Correlation Between Morphology and Device Performance of pBTTT:PC₇₁BM Solar Cells

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Abstract

Phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) could intercalate between the side-chains of poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene (pBTTT) creating a stable co-crystal structure, so optimal solar cell performance was obtained at high PC₇₁BM concentrations promoting phase separated electron conductive pathways. Neutron reflectivity, with the application of magnetic contrast variation, was used to investigate the concentration profile of PC₇₁BM within the active layer. And this profile was found to be homogeneous through the film thickness. Small angle neutron scattering was utilized to find there is amorphous PC₇₁BM even at 50 wt% of fullerene while previously it was believed that all fullerene was consumed to form co-crystals when its concentration is below 75 wt%. These fullerene molecules evolve into approximately 15 nm sized agglomerates to improve the electron transport when their concentration is above 75 wt%. Thermal annealing gives these agglomerates mobility to form micrometer sized crystals causing a decrease of device performance. These findings can therefore correlate the morphology, especially in terms of fullerene agglomerates, vertical concentration profile and percolat-

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ing structure they formed, with the device performance and provide valuable guidance for optimal morphology design of polymer:fullerene solar cells.

Keywords: Polymer:fullerene Solar cells, Co-crystal, Neutron scattering, Fullerene agglomerate, Exciton recombination

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1. Introduction

Polymer:fullerene solar cells have attracted substantial interest in scientific and industrial research because of their potential for low cost and fast roll-to-roll production on a flexible light weight substrate [1, 2]. The light absorbing
5 material is typically a mix of conjugated polymer acting as the electron donor and a fullerene derivative, which is the electron acceptor. They are blended together to form a phase separated interpenetrating structure at the nanometer scale creating the so called bulk-heterojunction (BHJ) solar cells [3]. Strongly Coulomb-bound electron-hole pairs (excitons) are generated when light excites
10 the polymer because of its low dielectric constant [4, 5]. The exciton diffusion length is only 5~10 nm, so it is required that they be created near the interface of the polymer and fullerene-rich domains to facilitate energetically favorable charge separation [6]. In order to warrant the charge transport, a certain degree of phase separation between donor and acceptor domains is also needed to form
15 continuous pathway throughout the active layer. Such dual requirements suggest an optimum morphology for the active layer consisting of long interpenetrating domains of order 5~10 nm in dimension [7, 8].

Therefore, much effort has been made to obtain efficient devices by controlling the morphology of the active layer through the use of various solvents,
20 solvent additives and inclusion of inorganic materials in addition to post processing procedures such as thermal and solvent vapor annealing [1, 9, 10, 11, 12]. A wealth of knowledge on the correlation between morphology and device performance has been obtained based on a number of structural characterization techniques, including small angle and soft X-ray scattering [13, 14], various

25 electron microscopies [15, 16] and atomic force microscopy [8].

Previous neutron reflectivity and small angle neutron scattering measurements on 1:1 weight ratio poly(3-hexylthiophene):[6,6]-phenyl-C₆₁-butyric acid methyl ester, P3HT:PCBM, have shown a nonuniform vertical distribution of phase segregated PCBM in the P3HT matrix after film deposition. Relatively
30 higher concentrations of PCBM were found near both the substrate and air interface than the active layer's bulk region, which is not a preferred structure, since PCBM is desired to be near the air interface and the subsequently deposited aluminum electrode can collect the electrons. By applying thermal annealing, the PCBM concentration near the air interface increases and PCBM agglomerates
35 grow into a larger size, creating percolating structure and better electron transport pathways resulting in improved device performance [17, 18, 19]. Therefore, relative high amount of fullerene near the cathode is proved to benefit the electron transport. Hence, it is necessary to study whether this phenomenon could be found in many systems optimized for best device performance with a
40 polymer:fullerene blend close to 1:4 by weight, such as poly(2-methoxy-5-(3',7'-dimethyloxy)-*p*-phenylene vinylene) (MDMO-PPV:PC₆₁BM) [20] and poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene:phenyl-C₇₁-butyric acid methyl ester (pBTTT:PC₇₁BM) [21].

It is discovered that in the pBTTT:PC₇₁BM system, PC₇₁BM can intercalate
45 late between the side chains to form a thermodynamically stable bimolecular structure because the side chains of pBTTT are further apart than they are in P3HT. A *bimolecular crystal*, i.e. co-crystal, of pBTTT and PC₇₁BM is formed when these two chemical species are in this ordered arrangement [22]. As a result of this intimate mixing, exciton harvesting is much better in pBTTT:PC₇₁BM
50 [21] in contrast to the P3HT:PCBM system [17]. Since the formation of the co-crystal consumes a large amount of PC₇₁BM, a high ratio of fullerene relative to the polymer must be used in the active layer to form continuous conductive pathways to the electrodes through phase separation. Indeed, the optimum device performance was obtained at 75%-80% PC₇₁BM weight fraction. Due to
55 the large amount of fullerene required, the limited solvent solubility and the

large band gap energy of pBTTT, this system is not expected to perform as well as other polymer systems.

In this study, we rationalize the correlation between the pBTTT:PC₇₁BM's morphology and device performance through an analysis of the fullerene intercalation, vertical distribution of fullerene molecules, optical properties of the active layers, and the shape and size of PC₇₁BM aggregates that form electron conductive pathways. Magnetic contrast neutron reflectivity (MCNR), small angle neutron scattering (SANS) and other complimentary characterization methods were applied to obtain insight of the active layer's morphology for a system that promotes a co-crystal while simultaneously requires a phase separated structure.

2. Materials and Methods

For device fabrication, an ITO (indium tin oxide) coated one inch square (1 inch square = 6.45 cm²) glass slide (sheet resistance of 8-12 $\Omega/\square$, Delta technologies, LTD) was cleaned by ultrasonic treatment in acetone and isopropanol sequentially for 15 minutes each. This was followed by spin coating a $\sim$ 33 nm thick layer of Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, H.C. Starck, Al 4083) which was then transferred to an oven and annealed for 20 minutes at $\sim$ 130 $^{\circ}$ C. After this, the slide was transferred to a nitrogen-filled glove box ($\leq$ 0.1 ppm of O₂ and H₂O) to fabricate a device. The solutions required for spin coating the active layer were prepared by dissolving pBTTT-C₁₄ (Luminescence Technology Corp.) and PC₇₁BM (Nano-C) in *ortho*-chlorobenzene in a nitrogen glove box. A wide PC₇₁BM loading range was used from 0 wt% to 91.7 wt% at a total polymer and nanoparticle concentration of 24 mg/ml. All materials were used as received. The solution preparation method was used as reported before [23]. In order to have complete dissolution, the solution was stirred for 9 hours at 90 $^{\circ}$ C. Before spin coating onto the PEDOT substrate, it was cooled to 60 $^{\circ}$ C. The solution was then spin coated at 600 rpm (60 rpm = 1 hertz) for 60 seconds, after filtering through a 0.2 μ m Teflon filter, to obtain an approximately 90 nm thick layer. A hotplate set at

180 °C was used to anneal the films for 10 minutes to obtain a high degree of polycrystallinity. This temperature is above the glass transition temperature of pBTTT ($T_g \sim 50$ °C) [24]. Lithium fluoride (0.8 nm thickness) and aluminum (80 nm thickness) were sequentially thermal evaporated in a deposition chamber at a vacuum of 2×10^{-6} mbar. The device area was approximately 0.1 cm^2 . The current-voltage curves were measured with a Keithley 2400 source meter, under illumination of 100 mW/cm^2 from 150 W solar simulator with AM1.5G filters.

For grazing incidence X-ray diffraction (GIXRD) measurements, the samples were prepared on silicon wafers instead of ITO glass. A Rigaku Ultimate IV multipurpose XRD system was used to perform all the X-ray scattering measurements which used a $1.54 \text{ \AA}$ wavelength Copper $K\alpha$ source with a 0.5° fixed incident angle in the 2θ mode. The UV-vis absorption spectra were measured on a Shimadzu UV-3600 spectrometer in transmission mode. All the samples were coated on soda-lime glass with a PEDOT:PSS layer, whose absorption was subtracted as a background signal. Photoluminescence measurement were performed on a Horiba Jobin Yvon Fluoromax-4 spectrofluorometer with an incident wavelength of 512 nm using identical samples to the UV-vis absorption measurements.

All neutron experiments were performed at the NIST Center for Neutron Research (NCNR). For neutron reflectivity, magnetic substrates with a permalloy and gold layer deposited on 2 inch (1 inch = 2.54 cm) diameter sapphire disks were prepared at NIST. Permalloy (thickness $\sim 115 \text{ \AA}$, 81% nickel, 19% iron) and gold (thickness $\sim 170 \text{ \AA}$) were deposited on the sapphire substrate sequentially in the same chamber by using a sputtering system. For neutron reflectivity, a rough film surface makes it difficult to collect high quality data during the limited available beam-time. So a higher spin coating speed was used to make a smoother film. In previous work done by Kiel *et al.*, a very similar P3HT/PCBM concentration profile was obtained for samples spin coated at 2500 rpm and 800 rpm [18], which gives us confidence to use a higher spin coating speed to make a flatter film surface without completely changing the

PC₇₁BM concentration profile. So a spin speed of 1500 rpm was used to have a uniform thin film to run the magnetic contrast neutron reflectivity (MCNR) test. The film thickness was ~ 30 nm. The NG-1 reflectometer was used for data collection with an incident neutron wavelength of $4.75 \text{ \AA}$ which had a spread
120 of 1.5% or less. In order to increase the signal to noise (S/N) ratio within the limited beam-time a smaller q -range was used to collect data. Fitting of the data was performed by using `ga_refl` program [25].

A one inch diameter (100) silicon wafer was used as the substrate for small angle neutron scattering and a PEDOT:PSS and active layer were spin coated
125 on it as described above. For SANS measurements, the film roughness is not as critical as it is for the reflectivity measurements. In order to mimic the active layer in actual devices, a spin coating speed of 600 rpm was used to make an active layer having a 90 nm thickness. Since the silicon substrate is essentially transparent to neutrons, a stack of 12 wafers was used as one sample
130 to increase the scattering signal [26]. The NG3 30m SANS instrument was used for the neutron scattering experiment. Three detector distances and two neutron wavelengths were used: distances of 1.33 meters and 4 meters were used with a wavelength of $6 \text{ \AA}$ and 13.2 meters with a wavelength of $8.4 \text{ \AA}$. Data were obtained over the scattering vector (q) range of $0.008 \leq q \leq 0.3 \text{ \AA}^{-1}$,
135 where $q = (4\pi/\lambda) \sin(\theta/2)$, and a total scattering count of $\sim 10^6$ was used to increase the S/N ratio. Empty cell scattering and background scattering were performed for data conversion to absolute scattering intensity versus scattering vector. Data reduction and SANS analysis was performed using NCNR SANS packages SANS Reduction v 5.20 and SANS Analysis v 7.1 [27]. The incoherent
140 scattering background was obtained by plotting $q^4 I(q)$ versus q^4 at large q [28]. The slope of this function is the sum of the incoherent scattering and a thermal scattering contribution both of which can be easily subtracted from the total scattering intensity. The magnitude of the background for all samples was small and around $0.7\text{--}1.8 \text{ cm}^{-1}$.

Figure 1: GIXRD pattern of pure pBTTT and pBTTT:PC₇₁BM blend thin film at various fullerene weight fraction: (a) as cast and (b) annealed at 180 °C for 10 min. For pure pBTTT, (100) and (200) diffraction peaks can be used to calculate the d -spacing between the polymer backbone. Blending with PC₇₁BM lowered the diffraction intensity, so only one peak was observed which shifted to lower q .

2.1. Disclaimer

Certain commercial equipment, instruments, materials, suppliers, or software, are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

3. Results and Discussion

3.1. Grazing Incidence X-ray Diffraction

Grazing incidence X-ray diffraction was used to determine the d -spacing, i.e. lamellar stacking spacing, for pure pBTTT polymer and pBTTT:PC₇₁BM blends and to examine the ordering of the structure. A series of peaks corresponding to the d -spacing ($h00$) are shown in Figure 1. For as cast samples, the d -spacing of pure pBTTT is about 21.2 Å. By increasing the PC₇₁BM weight fraction, an expansion in the lamellar stacking direction was seen until at a

Figure 2: Optical microscope of the annealed samples with various PC₇₁BM weight fraction. Large surface density of star-shaped micrometer sized PC₇₁BM crystal was seen with its higher loading.

concentration of 50 wt% where it remained constant at 29.4 Å. This expansion is caused by PC₇₁BM intercalation between the side chains of pBTTT as seen before [22, 23]. It should be noted more PC₇₁BM improves the ordering of the co-crystal. However, when the fullerene concentration is above 75 wt%, less polymer is available to form this co-crystal structure resulting in a weaker signal. After thermal annealing, the (100) peak shifted to a lower q value for all the samples below 75 wt% PC₇₁BM, which suggests a little larger distance between the polymer backbone [29, 30].

3.2. Optical Microscopy

Phase separation at micrometer length in annealed samples was observed through optical microscopy for PC₇₁BM weight fractions above 50% as shown in

Figure 2. Phase separation was only present for annealed samples while as cast samples showed none so they are not displayed here. Micrometer sized PC₇₁BM crystal are observed when the weight fraction is above 50% and the colored edges are due to light interference effects from changes in the film thickness. The size and substrate surface coverage of these crystal increased with higher PC₇₁BM weight fraction. Similar phenomenon in other polymer:fullerene blends has been observed previously by several groups [31, 32, 33, 34]. Obviously thermal annealing gave PC₇₁BM the mobility to form these large structures when the co-crystal could no longer incorporate more nanoparticles. Here we do a rough calculation assuming an average pBTTT molecular weight of 60 kDa based on the manufacturer’s specifications. The repeat unit of pBTTT has a molecular weight of 0.695 kDa, so the degree of polymerization is $N = 86$, PC₇₁BM has a molecular weight of 1031 Da. So for a PC₇₁BM 50 wt% mixture, there are 58 PC₇₁BM molecules per pBTTT molecule which has 86 repeat units. A 60 wt% mixture will have 87 PC₇₁BM molecules per pBTTT molecule, which is very close to the number of pBTTT repeat units. Based on this simple estimate, this implies the co-crystal fully formed at a concentration of approximately 60 wt%, which is consistent with the GIXRD data shown in Figure 1 since above this concentration the excess fullerene form agglomerates. However, the Figure 2c clearly shows fullerene agglomerates which are not supposed to be there because all the fullerene could have been mixed in the polymer matrix based on the calculations above. This suggests that not all PC₇₁BM may participate in forming co-crystals with pBTTT, and the amorphous fullerene forms agglomerations upon thermal annealing.

3.3. Magnetic Contrast Neutron Reflectivity

Kiel *et al.* demonstrated that the nanoparticle concentration profile played an important role in the performance of P3HT:PCBM solar cells and determined this by using phase sensitive neutron reflectivity (PSNR) [18, 35]. Air and D₂O were used as two reference layers to get multiple neutron contrast conditions to yield a unique concentration profile from reflectivity data. Analysis with neu-

Figure 3: Magnetic contrast neutron reflectivity from three PC₇₁BM weight fraction as cast pBTTT:PC₇₁BM films are shown in (a), (b) and (c). Black line is simultaneous fitting curve. Homogeneous nuclear SLD profiles are gained in (d) from PEDOT to air side. A 95% confidence interval was used when the raw reflectivity data were averaged.

neutron reflectivity gives the fullerene concentration profile throughout the whole active layer with quantitative accuracy [36, 37]. In this study, we used state-of-the-art neutron reflectivity methods, with the application of magnetic contrast variation, to investigate the concentration profile of fullerene in the active layers in order to understand the morphological difference from 50 to 83.3 wt% PC₇₁BM concentration and how it related to devices performance. There are two advantages in using magnetic contrast neutron reflectivity (MCNR): i) it is simple to obtain multiple neutron contrast data from a reference layer by tuning the polarization of neutron beam [38, 39, 40, 41], and ii) MCNR avoids the use of D₂O as a contrast agent which dissolves the PEDOT:PSS layer if PSNR was used. However, there is also limitation to this technique. High quality data is difficult to be obtained from annealed samples due to the roughness induced by phase separation of PC₇₁BM at micrometer length scale requiring much longer beam-time to increase the S/N ratio. Figure 3 shows the MCNR data from as cast samples and the extracted nuclear scattering length density (SLD) profile ($\rho(z)$), which is a function of PC₇₁BM volume fraction profile ($\phi_{\text{PC}_{71}\text{BM}}(z)$) within the active layer. We have

$$\rho(z) = \phi_{\text{PC}_{71}\text{BM}}(z) \rho_{\text{PC}_{71}\text{BM}} + (1 - \phi_{\text{PC}_{71}\text{BM}}(z)) \rho_{\text{pBTBT}} \quad (1)$$

195 , where $\rho_{\text{pBTBT}} (= 0.546 \times 10^{-6} \text{ \AA}^{-2})$ is the scattering length density of pure pBTBT and $\rho_{\text{PC}_{71}\text{BM}} (= 3.91 \times 10^{-6} \text{ \AA}^{-2})$ is the scattering length density of pure PC₇₁BM, which were determined by specular neutron reflectivity (shown in the supporting materials) [42, 43, 44]. Since the polarized neutron beam has two spin states (spin “up” and spin “down”), it interacts with the permalloy
200 (iron-nickel) layer to have a large magnetic scattering length density difference. Reflectivity of the spin “up” state is about an order of magnitude larger than the value for the spin “down” state. This allows one the ability to overcome the ambiguity from a single reflectivity data by simultaneously fitting these two reflectivity curves. The fitting approach was based on a slab model, in which
205 $\rho(z)$ is divided into a certain number of slabs each having a uniform thickness

Figure 4: Normalized PC₇₁BM concentration profile is shown in (a), the higher concentration profile accompanied with higher PC₇₁BM weight fraction. In (b), integration under PC₇₁BM vol% profile curve in (a) was used to compare with PC₇₁BM vol% from initial mixture to check the validity of fitting.

and constant SLD value [38]. Gaussian interfacial roughness was also added between slabs, and a certain number of steps can be chosen to smooth the overall profile [45]. Since the substrate's thickness and SLD is known beforehand, it is possible to make a set of constraints so only the PEDOT and active layer parameters like thickness and SLD profile are changed. The PEDOT's SLD was set at $1.64 \times 10^{-6} \text{ \AA}^{-2}$ based upon our previous results [18]. The active layer region is defined by putting a dividing line at the middle of the interfacial (Gaussian) roughness region at the PEDOT and air interface. The quality of fitting was very good judged by the small χ^2 values, between 1 to 3 ($\chi^2 = 1$ is an indicative of perfect fit) [46].

As shown in Figure 4a, the volume fraction profile of the PC₇₁BM within the active layer ($\phi_{\text{PC}_{71}\text{BM}}(z)$) converted from the SLD profile with Equation 1. By integrating under the PC₇₁BM vol% profile curve in Figure 4a, we can obtain the average value of the PC₇₁BM volume fraction throughout the active layer. Comparing the PC₇₁BM vol% from fitting the reflectivity data to the expected value from the initial mixture finds a good result, the difference between them is within 7% as shown in Figure 4b. This check of mass balance provides confidence

in the accuracy of the fits to MCNR data.

In P3HT:PCBM organic solar cells, the PCBM nanoparticles were found to
225 aggregate at both the substrate and near the air interface due to a balance of
convective flow and enthalpic and entropic forces [18, 47, 48]. However, this
phenomenon is not seen in the pBTTT:PC₇₁BM blend. From all these samples,
a fairly homogeneous PC₇₁BM concentration profile is formed throughout the
active layer with a decreasing concentration at both the substrate and air inter-
230 faces. It suggests that the formation of those co-crystals trapped most of the
fullerene molecules in the active layers' bulk region. Although the desired accu-
mulation of fullerene near air side is not seen in this system, the large amount of
fullerene, in 75 and 83.3 wt% samples, should be still able to form a percolating
structure to improve the transport of electrons to the cathode. It also should
235 be noted that the data sets fit perfectly well to a uniform layer, but in principle
we can not rule out inhomogeneity in general (for example a very thin increased
SLD layer at the surface).

3.4. Optical Properties

The results in Figure 5a,b depict the ultraviolet-visible absorption spectra
240 of the as cast and annealed samples coated on glass slices. The absorption co-
efficient maximum from the as-cast pure polymer centered around 530 nm and
decreases as PC₇₁BM is added. Compared with PC₆₁BM, PC₇₁BM has lower
structural symmetry allowing energy transitions which could improve light ab-
sorption also creating excitons [49]. However, this also induces exciton recom-
245 bination in the fullerene phase when free charges not created. Therefore, pho-
toluminescence (PL) data is plotted in logarithm scale in Figure 5c and 5d to
understand the degree of exciton recombination within these samples [17, 50].
PL quenching from both graphs was observed when fullerene was blended with
polymer due to fine mixing of the donor and acceptor materials forming a co-
250 crystal, which is consistent with previous findings from the McGehee group [23],
indicating exciton separation is highly efficient with the presence of a co-crystal
structure. The signature peaks at 770 nm and 820 nm clearly point to the pres-

Figure 5: The absorption spectra, normalized by active layer thickness, of the as cast and annealed samples are shown in (a) and (b). Photoluminescence from the same samples are shown in (c) and (d) respectively.

Figure 6: Power conversion efficiency (PCE) as a function of PC₇₁BM weight fraction of as cast and annealed samples. The improvement of PCE is mainly from the higher J_{sc} . Rough interface and exciton recombination in fullerene crystal also affect the fill factor and V_{oc} . A 95% confidence interval was used when the collected data were averaged.

ence of pure PC₇₁BM, which suggests the excitons recombination also occurs in the pure fullerene phase. The PL intensity slightly increases in the annealed samples due to the growth of star shaped PC₇₁BM crystals observed in Figure 2. This is expected since these large fullerene crystals at the length scale of micron meters (shown in Figure 2) is much larger than the exciton diffusion length (~ 10 nm), resulting in a higher degree of exciton recombination and PL intensity.

3.5. Device Performance

The corresponding device performance parameters as a function of PC₇₁BM weight fraction are shown in Figure 6. The maximum power conversion efficiency obtained at a PC₇₁BM concentration of 75% weight fraction for both the as cast and annealed samples is driven by the optimal short current density. Since the light absorption decreases due to less polymer in the blend, the higher current suggests more efficient exciton harvesting to compensate the negative

effect from the insufficient exciton generation. However, the lower fill factor for higher PC₇₁BM loading samples implies that the charge collection at the electrode interface is poor despite a higher current density [51]. As discussed above, the increased amount of pure fullerene not forming a co-crystal at high PC₇₁BM concentration, also absorbs light and induces exciton recombination, which leads to the reduction of the open-circuit voltage (V_{OC}) [52]. For annealed samples at higher fullerene loading, exciton recombination causes a drastic loss in V_{OC} due to the formation of large PC₇₁BM crystals.

3.6. Small Angle Neutron Scattering

By using SANS, morphological information on the length scale of 2 ~ 80 nm was obtained. Absolute intensity, $I(q)$, versus wave vector (q) as a function of PC₇₁BM weight fraction and thermal annealing are presented in Figure 7a and b. As shown in Figure 7b, for annealed samples having 75 and 83.3 wt% PC₇₁BM, the scattering curves follow a power-law of the form $I(q) \sim q^{-4}$ at small q , which arises from the surface roughness of the films caused by phase separation of fullerene at micrometer length scale as shown in Figure 2. A diffraction peak of (100) at $q = 0.21 \text{ \AA}^{-1}$ was observed after thermal annealing for the 50 wt% sample, which is caused by PC₇₁BM intercalation and consistent with the X-ray diffraction patterns seen in Figure 1. A much broader peak at the same position is also shown in as cast sample of 50 wt% suggesting a lower crystallinity of the co-crystal. For as cast samples, the scattering curves from 75 and 83.3 wt% fullerene concentration indicate polydisperse sphere behavior [53]. Modeling the PC₇₁BM agglomerates as polydisperse spheres (having a Schulz distribution) with a hard sphere interaction and surrounded by a matrix of pBTTT and solubilized PC₇₁BM allowed some general conclusions to be made. The fitting results were obtained and listed in Table 1, which are PC₇₁BM agglomerate diameter, PC₇₁BM agglomerate vol% and PC₇₁BM vol% trapped in pBTTT matrix [17, 19, 54, 55]. About 15 nm diameter size agglomerate formed in the matrix. The total volume fraction of PC₇₁BM was used to confirm the validity of fitting. The total PC₇₁BM vol% from fitting are 72% and 81%, which

Figure 7: Small angle neutron scattering for as cast and annealed samples are shown in (a) and (b). The solid curves in (a) are from polydisperse sphere (Schulz distribution) model fitting to give the PC₇₁BM agglomerate size and volume fraction within the active layer. The solid line in (b) is a power law fit indicating the scattering originating from rough surface. The arrow points to the (100) diffraction peak which indicates the d -spacing of the co-crystal. Kratky plots are shown in (c) and (d) to display the particle-like characteristic of the samples' morphology. A 95% confidence interval was used when the raw scattering data were averaged.

Table 1: Polydisperse spheres (with Schulz distribution) fitting results and distance between agglomerates of high concentration PC₇₁BM as cast samples. PC₇₁BM vol% in total was used to check the validity of fitting. A 95% confidence interval was used when the fitting procedures were performed.

	75 wt%	83.3 wt%
PC ₇₁ BM agglomerate radius (nm)	7.9 ± 0.5	7.1 ± 0.9
PC ₇₁ BM agglomerate vol%	22 ± 3	24 ± 2
PC ₇₁ BM vol% in pBTTT matrix	50 ± 4	57 ± 3
PC ₇₁ BM vol% in total (from initial mixture)	72	80
Distance between agglomerates (nm)	10.4 ± 1.3	8.6 ± 2.3

are in good agreement with PC₇₁BM vol% from initial mixture 71% and 80% respectively. By having the PC₇₁BM agglomerate vol%, we can also estimate the distance, H , between these agglomerates by assuming random packing, $H/D = (1/\phi)^{1/3} - 1$, where D is the agglomerate mean diameter, and ϕ is the volume fraction of PC₇₁BM agglomerate [17, 56]. The distance H decreases slightly from 10.4 nm to 8.6 nm simply because of the increased PC₇₁BM wt%. Thus, the electron transport could be improved by having shorter distance between fullerene agglomerates.

Kratky plots ($q^2 I(q)$ vs q) are shown in Figure 7(c) and (d) by plotting $q^2 I(q)$ as a function of scattering vector q , which allows one to find, $q^2 I(q) = 2\phi V (\Delta\rho)^2 / (R_g)^2$ in the high q limit ($q > 5R_g^{-1}$). Here, ϕ is the volume fraction of scattering centers, V is the volume of a single scattering center, $(\Delta\rho)^2$ is the square of the difference in the scattering length density between solvent and scatterer, i.e. contrast, and R_g is the radius of gyration of the scatterer. The curve should asymptotically reach a plateau (constant value) for an ideal Gaussian coil. However, the peak displayed in the low q regime is an indicative of particle-like feature caused by PC₇₁BM agglomerates in this case [56, 57]. For as cast 83.3 wt% sample, more PC₇₁BM molecules are kinetically trapped in less amount of pBTTT matrix compared with as cast 75 wt% sample. This results in lower contrast, $(\Delta\rho)^2$, between polymer matrix and PC₇₁BM, thus, lower curve maximum. It should be noted that the d -spacing ($d = 2\pi/q$) value converted from the peak position cannot be directly associated with the size of

the particles or the distance between them. It simply points out the featured
length scale of the studied structure. So in this case, for as cast samples, 75 and
320 83.3 wt% fullerene molecules form a structure at length scale of about 37 nm
($q \approx 0.017 \text{ \AA}^{-1}$). For annealed samples, 75 and 83.3 wt% samples show no peak
in obtained q range and their curves go upward at ultra low q regime. Since the
curve in Kratky plot has to reach origin point ($q^2 I(q) = 0$ when $q = 0$), so a
325 peak has to be formed at ultra low q regime suggesting a structural feature at
much larger length scale. This agrees with the micrometer sized fullerene crys-
tals as demonstrated in Figure 2. For 50 wt% samples, as cast sample shows
a broad hump in the range of 0.04 to 0.08 $\text{\AA}^{-1}$, a length scale of about 1.6 to
7.8 nm suggesting the existence of amorphous or small PC₇₁BM agglomerates.
330 The annealed sample's curve maximum is at $q \approx 0.03 \text{ \AA}^{-1}$ indicating a length
scale of about 21 nm, which suggests the formation of fullerene agglomerates
causing higher degree of phase separation after thermal annealing. In previous
section 3.2, the existence of PC₇₁BM not forming co-crystal below 60 wt% is
merely a speculation based on the optical microscopy images. Here, by analyzing
335 the SANS data, a more affirmative answer has been given. Therefore, based on
the above analysis, a schematic graph was drawn to summarize the morphologi-
cal changes caused by different fullerene weight fractions and thermal annealing,
as shown in Figure 8. For as cast 50 wt% samples, some PC₇₁BM molecules mix
into pBTTT and form not fully intercalated co-crystals, the others are amor-
340 phous or in the form of small agglomerates. After thermal annealing, these
amorphous or small agglomerates grow into larger size causing higher degree
of phase separation. For as cast 75–83 wt% samples, about 15 nm fullerene
agglomerates and fully intercalated co-crystals improve excitons harvesting and
electron transport to increase the device performance. However, after thermal
345 annealing, micrometer sized fullerene crystals cause rough interface between the
active layer and cathode resulting in low efficiency. From the MCNR results,
for as cast samples, PC₇₁BM concentration profile on the vertical direction of
active layers is basically homogenous. However, it is not for certain that the
thermal annealing would not affect this homogenous PC₇₁BM distribution along

Figure 8: Morphology schematic for as cast and thermal annealed samples with various PC₇₁BM weight fraction.

the vertical direction. Further study is required to answer this question.

4. Conclusion

The correlation between morphology and device performance of pBTTT:PC₇₁BM solar cells was studied in this article. Co-crystals of polymer and fullerene are formed by PC₇₁BM molecules intercalating between polymer side chains improving the excitons dissociation. The weight fraction fullerene molecules for a fully intercalated co-crystal was calculated yielding a value of 60 wt% PC₇₁BM. Kinetically trapped fullerene not forming co-crystal was observed even below 60 wt% giving a more precise picture of the morphology for pBTTT:PC₇₁BM system. By having large amount of PC₇₁BM agglomerates, electron transport was improved. Thus, as cast 75 wt% PC₇₁BM sample delivers the optimal efficiency by having excellent excitons harvesting and efficient electron transport at the same time. However, this improved electron transport costs the price of

less amount of polymer resulting in much less light absorbed in the system. So
a more balanced polymer:fullerene ratio with improved charge transport will be
the focus of future research. Both magnetic contrast neutron reflectivity and
small angle neutron scattering are proved to be very helpful in analyzing this
complex system. In the future, these advanced characterization techniques can
bring more exciting discoveries in the field of organic electronics.

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