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The Effect of Using 1-Dodecanethiol as a Processing Additive on the Performances of Polymer Solar Cells *

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We introduce 1-Dodecanethiol (DT) to poly(3-hexylthiophene) (P3HT)/[6,6]-phenyl-C_{61}-butyric acid methyl ester based polymer solar cells as a processing additive. When the amount of DT is 1vol%, the device performance is best. A final power conversion efficiency of 3.1% is achieved, which is an improvement of more than 40% compared to the reference solar cell without DT. To investigate the causes of improvement of the PCE, UV-vis spectroscopy, external quantum efficiency (EQE) is measured and an AFM is used. The enhanced photovoltaic performances are discussed in terms of optical properties and the film morphology.

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The energy problem is one of the most important problems facing the world today. Hence, there has recently been an increasing interest in polymer solar cells (PSCs) due to their numerous advantages, such as low fabrication cost, light weight, good flexibility, printability on plastic substrates, etc.[1−3] Organic PSCs have developed rapidly owing to their good performances. Especially, poly (3-hexylthiophene) (P3HT)/[6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) has received wide attention due to its high hole and electron mobility and good environmental stability. In order to further improve the PCE of PSCs, numerous efforts have been made by many researchers. For example, a LiF or ZnO layer had been added between the active layer and cathode to modify the cathode.[4,5] Solvent-treated poly(3,4-ethylenedioxythiophen-e): poly(styrenesulfonate)(PEDOT: PSS) was used to enhance the conductivity and optimized surface morphology of the PEDOT:PSS layer.[6] Annealing and a mixed solvent could also be utilized to improve the performances of the solar cells.[7,8] Metallic nanoparticles could cause a local enhancement in the electromagnetic field, which had been used to enhance light harvesting in PSC devices.[9]

In addition, the processing additives are proven to improve the optical properties and film morphology of the active layer, which is a special method that is worthy of learning. Hu *et al.*[10] demonstrated that 1,8-diiodooctane (DIO) can attribute to a favorable microscopic structure of the ternary blend and extended absorption on the red side of the visible spectrum up to 900 nm. Heo *et al.*[11] compared alkanediol series as processing additives in the photo-active layer on the power conversion efficiency of polymer solar cells and concluded that 1,3-propanediol was the best choice. Besides, Peet *et al.*[12,13] observed that alkane dithiols can increase the photoconductive response in conjugated polymer/fullerene composites and enable morphological control in bulk heterojunction materials. DT has the similar properties with alkane dithiols, especiallly a higher boiling point. Inspired by the above findings, DT was introduced to the active layer as a processing additive to improve the optical properties and film morphology of the polymer solar cells in this study, and we researched the effect of DT on the performances of PSCs.

The materials used for the active layer are P3HT and PCBM (purchased from Technology Corp). The processing additive is DT (1-Dodecanethiol, Aladdin, purity 98%). The chemical structures of P3HT, PCBM and DT are shown in Figs. 1(a), 1(b) and 1(c), respectively.

P3HT and PCBM were dissolved in a mixed solvent of chlorobenzene (CB)/chloroform (CF) (V/V = 1/1) in a weight ratio of 1:1 at a concentration of 20 mg/ml. DT was added to the solution to obtain volume percentages of 0vol%, 0.5vol%, 1vol%, 1.5vol% and 2vol% and stirred for more than 8 h on a table at room temperature. Pre-patterned ITO-coated glass with a sheet resistance of 12 Ω was used as the substrate and the anode electrode. The substrate was sequentially cleaned with detergent, de-ionized water, ethanol absolute, acetone, and isopropanol using an ultrasonic bath, followed by UV-ozone treatment for 4.5 min. PEDOT: PSS (Clevios P VP AI4083, H. C. Stark) treated by isopropanol according to the volume ratio of 5:1 was spin-coated on the substrate at

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3000 rpm for 30 s, then transferred into a glove box filled with high-purity nitrogen and dried at 130℃ for 10 min. The thickness of the dried PEDOT:PSS layer was about 40 nm. Subsequently, the absorber blend was spincoated at 1500 rpm on the top PEDOT:PSS layer and dried at 130℃ for 15 min. The resulting absorber thickness was about 10 nm. The cathode was formed by depositing 1 nm LiF and 130 nm Al through a shadow mask. Finally, these devices were annealed at 130℃ for 10 min. The architecture of PSCs was ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al, as is shown in Fig. 1(d). The active area of the PSCs is 16 mm^2 (4 mm×4 mm).

All the thicknesses were measured by using a Stylus Profiler (Dektak150). The variations of the morphology were measured by using an AFM. The photocurrent-voltage characteristics were measured using a solar simulator AM 1.5 (100 mW/cm^2, Japan, SAN-EI, ELS 155 (XE)) and a Keithley 2400 Sourcemeter, and the external quantum efficiency (EQE) was measured using an IPCE/QE/spectral response test systerm (USA, CROWNTECH).

Table 1. Device performances of solar cells with different volume percentages of DT as a processing additive.

DT (vol%)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	Calculated J_{sc} (mA/cm^2)
0	0.57	8.0	48.2	2.2	7.6
0.5	0.57	9.2	47.7	2.5	8.7
1	0.53	9.8	59.7	3.1	9.3
1.5	0.53	7.8	38.7	1.6	7.4
2	0.53	6.9	35.5	1.3	6.7

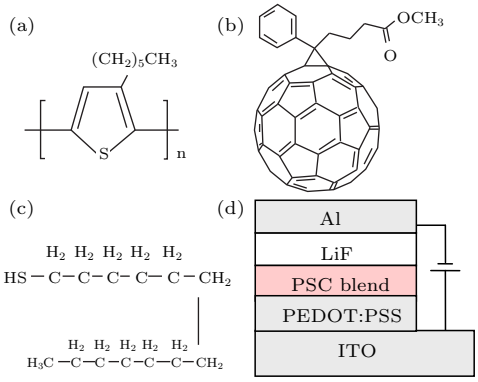


Fig. 1. The chemical structures of (a) P3HT, (b) PCBM and (c) DT processing additive; (d) the architecture of PSCs.

The photocurrent density-voltage (J–V) characteristics of the devices with DT at 0vol%, 0.5vol%, 1vol%, 1.5vol% and 2vol% are displayed in Fig. 2(a). Specific performance parameters are shown in Table 1. Changes of the performance parameters of solar cells with different volume percents of DT can be seen in Fig. 2(a). The trend of first increasing and then decreasing is observed compared to the reference solar cell without DT. In Table 1, the reference device prepared without DT exhibits an open-circuit voltage V_{oc} of 0.57 V, a short-current J_{sc} of 8.0 mA/cm^2, a fill factor (FF) of 48.2%, and the calculated PCE is 2.2%. After the addition of DT to the active layers, the values of V_{oc} do not show obvious differences (0.58–0.53 V) and stay the same later. The J_{sc} and FF also show a trend of first increasing and then decreasing. When 1vol% DT is added as processing additive, the performance parameters of the PSCs is best. V_{oc}, J_{sc}, FF and PCE are 0.53 V, 9.8 mA/cm^2, 59.7% and 3.1%, respectively. Theoretical J_{sc} values calculated by integrating the product of EQE with the AM 1.5 solar spectrum agree with the measured value with 5%. The increasing FF indicates that a better ohmic contact is formed between the active layer and the metal electrodes and that the morphology of film is improved.[14] DT has a high boiling pint of 266℃ and 283℃. When the addition of DT exceeds 1vol%, it may still be residual in the active layer. Therefore, the separation of excitons at donor-receptor interfaces and the transmission of carriers are both adversely affected, which leads to the decline of J_{sc}.

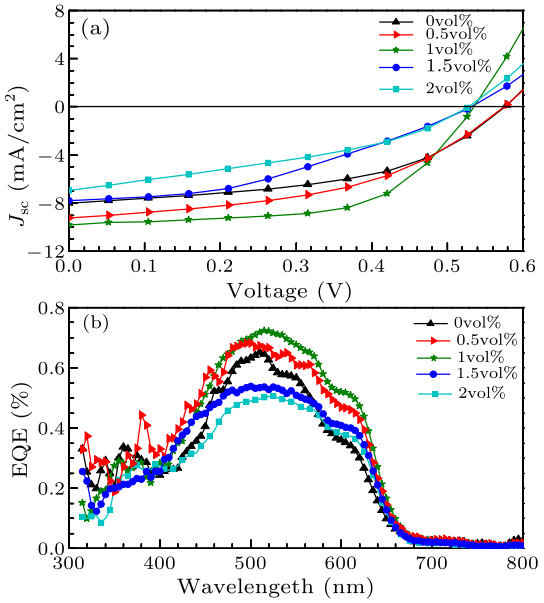


Fig. 2. (a) J–V characteristics and (b). EQE curves of solar cells incorporating different volume percents of DT as a processing additive.

Photo harvesting may be the first key issue to obtain the high performances of PSCs. The absorption spectra of active layers with different volume percents of DT are shown in Fig. 3. It can be seen that the absorption band of the active layers with DT clearly has

a "red shift", indicating DT as processing additive can help the devices to absorb more sunlight. The absorption intensity of active layers with different volume percents of DT also presents a trend of first increasing and then decreasing, which is in accordance with the J–V characteristics of solar cells. In addition, when 1vol% DT is added as a processing additive, the active layer exhibits higher absorption intensity at the peak positions of 500 nm, 550 nm, 600 nm than the reference solar cell. The increasing absorption will undoubtedly improve the performances of the PSCs.

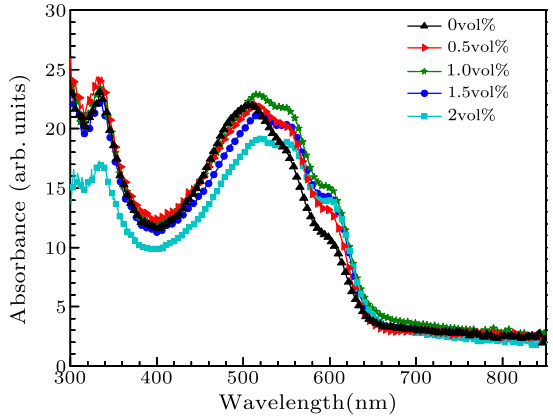


Fig. 3. Absorption spectra of films incorporating different volume percentages of DT as a processing additive.

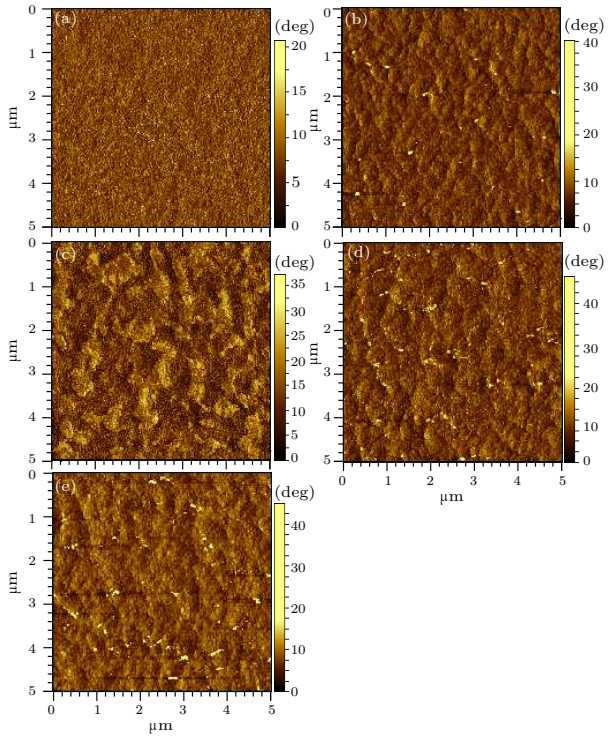


Fig. 4. AFM topographic images of active layers with different volume percentages of DT as a processing additive. (a) DT at 0vol%; (b) DT at 0.5vol%; (c) DT at 1vol%; (d) DT at 1.5vol%; (e) DT at 2vol%.

The high efficiency of converting photons into electrons enhances the performance of PSCs, which is also useful for the power source.[15] Figure 2(b) displays the EQE characteristics of devices with different volume percentages of DT as a processing additive. EQE curves of the devices show similar shapes, while peak values are different. When 1vol% DT is added, the EQE curve of PSCs exhibits the highest efficiency about of 70%, which is approximately 11% higher than the reference solar cell. The EQE curves indicate that DT incorporated in the active layers are beneficial to the photocurrent conversion of PSCs.

In order to better understand the effect of DT as a processing additive on the active layer, we measured the morphology by AFM. AFM images of the active layer incorporated with DT at 0vol%, 0.5vol%, 1vol%, 1.5vol% and 2vol% are shown in Figs. 4(a)–4(e), respectively. In Fig. 4(a), it can be seen that the active layer surface of the reference solar cell is smooth. The smooth film contributes to the separation of excitons, but migration is adversely affected. In Figs. 4(b)–4(e), it is shown that the surface roughness increases after being incorporated with DT in the active layers. A rough film usually has a good self-assembly property and can form better phase separation. An appropriate roughness of the film surface can effectively increase the D/A interfaces and decrease the transmission distance of charge in polymer, which is beneficial to the separation and transportation of charges.[16–18] Moreover, when 1vol% DT is added as a processing additive, the film presents a fibrous structure in Fig. 4(c). In other words, a good network interpenetrating structure is formed between the donors and receptors, improving the transportion of charges.[19] In general, the morphology of the active layer is effectively improved by DT.

In summary, we have demonstrated that the performances of PSCs can be improved by adding DT to the active layer of P3HT: PCBM blends. Optical property of the devices indicates that appropriate addition of DT can increase the intensity of light absorption and EQE. The variations of film morphology indicate that appropriate addition of DT to the active layers can improve the separation and transportation of charges. A comparison of performance parameters of all the devices shows that the device incorporated with DT as processing additive at 1vol% is optimal. The conversion efficiency of devices is improved from 2.2% to 3.1%, an improvement of more than 40% compared to the reference solar cell.

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