



# Solid solution phenomenon in the amorphous conjugated polymer:fullerene bulk heterojunction structure

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## ABSTRACT

The solid solution phenomenon in the amorphous PCDTBT:PC<sub>71</sub>BM blend was investigated. It has been disclosed that the PCDTBT:PC<sub>71</sub>BM blend with less than 20% PC<sub>71</sub>BM may form a kind of solid solution structure, which demonstrates a deeper HOMO level, a higher hole mobility, more free charges and less trap density than those of the pure PCDTBT film. It may well explain why the typical PCDTBT:PC<sub>71</sub>BM bulk heterojunction solar cells require higher PC<sub>71</sub>BM ratio to achieve a high power conversion efficiency. In that case, a portion of PC<sub>71</sub>BM is well intermixed with PCDTBT to form a solid solution phase and others form a pure PC<sub>71</sub>BM phase. It is the PCDTBT:PC<sub>71</sub>BM solid solution but not the pure PCDTBT to serve as the donor phases and to form interpenetrating networks with PC<sub>71</sub>BM phases. The PCDTBT:PC<sub>71</sub>BM solid solution phases favor to increase the V<sub>OC</sub> and enhance the charge collection leading to a high photovoltaic performance for the PCDTBT:PC<sub>71</sub>BM bulk heterojunction solar cells.

## 1. Introduction

Solar cells based on organic molecules and conjugated polymers have attracted more and more attention since they have some unique advantages including light weight, high flexibility and potential for low-cost and large-area solution-processed manufacturing, *etc* [1–4]. Up to date, the highest power conversion efficiency (PCE) of polymer solar cells (PSCs) approaches 15% [5], which has surpassed the record of commercial  $\alpha$ -Si solar cell modules. As the key component of PSCs, the bulk heterojunction (BHJ) active layer comprising of the donor and acceptor materials is responsible for converting all photon absorbed into charges. According to a traditional viewpoint, BHJ was considered as a donor phase-acceptor phase interpenetrating structure derived from the donor-acceptor phase separation for efficient exciton dissociation and charge collection [6,7]. However, more and more phenomena could not be well explained by the simple assumption and researchers realized that the practical status in BHJ may be more complex. McGehee and coworkers verified for the first time the existence of bimolecular crystal of fullerene and conjugated polymer in BHJ in 2009 [8]. Before long, Ade et al. found that the amorphous domains of donor polymer contain a significant concentration of fullerene acceptors, which means presence of a new phase in addition to pure donor and acceptor phases in BHJs [9]. In recent years, a lot of experiments have demonstrated that such kind of domains caused by

the miscibility of polymer and fullerene is ubiquitous in their BHJ and it is irrelevant to the crystallization behavior of polymer and fullerene derivatives [10–13]. More importantly, the new phase has many unique physical natures including energy level [14–16] and carrier mobility [17,18], which is quite different from those of polymer donor and fullerene acceptor. Obviously, this new phase may play a very important role in determining the final photovoltaic performance of PSCs. Deep insight into the nature of such kind of new phase is benefit to understanding the working mechanism and developing high-efficiency PSCs. In this work, the typical amorphous conjugated polymer poly [N-9'-heptadecanyl-2, 7-carbazole-alt-5, 5-(4', 7'-di-2-thienyl-2', 1',3'-benzothiadiazole)] (PCDTBT) is deliberately selected as donor material and combines with phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM) to form a BHJ structure. The miscibility between PCDTBT and PC<sub>71</sub>BM is investigated and it is found that low amount of PC<sub>71</sub>BM may disperse completely in PCDTBT matrix to form a kind of solid solution with a threshold PC<sub>71</sub>BM:PCDTBT value less than 1:4 (weight ratio). Further increasing the PC<sub>71</sub>BM ratio above the threshold value, PC<sub>71</sub>BM molecules in the solid solution phase is saturated and started to form pure PC<sub>71</sub>BM acceptor phase. It is further disclosed that the solid solution phase of PCDTBT:PC<sub>71</sub>BM has deeper the highest occupied molecular orbital (HOMO) energy level, lower work function and higher hole mobility compared with the pure PCDTBT film. Moreover, the solid solution phase has high free carrier concentration and low trap density

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due to more holes were activated at room temperature originated from its smaller activation energy. As a result, the solid solution/ $C_{60}$  bilayer device also showed a better photovoltaic performance than that of the control PCDTBT/ $C_{60}$  solar cell.

## 2. Experimental

PCDTBT and  $PC_{71}BM$  were dissolved in 1,2-ortho-dichlorobenzene to prepare their solutions. The concentration was 3.5 mg/mL for pure PCDTBT solution and 3.5–0.7 mg/mL for PCDTBT: $PC_{71}BM$  blend solution. The solid films were prepared via spin-coating their respective solutions on the substrate at 700 rpm for 150 s and then dried slowly at room temperature. It should be noted that post thermal annealing was not applied to keep good miscibility between PCDTBT and  $PC_{71}BM$  in the resultant films. The corresponding PCDTBT: $PC_{71}BM$  films are very uniform and phase separation is not distinctly observed in their atom force microscope (AFM) and transmission electron microscope (TEM) images. All procedures were completed in a glove box. Electrochemical measurements were carried out on a CHI660 electrochemical analyzer with a three-electrode cell at a scan rate of 100 mV/s. Tetrabutylammonium hexafluorophosphate ( $Bu_4NPF_6$ , 0.1 mol/L) was used as the supporting electrolyte. A glassy carbon with 10 mm diameter, a Pt wire and a saturated calomel electrode (SCE) were used as the working electrode, counter electrode and reference electrode, respectively. The PCDTBT or PCDTBT: $PC_{71}BM$  films were deposited on the working electrode and measured in anhydrous acetonitrile ( $CH_3CN$ ). The potential was calibrated by ferrocene/ferrocenium ( $Fc/Fc^+$ ). Field-effect transistor (FET) devices were prepared on the heavily n-doped Si wafer with a 300-nm-thick  $SiO_2$  as an insulator and the unit capacitance of  $SiO_2$  was 10 nF/cm<sup>2</sup>. The FET structure was bottom-gate and top-contact configuration. Gold was used as both the source and drain electrodes. The length and width of the channel are 200  $\mu m$  and 6 mm, respectively. The indium tin oxide (ITO) coated glass with a sheet resistance of 15  $\Omega/\square$  was used as substrate for the photovoltaic cells, which was ultrasonicated in acetone, alcohol and deionized water in sequence and then dried by pure  $N_2$  gas. Poly(3,4-ethylene dioxithiophene):poly(styrenesulphonate) (PEDOT:PSS) was spin-coated on the ITO glass and baked at 155 °C for 15 min. All samples were prepared on ITO/PEDOT:PSS substrate for UPS test. The devices with a structure of ITO/PEDOT:PSS/active layer/Au were used for conductivity test and the devices with a structure of ITO/PEDOT:PSS/active layer/ $C_{60}$ /LiF/Al were used for photovoltaic measurement.

## 3. Results and discussion

### 3.1. Ultraviolet photoemission spectroscopy (UPS)

The interfacial electronic structures of the non-annealed pristine PCDTBT: $PC_{71}BM$  blend films with various  $PC_{71}BM$  ratios were firstly studied via ultraviolet photoemission spectroscopy (UPS). UPS measurement using a He I radiation (21.22 eV) source was performed to determine the HOMO and the vacuum level positions of the PCDTBT: $PC_{71}BM$  blend films relative to ITO Fermi level. For the collection of secondary electrons, the samples were biased at  $-10$  V. Fig. 1(a) shows the evolution of the UPS spectra of the miscibility films with the  $PC_{71}BM$  ratio from 1% to 80% in regard to the pristine pure PCDTBT film. It is seen that at the initial stage with small amount of  $PC_{71}BM$  ratio, the work function shifts gradually toward the low binding energy side up to 0.2 eV, while the HOMOs remain unchanged with increasing the ratio to 20%. Ionization potential (IP) is the distance between HOMO and  $E_{vac}$ , which is an intrinsic property of a material. The change of IP indicated the formation of solid solution. When the  $PC_{71}BM$  ratio beyond 20%, the work function shifts toward to the high binding energy. For a high ratio of  $PC_{71}BM$ :PCDTBT blend films, the pure  $PC_{71}BM$  phase may gradually occur in addition to the PCDTBT: $PC_{71}BM$  miscibility phase, namely solid solution phase. As a

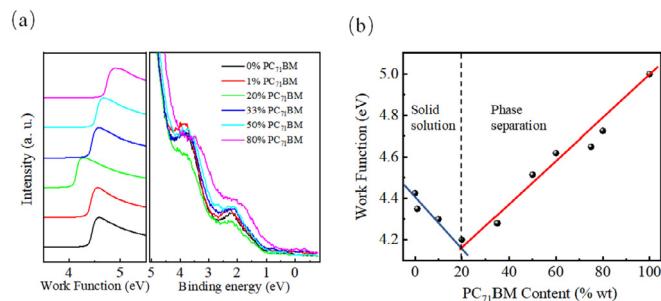


Fig. 1. (a) UPS spectra of the work function and HOMO in the PCDTBT: $PC_{71}BM$  blend films with varied  $PC_{71}BM$  content. (b) The measured work function changes of the PCDTBT: $PC_{71}BM$  blend films with varied  $PC_{71}BM$  composition.

result, a heterojunction effect may be presented between the solid solution phase and  $PC_{71}BM$  phase. The surface work function of the blend films shows an increase due to the alignment of their Fermi levels. Fig. 1(b) demonstrates the evolution of work function with various ratios of  $PC_{71}BM$  for the PCDTBT: $PC_{71}BM$  blend films. The cross point indicates the maximum  $PC_{71}BM$  ratio to form the solid solution in the PCDTBT: $PC_{71}BM$  blend film. Above the value, the pure  $PC_{71}BM$  phase is gradually presented.

### 3.2. Cyclic voltammograms (CV) and absorption spectra

As the UPS results of the PCDTBT: $PC_{71}BM$  blend film did not clearly detect the slight change of HOMO energy level, cyclic voltammograms (CV) method was further used to estimate HOMO energy level of the corresponding films, which was calculated by the equation:  $E_{HOMO} = -(4.8 + E_{ox}^{onset})$  eV. As shown in Fig. 2(a), the  $E_{HOMO}$  of pure PCDTBT was  $-5.61$  eV. The value is shifted to  $-5.68$  eV with the PCDTBT bringing in 1%  $PC_{71}BM$  and reaches the maximum of  $-5.71$  eV with 20%  $PC_{71}BM$  being incorporated. With gradually increasing the  $PC_{71}BM$  ratio to 33% and 50%, the  $E_{HOMO}$  values are slightly raised to  $-5.67$  eV and  $-5.66$  eV, respectively. The trend is completely consistent with the variation of work function measured with UPS. These results confirm that the amorphous PCDTBT and  $PC_{71}BM$  are well intermixed to form solid solution structure when the  $PC_{71}BM$  ratio is less than 20% in the blend. The PCDTBT: $PC_{71}BM$  solid solution show a deeper HOMO level than that of pure PCDTBT, which may be the real HOMO value of donor phase for determining the  $V_{OC}$  in currently reported PCDTBT: $PC_{71}BM$  BHJ PSCs. The absorption spectra of the PCDTBT: $PC_{71}BM$  solid solution films with different proportions of  $PC_{71}BM$  are shown in Fig. 2(b). The absorption of solid solution films is almost overlapped with the pure PCDTBT, indicating that the optical band gap of the solid solution was the same as pure PCDTBT.

### 3.3. Electric characteristic of the solid solution

The electrical characteristics of the pure PCDTBT and solid solution thin films with 15% wt.  $PC_{71}BM$  is investigated by using the field effect

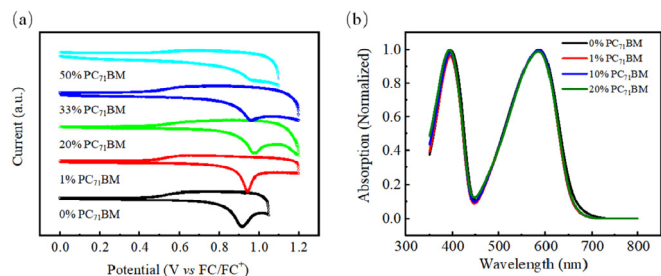


Fig. 2. (a) CV curves and (b) normalized absorption spectra of the PCDTBT: $PC_{71}BM$  blend films with various  $PC_{71}BM$  ratios.

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