Role of contact formation process in transport properties of molecular junctions: conductance of Au/BDT/Au molecular wires

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We report theoretical investigations on the role of contact formation process and its resulting structures to quantum transport in molecular wires and show that these processes critically control charge conduction. It was found, for Au(111)/1,4-benzenedithiol(BDT)/Au(111) junctions, the hydrogen atom in the thiol groups is energetically non-dissociative after the contact formation. The calculated conductances and junction breakdown forces of H-non-dissociative Au/BDT/Au devices are consistent with the experimental values, while the H-dissociated devices give conductances more than an order of magnitude larger. The results can be well understood by examining the scattering states that traverse the contacts. This work clearly demonstrates that the contact formation process must be carefully understood in order to correctly capture quantum transport properties of molecular nanoelectronics.

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In a very recent paper, Song et al.[1] reported experimental fabrications of three-terminal single molecule field effect transistors. The successful fabrication and characterization of such a molecular device can be considered an important milestone of nanoelectronics. In Song et al.[1] experiment, a gold wire was broken by electro-migration to produce a nano-meter gap in the wire. A molecule such as 1,4-benzenedithiol(BDT) may bridge the gap and form an Au/BDT/Au single molecule transport junction. The equilibrium conductances of 0.01 ~ 0.015G₀ (G₀ = 2e²/h) were reported[1] giving an average value of (0.0132 ± 0.0021)G₀. The Au/BDT/Au device was actually subjected to extensive studies in the past, for instance Xiao et al. reported a mean conductance of 0.011 G₀ by statistically measuring several thousand Au/BDT/Au junctions formed by BDT bridging the gap between a scanning tunneling microscope (STM) and a Au surface[2]. Their result has also been reproduced by other experiments[3]. The consistency of measured transport properties on devices fabricated by totally different methods suggests a degree of structural-function control at the single molecule level.

Despite the achievements, one realizes that the atomic structures of the fabricated devices were still unknown. In particular, the most important structural information - the metal-molecule contacts, is at best ambiguous for essentially all single molecule transport junctions investigated in literature. In general, a most important science issue concerning nano-systems is the relationship between structure and function. The experimental convergence of transport data for the Au/BDT/Au device provides a timely opportunity to shed considerable light on the structure-function issue of molecular nanoelectronics. It is the purpose of this Letter to report our first principles theoretical investigation on how the contact formation process can critically affect quantum transport properties of molecular junctions. In all theoretical analysis of molecular devices, one assumes an initial contact structure between the molecule and the metal electrodes — guided by intuition or by experiments, and then relaxes the structure. However, experimentally when a molecule is brought to contact the metal leads, a contact formation process occurs where chemical reactions may give rise to dissociation or formation of atomic groups from the original molecule. Such a process is likely lost when an initial atomic configuration is assumed without carefully considering it from ab initio point of view. As a result, the formation process has not been subjected to systematic investigations so far and, as we show below, it is a crucial effect that controls the interface transparency to charge flow.

We use the Au(111)/1,4-benzenedithiol(BDT)/Au(111) as a prototypical system for our investigation. As discussed above, the experimental conductance value is 0.011~0.015G₀[1,2] for this system. On the theoretical side[2,7], conductance obtained from quantitative analysis have not been able to reach a consensus. In particular, density functional theory (DFT) based first principles methods within local density approximation (LDA) or generalized gradient approximation (GGA) have mostly produced conductance values considerably larger — by more than one or even two orders of magnitude, than the experimental value of Xiao et al.[2] and Song et al.[1]. In this Letter, we shall show that such a qualitative discrepancy can be well understood by investigating the role of the device contact formation process. By extensive first principles calculations, it was found that a BDT molecule prefers to attach to ad-atoms when it is bonded to Au(111) and, much more importantly, the hydrogen atoms on the thiol groups of a BDT do not dissociate away after the formation of the device contacts. The calculated conductance of H-non-dissociated Au/BDT/Au
junctons as well as the junction breakdown force are consistent with experimentally measured values. On the other hand, all the H-dissociative contact configurations produce conductances at least one order of magnitude greater than the experimental value of Refs. [1, 2], while the junction breakdown force is also significantly larger than the experimental results. The quantum transport results can be well understood by analyzing the scattering states that traversing the metal-molecule contacts.

**Bonding structure of Au/BDT interface.** Despite the importance of bonding structure of the metal-molecule interface to transport [8, 9], detailed bonding geometry of Au/BDT/Au junctions have not been well established. In Au/BDT/Au, the conductance is dominated by the length of alkane molecule and not the Au/alkanethiol interface. In Au/BDT/Au, the benzene ring in BDT consists of a non-local \( \pi \)-bond dominated by the length of alkane molecule and not by the Au/alkanethiol interface. In Au/BDT/Au, the benzene ring in BDT consists of a non-local \( \pi \)-bond system which is rather transparent to electron conduction hence the conductance should be much more sensitive to the bonding structures at the Au/BDT interface. A very careful calculation on the interface is thus necessary. To this end, we use a standard DFT-PAW method with the Perdew-Burke-Ernzerhof 96 functional (GGA-PBE) as implemented in the electronic structure package VASP [11] to determine the atomic structure [12].

As suggested by a recent STM experiment [13], thiol molecules prefer to attach Au(111) surface through Au ad-atoms. We have therefore calculated BDT absorption on Au(111) with and without Au ad-atoms. It was found that if there are ad-atoms, the structures with BDT attaching to the surface via ad-atoms are more stable than their direct adsorption to the surface: the difference of binding energies is at least 0.4 eV per molecule. As a result we shall focus on a series of representative atomic configurations with BDT molecules adsorbed on Au(111) surface via Au ad-atoms. Figure 1(a,b) plots two initial structures of BDT attached to Au(111) via an ad-atom prepared for the structural relaxations, where the molecule is parallel or perpendicular to the Au(111). According to the C3 rotational symmetry of Au(111), another two sets of these structures with a rotation angle of −30° or 30° were also considered. Together these should likely cover most of the initial configurations. For the contact formation process, we consider three cases for the dissociative configuration: the dissociated H atom attaches to the ad-atom, to the surface, or escapes to vacuum to form an \( H_2 \) molecule, as shown in Fig. 1(c). The calculated total energies are summarized in Tab. I. It is striking to find that configurations with non-dissociative S-H bonds, (first row in Tab. I) are always energetically more stable than all dissociative structures by at least 0.2 eV per BDT throughout all systems investigated. Indeed, the non-dissociative S-H bond in thiol group absorbed on a perfect Au(111) surface was experimentally observed by Yates et al. [14] and more recently confirmed by ab initio calculations [15]. Furthermore, our calculated breakdown force of the junction (by elongation) is from 1.1 nN to 1.6 nN [16], fairly consistent to experimental measurements of molecular junctions with the same thiol linker [17]. These results strongly suggest that an H-non-dissociative structure should provide a more realistic model in terms of transport modeling of the BDT devices.

**Bonding structure in Au/BDT/Au device.** The parallel configurations were adopted to build the two-probe model of the junction, since they have lower ener-

![FIG. 1: (Color online) Top views of examples for (a) parallel and (b) perpendicular configurations. (c) Four positions of H have been considered for each configuration at several orientations: (A) is for non-dissociated H; (B), (C), and (D) are for dissociated H which attaches to the (B) ad-atom, (C) the surface, or (D) escapes into vacuum forming an \( H_2 \) molecule.](image1)

![FIG. 2: (Color online) Atomic models of the non-dissociated BDT linked by ad-atoms (a) without and (b) with stretching; and the H dissociated BDT connected to the surface via (c) ad-atoms or (d) Au atomic chains of various lengths.](image2)

| Energy (eV) | parallel | perpendicular |
|------------|----------|----------------|
| 0° | 0.00 | 0.09 |
| 30° | 0.08 | 0.06 |
| 60° | 0.08 | 0.06 |
| H-non-dissociative | 0.00 | 0.09 |
| H-dissociated to ad-atom | 0.28 | 0.25 |
| H-dissociated to surface | 0.41 | 0.40 |
| H-dissociated to vacuum | 0.24 | 0.25 |

**TABLE I: The difference of total energies (units eV) compared to the most stable structure (the parallel 0°) for typical configurations of Au/BDT interface.** For all situations, the H-non-dissociative structures have lower energies.
The basic idea of NEGF-DFT is to self-consistently calculate the Hamiltonian of the device by DFT and determine the non-equilibrium quantum statistical properties of the device operation by NEGF. For more details we refer interested readers to the original literature[18].

The non-equilibrium Green’s function (NEGF) formalism[18] is applied in the direction of current flow. Periodic boundary conditions are used in the left/right leads (see Ref.[16]). For comparison purposes, we have also investigated the widely assumed H-dissociated model. When the S-H bond is dissociated, the Au-S bond shows a stronger strength than the Au-Au bond in our calculation. Therefore, in the experiment of Xiao et al.[2], where a STM tip was repeatedly retracted from a Au surface, it is quite possible to drag an Au atomic wire out of the surface through the attached BDT molecule[2]. To cover this possibility, for the H-dissociative structure, we have calculated a few devices where the H-dissociated BDT is linked to the surface via gold atomic chains with various lengths (Fig. 2d). The geometries of the scattering region of all instances of Au/BDT/Au device is comprised of three parts[18]: the scattering region, the left/right leads, and the molecule is significantly different for H-non-dissociated Au/BDT/Au junctions which are energetically more stable, have conductance values much closer to the experimental data — by one order of magnitude, than the H-dissociated models. The transport results clearly suggest that the hybridization of electronic states from Au electrodes and the molecule is signiﬁcantly different for H-non-dissociative and dissociative models. To understand why this happens, we have analyzed the scattering states around the Fermi level for both models, as shown in Fig. 4.

FIG. 4: (Color online) Scattering states of: (a) H-dissociative; (b) H-non-dissociative models. Insets are the HOMO and LUMO of the corresponding molecule 1,4-benzenedithiolate and 1,4-benzenedithiol.
When the H is dissociated from a S-H group, an electron of the S atom becomes unpaired which has an overwhelming tendency to attract an additional electron to make a pair. The additional electron is most likely contributed by s-electrons of Au leads, resulting in a transfer of charge from leads to the molecule. The transferred electron dopes into the lowest unoccupied molecular orbital (LUMO) of the molecule and pushes down the s-LUMO bonding state just below the Fermi level, as found in a similar system.[10] The s-LUMO bonding states are expected to be very delocalized, since it was composed of a delocalized LUMO and a delocalized s state. We thus plot the scattering states around the Fermi level, as shown in Fig. 4(a). It was found that the conductance around the Fermi level is indeed dominated by a delocalized σ-LUMO state as expected. The plot shows the scattering states nicely passing through the junction, giving rise to a high conductance value. On the other hand, for the H-non-dissociative model, the above charge transfer can hardly happen since all electrons are paired already, hence the hybridized s-LUMO state around the Fermi level disappears. The bonding picture then switches to that of a lone-pair of the S atom donating to the partially unfilled σ-band of Au leads. The lone-pair is rather localized, like a σ-type orbital. The probable hybridization between the lone-pair and Au leads is therefore somewhat localized, which results in a tunneling mechanism for electrons going through the junction at low bias: a much smaller conductance is therefore expected. Indeed, as shown in the plot of scattering states in Fig. 4(b), very few incoming scattering states can pass through the junction. In this case, the conductance is mainly contributed by the HOMO of 1,4-benzenedithiol.

In summary, on the structural side our investigations reveal, surprisingly, that the H atoms in the thiol group of the BDT are non-dissociative after the Au/BDT/Au transport junctions are formed. On the functional side, the introduction of non-dissociative H atoms blocks charge transfer doping to the BDT from the Au electrodes, effectively induces an extra potential barrier that considerably reduces the electron transparency of the Au/BDT interface. Since thiol molecules provide perhaps the most popular binding linkers in experiments, these findings shed considerable light on charge transport properties. Finally, we believe that our findings resolved a long-standing theory-experiment discrepancy on the conductance of the most widely studied molecular transport junction.

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[12] A c(4 × 3) supercell consists of six layers of Au atoms separated by a vacuum layer of 15 Å was adopted to model the surface in Au/BDT interface. All atoms except the three bottom Au layers were fully relaxed with a force criterion of 0.022 eV Å applied for every ion. A planewave cutoff of 400 eV and a k-mesh of 4 × 4 × 1 were further checked by a cutoff of 500 eV and a mesh of 8 × 8 × 1 to ensure the convergence to 1 meV/atom. The cross-section in two-probe calculations is the same in the interface calculations, as shown in Fig. 2.
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[16] The supplemental information, EPAPS No. E-PRITA0-xx-xxxxxx, presents calculated results of the Au/BDT/Au junction formation. The calculated breakdown force due to elongation of the H-non-dissociated junction is consistent with experimentally measured force on the gold-thiol linkage[17]; while that of a lone-pair of the S atom donating to the partially unfilled σ-band of Au leads. The lone-pair is rather localized, like a σ-type orbital. The probable hybridization between the lone-pair and Au leads is therefore somewhat localized, which results in a tunneling mechanism for electrons going through the junction at low bias: a much smaller conductance is therefore expected. Indeed, as shown in the plot of scattering states in Fig. 4(b), very few incoming scattering states can pass through the junction. In this case, the conductance is mainly contributed by the HOMO of 1,4-benzenedithiol.
of H-dissociated junction is significantly higher than the measured values.

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