

Density Functional Theoretical Study on the Interchain Packing in Thiophene-Benzothiadiazole Based Polymers

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Received September 13, 2012, Accepted October 24, 2012

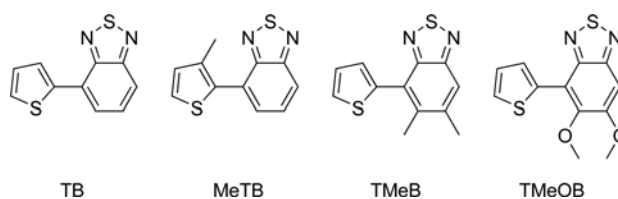
Key Words : DFT, Packing, Thiophene

Bulk-heterojunction polymer solar cells have attracted much attention due to their many advantages, which include mechanical flexibility, cost-effective low temperature processing, and tunable optoelectronic properties.¹ Recently, we reported the relationship between the molecular design and photovoltaic property of low band gap polymer based on a thiophene-benzothiadiazole (BT) alternating structure.² The electronic effects of substituents on thiophene or BT units in the polymer on photovoltaic cell performance were investigated experimentally.

In the present study, density functional theoretical (DFT, Jaguar quantum chemistry software,³ M06-2X/6-31G** level) calculations were performed to identify the optimized structures of the repeat units comprising thiophene-BT alternating copolymers. The interchain packing of two repeat units was explored with the torsional angle profiles of single repeat units, because this packing affects photovoltaic cell performance.

As shown in Scheme 1, four thiophene-BT linkages with or without substituents on the thiophene or BT rings: thiophene-BT (TB), methylthiophene-BT (MeTB), thiophene-dimethylbenzothiadiazole (TMeB), and thiophene-dimethoxybenzothiadiazole (TMeOB) were considered in the study. Methyl or methoxy substituents were chosen to simplify calculations.

Figure 1 shows calculated torsion angle profiles and the most stable structures based on minimum energy considerations. MeTB with a methyl-substituted linkage, which has often been used to increase the solubility of thiophene-based polymers, has a large torsional angle (130°) and TMeB also exhibits a similarly tilted structure (dihedral angle, 51°). This structural tilting is due to steric repulsion between the alkyl chain and the BT ring for MeTB, which leads to substantial twisting of the conjugated backbone and disrupts the coplanarity of the two rings essential for π - π interchain stacking and ordering. For TMeB, similar steric repulsion between the thiophene ring and the alkyl substituent in BT ring is responsible for the structural tilting. However, the torsion angle of TMeOB is similar to that of unsubstituted TB, which can be expected to have the most coplanar structure. The electron donating effect of the alkoxy groups, which increases the electronic conjugation and/or an attractive electrostatic interaction between the partially positive sulfur



Scheme 1

in the thiophene ring and partially negative oxygen atoms in the alkoxy linkage⁴⁻⁶ contribute to the coplanarity of TMeOB. In fact, this O...S contact between alkoxy substituents and thiophene has been employed to promote macromolecular planarity.^{7,8}

In order to estimate interchain packing interactions, the binding energies of two units of each repeat unit were calculated for various configurations. As in a previous study,⁹ three types of dimers were considered: 1) parallel head-to-head (HH), 2) parallel head-to-tail (HT) and 3) perpendicular (PE) dimers, which are schematically shown in Scheme 2. Binding energies between two repeat units are presented in Table 2.

As shown in Table 1, packed dimers of two TB repeat units were found to have similar binding energies around $-13 \text{ kcal}\cdot\text{mol}^{-1}$. Introduction of alkyl chain(s) in the ring causes destabilization around 1 or 2 $\text{kcal}\cdot\text{mol}^{-1}$, because the alkyl chains exert steric repulsion which disrupts comfortable π - π packing interactions and ring coplanarity. However, the introduction of the alkoxy linkage in TMeOB revives π - π interactions and ring coplanarity. Because Coulombic interactions between the partially positive sulfur atoms and the negatively charged oxygen atoms are also involved in TMeOB₂, binding energy recovery is not the same for all configurations, although the HH and PE conformers have almost the same stability.

In Figure 2, we show the most stable configurations of packed repeat units based on calculation results. In (TB)₂ and (TMeOB)₂, parallel geometries were obtained due to π interactions, whereas for (MeTB)₂ and (TMeB)₂, steric repulsion between methyl groups and the ring leads to slight deviations from parallel orientations

In order to take the effect of the length of the side chain attached at the alkoxy linkage in TMeOB into account, we changed the side chain from methyl to ethyl. This resulted in

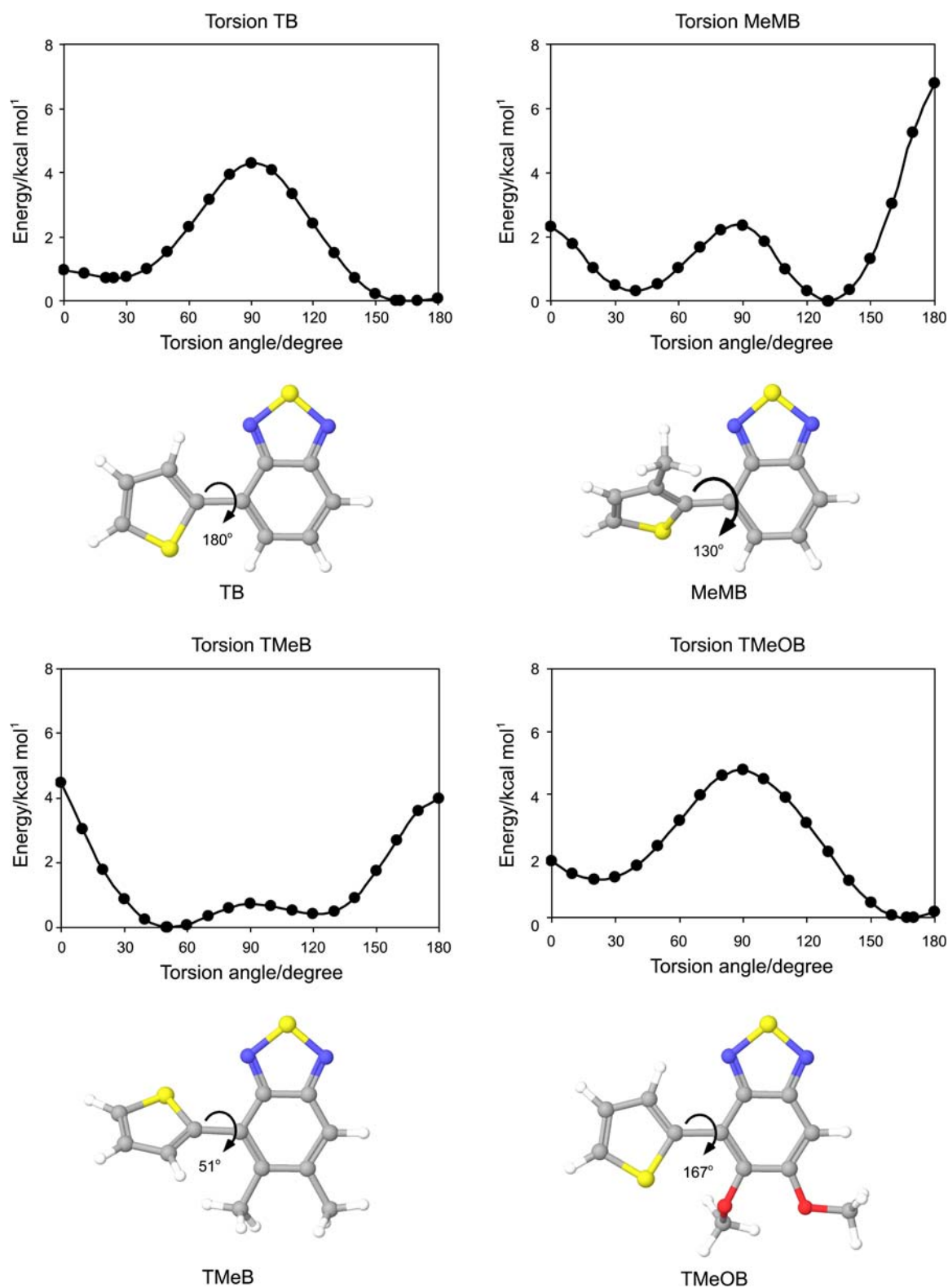
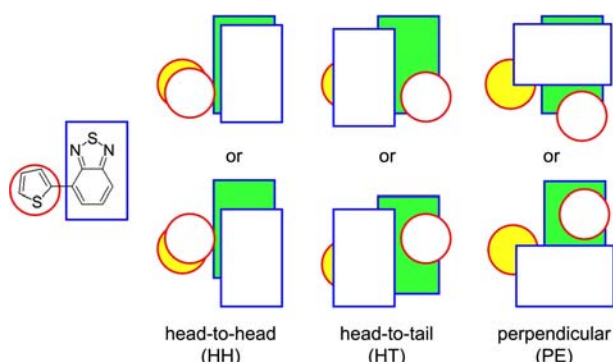


Figure 1. Minimum energy conformations and the torsional profiles of the repeat units.

a PE configuration that was less stable than the HH configuration by 2.4 kcal·mol⁻¹ (−16.8 kcal·mol⁻¹ vs −14.4 kcal·mol⁻¹), presumably due to steric hindrance between two side chains.

Summarizing, DFT calculations were applied to four

different BT units. Torsional profile and minimum energy conformation studies showed that the introduction of the alkoxy linkage provides a means of achieving improved solubility and ring coplanarity, which leads to good π - π packing between two chains.



Scheme 2. Schematic representation of the orientations of packed repeat units considered in the present study.

Table 1. Binding energy between two repeat units (unit: kcal·mol⁻¹)

	TB	MeTB	TMeB	TMeOB
HH	-13.8	-9.5	-12.2	-15.1
HT	-12.0	-9.0	-9.0	-12.1
PE	-12.8	-12.4	-12.0	-15.1

Acknowledgments. This work was supported by the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology, Korea (2009-00605, 2012R1A12005855).

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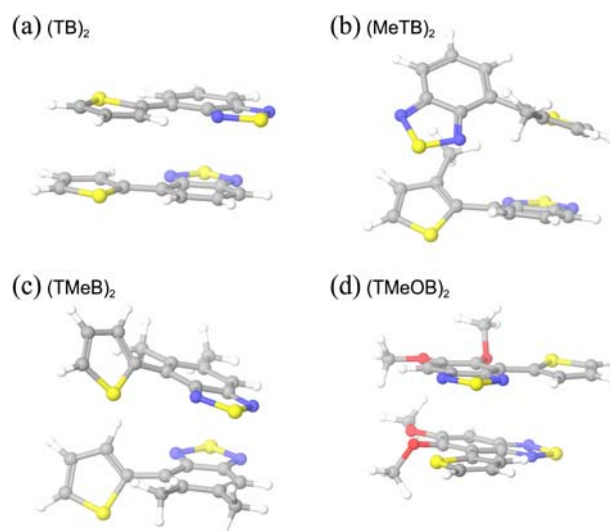


Figure 2. Structures of the most stable configurations of the packed repeat units.

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