High-conductance states of single benzenedithiol molecules

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Conductance of single 1,4-benzenedithiol (BDT) molecules is investigated in a wide range $(0-0.3)G_0$, exploiting mechanically controllable break junction technique. The authors observed a series of clear conductance steps both in low- ($\sim 0.01 G_0$) and high-conductance ($\sim 0.1 G_0$) regimes and corresponding two sets of peak structures in the conductance histograms. The two distinct conductance states are attributable to different Au–S bonding configurations of Au/BDT/Au junctions. The high-bias measurements reveal that the high-conductance state of single BDT molecules is stable up to 1.6 V and prospective for molecular device applications. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2363995]

Building reliable molecular devices requires fundamental understanding of molecule-metal contact effects on electron transport through molecular junctions and realization of highly transparent contacts with superior bias stability. Recently, conductance of various molecular junctions has been measured exploiting various types of experimental techniques.[1–3] These experiments, however, yielded vastly different results. In the case of 1,4-benzenedithiol (BDT) molecules, the reported conductance values vary from $< 10^{-4} G_0$ to $\sim 1.1 \times 10^{-2} G_0$,[1,4–6] where $G_0 = 2e^2/h \sim 77.5 \ \mu$S. Theoretically, it is well recognized that the single molecule conductance of BDT sensibly depends on the Au–S bonding geometry at the molecule-electrode contacts.[7,8] It is thus natural to attribute the huge discrepancy in the reported single molecule conductance to different bonding geometries and assume that there exist several stable contact configurations for Au/BDT/Au. This viewpoint has recently been put forward by Li *et al.*,[9] who demonstrated experimentally that single alkanedithiols bridging over scanning probe microscope break junctions take low- and high-conductance configurations. The authors suggested that each conductance state corresponds to one of distinct Au–S bonding geometries, i.e., top-molecule-top (top-top) geometry, where both S atoms of the molecule occupy the top site of the Au surface and the top-molecule-hollow (top-hollow) geometry with one S atom being connected to the threefold hollow site.[9] Similar geometry-dependent single molecule conductance states have also been reported recently by Ishizuka *et al.*[10] Furthermore, He *et al.*[11] pointed out that the conductance of smaller molecules is more significantly affected by changes in the bonding sites and predicted for BDTs that the top-top and hollow-hollow geometries would yield up to a tenfold difference in the conductance.

In the present study, we measured the single molecule conductance of BDT exploiting the mechanically controllable break junction (MCBJ) technique. In contrast to the previous experiments, which reported the low conductance of $\sim 10^{-2} - 10^{-4} G_0$,[1,4–6] we detected a high-conductance state of BDTs at $\sim 0.1 G_0$ simultaneously with the low-conductance state.

A fine Au wire was utilized for electrodes of the MCBJ. We first broke the MCBJ and formed a nanogap electrode in ethanol containing ~ 1 mM 1,4-BDT molecules (Tokyo Chemical Industry Co., Ltd.). After exposing the electrodes to the solution for a few minutes, the MCBJ was quickly loaded into a vacuum chamber which was first evacuated to 1×10^{-5} Torr and then backfilled with He gas. This procedure is necessary for leaving sufficient number of uncovered sites on the electrode surface which would become bonding sites for a one-side-bonded BDT to form a single BDT bridge over Au electrodes;[12] otherwise the entire electrode surface would be covered by a BDT monolayer and the electron transport would occur only through molecule-molecule overlapping.[13] Subsequently, we recorded the temporal evolution of the conductance (referred to as "conductance trace") with slowly squeezing the electrode separation at a rate of ~ 1.4 nm/s. The conductances of BDTs were measured up to $0.3 G_0$ in order to encompass the wide range of the reported conductance.[1,4–6] We repeated making and breaking the Au/BDT/Au junctions under different biases in the range of 0.4–1.6 V and acquired consecutive 200 conductance traces at each bias. Throughout the conductance measurements, a special care was devoted not to squash the bridging BDT by accidentally crushing the junction. All measurements were conducted in a He gas atmosphere at room temperature.

Typical conductance traces obtained at different biases are displayed in Fig. 1. Figure 1(b) is an expanded view of the low-conductance regime of Fig. 1(a). In many junction closures, we only observed an exponential increase in the conductance [such as the leftmost traces in Figs. 1(a) and 1(b)], which indicates electron tunneling but no molecular conduction between the electrodes. In some traces, however, the conductance exhibits clear steps, as depicted in Fig. 1(a). Once appeared, such stepwise structures can reproducibly be observed, with high probability of $\sim 80\%$, in successive junction closures. These conductance steps are naturally ascribed to formations of stable Au/BDT/Au junctions.[4] The conductance plateau tends to appear at $\sim 0.1 G_0$. In addition to the plateaus in the high-conductance regime, we observed another sets of conductance plateaus in the low-conductance region $< 0.02 G_0$, as shown in Fig. 1(b).

Following previous studies,[2–4] we analyzed the conductance states by constructing conductance histograms. The histograms obtained at 1.0 V are shown in Figs. 1(c) and 1(d). Corresponding to Figs. 1(a) and 1(b), the histograms cover the high- and the low-conductance regimes. Both his-
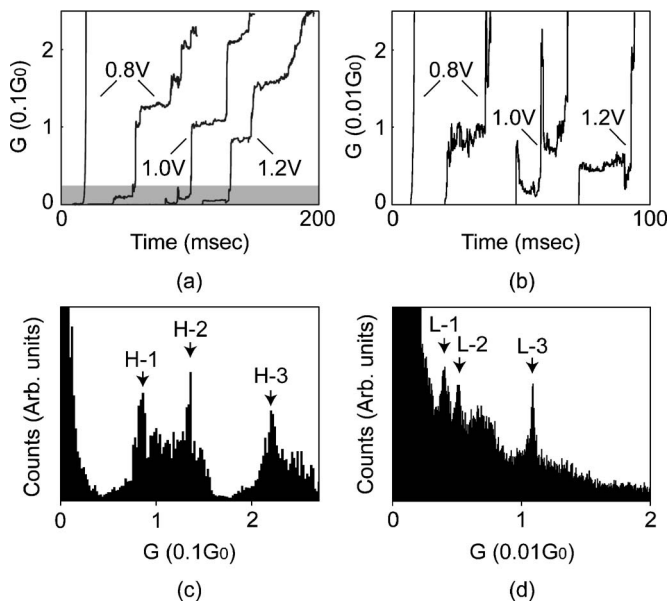
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FIG. 1. Transient conductance traces during the junction closures and corresponding conductance histograms. (a) Often, the conductance curves demonstrated exponential increase. Occasionally, however, clear conductance steps are observed at $\sim 0.1 G_0$. (b) When the conductance range at the dark region illustrated in (a) is expanded, we can also find several conductance steps below $0.02 G_0$. [(c) and (d)] The conductance histogram obtained at 1.0 V exhibiting two sets of peak structures at $\sim 0.1 G_0$ and $\sim 0.01 G_0$.
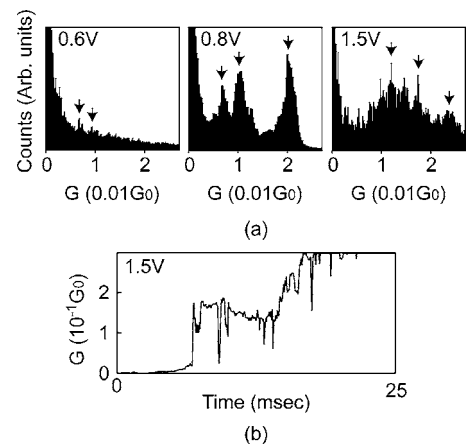

FIG. 2. Conductance histograms in the H regime obtained at 0.6, 0.8, and 1.5 V. The faint peaks in 0.6 V reflect a little chance for the H states being formed at the bias. The H peaks grow rapidly at 0.8 V and persist up to 1.6 V. At bias ≥ 1.5 V, however, the peak structure is significantly broadened perhaps due to the high-bias local heating of the molecular junctions that also causes conductance fluctuations, as depicted in (b).

tograms exhibit distinct peak structures around $0.1 G_0$ and $0.01 G_0$. We distinguish the high- and the low-conductance peaks and denote the corresponding conductance states as H and L, respectively. In Fig. 1(d), the L peaks are located at $G_{L-1} = 0.004 G_0$, $G_{L-2} = 0.005 G_0$, and $G_{L-3} = 0.011 G_0$. These peaks are narrow and little affected by the bias for 0.4–1.5 V. Similar multiple peak structures have previously been reported.[4,5] In particular, the conductance G_{L-3} of the L-3 peak agrees with the single BDT conductance observed by Xiao *et al.*[4] Thus, the observed L states can be identified with the conductance states reported in Refs. 4 and 5.

On the other hand, the H peaks are relatively broad and located at $G_{H-1} = 0.09 G_0$, $G_{H-2} = 0.14 G_0$, and $G_{H-3} = 0.22 G_0$. The bias dependences of the H peaks are in marked difference from those of the L peaks. Upon varying the bias, the H-peak profiles change appreciably, as shown in Fig. 2(a). There are only faint peaks at <0.8 V due to the fact that the H states emerged only under high biases ≥ 0.8 V. The peak structure evolves rapidly at higher biases and becomes most evident around 1 V. Further increase in the bias above 1.5 V, however, results in significant peak broadening. Also, the peak positions monotonically shift to the higher conductances with increasing the bias.

We now discuss the physical origin for the H states. The first point is possibility of multiple bridging of BDTs.[6] However, the conductance of the multiple bridging should be widely distributed and unlikely to form the well-defined large conductance steps nor the pronounced peak structures in the histograms. Moreover, we note that G_{H-3} is nearly a factor of 2 higher than G_{H-1} and G_{H-2}. Such a quantized peak structure cannot be expected for the multiple bridging but can be naturally interpreted that the H-1 and H-2 states represent single BDT junctions, while the H-3 state corresponds to double bridging of BDT molecules. It should also be argued that the H-state conductance of $\sim 0.1 G_0$ is typical for

contaminated Au single-atom chains.[14,15] Nevertheless, the chemisorbed atoms/molecules on the contacts are expected to desorb at high biases by the local heating, which contradicts to the fact that the H states are observable at high biases ≥ 0.8 V. Furthermore, we performed control experiments using solutions containing no BDT molecules and obtained featureless conductance histograms with no peak structures being identified. These observations ensure that the H states are genuine contact states of the Au/BDT/Au junctions.

We next discuss the difference in the bias stability of the L and the H states. Figure 3(a) plots the appearance frequency ratio H/L of the two states as a function of the bias. At <0.8 V, $H/L < 0.5$ so that the L states predominantly appear in the conductance traces. On the other hand, at 1.5 V, H/L increases steeply from 1.5 to 2.5 owing to the appreciable decrease in the appearance probability of the L states. This indicates that the L states are less stable under higher biases. What causes the high-field instability of nanocontacts is either current-induced forces[16,17] or local heating[17,18] (or both). Since the current-induced forces is estimated to be negligible in the bias range studied,[16,17] the local heating effects are more important. Recent measurements[17] on Au/octanedithiol/Au junctions estimated an ~ 25 K increase in the effective temperature at 1 V. Since the BDT conductance is two to three orders of magnitude higher than that of the octanedithiols,[9] we predict much se-
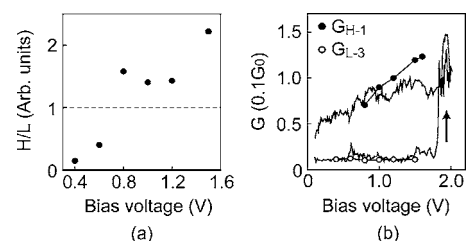

FIG. 3. (a) H/L appearance ratio at different biases. At low biases, $H/L < 0.5$ indicating the L states dominantly appear in the junction. In contrast, the H/L becomes >1.0 at ≥ 0.8 V suggesting that the H states are more preferred than the L states under high biases. (b) A typical G-V curve obtained from a single bias sweep, which shows the $H \to L$ transition at ~ 1.8 V. The G-V characteristic obtained from a single sweep accord quantitatively with that derived from the bias shifts of the histogram peaks.

vere overheating in our Au/BDT/Au junctions. In fact, at 1.5 V and above, the conductance trace often shows fluctuations, as seen in Fig. 2(b), which are indicative of the contact overheating.[4,18] The peak smearing in the histograms at >1.5 V also implies thermal broadening. Therefore, the $L \rightarrow H$ shift at ~0.8 V shown in Fig. 3(a) signifies a thermal transition in the contact configuration of the BDT molecule, from the initial bonding geometry to the one more stable under high biases.

We have also investigated the $L \rightarrow H$ transition by measuring the conductance versus bias voltage (G-V) characteristics of Au/BDT/Au junctions via a different scheme. In this procedure, an opened MCBJ is gradually closed until a conductance jump occurred, which signifies formation of a Au/BDT/Au junction. We then fixed the positions of the electrodes and subsequently measured the G-V characteristics by sweeping the bias up to 2.0 V. Figure 3(b) shows a typical G-V curve obtained by this method. A large conductance jump was often observed at high biases of 1.5–2.0 V [~1.8 V in Fig. 3(b)]. We have confirmed that the G-V characteristics before and after the conductance jump coincide well with those derived from the bias shifts of the L and H peaks in the histograms, respectively. Therefore, the high-bias conductance jump can unambiguously be attributed to the $L \rightarrow H$ transition. Furthermore, unlike the break junction approach, this measurement procedure involves no electrode motions during the G-V measurements, which corroborates that the $L \rightarrow H$ transition is a high-current/bias phenomenon, and denies the aforementioned possibility of multiple bridging of BDT molecules.

In the recent experiments on Au/octanedithiol/Au junctions, Li *et al.*[9] detected L- and H-conductance states similar to those of BDTs revealed in the present study. According to their interpretation, the L states correspond to the top-top geometry, while the H states represent the top-hollow geometry. Although the conductance of octanedithiols is approximately five times lower than that of the BDTs, the Au–S coupling should be equal for the two molecules. It is thus natural to assume that the same conception is also applicable for BDTs, i.e., L: top-top and H: top-hollow (or the hollow-hollow). This model is consistent with previous experimental and theoretical observations. First, the L-state conductance ~0.01G_0 is in accordance with the experimental single BDT conductance in the top-top geometry.[4] Also, recent calculations by Nara *et al.*[8] reported a tenfold increase in the BDT conductance when the bridging configuration transforms from top-top to hollow-hollow, which matches with the observed difference in the single BDT conductance of the L and the H states. Furthermore, the superior stability of the H states under high biases is consistent with the top-hollow geometry, where the increased coordination number of S atoms provides stronger electrode-molecule coupling. We finally point out that whenever the trace contains both H and L plateaus, the L plateau appears first, and then follows the H plateau, as seen in the traces in Fig. 1. Since the traces were recorded during squeezing the junctions, the appearance sequence of the plateaus seems plausible since the top-top should have slightly longer junction length than the top-hollow or the hollow-hollow.

In conclusion, we have measured the conductance of single BDT molecules bridging over the MCBJ electrodes and observed two distinct conductance states, the L and the H states with conductances ~0.01G_0 and ~0.1G_0, respectively. The conductance histograms reveal two sets of well-defined peaks in the two conductance regimes H and L. We showed that the high-bias stability and other characteristics can be consistently explained by attributing the top-top and the top-hollow (or the hollow-hollow) geometries of the Au–S bonding to the L and the H states, respectively. The present findings suggest that the Au/BDT/Au junctions can attain a high-conductance state which would be a useful element in practical molecular electronic devices.

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