



# Effects of different polar solvents for solvent vapor annealing treatment on the performance of polymer solar cells



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## ABSTRACT

The effects of different polar solvents on the performance of solvent vapor annealing treated polymer solar cell (PSC) with a structure of ITO/ZnO/PTB7: PC<sub>71</sub>BM/MoO<sub>3</sub>/Ag was systematically investigated by applying different polar solvents, including methanol, ethanol, dimethylsulfoxide, acetone and isopropanol. By analyzing the variation of PSC performance and the morphology of active layer, we found that both the solubility parameters ( $\Delta$ ) and viscosity of solvent were playing an important role in controlling the morphology of PTB7: PC<sub>71</sub>BM blend. Especially, the PSC treated by methanol with high  $\Delta$  and low viscosity exhibited a remarkable enhancement of power conversion efficiency from 6.55% to 8.13%. The performance improvement was mainly due to the formation of the nanoscale crystallization of PTB7: PC<sub>71</sub>BM blend and the moderated aggregation of PC<sub>71</sub>BM, resulting in efficient charge separation, balanced charge transport and suppressed charge recombination.

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## 1. Introduction

Polymer solar cell (PSC) is comparable to its inorganic counterparts such as amorphous silicon, CIGS, CdTe, and recently developed inorganic–organic hybrid perovskite solar cells by exhibiting great potential in low cost, easily manufactured, flexible and high efficiency of converting solar energy into electricity, which has attracted continue unabated interests in last decades [1–5]. The state-of-art PSCs are often incorporating bulk heterojunction (BHJ) to combine the electron donating with electron accepting organic semiconductors homogeneously for large D/A contact interface [6,7]. The donor and acceptor organic materials undergo phase separation, resulting in continuous phase domain sizes on the order of nanometers for facile charge separation and better charge transporting to the

responding electrode in best BHJs [8–10]. Moreover, both the orientation of crystallites within the domains and the molecular packing within each domain are both critical to the device performance [11,12]. A typical BHJ is obtained by spin casting a solution of conjugated polymer mixed with fullerene. However, as-cast PSC often exhibits low photovoltaic performance due to the fast evaporation rate of solvent, leading to more disorder morphology of the active layer [13,14]. In this regard, several strategies have been employed to modify and control the morphology of polymer–fullerene BHJs, such as thermal annealing, solvent treatment and solvent vapor annealing (SVA) [13,15,16].

Among them, thermal annealing is the most widely applied method for improving the power conversion efficiency (PCE) of PSCs, which has been demonstrated could benefit the charge transport, structure development and device performance [17,18]. However, the high temperature of thermal annealing limits its application, which may lead to both the crystals with large size and the

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degradation of conjugated polymers [19,20]. Alternatively, the above problems could be addressed by the incorporation of simple polar solvent SVA treatment. It can increase the ordering of polymer component and the local demixing of fullerene component through precisely controlling the morphology of active layer, resulting in the enhancement of short current density ( $J_{SC}$ ), fill factor ( $FF$ ) and  $PCE$  [21,22]. Compared with thermal annealing, SVA can also provide potential advantages over more controlled nanoscale phase separation and more thermodynamic stable morphology of active layer [23].

Effects of SVA are mainly dependent on the properties of applied polar solvents. And the solubility parameters ( $\Delta$ ) of polar solvents have been proved to be correlated with the changes in surface roughness of the active layer when directly exposed to the solvents [22]. Thus far, however, there has been no detailed investigation of the effects of polar solvents on the performance of SVA treated PSC. Also, the guidelines for how to select a compatible polar solvent for further achieving high efficiency PSC is still lack of research.

In this work, the systematic investigation of the effects of different polar solvents on the photovoltaic performance of thieno [3,4-b]thiophene/benzodithiophene (PTB7): (6,6)-phenyl-C71-butyril acid methyl ester (PC<sub>71</sub>BM) PSCs was performed by applying different polar solvents, including methanol, ethanol, dimethylsulfoxide (DMSO), acetone and isopropanol (IPA). It was found that both the  $\Delta$  and viscosity of solvent are critical to the SVA performance. Compared with other four solvents, methanol with high  $\Delta$  and low viscosity could significantly increase the  $PCE$  of PSC from 6.55% to 8.13%. The mechanism of polar solvents for SVA treatment was elucidated through characterizing both the morphology of active layers by atomic force microscopy (AFM) and the charge carrier mobility by theoretic simulation using space-charge-limited current (SCLC).

## 2. Experimental

For the inverted structure PSC, the device configuration is ITO/ZnO (40 nm)/PTB7: PC<sub>71</sub>BM (100 ± 15 nm)/MoO<sub>3</sub> (15 nm)/Ag (100 nm). ITO-coated glass substrates with a sheet resistance of 10 Ω/sq were consecutively cleaned in ultrasonic bath containing detergent, acetone, deionized water and ethanol for 10 min each step, then dried by nitrogen blow. Prior to film deposition, the substrate was treated by UV light for 10 min. The ZnO precursor was prepared by dissolving zinc acetate dihydrate (Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, Aldrich, 99.9%, 1 g) and ethanolamine (NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH, Aldrich, 99.5%, 0.28 g) in 2-methoxyethanol (CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OH, Aldrich, 99.8%, 10 ml) under vigorous stirring for 12 h for the hydrolysis reaction in air. 40 nm ZnO ETL was spin-cast from the precursor solution on top of the clean ITO-glass substrate, and annealed at 200 °C for 1 h in air [24]. Then, the active layer of PTB7: PC<sub>71</sub>BM was cast from a solution with PTB7: PC<sub>71</sub>BM ratio of 1:1.5 wt% in chlorobenzene at a concentration of 10 mg/ml, then spin coated at a rate of 1000 rpm for 60 s in a nitrogen glove box. The solvent vapor annealing process was completed by placing polymer films

in a vacuum desiccator full of solvent vapor for different time. Subsequently, ~15 nm MoO<sub>3</sub> and ~100 nm Ag layers were finally deposited at a pressure of  $3 \times 10^{-3}$  Pa in vacuum. Device architecture and schematic energy diagrams for flat band conditions of the PSC in this study are shown in Fig. 1a and b, respectively.

The morphology of active layer was characterized by AFM (MFP-3D-BIO, Asylum Research). Current density–voltage ( $J$ – $V$ ) curves under illumination were measured with Keithley 4200 programmable voltage–current source. A light source integrated with a Xe lamp (CHF-XM35, Beijing Trusttech Co. Ltd.) with an illumination power of 100 mW/cm<sup>2</sup> was used as a solar simulator [4]. All the measurements were carried out in air at ambient circumstance without any encapsulation.

## 3. Results and discussion

### 3.1. Performance of methanol treated PSC for SVA

Methanol is a typical polar solvent with great potential in surface engineering in photovoltaics [15,22]. It has been reported that the direct exposure of the methanol on the surface of PTB7: PCBM blend could lead to an enhancement of open circuit voltage ( $V_{OC}$ ) by increasing the surface charge density and reducing the surface traps. [15,25] Compared to the direct exposure treatment, SVA offers a more precise control of solvent to hinder the formation of amorphous morphology of active layer, resulted from uncontrollable overreaction between the solvent and active layer [26]. Therefore, herein, methanol was introduced at first to identify the effects of polar solvent for SVA treated PSC performance.

Fig. 2 shows the  $J$ – $V$  characteristics of methanol treated PSCs, and the detailed information is listed in Table 1. It can be seen that methanol SVA could obviously improve device performance. As SVA for 5 min, the  $FF$  increased from 61.1% to 63.7%, which may be due to the decrease of surface trap states [15]. When SVA for 10 min, the  $V_{OC}$  of the device increased from 0.69 V to 0.71 V. This phenomenon was consistent with the methanol solvent treatment, which was mainly ascribed to the enhanced  $V_{bi}$  in PTB7: PC<sub>71</sub>BM PSC via Fermi level pinning between cathode and PC<sub>71</sub>BM acceptor in the active layer [27]. As 15 min SVA,  $V_{OC}$  and  $FF$  of the PSC were significantly increased, corresponding to 0.73 V and 66.2%, respectively, resulting in the  $PCE$  as high as 8.13%. In general,  $J_{SC}$  and  $FF$  could be intimately affected by series resistance ( $R_S$ ), charge transport properties, charge extraction and charge recombination [24,28]. The  $R_S$  of PSC was 0.27 Ω cm<sup>2</sup>, which was only one fifth of that of as-cast PSC. The reduced  $R_S$  made a contribution to the high  $FF$  for more efficient charge transport and less charge recombination. While further increasing the SVA time to 20 min, the  $J_{SC}$  of PSC was decreased from 16.62 mA/cm<sup>2</sup> at 15 min SVA to 16.13 mA/cm<sup>2</sup> at 20 min SVA, which may be attributed to the increase of charge recombination.

To verify the above hypothesis, we examined the photocurrent density ( $J_{ph}$ ) of PSCs.  $J_{ph}$  is defined by  $J_{ph} = J_{light} - J_{dark}$ , where  $J_{light}$  and  $J_{dark}$  stand for the

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