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The role of polymer dots on efficiency enhancement of organic solar cells: Improving charge transport property

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ABSTRACT

In this work, poly(9,9-dioctylfluorene)-co-(4,7-di-2-thienyl-2,1,3-benzothiadiazole) (PF-5DTBT) and copolymer poly(styrene-co-maleic anhydride) (PSMA) dots were prepared as additive for active layer doping to enhance the power conversion efficiency (PCE) of organic solar cells (OSCs), which based on poly[N-9″-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole) (PCDTBT) and [6,6]-phenyl C₇₁ butyric acid methyl-ester (PC₇₁BM). A high efficiency of 7.40% was achieved due to increase of short-circuit current (J_{sc}) and fill factor (FF). The operation mechanism of OSCs doping with polymer dots was investigated, which demonstrated that the efficiency enhancement ascribes to improvement of electrical properties, such as exciton generation, exction dissociation, charge transport, and charge collection.

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1. Introduction

In the past few years, in order to solve the energy crisis and environmental issues, much research has been focused on solar cells. [\[1](#page--1-0)–[9\]](#page--1-0) Compared to their inorganic counterparts, organic solar cells (OSCs) possess more potential such as low cost, large area, flexibility, and lightweight $[10-16]$ $[10-16]$. However, the low power conversion efficiency (PCE) is still a crucial role for the commercial use of OSCs [\[17\].](#page--1-0) How to improve the PCE of OSCs is still a focus issue, which has been got increasing attention. The PCE of solar cells is decided by open-circuit voltage (V_{oc}), fill factor (FF), and shortcircuit current density $(J_{\rm sc})$. Therein, $V_{\rm oc}$ is mainly related to the work function of cathode, energy level gaps, and morphology of blended active layers $[18–21]$ $[18–21]$ $[18–21]$. The J_{sc} and FF are affected by many complicated factors, including incident light intensity and internal conversion efficiency which consists of separation and recombination of exciton and carrier mobility. The key to the success of PCE is the development of high performance materials possessing well matched photon-absorption with the solar spectrum, an efficient photoexcited charge separation to prevent electron–hole recombination and an adequate energy of charges that carry out the desired chemical reactions [\[22\].](#page--1-0) Low carrier mobility of active

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<http://dx.doi.org/10.1016/j.optcom.2015.11.062> 0030-4018/© 2015 Elsevier B.V. All rights reserved. layer material is one of the main disadvantages, which will slow down charge carriers to transport to electrodes, thus increasing the possibility of recombination in the process of transmission. The rapid recombination of photoexcited electron–hole pairs has been recognized as a key factor for the low photon–electron conversion efficiency. Therefore, there is competition between the sweep-out of the photogenerated carriers by the built-in potential and recombination of the photogenerated carriers within the active layer. Multidisciplinary efforts have been taken to solve this problem in recent few years, such as rational designs of lowbandgap conjugated polymers, optimization of film morphology, and developing new device architectures. Also, some tremendous efforts have been taken via doping or surface-tuning, when appropriate doping occurs in active layer, the probability of excition dissociation may be increased and carrier mobility enhanced possibly [\[23](#page--1-0)–[28\]](#page--1-0). Recently, metal nanoparticles and quantum dots have been employed to improve charge carrier transport and achieved high device performance [\[29](#page--1-0)–[31\]](#page--1-0).

In this work, we present the experimental studies of a poly[N-9″-hepta-decanyl-2,7-carbazole-alt-5,5 -(4′,7′-di-2-thienyl-2′,1′,3′ benzothiadiazole) (PCDTBT) and $[6,6]$ -phenyl C₇₁ butyric acid methyl-ester (PC_{71} BM) doped with poly(9,9-dioctylfluorene)-co-(4,7di-2-thienyl-2,1,3-benzothiadiazole) (PF-5DTBT) and copolymer poly(styrene-co-maleic anhydride) (PSMA) dots (PPdots) as active layer in OSCs. We show here that incorporation of PPdots exhibits

the following advantages: (1) enhanced exciton generation and dissociation; and (2) improved carrier transport. As a result, the PCE of photovoltaic devices increased from 5.73% to 7.40%, leading to a 29% enhancement.

2. Experimental section

Poly(9,9-dioctylfluorene)-co-(4,7-di-2-thienyl-2,1,3-benzothiadiazole) (PF-5DTBT) was synthesized according to previous report [\[32\]](#page--1-0). The functional copolymer poly(styrene-co-maleic anhydride) (PSMA) was purchased from Sigma-Aldrich. First, two kinds of solutions were prepared by stock solutions of PF-5DTBT (1.0 mg/mL) and PSMA (1.0 mg/mL) in THF, respectively. Second, the above solution was mixed sufficiently in order to form a homogeneous solution, and the function of PMSA is to reduce the size of PF-5DTBT dots. Then, the solution (3 mL) was injected quickly into deionized water (10 mL) under sonication and the mixture was sequentially sonicated for 3–5 min. Finally, the THF in the mixture was removed by nitrogen (N_2) flowing under a hotplate. The resulting PF-5DTBT and PSMA dots (PPdots) solution was concentrated by continuous heating, followed by filtration through a 0.22 μ m filter to remove larger particles. Meanwhile, we doped various doping amount of 10, 20, 30, and 40 μL PPdots solution into per milliliter PCDTBT:PC $_{71}$ BM solution, respectively. The mixture was sufficiently stirred, and no phase separation was found. The devices were fabricated with the structure of ITO/nanocrystal TiO2/PCDTBT:PC71BM: PPdots/MoO3/Ag. The schematic structure and energy levels are shown in Fig. $1(a)$ and (b) , and molecule structure of all active layer materials are exhibited in Fig. 1(c). The ITO substrates were cleaned by acetone, isopropyl alcohol, and deionized water firstly. Then $TiO₂$ layer was spin coated onto substrate as an electronic transport layer followed by postannealing at 450 \degree C for 2 h in the muffle furnace, and then cooling by nature. The active layer solution containing 7 mg PCDTBT and 28 mg PC_{71} BM in 1 mL 1,2-dichlorobenzene (DCB) doping of different concentration PPdots spinning coated at 2000 rpm on top of $TiO₂$ layer in air, then conducting a postannealing at 70 °C for 20 min in the glove box to remove solvent. Subsequently, $MoO₃$ with the ability of enhancing hole collection and Ag used as the anode were thermally evaporated. The devices without and with 10–40 μL PPdots were named as Devices A, B, C, D, and E, respectively.

3. Results and discussion

[Fig. 2](#page--1-0)(a) exhibits transmission electron microscope (TEM) graph of prepared PPdots, we can see that the average diameter of PPdots is about 5 nm. [Fig. 2](#page--1-0)(b) and (c) shows atomic force microscopy (AFM) images of active layer films without and with the PPdots doping in PCDTBT:PC $_{71}$ BM blender. It is found that the surface roughness of pristine PCDTBT:PC $_{71}$ BM is 1.55 nm, while that of film with PPdots is 1.28 nm. The addition of PPdots into PCDTBT: PC_{71} BM forms more homogeneous films and optimal do-main size with smooth surfaces [\[33\].](#page--1-0) The improved surface morphology and PPdots addition in active layer may provide a large interface for excition dissociation, as well as a continuous percolating path for hole and electron transport. Furthermore, a rather smoother surface allows doped films to produce a compact contact with the charge transport layers, which is benefit to charge transfer and collection.

[Fig. 3](#page--1-0)(a) shows the current density–voltage $(I-V)$ characteristics of all fabricated devices. Specific parameters including V_{oc} , J_{sc} , fill

Fig. 1. (a) The schematic structure and (b) energy levels of OSC devices, (c) sketch graph of molecular structure.

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