6.5% Efficiency of Polymer Solar Cells Based on poly(3-hexylthiophene) and Indene-C_{60} Bisadduct by Device Optimization

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Bulk heterojunction (BHJ) polymer solar cells (PSCs) have attracted more and more attention as a renewable energy source owing to their advantages of easy fabrication, low cost, light weight, and the possibility to fabricate flexible devices.\[1\]–[6] In this type of device, a blend of an electron-donating material (p-type conjugated polymers) and an electron-accepting material (n-type fullerene derivatives) is used as the active layer. One of the most representative BHJ PSCs is the device based on a blend of poly(3-hexylthiophene) (P3HT) as the electron donor and a soluble C_{60} derivative, (6,6)-phenyl-C_{61}-butyric acid methyl ester (PCBM) as the electron acceptor. The power conversion efficiency (PCE) of the PSCs based on P3HT:PCBM reached over 4%\([5\)–\[9]\] by thermal treatment,\[3\] solvent\[6\] and vapor\[8\] annealing, as well as mixture solvent treatment.\[9\] Moreover, the high efficiency of the devices is reproducible in different laboratories and insensitive to the active layer thickness of the devices in the range of ∼100–300 nm, which is very important for future low-cost and large-area fabrication of the PSCs by solution-processing. However, further improvement of the photovoltaic performance of the PSCs based on P3HT:PCBM is limited by the relatively large bandgap of P3HT (∼1.9 eV) (which limits the harvest of solar light) and the relatively small energy difference between the lowest unoccupied molecular orbital (LUMO) of PCBM and the highest occupied molecular orbital (HOMO) of P3HT (which results in a lower open circuit voltage \(V_{oc}\) of the P3HT:PCBM based PSCs to ∼0.6 V).

To further improve P3HT-based device performance, different C_{60} derivatives\[10\]–[16] have been synthesized for photovoltaic electron acceptors. Particularly, many efforts have been devoted to modify the substituent of PCBM in the introduction of additional substituents on its phenyl ring,\[10\] \[11\] or replacing the phenyl ring with other groups.\[12\] However, among these fullerene derivatives, most show poorer or just comparable photovoltaic properties to that of PCBM.\[12\]–[16]\[1] In recent years, PCBM bisadduct\[17\] or PCBM multi-adduct\[18\] and endohedral fullerenes\[19\] were reported for the application as photovoltaic acceptor materials. These fullerene derivatives possess higher LUMO energy levels which result in higher \(V_{oc}\) as well as higher PCE\[17\]–[19] of the P3HT based PSCs.

Recently, our group reported a novel indene-C_{60} bisadduct (ICBA) (see the inset of Figure 1)\[20\] with a higher LUMO energy level of ∼3.74 eV which is 0.17 eV higher than that of PCBM. The PSCs based on P3HT as donor and ICBA as acceptor showed a high \(V_{oc}\) of 0.84 V and a higher PCE of 5.44%,\[20\] which is very attractive for future low cost PSCs. For further exploring the potential of the new acceptor ICBA in the high performance PSCs, we carried out detailed device optimization of the PSCs based on P3HT:ICBA in this work, by optimizing the weight ratio of P3HT:ICBA and the pre-thermal annealing temperature. Under the optimized conditions with the weight ratio of P3HT:ICBA = 1:1, pre-thermal annealing at 150 °C for 10 min, a PCE as high as 6.48% was achieved with a \(V_{oc}\) of 0.84 V, a short circuit current \(I_{sc}\) of 10.61 mA/cm², and a fill factor \(FF\) of 72.7%. The PCE of 6.48%, the \(V_{oc}\) of 0.84 V, and the \(FF\) of 72.7% all are the highest values reported in the literatures so far for the P3HT-based PSCs. Absorption spectra and atomic force microscopy (AFM) morphology of P3HT:ICBA (1:1, w/w) blend films without or with thermal annealing were studied for understanding the origin of the thermal annealing effect on the photovoltaic performance of the PSCs. The results indicate that strong absorption and optimum surface morphology of the P3HT:ICBA blend films annealed at 150 °C for 10 min play key role in achieving the best performance of the PSCs.

We fabricated the PSCs with the structure of ITO/PEDOT:PSS/ P3HT:ICBA (1:1, w/w)/Ca/Al, where the polymer P3HT was used as electron donor and fullerene derivative ICBA was used as electron acceptor. The detailed experimental conditions for the device fabrication and characterization were described in Supporting Information. The blend films were prepared using the same method as that in the reported literatures\[6\]–[20] and annealed before the vacuum deposition of metal negative electrode (pre-thermal annealing) at different temperatures between 140–180 °C for obtaining the best photovoltaic performance. For comparison, the PSCs based on P3HT:PCBM (1:1, w/w) with commercial PCBM as acceptor were also fabricated. Figure 1 shows the \(I-V\) curves of the PSCs without or with pre-thermal annealing treatment under the illumination of AM1.5G, 100 mW/cm². The photovoltaic performance data of the PSCs, including \(V_{oc}\), \(I_{sc}\), \(FF\), and PCE values, are summarized in Table 1 for a clear comparison. As shown in Table 1, the pre-thermal annealing has obvious effect on the photovoltaic performances of the P3HT:ICBA based PSCs. The PSC without thermal treatment delivered a PCE of 4.84% with \(V_{oc}\) of 0.80 V, \(I_{sc}\) of 9.30 mA/cm², \(FF\) of 65.0%. While by annealing the active layer at 140 °C for 10 min, the \(V_{oc}\), \(I_{sc}\), \(FF\), and PCE of the device increased obviously

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to 0.84 V, 10.44 mA/cm², 72.2% and 6.33% respectively. The increment of the $V_{oc}$, $I_{sc}$, $FF$, and PCE after thermal annealing agrees with that of the P3HT-based PSCs reported in literature.

By annealing the active layer at 150 °C for 10 min, the PSC demonstrates the best performance with $V_{oc}$ of 0.84 V, $I_{sc}$ of 10.61 mA/cm², $FF$ of 72.7%, and PCE of 6.48%. Further increasing the annealing temperature to 160 or 180 °C, the PCEs of the PSCs decreased due to the decrease of $I_{sc}$. The photovoltaic performances of the P3HT:PCBM based PSCs with or without pre-thermal treatment are also listed in Table 1 for comparison. We can see intuitively that thermal annealing the P3HT:PCBM active layer at 150 °C for 10 min induces a little decrease of $I_{sc}$ from 10.51 to 9.91 mA/cm² which results in the decrease of PCE from 3.84% to 3.73%, although the $V_{oc}$ and $FF$ of the PSC under thermal treatment increased slightly. In comparison of the two acceptors of ICBA and PCBM in the P3HT-based PSCs with a weight ratio of donor:acceptor = 1:1 and by thermal annealing at 150 °C for 10 min, the $V_{oc}$ (0.84 V) of the device with ICBA as acceptor is increased by 42% than that (0.59 V) of the device with PCBM as the acceptor, which is consistent with our previous report.

Obviously, the $V_{oc}$ increment of the ICBA-based PSC is benefited from the higher LUMO energy level of ICBA, because it is well known that $V_{oc}$ of the PSCs is proportional to the difference between the HOMO of the donor (here it is P3HT) and the LUMO of the acceptor. The $I_{sc}$ of the ICBA-based device is 10.61 mA/cm² which is slightly higher than that (10.51 mA/cm²) of the PCBM-based PSC. $FF$ of the ICBA-based device reached 72.7% which is by 15% higher than that (63.0%) of PCBM-based device, and it is the highest value for the solution-processing organic solar cells reported so far. The $FF$ increment of the ICBA-based PSC means the decreased series resistance and optimum morphology of P3HT:ICBA blend film by the annealing at 150 °C for 10 min. The significant increase in $V_{oc}$ and $FF$, and a little higher $I_{sc}$ lead to the higher PCE of 6.48% for the ICBA-based PSC, which is 69% increased in comparison with the PCE of 3.84% for the traditional PCBM-based device. It should be mentioned that the reproducibility of the high efficiency of the P3HT:ICBA (1:1, w/w) PSCs with pre-thermal annealing at 150 °C for 10 min is quite good. We tested 20 devices with the same experimental conditions, and the PCEs of the PSCs are all higher than 6% (from 6.06% to 6.76%). The results indicate that the photovoltaic performance of ICBA as acceptor in the P3HT-based PSCs is greatly superior to that of the traditional PCBM.

External quantum efficiencies (EQEs) of the PSCs based on P3HT:PCBM and P3HT:ICBA, and the corresponding absorption spectra for P3HT:ICBA blend films (1:1, w/w) without or with thermal treatment are shown in Figure 2. High EQE values were observed in both PCBM-based device and ICBA-based device, suggesting that the photon-electron conversion processes are rather efficient. The shapes of EQE curves of P3HT:ICBA based PSCs are similar to the corresponding absorption spectra of the P3HT:ICBA blend films (1:1, w/w). And there are three vibronic absorption shoulders at 512, 555 and 600 nm, respectively, in the absorption spectra of the P3HT:ICBA PSCs.
The I-V curves and the corresponding photovoltaic data of the PSCs are shown in Figure S1 and Table S1, respectively in the Supporting Information. The device with P3HT:ICBA weight ratio of 1.5:1 shows the PCE of 5.77% with $V_{oc}$ of 0.85 V, $I_{sc}$ of 9.93 mA/cm$^2$, and $FF$ of 68.4%, and that of P3HT:ICBA = 1:1.5 (w/w) demonstrates the PCE value of 5.49% with $V_{oc}$ of 0.83 V, $I_{sc}$ of 8.81 mA/cm$^2$, and $FF$ of 75.1%. Obviously, the P3HT:ICBA weight ratio of 1:1 is the best from the viewpoint of $I_{sc}$ and PCE of the PSCs.

The morphology of the photoactive layer is very important for the photovoltaic performance of PSCs. We used the atomic force microscopy (AFM) to investigate the morphology of the P3HT:ICBA blend films without or with thermal treatment. The AFM topography and phase images are shown in Figure 3. We can see that the surface of the blend film before the visible region for the P3HT:ICBA blend films, which can be ascribed to the absorption of P3HT. The peak at 512 nm is the absorption of P3HT main chain, and the other two peaks in longer wavelength are due to the interchain interactions in the ordered P3HT crystalline regions in the films. The EQE values of the PSCs and the absorption intensities of the blend films in the wavelength range of 450–650 nm (which is the absorption range of P3HT) are both in the same order of P3HT:ICBA (150 °C, 10 min) > P3HT:1CBA (without thermal annealing) > P3HT:ICBA (180 °C, 5 min), which is consistent with the tendency of $I_{sc}$ of the PSCs based on the blend of P3HT:ICBA.

For investigating the effect of the weight ratio of P3HT:ICBA on the photovoltaic properties of the PSCs, we fabricated the PSCs with the P3HT:ICBA weight ratios of 1.5:1, 1:1 and 1:1.5, respectively, with pre-thermal annealing at 150 °C for 10 min. The I-V curves and the corresponding photovoltaic data of the PSCs are shown in Figure S1 and Table S1, respectively in the Supporting Information. The device with P3HT:ICBA weight ratio of 1.5:1 shows the PCE of 5.77% with $V_{oc}$ of 0.85 V, $I_{sc}$ of 9.93 mA/cm$^2$, and $FF$ of 68.4%, and that of P3HT:ICBA = 1:1.5 (w/w) demonstrates the PCE value of 5.49% with $V_{oc}$ of 0.83 V, $I_{sc}$ of 8.81 mA/cm$^2$, and $FF$ of 75.1%. Obviously, the P3HT:ICBA weight ratio of 1:1 is the best from the viewpoint of $I_{sc}$ and PCE of the PSCs.

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annealing is quite rough and the interpenetrating network of P3HT:ICBA is poor. When the blend film is annealed at 150 °C for 10 min, the surface of the blend film shows a higher PCE of 6.48%, the thickness-insensitivity and good reproducibility of the P3HT-PCBM device. However, a too rough surface morphology of the blend film may induce poorer contact between the active layer and cathode. It should be mentioned that the surface roughness of 7.9 nm of the active layer for the optimized device here is quite close to that (9.5 nm) of the best P3HT:PCBM device.

In conclusion, we carried out device optimization of BHJ PSCs based on P3HT as donor and PCBM as acceptor. The optimized PSC with the P3HT:ICBA weight ratio of 1:1, solvent annealing and pre-thermal annealing at 150 °C for 10 min, exhibits a high PCE of 6.48% with $V_{OC}$ of 0.84 V, $J_{SC}$ of 10.61 mA/cm², and FF of 72.7%, under the illumination of AM 1.5G, 100 mW/cm². The PCE of 6.48%, the $V_{OC}$ of 0.84 V, and the FF of 72.7% all are the highest values reported in the literatures so far for P3HT-based PSCs. Taking into consideration of the advantages of thickness-insensitivity and good reproducibility of the P3HT-based PSCs, these high-efficiency PSCs based on P3HT:ICBA are a very significant contribution to future commercialization of PSC devices. The solvent annealing and thermal annealing at 150 °C for 10 min are the key points for realizing the high performance, which benefits from the stronger absorption and the optimum surface morphology obtained by the treatment.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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