

A Study on the Electrical & Optical Properties of MEH-PPV Thin Films Using Different Solution Concentration

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Abstract- Polymer and organic light-emitting diodes (OLEDs), photovoltaic cells and field effect transistor are being focused towards commercialization. Poly [2-methoxy-5-(20-ethylhexoxy)-p-phenylene vinylene] or known as MEH-PPV, have been extensively studied for OLED applications. Two types of solvents prepared with MEH-PPV in this study are toluene and 1, 2-dichlorobenzene (1, 2-DCB). In order to have uniform thin film of MEH-PPV, spin coating technique is applied. The electrical properties of thin film were investigated and the optical properties were characterized by using UV-Visible-NIR (UV-VIS-NIR), Photoluminescence (PL) spectroscopy and Atom Force Microscope (AFM), high-resolution type of scanning probe microscopy. It is found that as the concentration of solution increased, thickness of thin film also increased as well as the resistivity of the thin film. However, MEH-PPV in 1, 2-DCB gives better conductivity compare to Toluene. There also significant difference between Toluene and 1, 2-DCB in PL spectra which Toluene exhibit higher peak compare to 1, 2-DCB.

Keywords—Polymer (MEH-PPV); different solvents and concentration; electrical and optical properties

I. INTRODUCTION

Remarkable progress has been made in synthesizing organics materials in understanding their properties and in developing them for use in optical and electronic devices, since enormous discovery of polymers and certain organic molecules conductivity [1]. As reported by Burroughes et al. [2], electroluminescence in conjugated polymers using poly (1, 4--phenylene vinylene) or known as PPV use as the active layer. Later, PPV and its derivatives have been widely studied for the fabrication of organic light-emitting diodes (OLEDs). However, there is a disadvantage exhibit from this type of conjugated polymer which it is insoluble in common organic solvents such as tetrahydrofuran (THF), chloroform, xylene, chlorobenzene (CB) and toluene.

Therefore, one of derivatives with alkoxy on phenyl groups known as poly [2-methoxy-5-(20-ethylhexoxy)-p-phenylene vinylene], MEH-PPV exhibits greater solubility in common organic solvents. MEH-PPV can be easily dissolved in non-aromatic and aromatic solvents to exhibit different optical properties [3]. Two types of solvents prepared with MEH-PPV in this study are toluene and 1, 2-dichlorobenzene (1, 2-DCB).

One of the easiest techniques to produce uniform films onto large area is the spin coating technique [3]. MEH-PPV is one of the conjugated polymers that have Newtonian rheological properties where the film thickness obtained by spin coating can be affected by polymer solution concentration, solution viscosity and spin speed [5]. Spin coated photo resists or waveguide materials film thickness typically in the range of several micrometers [6, 7, and 8]. On the other hand, spin coated conjugated polymers for electronic or optoelectronic devices typically have a thickness in the sub-micron range.[5] As example, the thickness of film in light emitting diode or photovoltaic cells generally in the range of 50-200nm.[9-14].

The objective of this study is to investigate the characteristic of MEH-PPV in terms of its optical and electrical properties. The electrical properties, the I-V characterization are measured by using two point probes (Solar Simulator), while the optical properties were investigated by using UV-Visible-NIR (UV-VIS-NIR), Photoluminescence (PL) spectroscopy and Atom Force Microscope (AFM) (Park system-XE 100).

II. EXPERIMENTAL

Basically, the completion of this study involve several processes which are substrate preparation, solution preparation, thin film formation by spin coating and thin film characterization in terms of electrical and optical properties characterization. The

flow of overall process can be clearly illustrated as in Figure 1.

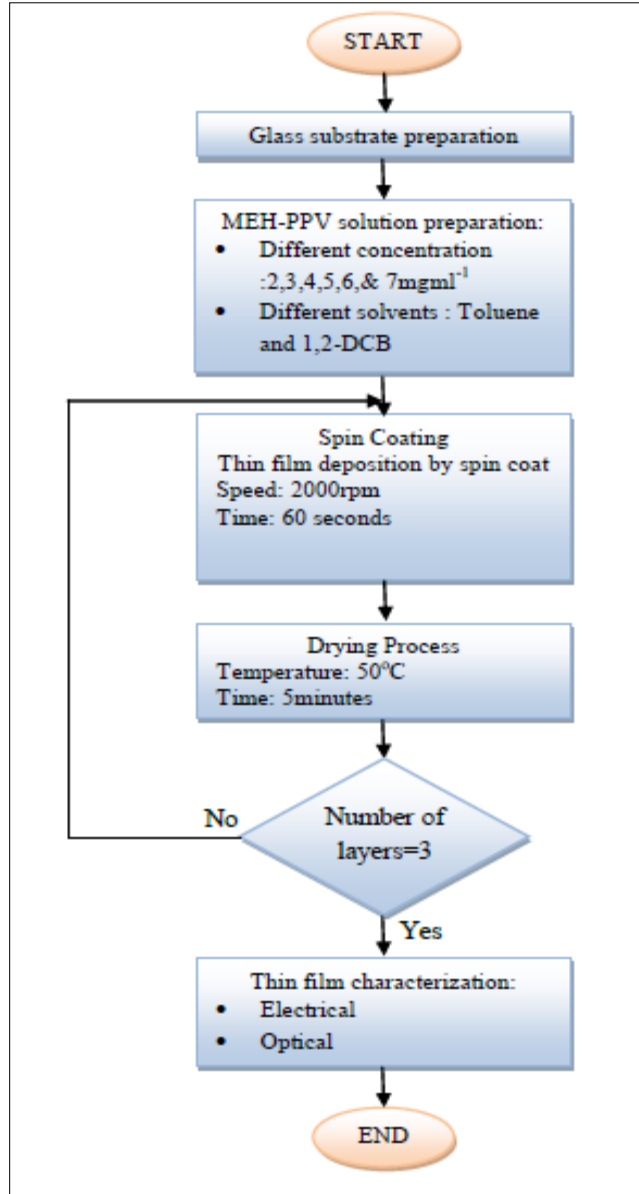


Figure 1- Flowchart of MEH-PPV thin film experiment

A. Substrate Preparation

The glass substrate was firstly prepared by cutting into dimension of 2cm x 2cm using diamond cutter. Later, the substrates proceeded for cleaning process to ensure glasses are free from dust or contamination. The substrates were sonicated into acetone in Ultra Sonic Cleaner (HWANSHIN, POWERSONIC 405) for 10 minutes and rinsed with deionized (DI) water. The steps were repeated by replacing acetone, then ethanol/methanol and lastly with DI water. Finally,

Nitrogen (N₂) gas was used to blow the glass to be dried.

B. Solution Preparation

The organic solvents involved in preparing MEH-PPV solutions are toluene and 1, 2-DCB. The concentrations of MEH-PPV are varied from 2mgml⁻¹ to 7mgml⁻¹ ml. The solutions were stirred for 48 hours at room temperature to ensure the reaction of the chemicals dissolved completely. The reaction mixture became red/orange during the addition.

C. Thin Film Formation by Spin Coating

The thin film was formed by deposited an amount of dissolved solution onto the substrate and spin coated. The speed was fixed to 2000 rpm for 60 seconds. After spin coated, the thin film then was dried at 50°C. Spin coating step was repeated for 3 times in order to reach desired thickness of thin film.

III. RESULTS AND DISCUSSIONS

A. Electrical Properties of MEH-PPV Thin Film

The resistivity of thin film can be explained by the equation below, Equation 1:

$$\rho = \frac{RA}{l}$$

$$\rho = \frac{R(w \times t)}{l} \quad (1)$$

Where

ρ = resistivity ($\Omega \cdot m$)
 R = resistance (Ω)
 A = cross sectional area
 l = length between metal contact
 w = width of metal contact
 t = thickness of thin film

Figure 2 shows how the parameters of the equation are applied. Gold (Au) was deposited by thermal evaporation process on top of the thin film which acts as the metal contact.

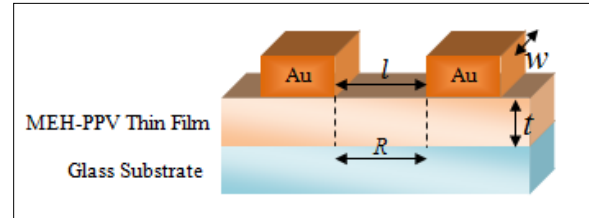


Figure 2. Gold (Au) as metal contact for current-voltage measurement

Table 1 shows the experimental result of the thin film average thickness at different concentration of MEH-PPV solutions. As reported, spin coated conjugated polymers for electronic or optoelectronic devices typically have a thickness in the sub-micron range [5]. In this study, the range of 3 layer thin film thickness obtained is between 50-300nm.

TABLE 1. MEH-PPV thin film average thickness at different concentrations

Thin film concentration (mgml ⁻¹)	Thin Film Average Thickness (nm)	
	Toluene	1, 2-DCB
2	49.52	53.91
3	67.75	75.17
4	100.73	99.81
5	131.01	110.51
6	195.84	170.06
7	281.88	236.23

Clearly seen that the thickness of thin film both for Toluene and 1, 2-DCB increased as the concentration increased. This result can be explained by Equation 2:

$$h_f = kx_{1,0}\omega^{-\beta} \quad (2)$$

The final thin film thickness, h_f , after spin coating of a polymer solution was found to be correlated to the initial polymer weight fraction, $x_{1,0}$ and the spin speed, ω [6,15]. k is the constant that depends on the concentration solution viscosity and other properties of the polymer and solvent. In this study, the spin speed was fixed at 2000rpm while the concentration of solution varied. Therefore, in this case, as the concentration increased, the value of k is increased and the thickness of thin film also increased by referring to Equation 2.

Now, looking at the current-voltage characteristics of the thin film shown in Figure 3 and 4, there are increasing in resistivity as the concentration of solution increased. As suggested by Equation 1, the resistivity of the thin film is proportional to the thickness. Therefore, as the thin film thickness increased due to increase of concentration, the resistivity also increased for both Toluene and 1, 2-DCB.

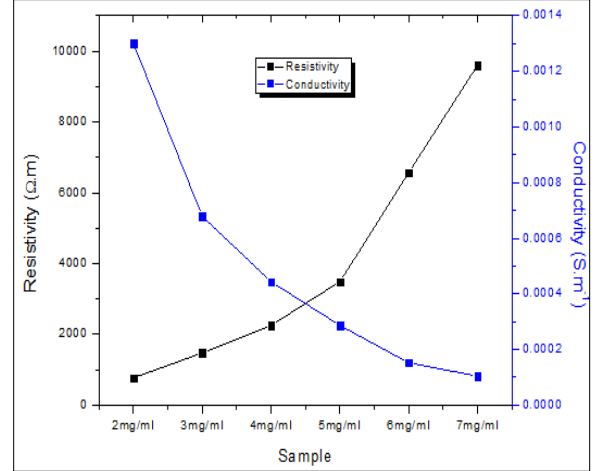


Figure 3. Resistivity and conductivity of MEH-PPV in Toluene

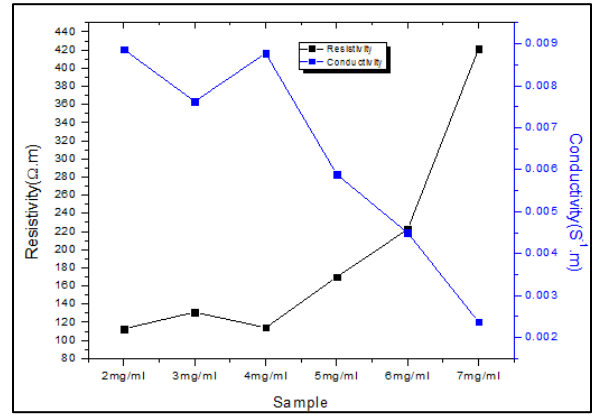


Figure 4. Resistivity and conductivity of MEH-PPV in 1, 2-DCB

The relationship between resistivity and conductivity can be explained by Equation 3:

$$\rho = \frac{1}{\sigma} \quad (3)$$

Where ρ =resistivity and σ =conductivity. Even though both Toluene and 1, 2-DCB are aromatic solvents, 1, 2-DCB gives better conductivity compare to Toluene by referring to the graph in Figure 4 due to the difference of aggregation in various solvents. Resistivity is also proportional to the resistance of thin film as suggested in Equation 1. By referring to the resistivity axis, can be seen that the range of resistivity from Toluene is much higher than 1, 2-DCB. This is due to that the resistance from Toluene is higher compared to 1, 2-DCB, which the comparison can be seen in Table 2.

TABLE 2. Resistance (Ω) in Toluene and 1, 2-DCB

Thin film concentration (mgml ⁻¹)	Thin Film Resistance (Ω)	
	Toluene	1, 2-DCB
2	2.58E+09	3.48E+08
3	3.62E+09	2.90E+08
4	3.72E+09	1.90E+08
5	4.43E+09	2.56E+08
6	5.58E+09	2.18E+08
7	5.67E+09	2.97E+08

B. Optical Properties of MEH-PPV Thin Film

• Photoluminescence (PL) Spectra

Photoluminescence (PL) is the spontaneous emission of light from a material under optical excitation and PL measurement is one of the methods to investigate the optical properties of MEH-PPV thin film. The PL spectra of Toluene and 1, 2-DCB is presented in Figure 5(a) and 5(b).

The range of wavelength in the measurement is between 450nm to 700nm. PL spectra of Toluene gives higher peak at range between 550nm to 600nm compare to 1, 2-DCB. The PL peak for 1, 2-DCB is increased as the concentration of thin film is increased. Same goes for Toluene however, at 6mgml⁻¹ and 7mgml⁻¹ concentration of Toluene, the peak gets lower compare at the concentration of 5mgml⁻¹ Toluene. The peak of PL from Toluene accompanied with small shoulder located at 650nm. The shoulder exhibited when aggregation is occurred and grows further as concentration increased caused by the increasing aggregation [17]. The degree of aggregation is both concentration and solvent dependent [18].

A broader PL spectra exhibited by Toluene compared to 1, 2-DCB due to its greater conformational disorder. Besides, MEH-PPV film prepared from Toluene is more red-shifted compare to 1, 2-DCB. The shifts exhibited by different solvents can be explained by considering that the conjugation length of polymer changes in different solvents [18]. Shorter average length of conjugation length will tend to exhibit blue shifted spectra. Thus, in this case, can be said that the polymer in Toluene has longer conjugation length compared to 1, 2-DCB. In

addition, the enhancement of red portion of film's PL by Toluene due to the amount of interchain interactions [18].

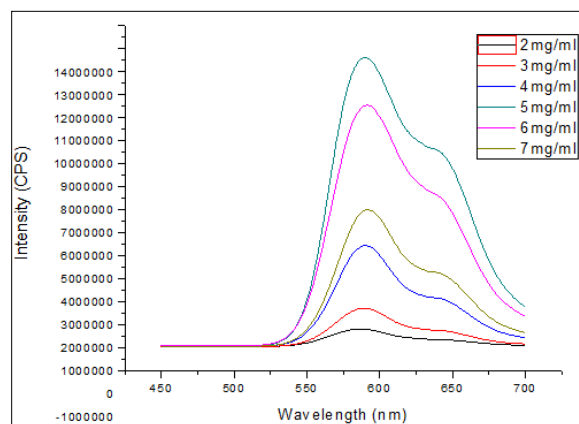


Figure 5(a)

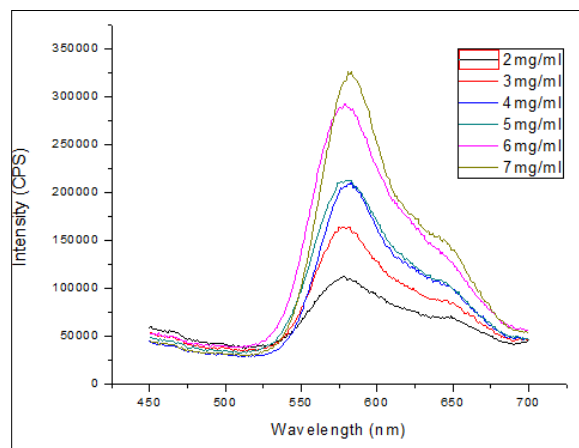


Figure 5(b)

Figure 5. PL spectra of MEH-PPV in (a) Toluene and (b) 1, 2-DCB

• Transmittance and Absorbance

Absorbance for both Toluene and 1, 2-DCB thin film results can be seen as indicated in Figure 6(a) and 6(b), while in Figure 7(a) and 7(b) shows the transmittance.

The highest peak of absorbance in Toluene range in between 450nm to 550nm is at the concentration of 5mgml⁻¹. The peaks observed to be lower as the concentration increased to 6mgml⁻¹ and 7mgml⁻¹. Different for 1, 2-DCB where the peak of absorbance continuously increased as the concentration increased from 2mgml⁻¹ to 7mgml⁻¹.

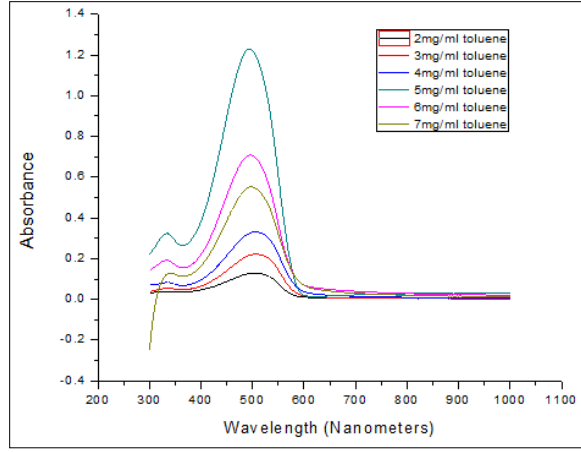


Figure 6(a)

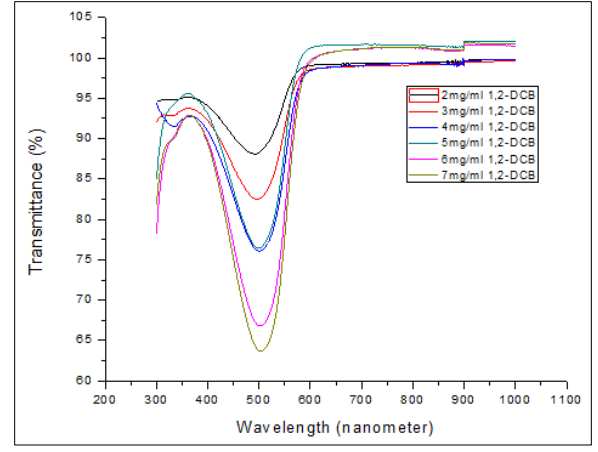


Figure 7(b)

Figure 7. Transmittance for (a) Toluene and (b) 1, 2-DCB

The absorption coefficient of MEH-PPV thin film in different solvents can be obtained from the transmittance spectra as indicated in Figure 7 and calculated by using Lambert's Law as in Equation 4:

$$\alpha = \frac{1}{t} \ln\left(\frac{100}{T}\right) \quad (4)$$

Where α is the absorption coefficient, t is the thin film thickness (nm) and T is the transmittance of the thin film. The determination of band gap energy of thin films was obtained by applying Tauc's Plot formula by extrapolation of the linear portion to the photon energy axis.

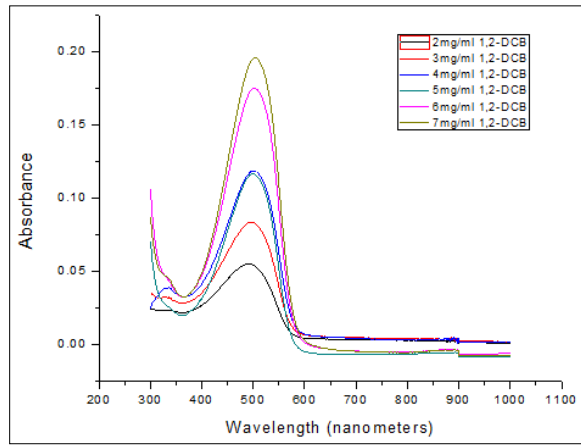


Figure 6(b)

Figure 6. Absorbance peak for (a) Toluene and (b) 1, 2-DCB

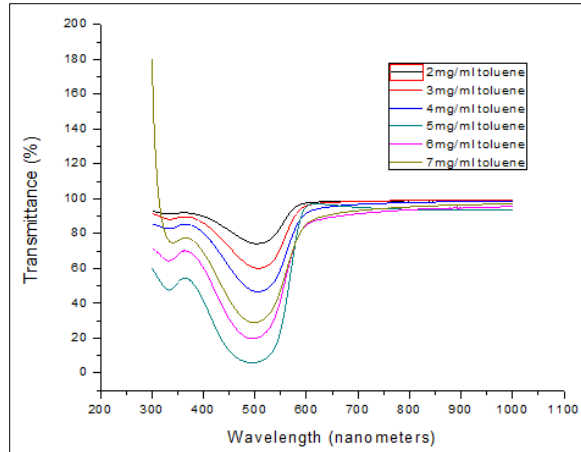


Figure 7(a)

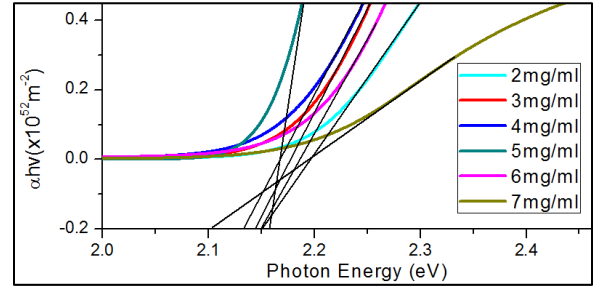


Figure 8(a)

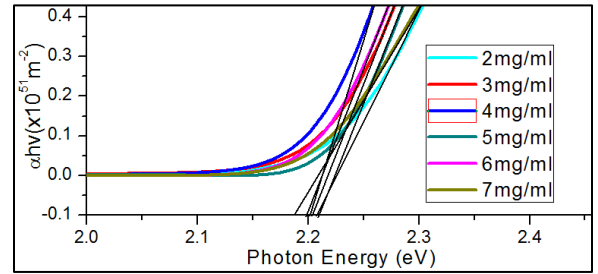


Figure 8(b)

Figure 8. Tauc's plot determined by transmittance data samples from (a) Toluene and (b) 1, 2-DCB

TABLE 3. Band gap energy by extrapolate of linear portion of transmittance to the photon energy axis

Thin Film concentration (mgml ⁻¹)	Thin film band gap (eV)	
	<i>Toluene</i>	<i>1,2-DCB</i>
2	2.151	2.208
3	2.144	2.204
4	2.133	2.202
5	2.159	2.211
6	2.156	2.202
7	2.103	2.188

Figure 8 shows the Tauc's plot determined by transmittance data samples and Table 2 shows the value of the band gap for each thin film from Toluene and 1,2-DCB. From the results, both thin film from Toluene and 1, 2-DCB has the highest band gap energy at 5mgml⁻¹ of solution concentration. These data also shows that by average, 1, 2-DCB requires higher energy to excite the electron from valence band to conduction band.

C. Atomic Force Spectroscopy (AFM) Surface Morphology

The morphology of the film is another important factor to achieve optimum device performance. The smooth surface is important factor for photovoltaic device to decrease internal resistance that limits electron transfer at polymer/metal interface [16]. Figure 9 and Table 3 shows the surface morphology of MEH-PPV in Toluene (9a) and 1, 2-DCB (9b) at different solution concentration. Thin film from Toluene have darker colour than 1, 2-DCB. Besides that, 1, 2-DCB has lesser surface roughness compare to Toluene. As the concentration of Toluene increased, can be seen that the surface of the thin film tend to have 'drain' structure. Higher concentration that consists pinholes or drain structure can affect to electrical properties such as a short circuit [16].

TABLE 4. Surface roughness of thin film.

Thin Film Concentration (mgml ⁻¹)	Surface Roughness (nm)	
	<i>Toluene</i>	<i>1,2-DCB</i>
2	2.677	1.911
3	3.676	1.993
4	3.920	1.334
5	3.192	1.854
6	3.508	2.240
7	3.247	2.737

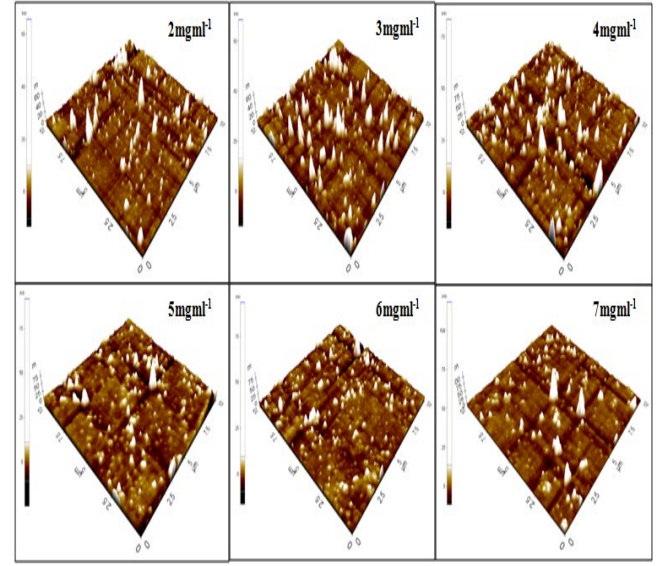


Figure 9(a)

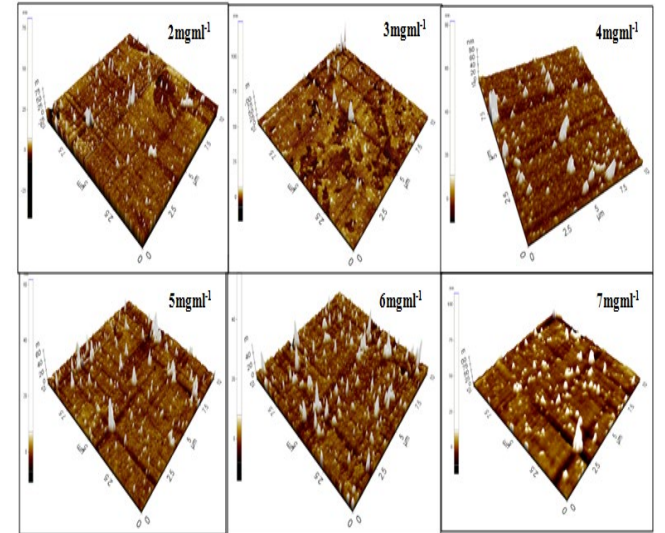


Figure 9(b)

Figure 9. AFM images obtained from 9(a) Toluene and 9(b) 1, 2-DCB.

IV. CONCLUSIONS

The optical and electrical properties of MEH-PPV thin film with different solvents and concentration investigated. From the results presented, the electrical properties of MEH-PPV thin film can be concluded that 1, 2-DCB offers better conductivity compare to Toluene. However, 1, 2-DCB requires higher energy band gap to excite electron from the lowest unoccupied molecular orbital, LUMO to the highest occupied molecular orbital, HOMO in OLED application. In terms of optical properties, PL spectra

shows Toluene gives higher peak compare to 1, 2-DCB as well as the absorbance of the thin film. A broader PL spectra exhibit by Toluene compared to 1, 2-DCB. Besides, MEH-PPV film prepared from Toluene is more red-shifted compare to 1, 2-DCB. For the better thin film is with fine structure in PL, sharper and redder absorption edge in the optical absorption spectra. 1, 2-DCB is chosen to be a better solvent due to its finer and sharper PL spectra. The surface roughness observed by AFM indicate that thin film from Toluene was rougher than 1, 2-DCB which can be concluded that 1, 2-DCB is preferable for OLED application due to its smooth surface that can avoid short circuit for any devices.

V. FUTURE RECOMMENDATION

In the future, the development of OLED will be interesting if there many approaches in fabrication process. The fabrication of OLED methods can be made in wide range of conditions. Hybrid composites which the combinations of organic and inorganic material would acquire better performance for OLED devices. The organic component offers efficient optical properties while the inorganic component would exhibit better conductivity.

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