



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

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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 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 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 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, solvent additives and inclusion of inorganic materials in addition to post processing procedures such as thermal and solvent vapor annealing [1,9–12]. 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 electron microscopies [15,16] and atomic force microscopy [8].

Previous neutron reflectivity and small angle neutron scattering measurements on 1:1 wt 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 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

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the subsequently deposited aluminum electrode can collect the electrons. By applying thermal annealing, the PCBM concentration near the air interface increases and PCBM agglomerates grow into a larger size, creating percolating structure and better electron transport pathways resulting in improved device performance [17–19]. 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 polymer: fullerene blend close to 1:4 by weight, such as poly(2-methoxy-5-(3',7'-dimethyloxy)-*p*-phylene 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 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 [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 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 in. square = 6.45 cm²) glass slide (sheet resistance of 8–12 Ω/□, Delta technologies, LTD) was cleaned by ultrasonic treatment in acetone and isopropanol sequentially for 15 min each. This was followed by spin coating a ~33 nm thick layer of Poly(3,4-ethylenedioxythio-phenylene): poly(styrenesulfonate) (PEDOT: PSS, H. C. Starck, Al 4083) which was then transferred to an oven and annealed for 20 min at ~130 °C. After this, the slide was transferred to a nitrogen-filled glove box (<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 di-*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 h at 90 °C. Before spin coating onto the PEDOT substrate, it was cooled to 60 °C. The solution was then spin coated at 600 rpm (60 rpm = 1 hertz) for 60 s, after filtering through a 0.2 μm Teflon filter, to obtain an approximately 90 nm thick layer. A hotplate set at 180 °C was used to anneal the films for 10 min 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 cm². The current-voltage curves were measured with a Keithley 2400 source meter, under illumination of 100 mW/cm² 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 Å wavelength Copper Kα 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 in. (1 in. = 2.54 cm) diameter sapphire disks were prepared at NIST. Permalloy (thickness ~115 Å, 81% nickel, 19% iron) and gold (thickness ~170 Å) 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 Å which had a spread 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 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 to increase the scattering signal [26]. The NG3 30 m SANS instrument was used for the neutron scattering experiment. Three detector distances and two neutron wavelengths were used: distances of 1.33 m and 4 m were used with a wavelength of 6 Å and 13.2 m with a wavelength of 8.4 Å. Data were obtained over the scattering vector (*q*) range of $0.008 \leq q \leq 0.3 \text{ \AA}^{-1}$, where $q = (4\pi/\lambda)\sin(\theta/2)$, and a total scattering count of ~10⁶ 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 scattering background was obtained by

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