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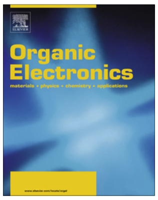

Acid-functionalized fullerenes used as interfacial layer materials in inverted polymer solar cells

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ABSTRACT

Two types of carboxylic acid functionalized fullerence derivatives, 4-(2-ethylhexyloxy)-[6,6]-phenyl C_{61}-butyric acid (*p*-EHO-PCBA) and bis-4-(2-ethylhexyloxy)-[6,6]-phenyl C_{61}-butyric acid (bis-*p*-EHO-PCBA), were synthesized and investigated as an interfacial layer for inverted polymer solar cells (iPSCs). The –COOH groups on the PCBAs chemisorb to inorganic metal oxide (TiO_X), generating fullerene-based self-assembled monolayers (FSAMs). The devices with the mono- and bis-FSAMs exhibited substantially lower series resistance (R_S) values of 2.10 Ω cm^2 and 1.46 Ω cm^2, compared to that (4.15 Ω cm^2) of the unmodified device. The TiO_X films modified with mono- and bis-FSAMs showed higher contact angles of 50° and 91°, respectively, than that of the pristine TiO_X film (33°). The increased contact angles were attributed to the enhanced hydrophobicity, improving the wetting properties with the organic photoactive layer. In addition, a comparison of device characteristics with electroactive FSAMs and non-electroactive benzoic acid SAMs clearly indicates that the FSAMs may suggest an additional pathway for photo-induced charge transfer and charge collection to ITO. After surface modification with FSAMs, the short-circuit current density (J_{SC}) and fill factor (*FF*) values increased substantially. The iPSCs based on poly(5,6-bis(octyloxy)-4-(thiophen-2-l)benzo[*c*][1,2,5]thiadiazole) (PTBT) and [6,6]phenyl-C_{61}-butyric acid methyl ester (PCBM) as an active layer showed remarkably improved power conversion efficiency up to 5.13% through incorporation of the FSAMs-based interfacial layer.

1. Introduction

Recently, all-solution processed polymer solar cells (PSCs) have been the subject of considerable research efforts for their potential applications in low cost, large-area and flexible energy sources. The power conversion efficiencies (PCEs) of polymer:fullerene-based bulk-heterojunction (BHJ) devices have reached ca. 5–8% in a conventional device architecture [1–11]. On the other hand, low work function metals such as aluminum (Al), calcium (Ca), and barium (Ba) as the top electrode in conventional thin-film devices, can be easily oxidized in air, resulting in poor temporal stability with deterioration in the device performance [12]. To circumvent this problem, an inverted device architecture was suggested using air-stable high work function metals (e.g. gold) as the top anode, where metal oxides e.g. TiO_X or ZnO, serve as an

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electron transporting and collecting layer on a transparent cathode (such as indium tin oxide (ITO)) [13–19]. Although the inverted PSCs (iPSCs) showed improved device stability under air, these devices still suffer from the inherent incompatibility and poor electrical contact at the organic photoactive layer and inorganic metal oxide interfaces [20,21].

To overcome the weak points of iPSCs, alkali metals, such as cesium carbonate (Cs_2CO_3), have been introduced as a buffer layer on ITO [22]. Through morphological optimization, iPSCs based on poly(3-hexylthiophene) (P3HT):[6,6]phenyl-C_{61}-butyric acid methyl ester (PCBM) with a Cs_2CO_3 interfacial layer showed an improved PCE of ~4.2% [22]. In addition, interface modification of metal oxides with self-assembled monolayers (SAMs) has been employed to improve the active layer/metal oxide contact in iPSCs [12,17,23,24]. Surface energy control of ZnO by incorporating two different SAMs with polar NH_2 or non-polar $–CH_3$ end groups led to successful morphology control of the active layer, improving photocurrent and device performance [24]. Fullerene-based SAMs (FSAMs) with different anchoring groups have also been designed to tune their self-assembling properties on metal oxides [25,26]. The use of interfacial SAMs was found to be efficient in facilitating charge transfer between the active layer and metal oxides, resulting in an improved fill factor (*FF*) and short-circuit current density (J_{SC}) by reducing the contact resistance and passivating the inorganic surface trap sites [17,26–28].

In this study, carboxylic acid functionalized fullerene derivatives, 4-(2-ethylhexyloxy)-[6,6]-phenyl-C_{61}-butyric acid (*p*-EHO-PCBA) and bis-4-(2-ethylhexyloxy)-[6,6]-phenyl-C_{61}-butyric acid (bis-*p*-EHO-PCBA), were prepared as an interfacial layer for iPSC devices. The –COOH groups in the PCBAs chemisorb onto TiO_X, generating SAMs on the TiO_X layer. An iPSC based on a thiophene–benzothiadiazole-based low band gap copolymer, poly(5,6-bis(octyloxy)-4-(thiophen-2-l)benzo[*c*][1,2,5]thiadiazole) (PTBT) and PCBM as an active layer [29], was fabricated using FSAMs to modify the interface between TiO_X and the organic active layer. The *p*-EHO-PCBA and bis-*p*-EHO-PCBA SAMs reduced the series resistance (R_S) and improved the wetting properties at the organic active layer and inorganic TiO_X interface. In addition, a comparison of device characteristics with electroactive FSAMs and non-electroactive benzoic acid SAMs (BA-SAMs) was also studied to verify additional pathways for photo-induced charge transfer and charge collection to ITO. The inverted device with FSAMs exhibited substantially improved J_{SC} and *FF* values with compared to the unmodified one, showing the best PCE value of 5.13% for the bis-FSAM treated photovoltaic device.

2. Methods section

2.1. Materials and instruments

All chemicals were purchased from either Aldrich or Acros and used without further purification. 4-(2-Ethylhexyloxy)-[6,6]-phenyl-C_{61}-butyric acid (*p*-EHO-PCBA) was synthesized by following a previous procedure [30]. ^1H NMR and ^{13}C NMR spectra were recorded on a VNMRS 600 (Varian, USA) spectrophotometer. MALDI MS spectra were obtained with Ultraflex III (Bruker, Germany). AFM images were obtained using a Park Systems XE-100 microscope in tapping mode. Contact angles were measured using DSA100 (KRUSS, Germany). Photoluminescence spectra were measured on a Cary Eclipse spectrofluorometer with a Xenon lamp excitation source (Edinburgh, UK). Cyclic voltammetry (CV) measurements were performed on a Solartron SI 1287 system. The electrochemical measurements were carried out at a scan rate of 50 mV/s under argon in *o*-dichlorobenzene containing 0.1 M Bu_4NClO_4 as a supporting electrolyte, relative to an internal ferrocene/ferrocenium standard.

2.2. Synthesis of Bis-4-(2-ethylhexyloxy)-[6,6]-phenyl-C_{61}-butyric acid methyl ester (bis-p-EHO-PCBM)

Bis-*p*-EHO-PCBM was synthesized by following the same procedure for the preparation of *p*-EHO-PCBM [30]. The bis-*p*-EHO-PCBM fraction was separated from monosubstituted *p*-EHO-PCBM (3.10 g, 34.0% yield) by silica gel column chromatography (eluent: toluene/dichloromethane, 30:70 v/v). The eluent was concentrated under reduced pressure, redissolved in a minimal amount of toluene and transferred to a centrifuge tube. The product was precipitated into MeOH, recovered by centrifugation and treated with MeOH several times. Isolated yield: 1.41 g (15.0%, brown solid). ^1H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.57–8.03 (m, 4H), 6.80–7.14 (m, 4H), 3.81–4.00 (m, 4H), 3.57–3.74 (m, 6H), 2.28–2.83 (m, 12H), 1.69–1.83 (2H), 1.25–1.60 (m, 16H), 0.89–1.01 (m, 12H). MALDI MS (*m/z*): 1358 ($(M+H)^{+\cdot}$). Elemental analysis. Calcd for $C_{100}H_{60}O_6$: C, 88.47; H, 4.45; Found: C, 88.25; H, 4.30.

2.3. Synthesis of Bis-4-(2-ethylhexyloxy)-[6,6]-phenyl-C_{61}-butyric acid (bis-p-EHO-PCBA)

To a solution containing bis-*p*-EHO-PCBM (1.40 g, 1.03 mmol) in chlorobenzene was added acetic acid (100 mL) and concentrated hydrochloric acid (40 mL). The mixture was heated under reflux overnight. The solvent was removed in vacuo and the precipitate was collected by filtration. The crude product was washed with methanol and a solvent mixture of MeOH:diethylether (1:1 v/v) several times. Isolated yield: 1.32 g (96.0%, brown solid). ^1H NMR($CDCl_3$, 600 MHz): δ (ppm) 11.86 (br m, 2H), 7.42–7.99 (m, 4H), 6.89–7.24 (m, 4H), 3.84–3.97 (m, 4H), 2.65–2.83 (m, 4H), 2.42–2.54 (m, 4H), 2.02–2.16 (m, 4H), 1.71–1.81 (m, 2H), 1.31–1.56 (m, 16H), 0.91–1.01 (m, 12H). MALDI MS (*m/z*): 1330 ($(M+H)^{+\cdot}$). Elemental analysis. Calcd for $C_{98}H_{56}O_6$: C, 88.53; H, 4.25; Found: C, 88.33; H, 4.08.

2.4. Solar cells fabrication and characterization

An ITO-coated glass was cleaned with detergent, water, acetone, and isopropanol. The TiO_X precursor solution prepared using a sol–gel method [8], was spin-coated onto an ITO substrate, annealed at 80 °C for 10 min and transferred