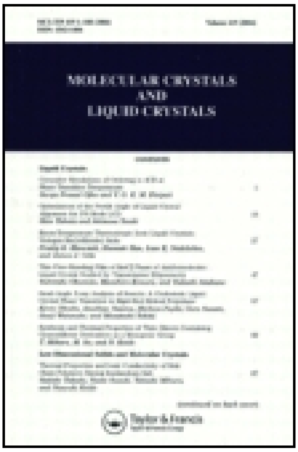

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Flexible Organic Solar Cells Based on Spin-Coated Blend Films of a Phenylene-Thiophene Oligomer Derivative and PCBM

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Flexible Organic Solar Cells Based on Spin-Coated Blend Films of a Phenylene-Thiophene Oligomer Derivative and PCBM

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*Flexible organic solar cells were fabricated on a polyethylene terephthalate (PET) substrate using a phenylene–thiophene oligomer, 3,7-bis[5-(4-*n*-hexylphenyl)-2-thienyl]dibenzothiophene-5,5-dioxide (37HPTDBTSO), as a photoactive donor. In bulk-heterojunction (BHJ) solar cells, many factors such as blend weight ratio, and solution and substrate temperatures have great effects on the photovoltaic performances. The flexible solar cell fabricated from the blend solution with a weight ratio of 1:2 of 37HPTDBTSO to phenyl-C61-butyric acid methyl ester (PCBM) and a temperature of 50°C, exhibited a high open-circuit voltage of 0.74 V and the highest power conversion efficiency of 0.26%.*

Keywords Flexible; oligomer; organic semiconductor; solar cell

1. Introduction

Organic photovoltaic (OPV) cell research is currently undergoing dynamic development, due to the advantages of low cost of production, light weight and capability to make flexible devices in comparison to the traditional silicon-based solar cells [1,2]. Tremendous efforts have been dedicated to developing novel materials and new device manufacture process. So far, the power conversion efficiency (PCE) of 8.62% was achieved in a solution-processed bulk-heterojunction (BHJ) solar cell based on a nanophase-separated blending film of a

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semiconducting polymer as the donor (D) and a soluble fullerene derivative as the acceptor (A) [3]. In small molecule solar cell devices, PCE of a solution-processed single-heterojunction (SHJ) device based on a D-A-D oligomer in combination with a C70-based fullerene reached 6.7% [4]. In these cases, indium tin oxide (ITO) glass substrates were selected, and could not be curved. For flexible and unbreakable characteristics and roll-to-roll manufacture of solar cells, plastic substrates such as polyimide (PI), polyethylene terephtalate (PET) and polyethylene naphtalate (PEN) have been extensively employed. While, much attention has been paid to the fabrication of flexible solar cells using semiconducting polymers as photoactive layer, especially poly(3-hexylthiophene) (P3HT)-based solar cells. Al-Ibrahim *et al.* [5] investigated a common BHJ solar cell based on P3HT and PCBM with PET substrate. Although without any special postproduction treatment, the flexible solar cell spin-coated from a blend solution with the weight ratio of P3HT:PCBM of 1:3 showed a high open-circuit voltage (V_{oc}) of 0.60 V and a PCE of 1.54%. Kuwabara *et al.* [6] easily fabricated a flexible PET-ITO/ZnO/PCBM:P3HT/PEDOT:PSS/Au inverted solar cell without warping of the thin PET film. The maximum PCE was 2.15% for the non-sealed device with 1 cm^2 of effective area in air.

Recently, much work has been focused on the oligomer (as small molecule) semiconductors as an alternative to replace the conjugated polymers in organic solar cells due to several intrinsic advantages. In general, the oligomer semiconductors exhibit higher hole and electron mobility than their polymeric counterparts because they are more likely to exhibit a long-range order [7,8]. Despite these advantages, flexible solar cells based on oligomers have attracted little attention in the area of the organic photovoltaic. Only a few oligomer materials such as pentacene and phthalocyanine were used to fabricate flexible solar cells by a troublesome vacuum thermal deposition method [9,10]. Thiophene-containing oligomers have been widely used in organic electronic, taking advantage of their high charge-carrier mobility, and facile synthesis to tune energy levels [11]. However, to the best of our knowledge, few flexible solar cell based on thiophene-containing oligomer have been reported by the spin-coating method.

In a previous work, we reported the facile synthesis, full characterization and the performances of BHJ solar cell devices of two thiophene-containing heteroaromatic oligomers that are based on a structural combination of a dibenzothiophene-5,5-dioxide core, and thienyl and end-cap hexylphenyl groups [12]. The results showed that 3,7-bis[5-(4-*n*-hexylphenyl)-2-thienyl]dibenzothiophene-5,5-dioxide (37HPTDBTSO, Fig. 1) was a new kind of organic photo-electronic material with D-A-D system, and had a V_{oc} of 0.83V and a moderate PCE of 0.52% in an un-optimized BHJ solar cell with ITO glass substrate. The weight ratio of donor to acceptor in particular significantly changes the morphology of the film and greatly affects the photovoltaic performance. By optimizing the weight ratio of 37HPTDBTSO to PCBM (1:1.5), the good performances of the BHJ solar cell with ITO glass substrate were achieved. Its short circuit current density (J_{sc}) was 2.75 mA/cm^2, the V_{oc} was 0.85 V, the fill factor (FF) was 0.35, and the highest PCE was 0.84% [13]. In this work, oligomer 37HPTDBTSO was extensively used to fabricate flexible solar cells on a PET substrate. The effects of device structure, blend weight ratio, solution and substrate temperatures, and surface morphology on photovoltaic performances would be further investigated.

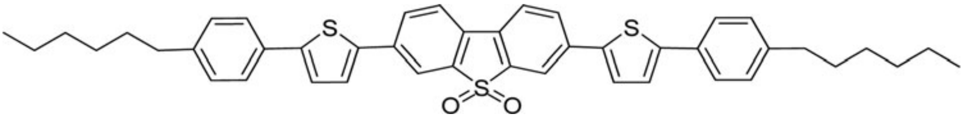

Figure 1. Chemical structure of oligomer 37HPTDBTSO.

2. Experimental

General Methods

All commercially available chemicals were purchased from Tokyo Kasei Industry or Sigma-Aldrich, and used without further purification. The oligomer 37HPTDBTSO was prepared according to the previously reported procedure [12]. Ultraviolet–visible (UV-vis) spectra were recorded using Shimadzu UV-3600 spectrophotometer with the chloroform as a solvent. The vacuum thermal deposition was performed using a MINI VACUUM SYSTEM (SVC-700TM/700-2, SANYU Electron Co., Ltd) in a high vacuum. The growth rate and the thickness of the films were determined by a thickness monitor (STM-100 Thickness/Rate Monitor, SYCON). The topography were imaged using a dynamic force mode atomic force microscope (AFM; SPI3800, SII). Solar cell device performances were investigated under simulated AM 1.5 irradiation (100 mW/cm^2) using a xenon-lamp-based solar simulator (OTENTO-SUNIII, Bunkoukeiki Co.). The Current density-voltage (J-V) were characterised with a Keithley 2400 source meter. The incident photo-to-electron conversion efficiency (IPCE) was recorded using a desktop spectral response and IPCE measurement system (SM-250TF, Bunkoukeiki Co.). All the measurements were carried out in air atmosphere.

Fabrication of Solar Cell Devices

Two types of the flexible solar cell devices were fabricated, and their geometries were depicted in Fig. 2. Several multi-layer heterojunction solar cell devices were prepared using the following device fabrication procedure: The PET/ITO substrates (Sanyo Vacuum Industries Co., Ltd, Japan, 30 $\Omega/\square$) were sequentially patterned lithographically, cleaned with detergent, ultrasonicated in isopropanol, and dried in a N_2 flow. The substrate was further cleaned with UV ozone for 30 min. An aqueous solution of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, 1.3 wt% dispersion in H_2O, conductive grade, Aldrich) was spin-coated onto the cleaned PET/ITO substrate at 4000 rpm for 90 s in air. As-prepared PET/ITO/PEDOT:PSS substrates were then baked at 100°C for 10 min in vacuum. A 40 nm layer of 37HPTDBTSO was first evaporated from a current-controlled crucible by the vacuum thermal deposition, followed by 25 nm of Fullerene-C60 (C60, 99.5%, Aldrich) and an 8 nm buffer layer of bathocuproine (BCP, 99.99%). The multi-layer solar cell devices were then completed by the deposition of a 100 nm aluminum top electrode (Al, 99.999%) through a shadow mask. All depositions were performed under a base pressure lower than 8×10^{-4} Pa, and the deposition rates were controlled at 0.1–0.2 nm/s.

All BHJ solar cell devices were fabricated mainly by the spin-coating technique. After PET/ITO/PEDOT:PSS was baked at 100°C for 10 min, active layers consisting of 37HPTDBTSO and PCBM (99%, Kanto Kagaku) with various weight ratios (1:0.5, 1:1, 1:1.5, 1:2, 1:2.5, 1:3) in the heated chloroform (10 mg/mL) were spin-coated on the top of the PEDOT:PSS layer at 1000 rpm for 150 s. Subsequently, the substrates were baked at 100°C for 30 min. The thickness of the resulting photoactive layers ranged from 30 to 40 nm. Finally, a 100 nm-thick aluminum top electrode was evaporated on the photosensitive layer using a shadow mask. The active area of final solar cell device was 4 mm^2. After the solar cell devices were annealed at 100°C for 30 min, solar cell device performances were estimated in air.

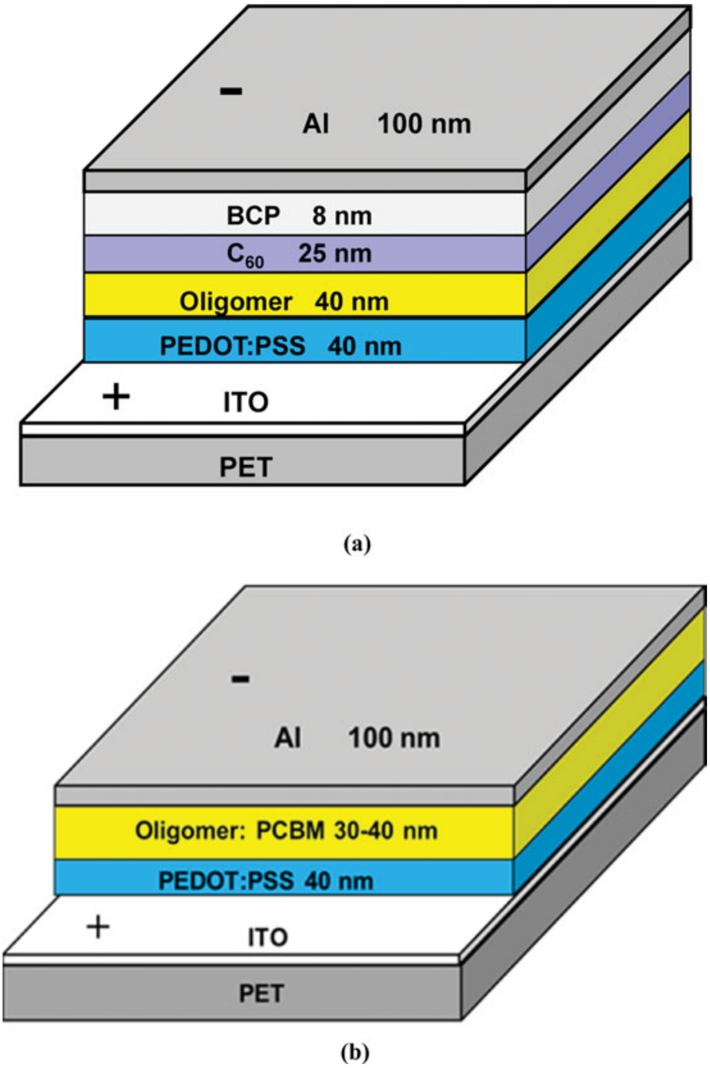

Figure 2. Schematic structures of (a) multi-layer heterojunction and (b) BHJ solar cell devices.

3. Results and Discussion

Effect of Device Structure on the Photovoltaic Properties

In order to minimize the difference between two types of solar cell devices, all the devices were fabricated with PET/ITO/PEDOT:PSS as an anode and Al as a cathode. In multi-layer heterojunction solar cell device, C60 and BCP were acted as an acceptor and a buffer layer, respectively. The BHJ solar cell device with common structure was based on the blend of 37HPTDBTSO and PCBM. The overall photovoltaic performances of the multi-layer heterojunction solar cell device were found to be nonideal, with a J_{sc} of 4.1 μA/cm^2, a V_{oc} of 0.77 V, a FF of 0.14 and a PCE of 0.00046%, while the BHJ solar cell device involved a J_{sc} of 0.17–1.20 mA/cm^2, a V_{oc} of 0.38–0.74V and a FF of 0.20–0.30. The maximum

PCE reached 0.26%. The PCE value of the BHJ solar cell device was about 3 orders higher than that of the multi-layer heterojunction solar cell device. The bulk heterojunction greatly increased the interfacial area of donor/acceptor, so that the higher PCE was obtained [2, 14]. Obviously, the structure of the BHJ solar cell device was the most effective configuration for high-efficiency organic solar cells based on the wet processing method.

Photo-physical Properties and Energy Levels

In order to study light absorption behaviors, normalized UV–vis absorption spectra of the individual solutions of 37HPTDBTSO and PCBM, the blend solution of 37HPTDBTSO and PCBM (1:2 wt.%) in chloroform, and the film of 37HPTDBTSO and PCBM (1:2 wt.%) were investigated (Fig. 3). UV–vis spectra of solution of 37HPTDBTSO showed that the absorption range was narrow with a strong absorption band at 350–450 nm and a weak band at 270–310 nm. And the absorption of PCBM originates at 480 nm and tends to increase with decrease in wavelength and reaches a maximum value around 330 nm. Apart from this maximum visible absorption, PCBM also possessed a high absorption around 260 nm. For UV–vis spectra of the blend solution of 37HPTDBTSO and PCBM (1:2 wt.%), the absorption intensity in near UV regime (350–450 nm) mainly attributed to 37HPTDBTSO. In the spin-casting film fabricated from 37HPTDBTSO and PCBM (1:2 wt.%), the absorption band became relatively broader in comparison to that of the blend solution. This indicated that some intermolecular interaction occurred in the solid state [15].

Cyclic voltammetry was also conducted to determine the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of 37HPTDBTSO. From the onset of the oxidation and reduction currents, the determined HOMO and LUMO levels of 37HPTDBTSO are −5.60 and −3.12 eV, respectively [12]. The relative position of donor LUMO and acceptor LUMO is crucial for the aimed charge transfer.

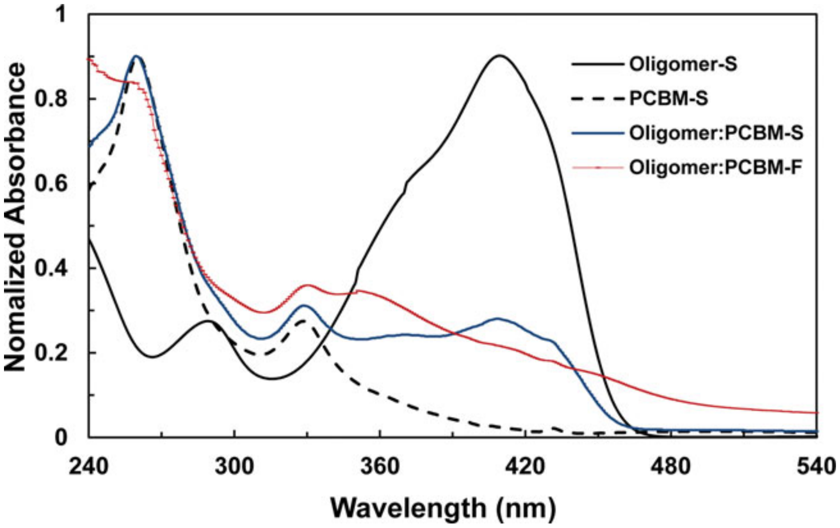

Figure 3. Normalized UV-vis absorption spectra of 37HPTDBTSO solution (Oligomer-S), PCBM solution (PCBM-S), and the blend solution (Oligomer:PCBM-S) and the blend film (Oligomer-PCBM-F) of 37HPTDBTSO and PCBM (1:2 wt.%).

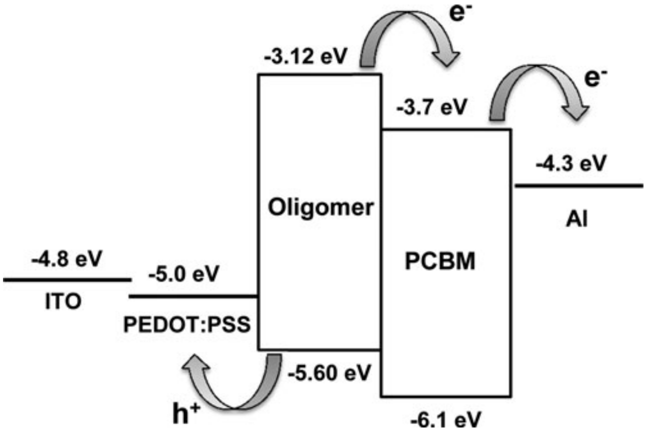

Figure 4. Energy band diagram of ITO, PEDOT:PSS, oligomer (37HPTDBTSO), PCBM and Al electrode.

Figure 4 shows the resulting energy diagram relative to the work function of the common BHJ solar cells applied ITO, PEDOT:PSS layer and Al electrode. There was a difference of 0.58 eV between LUMO of 37HPTDBTSO and that of PCBM. The energy of HOMO of 37HPTDBTSO was clearly higher than that of PCBM. On these conditions, it is energetically favorable for the photo-excited 37HPTDBTSO to transfer an electron to PCBM molecule. Therefore 37HPTDBTSO could be used as an electron donor with PCBM as an electron acceptor to prepare donor/acceptor solar cells [16, 17]. On the other hand, it has been reported that the thermodynamic limit of the V_{oc} was proportional to the difference between acceptor LUMO and donor HOMO [18]. The HOMO level of the oligomer, −5.60 eV, was lower than the HOMO of P3HT, −5.2 eV [5]. Therefore, the solar cell based on 37HPTDBTSO and PCBM exhibited relatively higher V_{oc}, compared with the solar cell based on P3HT and PCBM.

Effect of Blend Ratio on the Photovoltaic Properties

The optimum blend ratio of the electron donor and acceptor in the active layer was very important. At a particular ratio, the charge carrier mobility increases and, consequently, the power conversion efficiency also increased. In this work, several devices with 1:0.5 wt%, 1:1 wt%, 1:1.5 wt%, 1:2 wt%, 1:2.5 wt% and 1:3 wt% ratio of 37HPTDBTSO to PCBM in the active layer were made. Their photovoltaic properties are summarized in Table 1.

The device made up with an active layer, which was spin-coated from a heated solution with 37HPTDBTSO:PCBM (1:2 wt%) with a temperature of 50°C, had the maximum PCE of 0.26% under the illumination with AM 1.5G solar simulated light (100 mW/cm^2). Its J_{sc} was 1.20 mA/cm^2, the V_{oc} was 0.74 V, and the FF was 30%. Its current density-voltage (J-V) characteristic curves are presented in Fig. 5. Figure 6 shows the input photon to the converted current efficiency (IPCE) of the solar cell for the best device. The shape of the IPCE curve of the device based on 37HPTDBTSO was very similar as its absorption spectra. This indicated that all the absorption of the oligomer was contributed to the photovoltaic conversion. Besides the solar cell devices of 37HPTDBTSO:PCBM (1:0.5 and 1:1 wt%), all other devices had relatively high V_{oc} values, refered to previous reports about flexible solar cells based on P3HT and PCBM with PET substrate [5]. As above

Table 1. Summary of bulk-heterojunction solar cell device performances

Oligomer: PCBM (wt%)	Temperature (°C)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
1:0.5	50	0.17	0.50	20	0.02
1:1	50	0.31	0.38	25	0.03
1:1.5	50	1.00	0.70	28	0.20
1:2	50	1.20	0.74	30	0.26
	60	0.92	0.73	29	0.20
	50/50*	0.74	0.54	27	0.11
1:2.5	50	1.03	0.66	34	0.23
1:3	50	0.68	0.67	29	0.14

*Before the blend solution with a temperature of 50°C was spin-coated, the PET/ITO/PEDOT:PSS substrate was heated up to 50°C by a hair dryer.

discussion, it was attributed to the low-laying HOMO level of 37HPTDBTSO. If the active layers were identical, different devices with the same structure should theoretically display the approximated performances, such as V_{oc}. In previous work, the optimized BHJ solar cell device of 37HPTDBTSO:PCBM (1:1.5 wt.%) with a glass substrate showed a V_{oc} of 0.85 V and a PCE of 0.84%. However, the performance of the PET-based solar cell device of 37HPTDBTSO:PCBM (1:1.5 wt%) was remarkably poorer than its corresponding solar cell device with the glass substrate. There were many parameters that influenced the performances of oligomer-based BHJ solar cells, such as the solvent, the thickness of thin films, the thermal annealing temperature, and the weight ratio of donor to acceptor, etc.. Compared with the ITO/glass substrate, the PET/ITO substrate has a lower conductivity. Due to the limit of the glass transition temperature, the thermal annealing temperature

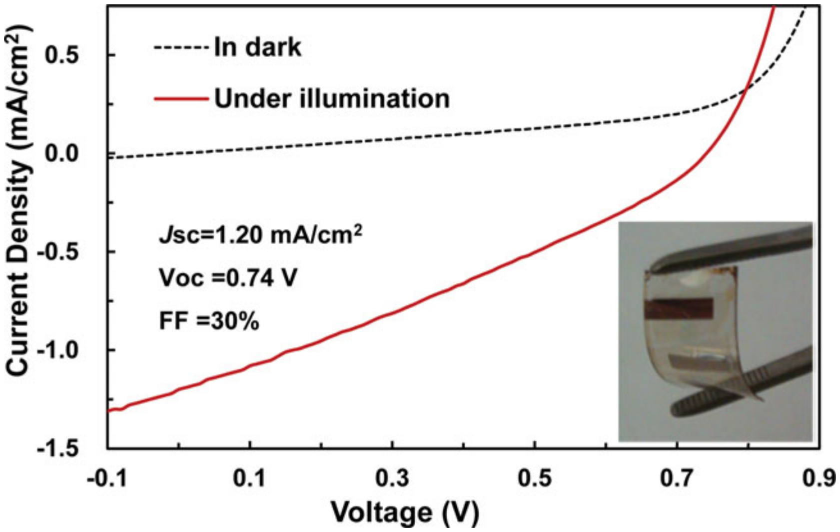

Figure 5. *J*-V characteristic curves of the BHJ solar cell device spin-casted from a heated solution with 37HPTDBTSO:PCBM (1:2 wt.%) and a temperature of 50°C.

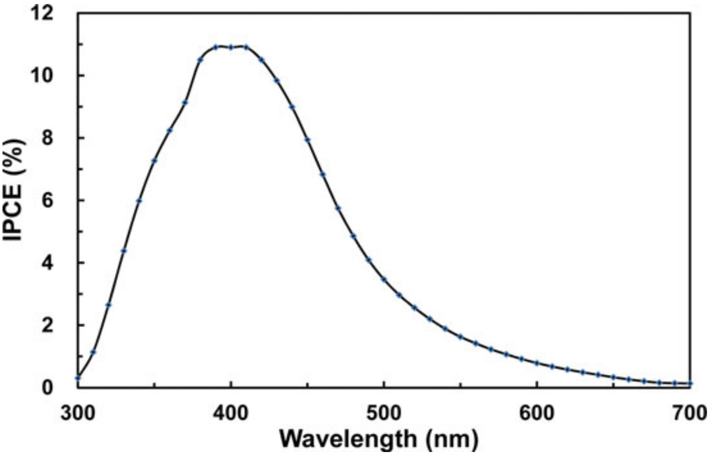

Figure 6. IPCE plot for the BHJ solar cell device spin-coated from a heated solution with 37HPT-DBTSO:PCBM (1:2 wt.%) and a temperature of 50°C.

of the solar cells on the PET substrate was 100°C, and lower than that of the solar cells with the glass substrate (150°C). More investigations are underway to clarify which factor plays the most important role in worsening the performances of solar cells fabricated on the PET substrate.

Effect of Temperatures of Solution and Substrate on the Photovoltaic Properties

Oligomer 37HPTDBTSO had a strong tendency to crystallize into well-defined structure. Additionally, its undesired solubility could occur in chloroform at room temperature, due to the π-π stacking and high self-assemble ability of 37HPTDBTSO in the solid state. In order to prepare the homogeneous spin-coating solution and the uniform film, the blend solution of 37HPTDBTSO and PCBM was heated by a bath-type ultrasonic cleaner to a temperature over 50°C before further processing. The surface morphology of the active layer, which was quite important for the photovoltaic performance, was investigated using AFM. The AFM image of the photoactive layer fabricated from a heated 37HPTDBTSO/PCBM (1:2 wt.%) solution with a temperature of 50°C is shown in Fig. 7a. Many grains with a diameter of over 100 nm appeared, and dispersed irregularly and discontinuously throughout the blend film. No obviously large-scale phase separation was observed. When the blend solution of 37HPTDBTSO and PCBM (1:2 wt%) was heated to 60°C, all characteristic factors of the solar cell device performance were worsened, thus resulting in a lower PCE of 0.20%. It can be clearly seen in Fig. 7b, large and regular microstructures appeared, presumably too large with respect to the exciton diffusion length to ensure the efficient exciton. These features might be responsible for the lower J_{sc}, V_{oc} and FF [19,20]. It was worth noting that the spin-coating chuck and substrate were at room temperature, the blend solution was being cooled during spin-coating in these processes. It was also necessary to investigate the effect of the substrate temperature on solar cell performance. Before the blend solution was spin-coated, the PET/ITO/PEDOT:PSS substrate was heated up to 50°C by an hair dryer. However, the quick removal of chloroform solvent resulted in poor active layer and worsened the performances of the final solar cell device, as shown in Fig. 7c and Table 1, respectively.

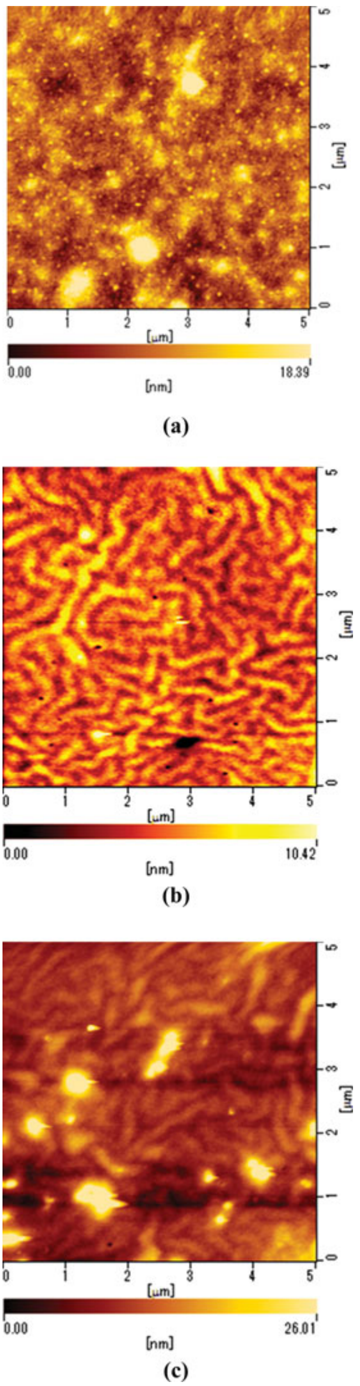

Figure 7. Surface AFM images of photoactive layers spin-coated from 37HPTDBTSO:PCBM (1:2 wt.%) blend solution at different solution and substrate temperatures: (a) 50°C and room temperature, (b) 60°C and room temperature, and (c) 50°C and 60°C, respectively.

4. Conclusion

A donor-acceptor-donor oligomer 37HPTDBTSO was utilized to harvest incident light and transfer electrons as a donor in flexible solar cells with a PET substrate. Compared with the structure of the multi-layer heterojunction device, the structure of BHJ device with blend layer of 37HPTDBTSO and PCBM was the effective configuration for high-efficiency organic solar cells. For BHJ solar cells, the blend weight ratio of donor/aceptor, solution and substrate temperatures, and surface morphology of photoactive layer had a remarkable influence on photovoltaic performances of solar cells. The best flexible solar cell was fabricated from the blend solution with the weight ratio (37HPTDBTSO:PCBM) of 1:2 and a temperature of 50°C. It had the highest PCE of 0.26% with a J_{sc} of 1.20 mA/cm^2, a V_{oc} of 0.74 V, and a FF of 30%. Higher temperatures of solution and substrate resulted in poor active layer, worsening its photovoltaic performance.

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