

Optical Properties of Poly (3-hexylthiophene-2,5-diyl) and Poly (3-hexylthiophene-2,5-diyl) / [6,6]-Phenyl C61-butyric Acid 3-ethylthiophene Ester Thin Films

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Thin films of Poly(3-hexylthiophene-2,5-diyl) (P3HT) were prepared from chloroform, 1,2 dichlorobenzene and toluene solutions by spin coating technique on quartz substrates. The absorption and photoluminescence (PL) measurements were performed on the P3HT films to investigate the influence of solvent on the optical properties of the films. The results shows that the UV-vis absorption of P3HT film spin-coated from toluene is red shifted compared to the spectra of the films spin-coated from either chloroform or 1,2 dichlorobenzene. The surface morphology of P3HT: [6, 6]-Phenyl C61-butyric Acid 3-ethylthiophene Ester (Modified Fullerene) thin films spin-coated from different solvents were studied using Atomic Force Microscope (AFM), the thin film spin-coated from 1,2 dichlorobenzene show the smoother surface.

Keywords: Poly (3-hexylthiophene), Modified fullerene, Optical properties, Thin films, AFM.

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1. INTRODUCTION

Polymer solar cells have shown a potential to harness solar energy in a cost-effective way. The concept of generating specific fullerenes that are compatible with specific polymers has great potential for increasing the performance of bulk heterojunction polymer solar cells through the optimization of the morphology. The nano-morphology of the organic photoactive layer has a strong relationship with the performance of the polymer solar cells [1]. The morphology of this layer can be strongly affected by the processing conditions used such as the donor-acceptor composition [2], the solvent and the thermal annealing of the organic layer [3, 4]. Several studies in the literature discussed the effect of solvent on the optical and surface morphology of Poly (3-hexylthiophene-2,5-diyl) (P3HT): [6, 6]-Phenyl C61-butyric Acid methyl Ester (PCBM) thin films [5, 6]. The design and synthesis of modified fullerene with a higher LUMO energies compared to PCBM is essential to have a higher open circuit voltage and higher efficiency in bulk heterojunction polymer solar cells [7, 8, 9].

To our knowledge there is no published study on the optical and surface morphology of P3HT: [6, 6]-Phenyl C61-butyric Acid 3-ethylthiophene Ester (Modified fullerene) thin films. In this paper we report on the effect of preparation conditions on the optical properties of the *p*-type donor polymer P3HT thin films and on the surface morphology of the thin films of P3HT: [6, 6]-Phenyl C61-butyric Acid 3-ethylthiophene Ester.

2. EXPERIMENTS

The *p*-type donor polymer P3HT and the *n*-type acceptor [6, 6]-Phenyl C61-butyric Acid 3-ethylthiophene Ester (modified fullerene) in this study were purchased from sigma-Aldrich Corporation and American Dye Source, Inc. respectively; the chemical structures are

shown in Fig. 1. All materials were used as received without further purification. For the UV-vis absorption and photoluminescence (PL) measurements, P3HT and P3HT: 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. P3HT films were prepared at the concentration of about 11 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).

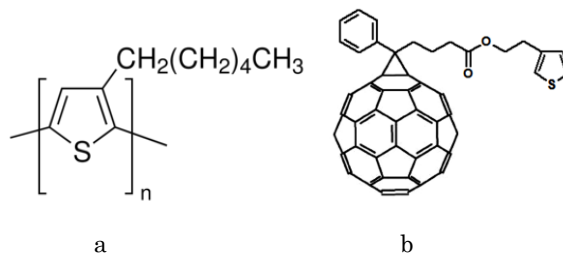


Fig. 1 – Chemical structure of (a) poly (3-hexylthiophene-2,5-diyl) and (b) [6,6]-Phenyl C61-butyric Acid 3-ethylthiophene Ester

For surface morphology characterization, P3HT and modified fullerene were dissolved in chloroform, 1,2 dichlorobenzene and toluene to yield a P3HT: modified fullerene (10.22 : 10.92 mg/ml chloroform, 10.41 : 10.38 mg/ml 1,2 dichlorobenzene and 10.50 : 10.56 mg/ml toluene) solutions. The quartz substrates were cleaned by ultrasonic treatment for 10 minutes using acetone and isopropyl alcohol sequentially. After cleaning of the quartz substrates the solutions were spin coated at 2000 rpm for 40 seconds. The surface morphology of P3HT: modified fullerene thin films spin coated from different solvents were characterized by atomic force microscopy (CP-II veeco).

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3. RESULTS AND DISCUSSIONS

The UV-vis absorption spectra of P3HT thin films spin-coated from chloroform, toluene and 1,2 dichlorobenzene solutions were recorded. Fig. 2 shows the UV-vis absorption spectra of the P3HT thin films fabricated from the different solvents. For the absorption spectra of P3HT film fabricated from chloroform, wavelength of the absorption peak (λ_{max}) is at 526 nm and two shoulders appeared at 488 nm and 588 nm. For the P3HT film fabricated from 1,2 dichlorobenzene, λ_{max} is 556 nm showing a red-shift and clear shoulders appeared at 527 nm and 603 nm. For the P3HT film prepared from toluene, the wavelength of the absorption peak is the same as the one prepared from 1,2 dichlorobenzene at 556 nm and the shoulders appeared at 522 nm and 603 nm. The strength of the maximum peak and the shoulder at higher wavelength of the films prepared from 1,2 dichlorobenzene or toluene is increased compared with that prepared from chloroform. It was clear that 1,2 dichlorobenzene and toluene promotes a higher degree of ordering in P3HT films than chloroform. The shift in the peak absorption wavelength in the different solvents may be attributed to an increased interchain interaction among P3HT chains. The absorption band edge of the films using chloroform, 1,2 dichlorobenzene and toluene solvents are observed at 660 nm (1.88 eV), 658 nm (1.89 eV) and 675 nm (1.84 eV), respectively.

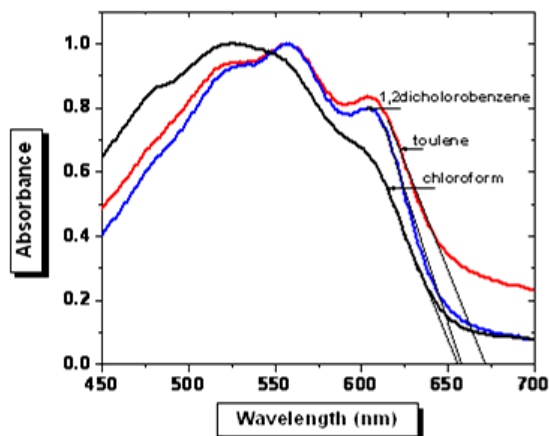


Fig. 2 – The UV-vis spectra of pure P3HT film spin-coated from chloroform, 1,2 dichlorobenzene and toluene

The photoluminescence (PL) emission spectra of P3HT was recorded in different solvents and are depicted in Fig. 3, the photoluminescence spectra do not show significant differences. The PL spectrums exhibit peaks at 643 nm, 649 nm and 650 nm for the films spin-coated from chloroform, 1,2 dichlorobenzene and toluene, respectively. The red shift in energy between the optical absorption and photoluminescence emission peaks is about 117 nm for thin film spin-coated from chloroform, 93 nm for the one spin-coated from 1,2 dichlorobenzene and 94 nm for toluene. Absorption and photoluminescence data for P3HT thin films are summarized in Table 1. Fig. 4 shows the UV-vis absorption spectrum of [6, 6]-Phenyl C61-butyric Acid 3-ethylthiophene Ester thin film. Two peaks appear at 266 and 336 nm and there is a broad tail of absorption extended to as long as 800 nm.

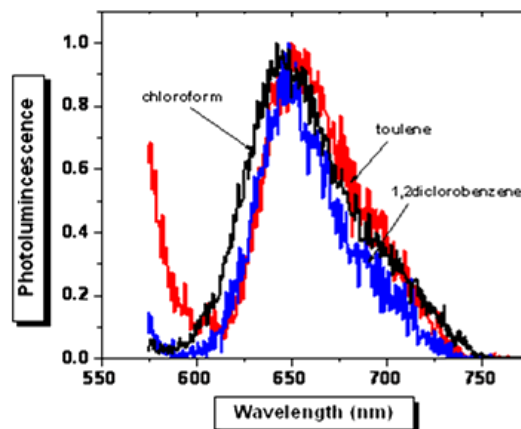


Fig. 3 – The PL spectra of pure P3HT film spin-coated from toluene, 1,2 dichlorobenzene and chloroform

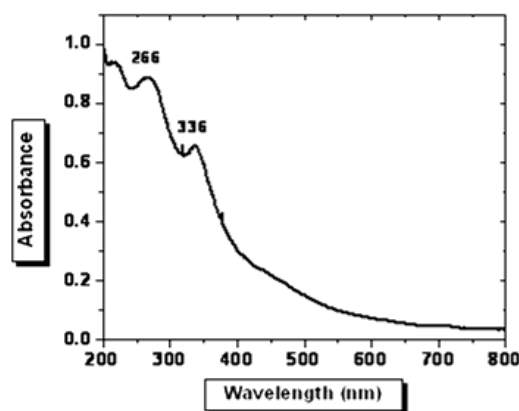


Fig. 4 – The UV-vis absorption of pure Modified Fullerene film spin-coated from chloroform

Fig. 5 display the UV-vis spectra of the P3HT: Modified fullerene (1:1) ratio blended film. The UV-vis absorption bands of the blend film appeared at 266 nm, 337 nm, 553 nm and 603 nm. The peaks 266 nm and 337 nm arise from the modified fullerene; the two other peaks with lower energies are caused by P3HT. We have extracted the onset wavelength of the blend with a linear fit near the absorption edge. The extracted onset wavelength was found to be 661 nm (1.88 eV). As shown in Fig. 6 the absorption of the films with increasing amount of Modified fullerene reduced significantly in the visible range, specifically between 450 nm and 650 nm which is the peak absorption wavelength band for P3HT. The maximum absorption wavelength for all films shows no change. However, in the wavelength lower than 400 nm, in the range of the peak absorption of the modified fullerene, the absorption of the films with increasing amount of modified fullerene is enhanced significantly. It has been reported by Vishal Shrotriya et al. [2] that there is a modification in the absorption spectra of P3HT:PCBM composite films with 67 wt % and higher amount of PCBM, the reason is due to the presence of PCBM which destructs the ordering in the P3HT chains. However, the amount of modified fullerene in our study is 50 wt % and less, so it has no effect on the chain ordering of P3HT. The film with the (3:1) P3HT: Modified fullerene shows the highest absorption in the range between 450 nm and 650 nm.

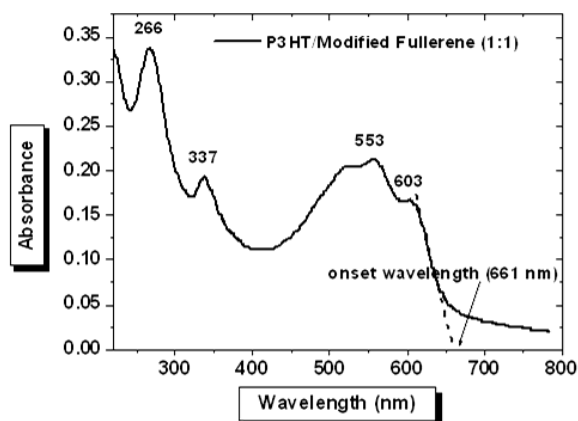


Fig. 5 – The UV-vis absorption of P3HT: Modified Fullerene (1:1) film spin-coated from 1, 2 dichlorobenzene

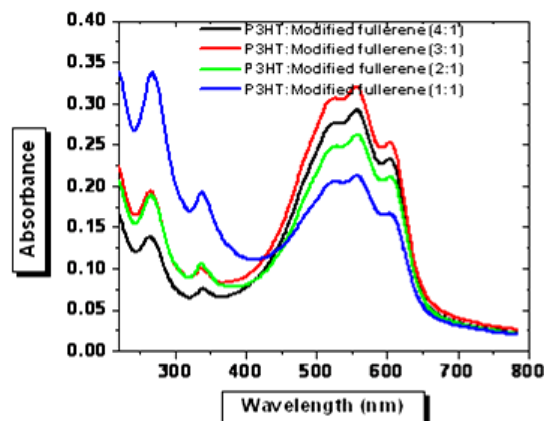


Fig. 6 – The UV-vis absorption spectra for P3HT: Modified fullerene films with different D/A ratio, spin coated from 1,2 dichlorobenzene with spin speed of 2000 rpm.

Table 1 – Optical data of P3HT in thin films spin-coated from different solvents

Solvent	$\lambda_{max,UV}$ (nm)	λ_{onset} (nm)	$\lambda_{max,PL}$ (nm)	Stokes shift (nm)	E_g E_t (eV)
chloroform	526	660	643	117	1.88
1,2 dichlorobenzene	556	658	649	93	1.89
toluene	556	675	650	94	1.84

AFM is a powerful tool to study the nanomorphology of organic blends in thin films. The surface topography usually gives a good insight into the film formation ability and the tendency of the components to phase separate. Fig. 7a displays AFM images of P3HT: Modified fullerene blended film prepared from chloroform; the area roughness is 8.8 nm. We observe phase separation of about 0.2 μm . The blended film prepared from

1,2 dichlorobenzene shows a smooth surface with an area roughness of 2.1 nm (see Fig. 7b). We observe a very small-scale phase separation (less than 0.1 μm) which is favorable for charge separation, charge transport, or charge collection in polymer solar cells. However, Fig. 7c shows that the blended film prepared from toluene have a rough surface area with area roughness of 22.5 nm and a large-scale phase separation.

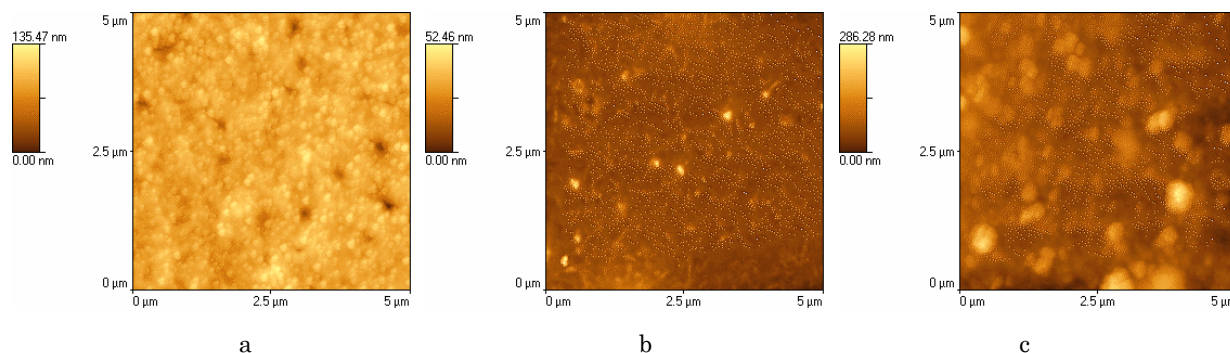


Fig. 7 – AFM images ($5 \times 5 \mu\text{m}^2$) of (1:1) P3HT: Modified fullerene film spin coated from (a) chloroform on quartz substrate (area roughness = 8.83 nm and average height = 86.67 nm) (b) 1,2dichlorobenzene on quartz substrate (area roughness = 2.11 nm and average height = 10.42 nm) and (c) toluene on quartz substrate (area roughness = 22.49 nm and average height = 71.47 nm)

4. CONCLUSIONS

In summary, we have shown that the absorption and photoluminescence of P3HT films are dependent on preparation conditions. Further, AFM images were used to study the P3HT: Modified fullerene film morphology spin-coated from different solvents. The results show that the surface morphology of the P3HT: Modified fullerene thin films depend strongly on the preparation solvent.

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