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Molecular orientation in polymer/fullerene blend films and the influence of annealing



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ABSTRACT

The molecular orientation of selected low band gap polymers for organic photovoltaics (Si-PCPDTBT, PCPDTBT, and PCPDTBBT) and the influence of PCBM on the orientation is studied using Near-Edge X-Ray Absorption Fine Structure spectroscopy (NEXAFS). The results are compared to the state of the art material P3HT. A clear angular dependence in the S-K NEXAFS spectra points to a preferred orientation of the π -conjugated system and thus to a high degree of ordering for most materials. Generally, the degree of ordering decreases after blending the polymer with the fullerene PCBM. In the case of P3HT and PCPDTBT, the degree of ordering could be improved considerably due to the annealing of the film. The annealing temperatures depend however on the considered polymer.

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1. Introduction

Compared to photovoltaic devices based on established inorganic materials the efficiency of organic solar cells today is lower. An approach to improve the efficiency of donor–acceptor based bulk heterojunction (BHJ) organic photovoltaic cells is the use of low band gap (LBG) polymers as donor materials [1,2]. The lowering of the band gap can be achieved due to the hybridization of electron-rich and electron-deficient sub-units which results in a reduction of the bond-length alternation [3]. The lower optical band gap results in a better efficiency by greater absorption in the visible and near infrared regions of the solar spectrum and by improving the offset of the frontier energy levels of the donor and acceptor [4,5].

In this work we focused on three such low band gap polymers – namely poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b'] dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT), poly[2,6-(4,4-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole)-alt-4,7-(2,1,3-benzothiadiazole)] (Si-PCPDTBT) and poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']-dithiophene)-alt-4,8-(benzobis[1,2-c:4,5-c'] thiadiazole) (PCPDTBBT). All three polymers are promising candidates for use in organic solar cells [6–9]. Most recently, very interesting

properties of a ternary bulk heterojunction system were reported, consisting of poly-3-hexylthiophene (P3HT), PCBM and Si-PCPDTBT [10].

The application and potential of these new polymers require detailed study of both electronic structure and molecular orientation as they are fundamental to the device properties: the orientation and quality of the film control the mobility of the charge carrier and hence device operation [11].

For the investigation of the molecular orientation and morphology of polymers a number of spectroscopic methods are available such as X-Ray diffraction (XRD) [12–14], optical methods [15,16] and Near-Edge X-Ray Absorption Fine Structure (NEXAFS) [17–22], the latter being a Synchrotron radiation technique. With NEXAFS the excitations from the occupied core levels to unoccupied states as a function of energy are probed. Due to the selection rules for these excitations, the change of the angular momentum quantum number ($\Delta l = \pm 1$) and also the direction of the electric field vector E of the linear polarized synchrotron light allows information about the unoccupied electronic structure of the polymer and also the molecular orientation to be obtained. This makes NEXAFS an ideal technique to study the orientation in ultrathin films [21,23]. Next to this geometric information NEXAFS also probes the electronic structure of the unoccupied orbital density of states, essential for determining the transport/mobility in such devices.

We have used the angular dichroism of the sulfur K-edge NEXAFS spectra of the respecting polymers to probe the orientation

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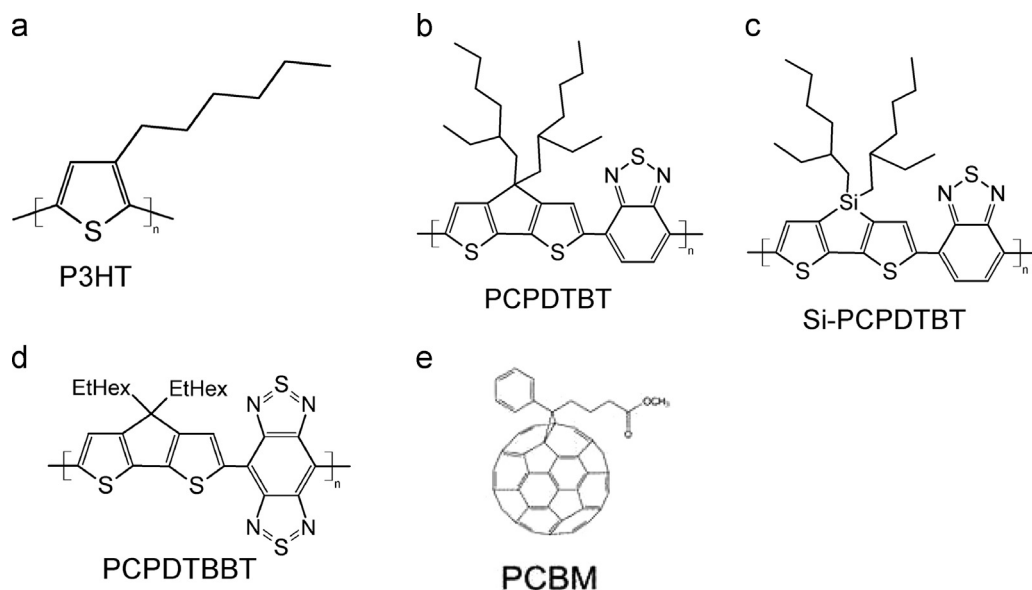


Fig. 1. Chemical structures of a) P3HT, the low band gap polymers b) PCPDTBT, c) Si-PCPDTBT, d) PCPDTBBT and the acceptor molecule e) PCBM.

of the extended π -conjugated system. A preferred molecular orientation also implies that the degree of ordering is high. Due to the relatively high photon energy of the sulfur K edge and fluorescence detection it is possible to study relatively thick layers (nanometers to micrometers) with NEXAFS, and therefore gain information more akin to bulk film properties instead of just the uppermost surface. For polymers such as Si-PCPDTBT and PCPDTBBT with different sulfur species (thiophene-unit and benzothiadiazole-unit), the orientation of each subunit and in particular a possible tilt angle between the subunits can be examined. NEXAFS is particularly useful in this respect as X-Ray diffraction is only sensitive to long-range order whereas NEXAFS also probes the short range order which in such systems often manifests itself in an increase of structural disorder. The optimal domain size in BHJ solar cells determined by the exciton diffusion length however is usually less than a few 10 nm [24–27]. The technique easily lends itself to the extension and measurement of other thin films such as polymer blends and other preparation routes providing complementary information to X-Ray diffraction.

In this work we focus on the effect of the acceptor molecule PCBM on the orientation and ordering of the LBG polymers Si-PCPDTBT and PCPDTBBT and we compare the results with the state of the art material P3HT and with pristine polymer films recently studied [28]. Furthermore the influence of temperature on the molecular orientation properties of polymer/fullerene blend films is studied for Si-PCPDTBT/PCBM, PCPDTBBT/PCBM as well as for the state-of-the-art polymer P3HT/PCBM. All chemical structures are summarized in Fig. 1.

2. Experimental section

Thin films of pure P3HT (Merck, $M_w=60,000$ g mol⁻¹, PD=1.5, RR=95%), Si-PCPDTBT (Belectric, $M_w=53,000$ g mol⁻¹, PD=2.9), PCPDTBT (Belectric, $M_w=56,000$ g mol⁻¹, PD=2.3) and PCPDTBBT (synthesized according to the published route [29], $M_w=18,000$ g mol⁻¹, PD=3.0) as well as the blend films with PCBM (Solenne BV, 99.5%) were coated on ITO (Hoya Corporation, $R=10$ Ω /sq) substrates from dichlorobenzene solution (1 mg polymer/100 mg dichlorobenzene) by doctor blade casting in a glove box (N₂-atmosphere). The ITO substrates were cleaned before the thin film application by ultrasonic treatment in acetone for 15 min.

Polymer samples with a film thickness of about 50 nm were prepared and the film thickness was determined by atomic force microscopy (AFM) and also UV/vis spectroscopy. Thermal annealing (120 °C) was performed in a glove box under N₂ and low light conditions.

Sulfur NEXAFS experiments were carried out at the XAS beamline at ANKA (synchrotron facility at the Karlsruhe Institute of Technology). The beamline at the sulfur K edge has a typical energy resolution of ≈ 300 meV (Si(111) double crystal monochromator) and a polarization degree of > 0.95 (*p*-polarized). The X-Ray absorption spectra were measured in a fluorescence yield mode using a special setup [30], which enables high quality data to be obtained in this energy region near 2.5 keV with a moderate incidence angle range (15–80°). Spectra were repeated and also taken from different sample regions in both slow and quick acquisition modes to check for the effect of radiation damage.

3. Results and discussion

3.1. Molecular orientation of new low band gap polymers

We first discuss sulfur K excitation spectra of Si-PCPDTBT and PCPDTBBT as a function of the excitation angle, which are shown in Fig. 2. Angular dependence of the sulfur K absorption peak is observed for Si-PCPDTBT (Fig. 2a). The intensity of the sulfur K absorption peak increases with decreasing incidence angle. Such angular dependence of the absorption signal can only be observed if the π -conjugated carbon system where the hetero-sulfur atom is involved forms a preferentially oriented film. However several peaks contribute to the absorption edge. The comparison with recently studied P3HT NEXAFS spectra enables the assignment of features for Si-PCPDTBT analogously to PCPDTBT [28]. Since P3HT only contains thiophene sulfur, a detailed peak fitting of the absorption spectra first enabled the assignment of related cyclopentadithiophene signals; other features were subsequently assigned to the benzothiadiazole moiety PCPDTBT [28].

In the same manner, four main peaks can be identified for Si-PCPDTBT, whereby the peaks labeled with T1 and T2 originate from the cyclopentadithiophene moiety and peaks B1 and B2 from the benzothiadiazole sulfur atoms. The shape and behavior of the absorption signal compare well with the Si-free analogue PCPDTBT [28].

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