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ARTICLE TYPE

Improving efficiency of inverted polymer solar cells by introducing inorganic dopants

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In this paper, molecular doping with polymer dots was designed to unravel its effect on the photoconductivity in organic solar cells. The photocurrent in organic solar cells received a considerable increase under optimal doping concentration, leading to an ultimate enhancement of power conversion efficiency from 2.30% to 3.64%. This can be attributed to the improvement primarily to an initial boost in charge carriers due to background carriers induced by polymer dots and increased tail absorption by active layer. Based on single carrier device and impedance measurements, polymer dopant can efficiently decreased charge recombination and improved charge carriers mobility. The obtained achievements pave an approach of molecular doping in affecting the operation of organic solar cells.

1. Introduction

Organic solar cells (OSCs) have attracted an increasing attention due to their merits, such as efficient solution-processing, capability for large areas, and the possibility of flexible devices compared to inorganic solar cells [1-6]. Although, the highest power conversion efficiency (PCE) of OSCs, as far as we know, have reached over 10%, which is still lower to meet commercial and industry application [7-9]. The bottleneck of the photons absorption range as well as the poor efficiency of exciton separation and charge transportation in organic material generates a relatively low photocurrent, leading to the restriction the improvement of PCE. Therefore some intensive research efforts has been carried out to achieve higher PCE such as synthesizing new polymers to better match the solar spectrum, the designing cascade and tandem structure, the using of different additives and the electrode interfacial engineering, etc [10-18]. Among such investigations, the using of additives has received more attention due to its great effect. The incorporation of additive may improve the morphology of active layer and increase photogenerated carriers, which can also enhance exciton dissociation and charge carriers transfer within the thin bulk heterojunction (BHJ) film [19-22]. Different approaches were taken to enhance the light absorption with the cautions to optimize cell absorption without increasing the thickness of active layer, so as to avoid the increase in charge recombination [23-25]. The optimized use of additives has resulted in remarkable increases in the photoconductivity, carrier mobility and incident photon-to-electron conversion efficiency (IPCE) [26,27]. Especially,

quantum dots (QDs) material due to its quantum effect and unique optical properties, which possesses potential to improve performance of PSCs in theory, became one of the most common additives. It has been reported that incorporating quantum dots such as CdS, PbS and CdSe into active layer to improve performance of PSCs in last decade [28-230]. Recently, polymer dots have attracted extensive interest in optoelectronic devices and biological monitoring[31-35]. Compared to inorganic additives, polymer dots is easy to dissolve in organic solvent and possesses better compatibility with polymer donor and acceptor materials.

In this paper, we prepared poly [(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-benzo-1-thiadiazole)] (PF-10BT) dots (Pdots) doping into active layer to improve the performance of inverted organic solar cells. The cells were employed a blend of poly[(4,4'-bis(2-ethylhexyl) dithieno[3,2-b:2',3'-d] silole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl] (PSBTBT) and fullerene derivative [6,6]-phenyl-C60-butyric acid methylester (PC₆₀BM) doping with various concentrations of Pdots as active layer. The photovoltaic performance of all finished cells was presented. We demonstrated that the PCEs of the PSBTBT: PC₆₀BM solar cells increase from 2.30% to 3.64% mainly due to improving photocurrent.

2. Experimental

2.1 Material preparation:

PF-10BT (average MW 15,000-200,000, polydispersity 3.0), was purchased from ADS Dyes, Inc. (Quebec, Canada).

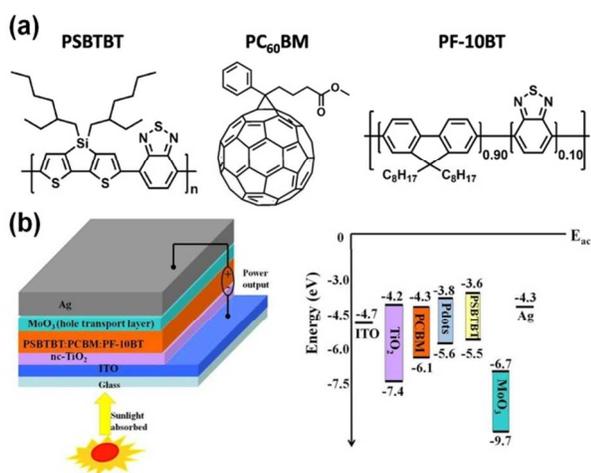


Figure.1 (a) Chemical structure of materials used in this study, (b) Device architecture and energy levels of the organic solar cell.

The functional copolymer poly (styrene-co-maleic anhydride) (PSMA, average Mw ~1,700, styrene content 68%), was purchased from Sigma-Aldrich (St. Louis, MO, USA). First, PF-10BT and PSMA were respectively dissolved in tetrahydrofuran (THF) to obtain stock solutions, and the concentrations are 5.0 mg/mL and 2.0 mg/mL. Second, PF-10BT solution (2 mL) and PSMA solution (1 mL) were mixed sufficiently in order to form a homogeneous solution. 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 (N₂) flowing under a hotplate. The resulting Pdots solution was concentrated by continuous heating, followed by filtration through a 0.22 μm filter to remove larger particles. The concentration of finally prepared Pdots solution was 3.6 mg/mL. The molecular structure of PSBTBT, PC₆₀BM, and PF-10BT are shown in Fig.1(a).

2.2 Device fabrication and characterization

Devices were fabricated with the structure of ITO (150 nm)/nano-crystal titanium dioxide (25 nm)/PSBTBT: PC₆₀BM: Pdots (100 nm)/MoO₃ (4 nm)/Ag(100 nm). The schematic structure and energy level are shown in Fig.1(b). The glass substrates coated with ITO was first precleaned acetone, isopropyl alcohol, and deionized water, and subsequently dried with nitrogen gun. Anatase TiO₂ layer was spin-cast at 3000 rotations per minute (rpm) onto ITO substrate in air then thermally annealed at 450°C for 2 h in the muffle furnace, and cooling by nature. TiO₂ layer acts as an electron-transport layer while block the hole at the same time. For the active layer, the 1,2-dichlorobenzene (DCB) solution composed of PSBTBT(15 mg/ml), PC₆₀BM(15 mg/ml) and Pdots were spin-coated (1000 rpm for 18 s) on the top of the TiO₂ layer to form a photosensitive layer in air. Active layer films of cells were made with different amounts of Pdots. The doping weight ratios (wt) of Pdots and PSBTBT:PC₆₀BM were 0, 0.12wt%, 0.24wt%, 0.36wt% and 0.48wt%, respectively. The cells with various doping concentrations were named as Device A, Device B, Device C, Device D, and Device E. All the films were subsequently annealed at 110°C for 20 min inside a nitrogen-filled glove box. Finally, the device fabrication was completed by the thermal

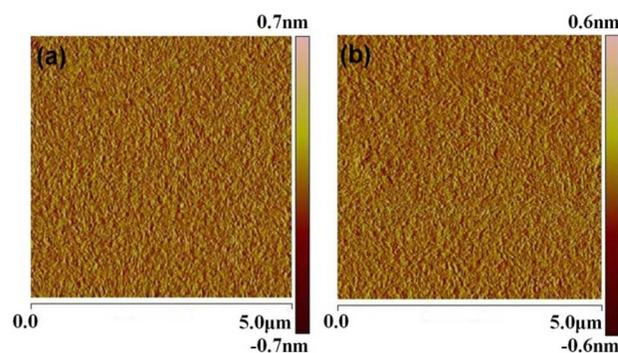


Figure.2 AFM images of PCDTBT:PC₇₁BM film (a) without and, (b) with Pdots doping.

evaporation of MoO₃ and Ag as a cathode. MoO₃ with the highest occupied molecular orbital (HOMO) level of -9.7eV, acts as a hole-transport layer, which is benefit to the hole collection at the photoactive layer interface [36-38]. The active area of the device was 6.4 mm² approximately. The current density-voltage (J-V) characteristics of devices were measured under AM 1.5G irradiation with the intensity of 100 mW/cm² (about one sun) in air without encapsulation by a programmable Keithley 2400 source meter. Crowntech QTest Station 1000 AD was used in IPCE measurement. The absorption and reflectance spectra were measured by means of ultraviolet/visible spectrometer (UV 1700, Shimadzu).

3. Result and discussion

In bulk-heterojunction solar cells, the surface morphology of active layer is very important to their photovoltaic performance[39]. Fig. 2 shows the surface morphology of active layers with and without 0.24wt% Pdots in Atomic Force Microscope (AFM) images. Their surfaces are quite smooth. The root-mean-square (RMS) roughness of two active layers is 1.03 and 0.74 nm. For doped active layer, the film surface exhibits relatively smooth and featureless structure, which is similar to the observation reported previously[40]. AFM results reveal that introducing Pdots in PCDTBT:PC₇₀BM blend leads to an obvious morphological variation. Pdots can interpenetrate into networks of donor and acceptor materials due to its small size. Pdots doping in active layer can increase donor/acceptor interfaces and produce connected pathways of each material type to facilitate charge extraction.

Fig.3(a) indicates the current density-voltage (J-V) characteristics of inverted cells. The contrast devices without Pdots demonstrate short-circuit current density (J_{sc}) of 9.50 mA cm⁻², open-circuit voltage (V_{oc}) of 0.63 V, fill factor (FF) of 38.48%, leading to a PCE of 2.30%. When doped with Pdots into active layer, the cells performance has been improved remarkably. The PCE of devices made with an optimal doping of 0.24wt% Pdote is 3.64%, with a J_{sc} of 12.85 mAcm⁻², V_{oc} of 0.65 V and FF of 43.72%. J_{sc} and FF were both increased, which directly leads an enhancement of PCE with 58.12% higher than control devices. Meanwhile, the cells doped with 0.12wt%, 0.36wt% and 0.48wt% Pdots were also conducted, and they also demonstrated relatively higher PCEs than control devices, exhibiting PCEs of 3.33%, 2.98%, and 2.86%. The corresponding J_{sc} of doped cells are 11.85 mAcm⁻², 10.46 mAcm⁻² and 10.34

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mAcm^{-2} , respectively. We found that J_{sc} and FF are all improved for the doped devices

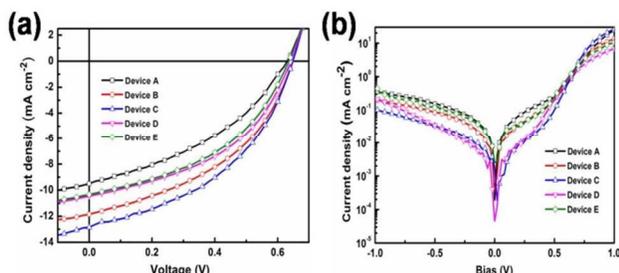


Figure.3 (a) The photocurrent characteristic and (b) dark J-V of all cells without and with various concentrations of Pdots.

irrespective of doping amounts while maintaining the V_{oc} at the same level. As we know, V_{oc} is mainly determined by the energy difference between the highest occupied molecular orbital (HOMO) of donor and the lowest unoccupied molecular orbital (LUMO) of acceptor [41-43]. Pdots have no large influence on the energy level distribution of the cells. With the increase of doping concentrations, J_{sc} and PCE of doped devices have obviously change trend. They increased first and then decreased. The detailed parameters of device performance are list in Table I,

Table I Solar cell parameters based on active layers of PSBTBT:PC₆₀BM without and with Pdots doping.

Device	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF(%)	PCE(%)	R_{s} (Ω)	R_{sh} (Ω)
A	0.63	9.50	38.48	2.30	280.01	2739.61
B	0.65	11.85	43.39	3.33	192.47	3195.41
C	0.65	12.85	43.72	3.64	185.04	3237.22
D	0.64	10.46	44.48	2.98	217.29	3305.63
E	0.64	10.34	43.49	2.85	267.88	3016.85

and the values are typical average of 50 devices. In the absence of illumination, the dark J-V curves of all five devices are shown in Fig.3(b). As expected, all the doped devices show smaller leakage current at negative voltages. Besides that, doped cells achieved higher current density in the space charge limited current dominated regime, suggesting an improvement of charge transport and a decrease of series or contact resistance. The dark J-V characteristics are in accordance with the increase of FF. With an apparently increase in J_{sc} , FF of cell with optimized doping value obtained 13.62% enhancement compared to the control device (from 38.48% to 43.72%), insinuating that the charge transfer properties are ameliorated. The possible operation mechanism of Pdots additive is that the presence a third material in active film provides an interface for charge transfer and enables the formation of percolation pathways for electron transport, thus reducing the effects of space charge formation and beneficial for mitigating the charge recombination, but excess doping will lead to conductivity degradation and worse device efficiency.

Fig.4 depicts the corresponding IPCE spectra of all solar cells. For the doping devices, IPCE exhibits significant increase

covering a broad wavelength range from 400 to 800 nm compared to the control device, corresponding to the J-V

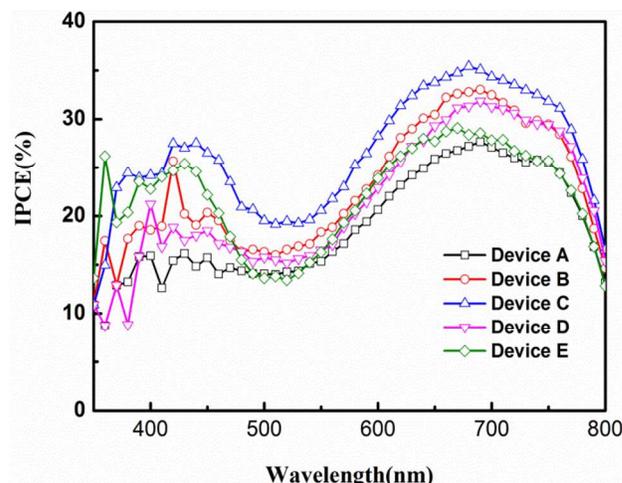


Figure.4 IPCE characteristic of cells without and with various concentrations of Pdots.

characteristics presented in Fig.3, and this indicates direct evidence for the enhanced J_{sc} . To better illustrate the J_{sc} enhancement, we also performed UV-vis absorption and reflectance spectra of PSBTBT: PC₆₀BM blended film with and without Pdots. The absorption and reflectance spectrum is shown in Fig.5. After Pdots were doped, the blended film shows greater optical absorption covering the wavelength range from 400 to 850 nm (Fig.5(a)). The active layer film indicates a higher reflectance in the region of 600-800 nm (Fig.5(b)), which is consistent with the lower absorption in Fig.5(a). It can be seen from Fig.5(c) that absorption spectra of Pdots peak locates in visible region, which contributes to increase light-harvesting of active layer. Moreover, doping Pdots could play a role of scattering center and more light was trapped through multiple and high-angle scattering. On the basis of IPCE and UV-vis absorption results, it is clear that Pdots doping greatly enhance light trapping of active layer. The increased absorption is in good agreement with the enhancement of IPCE. Thus, the introduction of Pdots into active film offers the possibility of increase optical absorption and correspondingly improves photo-induced carriers.

In order to investigate the effect of Pdots, we fabricated two kinds of single carrier devices. The electron-only device configuration is ITO/TiO₂/PSBTBT: PCBM: Pdots/BCP/Ag, where the BCP acts as hole blocking layer[44]. The hole-only device configuration is ITO/MoO₃/active layer/ MoO₃/Ag, where the MoO₃ acts as electron blocking layer and hole transport layer. The J-V characteristics of these two kinds of devices in dark were given in Fig.6 and charge carrier mobilities were calculated using the space-charge-limited current (SCLC) model, including field dependence [45]. At a typical applied voltage of 1.0V, corresponding to an electric field of 10^5V cm^{-1} across the bulk of a 100 nm device, hole mobility increased from $0.7 \times 10^{-4} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$

to $1.2 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{ s}^{-1}$, and apparent electron mobility increased from $0.9 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{ s}^{-1}$ to $1.3 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{ s}^{-1}$. It can be seen that

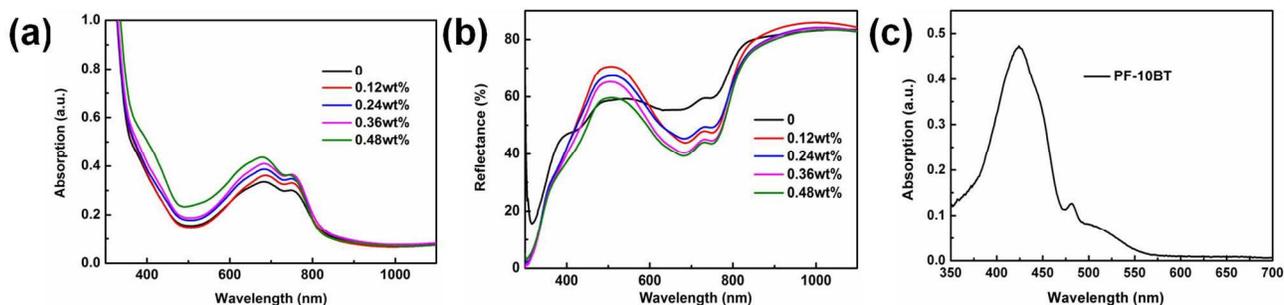


Figure.5 (a) the absorption and (b) the reflectance spectrum of active layer films without and with Pdots, (c) the absorption spectrum of Pdots

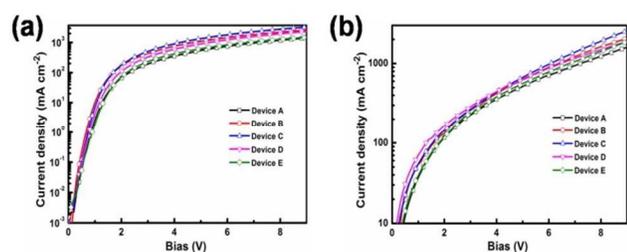
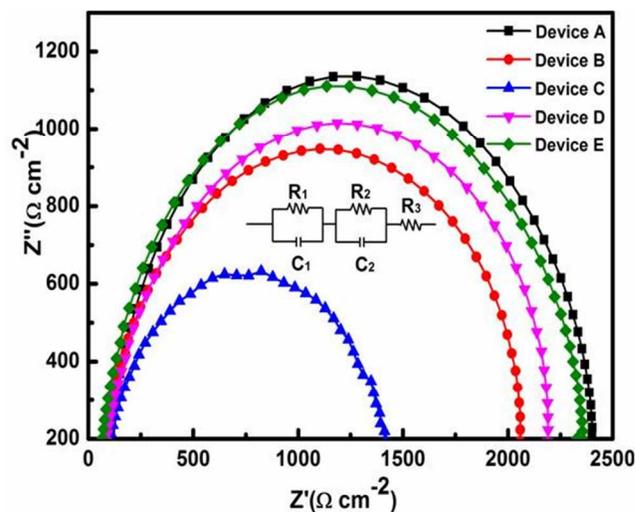


Figure.6 J-V characteristics of (a) single electron devices (b) single hole devices.

hole mobilities of doped devices were all enhanced compared to control devices. Fig.6(b) shows the same change trend for electron mobilities, which is consistent with Fig.6(a). Furthermore, active layer doping possessed an advantage to improve charge carrier transport and reduced charge recombination, which decreased the space charge buildup affecting the internal field in the case of undoped device, leading to an increase of FF. This proved that doping Pdots into active layer contributes to improvement of electron and hole transport properties.

One limitation of high-performance OSCs is the low charge carrier mobilities in the devices, which hinder the further improvement of the cell efficiency. A reasonable approach to overcome this drawback is to introduce the third material to form ternary OSCs, which have a cascade band structure and are favorable for prohibiting carrier recombination in the devices. In our research, the LUMO and HOMO levels of PF-10BT lie between that of PSBTBT and PCBM, which leads to the decrease in the injection barrier, making it less sensitive to the chosen contact. This kind of cascade band structure is critical to excitation dissociation and carrier recombination in OSCs. To deeply understand the kinetics and energetic processes governing the device performance, we measured the impedance spectroscopy of all cells with frequency range from 20 Hz to 1 MHz, which is shown in Fig.7 [46-48]. The data are satisfactorily described by the equivalent circuit model containing two RC components in parallel. The results give a series resistance (R_s) of 280.01 Ω for the PSBTBT:PC₆₀BM control device, and a reduced R_s of 195.47 Ω , 185.04 Ω , 217.29 Ω , and 267.88 Ω after adding Pdots in various concentrations, respectively. The decline of equivalent resistance means the incorporating Pdots could effectively improve the contact between active layer and electrodes, thus



decreasing the resistance of solar cells and contributing to FF enhancement. It is generally accepted that doping of conducting polymers leads to the chosen contact. As a result, the bias is mostly applied on the active layer than on the resistance across the contacts [49-51]. Lowering R_s undoubtedly benefits to decrease current losses across the contacting materials.

polymers leads to the chosen contact. As a result, the bias is mostly applied on the active layer than on the resistance across the contacts [49-51]. Lowering R_s undoubtedly benefits to decrease current losses across the contacting materials.

4. Conclusion

In summary, the role of PF-10BT Pdots in inverted solar cells was investigated. The achieved performances indicate that not only J_{sc} got apparently improvement but also slightly enhanced FF. The mechanism of J_{sc} enhancement is studied via single carrier test and impedance spectroscopy. We may safely draw a conclusion that incorporating Pdots into the active layer possess the capacity of enhancement of charge transport property. Upon the introducing of additive, both the hole and electron mobilities increased and a more balanced charge transport in the cells was achieved. As result, J_{sc} and FF are increased from 9.12 mA cm^{-2} to 12.85 mA cm^{-2} and 40.41% to 43.72%, respectively, leading a high PCE of 3.64% for optimized devices doped with 0.24wt% Pdots doping.

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Notes and references

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