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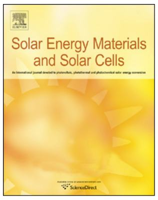

Relationship between photostability and nanostructures in DTS(FBTTh$_2$)$_2$:fullerene bulk-heterojunction films

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ABSTRACT

Successful fabrication and operation of highly stable organic photovoltaic (OPV) cells demand improved durability of the semiconductor materials used in the active layer. In this study, we performed photooxidation studies on DTS(FBTTh$_2$)$_2$:fullerene bulk-heterojunction (BHJ) films, one of the promising small-molecule materials for OPV cells, by using two-dimensional (2D) grazing-incidence wide-angle X-ray scattering (GIWAXS), absorption spectroscopy, and atomic force microscopy (AFM). The results of 2D-GIWAXS and absorption spectroscopic analyses indicate that increasing the crystallinity of DTS(FBTTh$_2$)$_2$:fullerene BHJ films improved their photostability. The AFM results suggest that the roughness of the original DTS(FBTTh$_2$)$_2$:fullerene films was also related to their photooxidation rates. The results obtained in this work show that changing the fullerene derivative species and controlling the nanostructures of the thin films are both important criteria for improving the photostability of OPV cells.

1. Introduction

Organic photovoltaic (OPV) cells have attracted much recent attention because of their flexibility, transparency, cost-effectiveness etc. [1–9]. The active layers, which convert light energy to electrical energy, consist of organic electron donor and acceptor materials. Poly(3-hexylthiophene) (P3HT) [1], poly[*N*−9″-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2″,1′,3′-benzothiadiazole)] (PCDTBT) [2], and poly({4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-*b*:4,5-b′] dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-*b*]thiophenediyl}) (PTB7) [3] have been developed as electron donors; together with small-molecule donor materials [4–9], they show high solubility in organic solvents and the ability to form thin films upon solvent evaporation. For the commercialization, it is necessary to improve both the power conversion efficiency (PCE) and stability of the materials. As a result, stability tests of OPV cells have been performed [10–13], and the International Summit on OPV Stability (ISOS) testing protocols were established in 2011 [14]. The importance of stability is also a critical issue for other types of organic solar cells. The stabilization of solar cells have been aimed for dye-sensitized solar cells [15] and perovskite solar cells [16]. Thus the degradation of organic solar cells is widely recognized to be important but is not completely understood in detail so far.

One trigger for the degradation of OPV cells is the photooxidation of the materials used in the active layers. The photooxidation of poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) [17–19], P3HT [20–27], PCDTBT [28], and PTB7 [29] has been studied. When the donor materials are mixed with acceptor materials such as fullerene derivatives, the photooxidation of the donor materials is suppressed generally suppressed [17,20,24,26,29]. This suppression may be the result of the acceptor materials working as radical scavengers. McGehee and co-workers reported that the suppression efficiency depends on the energy levels of the acceptor materials [17]. When the acceptor materials have small electron affinities, photogenerated electrons can be more easily transferred from the acceptor materials to oxygen, generating super oxide anions, an active oxygen species that can oxidize donor materials.

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These studies investigated the relationship between the energy levels of materials and the photooxidation rate of donor materials, or they focused on the molecular structures. However, the effects of the nanostructures of materials on the photostability are also significant, because polymer materials degrade faster in amorphous regions than in crystalline regions [30,31]. The research groups of both Rivaton and Krebs investigated the relationship between the nanostructures and photooxidative degradation of the donor material P3HT, using polymers with different regioregularity [22,23]. They reported that higher degrees of regioregularity in P3HT correspond to higher photostability. Recently, McGehee and co-workers performed photooxidation studies on 13 organic semiconductors, including polymers, oligomers, small molecules, and fullerenes, which exhibited changes in their morphologies [22]. They found that the photobleaching rates were correlated to the material density.

For OPV cells, the donor and acceptor materials are used in mixtures, which form randomly phase-segregated bulk-heterojunction (BHJ) structures. BHJ structures consist of amorphous and crystalline regions, and differences in the BHJ structures can affect the photooxidation rates of the materials. Here, we report the effects of structural differences, particularly those regarding the crystallinity and morphology, on the photooxidation rates of BHJ donor materials. We focus on donor materials because they absorb sunlight in OPV cells; they are approximately one or two orders of magnitude less stable under photoirradiation than phenyl-C_{61}-butyric acid methyl ester (PCBM) [32]. To examine the effects of BHJ structural differences, we investigated small-molecule donor materials because they have monodispersity and higher crystallinity than those of polymeric donor materials. In particular, we focused on 7,7′-(4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b*′]dithiophene-2,6-diyl)bis(6-fluoro-4-(5′-hexyl-[2,2′-bithiophen]-5-yl)benzo[*c*] [1,2,5] thiadiazole) (DTS(FBTTh$_2$)$_2$), whose molecular structure is shown in Fig. 1a [5–7]. Developed by Nguyen, Bazan, and their colleagues in 2012, DTS(FBTTh$_2$)$_2$ showed a maximum PCE of 7.0% when used with PC$_{71}$BM [5]. The photooxidation behavior of DTS(FBTTh$_2$)$_2$ was recently studied by McGehee and co-workers [32]; the investigation demonstrated that DTS(FBTTh$_2$)$_2$ was approximately twice as stable as P3HT and its stability could be improved by a factor of three by thermal annealing at 180 °C for 20 min. In our study, the effects of nanostructures in BHJ films of DTS(FBTTh$_2$)$_2$ were examined.

To prepare BHJ films consisting of DTS(FBTTh$_2$)$_2$:fullerene, we chose two fullerene derivatives of PCBM, shown in Fig. 1b [33] and indene-C_{60} bisadduct (ICBA), represents in Fig. 1c [34], as the acceptor materials. Since PCBM is the most common acceptor material in OPV cells, it is useful as a benchmark. Compared to PCBM, ICBA, which is composed of a mixture of isomers, has relatively high energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Thin films of DTS(FBTTh$_2$)$_2$, DTS(FBTTh$_2$)$_2$:PCBM, and DTS(FBTTh$_2$)$_2$:ICBA with different crystallinities and morphologies were prepared by changing the thermal annealing conditions. The photooxidation behavior of the films was studied systematically. If changes in the crystallinity or morphology, induced by differences in the materials or the annealing conditions, can affect the photooxidation behavior of these materials in OPV cells, design strategies for donor and acceptor materials with increased photostability can be developed from the results.

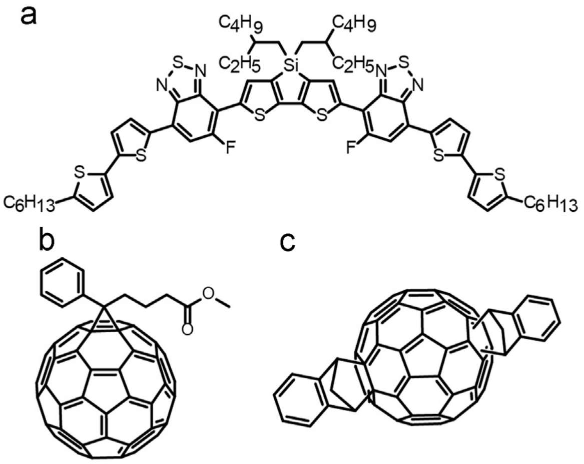

Fig. 1. Molecular structures of (a) DTS(FBTTh$_2$)$_2$, (b) PCBM, and (c) ICBA.

2. Experimental

2.1. Materials

Chlorobenzene, DTS(FBTTh$_2$)$_2$, PCBM, and ICBA were purchased from Aldrich, 1-Material, Solenne, and Luminescence Technology Corp., respectively. All reagents and solvents were used as received.

2.2. Sample preparation and photooxidation

The experimental samples were prepared by spin-coating the precursor solutions onto CaF$_2$ substrates for absorption spectra measurements or glass substrates for grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements. Thin films of DTS(FBTTh$_2$)$_2$ or DTS(FBTTh$_2$)$_2$:fullerene (molar ratio of 1:1) were prepared from chlorobenzene solutions. The films had a thickness of ~100 nm. After the thin films were deposited, they were heated at 60 °C to evaporate the solvent. The irradiation of the films was performed using a Bunkoukeiki BGS-50 solar simulator with an irradiation intensity of 100 mW cm^{-2} in air at 60 °C, without controlling the humidity. The absorption spectra were recorded using a Shimadzu UV2600 spectrophotometer.

2.3. GIWAXS measurements

Each sample was mounted on the gonio stage (HUBER X-ray diffractometer) of the SPring-8 beamline BL46XU for in situ X-ray diffraction (XRD) analysis. GIWAXS data were acquired using 12.398-keV X-rays ($\lambda = 1.000$ Å) at an incident angle of 0.12°; diffracted X-rays were captured at an exposure time of 1 s by a two-dimensional (2D) detector (PILATUS 300K) located at a distance of $L = 175$ mm from the sample.

2.4. Morphological characterization

Atomic force microscopy (AFM) measurements were performed with a Hitachi-Hi-Tech SPA-400 scanning probe microscope in the dynamic force microscopy mode.

3. Results and discussion

3.1. Photooxidation of DTS(FBTTh$_2$)$_2$ and DTS(FBTTh$_2$)$_2$:fullerene

To examine the photodegradation properties of DTS(FBTTh$_2$)$_2$, DTS(FBTTh$_2$)$_2$:PCBM, and DTS(FBTTh$_2$)$_2$:ICBA, absorption spectra were obtained after photoirradiation for 5, 10, 15, 20, and 25 h. The spectra of the as-prepared films, which were dried at 60 °C for 30 min after spin coating, are shown in Fig. 2a–c. All spectra obtained before irradiation (black line) show absorption bands from 500 to 800 nm, corresponding to the π–π* transition of DTS(FBTTh$_2$)$_2$. The absorbance of these bands was decreased upon irradiation, shown by the spectrum represented by the pink line, which indicates that photooxidation occurred at the π-conjugate