



Short communication

Annealing-free P3HT:PCBM-based organic solar cells via two halohydrocarbons additives with similar boiling points



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ABSTRACT

Efficient annealing-free inverted bulk heterojunction (BHJ) organic solar cells based on poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) (1:1, w/w) have been obtained using two easily accessible halohydrocarbons (1,6-dibromohexane (DBH) and 1-bromodecane (BD)) with the same boiling points as solvent additives. The devices treated with 2.5 wt% additives removed the grain boundary of the large PCBM-rich phase, resulting in more-uniform film morphology on the nanoscale. The more-uniform film morphology greatly improved the short circuit current density of the devices. Finally, PCEs of the devices processed with DBH and BD reached 3.81% and 3.68%, respectively. Both additives with almost the same boiling points had a similar impact on device performance, despite of different chemical structures with different polarities and other physical properties.

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1. Introduction

Bulk heterojunction (BHJ) polymer solar cells (PSCs) have been intensively explored in recent years for generation of affordable, clean, and renewable energy because of their light weight and potential for low-cost solution processing through roll-to-roll printing. Recently, PSCs incorporating low-bandgap conjugated polymers and fullerene derivatives have exhibited maximum power conversion efficiencies (PCEs) of over 8% [1–4]. Organic solar cells based on solution processable colloidal nanocrystals and conjugated polymers also have great improvement [5,6]. However, further improvement in efficiency is required for practical applications. There are some critical and complicated factors to determine the PCEs of the devices. One key step for PSCs with high photovoltaic performance is to form appropriate interpenetrating network morphology, which is comprised of the donor and acceptor components [1–4,7–10] through van der Waals crystal packing and nanoscale domains of the two phases [3,4,11–14]. It was proposed that a certain degree of phase separation of the two organic components would be beneficial to increase the PCEs of organic solar cells [15]. However, in polymer/fullerene based BHJ cells the crystallization of the polymer phase can be inhibited by the clustering of the fullerene in blend during drying [16,17]. This effect can be avoided

by choosing the appropriate solvent with required boiling point for either slow or high evaporation rate [18,19], thermal annealing [20], or using chemical additives [21,22]. Among these approaches, the addition of solvent additive during the active layer processing is the simplest and most effective method to optimize BHJ device's morphology; it can influence the size of the fullerene domains and enhance the crystallinity of the self-organized polymers by improving the solubility of the fullerenes and slightly elongating the drying time of the active layer. It has been already shown that the photoconductivity response is strongly increased in polymer/fullerene composites by adding a small amount of the alkyl thiol to the solution prior to the film deposition [23]. Besides alkyl thiols, there are some other solvent additives applied in poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) based BHJ solar cells. Notably, 1,8-di(X)octanes, one kind of the most popular additives, with different functional groups X (I, SH, etc.), can significantly improve the phase separation of the devices [24,25], while the effects on the morphologies of active layers need further investigation.

In this work, two halohydrocarbons 1,6-dibromohexane (DBH) and 1-bromodecane (BD), with similar boiling points, are applied in P3HT:PCBM based solar cells as new solvent additives. P3HT has been widely studied because of its self-assembly ability to form lamellae structures of ordered polymer chains [26–29]. The BHJ system with an inverted device structure is used to investigate the effects of solvent additives on the performance, because inverted structure of PSC has some advantages superior to conventional

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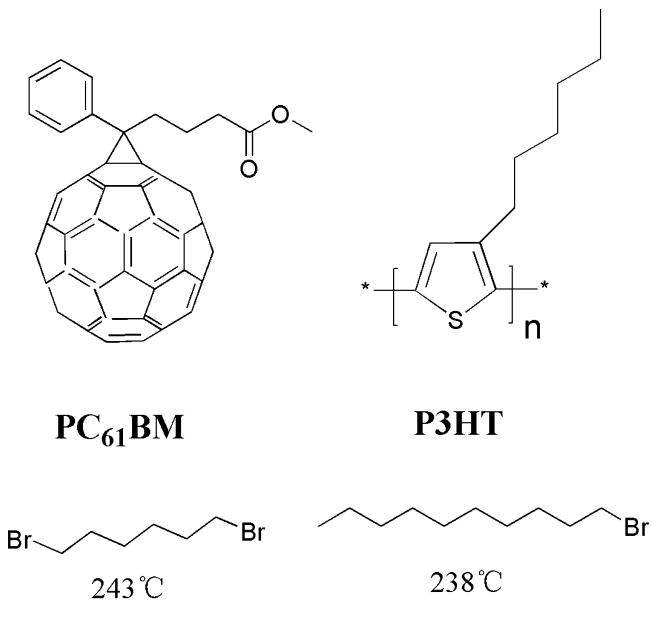


Fig. 1. Molecular structures of PCBM, P3HT, DBH and BD additives.

device structure, such as interface stability, a stable metal electrode, and design flexibility for tandem cells [30–32]. Moreover, the two easily accessible solvent additives are first used to explore the effects of alkyl chain length and the physical properties of the additives on the morphology of the active layer and the performance of the device. The mechanism of additives on the morphology of active layers will be further discussed.

2. Experimental

All cells were fabricated on ITO coated glass substrates with a sheet resistance of $15\ \Omega/\text{sq}$. The substrates were cleaned in an ultrasonic bath with detergent, ultra pure water, acetone, and isopropyl alcohol for 20 min, respectively. The ZnO precursor solution was prepared by using zinc acetate and the equally molar monoethanolamine dissolved in 2-methoxyethanol, and then the mixture was stirred vigorously at 60°C to yield a homogeneous transparent solution. The ITO surfaces were coated with the above ZnO precursor solution with spin speeds at 3500 rpm for 40 s, and baked in an oven at 100°C for 16 h. More details of ZnO films preparation have been described in our previous report [33]. A blend solution of P3HT (Rieke Metals Inc.) and PCBM (American Dye Sources Inc.) with a weight ratio of 1:1 (total solids concentration of 30 mg/mL) were spin-coated on ZnO coated ITO substrate to form the active layer ($\sim 110\ \text{nm}$, measured by Veeco Dektak 150 surface profiler) in glovebox filled with N_2 . The active layers with the additives (DBH or BD) were not thermal treated anymore, but in control device the active layer without any additive was thermally annealed on a hot plate at 150°C for 10 min in glovebox. Subsequently, all samples were immediately loaded into a thermal evaporation chamber, and then a 5 nm molybdenum oxide interlayer (MoO_3) and a 80 nm silver (Ag) layer were thermally deposited through a shadow mask to define the active area of the devices ($0.1\ \text{cm}^2$) and form a top anode. Fig. 1 presents the molecular structures of P3HT, PCBM, and the additives DBH and BD, and chlorobenzene (CB) as solvent was used to process the active layer.

UV-vis spectra were measured on Varian Cary 50 UV-vis spectrometer. Current density–voltage (J – V) characteristics were

Table 1
Device characteristics with different contents of additives.

Additive	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	η (%)
None, Annealed	0.624	8.42	62.74	3.29
DBH 1.5 wt%	0.638	7.10	55.11	2.64
DBH 2.5 wt%	0.643	9.90	60.67	3.81
DBH 4.0 wt%	0.614	9.36	61.87	3.55
BD 1.5 wt%	0.592	8.42	63.41	3.16
BD 2.5 wt%	0.583	10.11	63.04	3.68
BD 4.0 wt%	0.561	7.32	59.45	2.57

recorded with Keithley 2420 source measurement unit under simulated $100\ \text{mW}/\text{cm}^2$ (AM 1.5 G) irradiation from Newport solar simulator. Light intensity was calibrated with a standard silicon solar cell. External quantum efficiencies (EQE) of solar cells were analyzed by certified Newport incident photon conversion efficiency (IPCE) measurement system. Surface roughness and morphology of thin films were characterized by atomic force microscopy (AFM, Agilent 5400).

3. Results and discussion

3.1. Optical properties

Normalized UV-vis absorption spectra of P3HT: PCBM blend films with and without additives were characterized by Varian Cary 50 spectrophotometer. The absorption spectra of P3HT: PCBM blend film without additive annealed at 150°C for 10 min and films with different DBH contents are shown in Fig. 2(a). The absorption peak of P3HT is at 500 nm with two shoulders at 550 and 600 nm for the blend film without additive. The three bands can be attributed to the $\pi-\pi^*$ transition (500) and vibronic peaks (550, 600 nm), respectively, which are consistent with the reported results earlier [34]. The absorption peak of the blend films with DBH is red-shift to 510 nm with two shoulders at 560 and 610 nm. The absorption intensity is enhanced with increasing the DBH contents and higher than the annealed one without additive. The films with different contents of BD were also measured (Fig. 2(b)), and the absorption spectra are similar to the ones with DBH. According to Refs. [27,35,36], the optical absorption intensity of conjugated polymer increases gradually with higher degree of polymer crystallinity and extend conjugation length of polymer. The enhanced absorption in P3HT:PCBM layer is likely induced by higher degree of P3HT crystallinity and extend conjugation length of P3HT with increasing additives. Absorption spectra between 540 and 640 nm with different DBH (open) and BD (solid) contents are summarized in Fig. 2(c). One can observe that the absorption shoulder peaks at about 560 and 610 nm of P3HT: PCBM films with BD are stronger than those of corresponding DBH additive. The results show that compared with DBH, the introduction of BD could be more favorable to form crystalline of P3HT.

3.2. Photovoltaic properties

The P3HT:PCBM BHJ system with an inverted device structure (ITO/ZnO/P3HT:PCBM/MoO₃/Ag) was used to investigate the function of DBH and BD as solvent additives. For comparison, the device without additive annealed at 150°C for 10 min was simultaneously fabricated as reference. Fig. 3(a) shows the current–voltage (J – V) curves of the devices under illumination intensity $100\ \text{mW}/\text{cm}^2$ (AM1.5 G). The photovoltaic properties, including short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF) and PCE of all devices are summarized in Table 1. The reference device gives a PCE of 3.29% with J_{SC} , V_{OC} , and FF of $8.42\ \text{mA}/\text{cm}^2$, $0.624\ \text{V}$ and 62.74%, respectively, which is well consistent with the reported ones based on P3HT: PCBM with the same structure [37]. For the

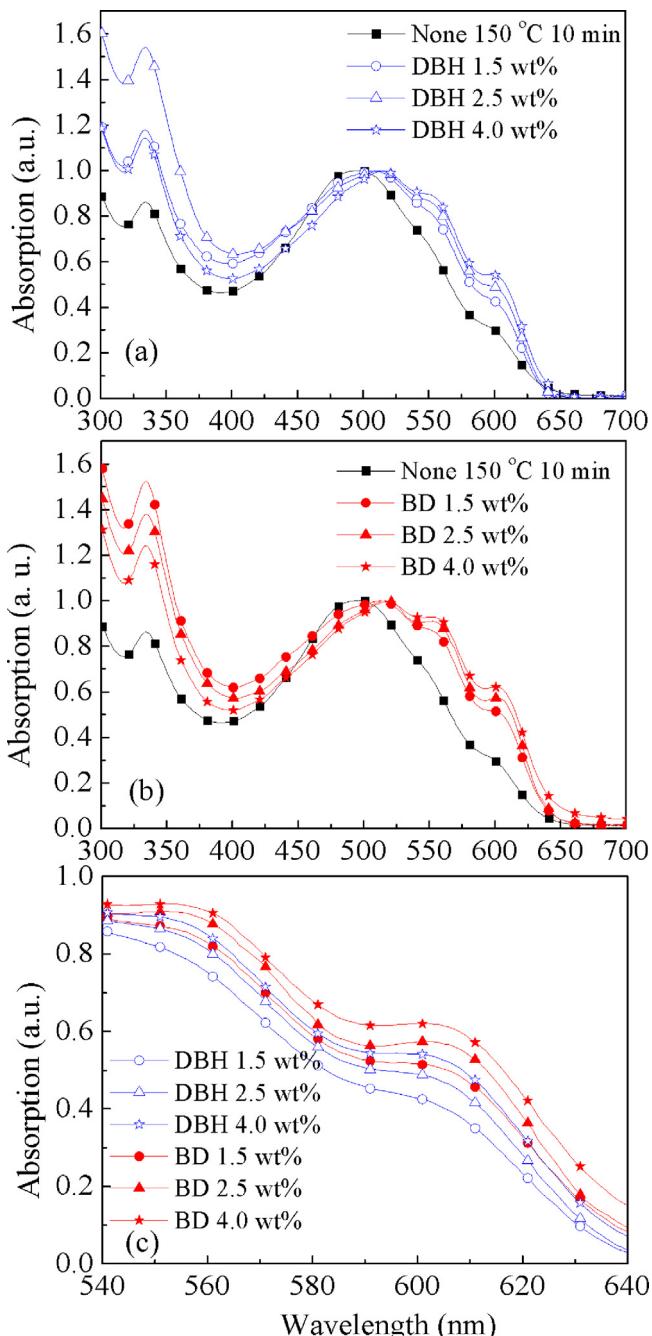


Fig. 2. Normalized UV-vis absorption spectra of P3HT:PCBM blend films: (a) with different DBH contents, (b) with different BD contents, (c) absorption spectra between 540 and 640 nm with different DBH (open) and BD (solid) contents.

devices with additive, the V_{OC} and FF are insensitive to the content of DBH. However, J_{SC} and PCEs are strongly dependent on the DBH content. The J_{SC} and PCE are only $7.10 \text{ mA}/\text{cm}^2$ and 2.64% when the addition of DBH 1.5 wt%, which are smaller than those of the reference device. After addition of DBH 2.5 wt%, J_{SC} and PCE increase to $9.90 \text{ mA}/\text{cm}^2$ and 3.81%. When the content of DBH further increases to 4.0 wt%, J_{SC} and PCE drop to $9.36 \text{ mA}/\text{cm}^2$ and 3.55%. When replacing DBH with BD, the devices show the similar change, and the best photovoltaic device gives a PCE of 3.68%, with a J_{SC} of $10.11 \text{ mA}/\text{cm}^2$, a V_{OC} of 0.58 V, and a FF of 63.04%. It is well known that a certain degree of phase separation of the two organic components would be beneficial to the PCEs of photovoltaic devices. With the content of DBH or BD increasing, the crystallinity

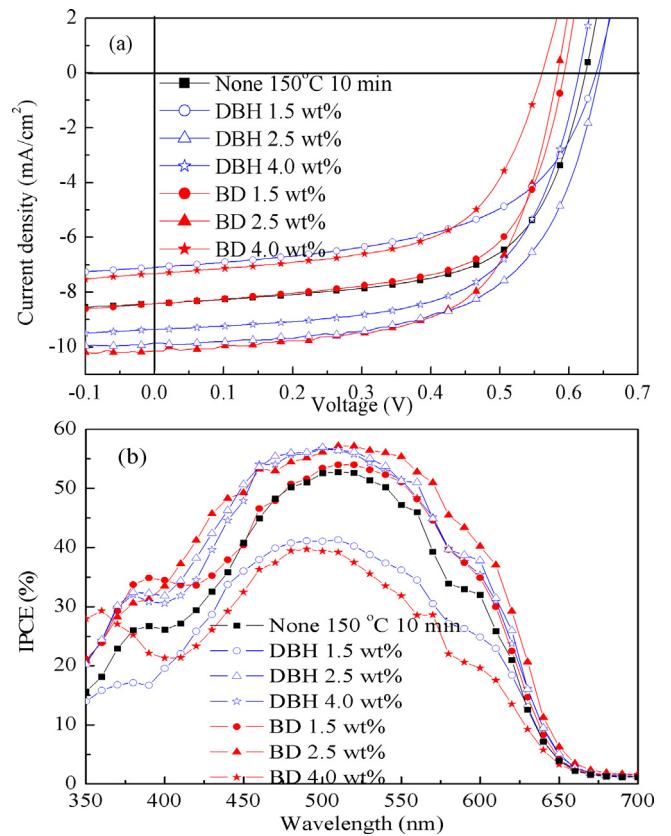


Fig. 3. (a) J - V curves and (b) IPCE spectra of P3HT:PCBM based devices with various additives and without additives after thermal treatment.

of P3HT increases gradually. The additive BD is easier to facilitate the crystallinity of P3HT than DBH, which is shown in Fig. 2. Therefore, when adding 1.5 wt% additives, the J_{SC} for BD is larger than that for DBH. When increasing the BD content to 4 wt%, the J_{SC} decreased to $7.32 \text{ mA}/\text{cm}^2$ quickly because large phase separation was formed. Interestingly, the most effective additive contents of DBH and BD are both 2.5 wt%, and thus their devices exhibit the best performance with PCEs of 3.81% and 3.68%, respectively, higher than that of the reference one.

The dependence of the photovoltaic performance on the DBH, BD content was further confirmed by the IPCE measurements of the devices, as shown in Fig. 3(b). The IPCE curves of the devices with and without additives show a main peak at around 510 nm, corresponding to the absorption maxima of the blend. The maximum IPCE is 52.8% for the device without additive after thermal treatment, and are 41.3% and 54.0% when addition of 1.5 wt% DBH and BD, respectively. With increasing the DBH and BD contents from 1.5 to 2.5 wt%, then to 4.0 wt%, the IPCE increases to 57.2%, 56.7%, and then decreases to 56.2%, 39.2%, respectively. The IPCE profiles varying with the DBH or BD contents are consistent with the changes of J_{SC} and PCE.

3.3. Surface morphology

The effect of the additives on the active layer morphology was examined by atomic force microscope (AFM) technique in tapping mode. Fig. 4 shows the AFM topographic ($5 \mu\text{m} \times 5 \mu\text{m}$) and phase ($2 \mu\text{m} \times 2 \mu\text{m}$) images of the blend films with different contents of DBH or BD. All the films were prepared under the same conditions used for the optimized photovoltaic devices. The additive-free film with thermal treated at 150 °C for 10 min is smooth and featureless, giving a uniform amorphous texture with a

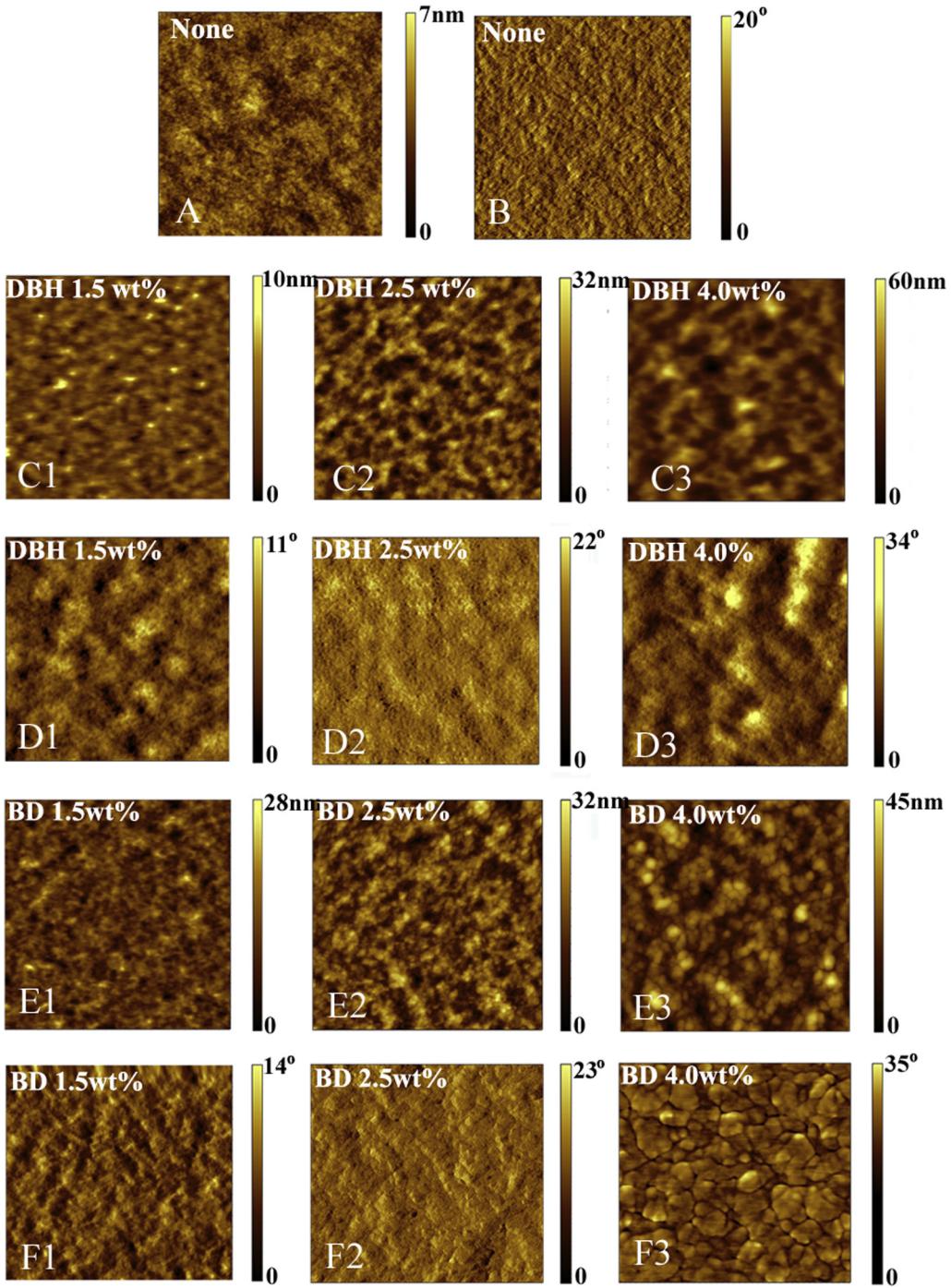


Fig. 4. Topographic (A, C1–C3, E1–E3, 5 $\mu\text{m} \times 5 \mu\text{m}$) and phase (B, D1–D3, F1–F3, 2 $\mu\text{m} \times 2 \mu\text{m}$) images of ITO/ZnO/P3HT:PCBM blend films: (A and B) without additive after thermal treatment, (C1–C3 and D1–D3) with different DBH contents, (E1–E3 and F1–F3) with different BD contents.

root-mean-square (RMS) roughness of 0.786 nm (Fig. 4(A)). It can be observed that partial PCBM-rich large domains (Fig. 4(B), darker phase) are embedded in the P3HT/PCBM blends [14]. In this condition, the J_{SC} of 8.42 mA/cm² and PCE of 3.29% are obtained from the reference cell. Apparently, the films change to typical cluster structures with more aggregated domains and larger roughness when additive DBH or BD is used. With increasing the content of DBH or BD, the domain sizes elongate gradually and the surfaces become much rougher (from 1.29 nm (C1), 3.27 nm (E1) to 6.95 nm (C3), 6.14 nm (E3), respectively). After optimization with DBH or BD 2.5 wt% as the solvent additive, nanoscale phase separation with proper domain sizes and bicontinuous interpenetrating network is formed (Fig. 4(C2, D2, E2, F2)). The performance of the fabricated

solar cells under these conditions (2.5 wt% additive) are improved greatly, especially J_{SC} (from 8.42 of reference device to 9.90 and 10.11 mA/cm² for DBH and BD, respectively). However, the AFM phase image of the film processed with BD 4 wt% shows large scale phase separation, and the round-shape domain size is larger than 100 nm, which are very unfavorable for exciton dissociation and charge transport. Consequently, the J_{SC} decreased to 7.32 mA/cm² and the PCE is only 2.57%.

4. Conclusion

In summary, two easily accessible halohydrocarbons DBH and BD were applied as the additives to improve the efficiencies of

P3HT/PCBM solar cells. Based on absorption, AFM, it was concluded that the additives affected the device performance by improving the crystallization of the polymer phase and enhancing absorption. Proper additive-processed film demonstrates a homogeneous nanoscaled phase separation and interpenetrating network morphology between the donor and the acceptor phases, which provide efficient exciton dissociation pathways for the charge carriers to reach the respective electrodes. The PCEs of PSCs based on films added with BD and DBH without thermal annealing reached 3.68% and 3.81%, respectively, whereas for annealed cells around 3.29% were obtained. The additives with almost same boiling points have similar impact on device performance, although the chemical structures are different. This work shows that introducing DBH or BD as solvent additive is an effective and simple method to optimize the morphology and thus improve the performance of the BHJ organic solar cells.

Acknowledgements

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