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Statistical *I–V* measurements of single-molecule junctions with an asymmetric anchoring group 1,4-aminobenzenethiol*

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Abstract

Molecular diodes are an interesting topic in the field of single-molecule electronics. Rectification of molecules such as 1,4-aminobenzenethiol (ABT) having different contact areas was reported. However, a more statistical approach is necessary to clarify the rectification of the ABT single-molecule junctions. In this research, we statistically measured the single molecular conductance and *I–V* characteristics of ABT single-molecule junctions using the scanning tunneling microscope break junction (STM-BJ) method. Two single molecular conductances caused to difference of bridging geometries were observed in the conductance measurements. Statistically significant rectification was not observed for ABT junctions. We concluded rectification does not appear only due to the difference of two anchoring groups in case of a small conjugate molecule such as ABT.

Keywords: single-molecule junction, *I–V* characteristics, molecular device, molecular diode
Classification numbers: 2.07, 6.01

1. Introduction

Much attention has been focused on achieving a molecular device since Aviram and Ratner proposed a theoretical single-molecule device [1]. Recently, research has progressed due to the development of measurement methods of single-molecule junctions, such as mechanically controllable break junction (MCBJ) technique [2–4] and scanning tunneling microscope break junction (STM-BJ) technique [5]. Functional single-molecule junctions that can work as transistors [6, 7] and switches [8, 9] have also been developed. Single-molecule diodes which were first proposed as molecular devices have also been investigated many times [10–14]. Asymmetric molecular backbones play an important role in the rectification of many molecular diodes that have been reported [10–13].

Rectification character is also expected by asymmetric molecule–electrode interface structure even without asymmetric molecular backbones [15]. Controlling the rectification with anchoring groups is useful in the design of molecules for use in devices. Some attempts to produce molecular diodes with different anchoring groups have been reported [14, 16–18]. Molecules which have different lengths of alkyl chains have functioned as molecular diodes [18]. Venkataraman's group have reported the rectification of single-molecule junctions consisting of a Au–C bond and Au–S bond [14]. 1,4-aminobenzenethiol (ABT) has the most frequently used anchoring groups for the single-molecule junctions, thiol group and amino group [19, 20]. Asymmetric current–voltage (*I–V*) curves of ABT single-molecule junctions were observed in *I–V* characteristics of an ABT single-molecule junction [16]. However, the conductance of single-molecule junctions is easily affected by external noise, shape of electrodes, and the geometries between molecules and metal electrodes [21]. Single molecule conductance should be determined statistically because only one conductance trace is insufficient to

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determine single molecule conductance [5]. It is well known that molecular junctions formed with thiol groups have several conductance states due to different metal-molecule interface geometries [20–24]. Moreover, breaking junction methods have a destructive nature where the metallic contacts formed by the approach of two electrodes are ruptured [25]. This destructive process prevents the precise control of the structures of metal electrodes. A previous report on the asymmetric *I–V* characteristics of symmetric molecules considers that the origin of the rectification is the difference between two metal-molecule interface structures [26]. However, the rectification of an ABT junction is not clear because single *I–V* curves cannot exclude the possibility of conductance change due to changing structure during bias sweeping or due to the presence of different electrode structures. In this research, we measured the conductance and *I–V* characteristics of a Au-ABT single-molecule junction more than 1000 times in order to statistically clarify the rectification of ABT containing different anchoring groups.

2. Experimental

2.1. Sample preparation

ABT was purchased from TCI Japan and was used without further purification. Au(1 1 1) substrate was prepared by thermal deposition of Au on mica at an elevated temperature and under high vacuum. The sample for the *I–V* measurement was prepared by dipping the Au substrate into 1 mM ethanol solution containing the target molecules. After evaporation of the solution, the substrate surface was washed with ethanol.

2.2. Conductance measurement of the molecular junctions

We used a commercially available STM (Nanoscope V, Bruker, Santa Barbara, CA) operating ambient conditions. Two current amplifiers of 1 μA V^{-1} each were used to access wide molecular conductance ranges from 10^{-5} to 10^1G$_0$ ($2e^2/h$). STM tips were prepared by mechanically cutting a Au wire (Nilaco, diameter $\approx$0.3 mm, purity >99%).

2.3. I–V measurement of the molecular junctions

The *I–V* curves of the single molecular junction were obtained by the following procedure (figure 1). First, the STM tip was made to approach the sample surface to make a Au point contact (~10 G$_0$) between the tip and substrate. Second, the tip was withdrawn by 10 nm at a speed of 38 nm s^{-1} to break the Au contact and to make a nanogap between the Au electrodes, resulting in a molecular junction. This process was done while monitoring the current at a fixed bias voltage of 20 mV. Third, the tip position was fixed and one *I–V* curve was recorded by scanning the bias voltage from 20 to 1000, −1000 mV and back to 20 mV within a time period of 10 ms at a constant tip-sample separation. Finally, the junction was broken by pulling the STM tip away from the substrate. In order to capture possible structural variation of the junction

structures, we repeated a cycle of the making and breaking process of the molecular junction and updated the junction-structure after every *I–V* curve. This *I–V* measurement scheme was performed using a signal access module III (Bruker, Santa Barbara, CA) using an external piezo driver (E-665 LVPZT-Amplifier, Physik Instrumente) and a data-acquisition-device with LabVIEW2014 (USB-6363, National Instruments). More than 1000 *I–V* curves of the molecular junctions were collected for each molecule. The *I–V* curves of the molecular junction were obtained by automatically removing *I–V* curves corresponding to Au-metallic junctions and vacuum gap formation. *I–V* curves with <100 nA current at the bias of 1.0 V is classified as vacuum tunneling, while *I–V* curves with >10 000 nA current at the bias of 0.2 V is classified as the charge transport through Au-metallic contact.

3. Results and discussion

Figure 1 shows a schematic illustration of conductance and *I–V* measurements. The Au tip approached the substrate to form a metallic junction. After the tip contacts the substrate, the conductance decreased with a break in the junction on withdrawing the tip. Figure 1 shows the conductance decay in this rupture process of the Au-ABT junction. For *I–V* measurements, the tip was held after breaking the Au atomic junction. At the same time, the bias voltage was swept to obtain *I–V* curves.

The single-molecule conductance measured using the STM-BJ method is shown in figure 2. Figure 2(a) represents the conductance traces during the rupture of the Au-ABT junctions. The conductance traces showed plateaus near 5 mG$_0$ and 13 mG$_0$. It is considered these plateaus represented the single-molecule conductance of Au-ABT junctions [16, 27]. Figure 2(b) represents a conductance histogram of Au-ABT junctions after statistical analysis. The conductance histogram showed two peaks near the conductance of plateaus in the traces. The single-molecule conductance of the Au-ABT junction was determined to be 5 mG$_0$ and 13 mG$_0$. This result is in agreement with previous reports on the conductance measurements of Au-ABT junctions [16, 27]. The possible origin of two single-molecule conductance is difference of orientation of the molecule between metal electrodes mentioned in [16] or absorption structures often observed for thiol molecules such as 1,4-benzenedithiol (BDT) [20–24].

Figure 3 represents the results of the *I–V* measurement of Au-ABT junctions. The examples of *I–V* curves are shown in figure 3(a). The rectification ratios were 2, 1, and 0.5 for a red, black curve, and a blue curve, respectively. Here, the rectification ratio was defined as $|I_{+1V}/I_{-1V}|$. Asymmetric *I–V* curves were observed in addition to symmetric *I–V* curves. The asymmetry of the curve varied with the samples. The rectification histogram which clarifies the asymmetric properties of Au-ABT junctions is shown in figure 3(b). The most common rectification ratio of the Au-ABT junctions was 1. Compared to BDT which has symmetric anchoring groups, Au-ABT junctions showed no significant difference. Based on the rectification analysis of molecular junctions, it was
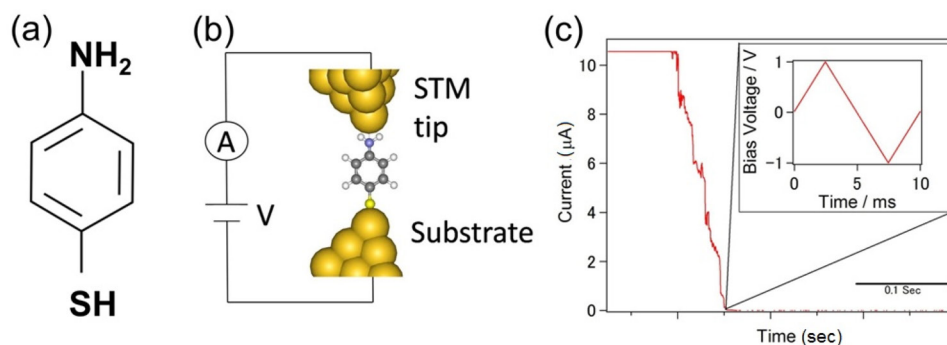
Figure 1. (a) Chemical formula of 1,4- aminobenzenethiol (ABT). (b) Schematic illustration of experimental setup. (c) Schematic illustration for current change as a function of time in one cycle of the *I–V* measurement. After making the metal contact, the contact was stretched at bias voltage of 20 mV. The bias voltage was scanned from 20 mV to 1000 mV, −1000 mV, and back to 20 mV to measure the *I–V* curve of the single-molecule junction after breaking the metal contact. The inset shows bias voltage sweeping during *I–V* measurements.
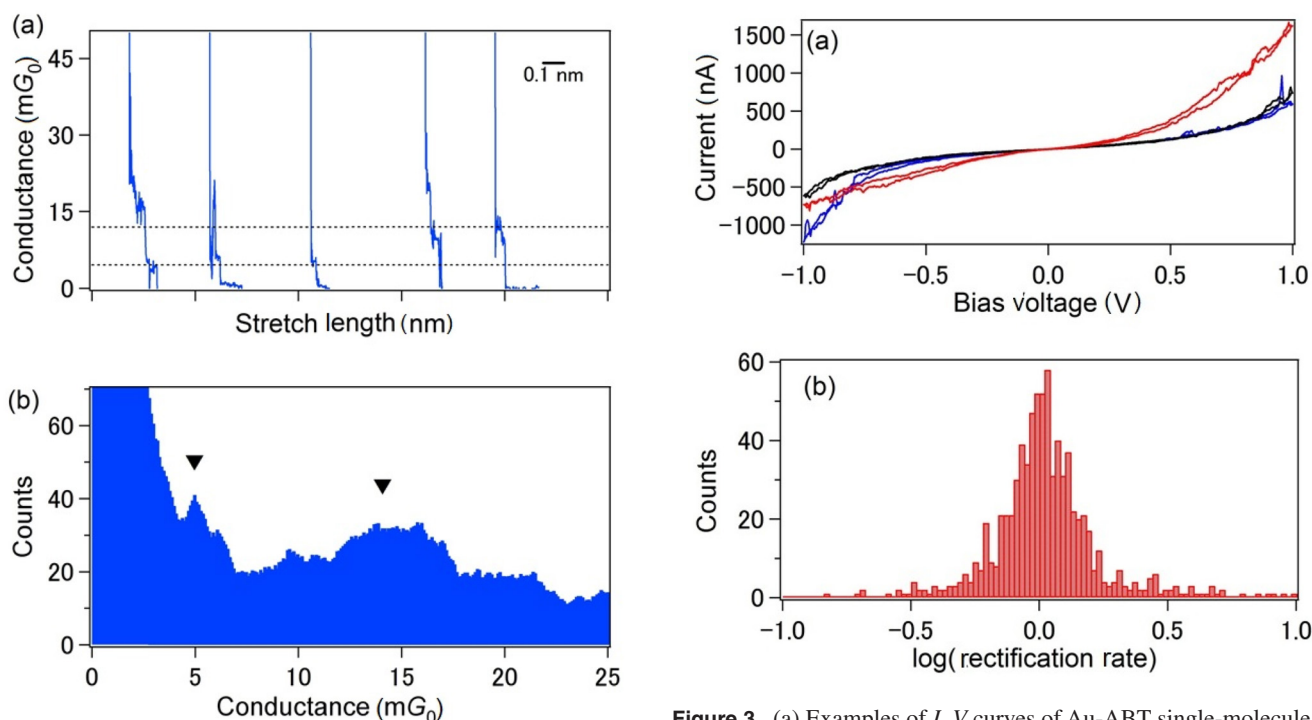

Figure 2. (a) Typical conductance trace of the Au-ABT junction. Each dotted line represents the single-molecule conductance of Au-ABT. (b) Conductance histogram of Au-ABT junctions. The histogram consisted of 300 conductance traces. Bias voltage was 20 mV.

Figure 3. (a) Examples of *I–V* curves of Au-ABT single-molecule junction. (b) Rectification rate histograms of ABT. Rectification rate was defined as |$I_{+1 V}/I_{−1 V}$|. Bin size was calculated as log (rectification rate) and was 0.02.

concluded that the rectification of the Au-ABT junction does not arise from the presence of two different anchoring groups. As shown in figure 3(a), some *I–V* curves of Au-ABT junctions showed a rectification ratio that is more than 2. However, these asymmetric *I–V* curves were also observed for Au-BDT and Au-benzendiamine junctions [24]. Hence, the origin of these rectification properties is not the asymmetric anchoring groups but rather uncontrollable differences such as structural changes of molecular junctions during the conductance sweep or geometric differences between two metal electrodes formed after the metal junctions break.

Statistically significant rectification was not observed in *I–V* curves. It means the conductance does not depend on molecular orientation. Moreover, some conductance traces also suggest that the origin of two conductance states is not the molecular orientation between metal electrodes. A conductance trace in figure 2(a) showed two plateaus. The molecular orientation does not change in one rupture process. It is considered that the appearance of the two peaks in the conductance histogram of STM-BJ is caused not by molecular orientation but by the change in the adsorption structures of the thiol group on the surface of Au electrode during the rupture process.

Here, we discuss the electronic structures of the Au-ABT single molecular junction. Transmission is described as follows for a single channel Breit–Wigner model [16, 17, 22, 28, 29]

$$\tau(E) = \frac{4\Gamma_L\Gamma_R}{(\Gamma_L + \Gamma_R)^2 + (E - \varepsilon)^2},$$

where ε, $\Gamma_{L(R)}$ are the energy of the conduction orbital from Fermi level of Au electrode, and the electronic coupling energy between the molecule and the left (right) electrode, respectively. Here, we assume the bias voltage dependence of conduction orbital level can be described using following equation

$$\varepsilon = \varepsilon_0 + \frac{\Gamma_L - \Gamma_R}{\Gamma_L + \Gamma_R}\frac{eV}{2} .$$

This assumption means that the conduction orbital level of the bridging molecule is significantly affected by a change in the bias voltage of the electrode coupled strongly with the molecule.

When the electronic temperature, T, is set to 0 K, the current through the molecular junction is represented by

$$I(V) = \frac{8e}{h}\alpha(1 - \alpha)$$
$$\times \Gamma\left\{\arctan\left(\frac{\alpha eV - \varepsilon_0}{\Gamma}\right) + \arctan\left(\frac{(1 - \alpha)eV + \varepsilon_0}{\Gamma}\right)\right\},$$

where $\Gamma = \Gamma_L + \Gamma_R$, $\alpha = \Gamma_L/\Gamma$. Note that at 300 K, the temperature effect of the Fermi–Dirac distribution is on the order of several percent on the $I(V)$ [29]. In the case of an asymmetric coupling molecule, the energy level from Fermi level is different between the positive and negative bias. Symmetric coupling does not show any rectification properties. Experimental I–V curves were fitted with the equation shown above, after clustering high state and low state. The I–V curve was distinguished as being in a high state when the conductance at 0.3 V was within the range of 6 mG$_0$ to 19 mG$_0$, and in a low state when the conductance at 0.3 V was in the range of 3.3 mG$_0$ to 5.8 mG$_0$. The range was determined by conductance $\pm 2\sigma$, where σ was the standard deviation of the peak position in the conductance histograms. Figure 4 shows histograms of the fitting results. The coupling of the high state and low state was 83 meV and 56 meV, respectively. The high conductance state had larger coupling. On the other, the position of the conduction orbital was 0.64 eV for the high state and 0.66 eV for the low state. The fitting results support that the two conductance states are caused by difference in absorption structures. This is because it is interpreted that coupling mainly depends on the strength of the contact between the molecule and electrodes and the energy orbital position depends on the molecular backbone. Compared to symmetric molecules, Γ of BDA is 85 meV. BDT has different three conductance states: the largest coupling is 129 meV for the bridge structure and the second largest coupling is 26 meV for the hollow structure. The bridging structures are suspected bridge structure for high conductance state and hollow structure for the low conductance state on comparing the coupling values.

The asymmetric factor, α, for dual coupling was 0.5 for both states. The coupling of the amino group to the Au electrode is as strong as the thiol group in a molecular junction. ABT is a small conjugated molecule which has a molecular orbital that is delocalized throughout the molecule. An anchoring
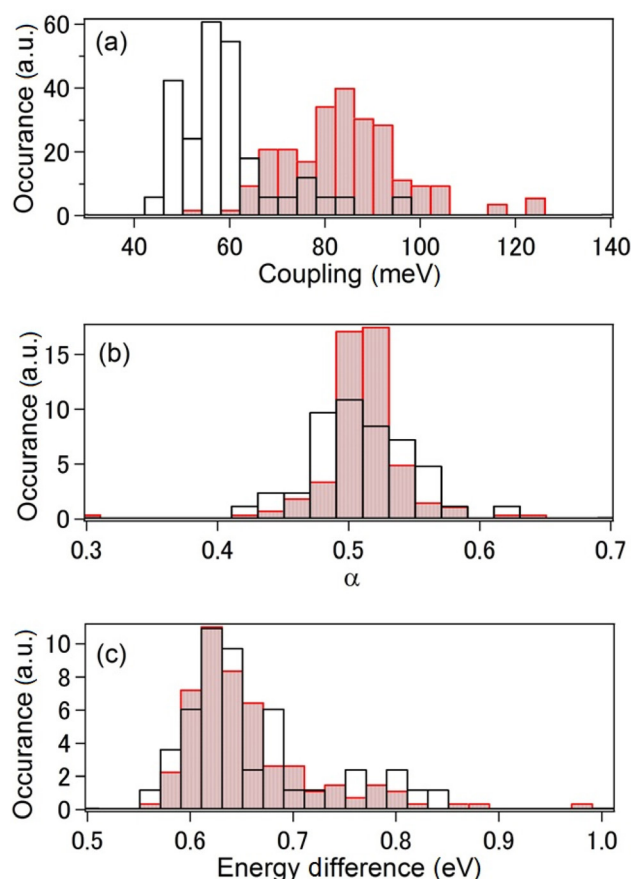

Figure 4. Fitting results of observed I–V curves. Each I–V curve was fitted with single channel Breit–Wigner model after the classified *H* (red) or *L* (black) conductance states. I–V curves were judged as high state when the conductance at 0.3 V was over 6 mG$_0$ and under 19 mG$_0$, and low state when the conductance was over 3.3 mG$_0$ and under 5.8 mG$_0$. (a) Histogram of coupling. Bin size was 4 meV. (b) Histogram of asymmetric factor α. Bin size was 0.02. (c) Histogram of energy difference. Bin size was 0.02 eV.

group could be not independent of any other anchoring group. Therefore, the I–V curves did not show rectification properties due to the coupling being the same, in spite of the presence of different anchoring groups.

4. Conclusions

In this research we statistically measured the single molecular conductance and I–V characteristics of ABT single-molecule junctions using the STM-BJ method. We reproduced an ABT molecular junction having two single molecular conductances as confirmed by the conductance measurements. These two conductance states are caused due to the difference in bridging geometries. Some I–V curves showed rectification. However, the ABT single-molecule junction did not show statistically significant rectification. We concluded that for small conjugate molecules such as ABT, the rectification does not solely occur due to the difference of the two anchoring groups.

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Acknowledgments

References

[1] Aviram A and Ratner M A 1974 *Chem. Phys. Lett.* **29** 277
[2] van Ruitenbeek J M, Alvarez A, Piñeyro I, Grahmann C, Joyez P, Devoret M H, Esteve D and Urbina C 1996 *Rev. Sci. Instrum.* **67** 108
[3] Smit R, Noat Y, Untiedt C, Lang N, van Hemert M V and Van Ruitenbeek J 2002 *Nature* **419** 906
[4] Reed M A, Zhou C, Muller C, Burgin T and Tour J 1997 *Science* **278** 252
[5] Xu B and Tao N J 2003 *Science* **301** 1221
[6] Song H, Kim Y, Jang Y H, Jeong H, Reed M A and Lee T 2009 *Nature* **462** 1039
[7] Xu B, Xiao X, Yang X, Zang L and Tao N 2005 *J. Am. Chem. Soc.* **127** 2386
[8] Kiguchi M, Ohto T, Fujii S, Sugiyasu K, Nakajima S, Takeuchi M and Nakamura H 2014 *J. Am. Chem. Soc.* **136** 7327
[9] Dulic D, van der Molen S J, Kudernac T, Jonkman H T, de Jong J J, Bowden T N, van Esch J, Feringa B L and van Wees B J 2003 *Phys. Rev. Lett.* **91** 207402
[10] Diez-Perez I, Hihath J, Lee Y, Yu L, Adamska L, Kozhushner M A, Oleynik I I and Tao N 2009 *Nat. Chem.* **1** 635
[11] Fu X X, Zhang R Q, Zhang G P and Li Z L 2014 *Sci. Rep.* **4** 6357
[12] Fujii S, Tada T, Komoto Y, Osuga T, Murase T, Fujita M and Kiguchi M 2015 *J. Am. Chem. Soc.* **137** 5939
[13] Zhang N, Lo W-Y, Cai Z, Li L and Yu L 2016 Molecular rectification tuned by through-space gating effect *Nano Lett.* **17** 308
[14] Batra A, Darancet P, Chen Q, Meisner J S, Widawsky J R, Neaton J B, Nuckolls C and Venkataraman L 2013 *Nano Lett.* **13** 6233
[15] Kornilovitch P E, Bratkovsky A M and Stanley Williams R 2002 Current rectification by molecules with asymmetric tunneling barriers *Phys. Rev.* B **66** 165436
[16] Wang K, Zhou J, Hamill J M and Xu B 2014 *J. Chem. Phys.* **141** 054712
[17] Kanthasamy K and Pfnur H 2015 *Beilstein J. Nanotechnol.* **6** 1690
[18] Yuan L, Nerngchamnong N, Cao L, Hamoudi H, del Barco E, Roemer M, Sriramula R K, Thompson D and Nijhuis C A 2015 *Nat. Commun.* **6** 6324
[19] Kim Y, Hellmuth T J, Burkle M, Pauly F and Scheer E 2011 *ACS Nano* **5** 4104
[20] Venkataraman L, Klare J E, Tam I W, Nuckolls C, Hybertsen M S and Steigerwald M L 2006 *Nano Lett.* **6** 458
[21] Li C, Pobelov I, Wandlowski T, Bagrets A, Arnold A and Evers F 2008 *J. Am. Chem. Soc.* **130** 318
[22] Kim Y, Pietsch T, Erbe A, Belzig W and Scheer E 2011 *Nano Lett.* **11** 3734
[23] Kaneko S, Murai D, Marques-Gonzalez S, Nakamura H, Komoto Y, Fujii S, Nishino T, Ikeda K, Tsukagoshi K and Kiguchi M 2016 *J. Am. Chem. Soc.* **138** 1294
[24] Komoto Y, Fujii S, Nakamura H, Tada T, Nishino T and Kiguchi M 2016 *Sci. Rep.* **6** 26606
[25] Frei M, Aradhya S V, Hybertsen M S and Venkataraman L 2012 *J. Am. Chem. Soc.* **134** 4003
[26] Guo S, Hihath J, Diez-Perez I and Tao N 2011 *J. Am. Chem. Soc.* **133** 19189
[27] Tsutsui M, Taniguchi M and Kawai T 2009 *J. Am. Chem. Soc.* **131** 10552
[28] Zhang G, Ratner M A and Reuter M G 2015 *J. Phys. Chem.* C **119** 6254
[29] Matsuhita R, Horikawa M, Naitoh Y, Nakamura H and Kiguchi M 2013 *J. Phys. Chem.* C **117** 1791