



[1]Benzothieno[3,2-*b*]benzothiophene (BTBT) derivatives: Influence in the molecular orientation and charge delocalization dynamics

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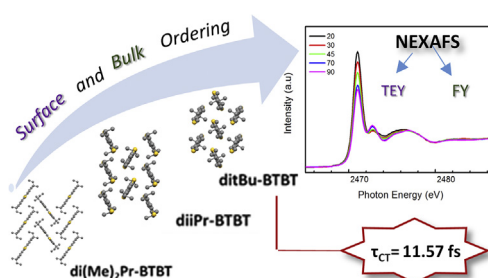
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HIGHLIGHTS

- Structure-property relationship are investigated for three BTBT derivatives.
- Ordering and molecular orientation show differences between surface and bulk.
- Alkyl chains of different sizes influence the charge transport properties.
- ditBu-BTBT has the highest molecular ordering and the lowest charge transfer time.

GRAPHICAL ABSTRACT



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ABSTRACT

Using near-edge X-ray absorption fine structure (NEXAFS) and resonant Auger spectroscopy (RAS) in conjunction with the core-hole clock methodology the electronic structure, molecular ordering and orientation and charge transfer dynamics in the femtosecond time scale of 2,7-di-tert-pentyl[1]benzothieno[3,2-*b*]benzothiophene (di(Me)₂Pr-BTBT), 2,7-di-iso-propyl[1]benzothieno[3,2-*b*]benzothiophene (diiPr-BTBT) and 2,7-di-tert-butyl[1]benzothieno[3,2-*b*]benzothiophene (ditBu-BTBT) films were investigated. Total electron yield (TEY) and fluorescence yield (FY) NEXAFS spectra were recorded with the aim of determining the preferred molecular orientation of the oligomers at the surface and in the bulk. Angular dependent sulfur 1s NEXAFS spectra for diiPr-BTBT and ditBu-BTBT films deposited onto FTO (fluorine doped tin oxide) point to well-organized films with a preferred edge-on geometry, while for the di(Me)₂Pr-BTBT film little variation is seen, indicating that the film matches its herringbone crystal packing. Films prepared on ITO (indium tin oxide) and silicon were also investigated by TEY and FY NEXAFS. Greater film ordering is observed in the bulk. The electron charge transfer time following sulfur K-edge main resonance was calculated. The ditBu-BTBT films showed the lowest charge transfer time as well as greater molecular organization, pointing to an increased coupling, as compared to the other oligomers.

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1. Introduction

The field of molecular semiconductors has been widely studied due to the promising optoelectronic properties that are offered for the construction of organic photovoltaics, light emitting diodes and field effect transistors. Some of the advantages that they offer are low cost of production and deposition in flexible substrates. Currently several research groups dedicate their studies to the optimization of the structure of organic compounds for use in the construction of optoelectronic devices [1–5].

[1]benzothieno [3,2-b]benzothiophene (BTBT) derivatives are among the molecular semiconductors with mobility values of $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, or even higher, that are crucial for the construction of performing optoelectronic devices [6–9]. Other important characteristics to mention are the viability of its synthetic route and high chemical stability [6]. Different studies have shown that the fine tuning of molecular packing of the BTBT core allows a better understanding of the structure-property relationship [10,11]. Previous research has shown successful results for various derivatives of the BTBT core [12–15]. Also the addition of alkyl chains of different sizes is a way to adjust the charge transport properties [10,13].

The electronic structure, molecular ordering and orientation and charge transfer processes are important parameters that will affect charge mobility in organic semiconductors. The knowledge of these parameters is of great importance for the optimization of the structure to be used in the manufacture of devices [16] and therefore they were systematically pursued here. Three different BTBT derivatives, namely 2,7-di-tert-pentyl [1]benzothieno [3,2-b]benzothiophene ($\text{di}(\text{Me})_2\text{Pr-BTBT}$), 2,7-di-iso-propyl [1]benzothieno [3,2-b]benzothiophene (diiPr-BTBT), and 2,7-di-tert butyl [1]benzothieno [3,2-b]benzothiophene (ditBu-BTBT), whose chemical structures are shown in Fig. 1, were studied aiming to gain further information on the structure-property relationship. ditBu-BTBT is the reference compound that shows the best charge transport [6]. The crystal structure of diiPr-BTBT is characterized by herringbone packing as for ditBu-BTBT but it exhibits a much greater structural disorder [6] that is anticipated to impact electronic properties. The crystal structure of $\text{di}(\text{Me})_2\text{Pr-BTBT}$ differs significantly from those of ditBu-BTBT and diiPr-BTBT . Aromatic core of $\text{di}(\text{Me})_2\text{Pr-BTBT}$ are much more separated from each other's. Intermolecular electronic interactions are expected to be considerably reduced (see

Figs. 1 and 2).

Electronic charge transfer times following sulfur K-edge were calculated by employing the so-called core-hole clock approach, a methodology that has been widely used for compounds containing thiophene units [1,2,17]. Photoabsorption spectroscopy (NEXAFS – near-edge X-ray absorption fine structure) allows the study of the unoccupied density of states, as well the analysis of the ordering and preferred molecular orientation at different depths of the films depending on the method of detection used [18,19]. NEXAFS spectra were obtained by detecting simultaneously the fluorescence yield (FY) and the total electron yield (TEY). Detection methods that involve the detection of electrons, such as TEY, depend on the inelastic mean free path of the electrons in the solid [20]. For tender X-ray photons, the sampling depth for TEY was estimated as being at least 40 nm [21]. On the other hand, the FY method involves the detection of photons that are much more energetic and penetrating. That is why this method offers information regarding the bulk of the films [20,22]. Films prepared on different substrates were also investigated by TEY and FY NEXAFS spectroscopy to learn about the influence of substrates in the morphology of the films.

2. Experimental

The diiPr-BTBT and ditBu-BTBT oligomers were synthesized according to previous publications [6]. The synthesis and characterization of $\text{di}(\text{Me})_2\text{Pr-BTBT}$ are given in supporting information.

2.1. Single crystal X-ray diffraction

X-ray diffraction data for crystals of compound $\text{di}(\text{Me})_2\text{Pr-BTBT}$ were collected at 123 K with graphite monochromated $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) using an Oxford Diffraction Gemini S instrument. The displacement parameters of all non-H-atoms were treated anisotropically. H-atoms were placed at calculated positions using suitable riding models with isotropic thermal parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for CH and CH_2 groups and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for CH_3 groups. The crystal structure was solved by direct methods and refined by full matrix least-squares methods based on F^2 using the SHELXL-2014 program [23]. Crystal data is summarized in Table S1 and full details are available in CIF format.

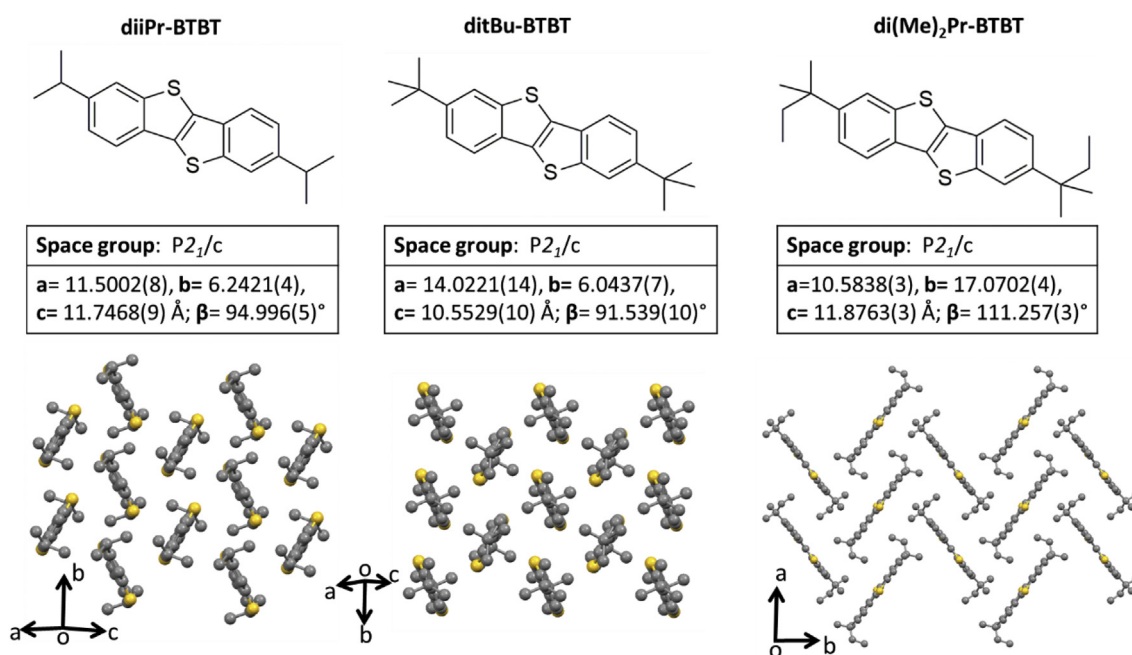


Fig. 1. Molecular and Crystal structure of compounds under study.

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