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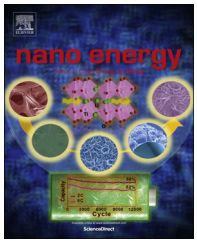

FULL PAPER

Highly efficient ternary polymer solar cells by optimizing photon harvesting and charge carrier transport

Miao Zhang[a], Fujun Zhang[a,*], Qiaoshi An[a], Qianqian Sun[a], Wenbin Wang[a], Jian Zhang[b], Weihua Tang[c]

[a]*Key Laboratory of Luminescence and Optical Information, Ministry of Education, Beijing Jiaotong University, 100044 Beijing, People's Republic of China*
[b]*Department of Material Science and Technology, Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, 1 Jinji Road, 541004 Guilin, Guangxi, People's Republic of China*
[c]*Key Laboratory of Soft Chemistry and Functional Materials, Ministry of Education, Nanjing University of Science and Technology, 210094, People's Republic of China*

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Abstract
Ternary strategy exhibits some apparent advantages to improve the performance of polymer solar cells (PSCs), such as using two donors or two acceptors to enhance photon harvesting and maintain the simple cell fabrication process. The power conversion efficiency (PCE) of PSCs was increased from 4.89% to 5.54% by doping 4 wt% SMPV1 into Si-PCPDTBT:$PC_{71}BM$ binary system. The PCE improvement should be attributed to the enhanced photon harvesting in the visible light range and optimized charge carrier transport by doping appropriate SMPV1 in the active layers. The champion PCE values were also increased from 4.89% to 5.73% or from 5.54% to 6.44% for binary or the optimized ternary PSCs by $CHCl_3$ solvent vapor annealing treatment. The positive effect of appropriate SMPV1 doping ratio should be attributed to the efficient energy transfer from SMPV1 to Si-PCPDTBT and the more balanced charge carrier transport in the ternary active layers. The energy transfer from SMPV1 to Si-PCPDTBT can be clearly confirmed from the absorption, photoluminescence (PL) spectra and time-resolved transient PL spectra of pure and blend films. The more balanced charge carrier transport can be further demonstrated from the corresponding hole-only and electron-only devices.

*Corresponding author. Tel.: +86 10 51684908.

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Introduction

Polymer solar cells (PSCs) have attracted extensive attention due to their advantages of light weight, low cost, easy fabrication and mechanical flexibility [1-6]. Nowadays, the power conversion efficiency (PCE) has exceeded 10% for single-junction PSCs based on narrow bandgap polymer as electron donor and fullerene derivations as electron acceptor [7,8]. It is known that one of the main restrictions to obtain high PCE is insufficient incident photon harvesting of the active layers, which is mainly ascribed to the following points: (i) relatively narrow absorption range (~100 nm) of organic materials due to its non-continuous absorption bands [9,10]; (ii) the limited active layer thickness for efficient charge carrier transport and collection [11,12]. The thick active layer is beneficial for photon harvesting, yet also results in the decrease of fill factor (FF) due to the increased charge carrier recombination (shunt) loss and bulk (serial) resistance [13]. Therefore, appropriate active layer thickness is required to make the balance between photon harvesting and the sweep-out of charge carrier prior to recombination for high performance single-junction PSCs [14]. Recent years, ternary strategy has been demonstrated as an effective method to improve the PCE of PSCs [15-18]. However, the working mechanism of the second donor or acceptor in the ternary PSCs is still in argue, such as energy transfer [19], charge transfer [20,21], alloy-model [22] or parallel-linkage model [23,24], which strongly depends on the energy levels and chemical structure of used materials. It has been commonly reported that the narrow band gap materials were commonly selected as the second donor to harvest low energy photon for highly efficient ternary PSCs with two donors. It should be kept in mind that narrow bandgap materials have relatively low photon harvesting ability for the light wavelength less than 600 nm and electron acceptor [6,6]-phenyl C71-butyric acid methyl ester ($PC_{71}BM$) also has a relatively weak photon harvesting ability for the light wavelength longer than 450 nm. Therefore, the enhancement of photon harvesting in the spectral range from 450 nm to 600 nm is very vital strategy to further improve the performance of PSCs based on narrow band gap materials as electron donor.

Yang et al. successfully synthesized a narrow band gap polymer poly[(4,4′-bis(2-ethylhexyl)dithieno[3,2-b:2′,3′-d]silole)-2,6-diyl-alt-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5′-diyl] (Si-PCPDTBT), which also has good hole transport property [25]. A series of binary PSCs based on Si-PCPDTBT:$PC_{71}BM$ as the active layers have been reported from different research groups, most of PSCs exhibited the PCE values from 3.8% to 5.9% [26-29]. However, the reported PCEs of PSCs based on Si-PCPDTBT as electron donor are not high enough due to its relatively weak absorption in the range from 450 nm to 650 nm. Ameri et al. reported that Si-PCPDTBT was used as the second donor to prepare ternary PSCs with P3HT:Si-PCPDTBT:$PC_{71}BM$ as the active layers, the champion PCE was increased from 3.1% for binary PSCs to 4.0% for ternary PSCs due to the increase of photon harvesting in the longer wavelength range [30]. Lin et al. also reported that the PCE of PSCs with Si-PCPDTBT:P3HT:$PC_{71}BM$ as the active layers was increased from 3.8% to 4.1% by adjusting P3HT doping ratios in donors due to the increased photon harvesting in the range from 450 nm to 650 nm [28]. The immiscibility of polymers may result in serious phase separation in the blend films, and the strategy of using two polymers may be not the best choice for obtaining high performance ternary PSCs. Up to now, the performance improvement of PSCs based on Si-PCPDTBT:$PC_{71}BM$ as the active layers was rarely reported by doping a relatively broad band gap small molecular material to compensate the weak photon harvesting of Si-PCPDTBT in visible light range. Therefore, the high absorption coefficient and broad band gap small molecular materials are needed to cover the photon harvesting in this spectral range for obtaining high performance PSCs. Recently, Liu et al. reported a two-dimensional conjugated small molecule material (5E,5′E)-5,5′-((5″,5‴′-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl)bis(3,3″-dioctyl-[2,2′:5′,2″-terthiophene]-5″,5-diyl))bis(methanylylidene))bis(3-octyl-2-thioxothiazolidin-4-one) (SMPV1) with high absorption coefficient about 4.8×10^4 cm^{-1} and broad photon harvesting range from 450 nm to 650 nm [31]. It can be envisaged that SMPV1 should be effectively compensate the weak absorption of Si-PCPDTBT:$PC_{71}BM$ in the range from 450 nm to 650 nm, suggesting the potential collocation of Si-PCPDTBT:SMPV1 as donors for highly efficient ternary PSCs.

In this work, two series of PSCs based on Si-PCPDTBT$_{1-x}$:SMPV1$_x$:$PC_{71}BM$ (x indicates SMPV1 doping ratios in donors) as the active layers were fabricated, the only difference is the active layers with or without solvent vapor annealing (SVA) treatment. The positive effect of SMPV1 on the performance improvement of PSCs can be adequately demonstrated from more than two hundred cells with or without SVA treatment on the active layers. For the binary PSCs based on Si-PCPDTBT:$PC_{71}BM$ as the active layers, the champion PCE arrives to 4.89% or 5.73% for the active layers without or with SVA treatment, respectively. The champion PCE of ternary PSCs with 4 wt% SMPV1 doping ratio in donors arrives to 5.54% or 6.44% for the ternary active layers without or with SVA treatment, respectively. The underlying reasons of SMPV1 doping ratios on the performance improvement of ternary PSCs are adequately discussed from the photon harvesting, exciton dissociation, energy transfer as well as charge carrier transport dependence on the SMPV1 doping ratios in donors. Some fundamental physical issues are still needed to be clarified for the further performance improvement of ternary solar cells, because there is no clear set of structure-function relationships for component selection and the operating mechanism for ternary solar cells.

Experimental

The used materials Si-PCPDTBT and $PC_{71}BM$ were purchased from Luminescence Technology Corp., organic small material SMPV1 was purchased from 1-Material Inc. The mixed SMPV1:$PC_{71}BM$ (1:1.5, wt/wt) and Si-PCPDTBT:$PC_{71}BM$ (1:1.5, wt/wt) powder were respectively dissolved in 1,2-dichlorobenzene (o-DCB) to prepare 25 mg/mL binary blend solutions. Ternary blend solutions of Si-PCPDTBT $_{1-x}$:SMPV1$_x$:$PC_{71}BM_{1.5}$ (x=2 wt%, 4 wt%, 6 wt%, 8 wt%, 10 wt%, 12 wt%, x represents SMPV1 doping ratios in donors) were prepared by mixing the binary solutions with different volume ratios. The prepared blend solutions were continuously heated and stirred at 100 °C for 12 h. The conjugated polyelectrolyte poly[(9,9-bis(3-(N,N-dimethylamino)-propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) was dissolved in methanol with addition of 0.25 vol% acetic acid