Stabilization of poly(3-hexylthiophene)/PCBM morphology by hydroxyl group end-functionalized P3HT and its application to polymer solar cells

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ABSTRACT

A new concept to stabilize the morphology of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) blend through H-bond formation by using a hydroxyl group end-functionalized P3HT (HOC-P3HT-COH) as a compatibilizer is presented. Domain size of the PCBM crystals in the annealed P3HT/PCBM film is diminished with addition of HOC-P3HT-COH. Surface roughness of the P3HT/PCBM film also becomes smoother with addition of HOC-P3HT-COH. Thermal stability of solar cell device is improved significantly through the H-bond formation between HOC-P3HT-COH and PCBM. A high performance and thermal stable polymer solar cell with 4.06% power conversion efficiency under AM1.5G irradiation is fabricated with 5% HOC-P3HT-COH in P3HT/PCBM layer.

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1. Introduction

P3HT and PCBM have been widely used as active layer materials for polymer solar cells since the introduction of bulk heterojunction (BHJ) [1–6] concept in 1995 [1]. Larger interfacial area in the BHJ device is created than that of planar heterojunction (PHJ) device and higher short-circuit current (I_{sc}) is obtained [7]. To further improve property of the heterojunction polymer solar cells, thermal treatment [8–11] of the P3HT/PCBM active layer is conducted to induce locally organized P3HT structures by aggregation of P3HT side chains and also agglomeration of PCBM [9,12]. The annealed P3HT/PCBM device achieves higher device performance because of enhanced bi-continuous phase morphology [10,13] and improved carrier mobility [10,14,15]. Although thermal treatment of the P3HT/PCBM film improves morphology of P3HT, it also decreases interfacial area between P3HT and PCBM because of formation

of larger P3HT and PCBM domains. Decreasing interfacial area lowers the possibility of exciton dissociation between P3HT and PCBM, which is not favorable in performance improvement of polymer solar cells. Therefore, an effective way of controlling the P3HT/PCBM morphology has become a very important issue in research of polymer solar cells.

Researchers [16–24] demonstrate that film morphology of P3HT/PCBM blends can be controlled by incorporation of additives such as 3-hexylthiophene [16], octanedithiol [17,18], block copolymers containing P3HT [19,20], and C_{60} end-functionalized P3HTs [21–24]. The C_{60} end-functionalized P3HTs act as compatibilizers to stabilize the morphology of P3HT and PCBM. Extent of PCBM agglomeration after thermal treatment is reduced and size of PCBM domains is decreased with these additives. In addition to the morphology stabilization, appropriate aggregation of P3HT is also crucial to performance enhancement of polymer solar cells. A bulky group at the chain end of P3HT may restrict aggregation of P3HT. It comes to our mind if a morphology stabilizer without large end group can be applied to the P3HT/PCBM system. Here, we present a new concept

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on morphology stabilization of P3HT/PCBM blend through H-bond formation of a hydroxyl group end-functionalized P3HT (HOC-P3HT-COH) and PCBM. The hydroxyl end group is a rather small functional group as comparing to C_{60}. It forms H-bond with the ester group of the PCBM molecules and diminishes the occurrence of large domain size PCBM formation during the thermal treatment process. Additionally, power conversion efficiency of a polymer solar cell is improved with the stabilized morphology.

2. Experimental

2.1. Materials

HOC-P3HT-COH was synthesized following McCullough's method [25]. The synthesized polymer has a $\overline{M}_w$ of 23,670, and a polydispersity index (PDI) of 1.89. P3HT and PCBM were purchased from Aldrich Corporation and were used without further purification. NMR analysis [26] showed the regioregularity of the synthesized HOC-P3HT-COH was 95% and that for the purchased P3HT was 93%.

2.2. Sample preparation

One percent of P3HT/PCBM (1:1) in *o*-dichlorobenzene (ODCB, spectroscopy grade, purchased from Aldrich) with different amounts of HOC-P3HT-COH were prepared by mixing appropriate amounts of P3HT, PCBM, and HOC-P3HT-COH in ODCB. The mixed solutions were rotated in an orbital shaker at 70 °C for overnight. The solutions were spin-coated on glass substrates and annealed at 150 °C for 30 min for UV–Vis spectroscopy, SEM and AFM measurements.

2.3. Device fabrication

ITO substrate (sheet resistance 12 $\Omega/\square$) was cleaned in an ultrasonic machine with isopropyl alcohol and deionized water following by treatment with O_2 plasma. A 300 Å PEDOT:PSS (Baytron PH from HC Starck) layer was coated on the ITO substrate and dried at 140 °C for 10 min under N_2 atmosphere. A 1000 Å P3HT/PCBM/HOC-P3HT-COH film was spin-coated and annealed at 150 °C for 10 min Ca (100 Å)/Al (1000 Å) film was thermally evaporated as cathode at 1.0×10^{-6} torrs.

2.4. Characterization

The molecular weight of P3HT was measured by a Viscotek DM400/LR40 Gel Permeation Chromatography (GPC) using standard polystyrene as reference. Regioregularity of P3HT was analyzed by a Bruker AV-300 Nuclear Magnetic Resonance. UV–Vis absorption measurements were carried out with a Shimadzu UV-2101C Spectrometer. The surface morphology of the P3HT/PCBM/HOC-P3HT-COH films was studied using a Hitachi S-3000N Scanning Electron Microscopy (SEM). AFM measurements were carried out by a MD-MDT model Semena-A. *I–V* parameters of the fabricated devices were measured by an Oriel Class A Solar Simulator

91160A under AM1.5G irradiation (100 mW/cm²) calibrated by a NREL certified reference solar cell.

3. Results and discussion

Loos [9,12] has demonstrated the formation of PCBM crystals after thermal treatment because of phase separation of the P3HT/PCBM film. The formation of large PCBM crystals decreases the interfacial area between P3HT and PCBM, which results in lower possibility of exciton dissociation and current generation. To stabilize the P3HT/PCBM morphology during thermal treatment process, HOC-P3HT-COH is added to the P3HT/PCBM film. As illustrated in Fig. 1, the hydroxyl end group of HOC-P3HT-COH forms H-bond with the ester group of PCBM. To characterize H-bond formation, 2-(hydroxymethyl)thiophene (Fig. 2) is used as model compound for HOC-P3HT-COH because moles number of hydroxyl group in HOC-P3HT-COH is rather small that may lead to low S/N ratio. Fig. 2a shows the chemical shift of 2-(hydroxymethyl)thiophene.

The chemical shift at δ = 2.01 ppm (in CDCl₃) is a broad peak that originated from a rapid proton exchange between 2-(hydroxymethyl)thiophene. As PCBM is added to the solution, the proton on 2-(hydroxymethyl)thiophene is fixed by the carbonyl group on PCBM because of H-bond formation. This broad peak splits into a triplet peak because of coupling from the adjacent protons (–CH₂–). The chemical shift at δ = 4.82 ppm (–CH₂–) also splits from a singlet peak into a doublet peak because the proton on hydroxyl group is fixed by PCBM that gives rise to the doublet splitting [27]. The H-bond restricts molecular motion of PCBM and diminishes the extent of PCBM agglomeration during the thermal treatment process. Fig. 3 shows SEM images of the decreasing PCBM crystal sizes in the annealed (150 °C, 30 min) P3HT/PCBM films by incorporation of different amount of HOC-P3HT-COH. The size of PCBM crystal is about 2 μm × 5 μm for the annealed P3HT/PCBM film without HOC-P3HT-COH. Upon addition of HOC-P3HT-COH, the size of the PCBM crystals becomes smaller with increasing amount of HOC-P3HT-COH in the P3HT/PCBM blend. The size of PCBM crystal is about 2 μm × 2 μm in diameter by addition of 5% HOC-P3HT-COH. The number of PCBM crystals decreases by blending 10% of HOC-P3HT-COH in the P3HT/PCBM film. The HOC-P3HT-COH behaves as compatibilizer to control the domain size of PCBM through the intermolecular H-bonding. An appropriate amount of HOC-P3HT-COH is important because the purpose of adding HOC-P3HT-COH to the P3HT/PCBM blend is to control the domain size of P3HT and PCBM, instead of forming a complete miscible blend.

As mentioned earlier, H-bonding between HOC-P3HT-COH and PCBM restricts molecular motion of P3HT and PCBM that may lead to poor P3HT aggregation. Indeed, absorption of P3HT in the as-prepared P3HT/PCBM/HOC-P3HT-COH film shows blue-shift to that without HOC-P3HT-COH (Fig. 4). The main absorption peak shifts from 500 nm (P3HT/PCBM film) to 485 nm (P3HT/PCBM/HOC-P3HT-COH film) before thermal treatment. Additionally, the intensities at 550 and 600 nm that represent
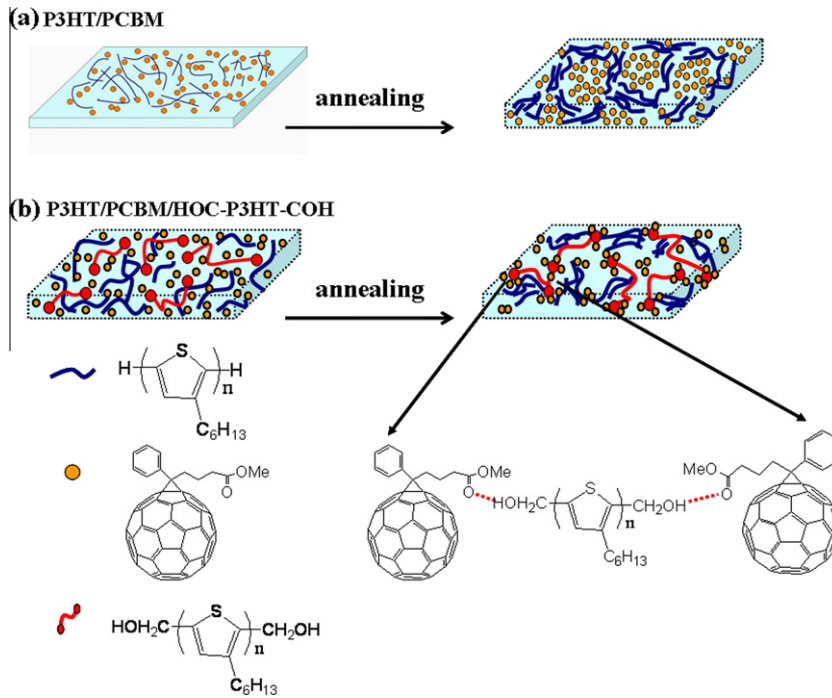
Fig. 1. Illustration of morphological difference in the fabrication of (a) P3HT/PCBM film and (b) P3HT/PCBM/HOC-P3HT-COH film.
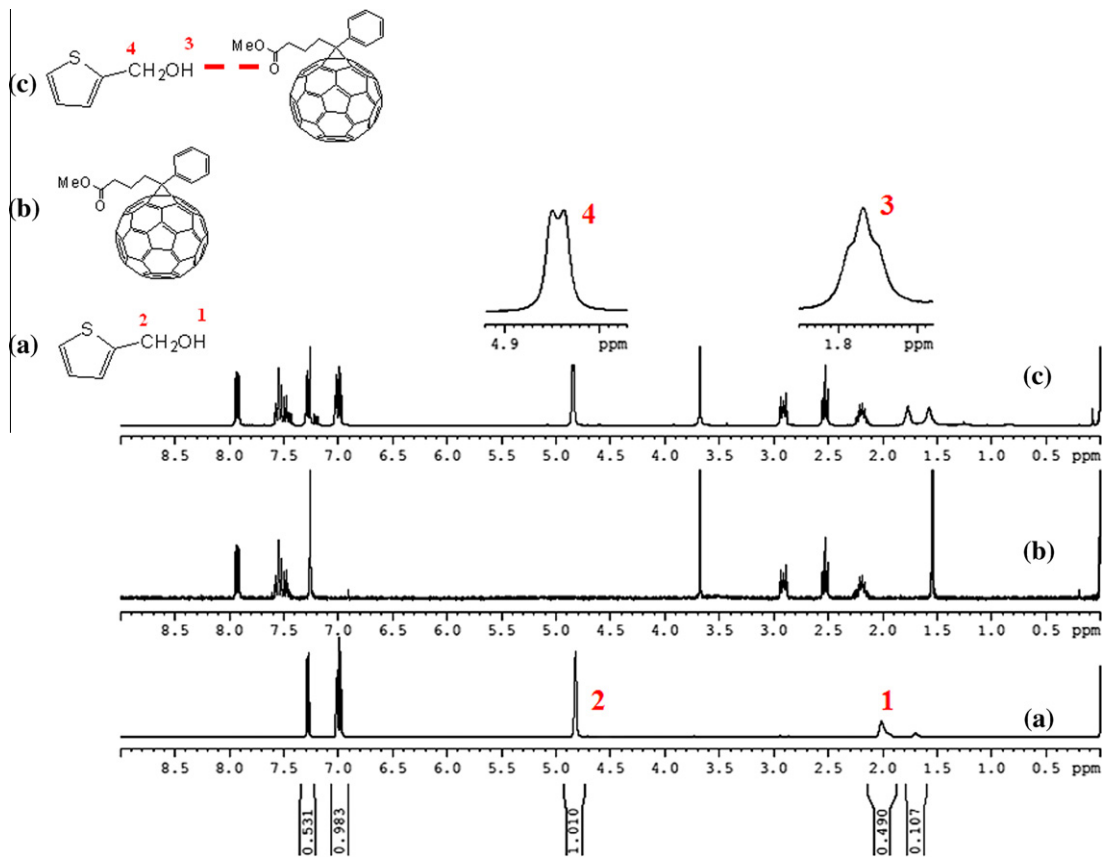
Fig. 2. NMR spectra of (a) 2-(hydroxymethyl)thiophene and (b) PCBM (c) 2-(hydroxymethyl)-thiophene blends with PCBM (1:1 by mole).
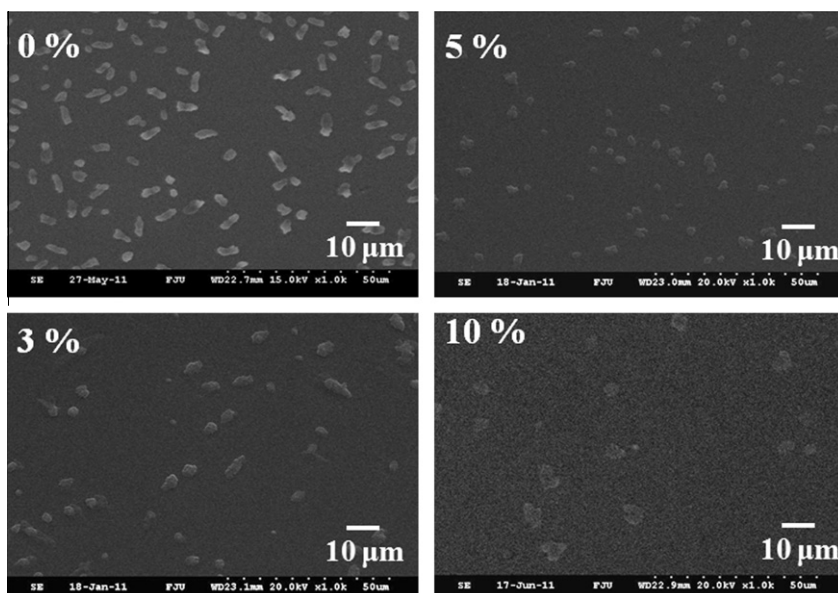
Fig. 3. SEM images of P3HT/PCBM/x% HOC-P3HT-COH films after annealing at 150 °C for 30 min.
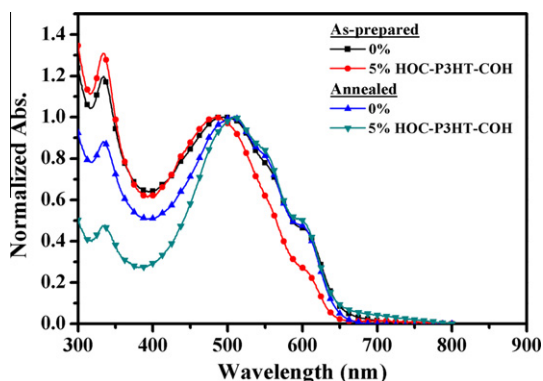

Fig. 4. UV–Vis absorption spectra of as-prepared and annealed (150 °C for 30 min) P3HT/PCBM and P3HT/PCBM/5% HOC-P3HT-COH films.

aggregation of P3HT are both lessened. This result indicates less aggregation of P3HT in the as-prepared P3HT/PCBM/HOC-P3HT-COH film. Researchers [28] find the steric hindrance effect of P3HT end group is important on the aggregation of P3HT. HOC-P3HT-COH forms H-bonds with PCBMs at both ends of HOC-P3HT-COH. The bonded PCBMs are bulky groups at the chain ends, which hinder the aggregation of P3HT molecules and result in blue shift of the absorption spectrum. Although the as-prepared film shows less aggregation with addition of 5% HOC-P3HT-COH, the thermally treated P3HT/PCBM/5% HOC-P3HT-COH film exhibits similar absorption spectrum and intensity between 400 and 650 nm to the annealed P3HT/PCBM film. Thermal treatment lowers the strength of H-bonds during the thermal treatment process and enlarges distance between HOC-P3HT-COH and PCBM. It allows the P3HT molecules to aggregate in a similar way to that without HOC-P3HT-COH. H-bonds are reformed after

the thermal treatment process as the temperature returns to room temperature.

Distribution of P3HT and PCBM in solvent is uniformed. However, evaporation of solvent induces phase separation [29] between P3HT and PCBM. Addition of HOC-P3HT-COH to the P3HT/PCBM blend creates H-bonds between PCBM and HOC-P3HT-COH, which will prevent the separation of PCBM from P3HT during the evaporation of solvent. PCBMs are more finely dispersed in the P3HT/PCBM/HOC-P3HT-COH film than that in the P3HT/PCBM film because H-bond between HOC-P3HT-COH and PCBM prevent severe agglomeration of PCBM. The size of PCBM gradually decreased and number of PCBM crystals also decreased as shown in Fig. 3. This result affects surface profile of P3HT/PCBM/HOC-P3HT-COH films. The surface profiles of the P3HT/PCBM/HOC-P3HT-COH films are shown in Fig. 5. The surface of the as-prepared film is smoother as the HOC-P3HT-COH content increases in the P3HT/PCBM/HOC-P3HT-COH films. R_{rms} of the as-prepared P3HT/PCBM is 10.95 nm (Table 1) without HOC-P3HT-COH. It decreases to 5.42 nm with only 1 wt.% HOC-P3HT-COH in the P3HT/PCBM film. The surface roughness becomes very small (R_{rms} = 0.68 nm) with 5% HOC-P3HT-COH in the P3HT/PCBM. Evidently, HOC-P3HT-COH acts as compatibilizer that decreases the domain size of PCBM by intermolecular H-bonding and the film surface becomes smoother. Upon thermal treatment at 150 °C for 30 min, surface roughness of the P3HT/PCBM/HOC-P3HT-COH films are about the same as the as-prepared films, which indicates the dispersion of PCBM in P3HT is uniformed and stable.

Performance of a P3HT/PCBM based solar cell is highly dependent upon the amount of interfacial area between P3HT and PCBM. The interface area affects the possibility of exciton dissociation and thus the generated current density of the solar cell device. By incorporation of HOC-P3HT-COH, domain size of PCBM becomes smaller that will effectively increase the interfacial area. Fig. 6
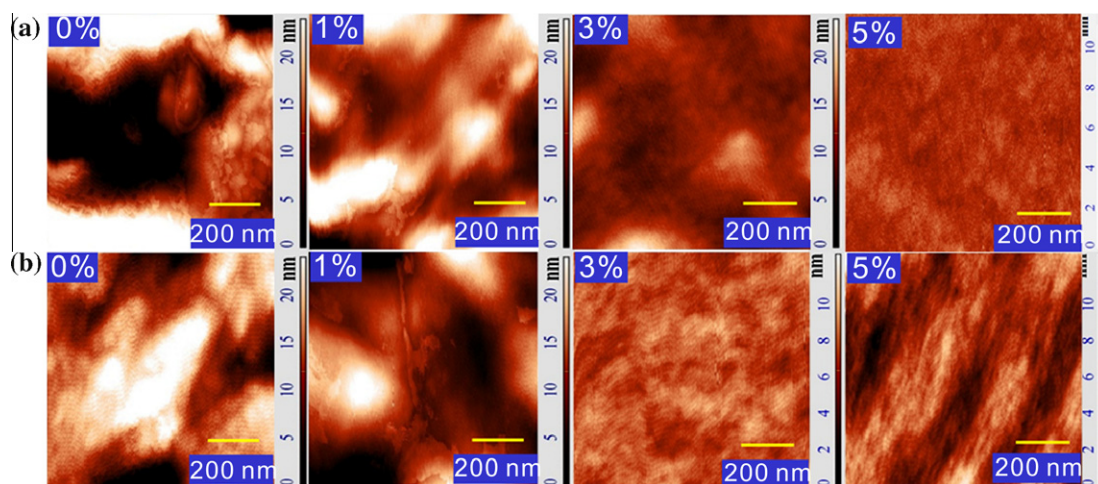
Fig. 5. AFM images (height) of P3HT/PCBM/x% HOC-P3HT-COH films (a) as-prepared and (b) annealed (150 °C for 30 min).

Table 1
Surface roughness of P3HT/PCBM/x% HOC-P3HT-COH films (measured by AFM). The annealed films are thermal treated at 150 °C for 30 min.

	R_a (nm)				R_{rms} (nm)			
% of HOC-P3HT-COH	0%	1%	3%	5%	0%	1%	3%	5%
As-prepared	8.38	4.27	2.07	0.54	10.95	5.42	2.75	0.68
Annealed	6.03	4.17	2.08	1.60	7.26	5.37	2.70	2.11

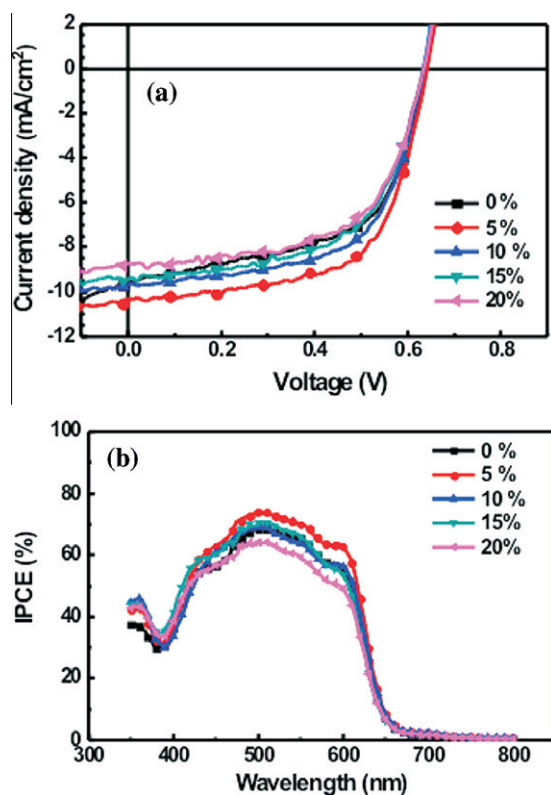**Fig. 6.** J–V and IPCE curves of P3HT/PCBM/x% HOC-P3HT-COH based polymer solar cells with a device structure of ITO/PEDOT:PSS(40 nm)/P3HT:PCBM:HOC-P3HT-COH active layer (100 nm)/Ca/Al.

shows the I–V-curves of P3HT/PCBM based solar cells with different amounts of HOC-P3HT-COH. Short circuit current density (J_{sc}) of the P3HT/PCBM based device increases from 8.70 to 10.27 mA/cm^2 (Table 2) by blending 5 wt.% HOC-P3HT-COH in the P3HT/PCBM active layer. However, it decreases gradually with increasing amount of HOC-P3HT-COH in the active layer. A complete miscible blend as an active layer does not necessarily generate higher current density. Possibly, the bi-continuous phase morphology disappears with heavy loading of HOC-P3HT-COH.

Addition of the HOC-P3HT-COH to the P3HT/PCBM film greatly enhances thermal stability of the P3HT/PCBM film through the H-bond formation. As shown in Fig. 7, P3HT/PCBM film is very sensitive to thermal treatment. Upon thermally treated at 150 °C for 10 min, many PCBM crystals appears. Continuing treatment on the P3HT/PCBM film allows intensified phase separation between P3HT and PCBM and results in formation of lots of PCBM domains. Through the H-bond formation between HOC-P3HT-COH and PCBM, PCBM molecules are finely dispersed in the P3HT/PCBM film and are less likely to separate from

Table 2
Solar cells performance of P3HT/PCBM/x% HOC-P3HT-COH based polymer solar cells. The active layer is thermal treated at 150 °C for 10 min.

HOC-P3HT-COH (%)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
0	8.70	0.62	0.58	3.14
5	10.27	0.62	0.63	4.06
10	9.70	0.64	0.61	3.76
15	9.45	0.64	0.58	3.53
20	8.73	0.64	0.60	3.37

(a) P3HT/PCBM film (x1000)
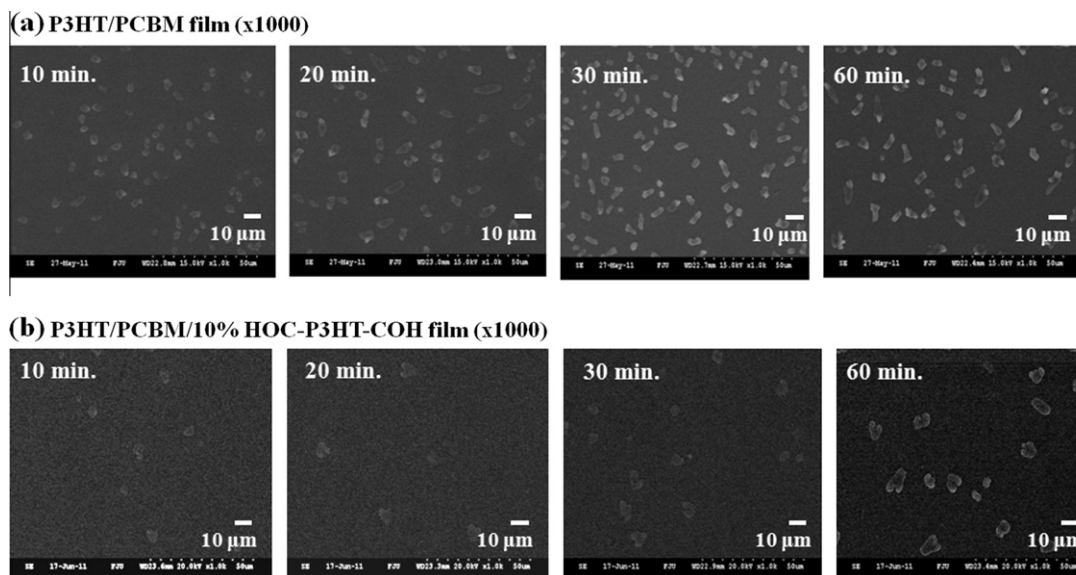

(b) P3HT/PCBM/10% HOC-P3HT-COH film (x1000)

Fig. 7. SEM images (×1000) of (a) P3HT/PCBM, and (b) P3HT/PCBM/10% HOC-P3HT-COH films after annealing at 150 °C for different period of time.

Table 3
Thermal stability of P3HT/PCBM and P3HT/PCBM/5% HOC-P3HT-COH based polymer solar cells. The active layer is thermal treated at 150 °C for different periods of time.

Anneal time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)	η/η_{max} (%)
P3HT/PCBM					
5	8.41	0.62	0.59	3.09	98.4
10	8.70	0.62	0.58	3.14	100
20	7.55	0.62	0.51	2.38	75.8
30	8.54	0.58	0.40	2.00	63.7
P3HT/PCBM/5% HOC-P3HT-COH					
5	9.89	0.64	0.60	3.79	93.3
10	10.27	0.62	0.63	4.06	100
20	10.44	0.64	0.59	3.94	97.0
30	10.33	0.64	0.59	3.91	96.3
60	9.23	0.64	0.61	3.61	88.9

P3HT during thermal treatment process. Miscibility of P3HT/PCBM blend can be enhanced if more HOC-P3HT-COH is added. However, as mentioned above, a complete miscible P3HT/PCBM blend does not necessarily result in higher performance device. An appropriate amount of HOC-P3HT-COH is more important to create the required morphology and enhanced stability. As shown in Table 3, fill factor of device without HOC-P3HT-COH decreases significantly from 0.59 to 0.40 upon thermal treatment at 150 °C for 30 min. However, fill factor of the 5% HOC-P3HT-COH containing device is rather stable during the thermal treatment process (~0.60). Additionally, current density and open circuit voltage are also improved. Finally, we observe significantly thermal stability improvement by using HOC-P3HT-COH as a compatibilizer. Power conversion efficiency of device without HOC-P3HT-COH decreases 36.3% (from 3.14% to 2.00%) upon treatment at 150 °C for 30 min. Power conversion efficiency of device with 5% HOC-P3HT-COH decreases only 3.7% (from 4.06% to 3.91%) during the same treatment process. It decreases

a little further to 3.61% (a 11.1% decrease in power conversion efficiency) for a 60 min treatment process, which is much better than that without HOC-P3HT-COH.

4. Conclusion

By introducing a hydroxyl group end-functionalized P3HT (HOC-P3HT-COH) to the P3HT/PCBM blend, morphology stabilization of P3HT/PCBM film is achieved through the H-bond formation. The hydroxyl group end-functionalized P3HT forms H-bonds with PCBM and diminishes the agglomeration of PCBM. PCBM is finely dispersed in the P3HT/PCBM film and interfacial area between P3HT and PCBM is increased, which results in higher current density. Additionally, thermal stability of the P3HT/PCBM based device is greatly improved because H-bonds minimize phase separation between P3HT and PCBM. A high performance and stable polymer solar cell with 4.06% power conversion efficiency under AM1.5G irradiation is

prepared. Finally, this concept shall be applicable to other polymer solar cell systems to stabilize phase separation during thermal treatment process.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.orgel.2011.11.019.

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