



# Effects of terminal connection and molecular length on electron transport in linear conjugated molecular wires



Jinjiang Zhang<sup>a</sup>, Wei Sun<sup>a</sup>, Hongmei Liu<sup>b</sup>, Yuanyuan He<sup>a</sup>, Jianwei Zhao<sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210008, PR China

<sup>b</sup> Institute of Condensed Matter Physics, Linyi University, Linyi 276000, Shandong, PR China

## ARTICLE INFO

### Article history:

Received 1 May 2013

Received in revised form 26 January 2014

Accepted 8 February 2014

Available online 3 March 2014

### Keywords:

Molecular wire

Nonequilibrium Green's function

Density functional theory

Quantum interference

## ABSTRACT

Electron transport through single linear conjugated molecular wires is investigated by using nonequilibrium Green's function method combined with density functional theory. The investigated molecule is sandwiched between two gold electrodes via S–Au bonds via three different kinds of terminal connections. One of the connections shows an obviously higher electrical conductance than the others. Several factors have been analyzed. Among them terminal coupling and destructive quantum interference play the main role. A significant structural feature of well conductive conjugated molecules has been pointed out which may provide a quick prediction before time-consuming calculations. Furthermore, we find that the conductance of all the studied molecular wires drops first and then increases with the molecular length increasing. This unusual phenomenon is investigated from the tunneling barrier, shift of molecular levels and electronic coupling between molecule and electrodes, and is ascribed to the competition between two opposite groups of factors.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Since the pioneer work on electron transport through single molecule by Aviram and Ratner [1] in 1974, it has been a long-standing goal for molecular electronics to understand the mechanism of electron transport. And in the meanwhile a wide variety of molecular devices have been designed and investigated, such as wires, rectifiers, switches, field-effect transistors and so on. As the most basic element in a molecular device, molecular wires have attracted much attention. During the past decades both experimental and theoretical studies have shown that a lot of factors could affect the electrical conductance of a molecular wire, such as molecular length [2–13], molecular conformation [7], molecular orbital (MO) levels [2,5,8,14–17], anchoring groups [6,18–20], anchoring sites [4,21] and so on. However, a more complete picture of the relationship between molecular structure and conducting behavior has been hitherto elusive. One of the least understood is the interface between the molecule and electrodes, especially the terminal binding site effects of conjugated systems on conductance. In addition, linear conjugated molecules are thought as the most potential candidate for molecular wires, and the length dependence of conductance still remains an interesting issue.

Terminal connection between the molecule and electrodes is a significant ingredient affecting the conducting behavior [22,23], especially for conjugated system. On one hand, the substituent groups may shift the molecular orbital levels, disturb the symmetry of the system, and determine the coupling between the molecule and electrodes. On the other hand, the topological structure of a conjugated system means that there could be multiple pathways for electrons to travel. There may be instances where a single pathway dominates and instances where many pathways contribute. These multiple pathways will not necessarily interact constructively since the coupling elements are signed terms and thus the quantum interference (QI) [24–31] will play an important role in electron propagation. Investigation on these intriguing topics will enable a variety of functional molecular devices to be developed.

As for molecular length, there are several typical sorts of length dependence of conductance. On one hand, it is well known that electrical conductance of many molecular junctions decreases exponentially with the molecular length [2–4,6–8], following the tunneling mechanism. The tunneling attenuation factor  $\beta$  is used to evaluate the exponentially decreasing conductance with the molecular length. And  $\beta$  values are quantitatively dependent on the molecular orbital levels [2,5]. On the other hand, it is reported that when the molecular size is large and  $\pi$ -conjugation is broken, electrons transport via a hopping mechanism [10–12]. In this case, the molecular conductance linearly decreases with the molecular

\* Corresponding author. Tel./fax: +86 25 83596523.

E-mail address: [zhaojw@nju.edu.cn](mailto:zhaojw@nju.edu.cn) (J. Zhao).

length, i.e. an Ohmic behavior. Except for these, other length dependence of conductance exists in some conjugated systems. For example, Visontai et al. [9] found the conductance of acene-based molecules oscillates with the length and ascribed it to quantum interference. Here, another unique length-dependent conductance in the linear conjugated molecules is reported, which involves competition between two opposite groups of factors.

In this work, the investigated conjugated molecules are sandwiched between two gold electrodes through S–Au bonds. They have a common body structure consisting of a dithiophene embedded in an acene chain. According to different terminal connections, they are divided into three series. This article is organized like this: In Section 2 we describe the details of the models, introduce the nomenclature, and then briefly show the computational methods. In Section 3, we analyze the transport behavior of the three series of molecules in details, using density functional theory (DFT) combined with the non-equilibrium Green's function (NEGF) method. Finally, we summarize the work in Section 4. The systematic investigation of the conduction mechanism would play a guidable role in designing molecular devices.

## 2. Methodology

The molecular structural formulas are divided into three series according to different terminal connections, as is shown in Scheme 1b. For example, when  $n = 1$ , in series S-A, the sulfur atoms in dithiophene and the terminal –SH groups are arranged in para-position and meta- position of the benzene ring; in series S-B, the arrangement is para- and para-positions; in series S-C, it is meta- and meta-positions. The molecular wires are extended by adding an equal number of benzene rings onto both sides. Thus the number (labeled as  $n$ ) of benzene rings on each side can be used to indicate the molecular length, for example,  $n = 4$  means there are eight benzene rings in the molecular chain totally. In this work, the molecular length ranges from  $n = 1$  to  $n = 6$ .

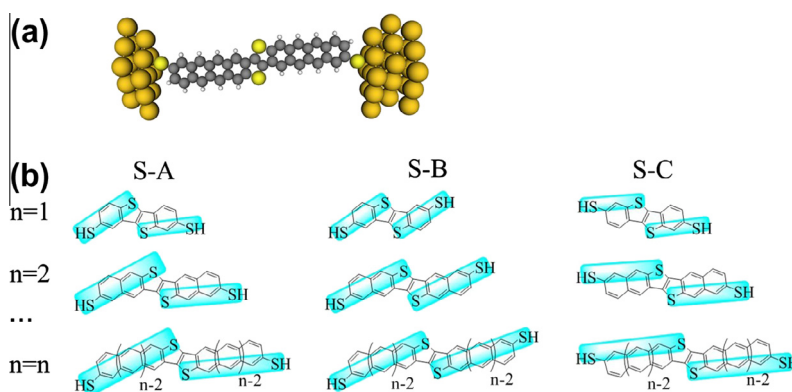
The geometric structure of each molecule in Scheme 1b was first optimized at the B3LYP/6-31G\* theoretical level by using Gaussian 03 software [32], as described in the previous papers [2,12,22,23,33,34]. Then each terminal thiol group lost the hydrogen atom, and the rest part of the molecule was sandwiched between two equilateral triangles consisting of three Au atoms with a side of 2.88 Å. The sulfur atom was chemisorbed to the hollow position of the Au triangle, reaching the local energy minimum [5,35–37]. This bonding approach was used to simulate the attachment to the Au (111) surfaces. Then the geometric structure of the metal–molecule–metal junction was optimized at the B3LYP level with a LANL2DZ basis set, during which the structure of each gold triangle was frozen.

Theoretical calculation of electron transport was performed with the Atomistix Toolkit (ATK) program [38] which is based on the first principles density functional theory (DFT) and non-equilibrium Green's function (NEGF) [39] approaches. The two Au triangle clusters used above were replaced with gold electrodes in the form of Au (111) surface. Scheme 1a shows a representation of S-B4 sandwiched between two gold electrodes. Two layers (18 atoms) were used for the left electrode and three layers (27 atoms) for the right one, as the common treatment in calculation with ATK software [2,12,22,23,33,34]. The molecule was perpendicular to the electrode surface with the terminal sulfur atoms placed at a three fold hollow site. In order to keep contact resistance the same and ascribe the divergence of conductance between series to the molecular structure, the distance between the terminal S atom and electrode surface was fixed at 2.0 Å, a favorable value within the computational accuracy, which can provide a good electrical contact between the molecule and electrodes [2,12,33–35]. More details and discussion about the geometry are given in the supporting information. In current calculation, single-zeta polarized basis set was utilized for Au atoms and double-zeta polarized basis set for other atoms. Bias voltage varying from –1.0 to 1.0 V was applied between the two metal leads (herein, the negative sign means a higher potential of right electrode than the left one). The current was calculated by integrating the transmission coefficients within the bias window according to the Landauer formula [39,40]. The bias window is defined as the energy interval  $[-eV/2, eV/2]$ , where  $V$  is the bias applied. Differential conductance,  $dI/dV$ , is the numerical differentiation of current–voltage curve.

## 3. Results and discussion

### 3.1. Different terminal connections

With different kinds of substitution sites of the sulfur anchoring groups, S-A1, S-B1 and S-C1 display different electron transport behaviors. From Fig. 1a, one could see that S-A1 and S-B1 have almost the same  $I$ – $V$  characteristics and their current was extremely lower than S-C1's when the same bias is applied. The inset shows the differential conductance curves. It is found that the connection in series S-C is much more conductive. For example, at zero bias the differential conductance of S-C1 (10.1  $\mu$ S) is about 20 times larger than that of S-A1 (0.5  $\mu$ S) and about 30 times larger than that of S-B1 (0.3  $\mu$ S). In addition, for longer molecular length, S-C $n$  (here,  $n = 1$ –6 indicating the number of benzene rings on each side of the molecule chain) connection always keeps predominant over the other two connections in electrical conductance (referring to Figs. 4d and S4 in the supporting information).



**Scheme 1.** (a) Schematic illustration of a simplified model of S-B4. (b) Chemical structures of the molecular wires studied in this article.

Download English Version:

<https://daneshyari.com/en/article/1560546>

Download Persian Version:

<https://daneshyari.com/article/1560546>

[Daneshyari.com](https://daneshyari.com)