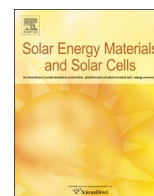




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# Electronic structure and self-organization properties of low band gap polymers: The effect of the introduction of additional thiophene moieties

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## ABSTRACT

An approach to improve the efficiency of donor-acceptor based bulk heterojunction (BHJ) organic solar cells is the use of low band gap (LBG) polymers as donor materials. The properties of these materials in BHJ solar cells are strongly influenced by their morphology and ability for self-organization in thin-films. We studied for two related polymer pairs the influence of the introduction of additional (hexyl-) thiophene moieties on both the electronic structure and ability for self-organization in thin films using Ultraviolet photoelectron spectroscopy (UPS) and Near-Edge X-Ray Absorption Fine Structure spectroscopy (NEXAFS). In addition, the influence of mixing with PCBM and post-processing annealing on the molecular orientation is investigated. We find that the introduction of additional (hexyl-) thiophene moieties in the polymer structure does not affect significantly the electronic structure of the polymers in thin films, but has a strong impact on their self-organization properties and consequently affects their behavior in devices.

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## 1. Introduction

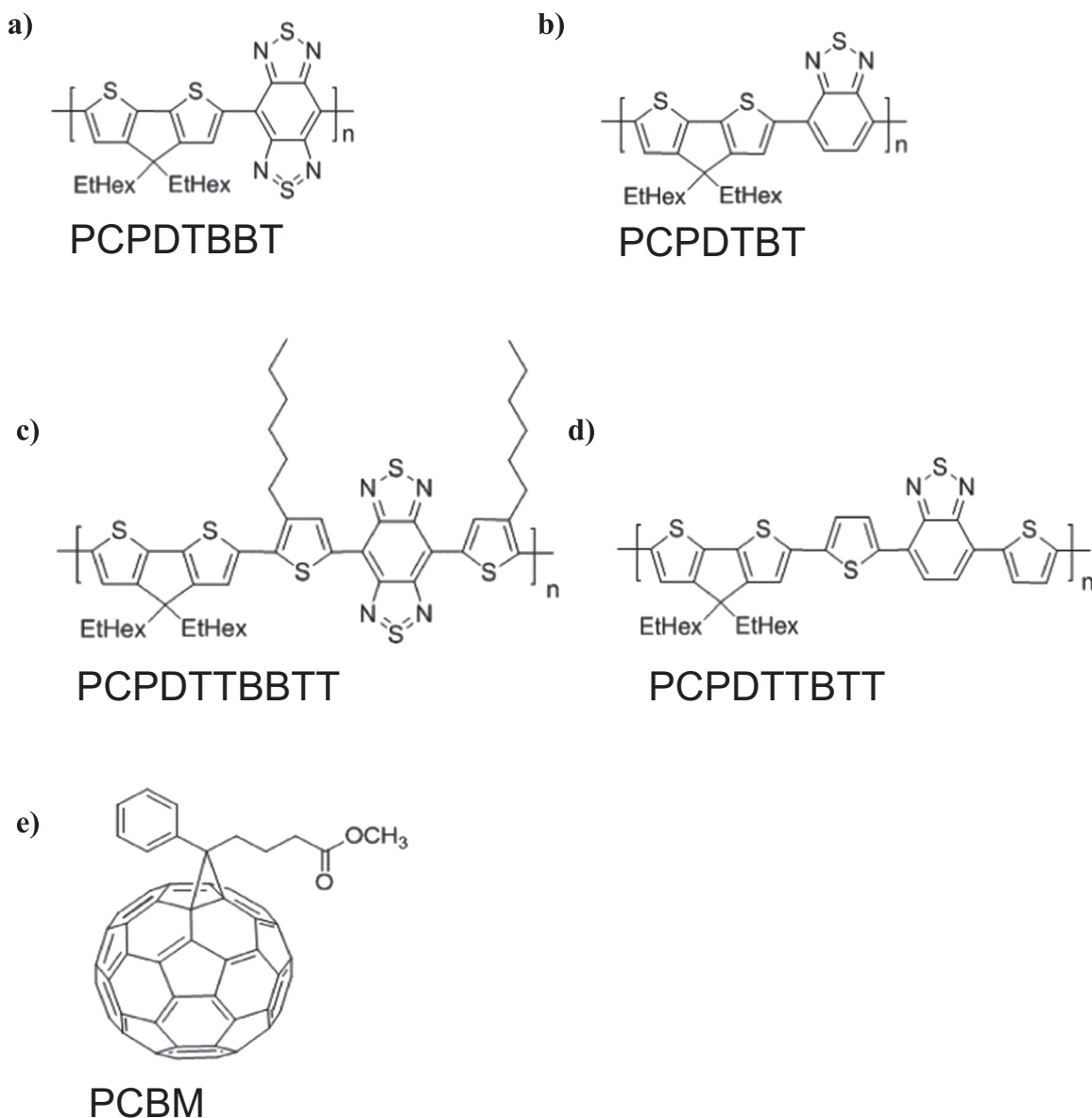
Due to the increasing necessity for renewable energy sources scientific and commercial interest in the last decade has also focused on organic semiconductors and consequently organic photovoltaics (OPV) technology is developing rapidly. OPV does not necessarily need to be seen as a competitor to the established photovoltaic devices it can be adopted in a wide range of other applications [1–3]. The most common device architecture for OPVs is based on thin films made of blends between a conjugated polymer as donor material and usually a fullerene derivative as an acceptor, the so-called bulk heterojunction (BHJ) solar cells [1–7]. In comparison to most photovoltaic devices based on inorganic semiconductors OPV's show typically lower efficiencies but have come close to amorphous Si:H [8]. A promising approach for improving the efficiency of donor-acceptor based BHJ organic photovoltaic cells is the usage of low band gap polymers (LBG) as donor materials [9,10]. One of the methods to build LBG polymers

is the synthesis of copolymers containing strong electron donating and withdrawing sub-units. The energy level hybridization results in a lowering of the band gap of the polymer enabling a more efficient absorption of sun light in the visible and near infrared spectral region [11]. In addition, the energy level alignment between the lowest unoccupied molecular orbitals (LUMO) of the donor and acceptor material of the blend can be improved [12,13].

The focus of this work is on two low band gap polymers containing dithiophene and benzothiadiazole moieties and including thiophene units with and without hexyl side chains: poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene)-*alt*-4,8-(bis(thiophene-2-yl)-benzobis[1,2-c;4,5-c']thiadiazole)] (PCPDTTBTT), poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene)-*alt*-4,7-(bis(thiophene-2-yl)-2,1,3-benzothiadiazole)] (PCPDTTBT). Chemical structures of the polymers are depicted in Fig. 1, together with related polymers (P3HT poly(3-hexyl-thiophene), PCPDTBBT (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)]) and PCPDTBT (poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)]) which we will use for comparison. Recent measurements using Near-Edge X-Ray

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**Fig. 1.** Chemical structures of studied low band gap polymers a) PCPDTBBT b) PCPDTBT, c) PCPDTTBBTT, d) PCPDTTBT and f) the acceptor molecule PCBM.

Absorption Fine Structure spectroscopy (NEXAFS) have shown that for the state of the art system P3HT and also the widely studied LBG polymer PCPDTBT, a highly preferred orientation in the thin films can be achieved [14]. Such an ability for self-organization depends strongly on the chemical structure, for example the introduction of an additional thiadiazole moiety to PCPDTBT (leading to PCPDTBBT) causes an almost complete loss of the preferred orientation in thin films [15]. However, the ordering and orientation of the polymer backbone in the active layers of bulk heterojunction solar cells can influence many device properties, such as the exciton diffusion, charge separation and charge carrier transport [16–20].

Since P3HT shows very good self-organization properties [21–24], the introduction of additional thiophene moieties might positively influence the ability for ordering of LBG polymers in thin films. We studied therefore the influence of the introduction of additional hexylthiophene spacer rings in the “polymer pair” PCPDTBBT/PCPDTTBBTT and the introduction of thiophene (without alkyl side chain) for the pair PCPDTBT/PCPDTTBT (see Fig. 1) on both the electronic structure and ability for self-organization in thin films.

These polymer pairs were also chosen due to their distinctly

different band gap: PCPDTBBT and PCPDTTBBTT exhibit a very small optical gap in comparison to the other two LBG polymers PCPDTBT and PCPDTTBT. The reason is the presence of benzo-bisthiadiazole (BB), which is a stronger electron withdrawing subunit in comparison to benzothiadiazole (BT) [25]. This could be of particular interest for the study of electronic interface properties. We use ultraviolet photoelectron spectroscopy (UPS) for the study of the electronic properties and near-edge X-ray absorption fine structure (NEXAFS) was employed mainly to investigate the molecular orientation of the polymers in thin films. By studying the angular dichroism of the sulfur K-edge NEXAFS spectra the orientation of the  $\pi$ -conjugated moieties of the polymer can be probed, allowing conclusions as to the short range structural ordering to be drawn. NEXAFS has been widely applied to the study of the molecular orientation in polymer films including polymer blends [20,26–28] providing complementary information to microscopy and X-ray diffraction (XRD) techniques the latter being more sensitive for probing long-range structural order. NEXAFS is therefore in particular suited for the studied polymer fullerene blend films - systems with a desired domain size of a few tens of nanometers. We use the fluorescence yield (FY) mode due to its

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