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Understanding the effect of heteroatoms on structural and electronic properties of conjugated polymers

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ABSTRACT

Heteroatom-containing conjugated polymers are promising candidates for designing efficient polymer solar cells. However, fundamental understanding of the role of heteroatoms on structure-property relationships of these polymers is not yet fully understood. This work, based on first-principles calculations at the molecular level, uncovers how fluorine and oxygen introduction on poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDT-BT) affect structural and electronic properties. Systematic computations of torsional defects, energy gaps, molecular electrostatic potential surfaces and dipole moments are carrier out for PCPDT-BT and its fluorine and oxygen derivatives. We found that oxygen derivative favors lowest energy planar conformation, low energy gaps and high ground to excited state dipole differences. The present results further suggest that oxygenation might increase charge dissociation and reduce charge recombination in the excited state, supporting the recent experimental findings.

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1. Introduction

Polymer solar cells (PSCs), bulk heterojunction (BHJ) devices containing conjugated polymers as electron donors and fullerene derivatives as electron acceptors, are potential candidates to meet the world's growing demand for clean, renewable and sustainable energy [1–3]. PSCs are environmentally friendly and are well recognized for their flexibility, lightweight, low cost, and ease of processing [4–6]. Despite their promise, PSCs are still suffering from their lower performance and stability compared to their inorganic counterparts [7]. The current power conversion efficiency (PCE) of PSCs has reached ~10.6% [8], but this would need to be at least doubled [9] for practical realization of PSCs by average citizens. Performance of PSCs depends on various factors such as band gaps of polymers, chemical structures and the bulk heterojunction morphology [10–12]. Among them, chemical structure of the conjugated polymer plays an important role because the chemical modification changes frontier molecular orbitals such as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) as well as intermolecular and intramolecular interactions [13,14]. Consequently, these interactions affect energy offset between the HOMOs of polymer and fullerene derivative changing open circuit voltage (Voc), and energy offset between the LUMOs of polymer and fullerene derivative changing the charge transport, which in turn affect the overall performance of PSCs.

In recent years, several experimental studies [15–27] have focused on structural modifications of the conjugated polymers by adding electronegative fluorine atoms and their effect on the performance of PSCs. These experimental studies are in agreement that the performance of PSCs is enhanced upon the partial fluorination of each monomer unit. In fact, our recent first-principles studies [28–30] on fluorinated derivatives of polythienothio phene-co-benzodithiophenes, that agreed with the experimental findings, have shown that the fluorination of thienothiophene unit increases the effective conjugation, HOMO offset and dipole moment, and decreases exciton binding energies.

Recently [8], oxygenated derivates of poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDT-BT) have been synthesized and revealed that oxygenated derivative poly[2,7-(5,5-bis-(3,7-dimethyl octyl)-5H-dithieno[3,2-b:2′,3′-d]pyran)-alt-4,7-(5,6-difluoro-2,1,3-benzothiadiazole)] (PDTP-DFBT) performs better than fluorinated derivative poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]-dithiophene)-alt-4,7-(2,1,3-

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difluorobenzothiadiazole) (PCPDT-DFBT) (Fig. 1). Although the synthesis and the performance of PCPDT-BT, PCPDT-DFBT and PDTP-DFBT are studied experimentally, many important aspects from the first-principles study remain unexplored. In particular, effect of oxygenation on conformation, frontier orbital energies and dipole moments have never been addressed so far.

In this study, we perform systematic first-principles calculations on the structural and electronic properties of PCPDT-BT, PCPDT-DFBT and PDTP-DFBT to investigate the effect of fluorine and oxygen additions. We compute torsional potentials, frontier molecular orbital energies, band gaps, molecular electrostatic potentials and dipole moments at the molecular level. The understanding of these fundamental properties is crucial for optimizing the design of efficient conjugated polymers for high performance PSCs.

2. Computational details

All calculations on PCPDT-BT, PCPDT-DFBT and PDTP-DFBT oligomers up to the hexamer were carried out using density functional theory (DFT) [31] and time dependant DFT (TDDFT) [32] combined with dispersion corrected [33] Becke's three–parameter Lee-Yang-Parr exchange-correlation functional (B3LYP) [34] and 6-31G(d) basis set. Our previous experience on the first-principles studies [28–30] of similar polymers has shown that the dispersion corrected B3LYP functional captures accurate nanostructural and electronic properties. This method has also been implemented to produce reliable structural and electronic properties of similar conjugated polymers in various studies [35–37]. In the context of the present work, some computations were also performed at the coulomb attenuated and long-rage corrected functionals, CAM-B3LYP [38] and LC-BLYP [39], respectively combined with the same basis set for the sake of comparison. The large-scale calculations were performed using Kraken and Blacklight computational resources that were provided by the extreme science and engineering discovery environment (XSEDE) [40]. NWChem 6.1 [41] and Gaussian 09 [42] ab initio packages were used to perform these computations.

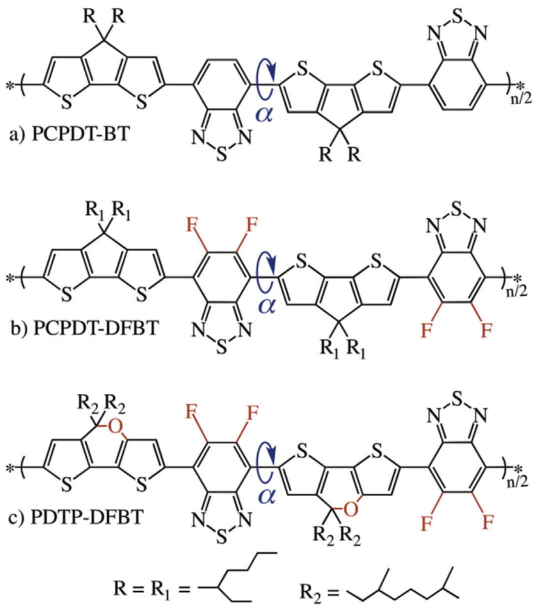

Fig. 1. Schematic representation of PCPDT-BT, PCPDT-DFBT and PDTP-DFBT. The inter-ring torsional angle, α, is zero when S-C-C-C (connected to N) angle is in trans conformations shown. In the present computations, the methyl group replaces R, R_1 and R_2.

Two different types of geometry optimizations of PCPDT-BT, PCPDT-DFBT and PDTP-DFBT oligomers were performed using DFT methods. First, oligomers were fully optimized without any constraint to determine the minimum energy conformations. Second, nanostructures were partially optimized at the constrained inter-ring torsional angle (α) by rotating two planar halves of each polymer in the range $0° \leq \alpha \leq 180°$ to investigate the effect of torsional disorder on structural and electronic properties. The exited state calculations were performed using TDDFT methods starting from the ground state optimized geometries.

3. Results and discussion

3.1. Nanostructures and torsional defects

All lowest energy conformations of PCPDT-BT, PCPDT-DFBT and PDTP-DFBT oligomers up to the hexamer investigated in the present study were found to contain planar backbones (Fig. 1). Vibrational frequencies of selected oligomers were calculated to ensure that each of the fully optimized conformations represented a local minimum of energy. Some additional fully relaxed geometry optimizations of dimers were also performed starting from non-planar geometries (for example, $\alpha \approx 25°$) as inputs to make sure that the optimized structure represented the lowest energy conformation. Irrespective of the starting geometry, the optimized geometry converged to the same conformation with the planar backbone. This shows that the solid-state packing structures of PCPDT-BT, PCPDT-DFBT and PDTP-DFBT are expected to have a planar backbone in the homogenous environment.

However, since the BHJ morphology of a PSC contains a blend of polymers and fullerene derivatives, the situation might be different because of the heterogenous environment. For example, different semicrystalline and crystalline domains have been reported in the BHJ morphology of PTB7 and fullerene derivatives [43–45]. These domains might be expected to contain substantial conformational disorder, which are usually caused by the inter-ring torsional defects in the polymer chains. A usual approach to probe these conformational defects is to calculate the torsional potential as a function of inter-ring torsional angle as was done in our previous studies on polythiophene (PT) and poly(3-alkylthiophenes) (P3ATs) [46–48]. These torsional profiles are very informative to investigate the propensity of conformational disorders in otherwise regular conformations.

Beginning with the planar PCPDT-BT, PCPDT-DFBT and PDTP-DFBT oligomers, the backbone torsional potentials were computed by rotating two planar halves in steps around the central inter-ring bond. Fig. 2 shows the one-dimensional torsional potentials for these polymers up to the hexamer. The relative torsional energy increases with the increase in torsional angle, reaches to the maximum and decreases with further increase in the torsional angle. Each of these torsional potentials has two minima: one at $\alpha \approx 0°$ and the other at $\alpha \approx 180°$. At $\alpha \approx 90°$, there is a maximum that is the highest barrier between the two torsional minima.

The major factor responsible for the nature of torsional profile depicted in Fig. 2 is the electronic conjugation along the conjugated backbone. At $\alpha \approx 0°$ or 180°, the planar geometry favors more extended electronic conjugation across the conjugated rings of monomer units (Fig. 3). The electronic conjugation is decreased when the non-planarity of the conjugated backbone increases and at $\alpha \approx 90°$, the electronic conjugation is broken thereby reducing the conjugation length from n to $n/2$ (Fig. 3). Consequently, frontier molecular orbitals get more separated and the torsional energy of an oligomer is increased. Hence, the barrier at $\alpha \approx 90°$ is a result of the breakage of the electronic conjugation. Other factors affecting

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