

Photovoltaic characterization of poly(2,5-bis(3-dodecylthiophen-2-yl)-2',2''-bisenophene) for organic solar cells

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ARTICLE INFO

Article history:

Received 3 September 2009

Received in revised form

24 October 2009

Accepted 30 October 2009

Available online 26 November 2009

Keywords:

Polymer

Organic solar cell

Photovoltaic properties

ABSTRACT

A novel regioregular selenophene and thiophene-based poly(2,5-bis(3-dodecylthiophen-2-yl)-2',2''-bisenophene) (PBTBS), was chosen as promising electron donor materials blended with [6,6]-phenyl-C61 butyric acid methyl ester (PCBM) to fabricate bulk heterojunction solar cells. The optical and photovoltaic properties of PBTBS were characterized and compared to those of poly(3,3''-didedocylquaterthiophene) (PQT-12). The PBTBS showed a higher ionization potential (IP) and improved oxidative stability than PQT-12 through the cyclic voltammetry (CV) measurements, which was due to stronger electron-donating properties of selenophene than that of thiophene analogue. A comparison of photovoltaic properties of cells between two polymer donors PBTBS and PQT-12 were also carried out. The result showed that cells based on the PBTBS had the comparable photovoltaic parameters with those of the PQT-12. An open voltage (V_{oc}) of 0.46 V, a short-circuit current (J_{sc}) of 0.17 mA/cm², a fill factor (FF) of 0.32 and a power conversion efficiency (η) of 0.34% were achieved at 100 mW/cm² (AM 1.5). The external quantum efficiency of cells based on the PBTBS exhibited much better performance with around 3.4% at 540 nm compared with that of the PQT-12.

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1. Introduction

Conjugated polymers-based photovoltaic cells have attracted a great deal of attention recently because of their potential application in fabrication low cost integrated circuit elements for large area and the feasibility of production using various ways such as spin coating, ink-jet printing and roll to roll through solution processes [1–9], and among them the polythiophene was one kind of the most promising materials, which has been widely exploited as the active layer in photovoltaic devices [10–13]. A commonly used hole transport material is well studied conjugated polymer poly(3-hexylthiophene) (P3HT), which has also been widely used in organic light emitting diodes and solar cells because of its beneficial properties such as high hole mobility (0.10 cm²/v·s), enhanced photo stability and an improved optical absorption in the visible region; however, the P3HT had a drawback of poor performances under the ambient atmosphere [14–17]. Recently another thiophene-based poly(3,3-didodecylquaterthiophene) (PQT-12) is similar to P3HT in structures and has shown similar absorption spectra, the hole mobility (0.18 cm²/v·s) as nearly double as large as that of P3HT. One

particular advantage of PQT-12 is the inherent stability in oxygen, as tested by degradation studies of organic field effect transistors (OFETs), due to its larger ionization energy [18]. Compared to P3HT, PQT-12 differs in term of alkyl chains in the fact that a better packing of polymer chains is possible inducing a better crystallinity and a higher hole mobility, its lower ionization energy could also be of interests for enhanced chemical stability of the compound as well as device lifetime [19,20]. The PQT-12 exhibits good oxidative stability and excellent device performances under the ambient condition with the unsubstituted thiophene affording rotational freedom along the backbone [20]. Crouch [21] reported that selenophene-containing polymers showed higher mobility than that of thiophene analogues, due to larger and more polarizable selenium atom; the oligoselenophenes had lower band gap energy than their oligothiophene analogues; and the mobility of OFETs based on oligoselenophene was slightly higher than that of oligothiophene deposited under the same condition [22]; a lower band gap poly(3-hexyl)selenophene with similar ionization potential compared to P3HT was reported [23]; OFETs based on fluorene and selenophene copolymer as an active layer showed better transistor performance with respect to fluorene and thiophene-based polymer [24].

In this article, a novel regioregular selenophene and thiophene-based poly(2,5-bis(3-dodecylthiophen-2-yl)-2',2''-bisenophene) (PBTBS) was chosen as electron donor material

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blended with [6,6]-phenyl-C61 butyric acid methyl ester (PCBM) to fabricate bulk heterojunction solar cells, the thiophene moieties were replaced with selenophene in the backbone of PQT-12. To our knowledge, there are few reports on the selenophene and thiophene containing copolymer for application in organic solar cells. A comparison between the photovoltaic properties of cells based on the polymer donors PBTBS and PQT-12 were also carried out.

2. Experimental details

In this paper, a novel regioregular selenophene and thiophene-based polymer PBTBS was chosen as electron donor materials blended with PCBM to fabricate bulk heterojunction solar cells, the photovoltaic properties of cells were compared to those of PQT-12. The chemical structures of the PBTBS, PQT-12 and PCBM used as the active layer materials are shown in Fig. 1. The solar cells were fabricated by spin coating the active layers onto the indium tin oxide (ITO) coated glass substrates; the ITO was thoroughly cleaned by an ultrasonic treatment in acetone, ethanol and de-ionized water sequentially; after drying the substrate, a layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT: PSS) at 3000 rps for 60 s was spin coated on the ITO substrate, followed by heating for 15 min at 140 °C in annealing oven. Afterwards, the active layer containing a mixture of the PBTBS and PCBM (1:1, wt%) was spin-coated from dichlorobenzene solution to the substrates in a N₂ glove box, while the blend film of PQT-12: PCBM (1:1, wt%) was deposited by spin coating from dichlorobenzene solution at 50 °C due to the poor solubility of PQT-12 at room temperature, all solutions were passed through 0.45 μm PTFE syringe filters prior to the deposition. And then the aluminum (Al) top electrodes were evaporated by thermal evaporation in vacuum (2×10^{-4} Pa) through a shadow mask. Post device annealing was carried out at 100 °C for 15 min in a N₂-filled glove box.

UV-visible absorption spectra were obtained on a UV-2501PC (UV-vis Spectrophotometer), the films of the two polymers and blended films with PCBM were formed through spin coating from dichlorobenzene solution on quartz substrates. The photoluminescence (PL) spectra were performed through a RF-5301PC Spectrofluorophotometer. The current-voltage characteristics of cells were measured by a Keithley 2400 source measurement unit under a Xe lamp illumination with power density of 100 mW/cm² (AM1.5). External quantum efficiency (EQE) measurements were tested by filtering the Xe lamp using a monochromator, the signal was collected by a merlin detector and preamplifier. All electrical measurements were made at room temperature in air.

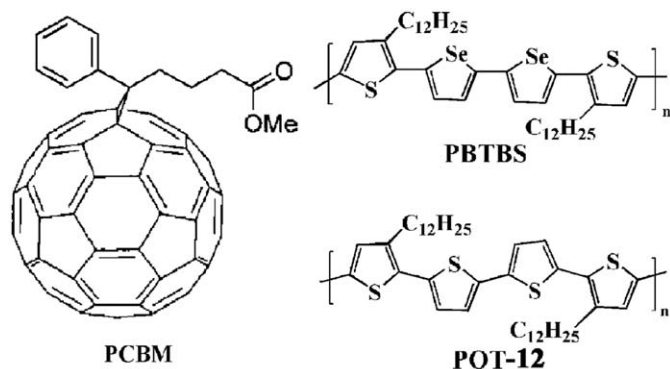


Fig. 1. The chemical structure of the PBTBS, PQT-12 and PCBM.

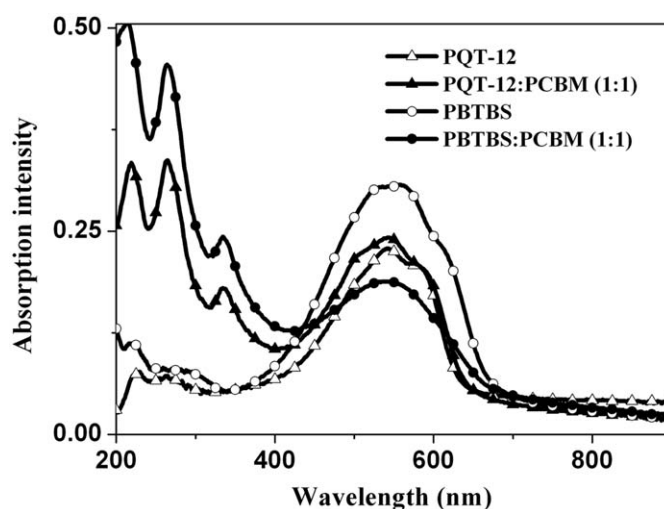


Fig. 2. The absorption spectra of the PBTBS, PQT-12 and their blend films with PCBM (1:1, wt%).

3. Results and discussions

3.1. Absorption spectra

Fig. 2 shows the UV-vis absorption spectra of PBTBS, PQT-12 and their blend films with PCBM (1:1, wt%) coated from the 1,2-dichlorobenzene solution. It's obvious that the absorption maximum for PQT-12 was found to be around 540 nm, whereas the absorption peak of PBTBS in the film was red shifted towards 555 nm compared to the PQT-12.

The red shift was attributed to the larger size of selenium atom and stronger electron-donating properties than that of sulfur atom [26]. The optical band gap (E_g) was determined from the onset absorption wavelength to be 2.1 eV, the HOMO and LUMO from the cyclic voltammetry (CV) measurements and optical band gap are -5.0 eV and -2.9 eV with respect to those of PQT-12 with (-5.35 eV, -3.39 eV). The ionization potential (IP) was calculated from the onset oxidation potential of 0.7 V to be 5.2 eV, which is 0.1 eV higher than that of PQT-12. The slightly higher IP of PBTBS was attributed to the tendency of the twisted conformation of selenophene moieties reducing π -electron delocalization along the backbone [25,26]. Therefore, the instead of the selenophene with thiophene in PBTBS was expected to bring about greater oxidative stability than PQT-12. The appearance of the weak shoulder absorption between 600 nm and 650 nm is indicative of π -stacking process in the solid state [27].

3.2. Photoluminescence properties

In order to check the possible application of PBTBS as electron donor in cells, the photoluminescence (PL) spectra of the pristine PBTBS and blend film with PCBM from dichlorobenzene solution were measured under the photo-excitation wavelength of 555 nm, which is corresponding to the absorption peak wavelength of the PBTBS. Fig. 3 shows the PL spectra of the pure PBTBS and the blend film of PBTBS: PCBM with the ratio of 1:1 in weight.

From Fig. 3, it can be seen clearly that the predominant PL band with central peaks around 537 nm for the pristine PBTBS occurs, but the blend is significantly quenched in the PBTBS: PCBM blended films. It is obvious that the intensity of PL spectra of the blend is quenched to about 2% of the pristine PBTBS emission indicating that 98% of the excitons are dissociated. The results indicate that electron is transferred from the photoexcited

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