

## Optical Properties of MEH-PPV and MEH-PPV/ [6,6]-Phenyl C61-butyric Acid 3-ethylthiophene Ester Thin Films

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Thin films of Poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) were prepared from chloroform, 1,2-dichlorobenzene and toluene solutions by spin coating technique on quartz substrates. Absorption and photoluminescence (PL) spectra of the polymer thin films prepared from different solvents were measured. It was concluded from the UV-Vis absorption and PL spectra that the optical properties of MEH-PPV films strongly affected by solvents used for spin coating. A strong photoluminescence quenching was observed in (1:4) MEH-PPV: [6,6]-Phenyl C61-butyric Acid 3-ethylthiophene Ester (Modified Fullerene) composite which provides evidence of photoinduced charge transfer. Further, with Atomic Force Microscope (AFM) it has been demonstrated that the surface morphology of the MEH-PPV: Modified fullerene thin films are strongly dependent on the preparation condition (solvents).

**Keywords:** MEH-PPV, Modified fullerene, Optical properties, Thin films, AFM.

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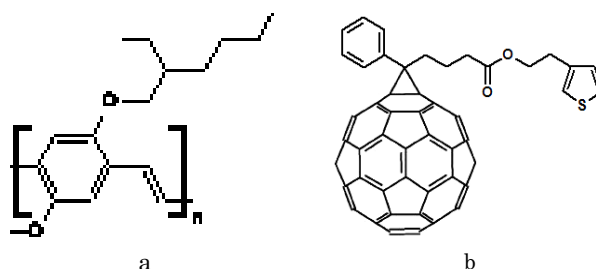
### 1. INTRODUCTION

Poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) is widely used in the fabrication of polymer light emitting diodes [1] and as donor material in the fabrication of bulk-heterojunction photovoltaic cells [2] because of its excellent processibility and favorable electronic and spectroscopic properties. It is very important to understand the relationship between the morphology and the processing conditions, and their influence on the electronic and photonic properties of polymer thin films. Among the many parameters which can affect the optical properties and surface morphology of the bulk-heterojunction solar cells the composition between donor and acceptor [3, 4, 5], the solvent used to make blend solutions [6, 7] and the thickness of the active layer [8, 9]. Shaheen et al. [10] reported a strong dependence of the performance of MDMO-PPV:PCBM bulk heterojunction solar cell on the solvent used. The toluene cast devices yielded power conversion efficiencies of only 0.9 %, while the use of chlorobenzene almost tripled the efficiency [10]. This increase was mainly due to an increase in the short circuit current and the authors attributed this to finer film morphology.

To our knowledge there is no published study on the optical and surface morphology of MEH-PPV: [6,6]-Phenyl C61-butyric Acid 3-ethylthiophene Ester (Modified fullerene) thin films. However, several papers in the literature discussed the effect of thin film preparation conditions on the device performance of MEH-PPV: [6,6]-Phenyl C61-butyric Acid methyl Ester (PCBM) photovoltaic cell [3, 6, 9]. In this paper we studied the solvent effect on the optical properties of the p-type donor polymer MEH-PPV and on the surface morphology of the thin film of MEH-PPV: Modified fullerene.

### 2. EXPERIMENTS

The p-type donor polymer MEH-PPV and the n-type acceptor modified fullerene in this study were purchased from sigma-Aldrich Corporation and American Dye Source, Inc. respectively; the chemical structures are shown in Figure 1. All materials were used as received without further purification. For the UV-Vis absorption and photoluminescence (PL) measurements, MEH-PPV and MEH-PPV: Modified fullerene films were prepared by using spin coating technique. Chloroform, 1,2-dichlorobenzene and toluene were used as solvents; the solutions were spin coated onto quartz substrates. MEH-PPV films were prepared at the concentration of about 3.3 mg/ml of solvent; the polymer solutions were spin-coated at 2000 rpm. The properties of the films were obtained on a Lambda-900 UV/Vis/NIR spectrophotometer (Perkin Elmer) and on LS55 luminescence spectrometer (Perkin Elmer).



**Fig. 1** – Chemical structure of (a) Poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] and (b) [6,6]-Phenyl C61-butyric Acid 3-ethylthiophene Ester

For surface morphology characterization, MEH-PPV and modified fullerene were dissolved in chloroform, 1,2-dichlorobenzene and toluene to yield a MEH-PPV: modified fullerene (3.19:12.68 mg/1 ml chloroform, 3.5:12.72 mg/1 ml 1,2-dichlorobenzene and 3.24:13.0 mg/1 ml toluene) solutions. The quartz substrates were cleaned by ultrasonic treatment for 10 minutes using acetone and

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isopropyl alcohol sequentially. After cleaning of the quartz substrates the solutions were spin coated at 2000 rpm for 40 seconds. The surface morphology of MEH-PPV: modified fullerene thin films spin coated from different solvents were characterized by atomic force microscopy (CP-II veeco).

### 3. RESULTS AND DISCUSSIONS

Absorption and photoluminescence spectra of MEH-PPV thin films were measured using chloroform, 1,2-dichlorobenzene and toluene as spin coating solvents. The spectra for MEH-PPV were examined as a function of solvent, to determine the change in optical properties upon different solvents. Figure 2 shows the effect of the different solvents on the UV-Vis absorption spectra for the thin films of MEH-PPV. In Figure 3 we show the absorption spectra near the absorption edge of the MEH-PPV thin films fabricated from the different solvents. For the MEH-PPV thin film fabricated from the chloroform, wavelength of the absorption peak ( $\lambda_{max}$ ) is 514 nm. For the MEH-PPV film fabricated from 1,2-dichlorobenzene,  $\lambda_{max}$  is 507 nm showing a little blue shift compared to chloroform. However, for the MEH-PPV film prepared from toluene, the absorption curve showed a wide broadening and  $\lambda_{max}$  was found at 519 nm. The shifts can be explained by considering that the conjugation length of the polymer changes in the different solvents. It is well known that the absorption band of oligomers shows a steady red shift with an increasing conjugation length [11]. All the spectra show a narrow low intensity peak at 334, 324 and 333 nm for the films prepared from chloroform, 1,2-dichlorobenzene and toluene, respectively. The optical band gaps ( $E_g^{opt}$ ) were calculated from the onset wave lengths ( $\lambda_{onset}$ ) according to the relation:

$$E_g^{opt} = \frac{hc}{\lambda_{onset}} \quad (1)$$

Where  $h$  is plank constants and  $c$  is the speed of light in vacuum. The  $\lambda_{onset}$  and the corresponding  $E_g^{opt}$  of MEH-PPV thin film fabricated from chloroform, 1,2-dichlorobenzene and toluene are 590 nm (2.10 eV), 588 nm (2.11 eV) and 620 nm (2.0 eV), respectively. The obtained optical band gaps are in agreement with the optical band gap of a MEH-PPV film cast from chloroform, 2.18 eV in the literature [12]. Figure 4 exhibits the photoluminescence (PL) emission spectra of MEH-PPV thin films prepared in the three different solvents. The PL spectrum of MEH-PPV has maximum peaks at 588 nm, 565 nm and 611 nm for thin films prepared from chloroform, 1,2-dichlorobenzene and toluene, respectively. The maximum peak of MEH-PPV film prepared from toluene is red shifted by 23 nm compared to that of chloroform. However; the maximum peak of MEH-PPV film prepared from 1,2-dichlorobenzene is blue shifted by 23 nm. The shorter average conjugation length for MEH-PPV in 1,2-dichlorobenzene compared to chloroform not only explains the blue-shifted absorption spectrum, but also the blue-shifted emission. The shift in PL may also attribute to formation of aggregates, which is solvent dependent. Significant changes into the values

of Stokes shift related with solvent used in thin films preparation were observed. The reason of the different in Stokes shift is due to polymer/solvent interaction through the solvent's optical parameters (refractive index and dielectric constant), it may also related to the magnitude of the change of dipole moment of the electronic ground state and the excited state. The PL spectra in all the cases are red shifted with respect to absorption spectra. Absorption and photoluminescence data for MEH-PPV thin films are summarized in Table 1.

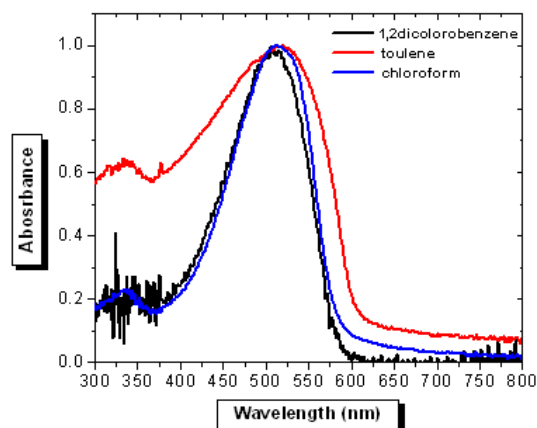


Fig. 2 – The UV-vis spectra of pure MEH-PPV film spin-coated from 1,2-dichlorobenzene, toluene and chloroform

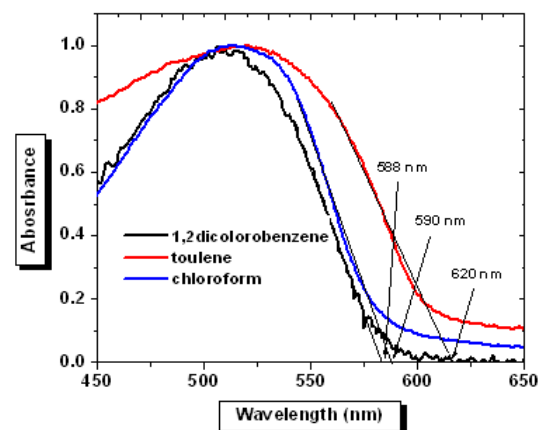


Fig. 3 – Optical absorption near the absorption edge of pure MEH-PPV film spin-coated from 3.32 mg/ml MEH-PPV in chloroform, 3.42 mg/ml MEH-PPV in 1,2-dichlorobenzene and 3.30 mg/ml MEH-PPV in toluene

Figure 5 compare the photoluminescence spectra of the pure MEH-PPV, pure Modified fullerene and (1:4) MEH-PPV: Modified fullerene films spin coated from Chloroform. As discussed previously for pure MEH-PPV, the characteristic PL peak was observed around 588 nm. This peak disappeared for the 1:4 composite films. The strong PL quenching in the composite film provides evidence of photoinduced charge transfer in the composite film. The same phenomenon was observed by different authors on polymer/PCBM composite [3, 4]. Figure 6 shows the absorption spectrum of a thin film of [6,6]-Phenyl C61-butyric Acid 3-ethylthiophene Ester (Modified Fullerene). Two peaks appear at 266 and 336 nm and there is abroad tail of absorption extended to as long as 800 nm.

**Table 1** – Optical data of MEH-PPV in thin films spin-coated from different solvents

Solvent	$\lambda_{max,UV}$ (nm)	$\lambda_{onset}$ (nm)	$\lambda_{max,PL}$ (nm)	Stokes shift (nm)	$E_g^{opt}$ (eV)
chloroform	514	590	588	74	2.10
1,2-dichlorobenzene	507	588	565	58	2.11
toluene	519	620	611	92	2.00

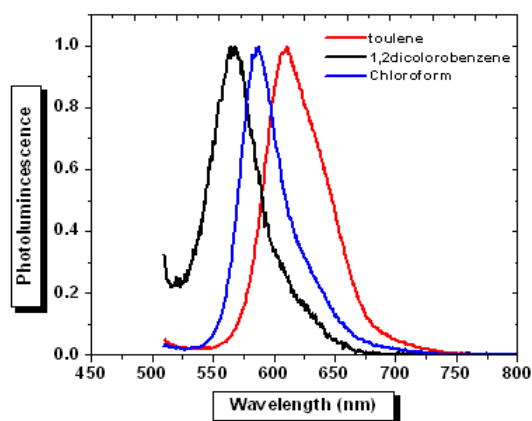
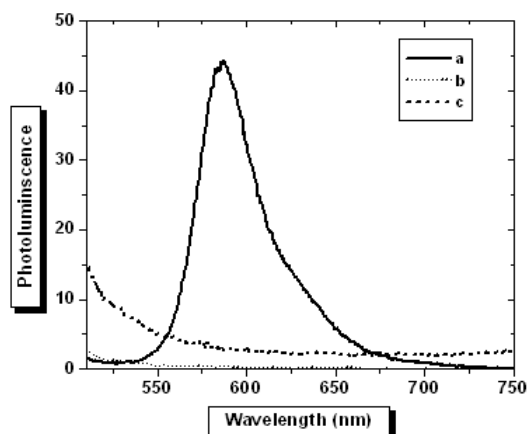
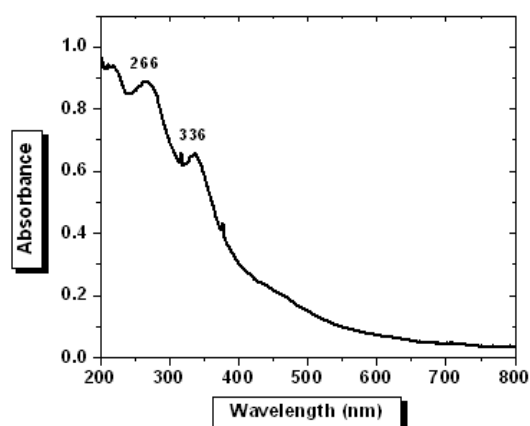
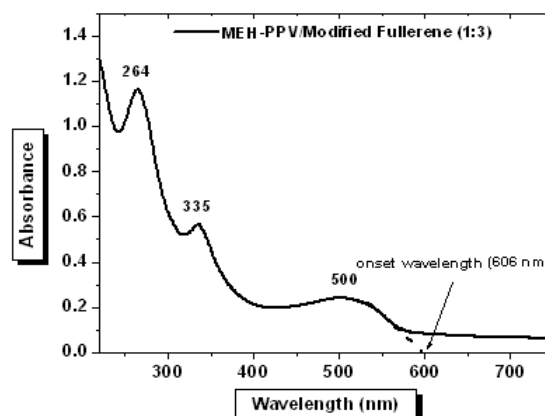
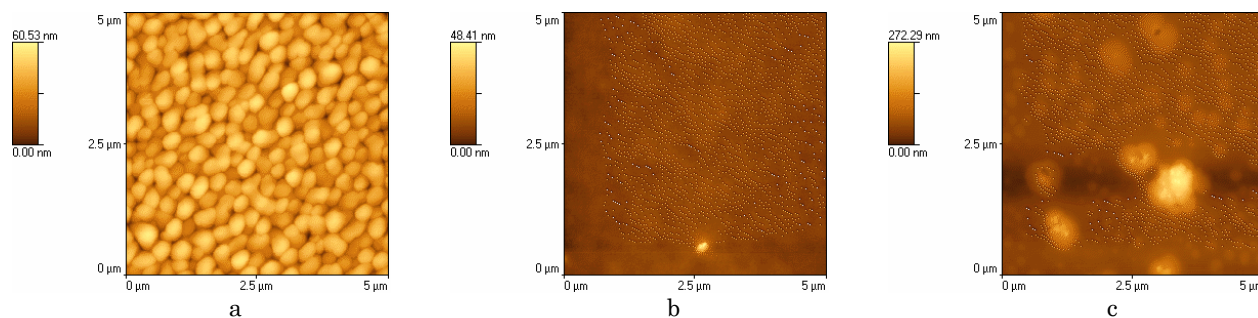
**Fig. 4** – The PL spectra of pure MEH-PPV films spin-coated from 1,2-dichlorobenzene, toluene and chloroform

Figure 7 shows the optical absorption spectrum of a MEH-PPV: Modified fullerene (1:3) thin film spin-coated from chloroform. Comparing this absorption spectrum with the absorption spectrum of the components alone shows that the peak at 500 nm is identified as the  $\pi$ - $\pi^*$  absorption of MEH-PPV, it is blue shifted by about 14 nm compared to the peak in the absorption spectra of MEH-PPV alone. The peaks at 335 nm and 264 nm are corresponding to modified fullerene. The onset wavelength of the blend is at 606 nm (2.05 eV), blue shifted by 16 nm compared to the onset absorption of MEH-PPV. In general the spectrum is a superposition of the two components. There is no indication of states below  $\pi$ - $\pi^*$  gap of the conjugated polymer that might arise from ground state interactions such as doping.

**Fig. 5** – Photoluminescence of (a) MEH-PPV, (b) Modified fullerene and (c) (1:4) MEH-PPV: Modified fullerene. All thin films spin-coated from chloroform**Fig. 6** – Optical absorption of pure Modified Fullerene film spin-coated from chloroform**Fig. 7** – Optical absorption of MEH-PPV: Modified Fullerene (1:3) film spin-coated from chloroform

The morphology of the spin-coated polymer thin films is an important factor on fabrication polymer solar cells. The surface morphological changes of MEH-PPV: Modified fullerene (1:4) films prepared from different solvents were monitored using AFM. Area roughness was used as parameter to quantitatively characterizes the surface of the thin films. In Figure 8a, the surface morphology of MEH-PPV: Modified fullerene film spin-coated from chloroform is shown as imaged by AFM; the area roughness is 7.33 nm. The film fabricated from 1,2-dichlorobenzene has a smooth surface with area roughness of 1.34 nm, (Figure 8b). Thin film prepared from toluene shows the rougher surface with area roughness of 15.18 nm, (Figure 8c). From AFM images it was clear that the thin film prepared from 1,2-dichlorobenzene shows much more homogeneous mixing of the photoactive layer in combination with a smoother surface.



**Fig. 8** – AFM images ( $5 \times 5 \mu\text{m}^2$ ) of (1:4) MEH-PPV: Modified fullerene film spin coated from (a) chloroform on quartz substrate (area roughness = 7.3 nm and average height = 34.25 nm). (b) 1,2-dichlorobenzene on quartz substrate (area roughness = 1.34 nm and average height = 8.09 nm) and (c) toluene on quartz substrate (area roughness = 15.18 nm and average height = 56.54 nm)

#### 4. CONCLUSIONS

We have shown that the absorption and photoluminescence of MEH-PPV thin films are strongly solvent dependent. We have shown that by varying the solvent used for polymer: modified fullerene spin coating, we can alter the thin film morphology. The thin film prepared from 1,2-dichlorobenzene shows the smoother surface.

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