Molecular Wires Composed of Thiophene Oligomers

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Molecular electronics, exploiting a cross-disciplinary bottom-up approach and using interconnected molecules to perform the basic functions of microelectronics, has attracted a great attention. Conjugated molecules, possessing delocalized π electrons, are pointed out being promising candidates to build new generations of electronic and photonic devices. It is essential to understand the electron conduction mechanism inside the molecules and at the interface between the molecule and electrodes. Thiophene-conjugated systems present generally higher stability than other conjugated systems and their properties can be easily chemically tailored [1]. We study the electron transport properties of molecular wires, which are composed of thiophene oligomers connecting to metal electrodes, using the first principles method [2] which is based on density functional theory and non-equilibrium Green's function. At the same time, thiophene films of dimers, tetramers and hexamers are synthesized and electron conductances of the films are measured with atomic force microscope.

To simulate the electron transport properties of thiophene oligomer based wires, we connect the thiophene oligomers to two gold (Au) electrodes to build atomic metal-molecule-metal junctions as in Fig. 1. The oligomers are connected to Au(111) surface via terminal groups which are located at Au(111) hollow site, the most energetically favored location [3]. The density of states (DOS), transmission functions (TF), and current-voltage (I-V) characteristics of the junctions are calculated to analyze their electronic properties. The effects of different substitutes, terminal groups and the wire lengths are focused.

Different alkyl substituents can modify the electronic properties of thiophene oligomers. This is done by changing the inter-ring torsional angles in thiophene oligomers. Considering the complexity in the relationship between the alkyl substituents and final conformations of the thiophene oligomers in an adsorbed film in the experiments due to the energy barriers for chain rotations, we simulate the effects of the alkyl substituents by varying the torsional angle systematically from 0 to 180 degrees instead. Figure 2 shows the simulation results of the thiophene dimers with three typical torsional angles 0, 90 and 180 degrees: DOS (Fig. 2a), TF (Fig. 2b), and I-V characteristics (Fig. 2c). Thiophene dimers with planar structures show better conductance due to better electron delocalization to the π orbitals.

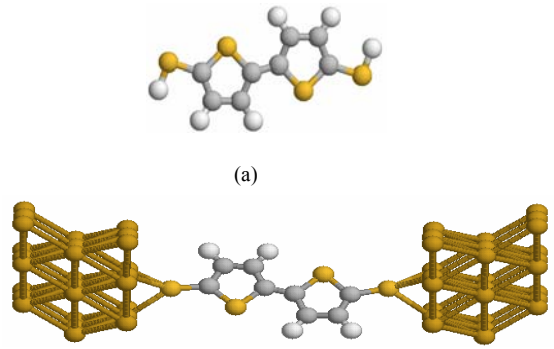
Terminal groups, which are used to build stable bonds between organic molecules and metal electrodes, will affect the electron transport of molecular systems [4]. In our experiments, S and CN have been used to connect the thiophene oligomers and Au substrates. Figure 3 shows the calculated I-V characteristics of thiophene tetramers connecting to Au electrodes with terminal group S and CN and the effects of terminal groups are clearly seen.

The resistance of molecular wires with different lengths will be fundamental for any kind of electronic wire applications. Thiophene dimers, tetramers and hexamers are synthesized and connected to Au electrodes to study the effects of the wire lengths. Figure 4 shows the simulated I-V characteristics of the dimer, tetramer and hexamer systems with torsional angle of 180 degrees. At bias less than 0.3eV (inset in Fig. 4), linear electron transport characteristics are observed in all three systems. The resistances of dimer, tetramer and hexamer wires are 16KΩ, 77kΩ, and 288 kΩ, respectively. The longer the wire is, the bigger the resistance will be.

More comprehensive analyses will be done once the measurement results come out in near term.

References

[1] J. M. Pernaut, P. Garcia and D. Delabouglise, *J. Chim. Phys.* **91**, 433 (1994).
[2] M. Brandbyge, J. L. Mozos, P. Ordejon, J. Taylor and K. Stokbro, *Phys. Rev. B,* **65**, 165401 (2002).
[3] P. Bai, E. Li, C. C. Chong and Z. Chen, "Effects of Metal-Molecule Interface Conformations on the Electron Transport of Single Molecule", *Cur. Appl. Phys.* In press.
[4] P. Bai, E. Li, Neerja, P. Collier, *IEEE T. Nanotech.,* **4(4),** 422, July 2005.



(a)

(b)

Fig. 1 Schematics of optimized thiophene dimer (torsional angle 180 degrees) with terminal group S (a) and the Au-thiophene-Au system composed of the thiophene dimer (torsional angle 180 degrees) sandwiched between gold electrodes with terminal atom S.

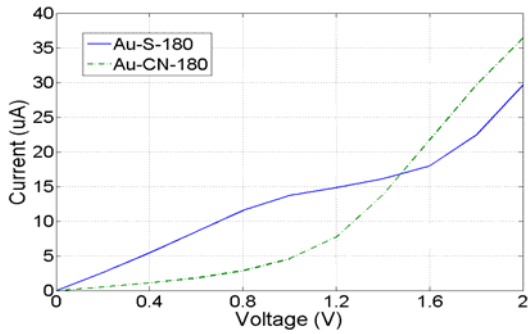


Fig. 3 I-V characteristics of thiophene tetramers (torsional angle 180) connecting to Au electrodes with terminal group S (solid) and CN (dashed).

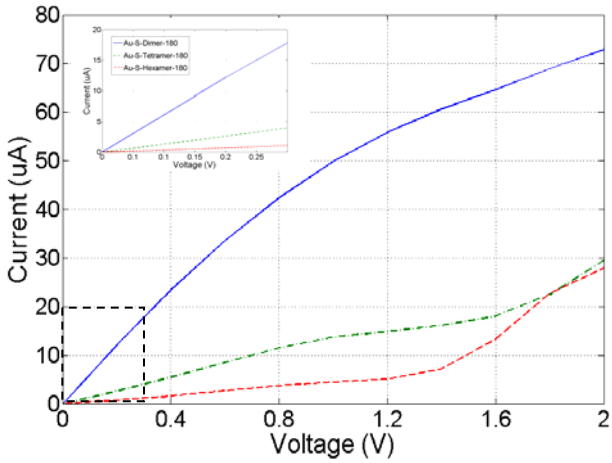
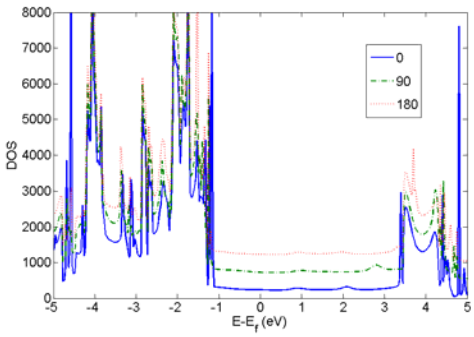
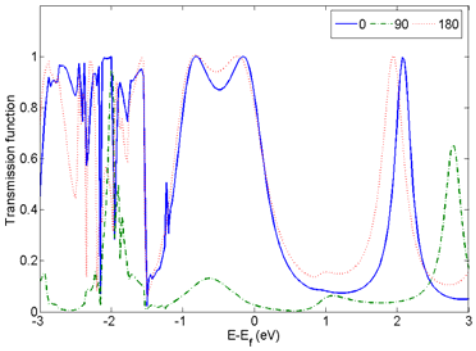


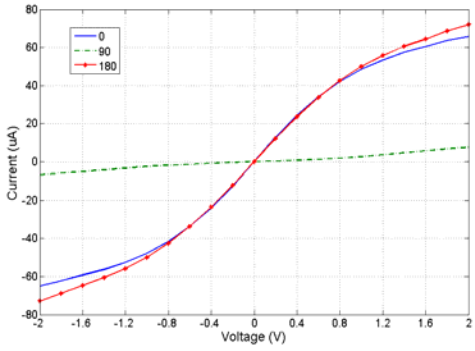
Fig. 4 I-V characteristics of the dimer (solid), tetramer (dashed), and hexamer (dotted) with torsional angle 180 connecting to Au electrodes with terminal group S.



(2a)



(2b)



(2c)

Fig. 2 Simulated density of states (a), transmission functions (b), and I-V characteristics (c) of three metal-molecule-metal junctions composed of thiophene dimers with torsional angle of 0, 90, and 180 degrees, connecting to Au (111) with terminal group S..