Reproducible Single-molecule Conductance Measurements of 1,4-Benzenedithiol with Break Junction Methods by Diluting It in a Thin Insulating Monolayer

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We demonstrate here a new sample preparation method satisfying requirements for ideal single-molecule conductance measurements using break junction methods. By diluting a targeted dithiol in an insulating self-assembled monolayer of a short methane thiolate with an adamantane cage on Au(111), we succeeded in constructing reproducible conductance histograms with clear peaks for the dithiol using all measured conductance traces.

Measurements and control of electrical currents through single molecules[1] have been attracting great interest in the field of molecular electronics,[2] in which an individual molecule acts as an active electronic component.[3] Among various methods to measure single-molecule conductance (SMC) values, the mechanically controllable break junction (MCBJ),[4] and the scanning tunneling microscopy based BJ (STM-BJ)[5] techniques have become popular, because these are applicable to various environments, such as gas, solution, and ultrahigh vacuum (UHV). In the BJ methods, conductance traces,[5–9,10a] or *i*–*V* curves[10b,11] have been analyzed statistically. Molecular junctions are usually formed by repeated formation and breaking of a metal point contact in the presence of molecules with two binding groups. During the cycles, the molecules stochastically bridge the gap between two electrodes. Therefore, conductance of such a molecular junction is considered to vary depending on atomic scale details, such as conformation of molecular backbone[6a,7,8,9b] and molecule-electrode contacts.[5c,7a–7c,8,9b,10,11b] In addition to these atomic scale details, the fluctuations in the number of bridging molecules,[7b,8a] tunneling background currents (TBCs),[7c,8a,9a] and the work function (Φ) of the electrodes[12,13] due to the change in coverage of dithiol can be other origins of variability of measured SMC values. To achieve ideal SMC measurements with UHV STM-BJ, it is preferable for samples to satisfy conditions that i) one thiolate of an isolated molecule is anchored to Au(111), while the other end oriented toward vacuum before contact,[8a] ii) a tunneling gap between a gold STM tip and a sample surface has high resistance to reduce the effect of TBC fluctuation during the current flow through the bridging molecule after contact, and iii) Φs of the electrode are kept constant to avoid current fluctuation caused by a relative change in energy levels between the highest occupied molecular orbital (HOMO) of the bridging molecule and the Fermi level of the electrodes during repeated contacts.

To realize such ideal measurements, we diluted conducting dithiol molecules with a SAM of a methane thiolate with a short insulating hydrocarbon cage,[14] rather than long alkanethiols.[11,14d] As such methane thiolates we have used ADT (that with tricyclo[3.3.1.1^{3,7}]decane (adamantane))[14b] and that with bicyclo[2.2.2]octane.[14a] These derivatives form stable SAMs on Au(111) with single-molecular defects that can be used to accommodate a *short* conducting single molecule such as phenylene oligomers.[14c] Here, we applied the previously reported two-step chemical-modification procedure[14c] to dilute the conducting dithiol molecules in the ADT SAM.

Figures 1a and 1b show STM topographic images of diluted and isolated single molecules of 1,4-benzenedithiol (BDT) and 4,4′-biphenyldithiol (BPDT), respectively, in the ADT SAM matrices.[15] Their STM topographic heights reflect the geometric heights as well as tunneling abilities of BDT and BPDT.[14c] Clear image contrast between ADT and BDT with almost the same physical heights reflects the higher tunneling ability of BDT than that of ADT.[16] Therefore, we expected the more reliable determination of SMC values of BDT by diluting it with the ADT SAM. We also expected additional preferable effects such as the stabilization of the Fermi level and the reduction of complexity of the breaking processes in multimolecular junctions.[7b]

In Figure 2 are shown logarithmic conductance histograms[9a] for four kinds of samples, i.e., a bare Au(111) (*Au*), an ADT SAM on Au(111) (*ADT*), diluted BDT molecules in an ADT SAM on Au(111) (*ADT+BDT*), and a BDT SAM on Au(111) (*BDT*) obtained with UHV STM-BJ at room temperature (rt). The histograms constructed from conductance traces measured with HV MCBJ at rt in Leiden were almost the same as those in Figure 2. First, the agreement between the histograms obtained with different methods guarantees reliability of the present sample preparation method for reproducible SMC measurements except *BDT*. The shape of the histograms and the magnitude of the probabilities on *BDT* were not reproducible.[6b] For *BDT*, a relatively well-structured histogram among a large number of obtained ones is shown in Figure 2. Second, all histograms confirm that typical conductance of gold atomic wires of 1, ≈2, and ≈3 G_0 was reproducibly observed after a metal point contact.[4b,5a] Third, the presence of ADT and/or BDT exhibits a peak between 0.1 and 1 G_0, probably due to insertion of $-S^-$ into the single-atomic wire, while no peaks are observed in this conductance range on *Au*. Fourth, the probabilities due to the TBCs is increasing in the order of *Au*, *ADT*, *ADT+BDT*, and *BDT* as we would expect.[7c] Fifth, three peaks with almost the same sep-

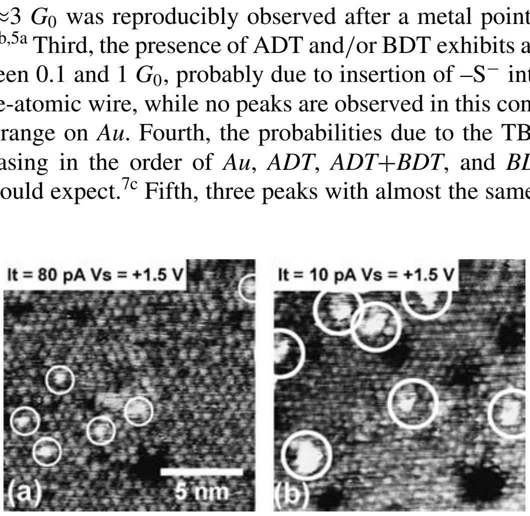

Figure 1. $15 \times 15\,\text{nm}^2$ STM topographic images of (a) BDT and (b) BPDT in ADT SAM matrices.

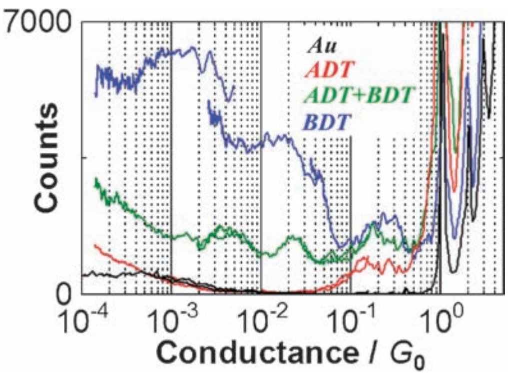

Figure 2. Logarithmic conductance histograms (the bin size: $\Delta\log(G/G_0) = 0.006$)[9a] of various samples constructed from 1000 conductance traces for each.

aration along the logarithmic conductance axis appear in the histogram for *ADT+BDT* or *BDT* in the same way as HC, MC, and LC for all-trans conformer of 1,6-hexanedithiol,[7a,7b] if a peak between 0.1 and 1 G_0 is included. Here, HC, MC, and LC denote high, medium, and low conductance, respectively. The higher probabilities for *ADT+BDT* and *BDT* than those for *ADT* in the HC range support the presence of the conductance peak due to the bridging BDT. The conductance peaks for BPDT in an ADT SAM, the molecular length dependence of currents through phenylene oligomers,[14c] and a report by Tsutsui et al.[11a] also confirm the peak for BDT in the HC range. Finally, the histogram with three peaks corresponding to HC, MC, and LC in comparison with reported histograms without structure on *BDT*[6b] demonstrates effectiveness of the present *ADT+BDT* sample.

The three peaks can be assigned to three different contact modes of i) high–high, ii) high–low (or low–high), and iii) low–low, reported as previously.[7a,7b] For rigid BDT, it is impossible to assign the LC peak to the gauche conformer[9b] as proposed recently for alkanedthiols. If the SMC of Au_1/BDT/Au_2 is described approximately as $G_{\mathrm{sm}} = T_{\text{contact-1}}\cdot T_{\pi\text{-system}}\cdot T_{\text{contact-2}}\cdot G_0$ according to the Landauer equation[13b] and the ratio of $T_{\text{contact}}(\text{high})/T_{\text{contact}}(\text{low})$ is n, the ratios of the three SMC values will be $n^2{:}n{:}1$.[7b] This expectation agrees with the appearance of three conductance peaks with almost the same separation on the logarithmic conductance scale.

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15 The sample was prepared by (a) immersing Au(111) in 1 mM ADT ethanol solution for 10 min, (b) rinsing it with ethanol, (c) blow-drying it with N_2, (d) dipping it in freshly prepared 1 mM ethanol solution of BDT or BPDT for 1 min, (e) repeating (b) and (c).

16 This is rationalized by previously measured ionization potentials (IPs) of phenyl ring and alkane of 6.95[17a] and 8.48 eV,[17b] respectively, against 4.47 eV[12a] of Φ of bare Au(111) in the condensed phases. Thus, the effective barriers[9b] for currents through phenyl- and alkane-HOMO are approximately 2.48 and 4.01 eV, respectively, by ignoring the effect of gold substrate on IPs[3a] and the change in Φ.[12,13a] It can be concluded from this observation that, in the presence of high concentration of BDT in the junction,[6b] the TBCs through the nonbonded BDT surrounding a few bridging BDT is not negligible,[7c] and thus, the apparent measured current through the bridging molecule becomes higher than the true one owing to the TBCs flowing in parallel.[8a] The same is probably true for SMC values in low conductance (LC) range measured in trimethylbenzene.[9b] In nonbonded BDT, only one of the two–SH groups binds to one of the two electrodes like thiol.[13b]

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