Solvent Vapor-Induced Self Assembly and its Influence on Optoelectronic Conversion of Poly(3-hexylthiophene): Methanofullerene Bulk Heterojunction Photovoltaic Cells

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ABSTRACT: Nanoscale-phase separation of electron donor/acceptor blends is crucial for efficient charge generation and collection in polymer bulk heterojunction photovoltaic cells. We investigated solvent vapor annealing effect of poly(3-hexylthiophene) (P3HT)/methanofullerene (PCBM) blend on its morphology and optoelectronic properties. The organic solvents of choice for the treatment have a major effect on the morphology of P3HT/PCBM blend and the device performance. Ultraviolet-visible absorption spectroscopy shows that specific solvent vapor annealing can induce P3HT self-assembling to form well-ordered structure; and hence, the absorption in the red region and the hole transport are enhanced. The solvent that has a poor solubility to PCBM would cause large PCBM clusters and result in a rough blend film. By combining an appropriate solvent vapor treatment and post-thermal annealing of the devices, the power conversion efficiency is enhanced. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1799–1804, 2009

Key words: conjugated polymer; fullerenes; phase separation; photovoltaics; charge transport

INTRODUCTION

Polymer photovoltaic (PV) cells have attracted considerable attention as a potential alternative to silicon-based PV technology for low-cost solar energy conversion. The potential advantages of polymer PV cells derive from their large-area manufacture capability, improved compatibility with low-cost flexible substrates, and the high degree of control over the optoelectronic properties of the conjugated polymers.[1,2] The donor/acceptor bulk heterojunction structure solves the contradiction between optical absorption and the diffusion length of photogenerated excitons in polymers because the typical optical absorption distance is an order of magnitude greater than the typical exciton diffusion length of 10–20 nm in conjugated polymers.[3,4] Regioregular poly(3-hexylthiophene) (P3HT) and 6,6′-phenyl C61-butyric acid methyl ester (PCBM) blend is one of the most promising pairs for realizing high power conversion efficiency (PCE) because P3HT possesses some unique properties over other polymers including its high self-organization capability, high hole mobility, and extended absorption in the red region. In case of the polymer PV cells based on P3HT/PCBM blend, the device performance is correlated to the nanoscale morphology of P3HT/PCBM blend, which strongly depends on the processing conditions including the donor-acceptor composition, the organic solvent used for spin coating, and the postproduction annealing. There have been many studies that investigate the effects of processing approaches of the blended films on the device performance.[5–9] Post-thermal annealing is found to be an effective approach for enhancing the power conversion efficiency. Padinger et al.[5] reported a power conversion efficiency of 3.5% in P3HT/PCBM blend system by annealing the cell simultaneously with an applied external potential higher than the open-circuit voltage. The burning of shunts and increasing of charge carrier mobility account for the enhancement of the device performance. Ma et al.[10] demonstrated a P3HT/PCBM blend-based photovoltaic cell with PCE approaching 5% via post annealing at 150°C, which is attributed to modified nanoscale morphology, increased crystallization of P3HT, and improved transport of charges. The self-organization of P3HT occurs not only under thermal annealing
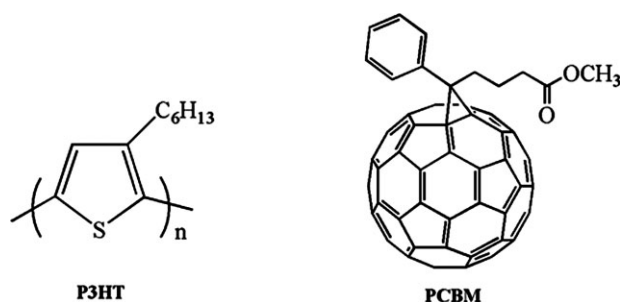
Figure 1 The chemical structures of P3HT and PCBM.

but also in proper solvent ambience. Li et al.[11] reported efficient photovoltaic cells based on P3HT/PCBM blend by controlling the growth rate of the active layer from solution to solid state. Our group also realized enhanced self-organization of P3HT in P3HT/PCBM blend films via 1,2-dichlorobenzene vapor treatment.[12] The questions are what kind of organic solvents is suitable for solvent vapor annealing of P3HT/PCBM blend and does it correlate to solubility of P3HT and PCBM. In this article, we investigate in detail how different organic solvents used for solvent vapor treatment influence the morphology of P3HT/PCBM blend and the optoelectronic characteristics.

EXPERIMENTAL

Preparation of films and PV cells

The indium tin oxide (ITO)-coated substrate used in this study has a sheet resistance of 10 Ω per square and is cleaned by ultrasonic treatment in detergent and deionized water, and then dried at 110°C for 40 min. The ITO substrate is spin coated with a 30-nm-thick poly(ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT:PSS, Baytron P4083) layer and baked at 120°C for 30 min. The 150-nm-thick P3HT/PCBM blend film is deposit onto the PEDOT: PSS layer by spin coating a chlorobenzene (CB) solution that contains P3HT and PCBM with a ratio of 10 : 8. Figure 1 shows the chemical structure of P3HT and PCBM. P3HT is synthesized in our lab with a weight-average molecular weight (M_w) of 3.86×10^4, a polydispersity of 1.59, and a regioregularity higher than 97%. PCBM with purity of 99% is purchased from Solenne Co. and used as received. The samples were transferred into a jar filled with organic solvent and stayed for different times. Various organic solvents including CB, 1, 2-dichlorobenzene (DCB), chloroform (CF), and toluene are used in this study. Finally, the samples were transferred into an evaporator, and 100-nm-thick aluminum (Al) cathodes were thermally deposited to produce an active area of 0.12 cm^2 for each cell. Post-thermal annealing was carried out at 150°C for 1 min on a

hot plate inside a nitrogen-filled glove box (<0.1 ppm of O_2 and H_2O), and the devices were encapsulated for measurement.

Measurements

Current density-voltage (J-V) characteristics of the devices under white light illumination were measured using a computer-controlled Keithley 236 source meter. The optical absorption of the P3HT/PCBM blend films were measured using a Perkin–Elmer 35UV-Visible spectrophotometer on quartz substrates. The atomic force microscopy (AFM) measurements were performed on SPA300HV with an SPI3800 controller, Seiko Instruments Industry, Co.

RESULTS AND DISCUSSION

It is well known that CB is commonly used to prepare the blend films of P3HT and PCBM because it has good solubility for both of them and can produce a smooth film. However, because of the fast evaporation of CB in P3HT/PCBM blend film, the orientation of P3HT supermolecules is restrained by the short timescale and does not form an ordered P3HT structure and phase-separated interpenetrating networks for charge collection. First, the P3HT/PCBM blend film is treated with CB vapor for increasing its orientation, and its time dependence is studied. Figure 2 shows The J-V curves of the PV cells with the P3HT/PCBM blend films as-produced and CB vapor-treated for different times under white light illumination with an intensity of 100 mW/cm^2. It can be seen that the as-produced PV cell demonstrates an open-circuit voltage (V_{oc}) of 0.55 V, a short-circuit current (J_{SC}) of 2.74 mA/cm^2. The overall PCE of this device is 0.71%. When the active layer of P3HT/PCBM blend is subjected to
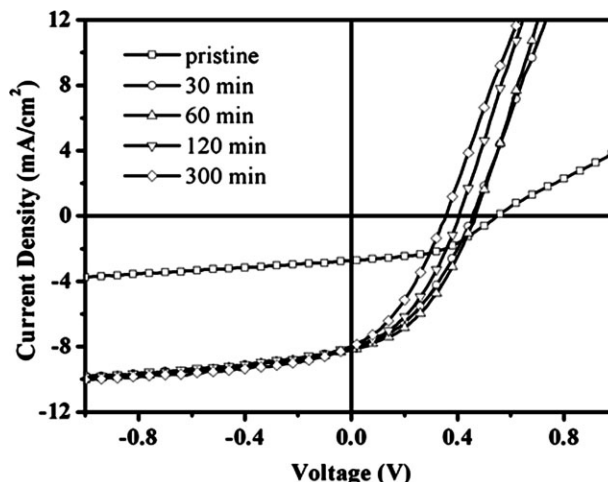

Figure 2 The illuminated J-V curves of the PV cells solvent vapor-annealed with CB for various times.
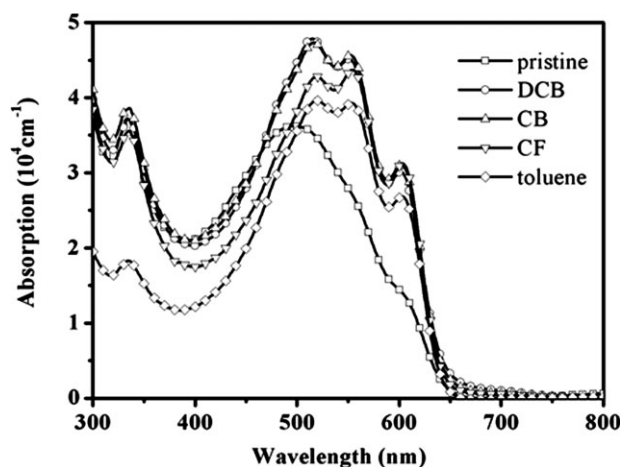
Figure 3 UV-Vis absorption spectra of P3HT/PCBM blend films solvent vapor-annealed with various organic solvents for 30 min.

Figure 4 The illuminated J-V curves of the PV cells solvent-annealed with various organic solvents.

the CB vapor treatment, the J_{sc} of the resulted PV cells increases over 8 mA/cm², almost threefold of the as-produced cell. A PCE over 1.40% is achieved for the PV cells with CB vapor treatment for 30 and 60 min. The J_{sc} of the PV cells change little while increasing the time of solvent vapor treatment. However, the V_{oc} and filling factor (FF) decreased with increasing the time of treatment, resulting in a reduced PCE. It indicates that a time of 30 min is enough for realizing the self assembly of P3HT in the solvent vapor ambience. Hence, the P3HT/PCBM blend films are treated with various organic solvents for 30 min in the following study.

To gain a better understanding of how the solvent vapor affecting the P3HT/PCBM blend morphology and optoelectronic properties, we select four different organic solvents to treat the active films prepared from CB including CB, DCB, CF, and toluene. Figure 3 shows the UV-Vis absorption spectra of P3HT/PCBM (1 : 0.8) films prepared from CB and treated with four different organic solvents for 30 min, and the absorption of the pristine P3HT/PCBM blend film is also plotted for comparison studies. For the untreated P3HT/PCBM blend film, the P3HT absorption peak is at 500 nm with a shoulder at 600 nm and the absorption at 340 nm is attributed to PCBM. Compared to the pristine P3HT/PCBM blend film, the absorption peak of the solvent vapor treated P3HT/PCBM films shifts red and becomes much stronger in the red region. The presence of the three vibronic absorption shoulders attribute to an enhanced conjugation length and the more ordered structure of P3HT. As the solvent molecules can penetrate into the film and increase the space between polymer chains, the chains become mobile and self-organization can occur to form ordering. Among the four organic solvents used, CB and DCB are the best candidates for realizing P3HT
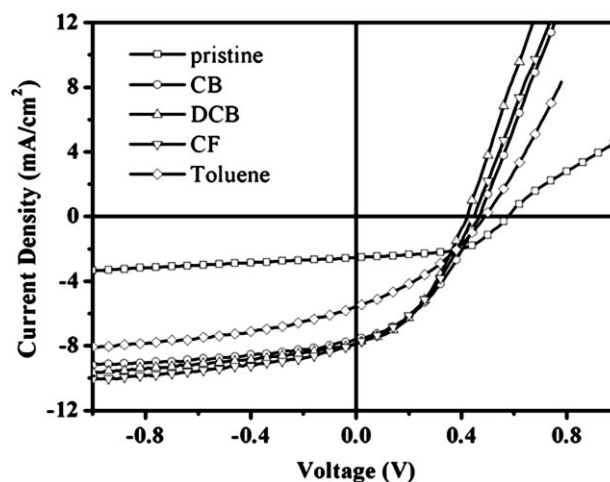
self-organization because of their good solubility in P3HT and PCBM. The self-organization of P3HT is not well realized with toluene treatment. The absorption of PCBM at 334 nm changes little with CB, DCB, and CF solvent treatment. However, the PCBM absorption deceases while treated with toluene, which may be correlated to the P3HT/PCBM morphology and will be discussed later.

Figure 4 shows the illuminated J-V curves under 100 mW/cm² white-light illumination for the PV cells with various organic solvents treatment. The parameters for these PV cells are summarized in Table I. It can be seen that the J_{SC} of the PV cells with CB, DCB, and CF vapor treatment increases to 7.60–7.85 mA/cm², threefold of the as-produced PV cells. The J_{SC} of the PV cell with toluene vapor treatment is enhanced to 5.57 mA/cm², twofold of the as-produced PV cell. The improvement is attributed to the self-organization of P3HT induced by solvent vapor treatment that enhances the optical absorption and the hole transport. The J_{SC} of the PV cells with CB, DCB, and CF is larger than that of toluene-treated device due to more efficient self-organization of P3HT as shown in Figure 3. The PCE of the PV cells with CB, DCB, CF, and toluene treatment are 1.39, 1.35, 1.34, and 0.95%, respectively, higher than 0.80%

TABLE I
Summary of PV Cells Performance, Solvent Vapor-Annealed with Various Organic Solvents under White Light Illumination with an Intensity of 100 mW/cm²

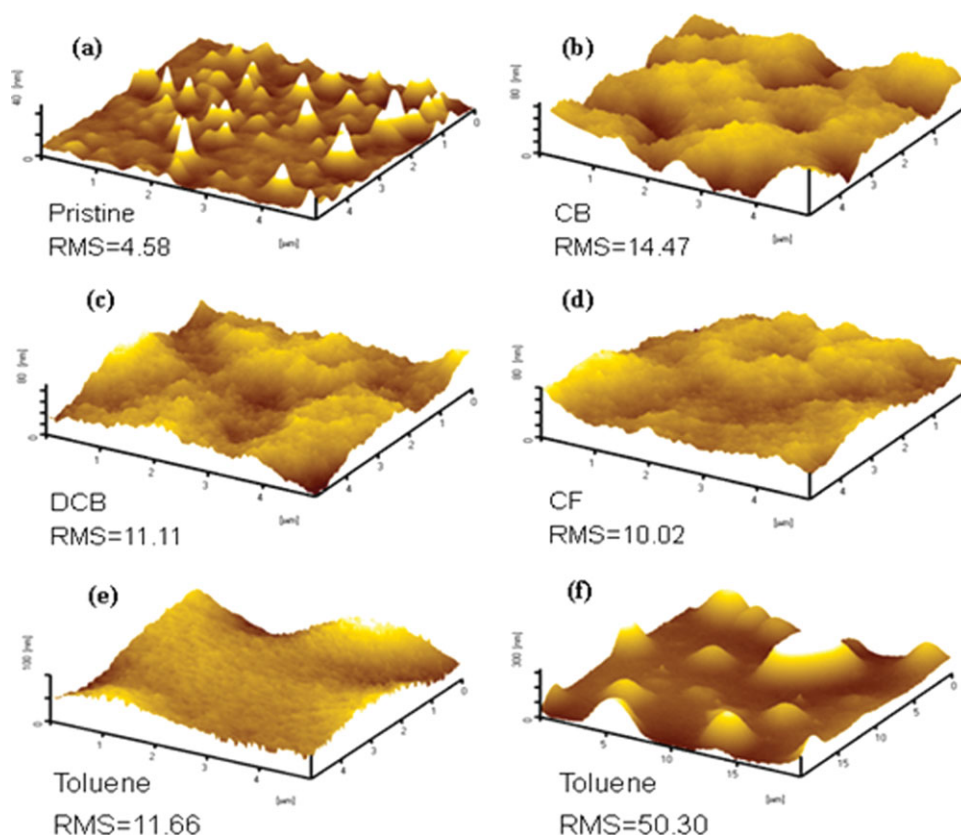| Solvent	V_{OC} (V)	J_{SC} (mA/cm²)	PCE (%)	FF
Pristine	0.58	2.54	0.80	0.55
CB	0.47	7.60	1.39	0.39
DCB	0.42	7.85	1.35	0.41
CF	0.45	7.86	1.34	0.38
Toluene	0.49	5.57	0.95	0.35

Figure 5 AFM height images of the P3HT/PCBM films solvent-annealed with various organic solvents for 30 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.].

of the as-produced device. FF decreases for the PV cells with organic solvent treatment. This may be due to the formation of defects or pinholes during solvent treatment, which results in a low shunt resistance.

The morphology of P3HT/PCBM blend films with organic solvents treatment are investigated, and the AFM height images of these P3HT/PCBM films are shown in Figure 5. For the as-produced film, a surface with r.m.s roughness of 4.58 nm is observed. The solvent vapor-treated P3HT/PCBM films are much rougher than the as-produced film. The CB-, DCB-, and CF-treated films show r.m.s roughness of 14.47, 11.11, and 10.02 nm at the 5 um ×5 um scan sizes, respectively. The roughness is considered to be a signal of polymer self-organization and phase separation.[11] The increase of the P3HT/PCBM film roughness is because the P3HT chains self-organize into ordered structure after organic solvent vapor treatment. However, the P3HT/PCBM blend film treated with toluene is quite rough as shown in Figure 5(f) at 20 um ×20 um scan sizes, and a roughness of 50.30 nm is calculated. As toluene has a poor solubility to PCBM,[13] the solvent molecules can not penetrate into the PCBM phase during the treatment. On the contrary, the mobile P3HT chains may push them to form an extremely large PCBM clusters dur-

ing toluene vapor treatment. This large scale phase separation of P3HT and PCBM can explain the decreased optical absorption of PCBM in Figure 3. This is because a portion of the P3HT/PCBM blend film is free of PCBM and transparent at 340 nm. The large scale phase separation also results in low power conversion efficiency.

Although the organic solvent vapor treatment can effectively induce P3HT chains self-organizing into the ordered structure resulting in the enhanced optical absorption in the red region and increased hole mobility, the low V_{oc} and FF still limit the PCE enhancement of the PV cells. Post-thermal annealing of the PV cells is carried out to further improve the device performance. Figure 6 shows the illuminated J-V curves under 100 mW/cm² white-light illumination for the PV cells with various organic solvents treatment and post-thermal annealing at 150°C for 1 min. The parameters for these PV cells are summarized in Table II. It shows that post-thermal annealing at a high temperature causes a great improvement of the device performance. The control device with post-thermal annealing has a V_{oc} of 0.63 V, a J_{sc} of 8.88 mA/cm², and a calculated FF of 0.61. The overall efficiency for this solar cell is therefore 3.43%. The J_{sc} of the CB and DCB vapor-treated PV cells with post annealing is much larger than
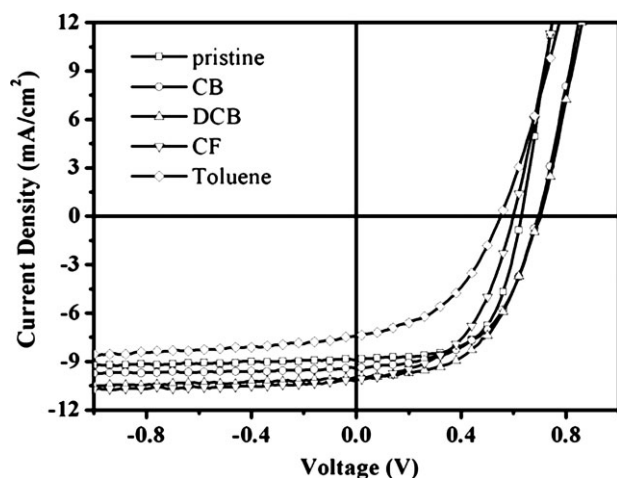
Figure 6 The *J-V* curves of the PV cells solvent vapor-annealed with various organic solvents and post annealed at 150°C for 1 min under white light illumination with an intensity of 100 mW/cm^2.

8.88 mA/cm^2 of the merely annealed device. This is attributed to the much more ordered structure of P3HT induced by proper solvent vapor treatment over the merely annealed device. Post-thermal annealing of the solvent vapor-treated devices favors activating PCBM molecules to diffuse and aggregate for better electron transport.[12] The increase of FF and V_{oc} of the solvent treated PV cells may attribute to the improved electron transport and burning of shunts after post-thermal annealing. Therefore by a combination of CB or DCB solvent vapor treatment and thermal annealing, P3HT and PCBM can self-organize into bicontinuous interpenetrating networks for enhanced optical absorption and efficient charge separation and transport resulting in a higher PCE.

To further testify our statement that thermal annealing favors activating PCBM molecules to diffuse and aggregate for better electron transport and solvent vapor treatment improves effectively hole transport, the hole-only devices with a structure of ITO/PEDOT(30 nm)/P3HT/PCBM(150 nm)/MoO$_3$ (20 nm)/Al (100 nm) and the electron-only device with a structure of Al(60 nm)/ P3HT/PCBM (150 nm)/LiF(1 nm)/Al (100 nm) are fabricated with

different treatments to investigate the influence of solvent treatment and thermal annealing on hole and electron transport. Here, CB is used as a solvent for vapor treatment. The measured dark *V-J* curves of the hole-only and electron-only devices are shown in Figure 7. The applied voltages are corrected for the built-in voltage (V_{BI}). As can be seen in Figure 7(a), although both thermal annealing and CB vapor treatment can improve the hole transport, the CB vapor treated device shows larger hole current than the thermally annealed device, indicating that CB vapor treatment is more effective than thermal annealing for inducing P3HT to self-ordering and enhance hole transport. It can be seen from Figure 7(b) that CB vapor treatment did not improve obviously the electron transport. However, the electron transport is drastically enhanced by thermal annealing the device, indicating that thermal annealing can effectively activate PCBM molecules to diffuse and aggregate into clusters for better electron transport. These results strongly support our above statement.
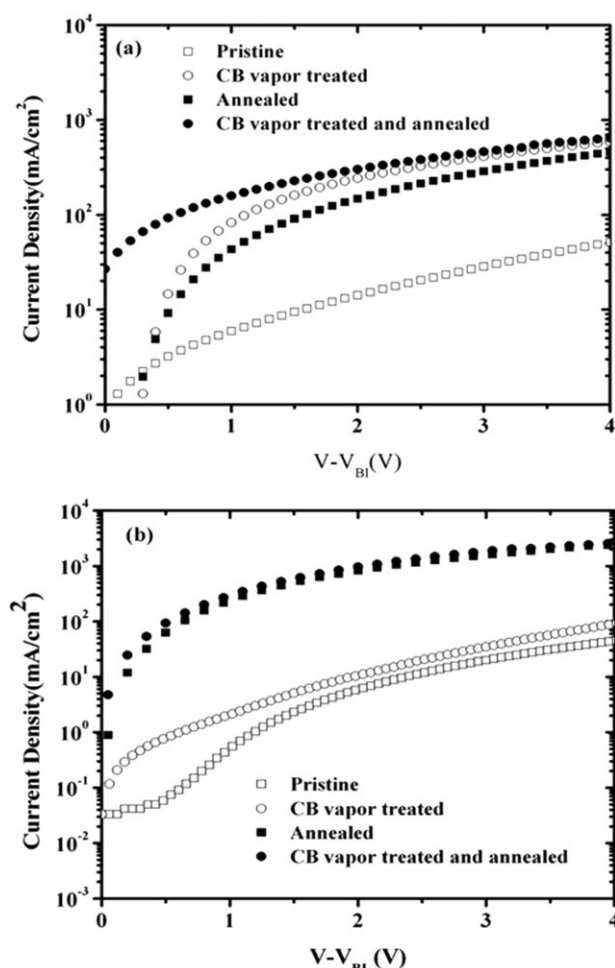
TABLE II
Summary of PV Cells Performance, Solvent Vapor-Annealed with Various Organic Solvents and Post Annealed at 150°C for 1 min under White Light Illumination with an Intensity of 100 mW/cm^2

Solvent	V_{OC} (V)	J_{SC} (mA/cm^2)	PCE (%)	FF
Pristine	0.63	8.88	3.43	0.61
CB	0.70	9.39	3.50	0.53
DCB	0.70	10.01	3.70	0.53
CF	0.60	10.12	3.01	0.50
Toluene	0.55	7.39	1.82	0.45

Figure 7 The *J-V* curves of the hole-only devices (a) and the electron-only devices (b) fabricated with different treatments.

Although a high J_{sc} of 10.12 mA/cm^2 is achieved in CF-treated PV cell, its PCE is merely 3.01% limited by a low V_{oc} of 0.60 V and a FF of 0.50. This may be due to a low shunt resistance in the device caused by pin holes in the film or the special orientation of alkyl side groups at the P3HT/PCBM/Al interface resulting from nonaromatic CF solvent.[14] As for the toluene-treated PV cells, its PCE is only about 1.82% even after post-thermal annealing. This may be attributed to the large scale phase separation of P3HT/PCBM blend due to a poor solubility of toluene to PCBM.

CONCLUSIONS

For the polymer bulk heterojunction PV cells, a nanoscale phase separation of electron donor and acceptor is necessary for efficient charge separation and collection. In case of P3HT/PCBM blend PV cell, well-ordered P3HT not only enhances the optical absorption but also increases the hole transport. Our studies indicate that the proper solvent vapor treatment is a more effective approach than thermal annealing for realizing the self-organization of P3HT and the phase separation of P3HT/PCBM blend. The solvent used for vapor treatment should have good solubility to both P3HT and PCBM. Post-thermal annealing is indispensable to activate PCBM molecules forming aggregates for better electron transport. By combining solvent vapor treatment and post-thermal annealing, high PCE may be achieved.

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