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ZnO hybrid photovoltaics with variable side-chain lengths of thienothiophene polymer

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ABSTRACT

The effect of the side-chain length of poly(3,6-dialkylthieno[3,2-b]thiophene-co-bithiophene) (pATBT) on the performance of hybrid polymer-metal oxide photovoltaics (PVs) utilizing zinc oxide (ZnO) acceptor is investigated. The pATBT attached with a dodecyl side chain (pATBT-C_{12}) in hybrid photovoltaics with ZnO was compared to pATBT with a hexadecyl side chain (pATBT-C_{16}). Atomic force microscopic analysis reveals a smoother surface for the pATBT-C_{16} photoactive layer compared to the pATBT-C_{12}. For hybrid PVs using pATBT-C_{16}, the relative intensity of the external quantum efficiency (EQE) increased particularly in wavelength region associated with the ZnO. Furthermore, the EQE spectrum shows a red shift for pATBT-C_{16} indicating better structural ordering compared to hybrid PVs with pATBT-C_{12}. As a result, the hybrid PV utilizing pATBT-C_{16}:ZnO blend layer is observed to display a better performance with a power conversion efficiency of 1.02% compared to 0.672% of pATBT-C_{12}:ZnO PV.

1. Introduction

Hybrid bulk-heterojunction (h-BHJ) solar cells based on blends of donor polymers and acceptor metal oxides are of interest as a low-cost, lightweight route for solar energy conversion [1], which is compatible with roll-to-roll fabrication [2]. Furthermore, metal oxides electron acceptors also present advantages such as the tunable absorption [3], the high electron mobility [4], chemical stability [5], and air stability over time [6]. Nonetheless, h-BHJ PVs incorporating metal oxides as acceptors presently exhibit poorer device performance than organic photovoltaics (PVs) [7]. As a result, much work has been carried out to improve the performance of such h-BHJ PVs [1,7–10].

A potentially interesting approach to improve performance would be to use a donor polymer, which has a higher ionization potential than poly(3-hexythiophene) (P3HT) currently utilized in the best h-BHJ cells. Recently, poly(3,6-dialkylthieno[3,2-b]thiophene-co-bithiophene) s (pATBT) was reported as interesting material for transistor applications[11] with improved oxidative stability compared to P3HT due to the lower lying HOMO energy level at 5.1 eV [11] compared to the HOMO level of P3HT (4.7 eV) [12]. Furthermore, studies of pATBT in blends with fullerene derivatives [13,14] have shown promise as a photoactive material.

In this work we investigate, the impact of the side-chain length of pATBT on h-BHJs. Control of side chains improves solubility of the polymer in organic solvents [15], as well as phase separation which impacts device performance [16,17]. Furthermore, side chains are also known organic PVs [18]. In this work, we have attempted to correlate the performance of h-BHJ PV devices utilizing pATBT with dodecyl (pATBT-C_{12}) or hexadecyl (pATBT-C_{16}) side chains (Fig. 1(a) inset) as the donor and ZnO [19,20].

2. Experimental section

pATBT-C_{16} (Mn 35,500 g/mol; Mw 84,000 g/mol, degree of polymerization = 47) and pATBT-C_{12} (Mn 26,500 g/mol; Mw 49,500 g/mol, degree of polymerization = 41) were synthesized as previously reported [11]. Devices were fabricated on indium tin oxide (ITO)-coated glass substrates with poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) (Baytron P VP AI 4083) (~50 nm thickness). The active layer was spin cast at different spin speeds for 60 s on the PEDOT:PSS layer under a relative humidity of 40% [9]. Upon drying for 30 min at a relative humidity of ~40 ± 5%, the samples were annealed on a hotplate at a 120 °C for a further 30 min. Finally, an 80 nm thick Al metal electrode thermally evapourated as the back contact. Device characterization was carried out under AM 1.5G 1 sun conditions. All measurements were carried out using an aperture (area of 0.385 cm^2). The measurement of surface

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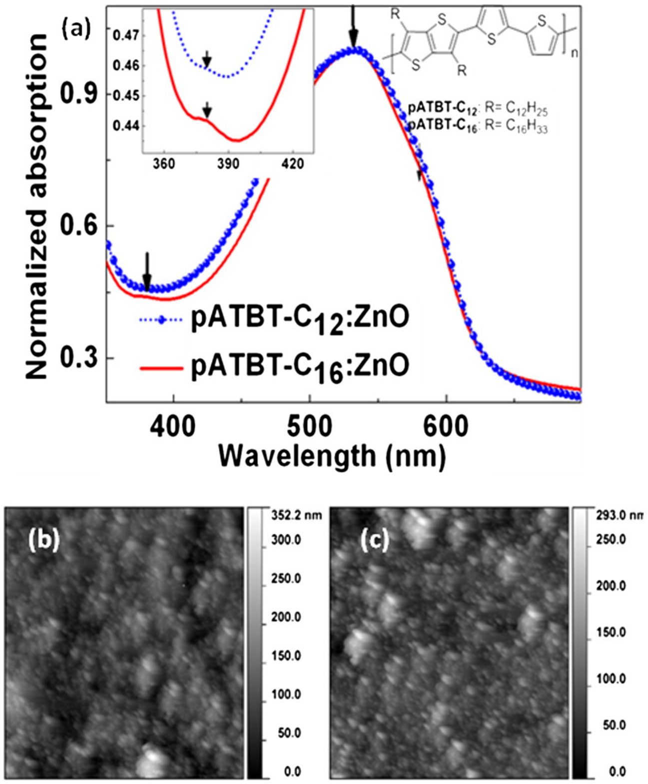

Fig. 1. (a) The absorption spectra of pATBT(-C12, -C16):ZnO composite layers on PEDOT:PSS/ITO/Glass and the AFM images of (b) pATBT-C12 and (c) pATBT-C16. Inset of (a) shows the absorption profiles for the composite layers between 350 - 430 nm. The molecular structure of pATBT(-C12, -C16) is also given in (a).

morphology and optical absorption was carried out using the atomic force microscopy (AFM) (Digital Instruments, Nanoscope IV) and Varian Cary 5000 UV-Visible spectrophotometer, respectively.

3. Results and discussion

The optical absorption of pATBT-C_{12}:ZnO and pATBT-C_{16}:ZnO composite layers are given in Fig. 1(a)). For both systems, the onset of the optical absorption is observed to be at ~625 nm, while a significant absorption in the wavelength region of 425–625 nm (due to the donor polymer) and an additional absorption edge at ~380 nm (Fig. 1(a) inset) due to the ZnO phase [21] are also observed. Furthermore, an absorption shoulder is observed for the polymer in the wavelength region of 550–600 nm. For P3HT, such transitions are attributed to interchain interactions due to ordering of the polymer [22]. Although an understanding is absent in the case of pATBT, it is suspected that similar interchain transitions lie behind the weak shoulder on the dominant peak observed. It is noted that the appearance of this shoulder peak is more prominent in the pATBT-C_{16}:ZnO blend layer compared to pATBT-C_{12}:ZnO, indicating that the longer side chains in pATBT leads to a more ordered structure in h-BHJ PVs incorporating ZnO [23]. This is in agreement with reports on longer side chains leading to better crystallization and shorter π-stacking distance between the chains due to micro-phase separation between the flexible side chains and the rigid backbone [24].

One of the key factors that determine the performance of h-BHJ PVs is the interface between the active layer and the Al electrode [25]. AFM images were obtained from the surfaces of 180 nm thick pATBT-C_{12}:ZnO (Fig. 1(b)) and 220 nm thick pATBT-C_{16}:ZnO (Fig. 1(c)) blend layer for optimized devices indicates a root mean square roughness of 57 nm and 34 nm, respectively. The decrease of roughness with increasing side-chain length related to the enhanced solubility and miscibility of polymer [26]. In this sense, the higher surface roughness for the active layer with the shorter polymer side chain is expected to lead to a poorer device in comparison to that of the smooth active layer with the longer polymer side-chain length.

Another factor that governs the device performance is the thickness of the photo active layer [27]. For both pATBT:ZnO blend layers, the open circuit voltage (V_{OC}) increased with the active layer thickness (Fig. 2(a)). For PVs with the 100 nm thick active layer, the V_{OC} of pATBT-C_{12}:ZnO PV was low at 0.183 V while pATBT-C_{16}:ZnO PV displays a V_{OC} of 0.590 V. However, the V_{OC} of both systems were observed to increase and then saturate at thicknesses greater than 180 nm. This indi-

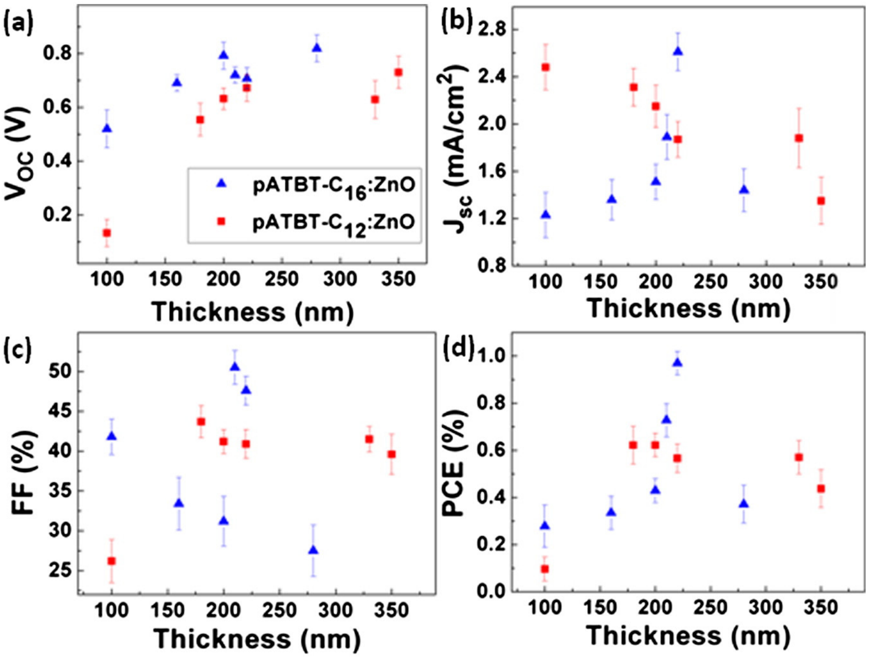

Fig. 2. (a) V_{OC}, (b) J_{SC}, (c) FF, and (d) PCE of pATBT-C_{12}:ZnO and pATBT-C_{16}:ZnO PVs verse active layer thickness. The average value depicted is for 30 large area devices for each system.