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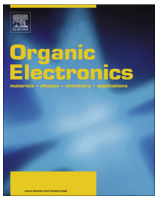

Enhanced efficiency in polymer solar cells by incorporation of phenothiazine-based conjugated polymer electrolytes

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ABSTRACT

The power conversion efficiency (PCE) of bulk hetero-junction type polymer solar cells (PSCs) based on poly(3-hexylthiophene) and (6,6)-phenyl-C61-butyric acid methyl ester can be enhanced by insertion of the thin layer of phenothiazine (PT)-based conjugated polymer electrolytes (CPEs), poly{10-[4-(*N*,*N*,*N*-trimethylammonium)butyl]-10*H*-phenothiazine} bromide (PHPT) and poly{10-butyl-10*H*-phenothiazine-alt-10-[4-(*N*,*N*,*N*-trimethylammonium)butyl]-10*H*-phenothiazine} bromide (PcoPT), at the cathode interface. The PHPT has quaternary ammonium salt on every side chains on PT rings whereas PcoPT has quaternary ammonium salt on the side chain on PT rings alternatively. Interestingly, regardless of high HOMO energy levels of PT-based CPEs (ca 5.0 eV), the thin layer of CPE at the cathode interface enhances the PCE by the formation of interface dipole which reduces the work function and a Schottky barrier at the cathode. It is also shown that the number of accumulated ionic groups of PcoPT on the photoactive active is larger than that of PHPT owing to the arrangement of side chain on the CPE backbone. In a similar way, the thin layer of PcoPT exhibits substantially better wetting ability on the photoactive layer than that of PHPT. Thus, the device with PcoPT exhibits higher short circuit current and fill factor than those of PSC with PHPT.

1. Introduction

Over the past decades, polymer solar cells (PSCs) have received great attention on account of many advantages such as light weight, flexibility and solution-based processibility [1]. Development of both the photoactive materials and the device engineering are essential to get high power conversion efficiency (PCE). To achieve high performance of PSCs, novel photoactive polymers with low band gap [2] and fullerene (C60 or C70)-based soluble electron accepting materials [3] have been developed. Also, device engineering such as morphology control by heat treatment [4,5] and addition of processing additives [6] and interface engineering by introducing interlayer [7,8] at the photoactive layer/electrode interface have been demonstrated to improve the efficiency of PSCs. Among them, interface modification is a crucial method to improve the performances of PSCs. A thin layer of LiF (ca. 1 nm) is well known as interfacial material [9,10], solution processible interlayer materials such as polyethylene oxide [11], neutral conjugated polymers with polar side chains [12], non-conjugated polyelectrolytes [13–16], and conjugated polyelectrolytes (CPEs) [17–22] have been also applied for interfacial layer in PSCs. These materials enable the fabrication of the devices without damaging the under-layer. By placing these materials at the cathode interface, the PCE of the devices are enhanced by the formation of interface dipole leading to reduction of a Schottky barrier.

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Here, two PT-based CPEs, poly{10-[4-(*N*,*N*,*N*-trimethylammonium)butyl]-10*H*-phenothiazine} bromide (PHPT) and poly{10-butyl-10*H*-phenothiazine-alt-10-[4-(*N*,*N*,*N*-trimethylammonium)butyl]-10*H*-phenothiazine} bromide (PcoPT), were polymerized (as shown in Scheme 1) to investigate the effect of the arrangement of side chain and the electronic properties of the main chain of CPEs on photovoltaic properties. The PHPT has quaternary ammonium salt in every side chains on PT ring whereas PcoPT has quaternary ammonium salt in the side chain alternatively. PT-based polymer has high-lying ionization potential [23]. Although PT-based CPEs have the HOMO energy level of ca. 5.0 eV, the PCE of the devices with PT-based CPEs are improved over the device without CPEs (reference device). Interestingly, it is also noticed that the arrangement of side chains affect the performances of the devices because of the conformation of backbone. The arrangement of side chains of CPEs may affect the effective work function of the cathode and the wetting ability of CPEs on the surface of the photoactive layer. For PcoPT, all the side chains with ionic group on backbone will be directed away from the surface of the photoactive layer whereas and the other side chains without ionic group will be pointed toward the semiconducting layer owing to the spontaneous organization of side chains on CPE. However, some of the side chains with ionic group in PHPT will be pointed toward the surface of the photoactive layer due to that all of the side chains have ionic group. One possible reason for this is that the zigzag conformation is preferred for PT-based polymers [23,24]. By different arrangement of side chains of CPEs, the interface between the thin layer of CPEs and the photoactive layer could be controlled and lead to the better PCE of PSCs.

2. Experimental section

2.1. Measurements

Synthesized compounds and polymers were characterized by ^{1}H NMR or ^{13}C NMR spectra, which were obtained with a JEOL JNM ECP-400 spectrometer. The elemental and MASS analyses of synthesized compounds were carried out an Elementar Vario macro/micro elemental analyzer and a Shimadzu GC–MS QP-5050A spectrometer. The gel permeation chromatography (GPC) measurements were conducted by GPC system equipped with a Varian 212-LC pump, a Rheodyne 6-port sample injection valve, a Waters Temperature Control Module, a Waters 410 differential RI detector and two Waters Styragel HR4E columns. The columns were calibrated by the polystyrene standards and toluene was used as an eluent. The work function was obtained by an ultraviolet photoelectron spectroscopy (UPS) (Thermo Electron Co. MultiLab 2000) with a He I source ($h\nu = 21.22$ eV) at a pressure of 1×10^{-8} Torr. A -3 V was applied to a sample during the measurements to distinguish between the analyzer and sample cut-off. For measurement of UPS, a thin film of CPEs with a thickness of approximately 5 nm was spin-coated from their ethanol (1 mg/mL) solution on top of a 200 nm-thick Al/glass substrate. The contact angle was measured by a KRUSS, Model DSA 100. The current density–voltage measurements under the 1.0 sun (100 mW/cm^2) condition form a 150 W Xe lamp with AM 1.5G filter were performed using a KEITHLEY Model 2400 source-measure unit. A calibrated Si reference cell with a KG5 filter certified by National Institute of Advanced Industrial Science and Technology was used to confirm 1.0 sun condition. The thickness of films was measured by an Alpha-Step IQ surface profiler (KLA-Tencor Co.). The geometric optimization of PT-based polymers considered in this study were performed according to density functional theory (DFT), utilizing the B3LYP hybrid density functional method in conjunction with the d-polarized 6-31G(d) basis set implemented in the Gaussian 03 program. All electrons were taken into account for the full geometric optimization, and the resulting molecular structures were classified as local minima on their respective potential energy surfaces.

2.2. Fabrication of PSCs

ITO-coated on glass substrates were cleaned with deionized water, acetone, methanol and isopropanol in ultrasonic bath. A layer (40 nm) of diluted poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Clevios P) with isopropanol (PEDOT:isopropanol = 1:2 by volume) was spin-coated on pre-cleaned ITO substrate (sheet resistance = 15 Ω/sq) which was pre-treated by UV/O_3 for 120 s. After being baked at 150 °C for 10 min under the air, the photoactive layer was spin-cast from the blend solution of P3HT/PCBM (20 mg of P3HT and 20 mg of PCBM in 1 mL of o-dichlorobenzene) at 600 rpm for 40 s. The solution was stirred for 12 h at 60 °C in the glove box. Prior to spin coating, the blend solution was filtered through a 0.20-μm PTFE membrane filter. The CPE layer was spin-coated from its ethanol solution (1 mg/mL) on top of the photoactive layer at 4000 rpm for 120 s. The typical thickness of the photoactive layer and the CPE layer was 150 and 5 nm, respectively. Finally, a 110 nm-thick Al electrodes were deposited by thermal evaporation at 2×10^{-6} Torr. Thermal annealing process was carried out on a hot plate at 150 °C for 10 min in a glove box filled with nitrogen gas. The typical photoactive area of the devices was 13 mm^2.

3. Results and discussion

3.1. Synthesis and electro-optical properties of CPEs

Syntheses of PT-based CPEs are shown in Scheme 1. The polymers, P1 and P2, were polymerized by the typical palladium-catalyzed Suzuki coupling reaction. PHPT and PcoPT were obtained by the reaction between P1 (or P2) and trimethylamine [25]. The CPEs were soluble in polar protic solvents such as methanol, ethanol and isopropanol (less than 2 mg/mL in ethanol). The weight average molecular weight of P1 and P2 were 20,350 Da with a polydispersity index (PDI) of 2.11 and 19,700 Da with a PDI of 1.98, respectively.

Fig. 1(a) shows the UV–Vis absorption spectra and the cyclic voltammograms (CVs) of PHPT are very similar to those of PcoPT. The HOMO energy levels of PHPT and PcoPT figured out from the onset oxidation potential (displayed vs. red-ox potential of ferrocene, Fc/Fc$^+$) of CVs (Fig. 1(b)