# CHAPTER 3 METHODOLOGY

## **3.1 Chemicals and Materials**

To get started with the study of tris (8-hydroxyquinolinate) metals for solutionprocessed organic solar cells, some chemicals and materials are needed to be in hand. These include the organic materials and solvents, quartz and/or glass substrates for depositing the organic films and active layers onto them, and the Indium Tin Oxide (ITO) coated glasses to realize the devices fabrication. Based on these approaches, the hydroxyquinolinate metals are widely characterized in terms of their optoelectronic, photophysical, morphological, structural, and thermal properties relating to the organic solar cells application and their mixing effects onto the active layers photo-absorption. Finally, the organic solar cell devices with and without incorporating tris (8hydroxyquinolinate) metals are fabricated and assessed. However, before the application of Mq3 materials in the solution-processed OSCs, various device architectural structures are studied to select the optimum active layer structure that is compatible for Mq3 inclusion.

## **3.1.1 Organic Materials and Solvents**

The organic materials used in the studies are divided into two types according to their charge carrier categories. Those with electron transport ability are acceptors, while the hole transporters are donors. Tris (8-hydroxyquinolinate) aluminium (Alq3) and gallium (Gaq3), having different central cation metals (M), have been selected as representatives of tris (8-hydroxyquinolinate) metals (Mq3), which are known as strong electron acceptors possessing a unique optoelectronic and thermal properties. In the fabrication of the solution-processed organic solar cells, the estimated optimal amount of Mq3 is added into the donor-accepter blends. The host donor and acceptor materials are  $\alpha, \omega$ -dihexylsexithiophene (DH6T) and methanofullerene (PC<sub>61</sub>BM), respectively. As it was mentioned in the previous chapters, the choice of these materials in the ongoing studies is due to the close values of their charge carrier mobilities, by which a more balanced hole-electron transfer is facilitated and the effect of incorporating Mq3 on the performance of the devices will be more easily understood. The chemical materials were purchased from Sigma-Aldrich Company/Malaysia branch in powder form and used as received. Besides, poly(3,4-ethylenedioxythiophene):poly(4styrenesulfonic) acid (PEDOT:PSS), which is a water soluble hole transport chemical, was purchased in solution form (H. C. Starck, Baytron P VPAI 4033) and filtered prior to use through a 0.45 µm PTFE syringe filter. The use of PEDOT:PSS between the active layers and ITO electrode in the organic solar cells was seen to effectively enhance their photovoltaic performance. This is basically due to its advantages of reducing the current leakage by preventing short circuiting, smoothing out the ITO surface layer to enhance the hole injection, and facilitating hole transport carriers between the active layer and ITO as a consequence of its higher work function (5.0 eV) compared to that of ITO (4.8 eV). Therefore, its utilization in the devices fabrication was chosen throughout. Figure 3.1 shows the chemical structures of the organic materials used in the studies, hereafter, their abbreviations are mentioned throughout the thesis.



Figure 3.1: The chemical structure of (a) Mq3 (M = Al, Ga, and q = 8-hydroxyquinolinate), (b) DH6T, (c) PCBM, and (d) PEDOT:PSS.

The choice of correct solvent is crucial to dissolve the chemical materials. However, it is difficult to get a solvent capable of dissolving all the organic chemicals efficiently, while Mq3 and DH6T are mostly known as poorly soluble materials (but comparably cheap materials). For that, among several pre-tried solvents, chlorobenzene (CLB) and/or carbon disulphide (CS<sub>2</sub>) was selected to be used for dissolving the blended system (DH6T/Mq3/PCBM). Chlorobenzene is the most favored solvent in preparing the bulk heterojunction solar cells due to the better solubility for PCBM and crystal packing structure (Baek, et al., 2009). As recent studies confirmed that the optimum condition of donor/PCBM ratio can be about (1:4) (Hoppe, et al., 2004), and higher ratio of PCBM compared to that of the donor (Bull, et al., 2009) is favorable. Besides, it was seen that adding a small amount of Mq3 into DH6T is needed to improve the photo-absorption properties of the mixture films (Muhammad & Sulaiman, 2011c). Consequently, the relatively low solubility of DH6T and Mq3 does not affect the solutions preparation. For instance, if a solution of DH6T/PCBM was needed to be

prepared in a weight ratio of (1:2) with concentration 30 mg/mL, only 10 mg of DH6T was required to be used, which was reasonably enough to be highly dissolved in the prescribed solvents. Table 3.1 shows the organic materials with their solvents and solutions concentration processed during the materials characterization and devices fabrication procedures.

Material	Solvent	Solution concentration	
Alq3, Gaq3	Dimethyl sulphoxide (DMSO)	5 mg/mL	
DH6T	Chlorobenzene or carbon disulphide	5 mg/mL	
РСВМ	Chlorobenzene or chloroform	5 mg/mL	
DH6T/Mq3	Chloroform/hexane (1:1 co-solvent) or carbon disulphide	5 mg/mL	
DH6T/PCBM	Chlorobenzene	30 mg/mL	
DH6T/Mq3/PCBM	Chlorobenzene or carbon disulphide	30 mg/mL	

Table 3.1: The organic materials, their respective solvent(s), and concentration of the solutions prepared for various studies.

## 3.1.2 Substrates and Electrodes

For the characterization purpose of the films, quartz and glass substrates were used, whereas for the devices fabrication, ITO coated glass substrates have been utilized. The importance of using quartz substrates is to help probing the photoabsorption behaviors of the films readily at higher photonic energy in the ultraviolet region. The substrates were purchased from H. W. Sands Co., Ltd., and then they were cut, patterned, and cleaned according to the desired sizes and shapes prior to their use. In the case of the organic solar cells fabrication, the cathode and anode electrodes were Al and transparent ITO, respectively. The ITO electrode having a sheet resistance of  $\approx$ 10  $\Omega$ /sq. is that side on which the devices are illuminated; therefore, it should provide a high possible transparency. ITO conductive electrodes usually show transparency of > 90%, which makes them a strong candidate to be applied in the OSCs. The difference between the work function of Al (4.2 eV) and ITO (4.8 eV), provides possible approach to design normal device structures by depositing the hole conductive materials onto the ITO side and electron conductive ones below the Al electrode.

#### 3.1.3 Substrates Patterning and Cleaning

The ITO substrates were patterned into a desired structure by means of a wet etching process. The whole procedure was performed as follows; the ITO part that was desired to be removed was first covered by vinyl tape stripes of equal width, then the remained uncovered part of ITO has been polished with blob nail. Once the nail polish was dried in air, the tape stripes were removed from the covered ITO part. Afterwards, the substrates were immersed in a bath of a diluted hydrochloric acid (HCl) in distilled water (DIW) with the ratio of 0.4:1, and then agitated for 15 min at a temperature of about 60 °C. By doing this, the ITO substrates have been correctly patterned. In the final step, before applying the various substrates for the films deposition or devices fabrication, the quartz, glass, and ITO coated substrates were cleaned ultrasonically for 15 minutes in Deacon® Neutracon foam solution, followed by 10 minute cleaning using acetone, ethanol and distilled water in an ultrasonic bath, subsequently. And then, they were dried thoroughly by blowing nitrogen gas.

#### **3.2 Thin Films Coating**

The Mq3 organometallic materials and DH6T/Mq3/PCBM blend systems were coated onto the specified substrates in order to characterize the films and to fabricate the solution-processed organic solar cells, respectively. In the next subsections, the coating procedures are demonstrated.

## 3.2.1 Gaq3 and Alq3 films

The tris (8-hydroxyquinolinate) metals, Gaq3 and Alq3 with their linear molecular formula of  $M(C_9H_6NO)_3$ , where M = Ga or Al, and having three ligands each with a phenoxide and pirydyl side group, are shown in Figure 3.2-(a). Figure 3.2-(b) shows the schematic diagram of the organic films deposited onto the transparent quartz slides, while Figure 3.2-(c) depicts the schematic of a home made thermal evaporator that has been utilized to grow the films. Films of Gaq3 and Alq3 were sequentially deposited onto the pre-cleaned quartz slides using the home-made thermal evaporator under a base pressure of about  $10^{-4}$  mbar. Initially, powder of Gaq3 or Alq3 was placed inside a quartz boat that has been surrounded by a tungsten coil capable of supplying sufficient heat to the materials upon passing the electrical current through this coil. Currents of about 30 to 35 Ampere were enough to start sublimating the powders. The quartz substrates were kept at the top of the chamber at room temperature (300 K) during the vapor application and throughout the whole deposition process. Prior to deposition, the quartz slides were cleaned as described in following the procedure in section 3.1.3. The quartz slides were selected because of their high optical transparency to just below 200 nm. All the measurements upon the deposited films were performed under ambient conditions and at room temperature, as to be discussed later. The choice of this method to deposit the Mq3 films was due to its simplicity and reliability into the films characterization (Muhammad & Sulaiman, 2011d) compared to the other techniques used in the field of small molecular organic films. However, for the Mq3 to be applied in OSCs, a solution-processed technique has been employed.



Figure 3.2: (a) The chemical structure of Mq3, (b) the schematic diagram of the deposited Mq3 films on the transparent quartz slides, and (c) the schematic diagram of the thermal evaporator set-up.

#### 3.2.2 DH6T/Mq3/PCBM Heterostructure Films

The linear molecular formula of DH6T is  $C_{36}H_{38}S_6$ , while that of PCBM is  $C_{72}H_{14}O_2$ . To study the photo-absorption response of DH6T upon Mq3 addition, which is an important property governing the photoactive layers performance in OSCs, and to estimate the optimum amount of Mq3 in this trend, the DH6T/Mq3 mixtures with different Mq3 contents (weight %) were dissolved in chloroform/hexane co-solvent (1:1) or chlorobenzene to obtain solutions of concentration 5mg/mL. The prepared blends were stirred on a magnetic stirrer at 550 rpm for about 48 hours. From these solutions, films of DH6T/Mq3 were coated onto the pre-cleaned quartz substrates by casting technique.

After analyzing and characterization of Mq3, as well as finding the optimum amount to be added to the DH6T donor, as mentioned previously, the patterned ITO coated glass substrates were used to fabricate the solution-processed OSC devices. Before the devices fabrication, DH6T/Mq3/PCBM blended films on the solid substrate were characterized. As such, all the PEDOT:PSS, DH6T:PCBM, and DH6T:Mq3:PCBM active layers were obtained from the materials solution and deposited by the spin coating machine as shown in Figure 3.3. The coating processes were undertaken at room temperature, i.e., without being performed under a controlled ambient or inside a glove box. By this, attempts have been made to realize the reduction in the costs and complexity of use.



Figure 3.3: The spin coating machine that is used to deposit active layers for the characterization and devices fabrication purposes.

#### **3.3 Characterization Techniques**

In this section, the experimental techniques and instruments that were used to carry out the studies from materials characterization to the devices fabrication and assessment are reported.

## 3.3.1 Ultraviolet-Visible-Near Infrared (UV-Vis-NIR) Spectrophotometer

A Jasco V-570 Ultraviolet- Visible- Near Infrared (UV-Vis-NIR) spectrophotometer, whose photograph shown in Figure 3.4, was used to measure the optical functions of the materials. Based on the absorption spectrum data, other optical functions can be calculated such as absorption coefficient, extinction coefficient, optical

energy gap, refractive index, dielectric parameters, etc, as well as, to find the optical thickness of the Mq3 films through their transmittance spectra measurement.



Figure 3.4: Photograph of Jasco V-570 UV-Vis-NIR spectrophotometer.

The word 'spectroscopy' is used as a collective term for all the analytical techniques based on the interaction of light and matter. In UV/Vis/NIR spectroscopy, various phenomena including reflectance, transmittance, and absorbance can be recorded for the samples (gas, vapor, liquid, or solids) under investigation. A standard spectroscope measures direct transmittance as a percentage (%T); this represents the percentage of the incident beam of light transmitted by the sample. This value is then used to calculate absorbance (A): A = log (1/T).

With the right kind of equipment, UV/Vis/NIR spectroscopy makes it possible to measure the different percentages of light reflected, transmitted, or absorbed by the sample. UV/Vis/NIR spectrophotometer can be used for optical absorption spectroscopy in the wavelength range from 175 to 3300 nm. The principle of UV/Vis lies in the fact that molecules have the ability to absorb ultraviolet and/or visible light, thereby promoting electrons from the HOMO to the LUMO level. The energy involved in this process is generally large and electronic spectra of molecules are usually found in the

visible and ultraviolet region of electromagnetic spectrum (Gupta, Kumar, & Sharma, 2007). In the absorption process various electronic transitions are involved as shown in Figure 3.5.

The wavelength at the maximum of the absorption band can give information regarding the structure of the molecule or ion and the extent of the absorption is proportional with the amount of the species absorbing the light. Moreover, in some cases absorption spectroscopy is an efficient tool to probe the charge-transfer phenomena, especially in the cases where two components of electron donor and acceptor are brought into a contact (D-A blend system).



Figure 3.5: Electronic energy levels and transitions involving in UV-Vis absorption.

The three main components of UV-Vis-NIR spectrophotometer are a suitable light source, monochromator to select the light with the necessary wavelength, and a detector to record the intensity of the light transmitted. In the solution form, the sample is placed into a sample quartz tube called a cuvette. The intensity measured by the detector is converted into an electric signal and is displayed as a certain absorbance on the readout. Figure 3.6 shows the block diagram of the UV-Vis spectrophotometer operation principle (Chemistry, date unknown).



Figure 3.6: Operating principle of the UV-Vis spectrophotometers.

#### **3.3.2** Photoluminescence (PL) Spectroscopy

A LS50B Perkin Elmer luminescence spectrometer, whose photograph shown in Figure 3.7, was used to study the photoluminescence (PL) behavior of the films in the wavelength range from 200 nm to 800 nm. PL experiments provide relatively direct information about recombination and relaxation processes, which are important phenomena in the photo-physical consideration for both of the organic light emitting diodes (OLED) and OSCs materials. Luminescence is the conversion of radiation or other forms of energy to visible light. It occurs when the incident radiation excites electrons from the valence band (HOMO), through the energy gap, and into the conduction band (LUMO). The excited electrons remain in the higher energy levels for a very short period of time, then they drop back to the valence band, photons are emitted. If the wavelength of these photons is in the visible light range, luminescence occurs. Figure 3.8-(a) shows this photo-excitation and emission process, while Figure 3.8-(b) is simply illustrating the operating principle behind the PL spectrometer instruments. Luminescence does not occur in metals. Electrons are merely excited into higher energy levels within the unfilled valence band and, when the excited electron returns to the lower energy level, the photon that is produced has a very small energy and a wavelength longer than that of visible light (Askeland & Phulé, 2006).



Figure 3.7: Photograph of LS50B Perkin Elmer luminescence spectrometer.

Conjugated polymers are easily placed into an excited state with UV light. Their PL spectra exhibits a broad structure (~200 nm wide) located in the visible range and may contain multiple peaks. One peak is due to the electronic ground state of the polymer (generally nondegenerate), the others are vibronic states. The broadening of the peaks is due to the range of energies each states may have.



Figure 3.8: (a) Luminescence process, and (b) operating principle of the PL spectrometers.

## 3.3.3 Fourier Transform Infrared (FTIR) Spectrophotometer

A Nicolet IS10-Thermo Scientific Fourier Transform Infrared spectrophotometer (FTIR), whose photograph shown in Figure 3.9, was used to analyze the molecular spectroscopic properties of the materials (powders and films) in the absorbance or transmittance mode within a wave-number range from 400 to 4000 cm<sup>-1</sup>. Almost any compound having covalent bonds, whether organic or inorganic, absorbs various frequencies of electromagnetic radiation in the infrared region of the electromagnetic spectrum. This region lies at wavelengths longer than those associated with visible light, which range from approximately 400 to 800 nm, but lies at wavelengths shorter than those associated with microwaves, which are longer than 1 mm.



Figure 3.9: Photograph of Nicolet IS10-Thermo Scientific FTIR spectrophotometer.

The absorption of infrared (IR) radiation is, like other absorption processes, a quantized process. A molecule absorbs only selected frequencies (energy) of infrared radiation. The absorption of IR radiation corresponds to energy range of 8 to 40 kJ/mole (Lampman, Pavia, Kriz, Vyvyan, 2010). Radiation in this energy range corresponds to the range encompassing the stretching and bending vibrational frequencies of the bonds in most covalent molecules (Gupta, et al., 2007). An IR spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. The size of the peaks in the spectrum is a direct indication of the amount of material present. As in the absorption process, those frequencies of IR radiation that match the natural vibrational frequencies of the molecule in question are absorbed; no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis, e.g., the quality or consistency of a sample, the amount of components in a mixture, and probing the complexation formation between molecular components (Griffiths & De Haseth, 2007). However, not all bonds in a molecule are capable of absorbing IR energy, even if the frequency of the radiation exactly matches that of the bond motion. Only those bonds that have a dipole moment that changes as a function of time are capable of absorbing IR radiation. Symmetric bonds, such as those of H<sub>2</sub> or Cl<sub>2</sub>, do not absorb IR radiation. Another important use of the IR spectrum is to determine structural information about a molecule. The absorptions of each type of bond (N-H, C-H, O-H, C-X, C=O, C-O, C-C, C=N, and so on) are regularly found only in certain small portions of the vibrational IR region. A small range of absorption can be defined for each type of bond. Outside this range, absorptions are normally due to some other type of bond. For instance, any absorption in the range 3000  $\pm$  150 cm<sup>-1</sup> is almost always due to the presence of a C=O bond (carbonyl group) in the molecule. The same type of range applies to each type of bond. Figure 3.10 illustrates schematically how these are spread out over the vibrational IR (Lampman, et al., 2010).

O-H N-H	С-Н	$C \equiv C$ $C \equiv N$ $X=C=Y$ $(C,O,N,S)$	Very few bands	C=O	C=N C=C N=O	C-Cl C-O C-N C-C N <del>T</del> O
4000	250	0 200 Frequ	00 180 1ency (cm <sup>-1</sup>	)0 165 )	50 155	650

Figure 3.10: The approximate regions where stretching vibrations occur for various common types of bonds.

Two types of IR spectrometers are in common use: dispersive and Fourier Transform (FT) instruments. Both of these types of instruments provide spectra of compounds in the normal range of 4000 to 400 cm<sup>-1</sup>. Although the two machines provide nearly identical spectra for a given compound, FTIR spectrometers provide the spectrum much more rapidly than the dispersive instruments. A schematic diagram of an FTIR is shown in Figure 3.11 and its normal instrumental process is as follows (Griffiths & De Haseth, 2007; Lampman, et al., 2010):

- The Source: Infrared energy is emitted from a glowing black-body source. This beam passes through an aperture which controls the amount of energy presented to the sample (and, ultimately, to the detector).
- The Interferometer: The beam enters the interferometer where the "spectral encoding" takes place. The resulting interferogram signal then exits the interferometer.
- The Laser: The Laser beam also passes through the interferometer. It is used for wavelength calibration, mirror position control, and data collection triggering of the spectrometer.
- The Sample: The beam enters the sample compartment where it is transmitted through or reflected off of the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed.
- The Detector: The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal.
- The Computer: The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation.



Figure 3.11: The approximate regions where stretching vibrations occur for various common types of bonds.

## 3.3.4 X-Ray Diffraction (XRD) Technique

To probe the structural nature of the investigated materials in powder or film forms, an X-ray diffractometer (Bruker AXS), using Cu K<sub>a</sub> radiation of wavelength  $\lambda =$ 1.5406 A° as a source and glancing angles in the range of 5°  $\leq 2\theta \leq 90^{\circ}$ , was utilized to record the XRD patterns. Figure 3.12 shows photograph of the XRD machine used in the experiments.



Figure 3.12: Photograph of the used X-ray diffractometer machine (Bruker AXS).

Diffraction can occur when any electromagnetic radiation interacts with a periodic structure. The repeat distance of the periodic structure must be about the same wavelength of the radiation. The interatomic distances in crystals and molecules amount to 0.15-0.4 nm, which correspond in the electromagnetic spectrum with the wavelength of x-rays having photon energies between 3 and 8 keV (Grieken & Markowicz, 2002). The X-ray photon interacts with a sample in many different ways and the form of interaction depends on the photon energy and the nature of the sample (Fewster, 2003; Warren, 1990). Accordingly, phenomena for instance constructive and destructive interference should become observable when crystalline and molecular structures are exposed to x-rays (Birkholz, 2006). The range of wavelengths which is commonly used for X-ray crystallography is namely from 0.5 to 2.5 A<sup>o</sup> (Guinier, 1963).

The diffraction phenomenon resulting from X-ray interaction with a matter can be understood as follows (Callister, 2007); when a beam of X-rays impinges on a solid material, a portion of this beam will be scattered in all directions by the electrons associated with each atom or ion that lies within the beam's path. Consider the two parallel planes of atoms A–A' and B–B' in Figure 3.13, which are separated by the interplanar spacing (*d*). Now assume that a parallel, monochromatic, and coherent (inphase) beam of X-rays of wavelength  $\lambda$  is incident on these two planes at an angle ( $\theta$ ). Two rays in this beam, labeled 1 and 2, are scattered by atoms *P* and *Q*. Constructive interference of the scattered rays 1' and 2' occurs also at an angle  $\theta$  to the planes, if the path length difference between 1–*P*–1' and 2–*Q*–2' (i.e.,  $\overline{SQ} + \overline{QT}$ ) is equal to a whole number, *n*, of wavelengths. That is, the condition for diffraction is:

$$n\lambda = \overline{SQ} + \overline{QT} \tag{3.1}$$

Or

$$n\lambda = d\sin\theta + d\sin\theta = 2d\sin\theta \tag{3.2}$$

Equation 3.2 is also known as Bragg's law, n is the order of reflection, which may be any integer (1, 2, 3 . . .) consistent with  $\sin\theta$  not exceeding unity. This is a simple expression relating the X-ray wavelength and interatomic spacing to the angle of the diffracted beam. If Bragg's law is not satisfied, then the interference will be nonconstructive in nature so as to yield a very low-intensity diffracted beam.



Figure 3.13: Diffraction of X-rays by planes of atoms (A–A<sup>'</sup> and B–B<sup>'</sup>).

The *diffractometer* is an apparatus used to determine the angles at which diffraction occurs; its features are represented schematically in Figure 3.14. A specimen or sample in the form of a flat plate is supported so that rotations about the axis labeled O are possible; this axis is perpendicular to the plane of the page. The monochromatic X-ray beam is generated at the source, and the intensities of diffracted beams are countered with a detector. The specimen, X-ray source, and detector are all coplanar. The detector is mounted on a movable carriage that may also be rotated about the O axis; its angular position in terms of  $2\theta$  is marked on a graduated scale. Carriage and specimen are mechanically coupled such that a rotation of the specimen through  $\theta$  is accompanied by a  $2\theta$  rotation of the detector; this assures that the incident and reflection angles are maintained equal to one another (see Figure 3.14). Collimators are incorporated within the beam path to produce a well-defined and focused beam. Utilization of a filter provides a near-monochromatic beam. As the detector moves at constant angular velocity, a recorder automatically plots the diffracted beam intensity (monitored by the detector) as a function of  $2\theta$ ;  $2\theta$  is termed the *diffraction angle*, which is measured experimentally.



Figure 3.14: Schematic diagram of an X-ray diffractometer.

## 3.3.5 Cyclic Voltammetery (CV)

In order to figure out the molecular energy diagram and calculate the ionization potential (*IP*), HOMO and electron affinity (*EA*), LUMO molecular energy levels of the Mq3 materials, electrochemical analyses using Cyclic Voltammetry (CV) measurements were carried out on MCA Microcell (ALS, Japan)/PGSTAT100 potentiostat electrochemical workstation interfaced with special auto lab CV software. The tests were done with 0.1 M solutions of the materials in  $CH_2Cl_2$  containing a supporting electrolyte of tetrabutylammonium perchlorate,  $(C_4H_9)_4NClO_4$  in an MCA three-electrode cell, where indium tin oxide (ITO) plate was used as the working electrode, platinum (Pt) wire was the counter electrode, and saturated calomel electrode (SCE) was used as the reference electrode. The concentration of Alq3 and Gaq3 in their solutions was fixed to 5 mg/mL. Figure 3.15 shows the MCA microcell and its components purchased from ALS Co., Ltd. MCA Microcells require only 50-200 µL of solution analyte (ALS, 2010). This is an advantage for the researchers who need to study with a small volume of sample.



Figure 3.15: The potentiostat and MCA microcell used for CV analysis experiment.

CV method (Angulo et al., 2009; Lee, Kwak, Kim, Cho, & Ohshita, 2008; Zhang, Yan, Li, Liu, & Chen, 2010) can be regarded as an efficient tool to be utilized successfully to investigate the molecular energy bands, e.g., higher occupied molecular energy level (HOMO), lower unoccupied molecular energy level (LUMO), and materials energy gap ( $E_g$ ), which are important parameters have to be accounted for in the OSCs consideration, especially in the selection of the correct donor and acceptor materials. Cyclic voltammetry experiment investigates the half cell reactivity of an analyte. This is performed by controlling the potential (Volts) of an electrode in contact with the analyte while measuring the resulting passed current (Amperes). To conduct such an experiment, at least two electrodes are needed (Bard & Faulkner, 2001). The working electrode, which makes contact with the analyte, must apply the desired potential in a controlled way and facilitate the transfer of charge to and from the analyte. A second electrode (counter electrode) acts as the other half of the cell. The counter electrode must have a known potential with which to gauge the potential of the working electrode; furthermore, it must balance the charge added or removed by the working electrode. While this is a viable setup, it is extremely difficult for an electrode to maintain a constant potential while passing current to the counter electrode. To solve this problem, the role of supplying electrons and referencing potential has been divided between two separate electrodes as shown in Figure 3.16-(a). The reference electrode is a half cell with a known reduction potential. Its only role is to act as reference in measuring and controlling the working electrodes potential and at no point does it pass any current. The counter electrode passes all the current needed to balance the current observed at the working electrode. To achieve this current, the counter will often swing to extreme potentials at the edges of the solvent window, where it oxidizes or reduces the solvent or supporting electrolyte.

When a potential is applied between the reference electrode and the working electrode and the current is measured between the working electrode and the counter electrode. This data is then plotted as current (I) versus potential (E) (see Figure 3.16-(b)). As the *I*-E curve shows, scanning from right to left produces a current peak for any analytes that can be reduced through the range of the potential scanned. The current will increase as the potential reaches the reduction potential of the analyte, but then falls off as the concentration of the analyte is depleted close to the electrode surface. If the reduction-oxidation (redox) couple is reversible, then when the applied potential is reversed, it will reach the potential that will oxidize the product formed in the first reduction peak will usually have a similar shape to the reduction peak. As a result, information about the redox potential and electrochemical reaction rates of the compounds is obtained.

The onset point of the reduction potential  $(E_{red})$  can be utilized to estimate the LUMO of the investigated material. In the case where the counter electrode is platinum and the reference one is saturated calomel electrode (SCE), then by accounting the

energy level of Pt which is 4.5 eV below the zero vacuum energy level (Bard & Faulkner, 2001), and the reduction potential of SCE versus Pt which is about 0.242 V, the equations below can be employed to calculate the molecular energy levels (Muhammad, et al., 2010). By having the obtained LUMO energy level from Equation 3.3 along with the energy gap ( $E_g$ ) that can be deduced from the spectroscopic measurements, the HOMO level is also estimated and a complementary optoelectronic study can be performed.

$$LUMO = [4.5 - (0.242 + |E_{red}|)] eV$$
(3.3)

$$HOMO = LUMO + E_g \tag{3.4}$$



Figure 3.16: (a) Set up of the CV cell electrodes connection, and (b) the current-voltage curve of a standard CV test.

## **3.3.6 Differential Scanning Calorimetry (DSC)**

In order to study the thermal properties of tris (8-hydroxyquinolinate) metals, Alq3 and Gaq3, Differential Scanning Calorimetric (DSC) measurements were conducted by using a TA instrument, Q200 thermal analyzer, shown in Figure 3.17, through the following procedure:

1- Films of Alq3 and Gaq3 were made by casting from their solutions in acetone.

2- Powders of Alq3 and Gaq3 were obtained by scraping these films.

2- Samples of Alq3 and Gaq3 (5 mg) were encapsulated in aluminum pans using a pan press.

3- The samples were heated from sub-ambient temperature to 300 °C (1<sup>st</sup> heating).

4- Then they were cooled down to 80  $^{\circ}$ C and heated again from 80  $^{\circ}$ C to 350  $^{\circ}$ C (2<sup>nd</sup> heating).

The heating and cooling steps were fixed at a ramp of 10 °C/min, and under flowing nitrogen gas (50 mL/min).



Figure 3.17: TA Differential Scanning Calorimetry instrument, DSC Q200.

DSC is considered to be an efficient tool for investigating the thermal history of organic, inorganic and polymeric materials (Alexandrou, Chrissafis, Vasiliadis, Pavlidou, & Polychroniadis, 2006; Cheng, Lin, & Wang, 2008; Kishi & Toraya, 2004; Klančnik, Medved, & Mrvar, 2010) due to its outstanding accuracy to measure the amount of energy absorbed or released by a sample when it is heated or cooled. By this, a quantitative and qualitative data on endothermic (heat absorption) and exothermic (heat evolution) processes is provided. DSC is the most frequently used method in the field of thermal analysis. Typical applications of DSC are glass transitions, melting-

crystallization, crystallinity of semi-crystalline materials, phase transition temperature, specific heat capacity, cross-linking reactions (Hatakeyama & Liu, 1998). Figure 3.18 shows the schematic diagram of a typical DSC instrument (Anderson, 2011). The sample is placed in a suitable pan and sits upon a constantan disc on a platform in the DSC cell with a chromel wafer immediately underneath. A chromel-alumel thermocouple under the constantan disc measures the sample temperature. An empty reference pan sits on a symmetric platform with its own underlying chromel wafer and chromel-alumel thermocouple. Heat flow is measured by comparing the difference in temperature across the sample and the reference chromel wafers. As such, the heat flow rate through the sample can be recorded as a function of time and temperature. Temperature can range from -120 to 725 °C, though an inert atmosphere is required above 600 °C. Pans of Al, Cu, Au, Pt, and graphite can be chosen to avoid reactions with samples, while the atmospheres could be nitrogen, air, oxygen, argon, vacuum, or controlled mixed gases.



Figure 3.18: TA Differential Scanning Calorimetry instrument, DSC Q200.

Figure 3.19 shows a DSC curve with the general features likely to be observed when thermal history is record for a sample. The DSC curve may show a step change (endothermic change), reflecting a change in heat capacity. The most common example, and a major application area of DSC, is the glass transition ( $T_g$ ) seen in amorphous polymers. This important region, in which the material changes from a rigid glassy state to a rubber, or very viscous liquid state, may be analyzed to give a wealth of information about the material.  $T_g$  may be used to identify polymers, as it varies over a wide range for commonly used materials. The amount or effectiveness of a plasticizer may be judged by how much it reduces  $T_g$  or affects the shape of the transition. Behind the rubbery state of amorphous materials, there will be a favorable tendency to the molecules to get crystallized. This feature is appeared as an exothermic peak in the DSC curve, while upon further materials heating, an endothermic peak will appear referring to the melting phase of the sample (see Figure 3.19).



Figure 3.19: The general feature of DSC curve.

#### 3.3.7 Scanning Electron Microscopy

A field emission scanning electronic microscope (FESEM, Quanta 200F) was utilized to capture the surface images of Mq3 films to visualize the surface morphology and structural distribution of the films. The photograph of this machine is shown in Figure 3.20. Electron microscope (EM) technique produces images of samples by using a beam of energetic electrons to scanning it on a very fine scale. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, morphology, and crystallographic information (Amelinckx, Van Dyck, Van Landuyt, & Van Tendeloo, 1997).



Figure 3.20: Field emission scanning electronic microscope (FESEM, Quanta 200F).

In scanning electron microscopy (SEM), a fine probe of electrons with energies typically up to 40 keV is focused on a specimen, and scanned along a pattern of parallel lines. Various signals are generated as a result of the impact of the incident electrons, which are collected to form an image or to analyze the sample surface. These are mainly secondary electrons, with energies of a few tens of eV, high-energy electrons backscattered from the primary beam and characteristic X-rays (Bogner, Jouneau, Thollet, Basset, & Gauthier, 2007). Electron microscopes were developed due to the

limitations of light microscopes which are limited by the physics of light. In contrast to light microscopy (LM) which uses visible light as a source of illumination and optical (glass) lenses to magnify specimens in the range between approximately 10 to 1,000 times their original size, EM is operated in the vacuum and focuses the electron beam and magnifies images with the help of electromagnetic lenses. The electron microscope takes advantage of the much shorter wavelength of the electron (e.g.,  $\lambda = 0.005$  nm at an accelerating voltage of 50 kV) when compared to the wavelengths of visible light ( $\lambda =$ 400 nm to 700 nm). Depending on the instrument used, specimens can be magnified roughly between 10 and 100,000 times in SEM. Figure 3.21 shows the basic components of a SEM. Conventional electron microscopy is used today have now been adapted to operate under the guidance of computers which makes sample viewing, photograph storage and labeling, as well as micrograph analysis easier for the investigator (Stadtländer, 2007).



Figure 3.21: Principal features of a SEM.

A field-emission cathode in the electron gun of a scanning electron microscope provides narrower probing beams at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage. The advantage of field emission scanning electron microscope (FESEM) over the SEM is basically including the followings (PhotoMetrics, date unknown):

- FESEM produces clearer, less electrostatically distorted images with spatial resolution down to 1-0.5 nm. That is 3 to 6 times better than conventional SEM.
- Smaller area contamination spots can be examined at electron accelerating voltages compatible with Energy Dispersive X-ray Spectroscopy.
- Reduced penetration of low kinetic energy electrons probes closer to the immediate material surface.
- High quality, low voltage images are obtained with negligible electricalcharging of samples. (Accelerating voltages range from 0.5 to 30 kV).
- Need for placing conducting coatings on insulating materials is virtually eliminated.

## 3.3.8 Surface Profilometer

Figure 3.22 displays a surface profilometer instrument, KLA Tensor P-6 photograph, which was used to measure the thickness of the active layer films. Surface Profilometer maps surface topography by dragging a sharp probe across the sample surface, thereby measuring the surface roughness or thickness depending on the interaction of the tip with the surface whether it is contact or noncontact mode. A Profilometer typically uses a mass cantilever system to keep the tip force constant during the scanning process. Profilometers utilize the same imaging fundamentals as a scanning probe microscopy (Bhushan, 2010; Kalinin & Gruverman, 2010), but with a

much larger tip (2.5 microns in diameter). The larger tip limits the vertical and horizontal resolution. The probe tip is usually made of diamond to reduce tip wear.



Figure 3.22: KLA Tensor P-6 surface profilometer instrument.

Modern Profilometers are capable of creating three dimensional topographical surface maps rather than traditional line scans (single horizontal direction scan while measuring feature height) (David, 2004). There are two basic surface profilometer technologies: contact and non-contact. Contact or stylus-based surface profilometers measure surface texture by dragging a sharp, pointed tool across the surface. Height variations of the tip are recorded and then used to form a texture profile like that shown in Figure 3.23-(a). Roughness and waviness are also calculated from the surface profile data. Non-contact surface profilometers measure the surface texture by optically scanning a surface with a light or laser, as shown in Figure 3.23-(b). With a proper selection of the stylus force both hard materials and soft materials can be measured. Examples of hard materials include silicon, silicon oxide, silicon nitride and metal films on rigid substrates. Examples of soft materials include organic and polymeric materials.



Figure 3.23: (a) A texture profile image recorded by surface profilometers, and (b) the process by which a surface is scanned under noncontact tip condition.

## **3.4 Devices Fabrication and Measurement**

In the previous Sections, the methodology of materials and solutions preparation, substrates patterning and cleaning, along with the techniques used to coat the films and their characterization procedures have been given. This Section is devoted to clarify the way of employing the investigated materials into the OSCs fabrication with different architectural geometry. Based on the Mq3 characterization, optimum photo-absorption condition for the active layers, and devices architecture, a final step of solution-processed OSCs fabrication with ternary bulk heterojunction structure was performed and assessed through their photovoltaic measurement.

#### 3.4.1 Bilayer and Bulk Heterostructures

Fabrication of the bilayer (BL) structure (composed of two layers each deposited over the other) and bulk heterojunction (BHJ) structure (composed of two or more components mixed each with others) of OSCs based on DH6T/PCBM thin film active layers, whose schematic of their devices geometry and molecular energy level of their components are shown in Figure 3.24-(a-d). The procedures undertaken to fabricate the complete devices are described as follows:

- Bilayer structure: The PEDOT:PSS layers were spin-coated onto the patterned ITO at 3000 rpm for 20 sec, then baked at 130 °C for 5 min to get the thickness of ~35 nm. Afterwards, the DH6T layer with thickness of ~ 120 nm was coated onto the PEDOT:PSS by a home-made thermal evaporator under a pressure of about 10<sup>-4</sup> mbar followed by ~80 nm layer of PCBM spin coated from 30 mg/mL solution of PCBM in chloroform. Finally, aluminum electrodes (50 nm) were thermally evaporated on the PCBM layer in a vacuum at 10<sup>-5</sup> mbar through a metal mask to give an active area of 14 mm<sup>2</sup> (2 x 7 mm<sup>2</sup>). For comparison, solar cells without the PEDOT:PSS layer were fabricated using an identical experimental procedure described above.
- Bulk structure: The PEDOT:PSS layer was first coated onto the patterned ITO substrates, then active layers of DH6T:PCBM blend (1:1 weight ratio), prepared with 30mg/mL solution in chlorobenzene, were coated onto the PEDOT:PSS layer to obtain thin layers of ~ 200 nm. Finally, aluminum electrodes (50 nm) were thermally evaporated on the PCBM layer in a vacuum at 10<sup>-5</sup> mbar through a metal mask to give an active area of 14 mm<sup>2</sup> (2 x 7 mm<sup>2</sup>).



Figure 3.24: Schematic views of the devices geometry; (a) ITO/DH6T/PCBM/Al with donor-acceptor bilayer structure, (b) ITO/PEDOT:PSS/DH6T/PCBM/Al with donor-acceptor bilayer structure, (c) ITO/PEDOT:PSS/DH6T:PCBM/Al with blended donor-acceptor structure and (d) the energy bands of their component materials.

## **3.4.2 Ternary Bulk Heterojunction**

Based on the characterizations of tris (8-hydroxyquinolinate) metals, the results to be discussed in Chapter 4 and 5 will reveal that the Mq3 are capable of enhancing the photoabsorption and charge transfer properties of DH6T films and DH6T/PCBM blends. As well as, due to the superior photovoltaic performance of bulk heterojunction devices of DH6T/PCBM over the bilayer ones, solution-processed OSCs based on ternary bulk heterojunction (TBHJ) of DH6T/Mq3/PCBM, in which Mq3 has been incorporated, were fabricated and analyzed. The ternary bulk heterojunction (gathering three materials component in the active layer together) and DH6T/PCBM bulk structures for comparison purpose, as shown in Figure 3.25, were fabricated as follows; the PEDOT:PSS layer was first coated onto the patterned ITO substrates, then active layers of DH6T:Mq3:PCBM blend [(0.75+0.25):2] weight ratio), prepared with 30 mg/mL solution in chlorobenzene, were coated onto the PEDOT:PSS layer to obtain thin layers of ~ 200 nm. Finally, aluminum electrode stripes (50 nm) were thermally evaporated on the PCBM layer in a vacuum at  $10^{-5}$  mbar through a metal mask to give an active area of 14 mm<sup>2</sup> (2 x 7 mm<sup>2</sup>). For comparison, solar cells without incorporating Mq3, having DH6T/PCBM (1:2) active layers, were fabricated using the identical procedures described above.



Figure 3.25: Schematic views of devices with (a) DH6T:Mq3:PCBM ternary bulk heterojunction, and (b) DH6T:PCBM bulk heterojunction active layers.

## **3.4.3 Photovoltaic Measurements**

The assessment and analyzing of fabricated OSCs can be realized via the photovoltaic (light power in – electrical power out) measurement. Photovoltaic measurement was performed by recording the current versus voltage response of the devices under the standard light illumination (100 mW/cm<sup>-2</sup>) that was discussed in Section 2.2.4 of Chapter two. The major photovoltaic parameters can be extracted from the current-voltage (*I-V*) measurements, while as the power-voltage (*P-V*) curve can also provide further significant estimation. In order to simulate the light intensity used for illuminating the devices under standard condition measurement, an Oriel solar simulator- model 67005 with an AM 1.5 filters was used. This solar simulator photograph is shown in Figure 3.26. Solar simulators can imitate the spectral

distribution of sunlight for a variety of environments by using high pressure xenon arc lamp sources to approximate the spectra emitted by the sun. The spectral distribution from the xenon arc lamp is altered and refined using Air Mass (AM) filters. The spectra emitted by the xenon source and the sun are both close to that of a 5800 K blackbody. Hence, by combination of the lamp and air mass filters the approximate standard light intensity condition of approximately 100 mW/cm<sup>2</sup> irradiance, AM 1.5 global reference spectrum at room temperature is being realized.



Figure 3.26: An Oriel solar simulator- model 67005.

The *I-V* characteristics were measured using a Keithley 236 Source Measure Units (SMUs), which can source and measure both current and voltage. These SMUs have four-quadrant source capability, and they can sink the cell current as a function of the applied voltage to up to 100 mA (Keithley, 1990). Figure 3.27-(a) and 3.27-(b) show the instrument photograph and a solar cell connected to its terminals for *I-V* measurement. One side of the solar cell is connected to the force and sense terminals of SMU1; the other side is connected to the force and sense terminals of either SMU2 or the ground unit (GNDU). With the four-wire method, a voltage is sourced across the solar cell using one pair of test leads (between Force HI and Force LO), and the voltage drop

across the cell is measured across a second set of leads (across Sense HI and Sense LO). The sense leads ensure that the voltage developed across the cell is the programmed output value and compensate for the lead resistance. Finally, to determine the current density (J) through the device, the measured current (I) values are divided by the device area (the total frontal area of the cell including the area covered by the grids and contacts). As such, the J-V and P-V characteristic curves can be readily derived.



Figure 3.27: Shows (a) a Keithley 236 source measurement instrument, and (b) a solar cell device connected to its terminal leads for the *I-V* measurement.