Variability of Conductance in Molecular Junctions

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The conductance of molecular junctions, formed by breaking gold point contacts dressed with various thiol functionalized organic molecules, is measured at 293 K and at 30 K. In the presence of molecules, individual conductance traces measured as a function of increasing gold electrode displacement show clear steps below the quantum conductance steps of the gold contact. These steps are distributed over a wide range of molecule-dependent conductance values. Histograms constructed from all conductance traces therefore do not show clear peaks either at room or low temperatures. Filtering of the data sets by an objective automated procedure only marginally improves the visibility of such features. We conclude that the geometrical junction to junction variations dominate the conductance measurements.

What are the conduction properties of an organic molecule bonded between metal electrodes? This question has been at the heart of research in molecular electronics for several years.[1] Experiments measuring the two-terminal conductance of ensembles of molecules[2−7] and single molecules[8−14] have been performed employing a variety of different techniques. The results vary widely: for example the low bias conductance of 1,8-octanedithiol (8DT) between Au electrodes measured by two different techniques was found to be 1.4×10^{-5} G_0[11] or 1.6×10^{-4} G_0,[13] where $G_0 = 2e^2/h$ is the fundamental quantum conductance unit. The published figures for π-conjugated molecules, which show special promise for molecular electronics, vary even more: the reported conductance of 1,4-benzenedithiol (BDT) between Au electrodes ranges from 4×10^{-4} G_0[8] (1 V bias) to 1.1×10^{-2} G_0.[14]

These values are also very different from several theoretically calculated conductance values, which depend critically on the detailed assumptions regarding the crystallographic orientation of the electrodes and the bonding site, length, and angle of the molecule relative to the metal lattice.[15−18,19] For example, for the Au/BDT/Au system, the calculated conductances range from 10^{-2} to 5×10^{-1} G_0,[18,20−23] depending on the nature of the S−Au bond (top site versus hollow site) and the geometry of the electrode (Au-111 versus Au-100). In addition, recent work by Basch, Cohen, and Ratner[24] suggests that the zero bias conductance of Au/BDT/Au, where the Au electrodes are chains of Au atoms, can differ by three orders of magnitude between different configurations of the BDT between the Au atoms.

The variations between experimental data and their deviations from the results of theoretical models suggest that the discrepancy in experimentally determined conductance values could

possibly originate from the different atomic-scale details of the contacts in the Au/molecule(s)/Au junction. To assess this variability, a statistical analysis of a large number of independent single-molecule junctions suggests itself, although it is usually not pursued. In the experiments of Cui et al.[11] and those of Xu, Xiao, and Tao,[13,14] such a statistical analysis has reportedly been applied, and the conductances of 8DT and BDT were found to vary by only a small percentage (1.4×10^{-5} $G_0 \pm 6\%$ for 8DT and 1.1×10^{-2} $G_0 \pm 10\%$[25] for BDT). Given that the model calculations yield conductances that vary by large factors, it is not clear how or why the experiments measure such a narrow range of conductances. Do experiments on molecular junctions record or select a few of the possible molecule−electrode configurations?

The experiments described in this paper address this question through a systematic statistical study of the conductance of thiolated molecules measured between Au electrodes both at room temperature (RT) and at low temperatures (LT). In our experiments, we find that the conductance of junctions formed between thiolated molecules and Au electrodes varies over a wide range of molecule dependent conductance values. Therefore, we cannot assign a value to the conductance of a molecule. In addition, we also find, from current−voltage measurements, that the conductance of one junction switches between different values in time.

We measure the conductance of molecules by repeatedly forming and breaking Au point contacts in the presence of the molecules[13] in two different experimental setups: a modified scanning tunneling microscope (STM)[13] and a mechanically controlled break junction (MCBJ),[4,8−10,26] enabling us to expand our statistical study by allowing measurements in different environments, temperatures, and junction formation rates (see Supporting Information for details). In the STM, which operates in ambient conditions at room temperature (RT), the junctions

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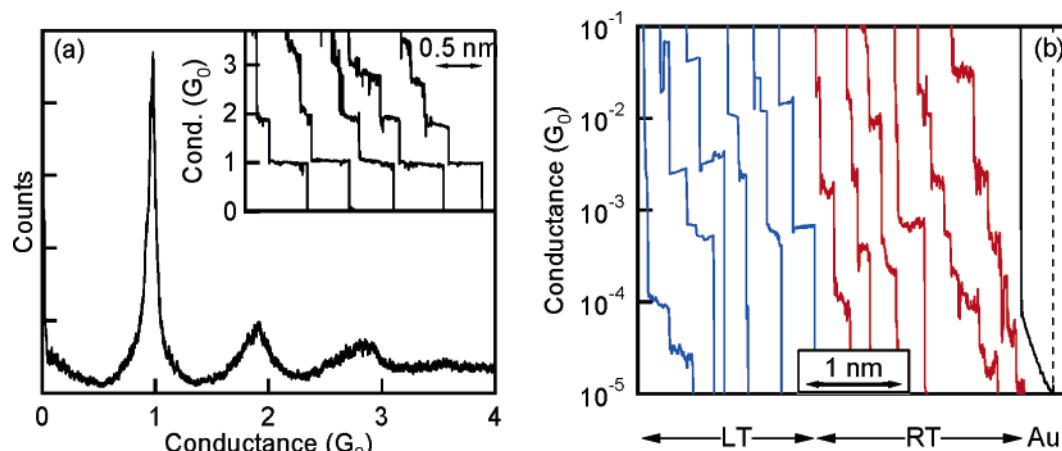[§] Department of Chemistry, Barnard College.

Figure 1. (a) Conductance histogram constructed from 500 traces measured while breaking clean Au point contacts at a bias of 25 mV in the STM setup at RT. The inset shows five traces at arbitrary x-axis offsets. (b) Conductance versus displacement traces of Au point contacts broken in the presence of BDT molecules measured at a bias of 100 mV with arbitrary x-axis offsets. The blue curves were measured with a MCBJ at 30 K, the red curves were measured in the STM at RT, the solid black curves show an exponential decay, and the dashed black curve shows a drop below our measurement limit after the Au contact is broken.

were broken in a dilute ($\sim$1 mM) solution of the molecules in 1,2,4-trichlorobenzene (TCB). In the MCBJ setup, which operates in vacuum at room and low temperatures, the Au was coated with molecules from solutions (typically $\sim$ 1 mM in ethanol) prior to forming and breaking the junctions.[27] Both systems rely on the trapping of one or more molecules between the ends of an Au point contact that is being broken by pulling the electrodes apart. In both experiments, currents were recorded at a fixed bias voltage while the electrodes were pulled apart, to generate conductance traces. To allow for detailed statistical analysis, many thousands of curves were collected, and to ensure that each measurement started from a different initial configuration, the electrodes were pulled apart only after being brought into contact with conductance greater than a few G_0.

When a clean Au contact is pulled and broken either in ambient conditions or in vacuum in the absence of molecules, the conductance decreases in a stepwise fashion (inset, Figure 1a). The steps are integral multiples of the fundamental conductance unit $G_0 = 2e^2/h$, indicating that the cross-section of the contact is reduced down to that of a few and eventually a single atom[28] with a single conductance channel. A conductance histogram, constructed from 500 consecutive traces, shows clear peaks around 1, 2, and 3$\times G_0$ (Figure 1a). When the single-atom chain is broken, in the absence of molecules, the conductance either decreases exponentially with the electrode displacement due to tunneling across the gap between the two Au electrodes (Figure 1b solid black curve) or drops from G_0 below the detection limit (Figure 1b dashed black curve), possibly due to the broken ends snapping back as the contacts relax.

When pulling the Au junctions in the presence of molecules, a large fraction of the traces show additional steps at conductance levels below G_0, as shown in Figure 1b for BDT, both in LT (blue curves) and RT (red curves) measurements. Following the work of Xu and Tao,[13] we interpret these steps in the conductance traces to result from the temporary formation of a stable Au/molecule(s)/Au system of fixed conductance value. Although the junction elongates during this process, this is probably due to Au atoms being pulled out of the electrodes rather than the stretching of the molecule itself.[13] Traces without steps below G_0, which are dominant ($\sim$90%) in the experiment without molecules, are also present when experiments are performed with molecules and are believed to represent cases when no molecule has been trapped in the junction.

In the traces shown in Figure 1b, additional steps are clearly visible in the conductance traces. However, to show that most of the traces collected when molecules are present around the contact have additional steps, a quantitative evaluation of the data is necessary. This is carried out by comparing each trace with two functions: a piecewise constant function, which tests for molecular conductance steps, and an exponential, which tests for tunneling conductance.[29] Both functions are fit to the logarithm of the region below 0.1 G_0 in each conductance trace so as to treat conductance steps in the full range of our data equally (See Supporting Information for details). The distribution of the least-squares deviations (LSD) obtained from the two fits to the region of the traces below 0.1 G_0 measured with and without BDT (Figures 2a and 2b) show clearly that a step function represents the BDT traces better than the Au traces, whereas the exponential function represents the Au traces better than the BDT traces. This confirms in a more objective way our previous interpretation: when breaking a clean Au point contact, the conductance follows an exponential tunneling decay, while in the presence of molecules low-conductance steps are seen in the breaking traces.

Although individual conductance traces show clear conductance steps below G_0, the statistical significance of particular step locations can only be assessed by histograms computed from such traces. In Figure 3a we show the histogram of all conductance traces taken by repeatedly breaking the Au contact in the presence of BDT at room temperature (red curve) along with a control histogram taken in the solvent without molecules (orange curve). Clearly, the conductance steps below G_0 that are so prominently visible in the individual traces do not add up to discernible peaks in the histogram, therefore we cannot deduce preferred conductance values of the Au/molecule(s)/Au system. Comparing the two histograms in Figure 3a, a large increase in the histogram counts can be seen for the Au/molecule/Au case over the entire conductance range shown, implying that the steps seen in individual curves occur everywhere in this range. In Figure 3b, we show data from low-temperature measurements, where the conductance histograms of all traces show some peak-like features (blue curve). These peaks are not at clear multiples of a single conductance value that can be associated with the conduction through 1, 2, or 3 molecules between the electrodes, as is the case for the 1-, 2-, and 3-G_0 conductance peaks of the Au point contact shown in Figure 1a. However, the fact that we do see peaks at LT could
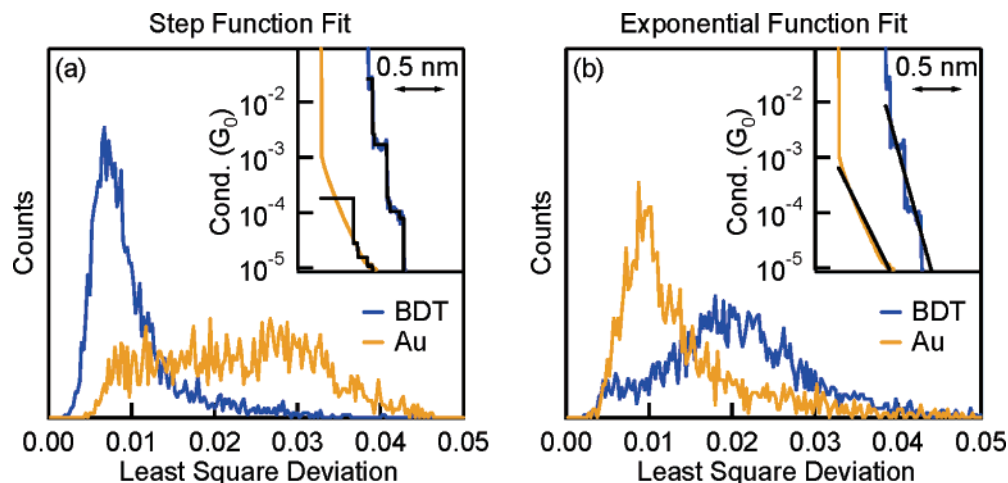
Figure 2. Histograms of the least-squares deviation calculated by fitting (a) a piecewise constant function or (b) an exponential to conductance traces collected while breaking Au contacts in ambient without (yellow) and with (blue) BDT molecules (normalized by the number of included curves). Only traces that do not drop immediately below the measurement range are included. Inset: Sample conductance curves with best exponential and step function fits that minimize the least-squares deviations.
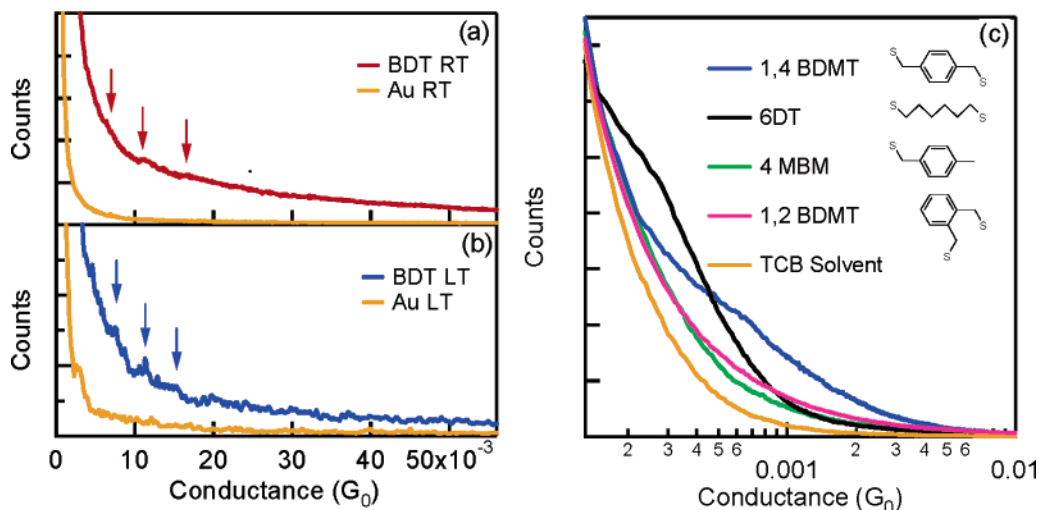

Figure 3. Conductance histograms constructed from 3000 consecutive traces similar to the ones in Figure 1a collected at (a) at RT in a 1 mM solution of BDT (red) in TCB and (b) LT in the presence of BDT (blue) at 100 mV bias. Arrows point to the position of the faint features. Control histograms (yellow) constructed from traces collected in the solvent alone or in vacuum are also shown. The bin size is 1×10^{-4} G_0. (c) Conductance histograms of 4000 breaking traces collected in 1 mM solutions of 1,4-BDMT, 6DT, 1,2-BDMT, and 4-MBM, as well as a control histogram in TCB alone shown on a semilog axis for clarity. The bin size is 1×10^{-5} G_0 and bias voltage is 25 mV.

imply that some Au/molecule(s)/Au configurations are more favorable than others at LT. The RT data, on the other hand, show that there is only a range of possible conductances that can be measured when an Au point contact is broken in the presence of BDT, but not a set of fixed values.

To explore the dependence of the histogram on molecular structure, we have performed RT experiments on four additional molecules: 1,4-benzenedimethanethiol (1,4 BDTM), 1,2-benzene-dimethanethiol (1,2 BDTM), 4-methylbenzylmercaptan (4MBM), and 1,6-hexanedithiol (6DT). We collected conductance traces in 1 mM solutions of these molecules in TCB and computed conductance histograms from 4000 traces (Figure 3c).[30] We first look in detail at the histograms of 1,4-BDMT, 1,2 BDMT, and 4 MBM (see inset of Figure 2c for molecule structures). Of these three molecules, only 1,4-BDMT has two thiol groups attached to opposite ends of the molecule, allowing it to attach easily to the two ends of the Au point contact as they are pulled apart. The fact that we clearly see more counts in the conductance histograms of 1,4-BDMT when compared with both 1,2-BDMT and 4 MBM provides additional evidence that the steps seen in individual traces below G_0 are due to conductance

through molecules which can bind to the two ends of the Au point contact.

We now compare the histograms of 1,4-BDMT and 6DT with that of a control histogram taken in pure TCB. Additional counts can clearly be seen when these two molecules are present in the solvent. For 1,4-BDMT (blue trace), the additional counts are primarily between 0.0002 G_0 and 0.004 G_0, whereas for 6DT (black trace), the additional counts are spread primarily between 0.0001 G_0 to 0.0015 G_0. This indicates that a larger fraction of the steps occur at higher conductance levels for 1,4-BDMT when compared with 6DT. While both molecules are of approximately the same length (1,4-BDMT is 0.76 nm and 6DT is 0.72 nm[31]), 1,4-BDMT contains an aromatic ring, but 6DT contains an alkane chain, and the latter is expected to have a lower conductance.[24] Our experimental data qualitatively agree with this expectation since we observe additional counts at a higher conductance range for 1,4-BDMT as compared to 6DT. However, this is in contrast to the work of Xu, Xiao, and Tao, who find the conductance of 6DT (at 0.0012 G_0)[13] to be higher than that of 1,4 BDMT (at 0.0006 G_0)[14] based on the peaks they find in their conductance histograms. A possible explana-

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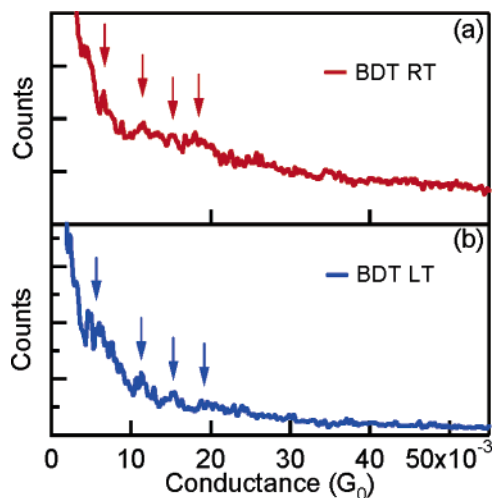*J. Phys. Chem. B, Vol. 110, No. 6, 2006* **2465**

Figure 4. Conductance histograms constructed from ∼400 traces selected from BDT data shown in Figure 3 at (a) RT and (b) at LT. The bin size is 1×10^{-4} G_0. The arrows point to the position of the features seen in these data. We note that the peak at ∼$0.011 \times G_0$ coincides with the conductance assigned to this molecule in similar experiments in the literature.[14]

tion for this difference could be that by constructing histograms including all measured traces without relying on a data selection process, we are including the conductance of all possible conformations of the Au/molecule/Au system.

To determine whether an objective data selection process would create prominent peaks also in our histograms, we construct histograms exclusively from traces that are best fit by a step function as opposed to an exponential. The selection criterion is based on the ratio of the LSD for the step and exponential fits. We keep traces for which this ratio is smaller than 0.3,[32] i.e., for which the step function is a much better fit than an exponential function. This provides an algorithm for an automated selection process for conductance traces that measure the conductance through Au/molecule(s)/Au. Figure 4 shows histograms constructed from such a filtered dataset of BDT at RT and LT.[33] After such data processing, weak peaks now appear in the RT histograms and the faint peaks in the LT histogram get sharper, although a broad background of counts is still present. The fact that we do not see clear peaks, even after an automated data selection process, implies that the steps

seen in individual traces occur over a wide range of conductance values, suggesting strongly that the variation in conductance shown in Figure 3 is a characteristic of the system. Thus our results support the hypothesis that the Au/molecule(s)/Au system has many possible conformations, each having a different conductance depending on its detailed structure.

If each Au/molecule(s)/Au system indeed has many possible configurations, each having a different conductance, it should be possible to see dynamic switching between them by performing current versus voltage (*IV*) measurements while keeping the distance between the electrodes fixed. To this end, we measured the *IV* characteristics of BDT coated Au electrodes in the MCBJ junctions at LT following a procedure similar to earlier published work.[8−10] Two series of *IV*s, each recorded consecutively over a few minutes without moving the electrodes, are shown in Figures 5a and 5b. The low bias conductance (shown in the insets of Figures 5a and 5b) is typically stable for several *IV*s and then switches abruptly. Some curves show a fast switching between conductance values. In addition, the low bias conductance of these IV curves also varies considerably from one establishment of a junction to the next, as can be seen by comparing Figures 5a and 5b. This is in contrast to *IV* curves measured for clean gold electrodes where, in the tunneling regime, we see symmetric featureless *IV* curves and do not observe any switching. This indicates that stable configurations with molecules, which have *IV*s that are stable over a period of a few minutes, can have significantly different conductance values, consistent with our hypothesis that there are multiple ways a molecule can bond to two electrodes.

In conclusion, we have measured the conductance of a variety of thiolated molecules on Au electrodes at RT and also of BDT at 30 K. The conductance traces measured as a function of electrode displacement show steps below G_0 in the presence of the molecules. These steps do not occur at multiples of a fundamental molecule-dependent value, and their position varies over a wide range of conductances. Clear peaks are therefore not discernible in the histograms created from all conductance traces, unlike the quantized conductance peaks from the Au contact at and above G_0. However, histograms constructed in this same fashion from equimolar solutions of different molecules differ characteristically and reveal trends. Specifically, the conductance of 6DT is smaller than that of 1,4-BDMT, qualitatively agreeing with expectation. The summary of these
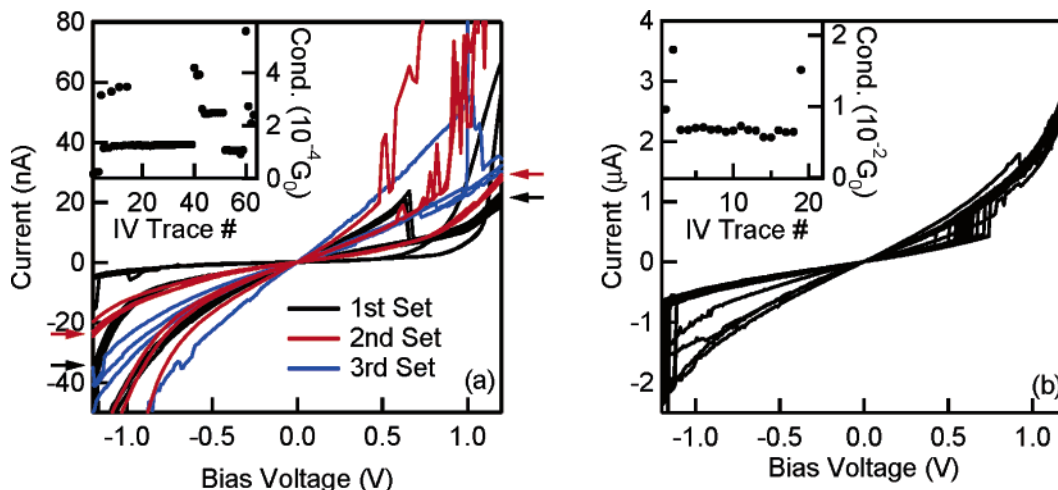

Figure 5. Current versus voltage characteristics of BDT measured in the MCBJ set up at 30 K at a constant electrode separation. The insets show the conductance at 100 mV for each measurement. (a) The traces were recorded consecutively in the order black, red, blue without further adjusting the electrode distance after one electrode approach. The arrows mark asymmetric traces of different polarity. (b) Consecutive current versus voltage traces after another independent electrode approach.

observations provide strong support for the hypothesis that each breaking of an Au wire in the presence of molecules results in a slightly different atomic arrangement of the junction; steps are distributed over a range of conductances that clearly depend on the molecule present. Additional support for such a conclusion comes from the *IV* measurements: the Au/dithiol−molecule/Au system is characterized by a high degree of static disorder (each realization of the junction is different from previous one) and dynamic disorder (the junctions can switch spontaneously between different configurations).

Supporting Information Available: Experimental details and fitting algorithm. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Aviram, A.; Ratner, M. A. *Chem. Phys. Lett.* **1974**, *29*, 277.

(2) Dhirani, A.; Lin, P. H.; GuyotSionnest, P.; Zehner, R. W.; Sita, L. R. *J. Chem. Phys.* **1997**, *106*, 5249.

(3) Tian, W. D.; Datta, S.; Hong, S. H.; Reifenberger, R.; Henderson, J. I.; Kubiak, C. P. *J. Chem. Phys.* **1998**, *109*, 2874.

(4) Chen, J.; Reed, M. A.; Rawlett, A. M.; Tour, J. M. *Science* **1999**, *286*, 1550.

(5) Wang, W. Y.; Lee, T.; Reed, M. A. *Phys. Rev. B* **2003**, *68*.

(6) Salomon, A.; Cahen, D.; Lindsay, S.; Tomfohr, J.; Engelkes, V. B.; Frisbie, C. D. *Adv. Mater.* **2003**, *15*, 1881.

(7) Selzer, Y.; Cai, L. T.; Cabassi, M. A.; Yao, Y. X.; Tour, J. M.; Mayer, T. S.; Allara, D. L. *Nano Lett.* **2005**, *5*, 61.

(8) Reed, M. A.; Zhou, C.; Muller, C. J.; Burgin, T. P.; Tour, J. M. *Science* **1997**, *278*, 252.

(9) Kergueris, C.; Bourgoin, J. P.; Palacin, S.; Esteve, D.; Urbina, C.; Magoga, M.; Joachim, C. *Phys. Rev. B* **1999**, *59*, 12505.

(10) Porath, D.; Bezryadin, A.; de Vries, S.; Dekker, C. *Nature* **2000**, *403*, 635.

(11) Cui, X. D.; Primak, A.; Zarate, X.; Tomfohr, J.; Sankey, O. F.; Moore, A. L.; Moore, T. A.; Gust, D.; Harris, G.; Lindsay, S. M. *Science* **2001**, *294*, 571.

(12) Reichert, J.; Ochs, R.; Beckmann, D.; Weber, H. B.; Mayor, M.; von Lohneysen, H. *Phys. Rev. Lett.* **2002**, *88*, 176804.

(13) Xu, B. Q.; Tao, N. J. J. *Science* **2003**, *301*, 1221.

(14) Xiao, X. Y.; Xu, B. Q.; Tao, N. J. *Nano Lett.* **2004**, *4*, 267.

(15) Kaun, C. C.; Guo, H. *Nano Lett.* **2003**, *3*, 1521.

(16) Ghosh, A. W.; Datta, S. *J. Comput. Electron.* **2002**, *1*, 515.

(17) Tikhonov, A.; Coalson, R. D.; Dahnovsky, Y. *J. Chem. Phys.* **2002**, *117*, 567.

(18) Emberly, E. G.; Kirczenow, G. *Phys. Rev. B* **1998**, *58*, 10911.

(19) Based on the multimode lead calculation in ref 18. The difference between (100) and (111) electrodes can be large as four orders of magnitude, when based on the one-band ideal leads.

(20) Stokbro, K.; Taylor, J.; Brandbyge, M.; Mozos, J. L.; Ordejon, P. *Comput. Mater. Sci.* **2003**, *27*, 151.

(21) Di Ventra, M.; Pantelides, S. T.; Lang, N. D. *Phys. Rev. Lett.* **2000**, *84*, 979.

(22) Bratkovsky, A. M.; Kornilovitch, P. E. *Phys. Rev. B* **2003**, *67*, 115307.

(23) Hall, L. E.; Reimers, J. R.; Hush, N. S.; Silverbrook, K. *J. Chem. Phys.* **2000**, *112*, 1510.

(24) Basch, H.; Cohen, R.; Ratner, M. A. *Nano Lett.* **2005**, *5*, 1668.

(25) He, J.; Sankey, O.; Lee, M.; Tao, N.; Li, X.; Lindsay, S. *Faraday Discuss.* **2006**, *131*, 145.

(26) van Ruitenbeek, J. M.; Alvarez, A.; Pineyro, I.; Grahmann, C.; Joyez, P.; Devoret, M. H.; Esteve, D.; Urbina, C. *Rev. Sci. Instrum.* **1996**, *67*, 108.

(27) In our MCBJ setup, we push the two Au electrodes, which are coated with molecules, together to form a contact of conductance greater than G_0 prior to breaking the junctions so as to produce the STM-like measurements.

(28) Ohnishi, H.; Kondo, Y.; Takayanagi, K. *Nature* **1998**, *395*, 780.

(29) We fit only the curves that do not drop below our detection limit after the contact breaks. This represents about 75% of curves without molecules (20% in MCBJ experiments) and about 95% of curves with molecules in solution (50% in MCBJ experiments).

(30) We note here that for a quantitative comparison of histograms, it is important to collect data in equimolar solutions of different molecules.

(31) Allen, F. H.; Motherwell, W. D. S. *Acta Crystallogr., Sect. B* **2002**, *58*, 407.

(32) Although this cutoff is arbitrary, it was chosen to keep ∼15% of the data. Varying this cutoff between 0.25 and 0.5 does not qualitatively affect the histograms.

(33) Similar results are also obtained for 6DT and BDMT data, and for BDMT our filtered data reproduces a faint peak-like feature at 0.0006 G_0, in agreement with ref 14.