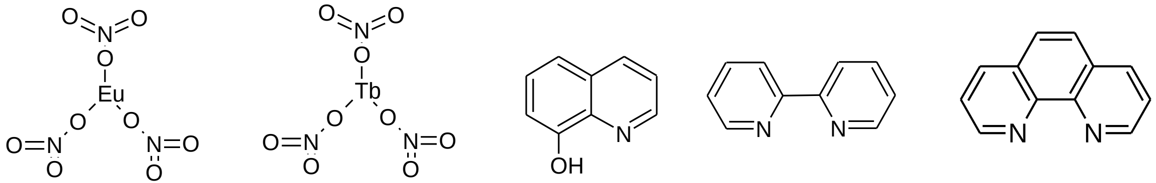
Chapter 3. Experimental Details

3.1. Introduction

This chapter provides the details on the experimental method involved in this research. The materials used in synthesizing all the molecular hybrid compound based on the rare earth metal quinoline ternary complexes (Req_3) chelated with 2,2-bipyridine (Bpy) and 1,10-Phenanthroline (Phen) as neutral ligand namely Euq_3bpy_3, Euq_3phen_3, Tbq_3bpy_3 and Tbq_3phen_3 ternary complexes as well as the synthesis process are presented in the first part. The second part will focused on the thin films deposition and device fabrication method respectively. The final part will focus on the measurement and characterization technique which utilizes Profilometer, UV-VIS/NIR spectrometer, Photoluminescence Spectrometer (PL), Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analyzer and Differential Scanning Calorimeter (TGA & DSC) and Keithly 236 Source Measurement Unit (SMU).

3.2. Materials

Europium(III)nirate [$Eu(NO_3)_3$] and terbium(III)nitrate [$Tb(NO_3)_3$] were purchased from Aldrich. 8Hq and Bpy compounds were purchased from MERCK. Phen compound were purchased from Systerm. The molecular structures of 8Hq, Bpy and Phen are shown in Figure 3.1.



(a) (b) (c) (d) (e)

Figure 3.1 Molecular structure of (a) europium(III)nitrate, (b) terbium(III)nitrate, (c) 8Hq, (d) Bpy and (e) Phen

3.3. Synthesis of molecular hybrid compound based on the rare earth metal quinoline ternary complexes (Req_3) chelated with 2,2-bipyridine (Bpy) and 1,10-Phenanthroline (Phen) as neutral ligand

The molecular hybrid complexes based on the rare earth metal quinoline ternary complexes (Req_3) chelated with 2,2-bipyridine (Bpy) and 1,10-Phenanthroline (Phen) as neutral ligand are synthesized by Prof. Dato' Dr. Muhammad Idiris Saleh et. al from School of Chemical Sciences, Universiti Sains Malaysia. Synthesis process is explained as followed (personal communication).

3.3.1. Europium (III) Tris-(8-hydroxyquinoline)-Tris-(2,2-Bipyridyl) (Euq_3bpy)

The molecular hybrid complex was obtained by the mixture of $Eu(NO_3)_3.6H_2O$, 8Hq and Bpy with molar ratio of 1:3:3 in ethanol. The solution of Bpy (0.03 mol) in 60 mL absolute ethanol was charged into a 250 mL, three neck flask equipped with stirrer. The solution is stirred in nitrogen atmosphere for 30 minutes. Then, a solution of 8Hq (0.03 mol) in 60 mL of absolute ethanol was added to the reaction mixture under stirring at 60 ˚C - 70 ˚C for two hours and cool to 50 ˚C. A solution of $Eu(NO_3)_3.6H_2O$ (0.01 mol) in 6 mL of deionized water was added dropwise, while the mixture in the flask was stirred for two hours. The resulting orange precipitate of the complex was filtered off, washed thoroughly with ether and dried in oven at 70 ˚C. The molecular structure of Euq_3bpy_3 is shown in Figure 3.2.

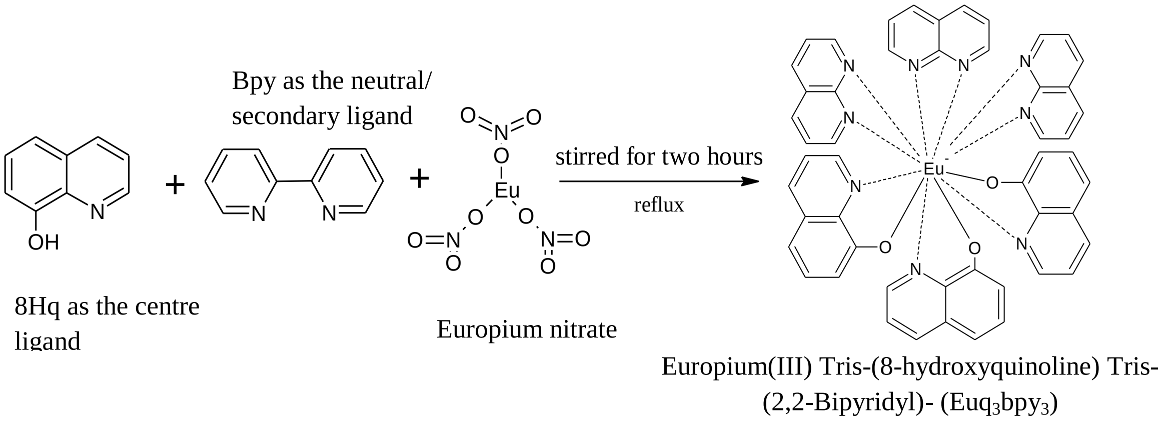


Figure 3.2 Synthesis process and molecular structure of Euq$_3$bpy$_3$.

3.3.2. Terbium (III) Tris-(8-hydroxyquinoline)-Tris-(2,2-Bipyridyl) (Tbq$_3$bpy)

The molecular hybrid complex was obtained by the mixture of $Tb(NO_3)_3.6H_2O$, 8Hq and Bpy with molar ratio of 1:3:3 in ethanol. The solution of Bpy (0.03 mol) in 60 mL absolute ethanol was charged into a 250 mL, three neck flask equipped with stirrer. The solution is stirred in nitrogen atmosphere for 30 minutes. Then, a solution of 8Hq (0.03 mol) in 60 mL of absolute ethanol was added to the reaction mixture under stirring at 60 ˚C - 70 ˚C for two hours and cool to 50 ˚C. A solution of $Tb(NO_3)_3.6H_2O$ (0.01 mol) in 6 mL of deionized water was added drop wise, while the mixture in the flask was stirred for two hours. The resulting orange precipitate of the complex was filtered off, washed thoroughly with ether and dried in oven at 70 ˚C. The molecular structure of Tbq$_3$bpy$_3$ is shown in Figure 3.3.

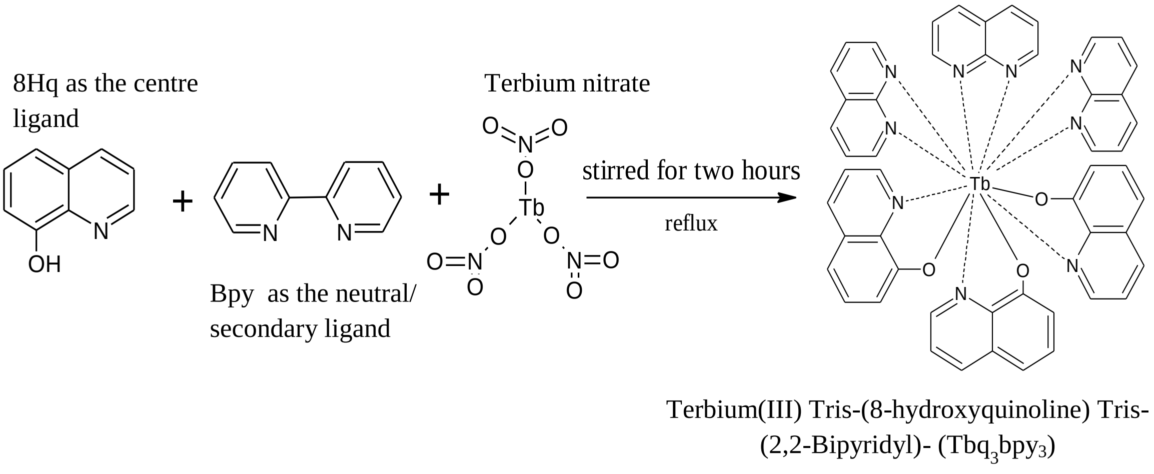
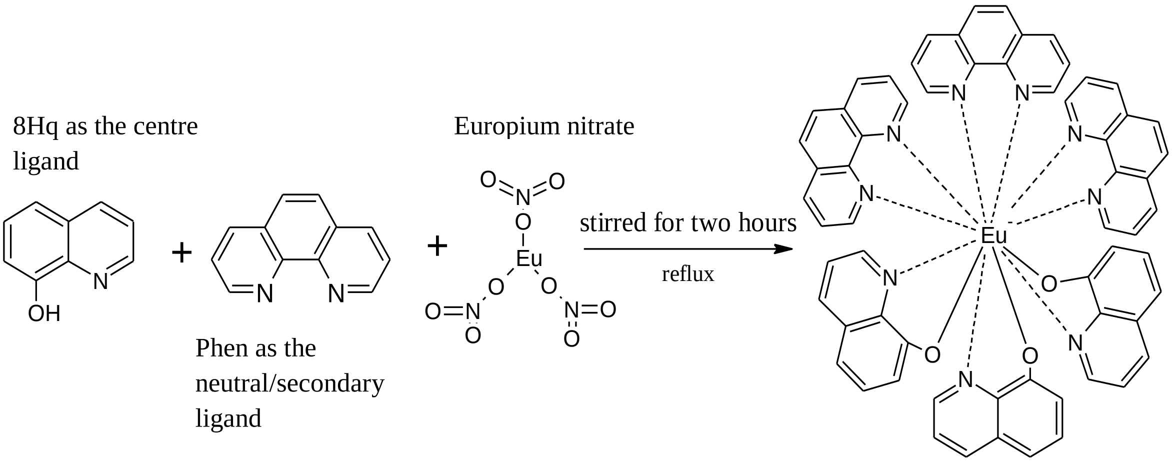


Figure 3.3 Synthesis process and molecular structure of Tbq_3bpy_3

3.3.3. Europium (III) Tris-(8-hydroxyquinoline)-Tris-(1,10-phenanthroline) (Euq_3phen3)

The molecular hybrid complex was obtained by the mixture of $Eu(NO_3)_3.6H_2O$, 8Hq and Phen with molar ratio of 1:3:3 in ethanol. The solution of Phen (0.03 mol) in 60 mL absolute ethanol was charged into a 250 mL, three neck flask equipped with stirrer. The solution is stirred in nitrogen atmosphere for 30 minutes. Then, a solution of 8Hq (0.03 mol) in 60 mL of absolute ethanol was added to the reaction mixture under stirring at 60 ˚C - 70 ˚C for two hours and cool to 50 ˚C. A solution of $Eu(NO_3)_3.6H_2O$ (0.01 mol) in 6 mL of deionized water was added drop wise, while the mixture in the flask was stirred for two hours. The resulting orange precipitate of the complex was filtered off, washed thoroughly with ether and dried in oven at 70 ˚C. The molecular structure of Euq_3phen_3 is shown in Figure 3.4.

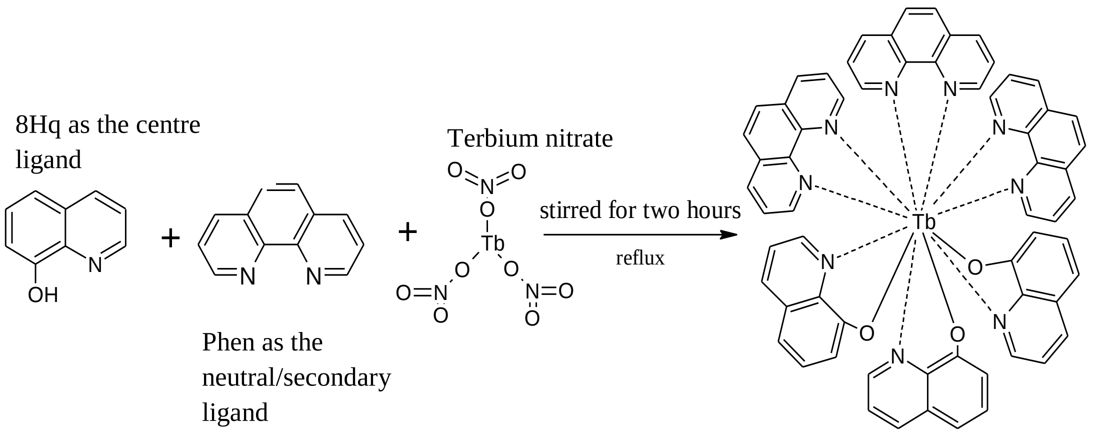


Europium(III) Tris-(8-hydroxyquinoline) Tris-(1,10-phenanthroline)- (Eu$q_3$phen$_3$)

Figure 3.4 Synthesis process and molecular structure of Eu$q_3$phen$_3$

3.3.4. Terbium (III) Tris-(8-hydroxyquinoline)- Tris-(1,10-phenanthroline) (Tb$q_3$phen$_3$)

The molecular hybrid complex was obtained by the mixture of $Tb(NO_3)_3.6H_2O$, 8Hq and Phen with molar ratio of 1:3:3 in ethanol. The solution of Phen (0.03 mol) in 60 mL absolute ethanol was charged into a 250 mL, three neck flask equipped with stirrer. The solution is stirred in nitrogen atmosphere for 30 minutes. Then, a solution of 8Hq (0.03 mol) in 60 mL of absolute ethanol was added to the reaction mixture under stirring at 60 ˚C - 70 ˚C for two hours and cool to 50 ˚C. A solution of Tb $(NO_3)_3.6H_2O$ (0.01 mol) in 6 mL of deionized water was added drop wise, while the mixture in the flask was stirred for two hours. The resulting orange precipitate of the complex was filtered off, washed thoroughly with ether and dried in oven at 70 ˚C. The molecular structure of Tb$q_3$phen$_3$ is shown in Figure 3.5.



Terbium(III) Tris-(8-hydroxyquinoline) Tris-(1,10-phenanthroline)- (Tbq_3phen_3)

Figure 3.5 Synthesis process and molecular structure of Tbq_3phen_3

3.4. Preparation of rare earth quinoline, Req_3 ternary complexes thin films by spin coating method

3.4.1. Overview

Spin coating is one of the solution processed method that is widely used in producing an organic thin film. It is a preferred method for organic thin film as it does not require high temperature that will cause the organic film to decompose upon heating if thermally evaporated. This method is a solvent based method, hence the organic material need to be dissolved in a volatile solvent first before spin casted as thin film. The deposition or spin cast process only requires a few seconds to produce a thin film. Therefore, this technique provide a less expensive production cost due to the fact that the production of the thin film has a simple approach and does not require a long time for deposition. On the other hand, the use of spin coated thin film for device application can prevents pin holes that cause leakage current and increase the degradation process of the device. Therefore in this research it has been demonstrated that Req_3 ternary complexes thin films can be deposited by using a spin coating method. Before producing the Req_3 ternary complexes thin films, the sample solution need to be prepared and the substrate need to be cleaned properly. The following sections of *3.4.2, 3.4.3* and *3.4.4* explain the experimental work including the substrate cleaning procedure, solution preparation and thin film deposition respectively.

3.4.2. Substrates cleaning procedure

Cleaning the substrates prior to thin film deposition is important as a small contamination on the substrate surface can severely affect the optical, electrical, structural and morphology properties of the thin films. In this research, three different substrates which are glass, glass coated with indium tin oxide (ITO) and silicon were used. The silicon substrate was utilized for FTIR analysis, glass substrate was used as the substrate for the optical characterization and ITO substrate was used for device fabrication. The cleaning process for each substrate was different. The glass substrate used in this experiment was cleaned by the following procedure. Initially, the glass substrate was immersed in a foam solution. Then, it was sonicated in an ultrasonic bath for 15 minutes to remove foam from the substrate. Next, the substrate was rinsed using deionized water, acetone and ethanol sequentially. After that it was rinsed again with deionized water and sonicated in ultrasonic bath for 15 minutes. Finally the substrates were purged with nitrogen gas to dry the substrate and remove the remaining moisture. P-type Si (111) (Boron dopant) wafer manufactured by the Polishing Corporation of America with resistivity of 0-10 Ω/cm and thickness of 625 ± 25 μm was used as the substrate only for FTIR measurement. For silicon substrate, the cleaning process is described as follow. Initially, the silicon was rinsed with deionized water. Then it was boiled in solution containing H_2O:H_2O_2:HCL with the ratio of 6:1:1 for 10 minutes. After that, it was rinsed again with deionized water. Then it was immersed in H_2O:H_2O_2:NH_4OH with the ratio of 5:1:1 and H_2O:HF with the ratio of 10:1 sequentially. The silicon substrate was rinsed with deionized water each time after immersing the substrate with different solution. The silicon substrate was then blown dry by nitrogen gas. The process of cleaning ITO substrate was performed as follow. Initially the substrate was immersed in DEACON^{TM}. After that it was sonicated in ultrasonic bath for 15 minutes. Then the substrate was rinsed by using deionized water, acetone and isopropanol sequentially. Finally the substrate was blown dry with nitrogen gas to avoid water spotting. All these cleaning procedures were carried out properly to ensure that the substrates are completely clean and free from contamination.

3.4.3. Solution preparation

All the Req$_3$ ternary complexes compound need to be prepared in a solution form before being cast into a thin film form. These compounds dissolve well in dimethyl sulfoxide (DMSO) compare to other solvent. However it is difficult to spin coat a solution of DMSO due to its high viscosity and boiling point (189 ºC) which consequently will cause a slow evaporation at normal atmospheric pressure. Therefore in order to achieve the essential viscosity and homogeneity of the solution for spin-coating, the solvent was mixed with acetone. The concentration of these solutions was fixed to 10 mg/ml where 10 mg of each compound were dissolved in 1 ml of solvent containing a mixture of DMSO and acetone with the ratio of 4:1. The procedure was proceed by placing the prepared solutions in an ultrasonic bath until a homogenous solution was obtained.

3.4.4. Thin film deposition

A machine utilized for spin coating is called a spin coater. The model of the spin coater used in this research is from LAURER model WS-400-6NPP-LITE (Figure 3.6). The substrate was first placed on the sample holder of the spin coater. The substrate was pumped down by a vacuum pump to prevent the substrate from being thrown out. A 100 µL substance of the Req_3 were dispensed on the centre of the stationary substrate surface by using a syringe. The substance was then allowed to dwell for 10 s. After that, the substance was spread over and covers the entire surface. Next, the substrate was accelerated to a spinning speed of 2500 rpm at 30 s. At this stage, a centrifugal force was transferred through the fluid and forms a wave front that will flow to the substrate edge leaving a uniform layer of thin film.

Figure 3.6 Photograph depicting the spin coater used in this research. The spin speed and time are set in the program provided by this machine

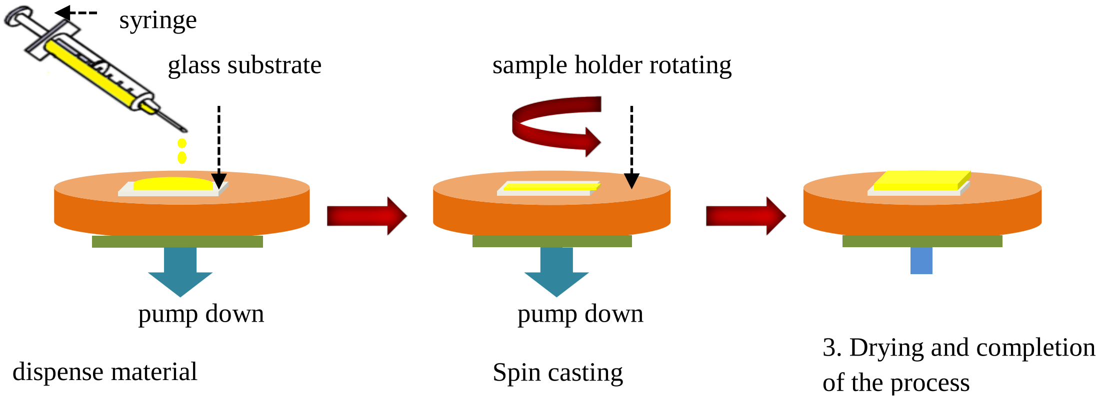


Figure 3.7 Schematic diagram showing process of spin coating to produce thin film. This spin coating process involve three major step which are; first, the dispense of an excessive amount of substance, second, spin casting and the third one is the drying process.

This process is known as spin casting. The evaporation process will occur throughout the process. Lastly, the thin film was permitted to dry for one minute before taken out from the spin coater and further heated for 50 ºC for 30 minutes to remove any trap solvent. A schematic diagram showing the spin coating procedure is shown in Figure 3.7.

3.5. Device Fabrication

3.5.1. Overview

The fabrication process for the device can be divided into three parts: (1) patterning the ITO substrate; (2) depositing the organic layer; (3) depositing the metal electrode. Sections of *3.5.2*, describes briefly the procedure used to prepare the ITO substrate. The deposition of the organic layer is not described in this section as the deposition process using the spin coating method was already described in the previous section. The metal cathode was evaporated by using a thermal vacuum evaporation system. An overview on the thermal vacuum evaporation system is shown and described in Section *3.5.3*. The metal electrode deposition process is discussed further in Section *3.5.4.*

3.5.2. ITO preparation

The ITO substrate was prepared by cutting out 2.0 cm x 2.5 cm rectangles. The substrate was then patterned by covering ½ of the ITO surface by nail polish and etched in hydrochloric acid at 90°C. The etching process was done in order to avoid short circuit between the positive and negative contact. After the etching process, the covered surface was removed by using acetone. Then the substrate was cleaned according to the cleaning procedure discussed earlier. The schematic diagram showing the ITO substrate before and after the etching process is shown in Figure 3.8.

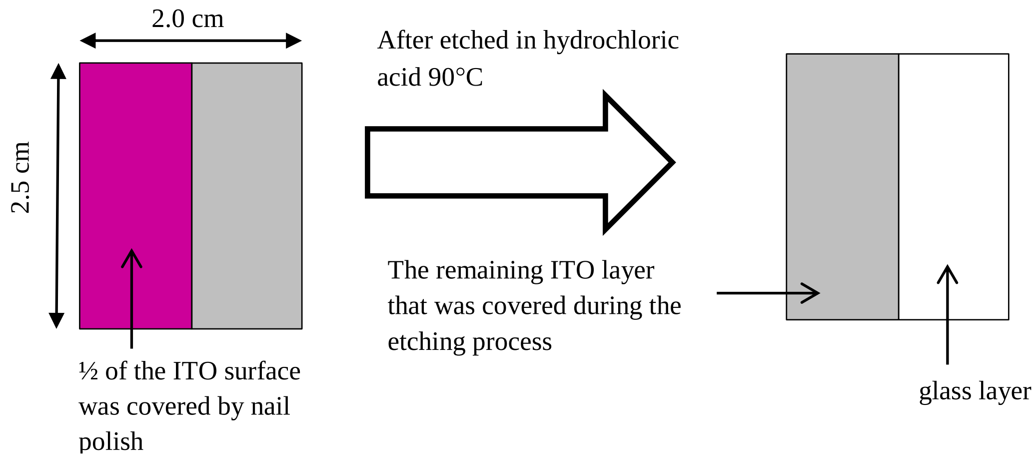


Figure 3.8 Schematic diagrams showing the preparation of ITO substrate for device fabrication

3.5.3. Thermal vacuum evaporation system

Thermal vacuum evaporation is one of the commonly used techniques that have been utilized for a metal deposition. The deposition process requires the metal to be vaporized by heating it to a sufficient high temperature and condensed onto a cooler substrate to form a thin film. The heating process occurs from the large current that passes through a spiral tungsten wire which has a finite electrical resistance. It is essential to carry out The evaporation process occurs in a vacuum chamber with a pressure less than 10^{-5} mbar to ensure that the evaporated metal will have a straight line path between the source and the substrate. Besides, the low pressure is use to avoid reaction between the vapor and the atmosphere as well as to prevent contamination of the source material (oxidation).

Figure 3.9 shows a schematic diagram of the thermal evaporation system arrangement within the vacuum glass chamber. The chamber contained a substrate table that was used to locate a shadow mask. The purpose of using the shadow mask is to obtain a desire aluminum electrode pattern. On top of the shadow mask was the ITO substrate. The crystal sensor used to monitor film thickness and deposition rate is located higher than the sample holder. A spiral tungsten wire consist of the deposition material was clamped and connected to the high current source. The current will flow through the tungsten wire and increase the temperature inside the chamber as well as regulating the deposition rate of the aluminum.

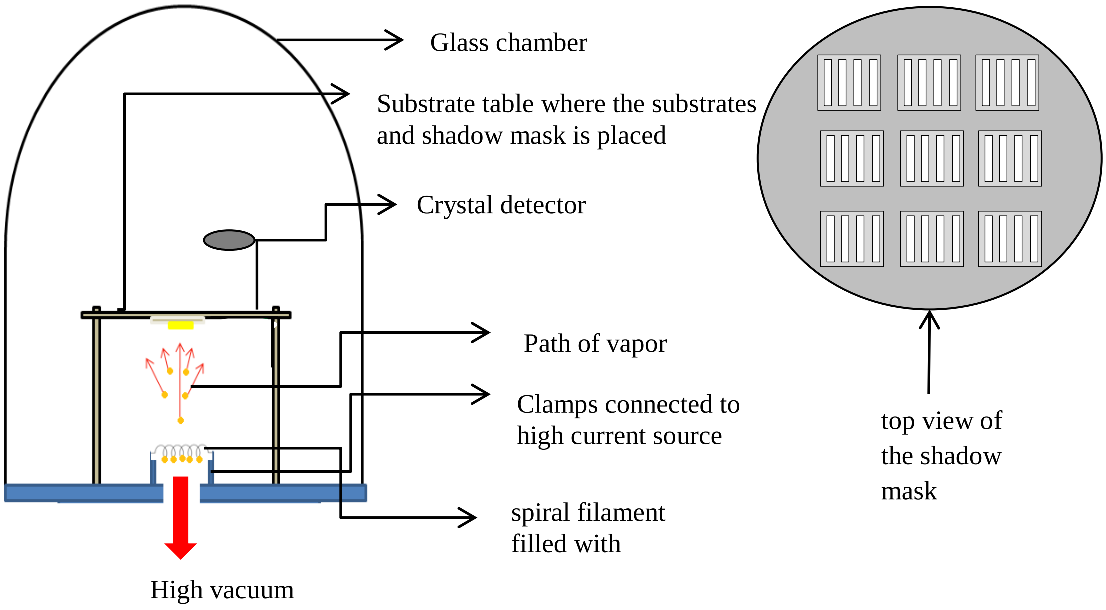


Figure 3.9 Schematic diagram showing thermal evaporation arrangement within the vacuum chamber

3.5.4. Aluminum electrode deposition

In this research, aluminum is used as the metal electrode for the device fabrication. The electrode is deposited using EDWARDS 306 thermal vacuum evaporator (Figure 3.10). A tungsten coil is mounted on a clamp which is connected to the high current source. A few strips of aluminum wire are hung on this coil. Then the ITO coated with the Req_3 ternary complexes is loaded together with the shadow mask which was placed above the substrate table. The top view of the shadow mask used in the deposition process is inserted in Figure 3.9. The desired deposition surface is directed downwards facing the tungsten wire. Following the loading of aluminum and proper substrate orientation, the chamber was pumped for two hours to achieve pressure of 2.5×10^{-5} mbar.

Figure 3.10 Photograph depicting the thermal evaporator (EDWARDS 306) used in this research

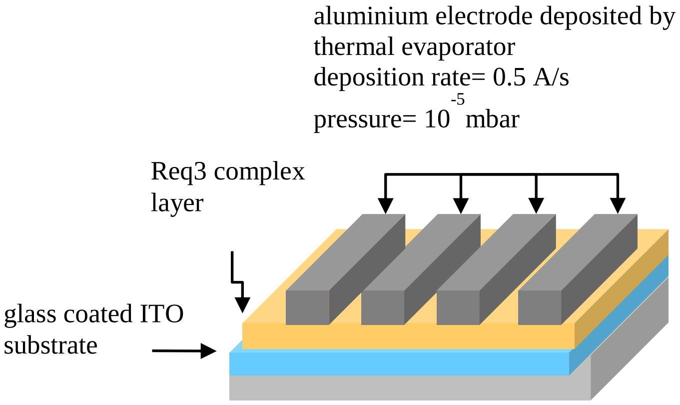


Figure 3.11 OLED architecture consists of spin coated Req3 ternary complexes layer sandwiched between the ITO and aluminum electrode

Consequently, a high current is supplied to the tungsten coil and heating it up to a sufficient temperature which will cause the aluminum to evaporate. The evaporated aluminum was condensed on the surface of the Req$_3$ ternary complexes layer which was not covered by the shadow mask. The growth rate of this aluminum layer depends on the current supplied. The deposition rate for evaporating the aluminum electrode is 0.5

A/s. This produces a single-layer device, in which consist of the Req_3 ternary complexes thin film sandwiched between the ITO and aluminum electrodes. The cross section of the resultant device is shown in Figure 3.11.

3.6. Measurement and Characterization

3.6.1. Overview

The structural, thermal, optical and electrical properties of the Req_3 ternary complexes were characterized by several methods. The structural properties of these materials were characterized by using Fourier transform infrared spectroscopy (FTIR) and X-ray diffractogram (XRD) while the thermal property was investigated using differential scanning calorimetry. The optical properties of the Req_3 ternary complexes were investigated by UV-Vis absorption and photoluminescence (PL) spectroscopy. The electrical characteristic of the Req_3 ternary complexes was performed by using Keithly 236 Source Measurement Unit (SMU) and the luminosity was measured using Konica Minolta CS-200 chromameter. KLA TENCO P-6 profilometer was used to determine the thin film thickness.

3.6.2. Thickness measurement

A contact profilometer is one of the instruments that have been used to measure the thickness of the thin films. Basically, it measures the thickness based on the difference height between the substrates and the thin films. Therefore, the films need to be scratched carefully in order to differentiate a different layer between the substrate and the thin film. A small needle or diamond stylus is moved vertically across the surface for a specific distance as shown in Figure 3.12. The surface profile is then generated based on the deflection of the stylus diamond and the films thickness is obtained.

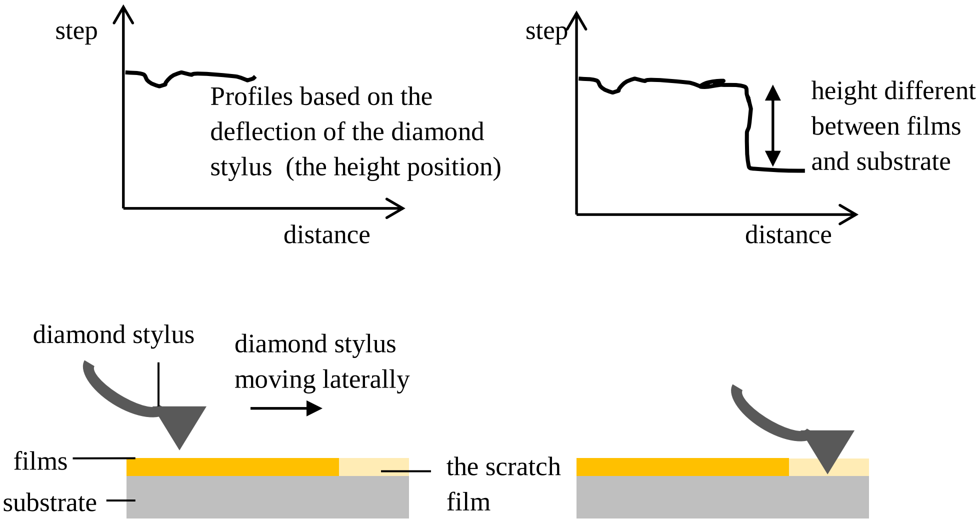


Figure 3.12Schematic diagram showing the thickness measurement

In this research, the Req_3 ternary complexes thin films were measured by using KLA TENCO P-6 surface profilometer (Figure 3.13). The films were scratched in different region across the surface to get several heights for the entire surface. The thickness is calculated from the average thickness of several locations on thin films.

Figure 3.13 Photograph depicting KLA TENCOR P-6 surface profilometer used to measure thickness in this research

3.6.3. Fourier Transform Infrared (FTIR)

The infra-red spectroscopy (IR) is one of the analytical techniques that can provide information on the structure and bonding of the molecules. It is known that the fundamental of IR spectroscopy involves the interaction of a molecule with the infrared radiation. These molecules have bands that are continually vibrating and moving around. As the absorbed infrared radiation matches the exact frequency as the energy difference between the ground and excited state, the bond will be promoted to the excited state. The specific frequencies that excite the specific bond to the excited vibrational state allow us to determine the bonds that exist in a molecule.

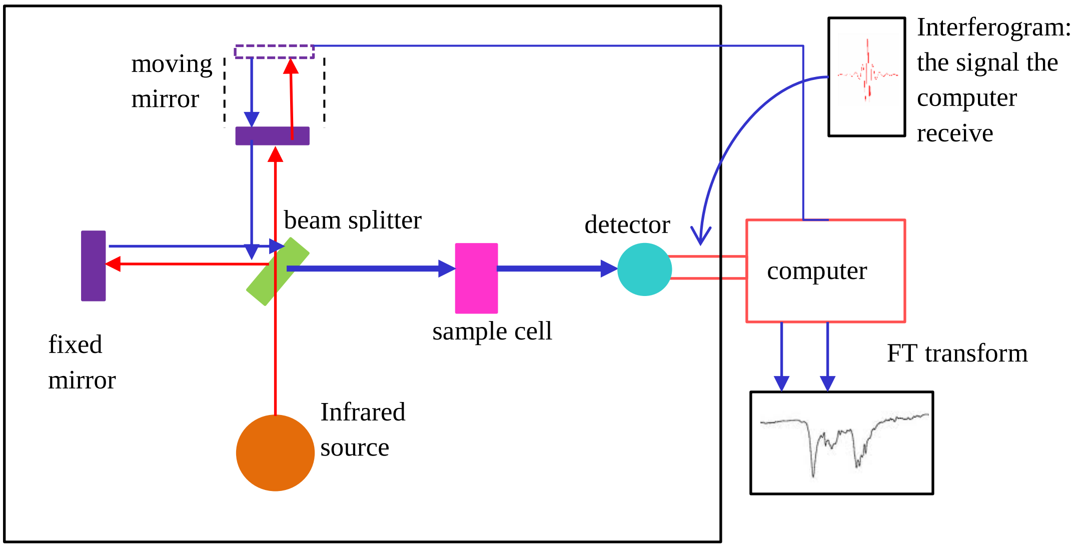


Figure 3.14 Schematic diagram showing optical path of Fourier transform infrared spectrophotometer

Fourier transform infrared spectrometer (FTIR) is the IR spectrometer that is performed to determine the absorption spectrum of a compound. The basic setup of FTIR spectrometer is shown in Figure 3.14. The interferogram is employed in order to generate Fourier transform from the infrared spectra. The interferogram that reaches the detector contains information about the amount of energy absorbed at every frequency. The computer is used to extract the individual's frequency that was absorbed by using Fourier transform mathematical process and to reconstructs and plot typical infrared spectra. In this research the chemical bonding of the Req$_3$ ternary complexes as thin films were investigated by using a Perkin-Elmer System 2000 FTIR spectrometer (Figure 3.15)

Figure 3.15 Photograph depicting the Perkin-Elmer System 2000 Fourier transforms infrared (FTIR) spectrometer that has been used to examining the FTIR spectra of the films

3.6.4. X-ray diffraction (XRD)

XRD is a non-destructive technique that reveals the crystalline structure of a material. The diffractogram that is generated from the measurement is due to the diffraction of the crystal lattice which can only occur when the Bragg's law is satisfying the condition for the constructive interference from plane with *d* spacing. However, for amorphous sample, a broad diffraction hump is observed due to the atoms arrangement that is not periodically located over large distances. In this research, the XRD measurement was performed by Siemens D5000 in order to determine the structure of the thin films

3.6.5. Analyzer and Differential Scanning Calorimeter

Thermo Gravimetric Analysis (TGA) is a thermal analysis technique used to measure changes in the weight (mass) of a sample as a function of temperature and/or time. TGA is commonly used to determine decomposition behavior of organic materials. The differential thermogravimetric (DTG) is the first derivatives of the TGA and is given as a visual aid to distinguish between the overlapping weight loss steps in TGA curve. It should be noted that DTG graph is exactly the same as the TGA except that, the weight loss versus time output is differentiated automatically to give the weight loss rate versus time. The peak temperature of maximum rate of weight loss, T_{DTG} is obtained from the intersection of tangents to the peak of DTG curve.

The basic setup of the TGA/DTG measurement is shown in Figure 3.16(a). The TGA/DTG measurement of the sample is described as follow. Initially the sample is placed into a TGA sample pan. This sample pan is attached to an electronic weighing machine and placed into a high temperature furnace. As heat is applied to the sample, the electronic weighing machine will measure the initial sample weight at room temperature and then continuously monitoring changes in the sample weight. The computer that is connected to the electronic weighing machine and temperature programmer will extract a typical weight loss profile for the amount or percent of weight loss at any given temperature, the amount or percent of non-combusted residue at some final temperature, and the temperatures of various sample degradation processes by using a software. In this research, the TGA/DTG analysis was performed by using Perkin Elmer (TGA)/ Pyris 1 (DSC). The picture of this instrument is shown in Figure 3.16 (b).

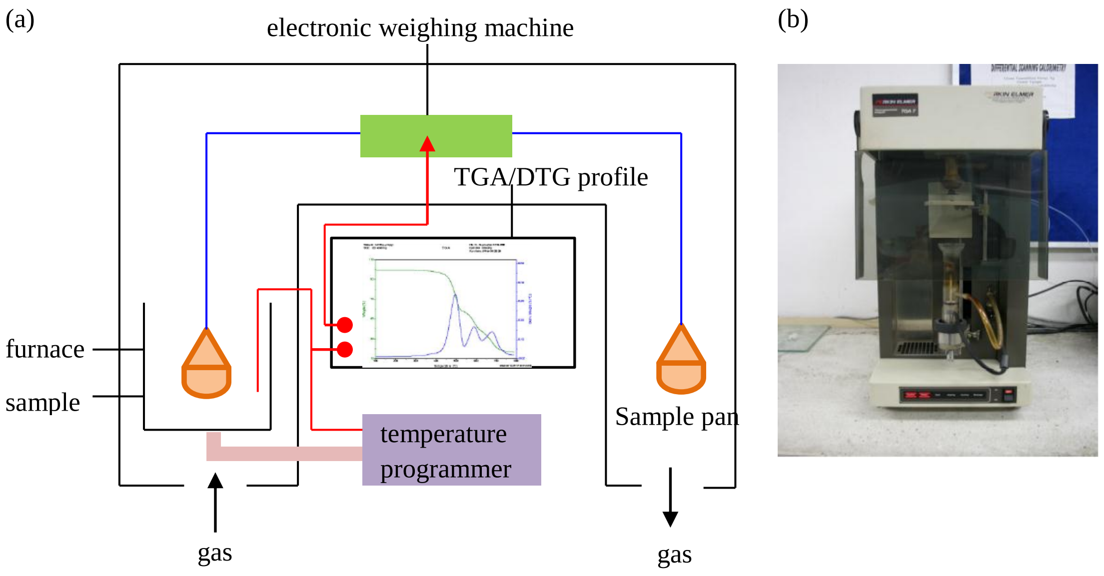


Figure 3.16 (a) schematic diagram of TGA/DTG and (b) photograph depicting the Perkin Elmer (TGA)/ Pyris 1 (DSC) Thermogravimetric instrument that has been used to investigate the thermal properties.

3.6.6. UV-vis Spectrometer

The UV-Vis spectrometer is used to measure the amount of optical absorption in a material as function of wavelength. The basic setup for measuring the absorption or transmission of light through a sample is shown in Figure 3.17. A simplified explanation of the absorption or transmission measurement may be described as follow. Basically, the light source will first pass through the monochromater and then directed to the collimating lens. Then the light is splitted into two light paths through a beam splitter and pass through the sample and reference cell. A photodiode which is usually connected to the difference amplifier will measures the amount of light that passes through the sample and reference cell. The different amount of light that passes through the sample and reference cell is amplified by the difference amplifier. The exact amount of light that passes through the sample is processed and executed by the software to reconstruct and plot typical UV-Vis absorption or transmittance spectra.

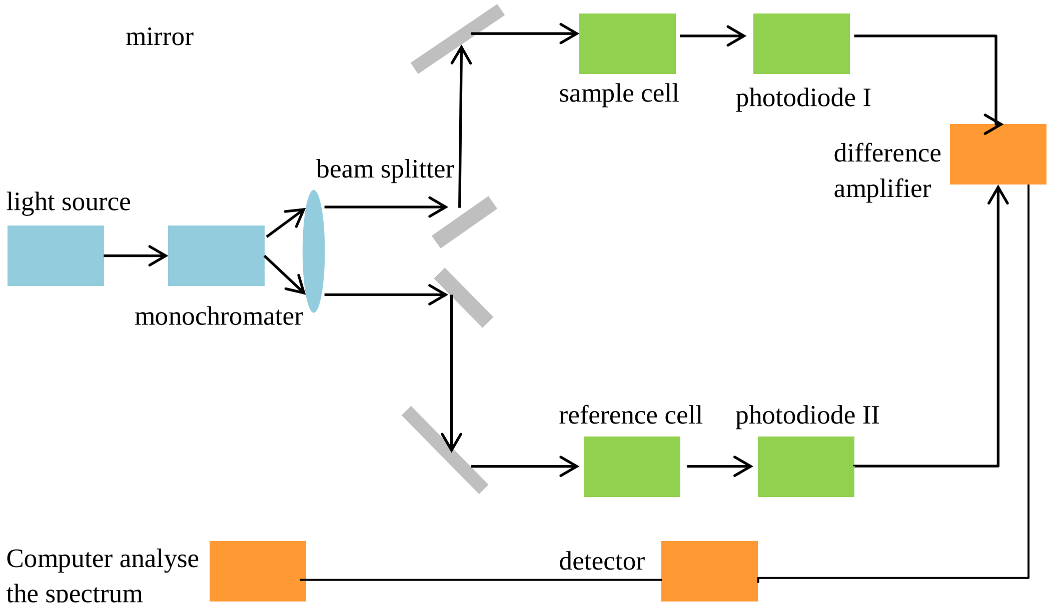


Figure 3.17 Schematic of double beam UV-Visible spectrometer to measure absorption spectra in the wave length range of 200 nm -2500 nm.

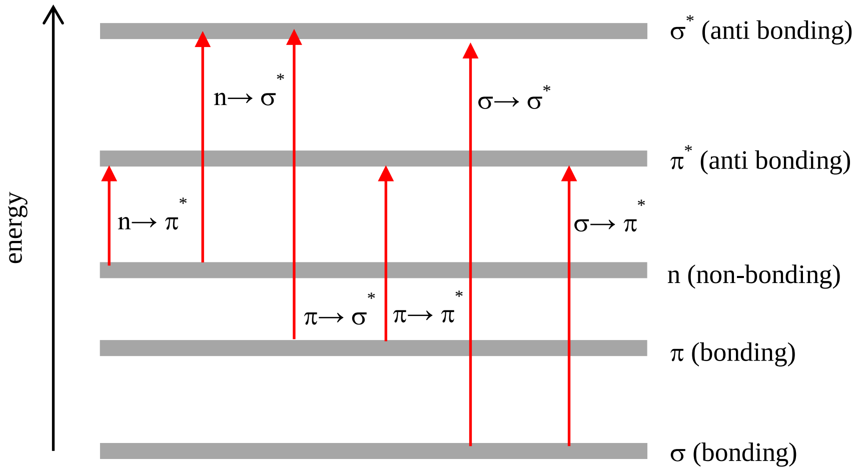


Figure 3.18 Possible electronic transition of π,σ and n electrons

. Typically, the UV-Vis absorption spectra of a sample determine the amount of energy required to promote an electron to an excited state from a ground electronic state. The sample that has been hit by the incident beam will absorb the photon energy to promote the electron to the excited state. Therefore, the UV-Vis absorption which is sometimes known as electronic spectroscopy can be used to identify the electronic excitation that has occurred in organic molecule. The various kind of electronic transition is shown in Figure 3.18. In the research, the absorption spectra measurements of Req$_3$, thin films were measured with the UV-VIS/NIR Spectrometer (model Jasco 570) as shown in Figure 3.19.

Figure 3.19 Photograph depicting the UV-VIS/NIR Spectrometer (model Jasco 570) that have been used to investigate the absorption properties.

3.6.7. Photoluminescence Spectrometer

The photoluminescence (PL) spectrometer is a non-destructive method that can provide the transition energy which can be used to determine the electronic structure of a material. Basically, PL is a process in which a material that absorb a photon and then re-radiates photons. When a light of a sufficient energy is incident on a material, photons are absorbed by the material to provide the energy for the electron to excite to higher energy level. (Gfroerer, 2000). Then the electrons will return to a lower energy state and the excess energy is released by an emission of light through a radiative process.

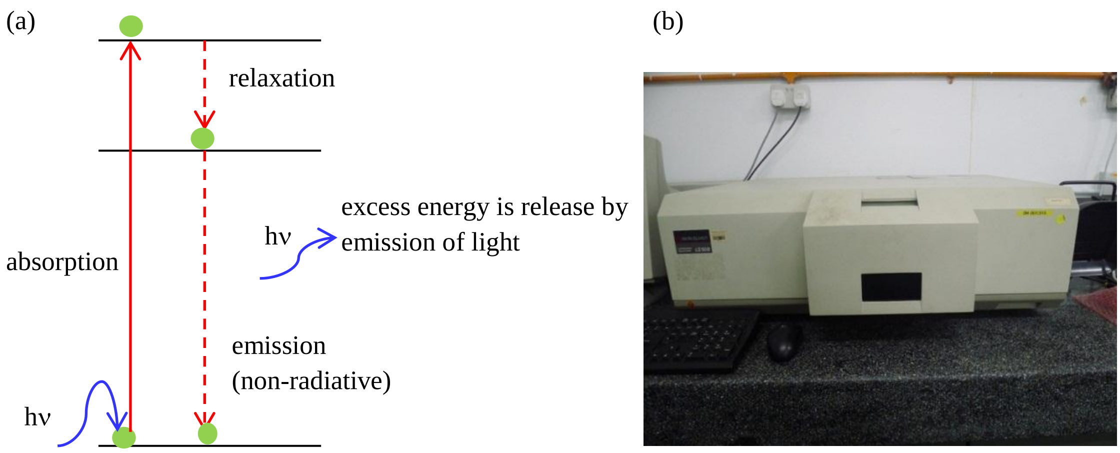


Figure 3.20 (a) A schematic diagram of the photoluminescence mechanism and (b) Photograph depicting Perkin-Elmer Luminescence Spectrometer (model LS50B) that has been used to investigate the photoluminescence properties

The emitted light is called photoluminescence (PL) which is related to the difference in energy levels between the emitted states and excited states as shown in Figure 3.20 (a). This light can be collected and analyzed to provide information about the material. A material that exhibits this characteristic is known as luminescent material. In this research the photoluminescence properties of the Req$_3$ ternary complexes thin films is performed with a Perkin-Elmer Luminescence Spectrometer model LS50B as shown in Figure 3.20 (b). The emission spectra of each Req$_3$ ternary complexes thin films are obtained from the PL spectroscopy. The measurement of the emission spectra enables parameter such as spectral width, position and intensity to be determined.

3.6.8. Current- voltage (I-V) and luminescence (L) measurement

The I-V characteristics of the single-layer devices with configuration the ITO/ Euq$_3$bpy$_3$/Al, ITO/ Euq$_3$bpy$_3$/Al, ITO/ Tbq$_3$bpy$_3$/Al and ITO/ Tbq$_3$phen$_3$/Al were examined using a Keithly 236 Source Measurement Unit (SMU). The SMU is used to source the supply voltage and measure the resulting current of the device. The luminosity of these devices is measured using Konica Minolta CS-200 chromameter which can measure as low as 0.01 cd/m^2. All measurements were performed at room temperature.