

# Effect of Composition on Conjugation Structure and Energy Gap of P3HT:PCBM Organic Solar Cell

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**Abstract:** in the present study we focus on the effect of donor/acceptor composition on the conjugation and ordered structure of the donor-polymer in the most common organic solar cell based on a bulk heterojunction of regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM). In addition, we try to illustrate the effect of composition, over a wide range, on the internal energy configuration and energy gaps of the donor polymer and acceptor fullerene in the solar cell active layer. Through the present investigations, we detected an improvement in conjugation length and ordered structure of the P3HT molecules under the increase its concentration in the solar cell active layer. This improvement is revealed through red shift of the P3HT absorption peak in optical absorption spectroscopy. In addition, we found a relation between energy gap and composition of the P3HT:PCBM combination, where the energy gaps of both P3HT and PCBM increase with increasing P3HT concentration in the solar cell active layer. The higher concentrations of P3HT or PCBM are the responsible for determining the energy gaps of the molecules in solar cell active layer, while the large variation in the energy gap of a molecule is a result of its poor concentration in the solar cell active layer. The device performance parameters are investigated under the wide composition range of P3HT:PCBM solar cell active layer. The best (optimized) solar cell composition in these investigations is the 50:50 wt.% of the P3HT:PCBM binary at which the J<sub>sc</sub>, V<sub>oc</sub>, FF, and PCE are 6.3 mA/cm<sup>2</sup>, 0.59 V, 0.55, and 2.03 %, respectively.

**Keywords:** Organic solar cells; P3HT:PCBM solar cell; Device performance parameters.

## 1 Introduction

Organic photovoltaic, the technology to convert sun light into electricity by employing thin films of organic semiconductors, has been the subject of active research over the past 20 years and has received increased interest in recent years by the industrial sector [1]. Organic solar cells offer considerable promise for use in new solar energy technologies due to their flexible material properties and potential for low-cost manufacture [2]. Solar cells based on a bulk heterojunction (BHJ) of regioregular poly(3-hexylthiophene) (P3HT) (which forms the hole-transport network) and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) (which forms the electron-transport network) have been reported among the highest performing material systems to date and have been considered as the largest in researchers' investigations and studies [3-8] for improving their power conversion efficiencies. Bulk heterojunction organic solar cells are composed of interpenetrating networks of p-type semiconducting donor material and n-type semiconducting acceptor material in a blend solution, which can be deposited by a printing process, and are thus

compatible with low-cost role-to-role fabrication technology. The BHJ blends provide an approach for high efficiency solar cells, since high interfacial area within BHJ material tends to large number of generated charge carriers and photocurrent in the solar cells. A BHJ is usually obtained by relying on the phase separation (on the nanometer scale) of donor and acceptor materials in a mixed layer, where insufficient phase separation often compromises the device performance owing to carrier recombination and poor charge transport [9]. In general, and as a result of phase separation on nanometer scale occurring in the active layer blend, the donor/acceptor interfaces (photoactive p-n heterojunction sites) spread within the entire volume of the BHJ composite layer. Therefore, the limitations of exciton migration and charge separation are overcome. Moreover, in the BHJ, both materials (donor and acceptor) have percolating paths to their respective electrode to ensure efficient charge transport and collection.

The variation in composition of the donor and acceptor materials in solar cell active layer can strongly affect phase separation and photoactive p-n heterojunction sites in the active layer of the organic solar cell. Then, the variation in

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donor/acceptor composition can affect light harvesting, exciton migration, charge separation, charge transport, the number of generated charge carriers, and photocurrent in the organic solar cell. Therefore, it is important to study the effect of donor/acceptor composition on optical properties and performance of the organic solar cell for understanding the device physics and to be able to improve the conversion efficiency of the organic solar cells. There are many works [10,11] done to study the influence of composition on the device performance parameters and for searching about optimum mixing ratio, which has the best performance parameters. However, in the present study we focus on the effect of donor/acceptor composition on the conjugation and ordered structure of the donor-polymer P3HT, and we try to illustrate the effect of composition on the internal energy configuration and energy gaps of the active layer materials.

In this work, we construct indium-tin-oxide (ITO)/poly(3,4-ethylene dioxothiophene)-blend-poly(styrene sulfonate) (PEDOT:PSS)/P3HT:PCBM/Al BHI solar cells with varying the composition of the P3HT:PCBM active layer in the most common organic solar cell. For studying the effect of composition on conjugation and ordered structure of the donor-polymer P3HT we measured optical properties of the solar cell active layer through optical absorption spectroscopy. The effect of composition on performance parameters of the organic solar cell is carried out through the current density/voltage (J/V) characteristics under AM1.5 white light illumination with an intensity of 100 mW/cm<sup>2</sup>. Our present study may increase the knowledge about the behaviour of P3HT:PCBM active layer under different composition.

## 2 Experimental procedures

### 2.1 Materials and solutions

Regioregular P3HT and PCBM (from Nano Spectra, Japan) were purchased and used without further purification. Using 1,2-dichlorobenzene (Tokyo Chemical Industry Co. LTD, Japan) as a solvent, we prepared P3HT:PCBM blend solutions of the solar cell active layer at different composition as 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20, 90:10, and 100:0 weight percentage (wt.%). The P3HT:PCBM blend solutions had 30 mg/mL as a concentration of the solar cell active layer. The active layer blend solutions were vigorously stirred for more than 24 h at room temperature under nitrogen atmosphere in a glove box to maximize mixing while avoiding touching the vial cap.

### 2.2 Film and device fabrication

For optical absorption measurement, the P3HT:PCBM blend films at different composition were prepared by spin-coating the blend solutions (2000 rpm) onto clean micro-

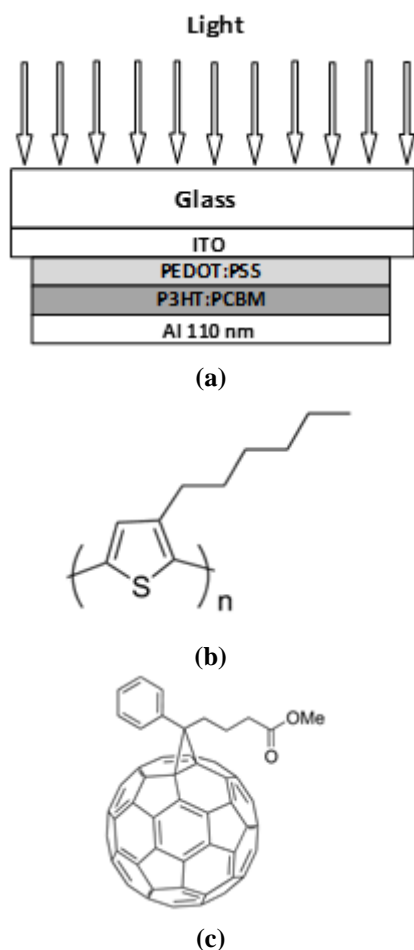
glass substrates with thermal annealing using a digitally controlled hotplate at 140 °C for 4 min under nitrogen atmosphere in a glove box. The film preparation and thermal annealing conditions were kept the same as those of the corresponding complete devices for accurate comparison.

For organic solar cell fabrication, the ITO-glass substrates (~10 Ω/□) were sequentially cleaned in an ultrasonic bath using acetone (twice) and methanol (once), rinsed with deionized water, and finally dried in flowing nitrogen. To increase the work function of the ITO electrode and to improve the electrical connection between ITO and organic active layer, a layer of PEDOT:PSS (from Sigma-Aldrich) was spin-coated (2500 rpm) onto ITO-glass substrate in air and dried using a digitally controlled hotplate at 100 °C for 10 min under nitrogen atmosphere in a glove box. On top of the insoluble PEDOT:PSS layer, the P3HT:PCBM blend solutions, at different composition, were spin-coated (2000 rpm) under nitrogen atmosphere in a glove box. An approximately 100-nm-thick Al electrode was thermally deposited onto the active layer using a vacuum deposition system at a pressure of about  $3 \times 10^{-4}$  Pa through a shadow mask to obtain 25 identical cells on one device with an active area of  $3 \times 3$  mm<sup>2</sup>. Then, the devices were annealed in a nitrogen atmosphere at 140 °C for 4 min for improving the conjugation and crystallinity of the P3HT chains and to increase the electrical contact between solar cell active layer and Al electrode. The complete organic solar cells, with the configuration shown in Fig. 1, were stored in the dark under suitable pressure until measurements.

### 2.3 Measurements

The optical absorption spectroscopy of the P3HT:PCBM blend films at different composition was measured using a JASCO V-570 ultraviolet/visible/near-infrared (UV/vis/NIR) spectrophotometer with incident optical light towards the coated side of the films using a micro-glass substrate in the reference position.

The external quantum efficiency measurement was performed for the complete devices using a halogen lamp and a monochromator. The J/V characteristics of the devices under white light illumination were determined using standard solar irradiation of 100 mW/cm<sup>2</sup> (AM1.5) with a JASCO CEP-25BX spectrophotometer J/V measurement setup with a xenon lamp as the light source and a computer-controlled voltage-current source meter (Keithley 238) at 25 °C under nitrogen atmosphere. All measurements were performed soon after preparation of the devices to avoid any change in the photoelectric properties caused by aging.



**Fig. 1.** (a) Cross-sectional view of P3HT:PCBM organic photovoltaic device and chemical structure of (b) P3HT and (c) PCBM.

### 3 Results and discussion

#### 3.1 Effect of P3HT concentration on optical properties of the solar cell

It is important to know that, the spectral range of the optical absorption compared to solar spectrum, absorption value, and absorption wavelength are the factors affecting the total number of absorbed photons by solar cell active layer, considering that the limitation in the light absorption across the solar spectrum limits the photocurrent of the solar cells. The number of absorbed photons and, therefore, the generated photocurrent in a solar cell increases when the absorption range and absorption peak value increase for solar cell active layer. The number of absorbed photons in a solar cell active layer, also, increases when the active layer absorbs in the red or near infrared region of the solar spectrum, where there is the dense number of the light photons.

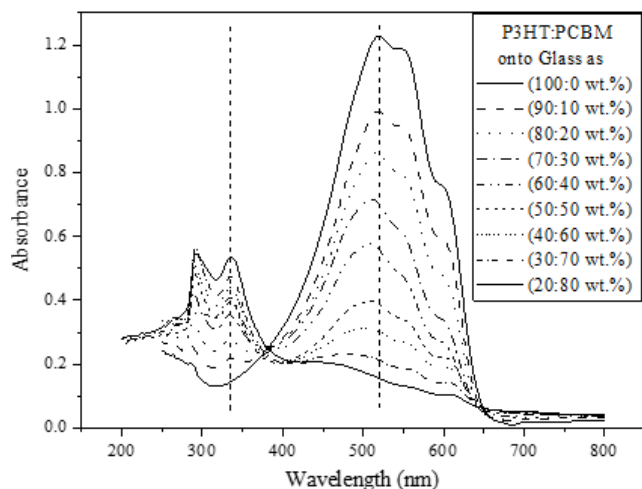
Figure 2 shows optical absorption of the P3HT:PCBM blend films at different composition. As shown in this figure, the absorption of P3HT in the active

layer occurs around the wavelength range of 380-660 nm, while the PCBM absorbs light around the wavelength range of 280-380 nm. We can observe from Fig. 2 that, with increasing P3HT concentration in the solar cell active layer, the absorption peak value of P3HT gradually increases, while the absorption peak value of PCBM decreases, continuously. The observed increase in the P3HT absorption peak value with increasing P3HT concentration is an indication of increase in the number of P3HT chains packed in the solar cell active layer. In addition, Fig. 2 shows that, the absorption peak of P3HT shifts to higher wavelength (redshift), from 438 to 520 nm with increasing P3HT concentration from 20 to 100 wt.%, respectively, while the absorption peak of PCBM (as a small molecule) remains unchanged under different P3HT:PCBM composition. It is important to consider that, the optical absorption spectroscopy is an efficient tool for detecting the organization of the molecules in crystalline domains as stated by Vanlaeke et al. [12]. Therefore, we can conclude from the observed results shown in Fig. 2 that, the observed red shift in the absorption peak of P3HT by increasing its concentration is an indication of improvement the conjugation length and ordered structure of the P3HT molecules in the solar cell active layer. As the polymer chains are extended through the crystallites, thicker crystallites would give a longer conjugation length [13]. The increase in P3HT conjugation length means that, the alternation of single-double bonds between carbon atoms increases along the polymer chains. Therefore, the P3HT absorbs larger amount of light photons, which have lower energy, and, consequently, the generation of charge carriers may increase in the solar cell.

Fig. 3 may amounts the variation in the red shift of the P3HT absorption peak as a function in the P3HT concentration in the P3HT:PCBM active layer. According to Fig. 3, we can see that, the red shift in the P3HT absorption peak seems to be large (from 438 to 510 nm) at the lower P3HT concentration (in the range of 20-50 wt.%), while it seems to be stable (in the small range of 510-520) at the higher P3HT concentration (from 50 to 100 wt.%). The improvement in P3HT conjugation length may enhance not only the light harvesting (by the absorption in the near red region) but also may enhance the charge carrier transfer in the solar cell active layer as a result of alternation of the single-double bonds between carbon atoms in the polymer chains. As a conclusion, the increase in P3HT concentration in the solar cell active layer tends to improve light harvesting of the P3HT:PCBM solar cell through the increase in absorption peak value of the P3HT molecules and through the red shift of the P3HT absorption peak in the optical absorption spectrum.

In addition to the valuable information about conjugation and ordered structure of the P3HT molecules determined by optical absorption study, the optical absorption measurement gives important information about band structure and optical band gaps of the P3HT and PCBM molecules in the solar cell active layer. In the organic

materials, the band gap is determined by the energy difference between highest occupied molecular orbit (HOMO) and lowest unoccupied molecular orbit (LUMO). Using Fig. 2 and by extension the low-energy absorption edge of the P3HT and PCBM to intersect the x-axis, we can determine the energy band gaps of both P3HT and PCBM under different composition. We found that, the increase in P3HT concentration in the P3HT:PCBM active layer tends to increase the energy gaps of both P3HT and PCBM, as shown in Fig. 3.

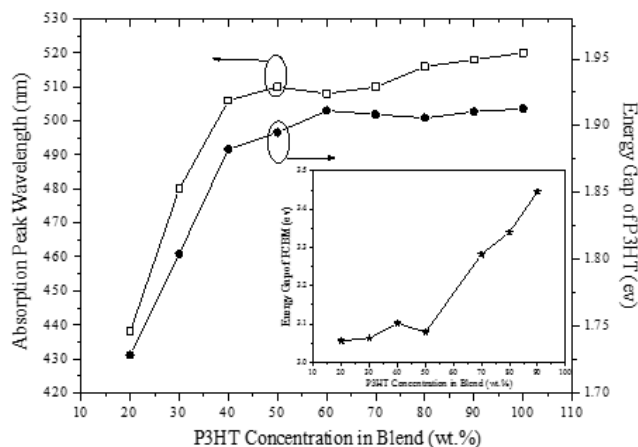


**Fig. 2.** Optical absorbance of P3HT:PCBM solar cell active layer at different composition.

The increase in the energy gap of the P3HT seems to be large (from 1.73 to 1.91 eV) at the lower P3HT concentration (in the range of 20-60 wt.%), while it seems to be stable (around the value of 1.91 eV) at the higher P3HT concentration (from 60 to 100 wt.%). The inset of the Fig. 3 shows the variation of energy gap of PCBM molecules at different P3HT concentration. The measured energy gap of the P3HT in the present work is in good agreement with that stated in the literatures [14]. As shown in Fig. 3, the energy gap of PCBM tends to be stable (around the value of 3.06 eV) at lower P3HT concentration (from 20 to 50 wt.%), while it increases largely (from 3.06 to 3.45 eV) at the higher P3HT concentration (in the range of 50-90 wt.%).

We can summarize the results shown in Fig. 3 and tell that, at the lower P3HT concentration (in the range of 20-50 wt.%), at which the energy gap of P3HT increases largely, the energy gap of PCBM stills stable. While at the higher P3HT concentration (in the range of 50-100 wt.%), at which the energy gap of P3HT stills stable, the energy gap of PCBM increases largely. Therefore, we can conclude that, the higher concentrations of P3HT or PCBM in solar cell active layer are the responsible in determining the energy gap of the molecule in active layer, and the large variation in the energy gap of a molecule is a result of its poor concentration in the solar cell active layer. By other words, we can say that, the increase in P3HT concentration in the P3HT:PCBM active layer increases the energy gap of

PCBM, while the increase in the PCBM concentration decreases the energy gap of P3HT. The observed variations in the energy gaps of both P3HT and PCBM through the present study may be attributed to the variation in the degree of covalent interactions between P3HT and PCBM, which varies with the variation in the P3HT:PCBM composition. Xie et al. [15] stated that, the P3HT band gap can be continuously enhanced by using the degree of covalent interactions with PCBM. The covalent interaction increases the P3HT band gap, leading to a lowering of the HOMO of P3HT.



**Fig. 3.** Absorption peak wavelength and energy gap of P3HT as a function of P3HT concentration. The inset shows the energy gap of PCBM molecules at different P3HT concentration.

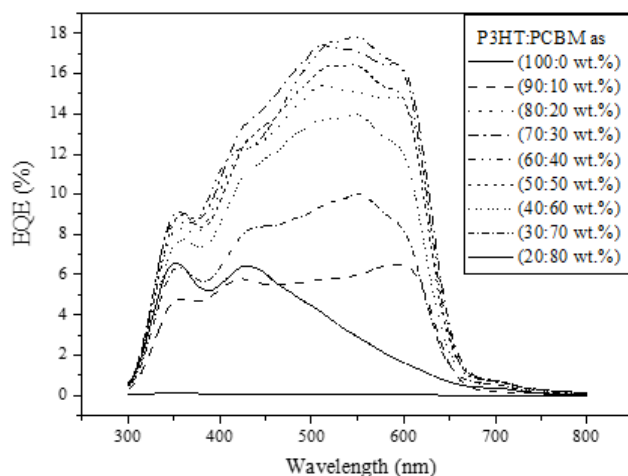
### 3.2 Effect of P3HT concentration on external photocurrent quantum efficiency of the solar cell

The external quantum efficiency (EQE) spectra of the ITO/PEDOT:PSS/P3HT:PCBM/Al solar cells with varying P3HT concentration in the solar cell active layer are shown in Fig. 4 in the wavelength range from 300 to 800 nm. The contribution of P3HT to photocurrent of the solar cells is observed in Fig. 4 around the wavelength of 550 nm, where the P3HT has an absorption peak at 520 nm, as shown in Fig. 2. The contribution of PCBM to photocurrent appears pronouncedly at lower P3HT concentration (such as 20 wt.%), at which the contribution of P3HT to photocurrent decreases pronouncedly, as shown in Fig. 4. The contribution of PCBM at 20 wt.% of the P3HT appears as two photocurrent peaks at the wavelengths of 360 and 430 nm. At the higher P3HT concentration, the photocurrent of PCBM at the wavelength of 430 nm overlaps with the photocurrent of P3HT. Hence, the shoulders appearing in the optical absorption of the P3HT:PCBM active layer around 430 nm at higher P3HT concentration is a part from PCBM contribution to photocurrent of the solar cell.

The photocurrent of P3HT:PCBM solar cell, as shown in Fig. 4, increases gradually with increasing P3HT concentration up to 60 wt.%, and after that, it decreases gradually with increasing P3HT concentration up to 100



wt.%. The observed increase in the photocurrent with increasing P3HT concentration up to 60 wt.% is attributed to the increase in optical absorption, which is able to generate excess of excitons from the solar cell active layer. The generated excitons can be easily dissociated at donor/acceptor interface as a result of increasing number of the photoactive p-n heterojunction sites, which increases with increasing P3HT concentration in the solar cell active layer. The subsequent decrease in the photocurrent of P3HT:PCBM solar cell with further increase in P3HT concentration up to 100 wt.% is attributed to decrease in the photoactive p-n heterojunction sites and deterioration in electron transfer at higher P3HT concentrations, at which the P3HT chains are entangled and form P3HT aggregations which restrict the transfer of mobile excitons and charge carriers through the solar cell active layer. The observed deterioration in the EQE occurs although the optical absorption of the P3HT:PCBM active layer is improved at higher P3HT concentration.

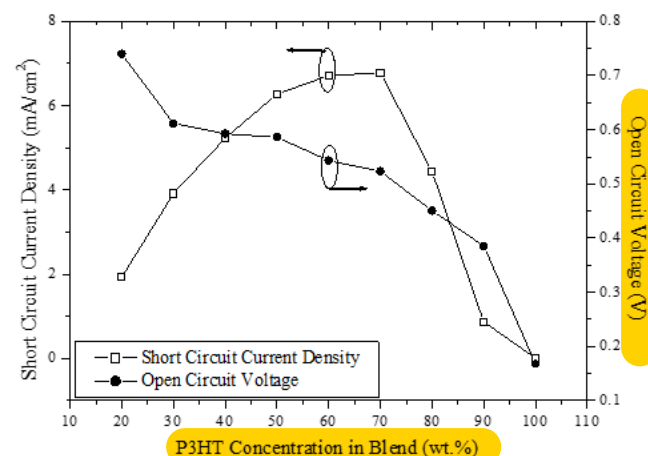


**Fig. 4.** EQE spectra of the P3HT:PCBM solar cell at different P3HT concentration.

### 3.3 Effect of P3HT concentration on the performance parameters of the solar cell

In the present work, we have measured J/V characteristics of the ITO/PEDOT:PSS/P3HT:PCBM/Al device as a function of P3HT concentration in the solar cell active layer. From the analysis of the J/V characteristics, we have obtained the photovoltaic performance parameters, i.e., open circuit voltage ( $V_{oc}$ ), short circuit current density ( $J_{sc}$ ), fill factor (FF), and power conversion efficiency (PCE), of the investigated devices. Figures 5 and 6 show the variation of these parameters with increasing P3HT concentration in the solar cell active layer. Figure 4 shows an increase in the  $J_{sc}$  with increasing P3HT concentration up to 70 wt.%, and after that the  $J_{sc}$  decreases with increasing P3HT concentration up to 100 wt.%. The  $V_{oc}$  of the P3HT:PCBM solar cell gradually decreases with increasing P3HT concentration. While, Fig.5 shows an increase in the FF and, consequently, PCE by increasing

P3HT concentration up to 40 and 50 wt.%, respectively. After that, the FF and PCE decrease by increasing P3HT concentration up to 100 wt.%.

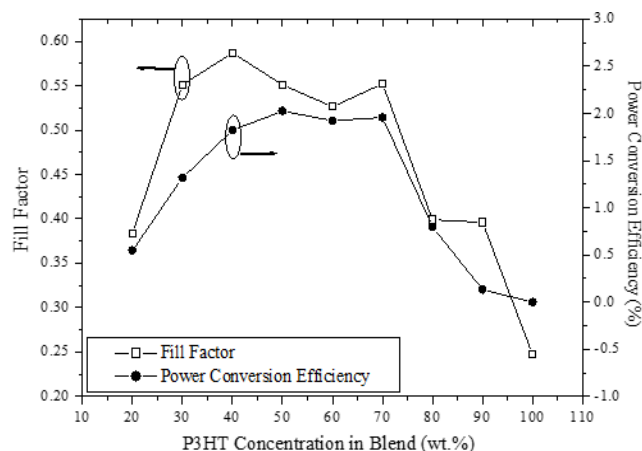


**Fig. 5.**  $J_{sc}$  and  $V_{oc}$  of the ITO/PEDOT:PSS/P3HT:PCBM/Al devices with varying P3HT concentration

It is well known that, the factors affecting the  $J_{sc}$  are the same of those affecting the EQE in the organic solar cells. This means that, the optical absorption (exciton generation), exciton dissociation at photoactive p-n heterojunction sites, and charge carrier transfer are the deriving factors affecting the increase in  $J_{sc}$  with increasing P3HT concentration, as discussed above for EQE. Therefore the subsequent decrease in the  $J_{sc}$  of P3HT:PCBM solar cell with further increase in P3HT concentration up to 100 wt.% is attributed to decrease in the photoactive p-n heterojunction sites and the deterioration in electron transfer at higher P3HT concentrations, at which the P3HT chains are entangled and form P3HT aggregations which restrict the transfer of mobile excitons and charge carriers through the solar cell active layer. For organic BHJ materials, the general perception is that the  $V_{oc}$  is determined by the energy difference between HOMO of the donor and LUMO of the acceptor [16]. Therefore, the decrease in the  $V_{oc}$ , observed in Fig. 5, may be attributed to the reduction in the energy difference between HOMO of the donor-polymer P3HT and LUMO of the acceptor PCBM. This reduction is a result of variation in energy gaps of both P3HT and PCBM in the solar cell active layer due to the variation in P3HT concentration, as discussed above.

The observed increase in the FF with increasing P3HT concentration up to 40 wt.%, as shown in Fig. 6, is attributed to the increase in interpenetrating networks for charge carrier transfer into electrode, where the increase in P3HT concentration tends to increase the conjugation length of the donor polymer indicated from the red shift observed in the optical absorption spectra. In the same time, the increase in the FF, as shown in Fig. 6, may be attributed to the increase in the amount of charge carriers generated by optical absorption, which is affected by the increase in P3HT concentration up to 40 wt.%. After that, the P3HT

aggregations formed at higher P3HT concentration (from 40 to 100 wt%) is the reason for increasing the series resistance in solar cell active layer, and therefore, the FF reduces in the solar cells, as shown in Fig. 6. The P3HT aggregations reduce the FF through restriction of the generated electrons to transfer into the electrode. Depending on the previously-measured device performance parameters, the PCE of the investigated solar cells can be shown in Fig. 6, which shows the best PCE at 50 wt.% of the P3HT. The best (optimized) P3HT:PCBM composition in these investigations is the composition of 50:50 wt.%, at which the  $J_{SC}$ ,  $V_{OC}$ , FF, and PCE are 6.3 mA/cm<sup>2</sup>, 0.59 V, 0.55, and 2.03 %, respectively. The values of device performance parameters in this work agree with several previous works [10,11,17].



**Fig. 6.** FF and PCE of the ITO/PEDOT:PSS/P3HT:PCBM/Al devices with varying P3HT concentration.

## 4 Conclusions

From the present investigations we may conclude that, the increase in P3HT concentration in the P3HT:PCBM solar cell active layer tends to increase the P3HT optical absorption, red shift the P3HT absorption peak, and increase both the P3HT and PCBM optical energy gaps. The observed red shift in the absorption peak of P3HT is an indication of improvement the conjugation length and ordered structure of the P3HT molecules in the solar cell active layer. From the presented results, we found a relation between energy gap and composition of the P3HT:PCBM combination, where the energy gaps of both P3HT and PCBM increase with increasing P3HT concentration in the solar cell active layer. We can summarize the results shown in the investigations and tell that, at the lower P3HT concentration (in the range of 20-50 wt.%), at which the energy gap of P3HT increases largely, the energy gap of PCBM stills stable. While at the higher P3HT concentration (in the range of 50-100 wt.%), at which the energy gap of P3HT stills stable, the energy gap of PCBM increases largely. The obtained variations in the energy gaps of both P3HT and PCBM may be attributed to the variation in the

degree of covalent interactions between P3HT and PCBM. The photocurrent of P3HT:PCBM solar cell increases gradually with increasing P3HT concentration up to 60 wt.%, and after that, it decreases gradually with increasing P3HT concentration up to 100 wt.%. The device performance parameters are investigated under the wide composition range of P3HT:PCBM solar cell active layer. The best (optimized) solar cell composition in these investigations is the 50:50 wt.% of the P3HT:PCBM binary at which the  $J_{SC}$ ,  $V_{OC}$ , FF, and PCE are 6.3 mA/cm<sup>2</sup>, 0.59 V, 0.55, and 2.03 %, respectively. The values of device performance parameters in this work agree with several previous works.

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