Critical role of domain crystallinity, domain purity and domain interface sharpness for reduced bimolecular recombination in polymer solar cells

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Abstract

Inverted bulk heterojunction solar cells were fabricated using poly(3-hexylthiophene) (P3HT) blended with two different fullerene derivatives namely phenyl-C₆₁-butyric acid methyl ester (PC₆₀BM) and indene-C₆₀ bis-adduct (IC₆₀BA). The effect of annealing temperatures on the morphology, optical and structural properties were studied and correlated to differences in photovoltaic device performance. It was observed that annealing temperature significantly improved the performance of P3HT:IC₆₀BA solar cells while P3HT:PC₆₀BM cells showed relatively less improvement. The performance improvement is attributed to the extent of fullerene mixing with polymer domains. Energy filtered transmission electron microscopy (EFTEM) and x-ray diffraction (XRD) results showed that ICBA mixes with disordered P3HT much more readily than PC₆₀BM which leads to lower short circuit current density and fill factor for P3HT:IC₆₀BA cells annealed below 120°C. Annealing above 120°C improves the crystallinity of P3HT in case of P3HT:IC₆₀BA whereas in P3HT:PC₆₀BM films, annealing above 80°C leads to negligible change in crystallinity. Crystallization of P3HT also leads to higher

domain purity as seen EFTEM. Further it is seen that cells processed with additive nitrobenzene (NB) showed enhanced short circuit current density and power conversion efficiency regardless of the fullerene derivative used. Addition of NB led to nanoscale phase separation between purer polymer and fullerene domains. Kelvin probe force microscopy (KPFM) images showed that enhanced domain purity in additive casted films led to a sharper interface between polymer and fullerene. Enhanced domain purity and interfacial sharpness led to lower bimolecular recombination and higher mobility and charge carrier lifetime in NB modified devices.

Keywords: polymer solar cells, bimolecular recombination, domain crystallinity, domain purity and domain interface sharpness

Introduction

Due to increased demand for clean energy and depletion of fossil fuels, alternative energy sources such as solar and wind are of interest currently. Organic semiconductors have gained significant amount of interest for photovoltaic applications in the last several decades due to their lower cost¹ and processibility from solution for lightweight and flexible devices². Polymer-fullerene bulk heterojunction (BHJ) solar cells have shown photovoltaic efficiencies up to 11%^{3, 4}. Nanomorphology plays a crucial role in BHJ solar cells as it dictates both charge generation and transport⁵⁻⁷. Nanomorphological features such as donor/acceptor crystallinity⁸, vertical/lateral phase separation^{9, 10}, domain purity¹¹, orientation¹² and domain interfaces¹³ can be tailored by optimizing the processing conditions to enhance device conversion efficiencies. Processing parameters such as solvent selection^{8, 14, 15}, annealing temperature¹⁶, donor-acceptor mixing ratio^{17, 18}, and coating techniques can be fine-tuned to attain high photovoltaic performance.

Molecular miscibility between polymer and fullerene is critical to acquire homogenous phase separation between polymer and fullerene components leading to efficient exciton dissociation¹⁹. However higher miscibility can lead to highly intermixed domains preventing ordering of polymer chains. These highly intermixed amorphous domains have shown to possess poor charge transport²⁰. It is desired to have pure polymer domains having sharp interface between polymer and fullerene phase (less intermixing at domain boundaries) to improve charge

transport and suppress trap assisted losses ²¹. Several studies have focused on the mixing of donor polymers and fullerene blend films and have shown that domain purity and crystallinity ^{5, 22, 23} plays an important role in enhancing device performance, but the physics behind efficient charge transport correlated to nanoscale morphology is still elusive. Further, the processing parameters required to achieve ideal morphology is dependent upon the material selection and needs to be studied. Such an insight will be beneficial to attain high power conversion efficiency at large scale.

P3HT:PCBM solar cells have been widely studied ²⁴ in the past decade and efficiencies of 4-5% have been regularly achieved. Device efficiencies were further improved to 5-7% ^{25, 26} by using a bis-adduct fullerene derivative namely indene-C₆₀ bisadduct (IC₆₀BA) resulting in higher open circuit voltage due to the higher LUMO level in ICBA. One of the most prominent approaches to improve efficiency in P3HT based blends has been slow drying of cast films. Slow drying leads to structural ordering of P3HT and diffusion of fullerene to achieve nanoscale phase separation between crystalline P3HT and fullerene domains. This approach has demonstrated efficient solar cells, however, is not practical for roll to roll processing. Lower boiling point solvents are preferred to increase throughput and thickness uniformity for roll to roll printing implementation ²⁷. Further it has been shown that mixing behavior of fullerene with P3HT is dependent upon the fullerene derivative used ²⁸. There exists a need for understanding the correlation between processing conditions and resulting morphology and between complex nanoscale morphological features and charge transport/recombination to achieve faster commercialization of low cost plastic solar cells.

In this study we found that mixing behavior of P3HT and fullerene is dependent upon the fullerene derivative used. ICBA was found to mix with P3HT more readily and the blend films require higher thermal energy to segregate into pure polymer and fullerene phases. Inclusion of additives that are poor solvents for P3HT and good solvent for fullerene lead to formation of ideal morphology consisting of interconnected pure polymer domains that have sharper interfaces for exciton dissociation and lower bimolecular recombination.

Results and Analysis

The chemical structures of the donor and acceptor materials used are shown in Figure 1a. The experimental procedures for film deposition, device fabrication and characterization are

given in detail in Supporting Information. To evaluate the effect of annealing on the optical properties and structural properties of P3HT:PC₆₀BM and P3HT:IC₆₀BA blend films, UV-Visible absorption and XRD diffraction spectra were taken as shown in Figure 1b and Figure 1c respectively. In both cases films without thermal annealing (as deposited) showed a single peak at 476 nm. For P3HT:PC₆₀BM films annealing at and above 80°C, the peak red shifted to 504 nm and also showed formation of vibronic shoulders around 545 nm and 595 nm. These vibronic shoulders formation at 545 nm and 595 nm is related to intrachain and interchain packing of P3HT respectively²⁹⁻³¹. When the P3HT:PC₆₀BM films were subjected to thermal annealing these shoulders start to form suggesting interchain and intrachain stacking. In particular the intensity of the shoulder at 595 nm (0-0 transition) was low in the as deposited films indicating poor packing between chains. When the films were annealed these shoulders become more pronounced which indicated that the P3HT chains assemble to form ordered chains as supported by the XRD spectra. However in P3HT:IC₆₀BA films, the vibronic shoulder at 595 nm had low intensities even when annealed below 120°C. The absorption peaks of P3HT:IC₆₀BA films also stayed at ~ 468 nm and did not show any red shift which represents less crystalline and defective P3HT when blended with IC₆₀BA up to 120°C. Annealing at and above 120°C led to red shift of the peak to 486 nm and annealing beyond 150°C, the vibronic shoulder at 595 nm became more pronounced leading to the conclusion that higher temperatures were required for P3HT chains to pack in P3HT:IC₆₀BA films. This could also be easily observed from the color of the film. The as deposited films had an orange color for both. P3HT:PC₆₀BM films turned purple when annealed at 80°C and above. However the orange color was still visible in P3HT:IC₆₀BA films when annealing temperatures were below 120°C which indicated that ICBA prevented P3HT chains to order at lower annealing temperatures. Figure 1c and d show the XRD spectra of P3HT:PC₆₀BM and P3HT:IC₆₀BA films. A peak at 5.4° was observed for all films corresponding to (1 0 0) diffraction of P3HT³². $2\theta = 5.4^\circ$ relates to d-spacing of 1.61 nm which corresponds to distance between hexyl side chains of P3HT. A small second order (2 0 0) diffraction peak was also observed at 10.5° in annealed films. The as deposited P3HT:PC₆₀BM and P3HT:IC₆₀BA show broad peaks indicating higher disorder and smaller crystallite size of P3HT phase. Annealing the films led to narrowing of (1 0 0) peak which indicated increased crystallite size of P3HT phase. In P3HT:PC₆₀BM negligible change is seen in the XRD peaks when films were annealed above 80°C. However in the case of P3HT:IC₆₀BA broad peaks are observed for as

deposited and 80°C annealed films. With increasing annealing temperatures above 100°C the peaks get narrower up to 150°C after which negligible changes were seen as shown in the inset. The trend in peak narrowing in P3HT:IC₆₀BA is similar to that observed in the vibronic shoulder formation seen in optical absorption spectra. Hence higher annealing temperatures were required for P3HT to aggregate into larger crystallites in P3HT:IC₆₀BA blend films.

Figure 1 (a) Chemical structure of P3HT, PC₆₀BM and IC₆₀BA. UV-Visible absorption spectra of (b) P3HT:PC₆₀BM and (c) P3HT:IC₆₀BA films with different annealing temperatures. X-ray

diffraction spectra of (d) P3HT:PC₆₀BM and (e) P3HT:IC₆₀BA films with different annealing temperatures. Inset shows the region from 4° to 6.5°

To observe the changes in the nanoscale purity of P3HT and PC₆₀BM/IC₆₀BA domains, energy filtered transmission electron microscopy (EFTEM) was performed to obtain donor and acceptor maps. The donor and acceptor maps were overlaid to find the donor purity in as deposited and thermally annealed P3HT:PC₆₀BM and P3HT:IC₆₀BA films as shown in Figure 2. The orange color in EFTEM composite maps corresponds to donor purity (sulfur) and green color shows the acceptor purity. Grey areas in the map are due to thickness variations in the films. In the as deposited films of P3HT:PC₆₀BM and P3HT:IC₆₀BA films small P3HT domains (5 nm – 10 nm width) distributed homogenously throughout the films were observed. P3HT:PC₆₀BM films when annealed at 120°C show larger P3HT domains aggregating together. When annealed at 150°C purer donor domains come together to form an interconnecting network. The donor purity was qualitatively analyzed by the enhanced contrast in the image. However in the case of as deposited and 120°C annealed P3HT:IC₆₀BA films negligible change in donor purity or domain size was observed. When annealed at 150°C formation of interconnected domains was observed. Due to thickness variations in the blend films quantitative analysis was not feasible. From XRD results in Figure 1, it was shown that annealing above 80°C led to the improvement in crystallization of P3HT domains in P3HT:PC₆₀BM blend films. On the contrary, higher annealing temperatures (>120°C) were required in P3HT:IC₆₀BA films to enhance crystallization of P3HT phase. Correlating the XRD and EFTEM results it can be concluded that crystallization of P3HT is the driving force to obtain higher purity polymer domains in the blend films consistent with the observation of other reports³³⁻³⁵. Hence IC₆₀BA mixes with disordered or smaller crystallites of P3HT and further impedes crystallization of P3HT phase to a higher extent than PC₆₀BM. Such a different behavior could be attributed to several different reasons such as higher solubility, molecular structure, size of the molecule, diffusion coefficient in solid state or intermolecular attraction between IC₆₀BA and P3HT. Our results with P3HT:PC₇₀BM shows the same trend as P3HT:PC₆₀BM even though PC₇₀BM has higher solubility than PC₆₀BM³⁶. Hence we believe that higher intermixing between P3HT and IC₆₀BA is not due to its higher solubility and real reason could be due to the physical properties of IC₆₀BA molecule and is not clear yet. The rigid molecular structure of IC₆₀BA due to two

symmetrical indene groups could be one of the major reason that could impede diffusion at lower temperatures, however such a claim requires further experimental proof.

Figure 2 Energy filtered transmission electron microscopy (EFTEM) donor and acceptor composite maps of P3HT:PCBM and P3HT:ICBA thin films with different annealing temperatures

The current voltage characteristics of P3HT:PC₆₀BM and P3HT:IC₆₀BA solar cells with different active layer thermal annealing temperatures are shown in Figure 3a and 3b respectively. As observed thermal annealing was essential to enhance the J_{sc} and fill factor for both P3HT:PC₆₀BM and P3HT:IC₆₀BA solar cells. The photovoltaic parameters are tabulated in Table 1. The best efficiencies (η) obtained for P3HT:PC₆₀BM and P3HT:IC₆₀BA are 3.08% and 4.19% respectively when the active layer was thermally annealed at 180 °C. Higher V_{oc} s (~ 0.25V) were observed for P3HT:IC₆₀BA solar cells attributed to the higher LUMO level of IC₆₀BA (3.74 eV) compared to that of PC₆₀BM (3.91 eV)^{25, 26, 37}. The dependence of V_{oc} , J_{sc} , FF and efficiency with

annealing temperature is shown in Figure 4. There is a small reduction (0.07 V - 0.09 V) in open circuit voltage with thermal annealing for both cases attributed to HOMO level shift formed as a result of improved P3HT crystallization^{38, 39}. In the case of P3HT:IC₆₀BA the J_{sc} and FF showed higher dependence with annealing temperature. J_{sc} increased from 1.66 mA/cm² to 6.22 mA/cm² when annealing temperature is increased from 80°C to 120°C and further increased with higher annealing temperatures till 180 °C. However for P3HT:PC₆₀BM bulk heterojunction solar cells J_{sc} increased from 4.16 mA/cm² in as deposited active layers to 6.62 mA/cm² in 80°C annealed films. No significant change in J_{sc} were observed higher annealing temperatures. Better performance in P3HT:PCBM cells is attributed to increase in fill factor increases with thermal annealing up to 180 °C and negligible decrease was observed when annealed at 200°C. Photovoltaic efficiency trend with annealing temperature shows similar behavior as J_{sc} with annealing temperature. Hence higher (150°C - 200°C) annealing temperatures was required to obtain comparable short circuit current density and photovoltaic efficiencies in P3HT:IC₆₀BA solar cells.

Figure 3 Current-voltage characteristics of (a) P3HT:PC₆₀BM and (b) P3HT:IC₆₀BA with different annealing temperature

Table 1 Photovoltaic parameters of P3HT:PC₆₀BM and P3HT:IC₆₀BA solar cells

Annealing Temperature	P3HT:PC ₆₀ BM				P3HT:IC ₆₀ BA			
	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	η (%)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	η (%)
As deposited	0.69	4.16	0.36	1.03	0.90	1.15	0.29	0.30
80°C	0.64	6.62	0.50	2.14	0.88	1.66	0.31	0.46
120°C	0.61	6.56	0.58	2.33	0.85	6.22	0.45	2.40
150°C	0.61	7.03	0.65	2.77	0.85	7.18	0.58	3.57
180°C	0.63	7.64	0.64	3.08	0.85	8.04	0.61	4.19
200°C	0.61	7.55	0.63	2.90	0.83	7.68	0.60	3.84

Figure 4 Effect of thermal annealing temperature on (a) Voc, (b) Jsc, (c) FF and (d) Efficiency on P3HT:PCBM and P3HT:ICBA solar cells

Figure 5 shows the topography and phase images of the as deposited, 80°C and 150°C annealed P3HT:PC₆₀BM and P3HT:IC₆₀BA blend films. For the as deposited P3HT:PC₆₀BM films fiber type morphology was seen in surface topography images whereas phase images shows both fiber type and agglomerated phases marked by dashed red circles in phase images. When P3HT:PC₆₀BM films were annealed the root mean square (RMS) roughness values increase from 0.77 nm for the as deposited films to 0.81 nm for 80°C annealed films. The RMS roughness for 150°C annealed P3HT:PC₆₀BM films is 1.001 nm. Roughness increase is attributed to swelling of the films due to packing of polymer chains to form larger fiber-like morphology. This can be seen clearly in phase images of P3HT:PC₆₀BM films when annealed. For P3HT:IC₆₀BA samples the aggregated phases are observed in both topography and phase images of as deposited and 80°C annealed films. The aggregated phase is largest in the as deposited films and gets smaller for 80°C films. The RMS roughness increases from 0.53 nm for as deposited films to 0.608 nm for 80°C films. For 150°C annealed films the RMS roughness was found to be 1.28 nm and showed fiber-like morphology. From XRD and optical absorption results, it was shown that P3HT was more disordered and possessed smaller crystallites in P3HT:PC₆₀BM and P3HT:IC₆₀BA films when no thermal annealing was applied. From EFTEM it was observed that in films without thermal annealing P3HT and fullerenes mix very well which led to low domain purity. It was also observed that low annealing temperatures ($\geq 80^\circ\text{C}$) were required for P3HT:PC₆₀BM films however relatively higher temperatures ($\geq 120^\circ\text{C}$) were required in the case of P3HT:IC₆₀BA films to enhance crystallization of P3HT. Based on this, the morphology evolution can be explained by taking into account following three different phases namely a) intermixed disordered polymer and fullerene phase b) crystalline polymer pure phase and c) fullerene nanocrystals or clusters. As deposited P3HT:PC₆₀BM and P3HT:IC₆₀BA films have higher intermixed polymer and fullerene phases that were observed in phase images as agglomerated regions marked by the dashed red circles. Upon thermal annealing of P3HT:PC₆₀BM films at 80°C P3HT crystallized in fibrillar form and these agglomerated phase disappeared. Upon further annealing at 150°C PC₆₀BM phase possibly diffused to form clusters⁷ as seen in the regions marked by yellow dashed circles. For P3HT:IC₆₀BA films the agglomerated phases regions were observed in both as deposited and 80°C annealed films attributed to higher degree of intermixing between disordered phase of P3HT and IC₆₀BA. Annealing at 150°C led to enhancement in P3HT domain size to form interconnected fibers due

to possible growth of IC₆₀BA phase form clusters, 150°C annealed P3HT:IC₆₀BA showed similar morphology as of 150°C annealed P3HT:PC₆₀BM films. Formation of fullerene clusters improved charge transport pathways and hence the fill factor as observed in the photovoltaic performance.

Figure 5 AFM topography and phase images of P3HT:PC₆₀BM and P3HT:IC₆₀BA films. Regions marked in red circles are indication of formation of intermixed phase. Regions marked in yellow circles are indication of formation of fullerene clusters

Further role of solvent additive namely nitrobenzene (NB) on the photovoltaic performance of P3HT:PC₆₀BM and P3HT:IC₆₀BA cells were studied and compared with best annealed devices as shown in Figure 6. 4 and 2 volume percent NB was added to P3HT:PC₆₀BM

and P3HT:IC₆₀BA blend solutions respectively before spin coating the active layers. 180°C was chosen as the annealing temperature for comparison and termed as ‘Annealed’ in all the future sections. It is obvious that NB additive improved the J_{sc} of solar cells with minor changes in V_{oc} and FF in both P3HT:PC₆₀BM and P3HT:IC₆₀BA cells when compared to annealed devices. The power conversion efficiencies were enhanced to 4.32% and 5.77% with the addition of NB in P3HT:PC₆₀BM and P3HT:IC₆₀BA solar cells respectively. The photovoltaic parameters are tabulated in Table 2. The dark curves are shown in supporting information and it is observed that NB modified devices possessed lower saturation current density as well as lower ideality factor than annealed and as deposited devices. Ideality factor has been linked to energy disorder in bulk heterojunction solar cells ⁴⁰, hence addition of NB could lower the energy disorder in the active layers.

Figure 6 Current-voltage characteristics of thermally annealed and solvent additive modified P3HT:PC₆₀BM and (b) P3HT:IC₆₀BA solar cells

Table 2 Photovoltaic parameters of thermally annealed and NB modified P3HT:PC₆₀BM and P3HT:IC₆₀BA solar cells

	V_{oc} (V)	J_{sc} (mA/cm²)	Fill Factor	Efficiency (%)	Enhancement (%)
P3HT:PCBM - Annealed	0.63	7.64	0.64	3.08	-
P3HT:PCBM - 4% NB	0.61	10.83	0.65	4.32	40.26
P3HT:ICBA - Annealed	0.85	8.04	0.61	4.19	-
P3HT:ICBA - 2% NB	0.83	10.99	0.63	5.77	37.71

To investigate the reasoning behind effect of NB on enhanced photovoltaic performance, the morphology was characterized by EFTEM and Kelvin probe force microscopy (KPFM) and compared with as deposited and annealed samples as shown in Figure 7. EFTEM images showed highly intermixed domains in as deposited samples and upon thermal annealing the domain purity increased. Addition of NB additives enhanced the P3HT domain purity with larger interconnected domains as observed from the higher sulfur contrast in EFTEM images. KPFM images of as deposited showed large aggregates (~ 100 nm – 150 nm diameter) of higher surface potential and fiber-like morphology (~ 20 nm mean diameter) as matrix. The RMS surface potential variation of as deposited films was 17.3 mV. In annealed film distinct fiber like domains (~ 15 nm mean diameter) were observed with smaller aggregates (~ 40 nm – 55 nm diameter). The RMS surface potential variation for annealed films increased to 27.5 mV. In the case of NB casted films predominantly fiber type of morphology was observed having average diameter of 20 nm and RMS variation of 41.4 mV. The length scales observed for features in annealed and NB films were consistent with the length scales of pure P3HT domains observed in EFTEM images. To further analyze the KPFM images of the films, surface potential distribution and line profiles were plotted as shown in Figure 7c and 7d. For the as deposited films, a narrow distribution is observed having full width half maximum (FWHM) of 40mV. For annealed and NB modified films, a broader distribution is observed having FWHM of 64 mV and 74 mV respectively were observed. Line profile variation of surface potential showed that as deposited films had the least variation over length. Annealed films showed higher variation and NB modified films showed the highest variation in surface potential. From EFTEM and KPFM

images it can be concluded that NB additive enhanced the domain purity that led to enhanced interfacial potential variation due to less intermixing at domain interfaces. No change in crystallite size was observed in XRD spectra of NB modified films (Supporting Information Figure 3). However optical absorption showed pronounced vibronic shoulders and red shift for films cast with NB additive. This discrepancy could be due to packing orientation of P3HT chains which might not be sensitive to Cu K α X-rays. Further insight is needed on the structural arrangement caused by NB addition and will be carried out in future. Nevertheless, Nitrobenzene (NB) effectively controlled the morphology of polymer-fullerene blends as it selectively solubilized the fullerene and induced self-ordering of purer polymer phase. Due to this selective solubility, blend films cast with NB additive possessed homogeneous interpenetrating network of nanoscale phase separated domains. Thermal annealing also induced crystallization of polymer but due to local inhomogeneity in domain purity⁴¹ and lack of free energy for diffusion of polymer or fullerene, homogenous phase separation between them was not achieved.

Figure 7 (a) EFTEM donor and acceptor composite maps of P3HT:PC₆₀BM films (b) Kelvin probe force microscopy images of P3HT:PC₆₀BM thin films (c) Pixel distribution of surface potential from KPFM images of P3HT:PC₆₀BM thin films. Values in parenthesis show the full width half maximum (FWHM) of Gaussian fits. (d) Line profiles of of P3HT:PC₆₀BM thin films

To evaluate the charge density and lifetime transient photocurrent (TPC) and photovoltage (TPV) spectroscopy were done on as deposited, annealed and NB modified solar cells. From TPV measurements, the charge carrier lifetime were measured with increasing light intensities which led to different V_{oc} in the cells as shown in Figure 8a. Charge carrier lifetime

decreases with increasing V_{oc} attributed to higher bimolecular recombination in the cells at higher light intensity. For the as deposited cells the charge carrier lifetime decreased to a much higher extent at higher V_{oc} s than annealed and NB modified devices. At 1 sun condition when the cell reaches the optimum V_{oc} the measured lifetime for as deposited, annealed and NB modified cells are 1.57 μ s, 3.87 μ s and 5.17 μ s respectively. Charge carrier lifetimes were plotted as a function of charge carrier density as shown in 8b. As deposited cells showed the lowest charge carrier density ($\sim 10^{16}$ cm⁻³) among all cells which decreased rapidly with increasing charge carrier density. For annealed devices, the charge carrier density increased by almost two orders of magnitude compared to as deposited cells. NB modified devices showed higher charge carrier density with lowest decline in lifetime. The slope of the linear region in charge carrier density vs lifetime plots was measured to evaluate the bimolecular recombination order. The bimolecular recombination order obtained for as deposited, annealed and NB modified devices are 8.02, 4.9 and 1.8 respectively. Higher interfacial potential variation in NB modified devices led to efficient exciton dissociation and suppressed interfacial bimolecular recombination^{23, 42}. Charge carrier mobility was evaluated using photo-charge carrier extraction by linearly increasing voltage (Photo-CELIV) technique. The Photo-CELIV at 10 μ s delay time for as deposited, annealed and NB modified solar cells are shown in Figure 8c. The Photo-CELIV current signal approached maximum earlier (lower t_{max}) in NB modified cells than annealed devices. The as deposited samples had the highest t_{max} of 5.35 μ s among all solar cells. t_{max} for annealed and NB cells were 4.7 μ s and 3.4 μ s respectively. Since the same voltage ramp was used for all cells lower t_{max} is related to lower bias voltage (field) required to extract the maximum charge carriers from the device. NB modified solar cells showed the highest mobility of 4.81×10^{-5} cm²/Vs and also resulted in the highest extracted charge carriers (n_{ext}) of 4.35×10^{16} cm⁻³.

Figure 8 Charge carrier lifetime as a function of (a) open circuit voltage and (b) charge carrier density. The values in the legend of (a) and (b) show the charge carrier lifetime at 1 sun Voc and bimolecular recombination order respectively. (c) Photo-CELIV spectra of P3HT:PC₆₀BM solar cells at 10 μs delay time between light pulse and voltage ramp, and (d) extracted charge carrier density (n_{ext}) from photo - CELIV curves with varying delay times.

Conclusions

Bulk heterojunction solar cells were fabricated with two different fullerene derivatives and the effect of thermal annealing on the active layer morphology and device performance was studied. It is seen that higher thermal annealing temperatures were needed for IC₆₀BA compared to PC₆₀BM for obtaining enhanced photovoltaic efficiency. The increase in efficiency was due to increased short circuit current density and fill factor. Increase in short circuit current density and fill factor is attributed to the polymer crystallization and formation of fullerene clusters respectively. Higher thermal annealing temperature was required for P3HT crystallization in

P3HT:IC₆₀BA blends due to higher intermixing between P3HT and IC₆₀BA. Domain purity was observed to increase when crystalline P3HT domains existed suggesting that fullerene mixing is only with disordered P3HT. It is well known that fullerene molecules cannot thermodynamically exist in between crystalline P3HT chains. In this case it was found that degree of mixing is dependent upon the fullerene derivative used which dictated the thermal energy required for adequate phase separation between pure polymer and acceptor phases. Further role of solvent additive on the device performance was evaluated and it was observed that small concentration (2-4 volume percent) of solvent additive (NB) significantly enhanced the short circuit current density that led to higher device efficiency. Detailed insight into domain purity and nanoscale surface potential variation was provided and compared for three different cases – as deposited, annealed and NB additive modified solar cells. It was observed that NB modified blends had higher domain purity consisting of interconnected crystalline P3HT domains. Higher domain purity led to sharper interfaces giving rise to higher surface potential variation. Due to these sharper interfaces, NB modified devices showed suppressed bimolecular recombination and enhanced charge carrier mobility and lifetime when compared to thermally annealed and as deposited solar cells. Addition of NB led to a morphology ideal for high efficiency bulk heterojunction solar cells as it gives rise to lesser energetic disorder and effective charge transport pathways. This led to less effective charge transport pathways due to the presence of impure domains which act as sinks for recombination. Hence inclusion of solvent additive provides a simple and effective technique to improve photovoltaic device efficiency of bulk heterojunction solar cells.

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Graphical abstract

Donor and acceptor composite mapping of energy filtered transmission electron microscopy (EFTEM) measurement in P3HT:PCBM and P3HT:ICBA thin films with different annealing temperatures.