Vol 14 No 5, May 2005
1009-1963/2005/14(05)/1032-04

Chinese Physics

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Efficient photovoltaic cells from low band-gap fluorene-based copolymer*

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(Received 9 July 2004; revised manuscript received 8 November 2004)

Polymer photovoltaic cells based on low band-gap copolymer, poly [2,7-(9,9-dioctyl) fluorene-co-5,5'-(4,7-diselenophenyl)-2,2'-yl-2,1,3-benzothiadiazole] (PFSeBT) are investigated, focusing on the effects of cathode and blend concentration on device performance. The best device, with active layer from PFSeBT:PCBM=1:2 blend and with LiF/Al as cathode, achieves an open-circuit voltage of 1.00V, a short-circuit current density of 4.42mA/cm^2, and energy conversion efficiency of 1.67% under AM1.5 illumination (100mW/cm^2). The short-circuit current density indicates the dependence of power law on the incident light intensity with a power index of 0.887. All devices have a spectral response up to 680nm. The results indicate that PFSeBT is a potential polymer functioning as an electron donor in polymer photovoltaic cells.

Keywords: polymer photovoltaic cell, low band-gap copolymer, spectral response
PACC: 7240, 7860, 8630J

1. Introduction

Polymer photovoltaic cells (PPVCs) are promising candidates for solar energy conversion due to their mechanical flexibility, light weight, easy fabrication, and potential low cost.[1−4] Energy conversion efficiencies exceeding 2.5% under AM1.5 illumination (100mW/cm^2) have recently been reported for bulk heterojunction polymer solar cells.[5,6] Yet, the energy conversion efficiency needs to be further improved for commercial applications. One of the limitations of polymer solar cells is the large band-gap of the polymer,[4,7,8] which serves as a donor phase in the device. In common use, electron donor conjugated polymers in PPVCs, such as substituted poly (*p*-phenylene vinylene)s (PPVs) and polythiophenes, have their optical band-gaps of 2.0–2.2eV, while the maximum photon flux of the solar emission is around 1.8eV. By use of low band-gap polymers ($E_g < 1.8$eV) to expand the spectral region of PPVCs the light absorption can be expected to be enhanced.

A series of low band-gap copolymers incorporating narrow band-gap comonomer into polyfluorene backbone has been successfully synthesized in our laboratory.[9−12] High-performance polymer photovoltaic cells have been made from one of the low band-gap copolymers: 9, 9-dioctylfluorene and 4, 7-di-2-thienyl-2, 1, 3-benzothiadiazole blending with methanofullerene [6, 6]-phenyl C61-butyric acid methyl ester (PCBM).[13] Our practice demonstrates that the band-gap of copolymer containing selenium element is smaller than that of sulphur element containing analogues.[10] Thus, selenium-containing PPVCs are expected to possess a higher energy conversion efficiency due to their smaller band-gaps and to be capable of absorbing more numbers of photons. In this paper, selenium-containing copolymer, poly [2, 7-(9, 9-dioctyl) fluorene-co-5, 5'-(4, 7-diselenophenyl)-2, 2'-yl-2, 1, 3-benzothiadiazole] (PFSeBT) blending

*Project supported by the National Natural Science Foundation of China (Grant No 90201023) and by the Fund from South China University of Technology (E5123286).

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with PCBM, is utilized in PPVCs. The devices exhibit a large open-circuit voltage of 1.00V and a high energy conversion efficiency of 1.67 % under AM1.5 illumination (100mW/cm^2), and the spectral response increased up to 680 nm.

2. Experiments

PFSeBT is synthesized from 9, 9-dioctylfluorene (DOF) and 4, 7-diselenophenyl-2, 2'-yl-2, 1, 3-benzothiadiazole (SeBT) with a feed ratio of DOF to SeBT 70: 30 by Suzuki coupling reaction. The molecular weight is measured to be 1690 and polydispersity index 2.221. The detailed synthesis route and characterization of PFSeBT will be reported elsewhere.[14] The chemical structures of PFSeBT and PCBM are presented in Fig.1.

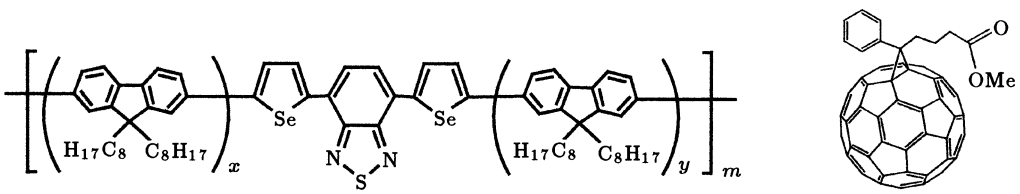


Fig.1. Chemical structures of PFSeBT and PCBM.

PPVCs with the structure of ITO/PEDOT: PSS/active layer/cathode are prepared, where ITO is the abbreviation for indium-tin oxide. Polyethylene dioxythiophene polystyrene sulfonate (PEDOT:PSS, Baytron P 4083, Bayer Co.) with thickness of 80nm is spin-coated from aqueous dispersion. The active layer is spin-coated from PFSeBT and PCBM blends, which are mixed in desired ratios from solutions of PFSeBT (toluene as solvent, 20mg/ml) and PCBM (chlorobenzene as solvent, 16mg/ml). The thickness of the active layer is about 55nm, which is an optimum thickness for PPVs based on PFSeBT and PCBM blends. Barium/aluminum (Ba/Al), lithium fluoride (LiF)/Al and Al are deposited on the active layer as the cathode at a background pressure of 10^{-5}Pa. The spectral response is measured with a commercial photo-modulation spectroscopic system (Model Merlin, Oriel). A calibrated Si photodiode is used for the determination of photosensitivity. Energy conversion efficiencies (η_e) are measured under an AM1.5 solar simulator (with 100mW/cm^2). The current density–voltage ($J-V$) characteristics are measured with a Keithley 236 source-measure unit. The η_e and fill-factor (F.F.) are calculated according to the following equations:[1]

$$\eta_e = \text{F.F.} \times J_{SC} \times V_{OC}/P_{in}, \quad (1)$$

$$\text{F.F.} = J_m V_m / J_{SC} V_{OC}, \quad (2)$$

where P_{in} is the incident radiation flux, J_{SC} and V_{OC} are respectively short-circuit current density and open-circuit voltage, J_m and V_m are respectively the current density and voltage at a maximum power output.

3. Results and discussion

3.1. Absorption of PFSeBT

UV–Visible absorbance of PFSeBT film is shown in Fig.2. Two independent peaks, maximum at 390nm and 560nm, respectively correspond to the absorption of DOF and BSeT segment.[9,11] The 560nm peak extends toward the red range until 680nm, corresponding to an optical band-gap of 1.8eV. The absorption of PFSeBT is very close to that of the terrestrial solar spectrum compared to that of substituted poly PPVs and polythiophenes which are typically used in PPVCs.

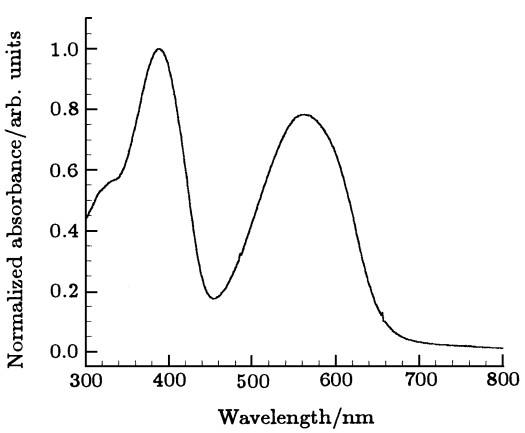


Fig.2. UV–Visible absorption spectrum of PFSeBT film.

3.2. Dependence of device performance on cathode

Under 100mW/cm^2 illumination, photovoltaic parameters of the devices based on PFSeBT:

PCBM=1:4 with different cathodes are listed in Table 1. Firstly, all devices have a high V_{OC} value of 1.00V, which is the highest open-circuit voltage of the polymer photovoltaic cells. Secondly, V_{OC} value remains almost constant despite the difference in the work function of the cathode (Ba is 2.7eV and Al 4.28eV [15]). Thirdly, J_{SC}, F.F. and η_e values may be different in the devices with different cathodes. Ba/Al, bare Al and LiF/Al devices show the improved performance in sequence.

Table 1. Photovoltaic parameters of ITO/PEDOT: PSS/PFSeBT: PCBM=1:4/Cathode.

Cathode	J_{SC}/(mA/cm^2)	V_{OC}/V	F.F./%	η_e/%
Ba(4nm)/Al	2.532	1.00	37.4	0.947
Al	2.945	1.00	38.6	1.137
LiF(2.5nm)/Al	3.283	1.00	40.6	1.332

It has been demonstrated that the obtained variation in V_{OC} is less than 200mV, is much smaller than the variation in work function of Ca, Ag, Al, and Au cathodes, for which a possible reason is suggested to be pinning of the Fermi level at PCBM surface states.[16] Possibly, the same is true of the devices based on PFSeBT and PCBM blend, leading to almost unchanged V_{OC}.

Concerning the overall performance, the device with LiF/Al cathode is superior to Ba/Al and bare Al cases (Table 1). As reported by several authors previously, thin LiF layer could prevent polymer and PCBM from reacting with alkali, alkaline earth metals or aluminum metals.[17–19] Here, the protection effects of LiF layer may also account for the best performance.

From the above study we can see that LiF/Al is a more selective contact to electron collection, so LiF/Al cathode will be used in the following study.

3.3. Dependence of the device performance on concentration

Table 2 summarizes the photovoltaic parameters of devices with various ratios of PFSeBT to PCBM. The ratio of 1:2 (by weight) is the optimized concentration, since device based on this ratio exhibits the best performance: J_{SC}=4.420mA/cm^2, V_{OC}=1.00V, F.F.=37.8% and η_e=1.670% under 100mW/cm^2 illumination. The concentration dependence is mainly determined by the bicontinuous network of donor–acceptor in the active layer.[1,13,20] The optimized concentration will result in the network morphology to favor charge separation in the bulk heterojunction and to leave holes to migrate in the donor phase and electrons in the acceptor phase.

Table 2. Photovoltaic parameters of ITO/PEDOT: PSS/PFSeBT:PCBM/LiF (2.5nm)/Al.

PFSeBT: PCBM	J_{SC}/(mA/cm^2)	V_{OC}/V	F.F./%	η_e/%
1:1	2.411	1.00	30.9	0.744
1:2	4.420	1.00	37.8	1.670
1:4	3.283	1.00	40.6	1.332

Figure 3 shows the $J-V$ characteristics (a) and spectral response (b) of the device with the structure of ITO/PEDOT:PSS/PFSeBT:PCBM (1:2)/LiF(2.5 nm)/Al. Local leakage currents due to weak spots in the film dominate the dark current under low bias voltages, so the dark $J-V$ characteristics can be used to estimate the quality of the active layer. Besides, the relatively low leakage current (Fig.3(a)) reveals the good quality of PFSeBT:PCBM film. Figure 3(b) shows that the peak and the onset of spectral response are 560nm and 680nm, which are red-shifted by 50–60nm, compared with that of the device based on the MEHPPV:PCBM blend.

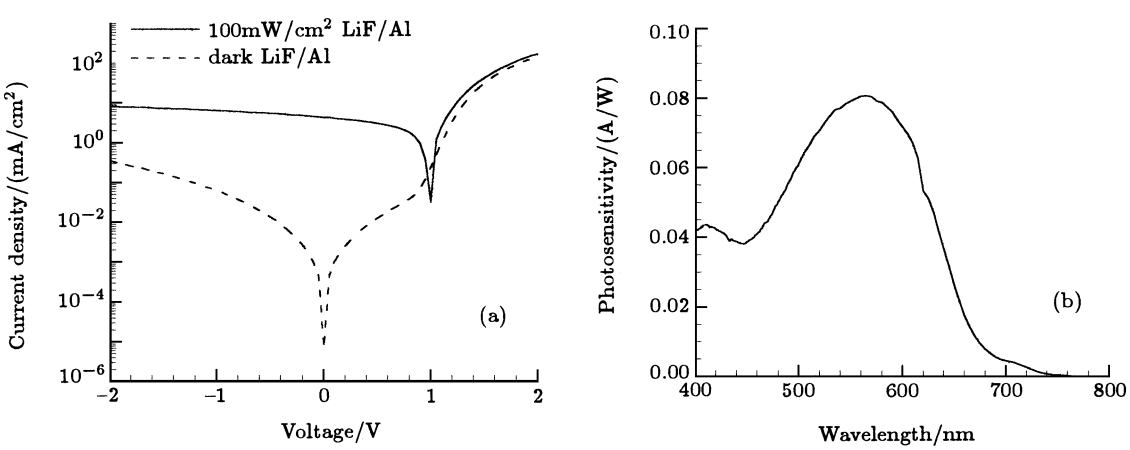


Fig.3. J–V characteristics (a) and spectral response at zero voltage (b) of device ITO/PEDOT:PSS/PFSeBT:PCBM=1:2/LiF/Al.

3.4. Dependence of performance on incident light intensity

Generally, the relation between J_{SC} and incident light intensity I can be described as: $J_{SC} \propto I^{\alpha}$, where α is the characteristic constant for the system studied. For the device of ITO/PEDOT: PSS/PFSeBT: PCBM=1:2/LiF/Al, the relation between J_{SC} and I and the relation between η_e and I are shown in Fig.4. The dependence of J_{SC} on I is fit by the power law,

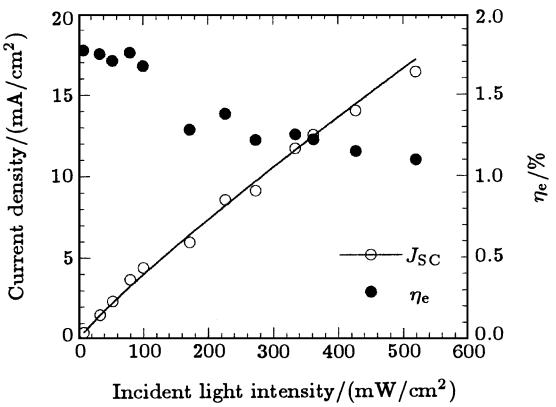


Fig.4. Dependence of short-circuit circuit current density and energy conversion efficiency on incident light intensity for the device ITO/PEDOT: PSS/PFSeBT:PCBM=1:2/LiF/Al.

$J_{SC} \propto I^{0.887}$, α=0.887. The energy conversion efficiency exhibits a higher value under low illumination and slightly decreases with the increasing of the incident light irradiation. Yet, the open-circuit voltage remains constant over the large span of incident light intensity.

4. Conclusions

Bulk heterojunction solar cells based on PFSeBT and PCBM blends are investigated, all devices showing spectral response up to 680nm due to the narrow band-gap of PFSeBT. The device from PFSeBT: PCBM=1:2 blend and with LiF/Al cathode shows an open-circuit voltage of 1.00V, a short-circuit current density of 4.42mA/cm^2, and an energy conversion efficiency of 1.67% under AM1.5 illumination (100 mW/cm^2); the short-circuit current density shows power law dependence on the incident light intensity with an index of 0.887; the energy conversion efficiency exhibits a higher value under low illumination and slightly decreases with the incident light irradiation increasing, while the open-circuit voltage remains constant over the large span of incident light intensity. The results indicate that PFSeBT is a promising polymer as an electron donor material in polymer photovoltaic cells.

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