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Electronic transport properties of molecular junctions based on the direct binding of aromatic ring to electrodes

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ABSTRACT

We have used the non-equilibrium Green's function in combination with the density functional theory to investigate the quantum transport properties of the molecular junctions including a terminated benzene ring directly coupled to surface of metal electrodes (physisorption). The other side of molecule was connected to electrode via thiolate bond (chemisorption). Two different electrodes have been studied, namely Cu and Al. Rectification and negative differential resistance behavior have been observed. We found that the electron transport mechanism is affected by the nature of benzene–electrode coupling. In other words, the transport mechanism depends on the nature of metallic electrode. Changing from sp- to sd-metallic electrode, the molecular junction changes from the Schottky to p–n junction-like diode. The transmission spectra, projected density of state, molecular projected self-consistent Hamiltonian, transmission eigenchannel, and Muliken population have been analyzed for explanation of electronic transport properties. Understanding the transport mechanism in junction having direct coupling of π-conjugate to electrode will be useful to design the future molecular devices.

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1. Introduction

Molecular devices have attracted great attentions due to their unique properties. Many experimental techniques, including self-assembled monolayers (SAMs) [1], scanning tunneling microscope (STM) [2], or mechanically controllable break junction (MCBJ) [3] have been employed to fabricate the molecular junctions. On the other hand, a lot of efficient theories have been developed to understand the quantum transport properties of molecule junctions [4–7]. Therefore, various interesting phenomena have been reported by both theoretical and experimental works, such as rectifying behavior [8–13] or negative differential resistance (NDR) [14–20]. Since Aviram and Ratner (AR) first proposed the idea of designing the rectifiers with donor–bridge–acceptor molecules [21], the molecular diodes have been widely investigated. Although the AR diodes have received the intensive study, their transport mechanism is still controversial [22–25]. Practically, the coupling between the molecule and metallic electrode plays the important role in the transport properties of junctions. Therefore, controlling the molecule–electrode coupling is another effective approach for designing the molecular rectifier [26–30]. This type of molecular diodes is similar to the Schottky

diode, which is formed from the contact between a metal and a semiconductor.

Usually, single molecules are attached to metallic electrodes *via* anchoring groups, including thiol ($-SH$), amine ($-NH_2$), isocyanide ($-NC$), cyanide ($-CN$), carbonxylic acid ($-COOH$), and so on. Although these groups make single molecular junctions become stable, they act as the resistance. Thus, the conductance in such devices is much lower than that of metallic atomic contact. To overcome this issue, Kiguchi et al. has recently proposed the direct binding of π-conjugated molecules to metallic electrodes, such as Pt–benzene, Ag–benzene, C_{60}–Au, C_{60}–Ag, and C_{60}–Pt (see Refs. [31,32] and references therein). Diez-Perez et al. [33] has proposed a new method to control the conductance of molecular junction. This method was based on the lateral coupling between the π-orbitals of molecule to the orbital of electrode attached to it. Indeed, the effect of orientation of π-conjugated molecule on the electron current was theoretically predicted by Toyoda et al. [34]. They found that electrons mainly transfer through the π-channels, which is the overlap between the molecular π-orbitals and the electrode orbitals. Recent experiments have shown that when the a metallic contact was physisorbed on the azobenezene monolayer without linker, the conductance of *cis*-configuration was larger than that of *tran*-configuration [35–37]. Wang and Cheng has theoretically confirmed this finding by employing the first principle calculation [38]. They suggested that in the case of *cis*-configuration the physisorbed contact shortens the effective tunneling

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pathway, leading to the conductance that is less sensitive to weak bonding. In our opinion, the coupling between the terminated benzene of *cis*-azobenzene and the top contact also comes into play to enhance the conductance of such junction. Most recently, Meisner et al. [39] has experimentally revealed the importance of direct metal-π coupling in electronic transport through the single molecular junctions. Meanwhile, several works including experiment [40,41] and theory [42,43] have shown the promising potential of molecular junctions based on the direct coupling of π-stacking to electrodes.

In this paper, we would like to study the transport mechanism of molecular junctions having the direct coupling of π-conjugate to metal surface. We have designed the biphenyl wire terminated by a benzene ring through the methyl group. This benzene ring was coupled face-to-face with the metallic surface (physisorption), while the other side of molecule was connected to electrode via thiolate bond (chemisorption). Two kinds of electrode materials have been investigated, namely Cu (111) and Al (111). We found that for the transport properties critically depend on the nature of benzene–electrode coupling. Our results suggest that the *p–n* junction-like diode can be obtained even without heteroatom doping.

2. Computational details

For all DFT calculations, we have employed the SIESTA program package [44]. In this code, the core electrons were modeled with the norm-conserving Troullier–Martins pseudopotentials [45] and the atomic orbital basis sets were used to describe the valence electrons. The double-ζ with polarization (DZP) and single-ζ with polarization (SZP) basis sets were used for light atoms and metal atoms, respectively.

We first designed the single molecule including a biphenyl-monothiol terminated by a benzene ring through the methyl group. We performed the geometry optimization by relaxing all atoms within the force tolerance of 0.02 eV Å^{-1}. After the geometry optimization, the molecule was translated into the metal junctions with the (111)–(3 × 3) surface. By varying the materials of two electrodes, we gained the models I and II where the materials are Cu and Al, respectively. Although the studying on the linker between the molecules and the Al surface via thiolate bond is rare in experiment, it has been reported in several theoretical works [46,47]. Three layers from each electrode are included to form the extended molecule as shown in Fig. 1. The extended molecules were optimized by computing the total energies of the system as a function of distance between two electrode. Every single energy point is calculated by performing the geometry optimization with a constrained separation of electrodes. The force tolerance was set at 0.05 eV Å^{-1}. Then, the equilibrium geometry is obtained as the distance at which the total energy is minima. Despite the fact that the pure GGA functionals fail to account for the Van der Waals interaction, they have been used to optimize the molecular junction including the direct binding of π-conjugated molecule to electrodes [41,48–50]. Therefore, because of computational reasons, we have employed the GGA Perdew–Burke–Ernzerhof (GGA-PBE) functional [51,52] being available in SIESTA for all geometry optimizations. The optimized distances between sulfur atom and metal surfaces are around of 2.1 Å. The average distances between the terminated benzene ring and metal surfaces are 2.91 and 3.52 Å for Cu (111) and Al (111) surfaces, respectively.

For the transport calculations, we used the TranSIESTA code [53] which uses SIESTA as the DFT platform. The GGA-PBE functional was also employed. According to the Landauer–Büttiker formula [4], the current was calculated by the integration of transmission function,
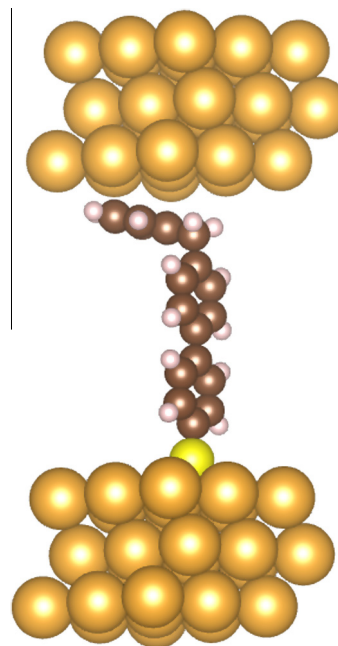

Fig. 1. The extended molecule. The backbone biphenyl is terminated by a benzene ring which is directly coupled to metal surface. The other side of molecule connects to metal surface via the thiolate bond.

$$I(V_b) = \frac{2e}{h} \int T(E, V_b)[f(E - \mu_L) - f(E - \mu_R)]dE, \quad (1)$$

where the $T(E, V_b)$ is the transmission coefficient at energy E and bias voltage V_b, μ_L and μ_R is the chemical potentials of left and right electrode, respectively. The *k*-point grid 3 × 3 was used for transport calculations. The transmission eigenchannel and molecular projected self-consistent Hamiltonian (MPSH) analyses were performed by using INELASTICA package [54].

3. Results and discussion

3.1. Zero-bias transport properties

We first consider the electron transport properties of molecular junctions at zero-bias. Fig. 2 presents the transmission spectra at zero-bias for model I and II. By default, the energy is relative to the Fermi level of leads. It is clearly shown that the transmission peak of model II is much closer to Fermi level than that of model
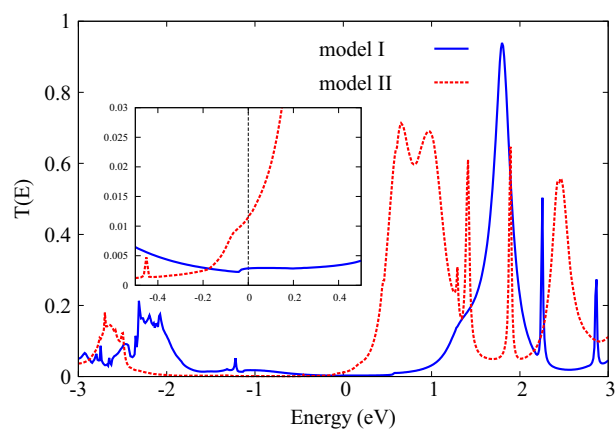

Fig. 2. The transmission spectra at zero-bias of models I and II.