Computational Study of Transmission Function in *p*-Phenylene Sulfide and Benzothiophene Oligomers

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The transmission function $T(E)$, which describes the conduction in molecule, and the density of state (DOS) of the helical *p*-phenylene sulfide oligomer and of the fused-planar benzothiophene oligomer were calculated by using the non-equilibrium Green's function formalism. Although both the oligomers consist of benzene-(1,4)-dithiolate subunit, they have different T(E) and DOS near the Fermi level. The effect of replacing a sulfur atom inside the oligomer by an oxygen atom was additionally investigated.

Interests and researches in nanotechnology have grown exponentially in recent years because of its potential applications in many areas of science and engineering. The use of molecules as components in a nano-sized electrical circuit is still one of challenging ultimate aims. Advancements both in experiment, such as the scanning tunneling microscope (STM)[1,2] that enables the manipulation of molecules, and in theory lead to more understanding in the electrical conduction by a molecule. Knowledge in the relationship between molecular structure and the required electrical properties is extremely helpful to the design of better 'tailor-made' molecules for the purpose of molecular electronics.[3]

In this short communication, we report the transmission function $T(E)$ of two forms of oligomer constructed from benzene-(1,4)-dithiolate subunit: the helical *p*-phenylene sulfide oligomer and the fused-planar benzothiophene oligomer (see Figure 1). The polymeric polybenzothiophene can be obtained by exposing poly(*p*-phenylene sulfide) to AsF_5.[4] The benzene-(1,4)-dithiolate subunit was selected in our works because it is frequently used in the theoretical studies of molecular conduction. Three units of benzene-(1,4)-dithiolate was chosen in our oligomers since both sulfur end atoms point in the opposite direction, hence leading to a plausible configuration between two metal tips required in an experiment. The effect of the heteroatom on the transmission function was additionally investigated by replacing a sulfur atom within the oligomer with an oxygen atom.

The structures of both types of oligomers were optimized at the semiempirical AM1 method by using the GAMESS program.[5] With these structures, the corresponding density of state (DOS) and the transmission function $T(E)$ were calculated using the non-equilibrium Green's function method as outlined by Datta.[6,7] With this $T(E)$, the conductance can be obtained through the Landauer formula.[6] The semiempirical extended-Hückel Hamiltonian was used to represent the electronic structure of the molecule.[8] The metal tip was modeled by a gold pad of six atoms with the self-energy estimated from the density of state of gold[7,9] (see Figure 1). Although qualitative in nature, we believed that this model should give some qualitative understanding for the system considered.[7] A sulfur atom in the oligomer was then replaced by an oxygen atom in order to study the effect of the heteroatom on the transmission of molecule. The transmission function and the density of state of the helical and the fused-planar form are shown in Figures 2 and 3, respectively.

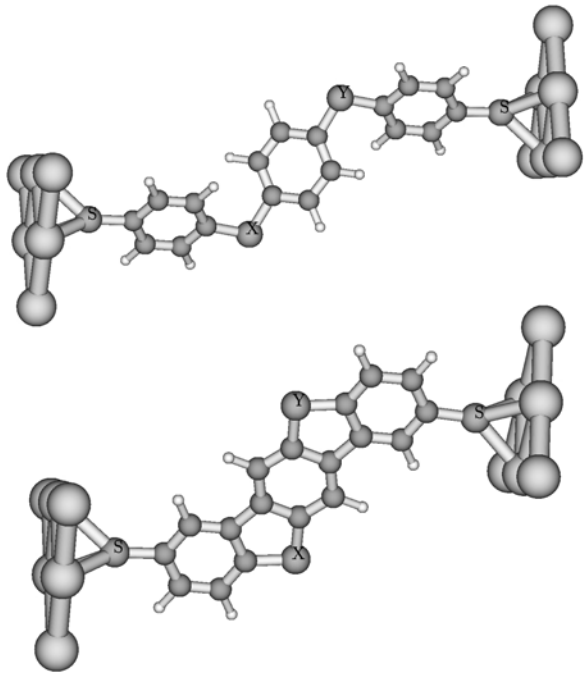

Figure 1. Optimized structures of the helical *p*-phenylene sulfide oligomer and the fused-planar benzothiophene oligomer in which each sulfur end atom is connected to a gold pad of six atoms. The X and Y atoms denote the heteroatom pair inside the molecules.

The Fermi energy of the system was estimated by integrating the DOS curve. The Fermi energies of helical and fused-planar forms are, to the numerical accuracy, the same and have the values of −9.72, −9.90 and −9.92 eV for the heteroatom pair (X, Y) of (S, S), (O, S) and (O, O) respectively. We considered these values qualitatively as it was commented by Tian et al. that small numerical error could lead to large error in the Fermi energy.[7]

At the Fermi energy of all the compounds considered there is a very low transmission due to a very low density of state; this can be compared to the semiconductor situation. The transmission function at the Fermi energy of both helical and fused-planar forms is also similar. Near the Fermi energy level, there is very low density of state in the helical form whereas a peak of an unoccupied low-lying state exists in the fused-planar form. In other word, the HOMO-LUMO gap of the fused-planar form is

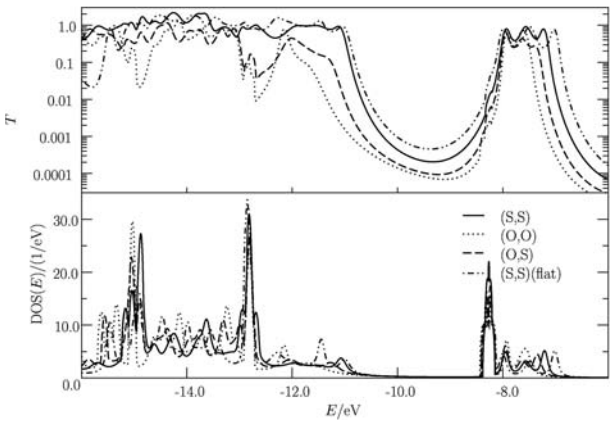

Figure 2. The transmission function $T(E)$ (unitless) and the density of state (DOS) of the helical *p*-phenylene sulfide oligomer. A sulfur atom is replaced by an oxygen atom at the (X, Y) position defined in Figure 1. The result of the planar form of *p*-phenylene sulfide oligomer is also shown.

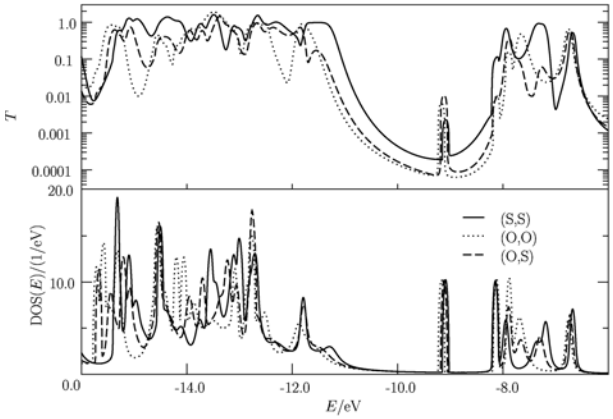

Figure 3. The transmission function $T(E)$ (unitless) and the density of state (DOS) of the fused-planar benzothiophene oligomer. A sulfur atom is replaced by an oxygen atom at the (X, Y) position defined in Figure 1.

less than that of the helical form. The LUMO band of fused-planar oligomer should contribute to the transmission and therefore enhance the conduction when the voltage is applied across the metal tip junction.

A small energy gap and a transmission peak near the Fermi energy are intrinsic to the electronic structure in the fused-planar form. This behavior does not occur even when the helical form is forced into the planar configuration. There is only some increases in the transmission function near the Fermi energy (see Figure 2) but the features of both DOS and $T(E)$ are essentially the same.

Considering the effect of the heteroatom on the transmission function, we observed that the transmission is decreased when the sulfur atom is replaced by oxygen atom. The substitution of one sulfur atom by one oxygen atom leads to an observable decrease in the transmission near the Fermi energy. The second substitution, however, has much smaller effect on the decrease of the transmission near the Fermi energy. This trend of change is also similar to the Fermi energy obtained in the case of one substitution. The transmission function at the highest occupied state decreases considerably in the helical form.

To summarize, the transmission function of two oligomers of benzene-(1,4)-dithiolate was theoretically studied. The helical form has wider HOMO-LUMO gaps than the fused-planar form. There is a transmission peak corresponding to the LUMO peak in the fused-planar form that lies near the Fermi energy. This should lead to a greater conductivity than in the helical form. This feature is intrinsic to the fused-planar form which cannot be obtained by flattening the helical form.

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