Thermally induced anchoring of fullerene in copolymers with Si-bridging atom: Spectroscopic evidences

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ABSTRACT

We use X-ray photoelectron spectroscopy (XPS), Near-edge X-ray absorption fine structure (NEXAFS), resonant Auger spectroscopy (RAS), Attenuation Total Reflection Infrared (ATR-IR) and Atomic Force Microscopy (AFM) to study the blend between the copolymer poly[2,7-(9,9-bis(2-ethylhexyl)-dibenzosilole)-*alt*-4,7-bis(thiophen-2-yl)benzo-2,1,3-thiadiazole] (PSiF-DBT) and the fullerene derivative $PC_{71}BM$ submitted to different annealing temperatures. Those measurements indicate that there is an incidental anchoring of a fullerene derivative to the Si-bridging atoms of a copolymer induced by thermal annealing of the film. Insights about the physical properties of one possible $PSiF-DBT/PC_{71}BM$ anchored structure are obtained using Density Functional Theory calculations. Since the performance of organic photovoltaic based on polymer-fullerene blends depends on the chemical structure of the blend components, the anchoring effect might affect the photovoltaic properties of those devices.

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1. Introduction

Bulk heterojunction organic solar cells are composed blends between a hole transporting donor (usually a conjugated polymer) and an electron transporting acceptor (usually a fullerene derivative). In order to tune the photovoltaic properties of this active layer, an enormous variety of low bandgap copolymers was synthesized by combining different chemical groups along the polymeric chain. In particular, Si-bridging copolymers are very promising materials for active layer in organic solar cells [1–3]. The longer C-Si bond lengths linking the lateral alkyl groups to the polymer's main backbone drastically modifies interchain interactions, leading to higher degrees of crystallinity [4]. This effect allows a better stacking between chains [5] which improves the photovoltaic performance of the film [6]. For instance, a device with 5.4% of power conversion efficiency (PCE) was reported using the Si-bridging copolymer poly[2,7-(9,9-bis(2-ethylhexyl)-dibenzosilole)-*alt*-4,7-bis(thiophen-2-yl)benzo-2,1,3-thiadiazole] (PSiF-DBT) [7]. Moreover, the efficiency of BHJ devices is strongly dependent on the film morphology [8]. A nanoscale phase separation is desired to ensure the best donor-acceptor contact leading to higher exciton dissociation efficiencies. Even after achieving this ideal morphology, phase segregation during the device lifetime can compromise the solar cell performance. One elegant strategy to circumvent this problem was the synthesis of polymers with thermocleavable side groups that employs the easy thermal cleavage of esters between carboxylic acids and a tertiary alcohol at temperatures around 200 °C [9]. The higher density of the film that was obtained after the thermocleavage slowed down the diffusion phenomena which results in an improved morphologic stability [10]. Another approach to increase the film stability is to covalently link the fullerene to the polymeric chain using a non-conjugated bridging chain [9–12]. Yet there are issues related to the processability of these systems as well as their fraction loading with fullerenes [13]. In addition, all devices built using this approach showed very low power conversion efficiencies [13,14].

Here we report spectroscopic evidences indicating that the thermal treatment of $PSiF-DBT/PC_{71}BM$ blends is able to induce an anchoring process of the fullerene in the Si bridging atom of the copolymer. Thermal annealing of polymer/fullerene blends is commonly applied as an after deposition treatment to improve the photovoltaic properties of the corresponding film. Due to the low binding strength of the Si—C bond between Si atom and the non-conjugated side chain [15], thermal annealing is effective to break Si—C bonds and promote the attachment of $PC_{71}BM$ by forming a bond between the Si and the O heteroatom present in $PC_{71}BM$ ester group. Those evidences were obtained using a multitechnique approach based on X-ray photoelectron spectroscopy (XPS), near edge X-ray absorption fine structure (NEXAFS), resonant photoemission spectroscopy (RPES), Attenuation Total Reflection Infrared (ATR-IR) and atomic force microscopy (AFM).

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For future applications in photovoltaic devices, our findings open the possibility of an after deposition treatment of OPVs under non-controlled atmosphere to develop photovoltaic heterojunctions with improved stability.

2. Experimental section

2.1. Materials and film deposition

Bulk heterojunction films were fabricated as follow: a solution of 11 mg/mL in o-dichlorobenzene of PSiF-DBT:PC$_{71}$BM with mass proportion 1:3 were prepared in inert nitrogen atmosphere and stirred and heated at 40 °C for 12 h. After stirring the film were spin-cast onto a pre-cleaned glass/ITO substrate and submitted to thermal annealing at temperatures of 100 °C and 200 °C in vacuum for 15 min. The same processes were adopted to as cast samples, except for the annealing step. All steps after solution preparation were done outside of the glovebox, in ambient atmosphere. Before the active layer deposition, a treatment with methanol was done in pre-cleaned glass/ITO substrates to improve the wettability. After this treatment, a PEDOT:PSS layer was spin-coated with a thickness of 40 nm and submitted to annealing treatment at 120 °C for 15 min. In sequence the active layer was deposited as described above and the films were submitted to annealing treatment using the same temperature and conditions cited before. The thickness of the PSiF-DBT:PC$_{71}$BM films was around 60 nm. The surface morphology of PSiF-DBT:PC$_{71}$BM film was probed in an atomic force microscope (AFM, Shimadzu) in dynamic mode using a silicon tip with radius of curvature of 10, a resonance frequency of 204–497 kHz, and a force constant of 10–130 N/m.

XPS spectra were acquired using the Thermo Scientific ESCALAB 250Xi spectrometer equipped with a hemispherical electron energy analyzer. A flood gun source for generating a diffuse beam of low energy electrons and Ar$^+$ ions was used during all measurements in order to prevent surface charging. The monochromatized Al $K\alpha$ (hν = 1486.6 eV) excitation energy with 650 μm X-ray spot size was used for the XPS measurements. The electron energy analyzer was operated at constant pass energy of 25 eV and 40 eV for high resolution and survey spectra, respectively. The error in the energy values at high resolution XPS experimental conditions is estimated to 0.2 eV.

Thermo Scientific Avantage XPS software package (version 4.61) was used to acquire and processing the XPS spectra. A linear combination of Gaussian and Lorentzian line shapes was select for the spectra fitting, while Shirley function was used for background correction. For all spectra the binding energy calibration was performed using the Au (4f$_{5/2}$) line at 84.0 eV. A set of constrains was used for the spin-orbit splitting doublets in Si2p high resolution spectra fitting. We used the same full width at half maximum (FWHM) and line shape for these doublets, and the intensity of 2p$_{3/2}$ and 2p$_{1/2}$ was constrained to I(2p$_{3/2}$) = 2 ∗ I(2p$_{1/2}$). The 2p$_{3/2}$ and 2p$_{1/2}$ binding energy difference was set to 0.62 eV for Si2p core level spectra [16].

Near-edge X-ray absorption fine structure (NEXAFS) spectra were measured at the soft X-ray spectroscopy (SXS) beamline at the Brazilian Synchrotron Light Source (LNLS). InSb(111) double-crystal monochromator was used to cover the silicon K-edge. NEXAFS spectra were collected in the total electron yield mode (electron current at the sample) simultaneously with a photon flux monitor (Au grid). The final data was normalized by this flux spectrum to correct for fluctuations in beam intensity. The energy calibration was performed using the 1s → 3p transition of a silicon wafer. Resonant Auger spectra (RAS) were also measured at the SXS beamline in the same ultrahigh vacuum chamber (UHV) with a base pressure of 10^{-8} mbar using a hemispherical electron energy analyzer with pass energy of 20 eV.

Attenuation Total Reflection Infrared spectra were obtained for PSiF-DBT and PSiF-DBT:PC$_{71}$BM films deposited onto a flexible plastic substrate, using a Bruker Vertex 70 FT-IR spectrometer with a resolution of 4 cm^{-1}.

2.2. Computational procedure

The simulations discussed in this work were based on the model oligomer of PSiF-DBT fully optimized for the simulations discussed in ref. [17]. Instead of a five units oligomer here we use a small symmetric structure containing the alkyl-dibenzosilole unit in the center of two thiophene-benzothiadiazol-thiophene units, one in the left and another one in the right of the alkyl-dibenzosilole unit. This small structure was used in this study in order to save computational effort. As we take just a part of the previously studied structure, we optimize the structure using HF theory level and the basis set 3-21G** [18–20]. The same theory level was used to optimize the PC$_{71}$BM structure. After optimization of the isolated structure, we linked the PC$_{71}$BM molecule to the PSiF-DBT model structure, by replacing one of the alkyl side chain bridged in Si atom. PC$_{71}$BM structure was linked to PSiF-DBT by bonding the O heteroatom of the ester group to the **Si**-bridging atom in dibenzosilole group. After this, the PC$_{71}$BM anchored structure was optimized using the HF/3-21G**. After this optimization, electronic structure and IR spectrum were simulated using Density Functional Theory. We used B3LYP [21,22] as exchange-correlation functional and 3-21G** as basis set. We have also obtained the IR spectrum for the isolated PSiF-DBT using the same method cited before. All simulations were performed using the Gaussian03 package [23].

3. Results and discussion

3.1. XPS

To investigate the **Si**—O bond formation the survey XPS spectra for PSiF:PC$_{71}$BM thin film without thermal annealing (PSiF:PC$_{71}$BM-as cast) and thermal annealed thin films at 100 °C (PSiF:PC$_{71}$BM-100) and 200 °C (PSiF:PC$_{71}$BM-200) were measured (see Figure SI 1 of Supplementary Information Files). The peaks associated with the characteristic elements (i.e., Si2p, S2p, C1s, N1s and O1s) of these blends were measured. Here, we will concentrate our discussion on the **Si**-bonds and for that we investigate high resolution Si 2p and O 1s XPS spectra for these films. Those measurements are shown in Fig. 1.

High resolution XPS spectra of Si2p core level are displayed in the left panel of Fig. 1. The spectra deconvolution procedure was performed using two contributions for the as-cast film, one attributed to **Si**—C bond at 100.3 eV in the dibenzosilole unit and the other one located at 102.5 eV. According to previous reports [24–26], the latter contribution is associated to the O—**Si**—C bond, which becomes more pronounced for thermal annealed films. Additionally, a more defined profile of the signal is observed after thermal annealing (see FWHM parameter in Table SI 1). Surprisingly, it is possible to observe from Fig. 1(left) that the **Si**—O signal becomes more intense in relation to the Si—C signal after the thermal annealing treatment. This result suggests that this treatment is able to break the Si—C bonds while it induces the formation of Si—O bonds.

The right panel of Fig. 1 shows O 1s core level XPS spectra for as-cast and thermal annealed films. For the discussion of this figure one has to keep in mind that the O atom is only present in the PC$_{71}$BM structure while the Si atom is the bridging atom in the copolymer structure, being bonded to the alkyl side chains (see Fig. 1, bottom scheme). As a consequence, the O 1s XPS spectrum corresponding to the as-cast sample is characteristic of the O 1s XPS spectrum of PC$_{71}$BM, which is composed by two features, one assigned to the oxygen labeled as 2 (532.2 eV) and another correspondent to the oxygen labeled as 1 (533.7 eV) respectively [27,28] (the oxygen labels are depicted in the bottom scheme of Fig. 1). The intensity of the O 1 signal decreases with increasing temperature of the thermal treatment, while the signal attributed to the O 2 remains unchanged. This last result is an indication that the C—O bond involving oxygen 1 becomes weaker under the thermal treatment and that this oxygen tends to form concomitantly a **Si**—O bond that links the polymer to the PC$_{71}$BM. With **Si**—O formation two