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Letter

Origin of high fill factor in polymer solar cells from semiconducting polymer with moderate charge carrier mobility

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ABSTRACT

The fill factor of polymer bulk heterojunction solar cells (PSCs), which is mainly governed by the processes of charge carrier generation, recombination, transport and extraction, and the competition between them in the device, is one of the most important parameters that determine the power conversion efficiency of the device. We show that the fill factor of PSCs based on thieno[3,4-b]-thiophene/benzodithiophene (PTB7):[6,6]-phenyl C_{71}-butyric acid methylester ($PC_{71}BM$) blend that only have moderate carrier mobilities for hole and electron transport, can be enhanced to 76% by reducing the thickness of the photoactive layer. A drift–diffusion simulation study showed that reduced charge recombination loss is mainly responsible for the improvement of FF, as a result of manipulating spatial distribution of charge carrier in the photoactive layer. Furthermore, the reduction of the active layer thickness also leads to enhanced built-in electric field across the active layer, therefore can facilitate efficient charge carrier transport and extraction. Finally, the dependence of FF on charge carrier mobility and transport balance is also investigated theoretically, revealing that an ultrahigh FF of 80–82% is feasible if the charge mobility is high enough ($\sim 10^{-3}$–10^{-1} cm^2/V s).

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1. Introduction

Polymer bulk heterojunction solar cells (PSCs) have attracted tremendous interest in the past decade because of their potential as low-cost, large-area, flexible and renewable energy sources [1–6]. To date, the power conversion efficiency (PCE) of PSCs, which is determined by the open-circuit voltage (V_{OC}), the short-circuit current (J_{SC}), and the fill factor (FF), has reached 10% in both single junction devices and tandem cells [7–13]. In general, among all of the three device performance parameters, FF is the most sensitive one, which is closely related to the bulk properties of the photoactive layer and the interfacial properties between each layer. Specifically, as revealed by many experimental works and device modeling studies [14,15], the FF of PSCs is primarily limited by the charge carrier transporting/collection properties [15,16], charge recombination [17–19], and space charge effects [20,21], where charge carriers mobilities [22–25] and the balance between them [26] play important role. Recently Guo et al. demonstrated high FF (up to 80%) in PSCs by using highly ordered polymer with enhanced hole mobility on the order of 10^{-3} cm^2/V s as electron donor [27], highlighting the importance of hole mobility

[28] and optimized film morphology in PSCs. The results also clearly indicated that the FF of PSCs can be as high as that of the conventional silicon-based solar cells ($\sim$81% for monocrystaline devices and $\sim$78% for noncrystalline devices, respectively) [29], despite the huge charge mobility difference between them (10^{-3} cm^2/V s versus 10^3 cm^2/V s). On the other side, limited by their disordered nature, the vast majority of the widely-studied polymer donors only show low or moderate hole mobilities (much less than 10^{-6}–10^{-4} cm^2/V s). As a result of the low mobility and the consequent severe recombination loss, the FF of many PSCs reported to date from many promising donor material systems is typically in range of 50–70%. Given these facts, it is crucial to achieve high FF in the PSCs from these donor materials. We also note that in the past few years, more and more conjugated polymers with high hole mobility (over 10^{-2} cm^2/V s) [30–37], have been successfully developed for organic photovoltaic application. Among various types of high mobility polymers, state-of-the-art polymers based on diketopyrrolopyrrole (DPP) exhibits very high hole mobility on the order of 10^1 cm^2/V s [32,36], and were expected to deliver high FF values in polymer solar cells if device fabrication are fully optimized.

Here we report the realization of high FF ($\sim$73–76%) in polymer solar cells from a semiconducting donor with moderate hole mobility on the order of 10^{-5}–10^{-4} cm^2/V s magnitude.

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Furthermore, the FF shows a clear dependence on the active layer thickness, with a FF of 76% for a thinner active layer and a FF of 73% for a thicker active layer. Supported by the simulation results as obtained from a drift–diffusion model [14,15], redistribution of charge carriers in the photoactive layer and the concomitant reduced bimolecular recombination loss were quantitatively indentified as the major reason responsible for the improved FF. In addition, our results also show that higher hole carrier mobilities (on the order of 10^{-3}–10^{-1} cm^2/V s) are needed in order to further push the FF of PSCs toward its theoretical upper limit (80–82%). In very high hole carrier mobilities region (exceeding 10^{-1} cm^2/V s), FF is found to decrease as a result of increased recombination loss, which can partially explain why state-of-the-art polymers with high hole carrier mobilities did not lead to record high FF in polymer solar cells.

2. Results and discussion

The polymer solar cells were fabricated from blend of a low bandgap semiconducting polymer thieno[3,4-b]thiophene/benzodi thiophene (PTB7) and [6,6]-phenyl C$_{71}$-butyric acid methyl ester (PC$_{71}$BM), on ITO coated rigid glass substrate, following the procedures described in our previous papers [4]. The device structure is ITO/PEDOT:PSS/PTB7:PC$_{71}$BM/PFN/Ca/Al, where PEDOT:PSS is poly (3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Clevios P PVP AI 4083, H.C. Starck Inc.) and PFN is poly ((9,9-bis(3′-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)) (PFN) used as anode and cathode buffer layer [38–40], respectively.

Shown in Fig. 1 is the typical current density versus voltage (*J–V*) characteristics of the PSCs with different active layer thicknesses, tested under 1000 Wm^{-2} air mass 1.5 global (AM 1.5 G) illumination. The deduced device performance parameters were summarized in Table 1 for comparison. The device with an active layer of 100 nm showed the highest PCE of 8.27%, with an open circuit voltage (V_{OC}) of 0.73 V, a short-circuit current density (J_{SC}) of 15.7 mA cm^{-2}, and fill factor (FF) of 73%, in good agreement with our previous report [4]. It is worthy to note that following the reduction of the thickness of the photo active layer, the FF was enhanced to 75% (80 nm) and 76% (70 nm), respectively, although the overall device performance declined as a result of reduced photon absorption.

To investigate the origin of the increase in FF with decreased active layer, we firstly examined the charge carrier mobility in single-carrier devices with different active layer thicknesses. The charge mobility was measured by fitting the current-bias characteristics in dark using a field-independent space charge limited

Table 1
The device performance parameters of the devices with different active layer thicknesses, tested under 1000 Wm^{-2} air mass 1.5 global (AM 1.5 G) illumination.

Thickness (nm)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
100	0.73	15.7	73	8.27
80	0.73	14.5	75	7.91
70	0.73	13.9	76	7.66

current (SCLC) model or by transient photoconductivity. These charge transport studies will be published elsewhere. For all of the devices with different thicknesses studied in this study, the hole and electron as of 7.0×10^{-5} cm^2/V s and 2.5×10^{-4} cm^2/V s respectively, thus excluding the change in charge carrier mobilities as the origin of observed enhancement in FF. It is important to note that the measured hole and electron mobilities here are only moderate when compared to those of highly ordered polymer: PCBM blend [27], suggesting that the physical origin of the high FF in this system may be different between these systems.

Nevertheless, the clear dependence of FF on active layer thickness can be attributed to the alleviation of space charge effects in a first order of approximation, as a result of a more efficient charge extraction as a stronger average electric field across the devices [21]. To illuminate the influence of the different active layer thicknesses on FF, we employed the numerical model developed by Bolm et al. [14] to describe the *J–V* characteristics of the PSCs with different active layer thicknesses. The numerical model includes field and temperature dependent generation of free charge carriers, the bimolecular recombination of charge, and the drift and the diffusion of charge.

The course of photo-generated of free charge carriers is described by an optimized geminate recombination theory of Onsager [41], which was proposed by Braun in 1984 [42]. In that model, the probability of the dissociation of bound electrons and holes at the donor/acceptor interface is given by [14]

$$p(x, T, F) = \frac{k_{\text{diss}}(x, T, F)}{k_{\text{diss}}(x, T, F) + k_f(T)} \tag{1}$$

where T and F represents the temperature and field strength, x is the electron–hole pair distance, and the dissociation rate constant is given by

$$k_{\text{diss}}(x, T, F) = \frac{\frac{3R}{4\pi x} \exp\left(-E_B/k_B T\right) J_1\left(2\sqrt{-2b}\right)}{\sqrt{-2b}}$$
$$= \frac{3R}{4\pi x} \exp\left(-E_B/k_B T\right)\left(1 + b + b^2/3 + \cdots\right) \tag{2}$$
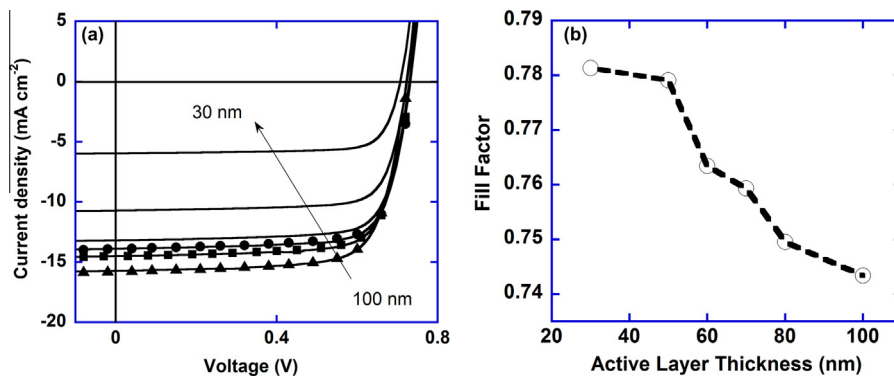

Fig. 1. (a) The experimental current density versus voltage (*J–V*) characteristics of PTB7:PC$_{71}$BM devices with different active layer thickness of 70 nm (solid circles), 80 nm (solid squares) and 100 nm (solid triangles). The solid lines represent the simulated *J–V* characteristics for devices with different active layer thickness (30–100 nm), as obtained from numerical modeling using identical fitting parameters shown in Table 2. (b) The deduced FF for each device with different active layer thickness from the simulated *J–V*.