Absorption spectra modification in poly(3-hexylthiophene):methanofullerene blend thin films

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Abstract

The absorption spectra and the photovoltaic effect in thin films consisting of a blend of p-type poly(3-hexylthiophene) and n-type acceptor [6,6]-phenyl C60 butyric acid methyl ester have been studied and a decrease in inter-band absorption in the wavelength range of 450–600 nm is observed. This absorption quenching is attributed to the disordering of the poly(3-hexylthiophene) chains and a charge transfer between poly(3-hexylthiophene) and [6,6]-phenyl C60 butyric acid methyl ester, as evidenced by FTIR and X-ray photoelectron spectra. Finally, photovoltaic cells were fabricated utilizing the blend as the active layer and the device characteristics were studied.

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1. Introduction

Polymer based photovoltaic devices, incorporating 3-D interpenetrating network of conjugated polymers and C_{60} derivatives, have shown potential for application as renewable source of energy [1]. There have been several efforts in last few years to improve the efficiencies of these devices and reach the levels where they can be put into practical applications [2–5]. To further improve power conversion efficiency of the photovoltaic cells, it is important to use high-mobility polymers as the active material. In terms of literature, poly(3-hexylthiophene) (P3HT) has the highest charge carrier mobility among the conjugated polymers and hole mobility as high as $0.1 \, \mathrm{cm^2 \, V^{-1} \, s^{-1}}$ has been reported [6]. Moreover, P3HT has a band gap of 1.9–2.0 eV, which matches well with the strongest sun light [7]. These merits render P3HT good candidate for the polymer in polymer photo-

voltaic cells [8–10]. Several laboratories have reported high-performance photovoltaic cells using P3HT as the donor and [6,6]-phenyl C60 butyric acid methyl ester (PCBM) as the acceptor. A power efficiency of 3.5% has already been reached for the device utilizing a blend of P3HT and PCBM (in 1:2 wt. ratio) after a treatment of thermal annealing and electrical conditioning of the devices [9]. Recently, it has been shown that for photovoltaic devices utilizing P3HT:PCBM blends, the donor to acceptor ratio of 1:1 by weight gives the best device performance [11,12], with power conversion efficiency of about 3% being reported [11]. To further enhance the device performance, a study on the interaction between P3HT and PCBM is very important. We observed that the absorption spectra of thin films obtained by spin-coating a blend of P3HT:PCBM from solution showed a significant blue-shift when the amount of PCBM is 67 wt.% or more (i.e., at 1:2 wt. ratio of P3HT:PCBM), resulting in reduced red part absorption. Chirvase et al. [12] have reported similar trend in the absorption spectra modification and have

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attributed this change to destruction of ordering in the P3HT chains in the presence of PCBM. From our experiments, we demonstrate that the absorption spectra modification in P3HT:PCBM composite films is due to two possible interactions: first, the destruction of ordering of P3HT chains, as suggested earlier by Chirvase et al. [12], and second, due to a non-photoinduced charge transfer between P3HT and PCBM.

2. Experimental

A typical polymer photovoltaic device in this study consisted of a layer of polymer thin film sandwiched between a transparent anode (indium tin-oxide, ITO) and a metal cathode. The active polymeric material is an admixture of P3HT, a p-type polymer, and PCBM, an n-type acceptor. For fabricating the devices, the ITO glass substrates were cleaned by ultrasonic treatment in detergent, de-ionized water, acetone and isopropyl alcohol sequentially. The ITO surface was then modified by spin-coating a thin layer (about 30 nm) of PEDOT:PSS (Baytron® P VP Al 4083) from water. This was followed by thermal treatment of the substrates at 120 °C for 2 h. Then, solutions of P3HT blended with different wt. ratios of PCBM, were spin-coated from 1,2-dichlorobenzene (DCB) on the prepared anodes. The thickness of the polymer films was controlled by changing and optimizing the spinning speeds. Finally, the cathode, consisting of 30 nm of Ca and 80 nm of Al layers, was thermally deposited on top of the polymer film under vacuum of $\sim 10^{-6}$ Torr. The active area of the device was around 0.11 cm^2. For obtaining absorption spectra, thin films of P3HT:PCBM blend were spun-cast from solution in DCB onto quartz substrates and the spectra were obtained from Varian Cary 50 UV–Visible spectrophotometer. Similarly for obtaining infrared (IR) spectra the films were spun-cast on potassium bromide (KBr) palates and the measurements were done using Nicolet Avatar 360 FTIR Spectrometer. The X-ray Photoelectron Spectroscopy (XPS) data was obtained using monochromatic Al Kα radiation (1486.6 eV, 300 W) source with analyzer pass energy of 50 eV. The base pressure of analysis chamber was lower than 10^{-9} Torr. The film samples were prepared by spin-coating thin polymer layers on Au-plated Si substrates mounted on stainless steel holder. From all the spectra, a linear constant background was subtracted and the peak fitting was performed with a symmetric Gauss–Lorentz function. The spin–orbit splittings were set at 1.20 eV for the S 2p signals. The resolution of the measurement is about 0.1 eV. The current–voltage (I–V) curves were measured by a Keithley 2400 source-measure unit. The photocurrent was measured under illumination supplied by a ThermalOriel 150 W solar simulator (AM1.5G conditions). The thick-

nesses of the various films were measured using Dektak profilometer. All devices were fabricated and tested in oxygen and moisture free nitrogen ambient inside the glove-box.

3. Results and discussion

Fig. 1a shows the UV–Vis absorption spectra measured for P3HT from film and solution and for P3HT:PCBM films, for different wt. ratios of the two components. For pure P3HT film the solid-state absorption spectra showed two peaks at 493 nm and 517 nm and one shoulder at 572 nm. These three bands can be attributed to the π–π* transition. These values were similar to the ones that have been reported earlier for regioregular P3HT [13]. The absorption of the films with increasing amount of PCBM reduced significantly in the visible range, specifically between 450 and 600 nm
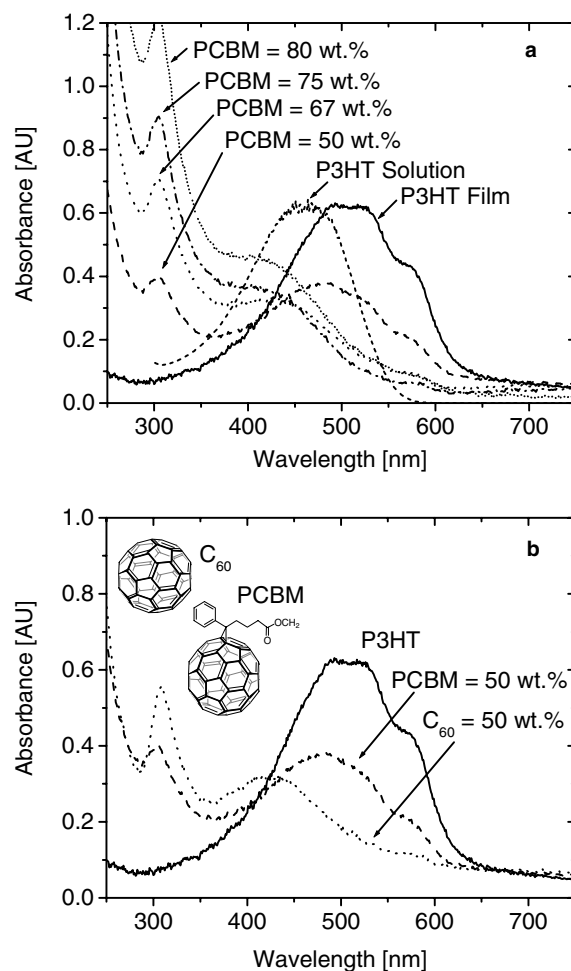

Fig. 1. UV–Vis absorption spectra for (a) P3HT (measured from film and solution) and P3HT:PCBM composite films for different amount of PCBM, and (b) thin films of pure P3HT, and P3HT with 50 wt.% of C$_{60}$ and PCBM. The chemical structures of C$_{60}$ and PCBM are also shown in the inset for comparison.

which is the peak absorption wavelength band for P3HT. The maximum absorption wavelength for the film with 50 wt.% PCBM was at ∼484 nm with shoulders at ∼516 and ∼570 nm. The peak absorption wavelength and the maximum absorption intensity changed significantly for films with 67 wt.% and higher amount of PCBM. The characteristic peak absorption wavelength (λ_{max}) for film with 67 wt.% PCBM was at ∼421 nm showing a blue-shift of 63 nm compared to the film with 50 wt.% PCBM, whereas for 75 wt.% and higher amount of PCBM, λ_{max} was around 403–404 nm showing blue-shift of about 80 nm. Since the concentration of P3HT was always kept the same in the solutions used for spin-coating, that is, the total amount of P3HT may be almost the same for all films, the quenching of the absorption for the film with the presence of PCBM can be attributed to the interaction between the polymer and PCBM. One possible effect of the presence of PCBM molecules is the lowering of the interaction among the P3HT chains. This is evidenced by the comparison of the film absorption and the solution absorption as seen in Fig. 1a. The absorption of the solution has a blue-shift compared to the absorption of the film. The extinction coefficients (ε_{abs}) were calculated by using Beer–Lambert Law [14] from the absorption spectra for both films and solutions of P3HT:PCBM. For the films, the values of ε_{abs} were 5260, 2830, 1780, 1670 and 1730 for PCBM concentration of 0%, 50%, 67%, 75% and 80%, respectively. However, for the solutions, the values of ε_{abs} were 41, 44, 43, 45 and 44, for similar concentration of PCBM. The extinction coefficients of the solutions were lower than that of the films by about two orders of magnitude. Hence, the inter-chain interaction among the P3HT chains results into more delocalized conjugated π electrons, the lowering of the bandgap between π and π^*, and the increase of the optical π–π^* transition. However, this may not be the sole reason for the absorption quenching. The envelope of film with 50 wt.% PCBM is similar to that of pure P3HT film, while the absorption quenching has already occurred. If the decrease in the inter-chain interaction is the sole factor for the absorption quenching, the absorption band should significantly shift towards blue for the film with 50 wt.% PCBM. This suggests that there may be another factor for the absorption quenching. Another possible interaction between P3HT and PCBM may be a charge transfer, since P3HT can be oxidized while PCBM can be reduced. This charge transfer becomes clear when PCBM is replaced by C_{60} in the blended film. Fig. 1b presents the UV–Vis absorption spectra for films of P3HT blended with 50 wt.% C_{60} and PCBM. The difference between these two spectra is remarkable. The absorption peaks, which appear at 484 nm with shoulders at 516 and 570 nm for 50 wt.% PCBM, exhibit a blue-shift to ∼423 nm with a small shoulder at ∼570 nm for P3HT:C_{60} film. The

absorption for P3HT:C_{60} film becomes even lower. This suggests that PCBM or C_{60} may not only play a role to de-structure the P3HT but there may be a charge transfer between P3HT and PCBM or C_{60}, since P3HT can donate an electron and PCBM or C_{60} can accept an electron. The remarkable difference may be attributed to the chemical structure of these two compounds. The PCBM molecule is a derivative of C_{60} where alkyl side chains are attached to C_{60} molecule to increase is solubility in organic solvents (see Fig. 1b – inset). These side chains might act as preventive element for the possible interaction between P3HT and C_{60} molecules. Therefore, in absence of these side chains, the interaction between the p-type polymer and the C_{60} molecule, which is a strong electron acceptor, is significantly increased resulting in further shift and reduction of absorption peak. If the absorption spectra modification is solely due to destruction of order in P3HT chains by presence of PCBM or C_{60}, then such disordering should be more in case of PCBM than for C_{60}. However the blue-shift in the absorption spectra is significantly more for P3HT:C_{60} film compared to P3HT:PCBM. The difference in the absorption spectra for P3HT:PCBM and P3HT:C_{60} films provides the evidence for a charge-transfer reaction between the donor polymer and the acceptor PCBM molecules.

It has been reported by Chirvase et al. [12] that the modification in the absorption spectra of P3HT:PCBM composite films is due to the presence of PCBM which destructs the ordering in the P3HT chains. It was also mentioned in the above reference that the absorption spectra can be recovered upon thermal annealing of the films. We performed thermal annealing on two types of P3HT:PCBM composite films, with PCBM concentration of 50% and 67% by weight. The results are shown in Fig. 2a and b. When thermal annealing was performed on the composite films, the absorption shift in the spectra showed some recovery for both types of films, which suggests that annealing induced some ordering in the polymer chains. However, after annealing, the absorption peak for the 50 wt.% PCBM film was at ∼510 nm, whereas for 67 wt.% film it was at ∼467 nm, a blue-shift of 43 nm. Compared to the untreated films, there was some recovery but the blue-shift in the absorption spectra upon mixing PCBM was not completely recovered upon annealing. Also, the amount of recovery for films with different concentration of PCBM was different, suggesting that the presence of PCBM in the films not only has an effect on the ordering of P3HT chains, but there is another irreversible interaction in the form of non-photoinduced charge transfer between the two components. The annealing process can result in recovery of the ordered structure of the polymer chains, which results in red-shift of the absorption spectra after annealing, as shown in Fig. 2. The charge-transfer process, on the other hand, is not revers-
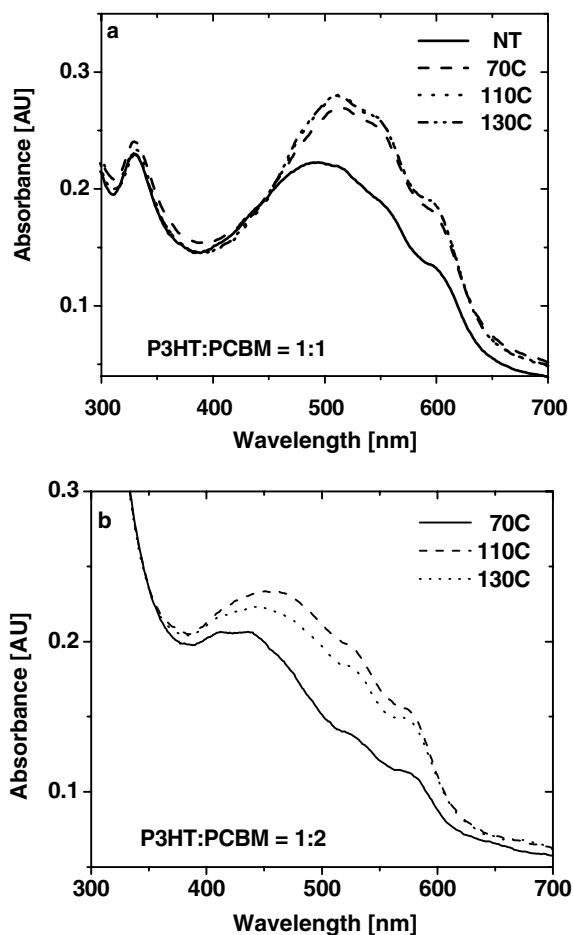
Fig. 2. Effect of thermal annealing on the absorption spectra of P3HT:PCBM composite films for P3HT:PCBM ratio of (a) 1:1 and (b) 1:2 by weight. The annealing time for all the films was 30 min.

Fig. 3. FTIR spectra for thin films of pristine PCBM, pristine P3HT, and P3HT:PCBM in 1:1 and 1:2 wt. ratios.

ible and therefore the absorption spectra cannot be recovered completely upon annealing. The recovery was less for PCBM concentration of 67% suggesting that at this concentration, there has been significant non-reversible non-photoinduced charge transfer between PCBM and P3HT.

This charge transfer between P3HT and PCBM was further studied by the FTIR spectroscopy (Fig. 3). The vibrations of some compounds are sensitive to the charge on the compounds. Both the C=C and C—S stretching vibrations may shift when the amount of charge present on the compound changes [15,16]. The C=C stretching vibrations are really complicated since both P3HT and PCBM have C=C stretching vibrations, and therefore, it is difficult to explain the charge-transfer effect by analyzing the C=C vibrations. Also it is not easy to find C—S peak in the IR spectra of P3HT [15]. However, the thiophene ring associated with P3HT shows an out of plane deformation of C—H, and the band at 819 cm^{-1} is assigned to this C—H deformation vibration of P3HT and can be used to study the charge-transfer effect in P3HT. A new band appears at
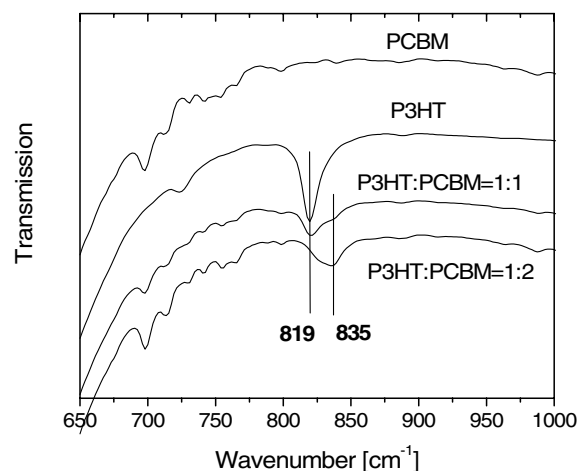
835 cm^{-1} as a shoulder for the 1:1 P3HT:PCBM film. This band becomes intense with the increase of the amount of PCBM. This band at 835 cm^{-1} is not from PCBM. Hence, this change in vibration energy might be due to the charge transfer that occurs between sulfur atom in P3HT molecule and PCBM. Some charge is transferred from the sulfur atoms, to the conjugated chains of the PCBM molecules, and this result in a slight positive charge being present on the sulfur atoms.

X-ray photoelectron spectroscopy measurements were performed on the thin films of pristine P3HT, and P3HT blended with PCBM and C$_{60}$. No apparent shift was observed in C 1s peak, which was located at 284.65 ± 0.1 eV. The XPS S 2p core level spectra in various samples corresponding to various P3HT films (pristine, and blended with PCBM and C$_{60}$) are presented in Fig. 4a. The inset shows the curve fitting of S 2p doublet of P3HT. A respective intensity ratio of S 2p3/2 and S 2p1/2 is about 2:1 ratio. The S 2p peak showed a shift towards lower binding energy (BE) when P3HT was blended with PCBM or C$_{60}$. Also, the shift to the lower BE was maximum when P3HT was blended with 67 wt.% PCBM (−0.5 eV), followed by 50 wt.% C$_{60}$ (−0.3 eV), and then 50 wt.% PCBM (−0.1 eV). Such shift in BE corresponds to the shift in absorption spectra where we observed similar relative blue-shift when P3HT was blended with PCBM or C$_{60}$. The shift of S 2p peak to lower BE suggests the presence of a slight negative charge on sulfur in P3HT. However, when the S 2p peak was measured for the oxidized P3HT film (the film was oxidized by treating in a solution of ferric chloride in nitromethane), a shift towards higher binding energy (+0.1 eV) relative to the oxidized P3HT was observed, suggesting the presence of positive charge on sulfur which is consistent with the result of oxidized P3HT by chemical doping [17]. The presence of negative charge on sulfur upon mixing P3HT with PCBM does
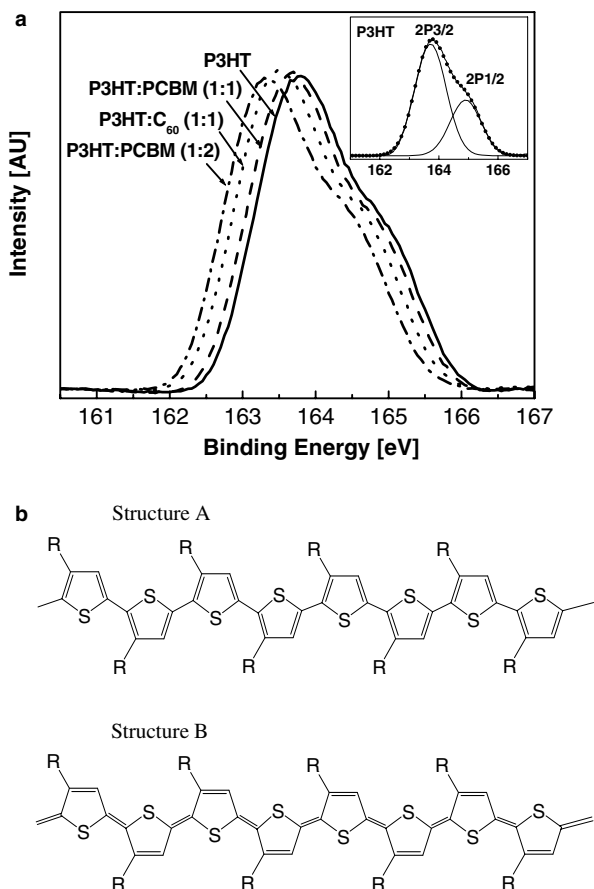
Fig. 4. (a) XPS spectra for films of pristine P3HT, P3HT with 50 wt.% C_{60}, and P3HT with PCBM (50 wt.% and 67 wt.%); (b) two resonant structures, aromatic (A) and quinoid (B), of P3AT chains.

not agree with the observation for the case of oxidized P3HT. This can be explained by the localized charges stabilized by the disorder degree in P3HT film [18]. We assume more disorder is created by blending PCBM or C_{60} resulting in charge transfer from the inter-chain to intra-chain on the sulfur atom, corresponding to the localization of these charges. The disorder of the polymer chains would cause the bleaching of $\pi–\pi^*$ absorption in neutral chains of P3HT [18], and thus provide further absorption quenching as seen in the absorption spectra.

When PCBM was blended with P3HT, we observed a quenching (or reduction coupled with a blue-shift) in the absorption spectra suggesting an interaction between the two components in the active layer. This absorption quenching has adverse effect on device performance because less absorption means less photogenerated charge carriers and lower efficiency. Also, this quenching became significantly large when the amount of PCBM was about 67 wt.% or more, resulting in reduced photocurrent. There are two possibilities for interaction between P3HT and PCBM: (i) a non-photoinduced (under dark or without light) charge transfer between

P3HT and PCBM, similar to oxidation of P3HT; (ii) blending PCBM with P3HT will result in destruction of ordered structure of polymer chains and this disordering will reduce the inter-chain interaction in the polymer,

thus reducing the absorption. XPS measurements on P3HT:PCBM films showed a small negative charge present on S. To explain this effect we need to consider an important issue. The polymer chains can exist in two resonant structures [19]: aromatic (structure A) and quinoid (structure B), as shown in Fig. 4b. When the polymer chains have more disordering, which happens when PCBM is blended into the polymer, the structure A will be more favorable compared to B, because in A the adjacent rings are connected by a single bond making the chains more flexible. When there is more disorder, polymer chains will be highly coiled and flexibility becomes important. Now in A, the ring has more charge density because of the presence of two double bonds in the ring (compared to only one in B) and XPS will measure this negative charge present on S. This implies that although there will be charge transfer, the effect of disordering overcomes the effect of charge transfer and S atoms end up with a small negative charge. Both the effects, however, reduce the absorption spectra of the polymer.

When the blended film P3HT and PCBM is used as the active film of a polymer photovoltaic cell, both the absorption and the amount of PCBM should be considered. As discussed above, the absorbance decreases with the increase of the PCBM amount in the film, while the electron mobility in the film should increase. We investigated the effect of these two factors on the device performance by fabricating photovoltaic cells utilizing P3HT:PCBM blend as the active layer, with varying weight fraction of PCBM, and the *I–V* characteristics under illumination for the devices are shown in Fig. 5.
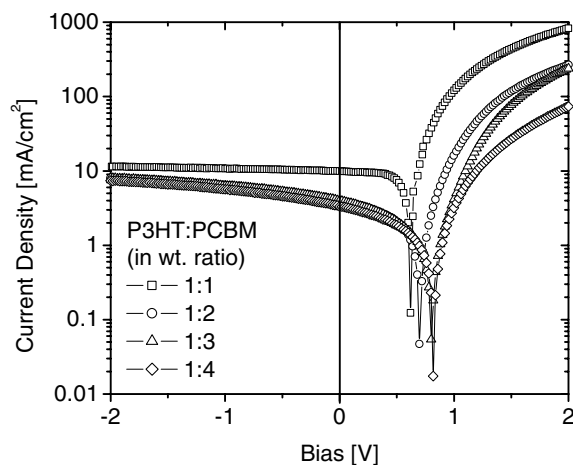

Fig. 5. *I–V* characteristics for photovoltaic devices with P3HT:PCBM system used as the active layer containing different wt. ratios of the two components.

From the figure, it can be seen that the short-circuit current (I_{SC}) was highest for the device with 1:1 wt. ratio ($I_{SC} = 9.9$ mA/cm^2), and reduced with increasing concentration of PCBM in the active layer. For device with P3HT:PCBM wt. ratio of 1:4 wt. ratio, the I_{SC} was only 3.3 mA/cm^2. This is in agreement with the reduced absorption that is observed for active layer when the amount of PCBM exceeds 50 wt.%, which will result in reduced carrier generation and therefore lower current density. The open-circuit voltage (V_{OC}) however, increases with the increasing amount of PCBM as a result of increased shunt resistance of the device, which also results in a lower fill factor (FF). The V_{OC} of 0.61, 0.71, 0.80, and 0.83 V are observed for the devices with P3HT:PCBM wt. ratios of 1:1, 1:2, 1:3, and 1:4, respectively. Therefore, we observed the best performance for the device with 50 wt.% PCBM in the active layer, which gave highest short-circuit current of about 10 mA/cm^2 and a power conversion efficiency of up to 3.85% as a result of better absorption and carrier transport in the active layer.

4. Conclusions

In conclusion, the interaction between P3HT and PCBM in solid-state thin films was studied by UV–Vis absorption, FTIR, and XPS spectroscopy. The absorption of P3HT in the visible range shows significant shift with the increase of the PCBM amount in the polymer film. This absorption spectra modification was attributed to the lowering of the inter-chain interaction due to the presence of PCBM molecules, and a non-photo-induced charge transfer between P3HT and PCBM in solid state. The charge transfer was evidenced by the comparison of absorption spectra between films of P3HT:PCBM and P3HT:C$_{60}$. The FTIR spectroscopy showed the change in peak assigned to C─H deformation vibration associated with the thiophene ring which further proved the occurrence of charge-transfer process. XPS spectroscopy results on the P3HT:PCBM and P3HT:C$_{60}$ films confirmed the interaction between the two components and a shift in S 2p core level peaks was observed. Finally, photovoltaic devices were fabricated with different wt. ratios of donor and acceptor and a sharp reduction in short-circuit current was observed on increasing the amount of PCBM in the active layer, which is due to reduced absorption in the polymer. An increase in V_{OC} was also observed on increasing the amount of PCBM in the film. The best performance

was observed for devices with the active layer containing 50 wt.% PCBM with efficiency of about 3.85%.

Acknowledgments

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