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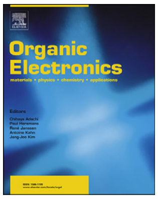

Influence of anchoring groups on single-molecular junction conductance: Theoretical comparative study of thiol and amine

Fang Xie [a, b], Zhi-Qiang Fan [c, *], Ke-Qiu Chen [a, **], Xiao-Jiao Zhang [b], Meng-Qiu Long [d]

[a] Department of Applied Physics, Hunan University, Changsha, 410082, China
[b] Physics Science and Engineering Technology College, Yichun University, Yichun, 336000, China
[c] School of Physics and Electronic Science, Changsha University of Science and Technology, Changsha, 410114, China
[d] School of Physics and Electronics, Central South University, Changsha, 410083, China

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ABSTRACT

Understanding the transport characteristics of single molecules bonded between metal electrodes is of fundamental importance for molecular scale electronics. By performing first-principle quantum transport calculations, we investigate the influence of anchoring groups on the conductance of a single molecular junction. The results indicated that the conductance of a single-molecule anchoring the Au electrode with thiol can be enhanced obviously by changing the anchoring group with amine. More importantly, the negative differential resistance behavior is found in the I-V characteristic of this single-molecule junction with thiol anchoring group, which also can be enlarged remarkably by replacing the anchoring group with amine. The results suggest that the diamine as anchoring group has a great potential in molecular electronics.

1. Introduction

Since it was first suggested that a single molecule might function as an active electronic component [1], molecular electronics has attracted tremendous attention and holds the most promise for the miniaturization of electronics [2–5]. Numerous molecular devices have been made to realize the functions existing in microelectronic devices such as switching [6–8], rectification [9–11], negative differential resistance (NDR) [12–15], and spin filter [16,17]. However, there are still a number of challenges in researching the molecular devices. It is because the electronic transport properties of the molecular devices can be influenced by intrinsic molecular properties such as their length [18,19], conformation [20,21], and the alignment of molecular orbitals to the metal Fermi level [22,23]. In addition, chemical linker groups used to bind molecules to metal electrodes also play an important role in the single molecular junction's conductance [24,25]. A suitable anchoring group should have a efficient binding and a strong electronic coupling between the molecule and the electrode, so as to improve the charge transport, reduce the charge injection barrier across the metal-molecule interface and form reproducible and mechanically stable contacts.

In the previous experiment, thiol moieties had been used extensively to attach single molecules to gold electrodes [26,27]. However, the thiol-gold bond exhibits variations and fluctuations that are reflected in the electronic properties of molecular junctions [28–30]. Compare to thiol, the amine anchoring group was reported be able to achieve a better defined contact geometry and to get more well-defined transport properties in recent experimental studies [31–34]. Although there are plenty of experimental investigations, the deep understanding of why the amine anchoring group is superior to the thiol anchoring group is still not clear. Therefore, in this paper, we show the comparative study of anchoring groups thiol and amine on the conductance of a single molecular junction.

2. Model and method

For showing the comparative study of anchoring groups thiol and amine, we choose a particular molecule which is characterized by two planes corresponding to a left and a right conjugated

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[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: zqfan@csust.edu.cn (Z.-Q. Fan), keqiuchen@hnu.edu.cn (K.-Q. Chen).

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fragments coupled together through a saturated bridge, that efficiently prevents the π-coupling between two fragments [35]. As a result, the alignment of each fragment tends to be independent, promoting an independent pinning of each fragment to its respective electrode [35,36]. For simplicity, these three parts of molecule are named LM, CM and RM from left to right. As anchoring groups, we first use two thiol groups on the left side and the right side of the molecule covalently binding to Au electrodes on top of a gold atom, as can be observed in Fig. 1. Then we replace the right thiol anchoring group by one amine anchoring group or replace two thiol anchoring groups by two amine anchoring groups together obtaining other two different junctions. The relaxed Au-S bond length is 2.29 Å which is larger than that of Au-N bond length (2.01 Å). For simplicity, we name three junctions as SS, SN and NN, respectively. From the figure, one can see that the junction is divided into three regions: left electrode, right electrode, and central scattering region. The central scattering region contains four layers of Au electrode on each side, thereby establishing the bonding between the molecules and the electrodes, the common Fermi level, and charge neutrality at equilibrium.

The geometric optimizations and the electron transport properties were calculated by using the first-principle software package Atomistix ToolKit (ATK), which is based on density-functional theory (DFT) in combination with the non-equilibrium Green's function (NEGF) [37,38]. The structures of the Au electrode and the molecule with anchoring groups thiol or amine are optimized separately. Then, we connect the molecule to the Au electrode and optimize the whole device again with Au atom in electrode region fixed. The geometries are optimized until all residual force on each atom was less than 0.05 eV $Å^{-1}$. The exchange-correlation potential is described by the local density approximation (LDA) and the wave function is expanded by the double-zeta plus polarization (DZP) basis for all atoms. The k-point sampling is 3, 3, and 100 in the x, y, and z directions, respectively, where the z is the transport direction. The real space grid techniques are used with the energy cut off of 150 Ry as a required cut off energy in numerical integration and the solution of Poisson equation using fast Fourier transform (FFT). The current $I(V_b)$ can be calculated by the Landauer formula: $I(V_b) = \frac{2e}{h}\int T(E,V_b)[f_L(E,V_b) - f_R(E,V_b)]dE$[39,40]. Here, V_b is the bias voltage, $T(E,V_b)$ is the transmission coefficient, and $f_L(E,V_b)$, $f_R(E,V_b)$ are the Fermi-Dirac distribution functions of the left and the right electrodes.

3. Results and discussion

In Fig. 2(a), we show current-voltage (I-V) characteristics of three junctions SS, SN and NN in a bias region from 0.0 to 1.0 V. One can see that currents of SS device increase with bias voltage first and then decrease after 0.3 V, showing a weak NDR behavior. When the right thiol anchoring group is replaced by one amine anchoring group, the conductance of SN device is enlarged a little in comparing with SS device. As a result, the NDR behavior becomes more intense due to the rise of peak current. After the thiol anchoring groups in SS device are replaced by two amine anchoring group together, the conductance of SN device is improved enormously leading to a huge improvement of the NDR behavior. The peak current of NN device increases to 5620 nA which is nearly 10 times bigger than the peak current of SS device. Because two devices have a similar valley current, the peak-to-valley current ratio of NN device is also nearly 10 times bigger than that of SS device. The results indicate that the amine anchoring group indeed can achieve better defined contact geometry and get more well-defined transport properties in comparing with thiol anchoring group. In order to explain the above calculated results, the transmission spectra of three junctions SS, SN and NN at zero bias are presented in Fig. 2(b). One can see that there is always one transmission peak for three devices in the energy region [-1eV, 1eV]. However, the energy locations of the transmission peaks are sensitive to the anchoring groups. For SS device, its transmission peak locates on −0.18 eV and the corresponding coefficient is small (0.13). When the right thiol anchoring group is replaced by one amine anchoring group, we find that the transmission spectrum of SN device moves to right in comparing with that of SS device. More importantly, its transmission peak just locates on Fermi level and the corresponding coefficient increases to 0.28 which is two times bigger than that of SS device. That's why the conductance of SN device is bigger than that of SS device in Fig. 2(a). After the thiol anchoring groups in SS device are replaced by two amine anchoring group together, the transmission spectrum of NN device moves to right a little in comparing with that of SN device. Its transmission peak still locates on Fermi level and the corresponding coefficient increases to 0.98 which is about 8 times or 4 times bigger than that of SS device or SN device. So, the conductance of SN device is improved enormously leading to a huge improvement of currents at the low bias region.

In order to explore the differences of the transmission coefficient at Fermi level, we show the zero bias local density of states (LDOS) and zero bias transmission pathways (TP) at Fermi level of

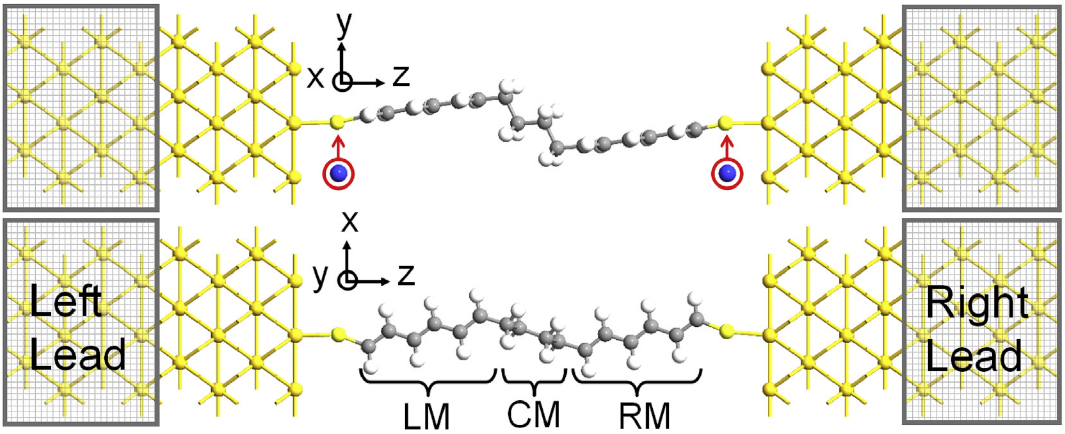

Fig. 1. Side and top views of the schematic illustration of the single molecular junction with two thiol anchoring groups. The gray, white, yellow and blue atoms in the molecule represent carbon, hydrogen, sulfur and nitrogen atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)