Bulgarian Chemical Communications, Volume 49, Special Issue J (pp. 75 – 81) 2017

Investigation of three important parameters on performance of organic solar cells based on P3HT:C_{60}

A. Azimy[1*], S.M.A. Hosseini[2], N. Ramezanian[3]

[1,2] Department of Chemistry, Shahid Bahonar University of Kerman, 76169 Kerman, Iran

[3] Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran

Submitted May 15, 2017; Revised August 21, 2017

In order to fabricate high performance polymer solar cells, donor:acceptor mixture must be prepared using a proper solvent. Since selection of the solvent is the key for obtaining good morphology of the films as well as the efficiency and stability of the photovoltaic devices, finding a suitable solvent could considerably enhance the Poly(3-hexylthiophene) (P3HT):C60 based cell performance in terms of short circuit current (JSC), fill factor (FF) and finally power conversion efficiency (PCE). The formation of C60 aggregates and donor material, i.e. Poly(3-hexylthiophene), crystallinity depend on the selection of proper solvent. In this paper, photovoltaic (PV) solar cells have been fabricated using tree solvents: chloroform (CHCl3), chlorobenzene (CB) and 1-Chloronaphthalene (Cl-Naph). The active layers were composed of poly(3-hexyl)thiophene (P3HT) as a donor and (C60) as an acceptor. P3HT:C60 films casted from 1-Chloronaphthalene solution absorb more red light than the films casted from other solution.. On the other hand the donor/acceptor composition ratio were Investigated and reported.

Keywords: solar cell, P3HT, annealing, organic photovoltaic, donor, solvent effect

1.INTRODUCTION

Organic photovoltaic cells have recently attracted considerable attention of their low cost and easy to process [1-4]. During the last few years, increased effort of many research groups has been devoted to the development of solar cells based on conjugated polymers. OPVs based on conjugated polymer/fullerene to form a donor/acceptor bulk heterojunction blend system have been reported recently [5-10].

C_{60} is an acceptor material for photovoltaic cells with favorable characteristics, such as solubility and absorption profiles. The major difference in the functionalities of donor and acceptor is that the acceptor molecules stabilize free electrons. C_{60} has a high electron affinity and absorb at wavelengths shorter than 400 nm [11].

. The difference between the HOMO / LUMO energy levels of the two materials creates an energy level offset at the heterojunction. A donor (D) material typically has low ionization energy, and an acceptor (A) material has high electron affinity. Good donor-acceptor candidates also have high charge-carrier mobility and conductance.

The evaporation rate of solvent is a straight forward factor to tune the crystallinity of P3HT. For instance, Bao et al. [12] and Joung et al. [13] found that the field effect mobility of pure P3HT varies significantly as a function of solvent. Equally, other research groups [14 -16] reported the relationship between the morphology of pure P3HT and the charge carrier mobility. Chang et al. [14] have also observed a clear correlation between field-effect mobility and degree of microcrystalline order by means of X-ray diffraction.

The effect of solvent on the performance of organic photovoltaic (OPV) solar cells based on P3HT:C_{60} blends has also been investigated by many groups. The studies on the blend of PPV (polyp-phenylene vinylene) and fullerene were generally conducted with a weight ratio of 1:4 [17–19], which corresponds to a high concentration of fullerene. Therefore, the segregation of fullerene in large domains is favorable. The size of clusters of C_{60} within thin film changes enormously with the choice of solvent [17,18,20].

The most suitable condition to establish efficient exaction dissociation in a bulk heterojunction is that the LUMO (D) > LUMO (A) and HOMO (D) > HOMO (A) and the difference between these levels respectively is higher than the binding energy of a photo-generated exciton.

Elementary steps in the process of photo induced charge separation for a donor (D) and an acceptor (A) : (1) The active layer of the cell absorbs photons, causing the generation of excitons (electron-hole pairs) within the cell, (2) Excitons diffuse to a heterojunction comprising a donor and acceptor, (3) A favorable energy offset between the organic layers separates the electron-hole pair into free charge

---

To whom all correspondence should be sent:
E-mail: ahmad.azimy@gmail.com

carriers, (4) Electrons are collected at the cathode, and holes are collected at the anode.

In this work, P3HT is used as electron donor, which has a significant absorption in the visible spectral range. Fullerene C_{60} is used as electron acceptor. Therefore, blending these materials is thought to be very promising as photoactive layer for photon-to-electric energy conversion. In addition the silver cathode and an electron blocking layer, Poly (3,4-ethylene dioxy thiophene): poly (styrenesulfonate), PEDOT:PSS, on top of the indium tin oxide ITO anode .

2.EXPERIMENTAL

C_{60} and P3HT were used as the acceptor and donor layer materials respectively. P3HT:C_{60} were prepared at a concentration of 50 mg/mL chloroform (CF), chlorobenzene (CB) and 1-Chloronaphthalene (Cl-Naph) solutions, stirred for 60 min at 50 °C and allowing them to cool before filtering through a 0.45 µm PTFE filter. To deposit the P3HT/C_{60} film a micro-pipette was used to drop 20 µL of solution onto a spinning substrate. PEDOT:PSS was used as a buffer layer between the anode and active layer. ITO (indium tin oxide) on glass (from Esfahan Inc. Iran) was used as the substrate, and silver was used as the cathode. Finished devices were stored in the glove box under nitrogen atmosphere in order to prevent degradation.

Before to device fabrication, ITO substrate was cleaned. Substrate was sonicated in a detergent solution for 5 min, and subsequently transferred to deionized water and acetone where they were sonicated for 5 min in each solution. After being sonicated, substrates were placed in boiling isopropanol for 5 min. Substrates were blow-dried using pure nitrogen, and placed in an O_2 plasma environment for 15 s to complete the cleaning process.

Bilayer devices were constructed in a stack formation, starting with the ITO-glass substrate. On the ITO substrate, PEDOT:PSS was spin coated at 5000 rpm for 60 s and baked for 10 min at 50 °C. This produced a film having a thickness of approximately 40 nm. For deposition of the P3HT:C_{60} layer, devices were transferred to the glove box, and the P3HT:C_{60} solution was spin coated at 1000 rpm for 90 s. The P3HT:C_{60} films were dried in vacuum. Ag was added as the top contact of the device (PVD) to create four individual testing pads. Evaporation of the cathode was performed through a shadow mask and typically consisted of 100 nm of silver, each with an active area of 0.15 cm^2. Devices were annealed at 110 °C on a hot plate for 60 min; some devices were tested before and after annealing. In total, 9 devices (The following devices) were fabricated and tested.

Table 1. Composition of devices were tested

Cell	Ratio of P3HT to C_{60}	Solvent type	Annealing temperature (°C)
1	1-1	Chloroform (CF)	50
2	1-1	chlorobenzene (CB)	50
3	1-1	1-Chloronaphthalene	50
4	1-0.5	Chloroform (CF)	50
5	1-0.5	chlorobenzene (CB)	50
6	1-0.5	1-Chloronaphthalene	50
7	1-0.5	Chloroform (CF)	110
8	1-0.5	chlorobenzene (CB)	110
9	1-0.5	1-Chloronaphthalene	110

The current density versus voltage characteristics were measured with J–V curve tracer (PG- State -30 from Autolab company) with solar simulator under AM 1.5 G (100 mW/cm^2) irradiation intensity. UV/visible spectrophotometer (Agilent 8453) was empolyed to study absorption spectra of the P3HT:C_{60} films.

3.RESULTS AND DISCUSSION

In our optimization of the P3HT:C_{60} active layer, three different parameters were varied: Selection of the solvent, Ratio of P3HT to C_{60}, and the annealing temperature.

For the measurement of the absorption spectra

P3HT:C_{60} layers (1:1 and 1:0.5 wt %) were spin coated from chloroform, chlorobenzene and 1-Chloronaphthalene solutions on ITO glasse. The absorption spectra of the nonannealed layers were measured, then these layers were heated at 110 °C for 60 min and measured again.

3.1. Selection of the solvent

Selection of the solvent is the key for obtaining good morphology of the films as well as the efficiency and stability of the photovoltaic devices. Several solvents such as chloroform (CF), chlorobenzene (CB) and 1-Chloronaphthalene (Cl-Naph) solutions were investigated to prepare thin films.

To prepare a P3HT/C_{60} solutions, P3HT powder was dissolved in the mentioned solvents to achieve a concentration of 50 mg/mL. Similarly, C_{60} was dissolved in this solvent at the corresponding concentration, followed by mixing P3HT and C_{60} solutions, stirring and heating at 50 ºC for ~12 hours. Afterwards, the P3HT:C_{60} blend solution was spin coated onto the cleaned ITO glass substrates [21].

Figure 1 shows the absorption spectra of P3HT:C_{60} composite films 1:1 wt % casted from chloroform, chlorobenzene and 1-chloronaphthalene solutions. The absorption maximum of the film casted from chloroform solution is observed at a wave length of 440 nm. This maximum is observed at 450 nm when the film is casted from chlorobenzene solution and 465 when the film is casted from Cl-Naph solution. This indicates that the degree of the P3HT chain ordering is higher in the case of using Cl-Naph.

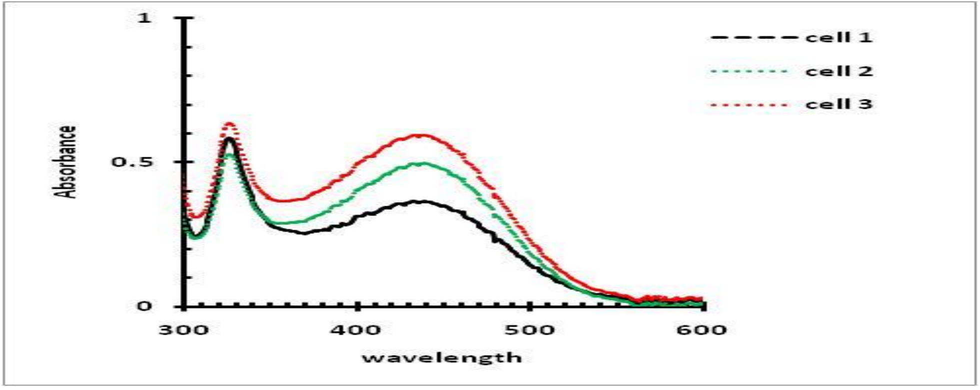


Fig. 1. Absorption spectra of P3HT: C_{60} composite films (1:1 wt %) casted from (CF), (CB) and (Cl-Naph) solutions

To prepare solar cell for investigation the effect of ratio of P3HT to C_{60}, solvent effect and the annealing temperature on active layer were done according to the method which have been described at experimental section.

The measurement method used to characterize the voltage-current curves was according to the method which has been described at experimental section.

Figure 2 illustrates the current-density vs. voltage (J-V) characteristics of the P3HT: C_{60} composite films (1:1 wt %) casted from chloroform (CF), chlorobenzene (CB) and 1-chloronaphthalene (Cl-Naph) solutions under AM 1000 light.

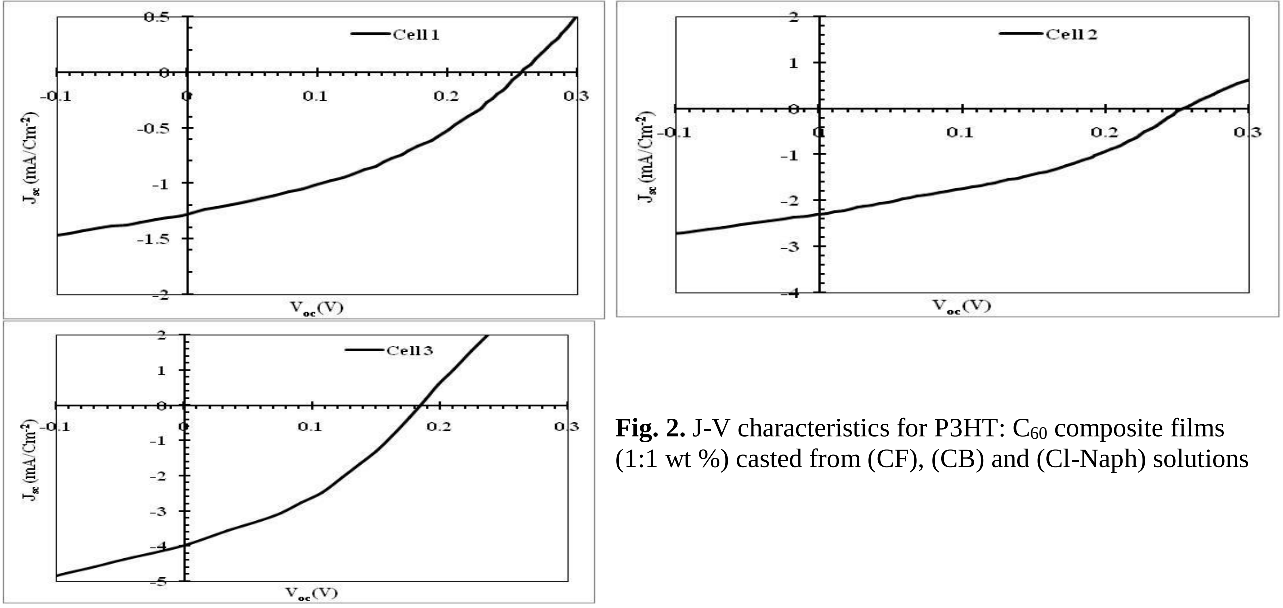


Fig. 2. J-V characteristics for P3HT: C_{60} composite films (1:1 wt %) casted from (CF), (CB) and (Cl-Naph) solutions

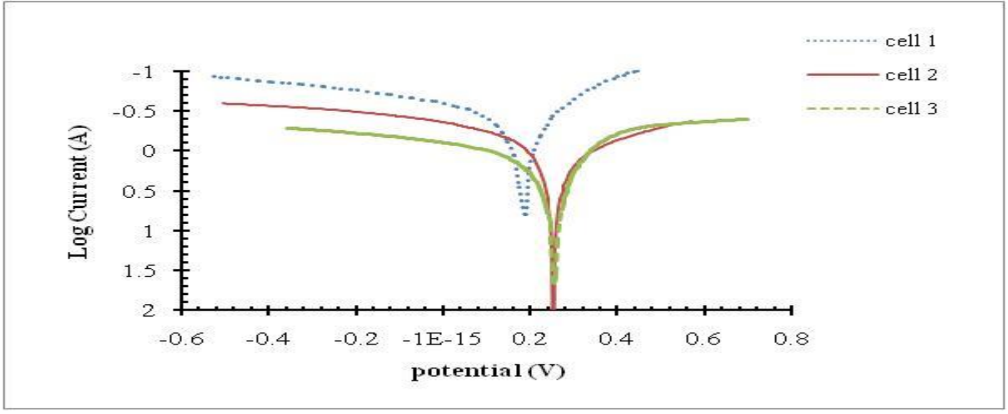
The photovoltaic characteristics, namely, Voc, Jsc, fill factor (FF), and PCE, for OPVs, are given in Table 2.

Table 2. The photovoltaic characteristics for OPVs

Cell	J_{SC} (mA /cm^2)	V_{OC} (V)	I*V	FF	PCE
1	1.3	0.260	3.38	0.04	0.12
2	2.3	0.26	0.59	0.37	0.22
3	4	0.19	0.76	0.35	0.27

It was found that short-circuit current density (JSC) and fill factor (FF) of a cell with a photo-active layer made using materials dissolved in a with Cl-Naph to be slightly higher than those of a cell made using the same materials dissolved in choloroform and chlorobenzene. Evaluating the absorption spectra, characterizes the voltage-current of photo active films made by different solvents, it is concluded that the higher JSC and FF were due to a larger interfacial area between the photo-active materials in the layer.

Figure 3 depicts a semi-log plot of the absolute value of current vs voltage for P3HT: C_{60} composite films (1:1 wt %) casted from chloroform (CF), chlorobenzene (CB) and 1-chloronaphthalene (Cl-Naph) solutions under AM 1000 light. The device exhibit improvement in current response under illumination. The V_{OC} is the point at which the absolute value of current reaches a minimum.



.

Fig. 3. Semi-log plot of the absolute value of current vs voltage for the P3HT:C_{60} blend ratio

3.2. The composition of donor/acceptor

The composition of donor/acceptor plays an important role to achieve good device performance. If the concentration of the acceptor is too high, the films will have kinks, overlapping chains, and the photo-induced charge transfer rate will be low, which result in low photon absorption [8]. On the other hand, if the concentration of the acceptor is low, the interface of the organic layer and the electrode will become smooth, and the exciton will not have enough space to diffuse, resulting in low exciton generation efficiency [8].

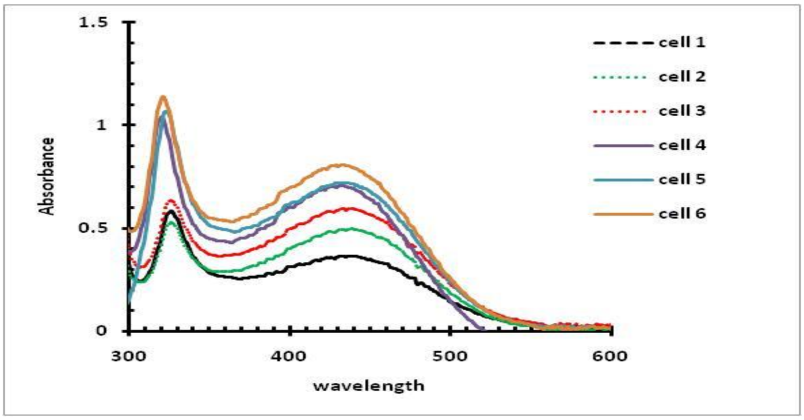
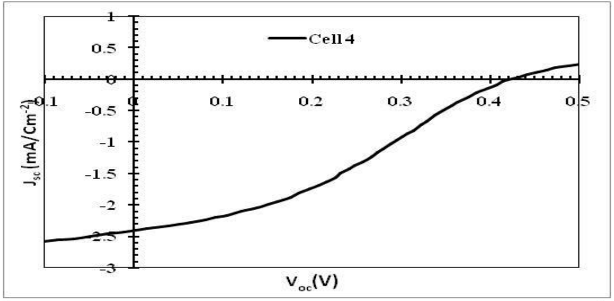
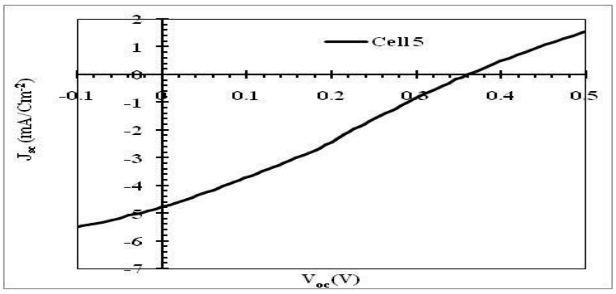


Fig. 4. Absorption spectra of P3HT:C_{60} composite films (1:1 and 1:0.5 wt %) casted from (CF), (CB) and (Cl-Naph) solutions.

Comparing the absorption spectra of P3HT:C60 films with different composition ratio 1:1 and 1:0.5 wt % casted from solvents, we found that the maximum absorption peak is red shifted only by 15 nm upon going from 1:1 to 1:0.5 wt % for Cl-Naph and blue shifted by 5 nm upon going for chloroform.

Figure 5 shows the current-density vs. voltage (J-V) characteristics of the P3HT: C_{60} composite films (1:0.5 wt %) casted from chloroform (CF), chlorobenzene (CB) and 1-Chloronaphthalene (Cl-Naph) solutions under AM 1000 light. It was found that an increase in η and Jsc and decrease in Voc are due to an increased interchain interaction among P3HT chains and the increase of the optical π-π* transition's. It can be seen that device having a P3HT:C_{60} blend ratio of 1:0.5 seems to be relatively better than a blend ratio of 1:1. The photovoltaic characteristics, namely, Voc, Jsc, fill factor (FF), and PCE, for OPVs, are presented in Table 3.





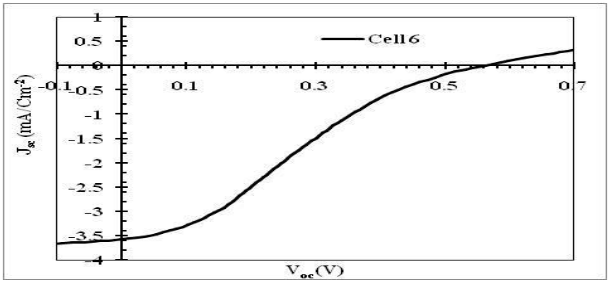


Fig. 5. J-V characteristics for two OPVs having their active layer deposited at different of the P3HT:C_{60} blend ratio of 1:1 and 1:0.5.

Table 3. The photovoltaic characteristics for OPVs

Cell	J_{SC} (mA/cm^2)	V_{OC} (V)	I*V	FF	PCE
4	2.4	0.43	1.03	0.34	0.35
5	4.8	0.38	1.82	0.27	0.49
	3.5	0.56	1.96	0.26	0.50

3.3. Thermal annealing

Thermal annealing was found to be a possible approach to enhance the photon absorbance, improve the short circuit current, fill factor, and therefore the efficiency of the device [9]. To achieve a high efficiency, the optimal annealing conditions of P3HT/C_{60} film must be determined. In this study, the research carried out to address these aspects in order to discover optimal parameters for sample preparation as well as optical constants of thin films for multilayer design and performance improvement

Figure 6 shows the absorption spectra of P3HT:C_{60} composite films (1:0.5 wt %) casted from (CF), (CB) and (Cl-Naph) solutions before and after thermal annealing at 110 °C.

After thermal annealing of the two layers the C_{60} peak as well as the whole spectrum of the film casted from 1-Chloronaphthalene is redshifted by 15 nm, while the absorption spectra of the film casted from chloroform changes significantly. The maximum absorption peak is redshifted by 50 nm,. The changes in the absorption spectrum of the film casted from chloroform solution upon annealing are due to the molecular diffusion of C_{60} out of the polymer matrix, which increases the degree of the P3HT chain ordering [9], which indicates the same type of increased structural order caused by thermal annealing and by changing of the solvent from chloroform to chlorobenzene.

Figure 7 shows the J-V characteristics of annealing temperatures plot of the absolute value of current vs voltage for the P3HT:C_{60} blend ratio of 1:0.5 under AM 1000 light. The experiments data reported in Table 4 and explored annealing 1:0.5 P3HT:C_{60} blend at a temperature at 110 °C (for 60 minutes after deposition of the device cathode). Here, it can be seen that an optimum anneal temperature for this blend appears to be ~110°C (for 60 minutes).

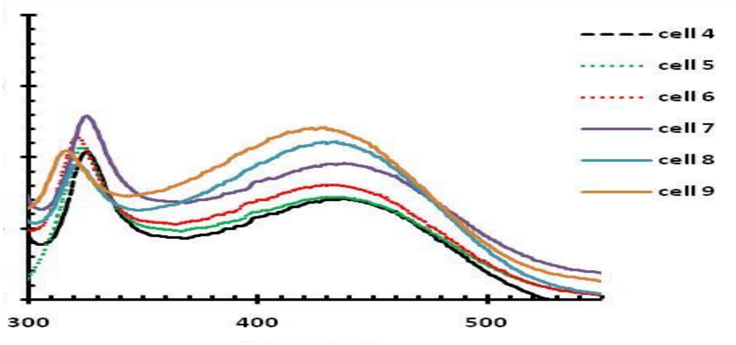


Fig. 6. Absorption spectra of P3HT:C_{60}.

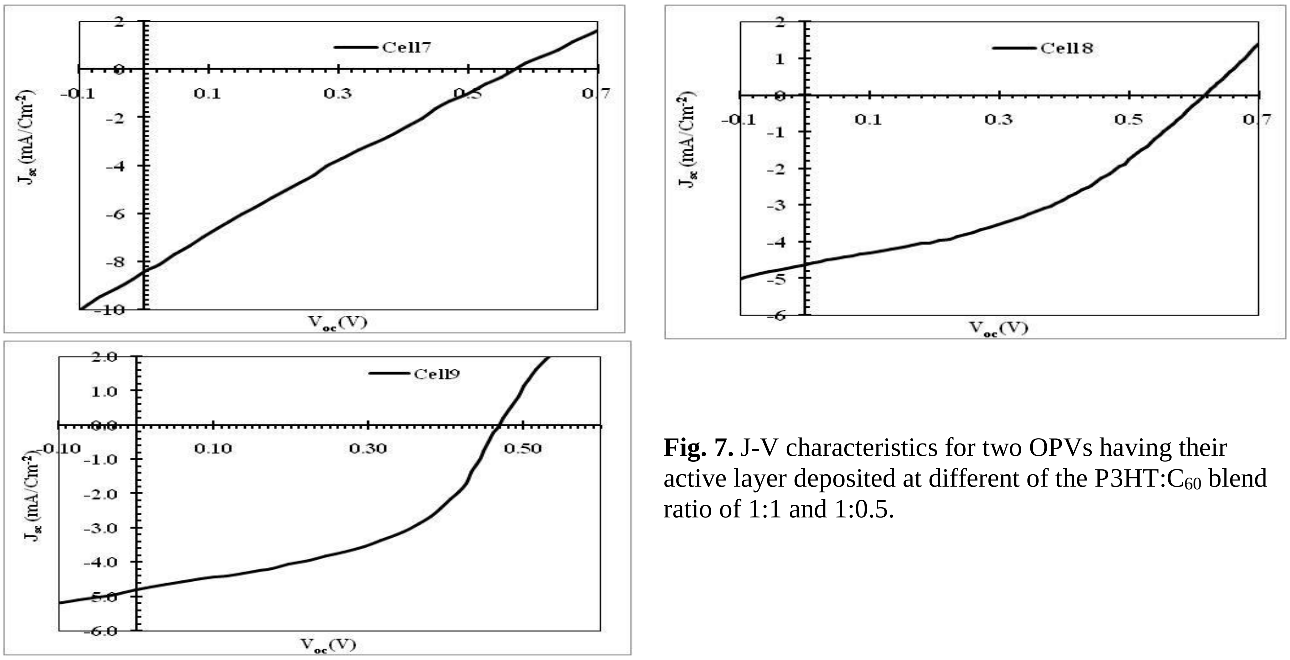


Fig. 7. J-V characteristics for two OPVs having their active layer deposited at different of the P3HT:C_{60} blend ratio of 1:1 and 1:0.5.

Table 4. The photovoltaic characteristics, namely for OPVs.

Cell	J_{SC} (mA/cm^2)	V_{OC} (V)	I*V	FF	PCE
7	8.2	0.58	4.76	0.24	1.15
8	4.6	0.62	2.85	0.40	1.14
9	4.8	0.47	2.26	0.48	1.08

Figure 8 shows a semi-log plot of the absolute value of current vs voltage for the P3HT:C_{60} blend with range of annealing temperatures under AM 1000 light, such as previous the semi-log plot re-emphasizes the findings from Table 4 and J-V plot.

The majority of device studied on P3HT:C_{60} blends utilize annealing to increase device efficiency. This is believed to be due to changes in both the morphology of the active layer (where by the P3HT and C_{60} self-organize into nanoscale domains) as well as because of the better intermolecular alignment of the P3HT giving higher hole mobilities [21].

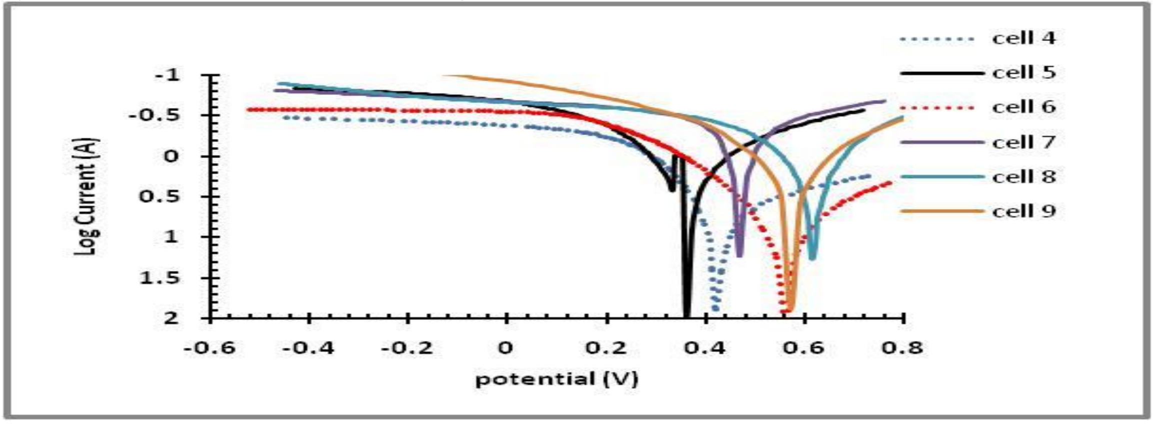


Fig. 8. Semi-log plot of the absolute value of current vs voltage for the composite films (1:0.5 wt %) casted from (CF), (CB) and (Cl-Naph) solutions.before and after thermal annealing at 110 °C.

4. CONCLUSIONS

In this paper, important factors for improving the performance of donor acceptor bulk heterojunction photovoltaic cells have been investigated, which include identification of optimal solvent to dissolve organic materials and composition of the blend and optimization of thermal annealing parameters. Absorption spectra of the P3HT/C_{60} film annealed at different temperatures reveals that the absorbance of the film increases as the annealing temperature increases. Thus, the best annealing condition for the P3HT/C_{60} films are thermal treatment at 110°C for 60 minutes. The absorption coefficients of the P3HT/C_{60} films increase as the annealing temperature increases. The information on the optical constants of the photovoltaic films is very important for multilayer design and device optimization.

Organic photovoltaic solar cells have been fabricated from various solvents with different boiling points and we conclude that a notable correlation in performance with boiling point of solvents was observed. The slower evaporation of solvent leads to higher efficiency.

On the other hand We conclude that molecular diffusion of C_{60} in the P3HT matrix is higher in the films casted from chloroform in comparison to films casted from chlorobenzene and 1-chloronaphthalene solutions, This effect depends on the amount of C_{60} in the composite.

In summary, we have found that the processing conditions (solvent, P3HT:C_{60} composition, thermal annealingd) strongly effect the optical properties of the P3HT:C_{60} films. The improved absorption of the composite films, the enhancement of the degree of polymer chain ordering lead to an improved performance of polymer solar cells based on P3HT.

REFERENCES

1. G. Li, V. Shrotriya, Y. Yao, Y. Yang, *J. Appl. Phys.*, **89**, 04 (2005).
2. R. Schueppel, R. Timmreck, N. Allinger, T. Mueller, M. Furno, C. Uhrich, K. Leo, M. Riede, *J. Appl. Phys*., **107**, 503 (2010).
3. R. Aïch, B. Ratier, F. Tranvan, F. Goubard, C. Chevrot, *Thin Solid Films*, **516,** 7171 (2008).
4. R. Franke, B. Maennig, A. Petrich, M. Pfeiffer, *Solar Energy Materials and Solar Cells*, **92,** 732 (2008).
5. J. Peet, J.Y. Kim, N.E. Coates, W.L. Ma, D. Moses, A.J. Heeger, G.C. Bazan, *Nat. Mater.*, **6**, 497(2007).
6. F. Yang, M. Shtein, S.R. Forrest, *Nat. Mater.*, **4**, 37 (2005).
7. J.Y. Kim, S.H. Kim, H. Lee, K. Lee, W. Ma, X. Gong, A. J. Heeger, *Adv. Mater.*, **18**, 572 (2006).
8. G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, *Science*, **27**, 1789 (1995).
9. J.Y. Kim, K. Lee, N.E. Coats, D. Moses, T.Q Nguyen, M. Dante, A.J. Heeger, *Science*, **31**, 222 (2007).
10. R. Gómez, J. L. Segura, N. Martin, *Org. Lett.*, **7**, 717 (2005).
11. W. Zhang, Y. Xu, H. Wang, C. Xu, S. Yang, *Solar Energy Materials and Solar Cells*, **95**, 2880 (2011).
12. Z. Bao, A. Dodabalapur, A.J. Lovinger, *Appl. Phys. Lett.*, **69**, 4108 (1996).
13. M.J. Joung, C.A. Kim, S.Y. Kang, K.-H. Baek, G.H. Kim, S.D. Ahn, I.K. You, J.H. Ahn, K.S. Suh, *Synth. Met.*, **149**, 73 (2005).
14. J.F. Chang, B. Sun, D.W. Breiby, M.M. Nielsen, T.I. Solling, M. Giles, I. McCulloch, H. Sirringhaus *Chem. Mater*. **16**, 4772 (2004).
15. H. Yang, T.J. Shin, L. Yang, K. Cho, C.Y. Ryu, Z. Bao, *Adv. Funct. Mater*., **15**, 671 (2005).
16. K. Sethuraman, S. Ochiai, K. Kojima, T. Mizutani, *Appl. Phys. Lett.*, **92**, 302 (2008).
17. X. Yang, J.K.J.v. Duren, R.A.J. Janssen, M.A.J. Michels, J. Loos, *Macromolecules*, **37**, 2151 (2004).
18. H. Hoppe, M. Niggemann, C. Winder, J. Kraut, R. Hiesgen, A. Hinsch, D. Meissner, N.S. Sariciftci, *Adv. Funct. Mater*., **14**, 1005 (2004).
19. J.K.J. van Duren, X. Yang, J. Loos, C.W.T. Bulle-Lieuwma, A.B. Sieval, J.C. Hummelen, R.A.J. Janssen, *Adv. Funct. Mater*., **14**, 425 (2004).
20. S.E. Shaheen, C.J. Brabec, N.S. Sariciftci, F. Padinger, T. Fromherz, J.C. Hummelen, *Appl. Phys. Lett*., **78**, 841 (2001).
21. G. Li, V. Shrotriya, Y. Yao, J. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, *Nat. Mater*., **4**, 864 (2005).