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Conformational and electronic properties of small benzothiadiazole-cored oligomers with aryl flanking units: Thiophene *versus* Furan

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ABSTRACT

Symmetrical benzothiadiazole-cored (*BTZ*) oligomers with aromatic flanks are widely used in experiments as structural blocks for organic electronic materials. Along with chemical composition, the molecular conformation plays a crucial role in crystal packing/self-assembly of these building blocks in thin films. In this study, we perform an extensive theoretical comparison of conformational preferences, electronic and optical properties of small π-conjugated molecules having BTZ central unit symmetrically decorated with thiophene (*Th*) or furan (*Fu*) rings using DFT calculations. In addition to the conformational screening of small molecules, the torsion potentials of the internal rotation and the energetics of weak intramolecular S···N, O···N, O···H and N···H nonbonded interactions stabilizing certain conformations are evaluated. The conformational properties of $–[BTZ\text{-}Fu]_n–$ and $–[BTZ\text{-}Th]_n–$ chains are predicted applying the hindered rotation model. Our calculation shows that substitution of one atom, here sulphur by oxygen, leads to huge stiffening of the resulting polymer as estimated by the Kuhn length based on the rotational isomeric model. On the other hand, the calculation of the band gaps and the UV–vis spectra shows that the electronic and optical properties of both compounds are almost identical. This offers the possibility to decouple the intramolecular electronic properties from the intermolecular arrangement and the morphology of the materials since the latter properties are sensitive to the local stiffness of oligomers and polymers.

1. Introduction

The most well-studied and high-performance compounds for plastic electronics rely on thiophene-based units [1]. Polythiophene homopolymers with a variety of side chains, polythiophene-based donor-acceptor block copolymers or small conjugated molecules, diverse mixtures and complexes have been engineered by materials scientists for target applications in organic electronics and photonics. Recently, there has been increased interest in exploring how the incorporation of other electron-rich units into the polymer backbone will influence the properties of conjugated macromolecules. One possible approach to this issue is to take an advantage of heteroaromatic compounds with another heteroatom of the chalcogen group (16th group of elements of the periodic table). Thus, not only five-membered thiophene, but also furan and selenophene rings have been introduced, and both the properties and device performance have been tested [2–6].

The aforementioned heterocyclic compounds are usually introduced as peripheral substituents of electron-deficient units known for their easy synthetic process, good stability and electrooptical characteristics. These peripheral substituents are also called “flanks” (Fig. 1) highlighting their position on both sides from the central unit in small π-conjugated molecules, or “spacers/bridges” if they connect donor and acceptor units in alternating all-conjugated block copolymers. For instance, benzothiadiazole (BTZ) as central unit with flanking thiophene or rarely with furan rings is used in synthetic approaches for further development of conjugated polymers and block copolymers for advanced applications [7–14].

In recent publications it has been suggested that upon thiophene for furan substitution, the conjugated polymers could experience improved conjugation length/planarity, electronic properties, intermolecular interactions and crystal packing. Indeed, the lower aromaticity of furan ring causes better stabilization of

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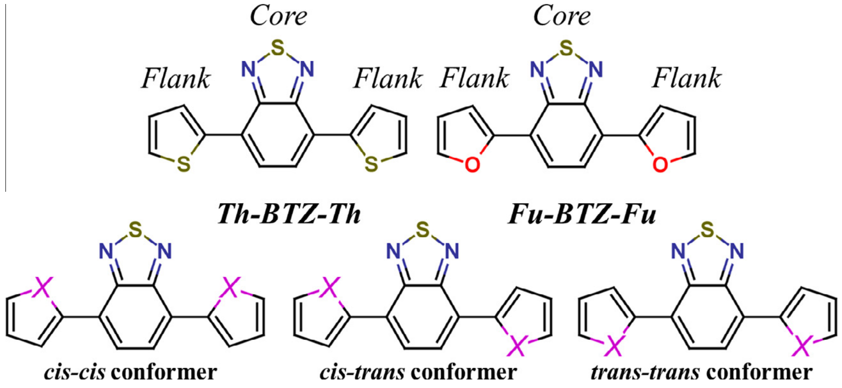

Fig. 1. Structural formulae of two objects of the study: dithienylbenzothiadiazole (*Th-BTZ-Th*) and difurylbenzothiadiazole (*Fu-BTZ-Fu*) and schematic representation of three conformers for each molecule, where *X* denotes the chalcogen atom (sulphur S or oxygen O) of the flanking units. The figure also provides the nomenclature used in this work.

the quinoid form leading to narrower band gaps [15]. Because of the smaller van der Waals radius of oxygen, as compared to sulphur, *trans*-bifuran and higher furan homologues are more planar and rigid molecules, whose geometry guides tighter packing, more efficient π-π stacking interactions and slightly larger extent of electron delocalization in various furan-bridged conjugated systems as compared to thiophene-containing analogues [3,16–18]. Besides, incorporating furan into polymer backbones increases the solubility in common organic solvents as compared to oligothiophenes. As a result, polymers with higher molecular weights can be synthesized, which is an important factor for large-scale materials processing [19]. Finally, furan is considered as a promising candidate for sustainable organic electronics as that it is biodegradable and can be produced from renewable resources [20].

However, as some authors point out, thiophene for furan substitution may enhance the electronic, optical and other material properties or may cause complete loss of beneficial characteristics [5,21]. In addition, the findings strongly suggest that the effect of heteroatom substitution is system-dependent, i.e. is determined by the combination of central core and flanking units. Therefore, further efforts in this field should be made in order to reveal the effects of heteroatoms on the properties of simple model systems of interest.

In this work we describe the results of a comparative theoretical study of two BTZ-cored molecules as solution-processable molecular semiconductors comprising furan or thiophene rings used as flanks (Fig. 1). Despite the fact that both, difurylbenzothiadiazole and dithienylbenzothiadiazole fragments are common repeat units of π-conjugated polymers which have shown attractive photovoltaic performance [22], to the best of our knowledge there is no complete and systematic theoretical comparison of these systems.

The published theoretical studies are mainly related to very specific BTZ-containing molecules. For instance, using classical all-atom molecular dynamics Netz modelled a series of biologically active BTZ derivatives as DNA intercalators [23], Jackson et al. studied the conformational properties of long-chain BTZ-based polymers in solution [24], Guilbert et al. described the properties of BTZ block copolymers in crystalline phases [25]. In quantum-chemical studies the main emphasis has been laid on the characterization of (i) frontier molecular orbitals (MOs) and band gaps of BTZ model oligomers [26–29], (ii) geometry and UV–vis absorption spectra of BTZ block copolymers and small molecules [4,9,12,30–32], (iii) photoexcitations in BTZ-cored sensitizers containing thiophene spacers [33], (iv) optoelectronic properties of BTZ short chains [34], (v) intra- and interchain electron transport in BTZ-based block copolymers [35]. The following factors defining the conformational properties of related systems have been considered as well: the extension of the conjugation pathways along the backbone, the control over chain flexibility/rigidity/conforma tion [36] and chain curvature, the effects of mutual orientation of the BTZ core and thiophene flanks on excitations in conjugated block copolymer [37] and finally, the control over intramolecular locking interactions that tune the backbone planarity [38].

The analysis of literature data has shown the absence of systematic research work concerning the BTZ-cored molecular semiconductors. There are several important questions remaining unanswered in recent reports: (i) What is the impact of heteroatom in flanking units of BTZ-cored molecules on the electronic and optical properties? (ii) What is the function of a flank in the intramolecular locking interactions? (iii) Can the design of monomers be used to control the conformational macromolecular properties without changing the electronic properties of the repeating units?

To answer these questions, the present work focuses on two structural analogues having a common conjugated core and different heterocyclic five-membered furan or thiophene flanking units with an aim to establish the relationship between the structures and properties of two molecular semiconductors. First, we consider the stability of the conformers for each molecule and analyse possible factors and weak intramolecular interactions involved in stabilization of particular conformation. Further, the conformational screening is performed, and the 1D potentials to the internal rotation and 2D potential energy surfaces are evaluated. In order to predict the conformational properties of related polymers, the hindered rotation model is applied. Finally, the optical properties and frontier orbitals/band gaps of model compounds both in gas phase and in solvents are described. These basic structural and electronic properties can be used further for the calculation of intrinsic charge transport rates and mobilities in conjugated polymers and in crystalline phases of difurylbenzothiadiazoles and dithienylbenzothiadiazoles.

The remainder of this work is structured as follows. The next section gives an overview of methods and computational details. The third section comprises the description of the results, their analysis and comparison with available experimental data. The last section provides a brief summary of the conclusions.

2. Computational details

The ground-state molecular geometries of three conformers for each molecule are optimized without any symmetry constrains. In this work one conformer is called *cis-cis* when both heteroatoms of the flanks, i.e. oxygen from furan or sulphur from thiophene, are pointing out in the direction of 1,2,5-thiadiazole. For *trans-trans*