Improved performance of P3HT:PCBM solar cells by both anode modification and short-wavelength energy utilization using Tb(aca)$_3$phen*

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The performance of P3HT:PCBM solar cells was improved by anode modification using spin-coated Tb(aca)$_3$phen ultrathin films. The modification of the Tb(aca)$_3$phen ultrathin film between the indium tin oxide (ITO) anode and the PEDOT:PSS layer resulted in a maximum power conversion efficiency (PCE) of 2.99% compared to 2.66% for the reference device, which was due to the increase in the short-circuit current density (J_{sc}). The PCE improvement could be attributed to the short-wavelength energy utilization and the optimized morphology of the active layers. Tb(aca)$_3$phen with its strong down-conversion luminescence properties is suitable for the P3HT:PCBM blend active layer, and the absorption region of the ternary blend films is extended into the near ultraviolet region. Furthermore, the crystallization and the surface morphology of P3HT:PCBM films were improved with the Tb(aca)$_3$phen ultrathin film. The ultraviolent–visible absorption spectra, atomic force microscope (AFM), and X-ray diffraction (XRD) of the films were investigated. Both anode modification and short-wavelength energy utilization using Tb(aca)$_3$phen in P3HT:PCBM solar cells led to about a 12% PCE increase.

Keywords: P3HT:PCBM, anode modification, polymer solar cells

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1. Introduction

Recently, polymer solar cells (PSCs) have attracted much attention due to their low production cost, light weight, mechanical flexibility, and use as a green and renewable energy source.[1,2] The performance of PSCs is greatly improved when the bulk-heterojunction (BHJ) device is used, because of a highly increased interfacial area between donor and acceptor materials, the ultra-fast charge separation from the conjugated polymer to acceptors, and the formation of interpenetrating polymer networks for charge transport.[3–5] Poly(3-hexylthiophene) (P3HT) has been used as a traditional material for the polymer BHJ solar cells because of its low production cost, high charge carrier mobility, and solution processing.[6–8]

The performance of PSCs is always limited by the relatively narrow absorption range of the active layer in the visible light, the short-exciton diffusion length, the low charge carrier mobility, and the poor morphology of the active layer.[9] To improve the active layer light harvesting capability, many researches exploring small band gap materials or combining different organic materials with complementary absorption spectra in one device have been carried out.[10–14] Various methods, such as solvent annealing,[15] additives,[16–19] thermal annealing,[20] and electrode modification,[21,22] have been empolyed to increase the power conversion efficiency (PCE). Buffer layers or ultrathin films, including PEDOT:PSS, LiF, MoO_3, WO_3, V_2O_5, $CsCO_3$, and TiO_2, have been used to modify the electrodes to improve the device performance.[23–29] However, most of the buffer layers or ultrathin films can hardly improve the short-wavelength energy utilization and little attention has been paid to using rare earth (RE) elements for anode modification. RE metal complexes, especially europium (III) and terbium (III) complexes, have some good characteristics, including extremely strong absorption in the near visible light range, strong photoluminescence (PL) in the visible range, and high internal quantum efficiencies,[30] which have found wide applications in luminescence devices.[31–33] The luminescence behaviors of terbium and europium complexes have been reported.[34–36] These complexes are probably suitable for broadening the absorption spectra of active layer materials in PSCs.

In this paper, we explored ultrathin film Tb(aca)$_3$phen for the anode modification of PSCs. The effect of the anode modification with an ultra thin Tb(aca)$_3$phen film on the device performance was studied. The ultravieloet–visible absorption peak of P3HT:PCBM showed broader and stronger absorption after inserting Tb(aca)$_3$phen, which should be beneficial for

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the solar cell due to the improved device light harvesting ability. Moreover, the crystallization and the surface morphology of the active layer improved by the Tb(aca)$_3$phen film were explored by X-ray diffraction (XRD) and atomic force microscopy (AFM), respectively. An increase of 12% in PCE was achieved by the anode modification with Tb(aca)$_3$phen.

2. Experimental details

Indium tin oxide (ITO) coated glass substrates with a sheet resistance of 15 Ω/□ (purchased from Shenzhen Jinghua Display Co. Ltd) were cleaned consecutively in ultrasonic baths containing acetone, ethanol, and de-ionized water and then dried by nitrogen blowing. UV-ozone treatment on the pre-cleaned ITO substrates was carried out for 10 min to enhance the work function of the ITO substrates. Tb(aca)$_3$phen was dissolved in chlorobenzene (concentration: 2 mg/ml), then spin-coated onto the ITO substrates under 5000 rpm in 40 s. The ultrathin film Tb(aca)$_3$phen-coated ITO substrates were heat-treated at 120 °C for 10 min in atmosphere. The poly (3,4-ethylenedioxythiophene)-poly (styrenesulfonate) (PEDOT:PSS) (Lumtec) was spin-coated onto the Tb(aca)$_3$phen-coated ITO substrates under 3000 rpm in 40 s. Then the PEDOT:PSS-coated ITO substrates were heat-treated at 120 °C for 10 min in atmosphere. Polymer materials P3HT and PCBM (Lumtec) were dissolved in chlorobenzene (concentration: 20 mg/ml) and then mixed together with an equal volume ratio. Then the 0.8 nm LiF buffer layer and 100 nm aluminum (Al) cathode, consisting of an active area of about 0.09 cm^2, were deposited by thermal evaporation through a four-square shadow mask under 5×10^{-4} Pa. All cells were annealed at 120 °C for 10 min in atmosphere, which is the post-annealing treatment.

The absorption spectra of the active layers were measured with a Shimadzu UV-3101 PC spectrometer. The current–voltage (I–V) characteristics of the PSCs were measured both in the dark and under illumination at 100 mW/cm^2 under an AM 1.5 condition. All measurements were carried out in atmosphere and at room temperature.

3. Results and discussion

The J–V characteristics of the PSCs with structures (I)–(III) listed below were prepared under the same conditions and were measured in the dark and under illumination:

(I) glass/ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al (reference, without Tb),

(II) Tb(aca)$_3$phen/glass/ITO/PEDOT : PSS/P3HT : PCBM/LiF/Al (with Tb outside),

(III) glass/ITO/Tb(aca)$_3$phen/PEDOT : PSS/P3HT : PCBM/LiF/Al (with Tb inside).

The results are shown in Fig. 1. The characteristic parameters abstracted from the J–V curves are listed in Table 1. Device (II) exhibits a small improvement in the photovoltaic performance compared with the reference devices due to J_{sc} increasing to 8.5 mA/cm^2. The PCE of device (III) with a Tb(aca)$_3$phen film is very successfully increased, along with FF slightly decreased and J_{sc} increased remarkably. The J_{sc} is increased from 8.1 mA/cm^2 to 9.4 mA/cm^2, and the best PCE is increased from 2.66% to 2.99%.

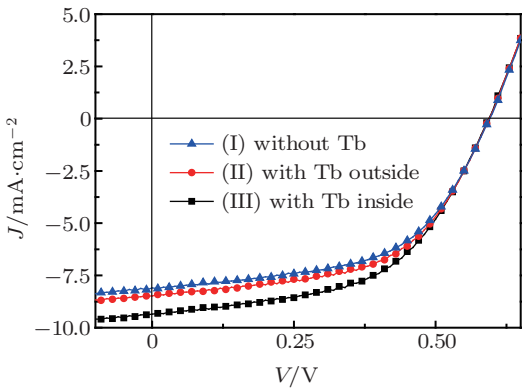


Fig. 1. (color online) The J–V characteristics of solar cells with and without Tb(aca)$_3$phen (Tb) film under the AM 1.5 condition.

Table 1. Photovoltaic parameters for the devices with and without anode modification.

	Device (I)	Device (II)	Device (III)
V_{oc}/V	0.59	0.59	0.59
J_{sc}/mA·cm^{-2}	8.1	8.5	9.4
FF/%	55.6	55.6	53.9
Best PCE/%	2.66	2.77	2.99
Ave. PCE/%	2.54	2.68	2.85

*For the average PCE, more than 24 cell samples were evaluated.

To study the characteristics of Tb(aca)$_3$phen, the absorption and PL spectra were measured. Figure 2(a) shows photos of Tb(aca)$_3$phen powder excited by 330 nm light under room conditions or in the dark, which exhibit a strong photoluminescence due to high internal quantum efficiencies of RE metal complexes. The PL intensity of Tb(aca)$_3$phen powder does not show any apparent decay after seven days preservation under room conditions. Tb(aca)$_3$phen was spin-coated onto quartz substrates under 5000 rpm in 40 s, then the ultrathin film Tb(aca)$_3$phen-coated quartz substrates were heat-treated at 120 °C for 10 min in atmosphere. The absorption and PL spectra of the ultrathin Tb(aca)$_3$phen film are shown in Fig. 2(b). Tb(aca)$_3$phen has a strong and broad absorption in the range near ultraviolet. Under 330 nm light excitation, the terbium ion (Tb^{3+}) characteristic emissions peaking at 488 nm, 545 nm, 582 nm, and 620 nm are obtained, which correspond to the energy level transitions $^5D_4$–^7F_J (J = 3, 4, 5, 6) of Tb^{3+}, respectively,[30,37] as shown in Fig. 2(c). Here

symbols $^{2S+1}L_J$ are used, where S is the total spin quantum number; L is the total orbital angular momentum quantum number in spectroscopic notation, $L = 0, 1, 2, 3, \ldots$ for S, P, D, F, ...; and J is the total angular momentum quantum number. It is known that the Tb^{3+} ions in $Tb(aca)_3phen$ are always at the symmetrical center, a strong emission exists due to the transition of $^5D_4$–$^7F_5$.[38] According to the luminescent mechanism of the RE metal complex, a singlet-to-triplet conversion by intersystem crossing and an intra-molecular energy transfer from the ligand to the metal ions will occur. The excited state of the luminescent Tb^{3+} ion is populated due to the energy transfer from the triplet state of the ligand. The UV–visible absorption spectra of the P3HT:PCBM thin film after annealing treatment and the PL spectra of the $Tb(aca)_3phen$ thin film are shown in Fig. 2(d). P3HT has a strong and broad absorption in the visible light range, especially in the range from 400 nm to 600 nm. The spectral overlapping between the emission spectra of $Tb(aca)_3phen$ and the absorption spectra of P3HT assists the energy transfer from $Tb(aca)_3phen$ to P3HT. It may be one of the reasons for improving the J_{sc} of PSCs with $Tb(aca)_3phen$ as the short-wavelength energy utilization material.

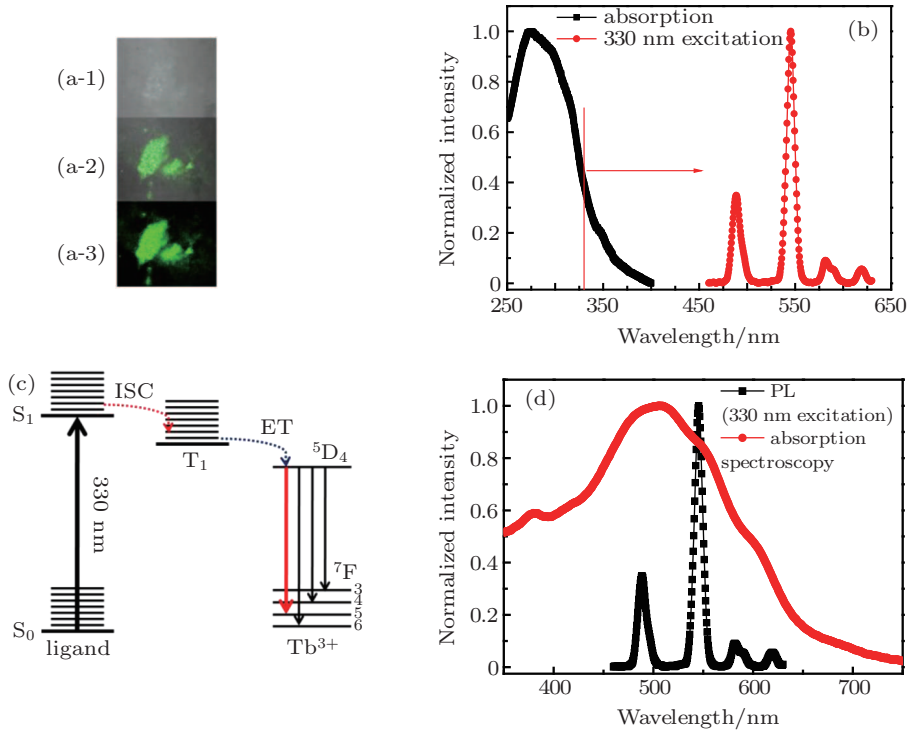


Fig. 2. (color online) Photos of $Tb(aca)_3phen$ powder (a-1) under room conditions, (a-2) excited by 330 nm light under room conditions, (a-3) excited by 330 nm light in the dark. (b) The absorption and photoluminescence spectra of the ultrathin $Tb(aca)_3phen$ film. (c) Schematic diagram of the processes of ligand light absorption, charge transfer, energy transfer, and luminescent transition on Tb^{3+}. (d) PL spectra of $Tb(aca)_3phen$ and absorption spectra of P3HT.

In order to demonstrate the effect of anode modification of $Tb(aca)_3phen$ ultrathin films, the UV–visible absorption spectra of PEDOT:PSS/P3HT:PCBM, $Tb(aca)_3phen$/PEDOT:PSS/P3HT:PCBM thin films with and without annealing treatment were measured, as shown in Fig. 3. It is believed that the absorption spectra of the P3HT:PCBM active layer between 450 nm and 650 nm increase after an annealing treatment, the full width at half maximum (FWHM) broadens, and the spectra exhibit more vibrations and are red-shifted.[39] It is known that the shoulder peak at about 545 nm is attributed to the absorption of the extended conjugation of P3HT in the solid state and the absorption shoulder peak at around 610 nm, which is assigned to the inter-chain interactions, becomes bigger and more obvious.[40] As shown in Fig. 3, the $Tb(aca)_3phen$ ultrathin film nearly has no absorption in the range of 400–800 nm, which is an essential requirement for the anode interfacial layer in order to maintain the high transparency. However, the $Tb(aca)_3phen$/PEDOT:PSS/P3HT:PCBM ternary layers after annealing exhibit stronger absorption compared to the PEDOT:PSS/P3HT:PCBM binary layers. It is due to the closer chain packing of P3HT which results from the strong interchain interactions with the $Tb(aca)_3phen$ ultrathin film. The increased absorption intensity gives the possibility to increase the J_{sc} of PSCs with anode modification.

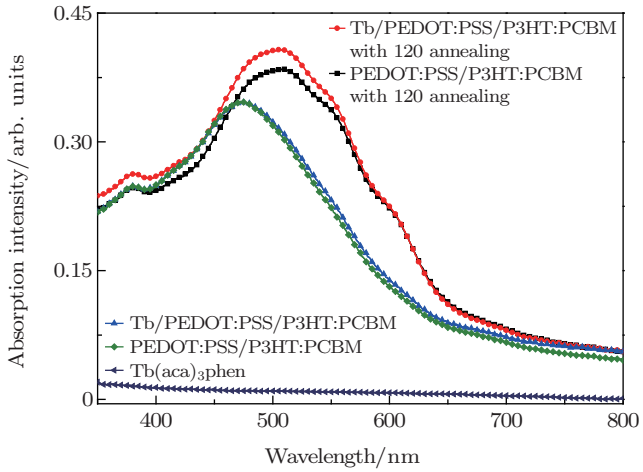


Fig. 3. (color online) UV–visible absorption spectra of $Tb(aca)_3phen$ ultrathin films, PEDOT:PSS/P3HT:PCBM blend thin films with and without $Tb(aca)_3phen$ (Tb) ultrathin film before and after annealing.

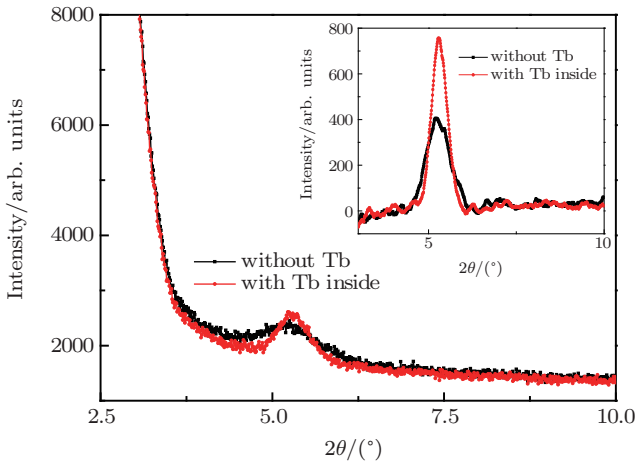


Fig. 4. (color online) XRD diagrams of P3HT:PCBM with and without $Tb(aca)_3phen$ (Tb) ultrathin film.

For the further investigation of the effect of $Tb(aca)_3phen$ ultrathin films on P3HT molecular arrangement, the XRD patterns of the P3HT:PCBM active layers on ITO/PEDOT:PSS or ITO/$Tb(aca)_3phen$/PEDOT:PSS are shown in Fig. 4. The XRD patterns in Fig. 4 depict the crystallization of P3HT, which is shown by the changes of the peak intensity and the FWHM. The size of the crystallites is calculated from the broadening of a peak in the diffraction pattern with Scherrer's equation $\tau = \frac{K\lambda}{\beta \cos\theta}$. A characteristic peak around $2\theta = 5.4°$, which is associated with the lamella structure of thiophene rings in P3HT,[41] is used. This diffraction peak of P3HT:PCBM is increased for the films prepared on the $Tb(aca)_3phen$ ultrathin film, meanwhile its half width decreases. The calculated size of the crystallite increases for P3HT:PCBM with the $Tb(aca)_3phen$ ultrathin film. The results of the XRD exhibit that the volume fraction of the π-conjugated planes of the P3HT (1 0 0) phase normal to the substrate increases after the anode modification. The enhanced π-conjugated planes might be responsible for the enhanced charge carrier transport in the composite films, resulting in the J_{sc} improvement.

AFM was employed to characterize the surface morphology of the active layers on different substrates. The AFM height images of blend films are shown in Fig. 5. The root mean square (RMS) values of P3HT:PCBM thin films with and without the $Tb(aca)_3phen$ layer are 1.63 nm and 1.74 nm, respectively. The RMS values of the films are nearly the same, and both films are very smooth, which sustains good J_{sc} of the devices. According to the AFM images, the P3HT:PCBM active layer has smaller domains with $Tb(aca)_3phen$ ultrathin films. The slight decrease in roughness is attributed to the formation of small PCBM domains and P3HT domains. The small domains may increase the interfaces between donor and acceptor, which are beneficial for a better charge separation as well as a good charge carrier transport efficiency.[42]

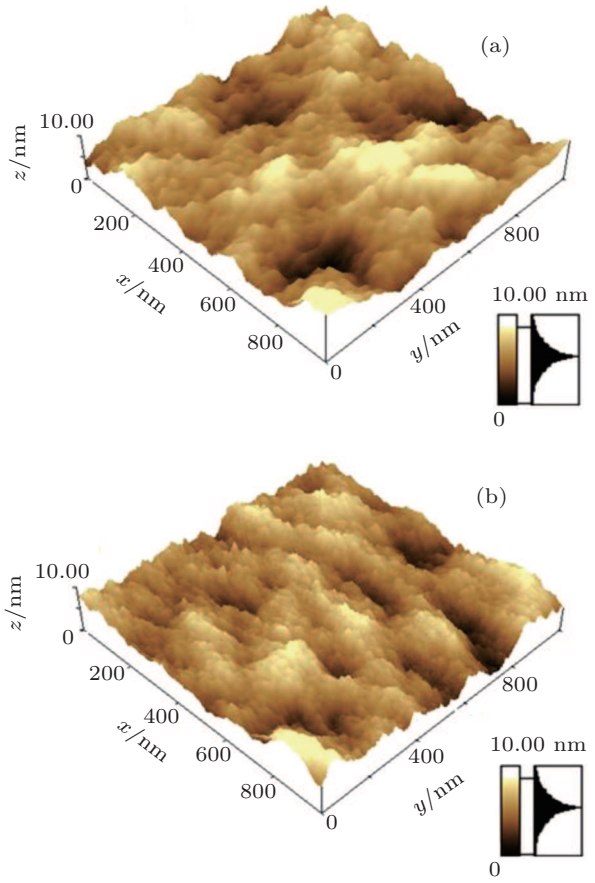


Fig. 5. (color online) AFM images of the P3HT:PCBM composite films (a) without and (b) with $Tb(aca)_3phen$ ultrathin film.

According to the above results, the reasons for improving the performance of P3HT:PCBM solar cells lie in short-wavelength energy utilization and anode modification using $Tb(aca)_3phen$. It is believed that $Tb(aca)_3phen$ tunes the short-wavelength of the incident light to the absorption wavelength of the P3HT:PCBM active layer, thus increasing J_{sc} and improving the PCE of the PSCs.[43,44] The other improvement are likely to be attributed to the anode modification, which then exhibits beneficial crystallization and phase separation

of P3HT domains in the active layer itself. These explanations are also supported by XRD and AFM experimental results. Meanwhile, there is no change in V_{oc} with and without the Tb(aca)$_3$phen ultrathin layer. The V_{oc} strongly depends on the interfacial contact and the energy level difference between the highest occupied molecular orbital (HOMO) of the electron donor (P3HT) and the lowest unoccupied molecular orbital (LUMO) of the electron acceptor (PCBM). The balance of these dynamic processes, such as exciton formation, diffusion, and dissociation, charge carrier transporting and collection, plays a very important role for improving the PCE. The PCE of PSCs with short-wavelength energy utilization is increased to 2.77% from 2.66% for the reference ones. Meanwhile, the optimized PCE with both short-wavelength energy utilization and anode modification is increased to 2.99%.

4. Conclusion

In summary, the best PCE of P3HT:PCBM bulk heterojunction solar cells with Tb(aca)$_3$phen ultrathin film as the anode modification was improved to 2.99%. In comparison to the reference devices, the devices with the anode modification exhibited an increase of 12% in PCE due to the improved J_{sc}, which could be attributed to the effect of Tb(aca)$_3$phen on the widened absorption spectra of the blend films, the improvement of crystallized P3HT inter-chain packing for photon harvesting and charge carrier transporting. These results demonstrate that Tb(aca)$_3$phen may be an efficient short-wavelength energy utilization and anode modification for enhancing the performance of PSCs.

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