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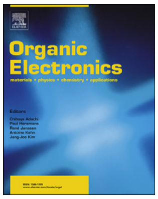

Morphology-driven photocurrent enhancement in PTB7/PC$_{71}$BM bulk heterojunction solar cells *via* the use of ternary solvent processing blends

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ABSTRACT

PTB7/PC$_{71}$BM bulk heterojunction solar cell devices with high photocurrents were fabricated through processing their active layers from a ternary solvent system. The active layers were deposited from solutions where chlorobenzene (CB) was used as the main solvent, DIO (3%) as the solvent additive and cyclohexanone (CHN), a solvent in which both the polymer and fullerene are poorly soluble. The morphology of the different active layers was characterized by atomic force microscopy (AFM) and grazing incidence X-ray scattering (GIXRS) while charge extraction (CE) and transient photovoltage (TPV) techniques were used to measure charge carrier recombination kinetics. It was found that this ternary solvent system affects the *J-V* characteristics to a significant extent, mainly affecting the J_{SC} and FF, in a trend where the J_{SC} is seen to increase with increasing ratio of CHN/CB, while the FF decreases concomitantly. This increase in J_{SC} has been correlated with an increase in crystallinity of the active layer and more specifically with an increase of the crystalline volume of the fullerene domains and the increase in the polymer crystallites size, while the decrease in FF was linked to non-optimal vertical segregation. Despite the drop in FF, the addition of CHN in the blend still leads to an overall increase in power conversion efficiency (PCE) with respect to the devices processed from pristine CB (6.86% vs. 7.31%).

1. Introduction

Organic solar cells hold great promise for commercial applications due to numerous advantages over conventional technologies, *e.g.* mechanical flexibility and low manufacturing costs [1–3]. In the past decade, solution processed bulk heterojunction (BHJ) polymer solar cells (PSC) with high efficiencies have been reported and, although power conversion efficiencies (PCEs) over 11% have been achieved [4–7], a significant increase is still necessary if PSCs are to reach the market. In recent years, many studies have focused on the development of new donor and acceptor materials with optimized band gaps for enhanced spectral coverage. Focus has also been on tuning the charge transport layers to ensure all photo-generated charges in the active layer are extracted [8–12]. While the intrinsic properties of the materials must be finely tuned, it is also imperative that extrinsic loss mechanisms are minimized. This can be achieved through careful control of the BHJ morphology [13–15]. As such, it has been demonstrated that the crystallinity of the active layer, in particular, has a dramatic impact on numerous properties of solar cell devices [16,17]. More specifically, the crystalline volume, crystallite size and crystallite orientation of the polymer domains, have shown to be key in obtaining higher PCEs [18–20]. These parameters have been shown to be tunable by the thermal or solvent annealing post deposition processes, and more recently, by the use of solvent additives in the processing solution [21–24]. High boiling point solvents such as dichlorobenzene (DCB) or 1,8-diiodctane (DIO) in addition to the main processing solvent have shown to promote the formation of homogeneously distributed crystalline domains of polymers in the active layer resulting in a significant improvement of the solar cells characteristics [25,26]. Ternary solvent mixtures have, in some cases, led to further improvement with respect to the single solvent and binary solvent systems [27]. In the case of PDPP3T/PCBM blends, for example, processing the active layers from a ternary solvent mixture (DCB/Chloroform/DIO) has shown to have a positive impact on the interface between donor and acceptor domains resulting in solar

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cells with higher PCEs [28].

The use of additive has, as well been a requisite for obtaining record PCEs in benchmark PTB7/$PC_{71}BM$ devices [29–34]. However, the effect of ternary solvent systems on the morphology and the crystallinity of PTB7/$PC_{71}BM$ active layers has not yet been reported. We thus chose to investigate the effect of processing the active layer of PTB7/$PC_{71}BM$ devices with a ternary solvent system on the devices characteristics. Basing our approach on previous reports [35,36] the active layers were processed using chlorobenzene (CB) as the solubilizing solvent, DIO as the solvent additive and cyclohexanone (CHN), a solvent in which both the polymer and fullerene are poorly soluble. We examined the effect of processing the PTB7/$PC_{71}BM$ blend with a CB/CHN/DIO solvent mixture on the crystallinity of the active layers, the *J-V* characteristics of the devices, and on the charge carrier recombination kinetics. The morphology of the active layer was characterized by atomic force microscopy (AFM) and grazing incidence X-ray scattering (GIXRS) while we used the charge extraction (CE) and transient photovoltage (TPV) techniques to assess the effect on charge carrier recombination kinetics. We found that this ternary solvent system affects the *J-V* characteristics to a significant extent, mainly affecting the J_{SC} and FF. This effect has been correlated with an increase in crystallinity of the active layer and most significantly with an increase of the crystalline volume of the fullerene domains and the increase in the polymer crystallites size.

2. Results and discussion

A 1:1.5 (w/w) donor/acceptor (D/A) ratio of PTB7 to $PC_{71}BM$ and the use of solvent additive (3% DIO v/v) have been reported to lead to the highest PCEs for PTB7-based devices [32]. Therefore, PTB7:$PC_{71}BM$ blend solutions of identical D/A ratio and a constant volume of DIO (3% in volume of total solvent) was used in the present study. However the active layers were processed using pure CB and solvent mixtures of CB/CHN in different ratios (3:1, 2:1 and 1:1). The blend solution were aged for 24 h prior to the active layer deposition. The aging time was optimized in a preliminary study (see Fig. S1, ESI). The devices were fabricated with the standard ITO/PEDOT:PSS/PTB7:$PC_{71}BM$/Ca/Ag configuration and their performance was evaluated at 1 SUN (AM 1.5G) illumination. The *J-V* characteristics of the devices processed with different ratios of CB/CHN are depicted in Fig. 1a. The relevant parameters extracted from the *J-V* curves are summarized in Table 1. Devices whose active layer was processed from CB/DIO exhibit a PCE of 6.86% with an open circuit voltage (V_{OC}) of 0.73 V, a short circuit current (J_{SC}) of 14.55 mA/cm^2 and a 64% fill factor (FF). All the devices fabricated with and without CHN exhibited similar V_{OC} values ranging from 0.72 V to 0.74 V. Upon the introduction of CHN into the blend, the performance improved significantly mainly due to an increase in the J_{SC}. Devices processed from a 3:1 CB/CHN ratio exhibit a short circuit current of 15.24 mA/cm^2 with a corresponding PCE of 7.1%. When the ratio of CB/CHN is increased to 2:1, the PCE further increases to 7.31% concomitant with an increase in J_{SC} (16.20 mA/cm^2) and a slight reduction of the FF to 61%. Further increasing the ratio of CB/CHN to 1:1, induces an additional increase in J_{SC} to 16.92 mA/cm^2, however the PCE decreases to 6.82% due to a strong reduction of the FF (56%). In addition, it should be noted that devices made solely with a CB:CHN blend (without DIO) showed very poor *J-V* characteristics further confirming the superiority of the ternary blend with respect to the binary blend (Fig. S7).

In order to investigate the origin of the increase in J_{SC}, we recorded the external quantum efficiency (EQE) of the devices processed with and without CHN (Fig. 1b). All EQE spectra show a broad optical response in the entire visible spectral range (from 350 nm to 850 nm).

The contribution to the J_{SC} in the region from 350 to 600 nm is mainly due to the absorption of $PC_{71}BM$, while it is due to the absorption of PTB7 from 600 to 800 nm (Fig. 1b, absorption

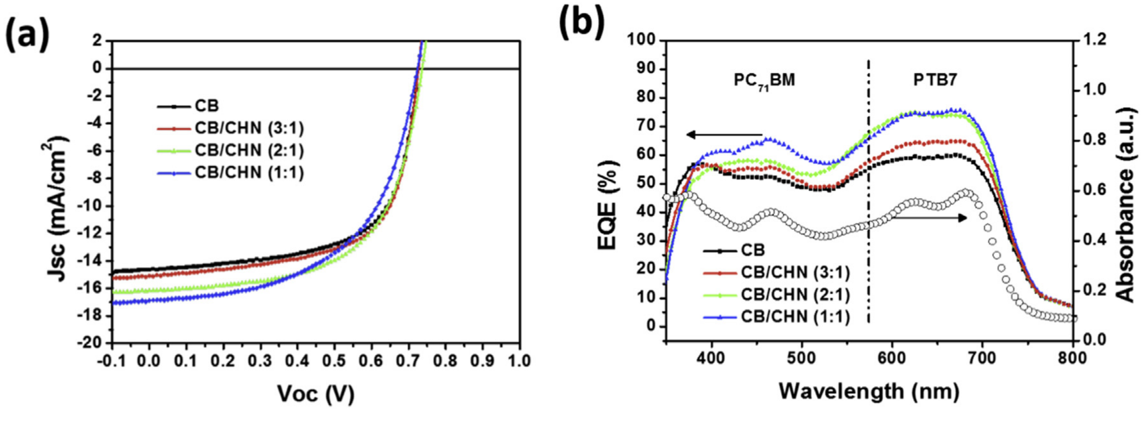

Fig. 1. (a) *J-V* characteristics recorded at 1 SUN illumination (AM 1.5 G) of devices processed from different solvent blends: CB, CB/CHN (3:1), CB/CHN (2:1) and CB/CHN (1:1). All the blends contain 3% DIO in volume. (b) EQE spectra of the corresponding devices, and absorbance spectrum of the active layer processed from pristine CB (see ESI for individual absorbance spectra).

Table 1
Photovoltaic performance of device processed from different solvents.

Solvent	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)[a]	R_s (Ω)	R_{sh} (Ω)	Hole mobility cm^2/(V·S)
CB	0.73	14.55	64	6.86 (6.82)	13	7077	5.7 (±0.016) × 10^{-5}
CB/CHN (3:1)	0.73	15.24	64	7.1 (6.96)	13	5310	3.5 (±0.013) × 10^{-5}
CB/CHN (2:1)	0.74	16.2	61	7.31 (7.16)	28	10011	4.8 (±0.023) × 10^{-5}
CB/CHN (1:1)	0.72	16.92	56	6.82 (6.68)	40	5277	2.3 (±0.015) × 10^{-5}

[a] The value under parenthesis corresponds to the PCE averaged over 7 devices (see Fig. S5, for individual devices PCEs and corresponding device parameters).

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