Solar Energy Materials & Solar Cells 95 (2011) 1219–1223

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Letter

Improved power conversion efficiency of bulk heterojunction poly(3-hexylthiophene):PCBM photovoltaic devices using small molecule additive

S.S. Sharma [a], G.D. Sharma [b,c,*], J.A. Mikroyannidis [d,**]

[a] Department of Physics, Government Engineering College for Women, Ajmer, Rajasthan, India
[b] Physics Department, Molecular Electronic and Optoelectronic Device Laboratory, JNV University, Jodhpur, Rajasthan 342005, India
[c] R & D Centre for Engineering and Science, Jaipur Engineering College, Kukas, Jaipur, Rajasthan, India
[d] Chemical Technology Laboratory, Department of Chemistry, University of Patras, GR-26500 Patras, Greece

ARTICLE INFO

Article history:
Received 22 October 2010
Received in revised form
29 November 2010
Accepted 6 December 2010
Available online 30 December 2010

Keywords:
Bulk heterojunction solar cells
Poly(3-hexylthiophene)
Small molecule additive
Photovoltaics
Thienothiadiazole

ABSTRACT

We report that the power conversion efficiency (PCE) of the bulk heterojunction organic photovoltaic device based on poly(3-hexylthiophene):[6,6]-phenyl-C_{61}-butyric acid methyl ester (P3HT:PCBM) blend was improved by incorporating a small molecule **SM** having absorption band in the longer wavelength region. **SM** is a small molecule containing thienothiadiazole central unit with terminal cyanovinylene 4-nitrophenyl at both sides, which were connected to the central unit via a thiophene ring. The combination of **SM** with P3HT and PCBM allows not only a broad band absorption up to longer wavelength, but also tuning the inter-energy level leading to a higher short circuit current (J_{sc}) and open circuit voltage (V_{oc}). The device based on the as cast P3HT:PCBM:**SM** exhibits a PCE of 3.69%, which is higher than the device based on P3HT:PCBM and **SM**:PCBM blends. The overall PCE of the device based on thermally annealed blend is further improved up to 4.1%. The improvement of the PCE has been attributed to a better charge transport in the device, due to the increased crystallinity of the blend through thermal annealing.

1. Introduction

Organic photovoltaic devices (OPVs) have attracted attention and are a promising effective alternative for converting solar energy into electrical energy. In addition, they possess low cost, light weight and flexibility advantages [1]. The low power conversion efficiency (PCE) of these PV devices is still considered a major obstacle to commercialization [2], although PCEs in the range of 5–8% have been recently reported for bulk heterojunction (BHJ) solar cells [3]. The research in the field of OPVs is focused on achieving PCEs in the range of 10–15% [4]. The photoactive layer of OPVs is commonly composed of a blend film of a conjugated polymer (donor) and soluble fullerene derivatives (acceptor). There are many factors limiting the performance of the BHJ solar cells [5]. Among them, the properties of materials of the active layer are the most determining factors in the overall performance of the polymer solar cells [2i,6]. Ideally, the polymers should have a broad absorption in the solar spectrum to ensure effective harvesting of the solar photons and high charge carrier mobility for charge transport. The most representative polymer donor is poly(3-hexylthiophene) (P3HT) and the most important soluble fullerene derivative acceptor is [6,6]-phenyl–C61–butyric acid methyl ester (PCBM). However, further improvement of the PV efficiency of the PSCs based on P3HT:PCBM is limited by the mismatch of the P3HT absorption band with the solar spectrum. Although great process developments have improved the charge transport properties of the solar cells based on P3HT/PCBM, the large offsets of the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of P3HT and PCBM, there are still limitations of high performance and commercialization of these devices [7]. Therefore, one way to enhance the PCE has been to match the absorption profile of donor polymers with the solar spectrum, usually by developing low band gap conjugated polymers [8]. For improving the exciton/charge transfer and transport with the morphology control of the active layers in BHJ OPVs numerous approaches such as thermal [9] and solvent [10] annealing, selective (differential) solubility by processing additives [11], control of the solvent rate [12] and phase polarity control by nonvolatile additives [13] have also been pursued and have a crucial impact on increasing exciton/charge transport, thus enhancing the PCE.

Recently, the energy harvesting capabilities of OSCs have been improved through the use of low band gap conjugated polymers [14].

* Corresponding author at: R & D Centre for Engineering and Science, Jaipur Engineering College, Kukas, Jaipur, Rajasthan, India. Tel.: +91 0291 2720857; fax: +91 0291 2720856.
** Corresponding author. Tel.: +30 2610 997115; fax: +30 2610 997118.
E-mail addresses: sharmagd_in@yahoo.com (G.D. Sharma), mikroyan@chemistry.upatras.gr (J.A. Mikroyannidis).

0927-0248/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.solmat.2010.12.013

Although the absorption spectra of these polymers extend into the longer wavelength region (e.g., near infrared), they still sacrifice some absorption in the visible region. Moreover, the offsets of the HOMO energy levels of the donors and acceptors lead to significant energy losses upon exciton dissociation. Therefore, in order to enhance the photocurrent generation, there is still great interest in combining organic semiconductors that exhibit complementary absorption spectra. In addition to polymer, π-conjugated small molecules have been found attractive as alternative solution processable p type donor materials. Solution processable small molecules are attractive for OSCs as they are easier to be synthesized and purified, offer easier processing compared to polymers, and show, in general, higher charge carrier mobilities [15]. The PCE of solution processable small molecules as donor with PCBM as acceptor, has steadily been improved over the past decade from about 0.03% to over 4.4% [16]. A possible approach to enhance the absorption capabilities of the polymer BHJ active layer throughout the solar spectrum might be the incorporation of a small molecule having absorption band in the region of 600–800 nm in the blend of polymer and PCBM [17]. In ternary blend solar cells, low band gap small molecules are simply blended into the polymer/fullerene matrix as the third component to harvest solar photons at longer wavelengths, where the original donor and acceptor do not absorb.

Very recently, we have synthesized a small molecule, **SM**, having thienothiadiazol central unit and terminal cyanovinylene 4-nitrophenyl segments at both sides, which were connected to the central unit via a thiophene ring (Fig. 1(a)) [18]. A BHJ OPV fabricated from a blend of **SM** (electron donor) and PCBM (electron acceptor) had yielded only a modest PCE of about 1.24% [18]. The present paper focuses on the improvement of PCE by blending **SM** as an additive into the currently most promising P3HT:PCBM OPVs, to provide a simple method for improving the PV efficiency. Owing to the wide light harvesting range up to 780 nm the ternary blend solar cell of P3HT:PCBM:**SM** exhibits a higher PCE of 3.69% than that of the solar cells based on individual P3HT:PCBM and **SM**:PCBM. This is mainly attributed to light harvesting throughout the whole visible region leading to the increase in the photocurrent. The PV device based on thermally annealed ternary blend is further increased up to 4.1%.

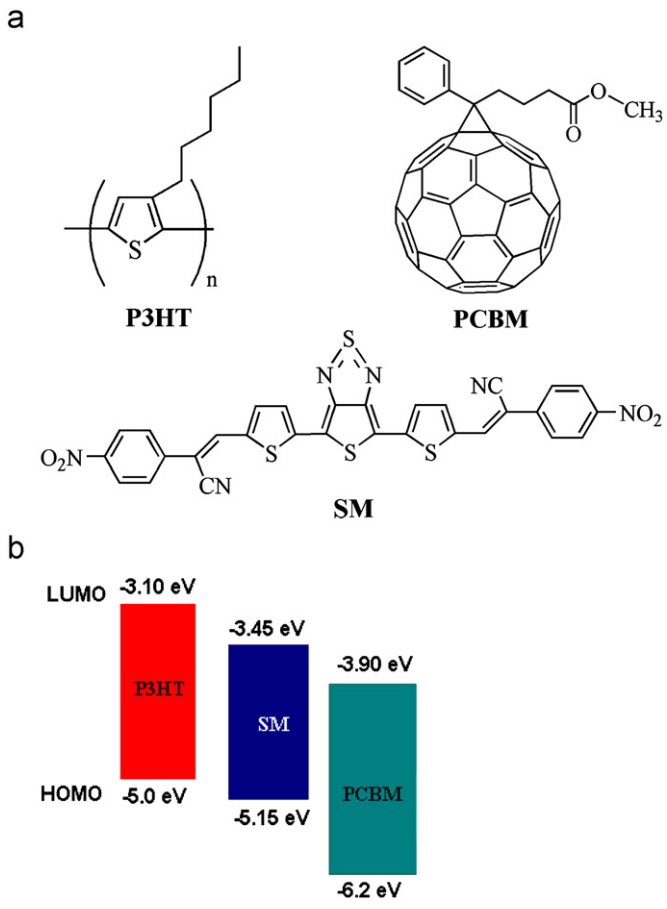

Fig. 1. (a) Chemical structures of P3HT, PCBM and small molecule (**SM**) used for ternary blend and (b) energy level diagram for P3HT, **SM** and PCBM.

2. Experimental

The solutions of the blend P3HT:PCBM:**SM** (1:1:1 w/w) were prepared in concentration 10 mg/ml using chloroform as the solvent and then stirred for 2 h. The PSCs were fabricated according to the following procedure. First, the indium doped tin oxide (ITO) coated glass substrate was cleaned with a detergent, then ultrasonicated in distilled water and isopropyl alcohol and finally dried overnight in an oven at 80 °C. To supplement this bottom electrode, a hole transport layer of PEDOT:PSS (Bayer AG) was spin-casted from aqueous solution on the ITO coated glass substrate, and was subsequently dried at 80 °C for 20 min. The photoactive layer of the blend P3HT:PCBM:**SM** (90 nm) was deposited by spin coating the prepared blend solutions on the top of the PEDOT:PSS layer. Finally, an aluminum (Al) electrode (thickness about 100 nm) was deposited by thermal evaporation under high vacuum (1×10^{-5} mbar). The effective area of the devices is 20 mm^2. For thermal annealing, the blend films were placed on a hot plate and annealed at the temperature of 120 °C for 2 min, before the deposition of Al electrode. The current–voltage (*J–V*) measurement of the devices was carried out on a computer controlled Keithley 238 source meter. A xenon light source was used to give an irradiance of 100 mW/cm^2 (equivalent to one sun at AM 1.5) at the surface of the device. We have fabricated seven devices and found similar *J–V* characteristics for each device.

3. Results and discussion

The chemical structures of the conjugated polymer P3HT, PCBM and **SM** are shown in Fig. 1(a). The HOMO and LUMO energy levels of PCBM, P3HT and **SM** [18] were estimated by cyclic voltammogram studies and are shown in Fig. 1(b). In order to avoid the charge trapping in the ternary BHJ, using a small molecule of which the energy level should lie between the energy levels of conjugated polymer and PCBM. On the basis of electrochemical data, the HOMO and LUMO levels of **SM** are −5.15 and −3.45 eV, respectively [18]. **SM** possesses intermediate energy band edges between PCBM and sufficiently large band edge offsets with P3HT and PCBM, which suggests that photogenerated excitons might be dissociated efficiently at P3HT/**SM**, P3HT/PCBM and **SM**/PCBM interfaces and that the carriers can be effectively driven to respective electrodes. The synthesis of **SM** and its other photophysical properties have been reported [18]. The optical absorption spectra of P3HT, PCBM and **SM** thin films are shown in Fig. 2(a). **SM** exhibits a wide absorption band in the wavelength region of 580–680 nm having absorption edge approximately at 760 nm, while P3HT shows an absorption band at 500–560 nm having edge at ~610 nm. The optical absorption spectra of the P3HT:**SM**:PCBM blend are shown in Fig. 2(b). It can be seen from this figure that there are broad absorption bands at the regions of 300–350, 510–570 and 600–700 nm, corresponding to PCBM, P3HT and **SM**, respectively. The absorption spectrum of the blend is a simple superposition of P3HT and **SM** absorption spectra with a small contribution of PCBM in the lower wavelength region, indicating a homogeneous mixing of components. Fig. 2(b) reveals