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## Conductance of single 1,4-disubstituted benzene molecules anchored to Pt electrodes

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The authors have studied the conductance of a 1,4-disubstituted isocyanide(–NC) or thiol(–SH) benzene molecule anchored to two Pt electrodes. A single molecular junction showing a well-defined conductance value ( $\sim 3 \times 10^{-2} G_0$ ,  $G_0 = 2e^2/h$ ) was fabricated with the Pt electrodes. The conductance of the molecular junction was one order higher than the previously documented value using Au electrodes. These observations could be explained by differences in the local density of states of the contact metal atom at the Fermi level and the extent of the hybridization and energy difference between the molecular and metal orbitals. Further insight into the binding strengths of the metal-anchoring group bond was obtained by statistically analyzing the stretching length of the molecular junction. © 2007 American Institute of Physics. [DOI: 10.1063/1.2757592]

There is a growing interest in the electron transport properties through single molecules due to their potential use in ultrasmall electronic devices.<sup>1</sup> In studying the electron transport properties through a single molecule, it is important to design an appropriate molecule-electrode contact, since the contact plays a decisive role on the electron transport process through the molecule. Conductance measurements have been investigated for various single molecules using scanning tunneling microscope (STM) and mechanically controllable break junctions.<sup>1–3</sup> In most of the studies, the Au–S bond is used to connect molecules to metal electrodes because stable molecular junctions can be easily obtained with this Au–S covalent bond. On the other hand, the conductance of a single molecular junction depends on the extent of the hybridization and energy difference between the molecular and metal orbitals and the local density of states (LDOS)  $\rho$  of the contact metal atoms at the Fermi level  $E_F$ .<sup>4</sup> An effective hybridization and a small energy difference between the molecular and metal orbitals, and also large  $\rho$  of the contact metal atom at  $E_F$  are essential for the molecular junction to achieve high conductivity. Generally, the energy of the molecular orbital varies, depending on the molecule and its anchoring group. The  $\rho$  of Au is relatively low compared with other *d*-orbital metals at  $E_F$  because of their *sp* state characteristics. Therefore, the Au–S bond is not always the best anchoring group for the single molecular junction showing high conductivity. It is important to develop a pair of metal and anchoring group other than Au–S to establish highly conductive single molecular junctions.

In developing anchoring groups, the conductance of single molecules anchored by isocyanide (–NC),<sup>5</sup> carboxylic acid (–COOH),<sup>6</sup> or amine (–NH<sub>2</sub>) (Ref. 7) anchoring groups to Au electrodes has been studied. Still, the metal of the electrode is restricted to Au. In spite of the variation in the choice of molecules, there have been few studies of single molecular junctions using metals other than Au. Among various metals, we pay attention to Pt for the following three

reasons. First, Pt is chemically stable, which is essential for preparing a clean surface on the metal electrodes. Second, air stable thiol and isocyanide self-assembled monolayer (SAM) films are formed on Pt surfaces.<sup>8</sup> The formation of stable SAMs indicates that the stable Pt–S or Pt–CN bond is formed and molecules are not decomposed on a Pt surface. Third, the  $\rho$  is high for Pt compared with Au at  $E_F$ , since a narrow *5d* band is located at  $E_F$  for Pt.<sup>9</sup> The conductance of a single molecule anchored to the Pt electrodes would be higher than that of the Au electrodes due to the high  $\rho$  of Pt. Recent theoretical calculations show promise for high conductivity of the molecular junctions with Pt electrodes.<sup>10,11</sup> The calculated conductance of the molecular junction binding a benzene molecule to Pt electrodes by thiol or isocyanide coordination was estimated to be one order higher than that of the Au electrodes.<sup>10,11</sup>

In the present study, the effect of the metal and anchoring group on the conductance of single molecular junctions was investigated for 1,4-disubstituted (–NC– or –S) benzene molecules anchored to two Pt or Au electrodes. The metal-anchoring group bond strength was qualitatively estimated by the distance over which the molecular junction was stretched before breakdown. The conductance of the single molecular junction is discussed, considering a simple tunneling model.

The experimental design used in this study was the same as described in our previous report.<sup>5</sup> A sharp tip was used, comprising a Pt wire (diameter of  $\sim 0.25$  mm,  $>99.9\%$ ). The substrate was Pt(111), prepared by flame annealing and quenching method.<sup>12</sup> The measurements were carried out in tetraethyleneglycol dimethyl ether (tetraglyme). The solution contained 1mM 1,4-diisocyanobenzene and 1,4-benzenedithiol. A STM tip was repeatedly moved into and out of contact with a metal substrate at a rate of 50 nm/s in the solution. Respective molecules terminated with two isocyanide or thiol anchoring groups can bridge the tip and the substrate electrodes via their anchoring groups. Conductance was measured during the breaking process under an applied bias of 20 mV between the tip and substrate.

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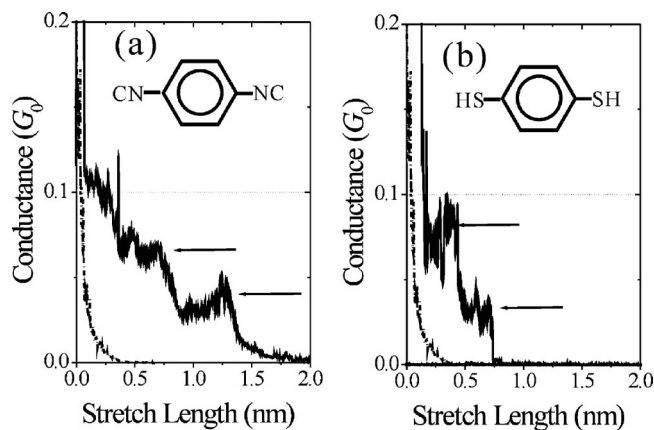


FIG. 1. Typical conductance traces of Pt contacts during breaking the contact in a tetraglyme solution containing (a) 1,4-diisocyanobenzene and (b) 1,4-benzenedithiol. The dotted line shows the result in the absence of molecules.

All statistical data were obtained from a large number (over 1000) of individual conductance traces.

Figures 1 and 2 show the typical conductance traces and histograms of the Pt contacts during breaking the contact in a tetraglyme solution, with and without 1mM 1,4-benzenedithiol or 1,4-diisocyanobenzene. In the absence of molecules, neither plateaus nor peaks were observed both in the conductance traces and histograms (see Figs. 1 and 2). In solution containing the molecules, there are two characteristics in the conductance traces. First, the conductance trace shows a conductance fluctuation, which would originate from the structural transformation of the molecular junction.<sup>13</sup> Second, the trace shows a plateau in which the conductance is nearly constant (arrow in Fig. 1), and the conductance value of the plateau is an integer multiple of  $\sim 3 \times 10^{-2} G_0 (=2e^2/h)$ . The corresponding histogram shows a feature at  $3 \times 10^{-2} G_0$  [see Figs. 2(a) and 2(b)]. The last plateau before the contact is broken in the conductance trace and a peak observed in the conductance histogram likely originates from the formation of stable single Pt/1,4-benzenedithiol/Pt and Pt/1,4-diisocyanobenzene/Pt junctions. The conductance of a single molecular junction was determined to be  $3 \times 10^{-2} (\pm 1 \times 10^{-2}) G_0$  for both molecular junctions. A benzene molecule is possibly bound to Pt atoms via

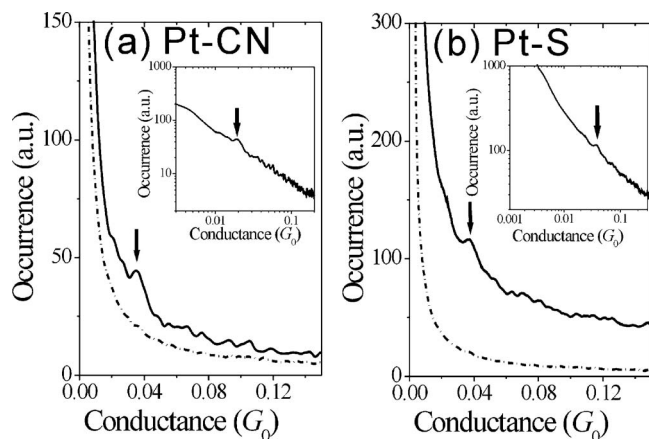


FIG. 2. Conductance histogram of Pt point contacts broken in the tetraglyme solution containing (a) 1,4-diisocyanobenzene and (b) 1,4-benzenedithiol. The dotted line shows the result in the absence of molecules. The insets show the conductance histograms shown on a log-log plot.

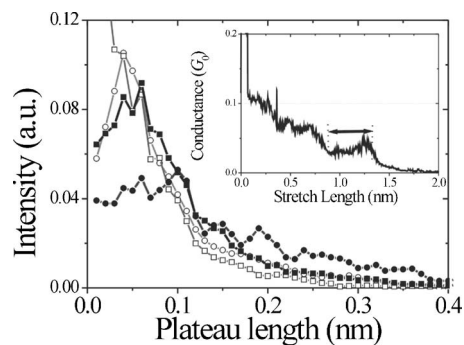


FIG. 3. Distribution of lengths for the last conductance plateau for Pt-S (filled circle), Au-S (circle), Au-CN (box), and Pt-CN (filled box). The inset shows the typical conductance trace for the 1,4-diisocyanobenzene junction on Pt electrodes. The plateau regime is shown by the arrows. The length of the last conductance plateau was defined as the distance between the points (set points) at which the conductance dropped below  $4 \times 10^{-2} G_0$  and  $3.0 \times 10^{-2} G_0$  for the molecular junctions with the Pt-S bonds. The set points were  $4.3 \times 10^{-2} G_0$  and  $2.7 \times 10^{-2} G_0$  for the Pt-CN bond,  $4.8 \times 10^{-3} G_0$  and  $3.0 \times 10^{-3} G_0$  for the Au-S bond, and  $3.2 \times 10^{-3} G_0$  and  $2.0 \times 10^{-3} G_0$  for the Au-CN bond, respectively.

S atoms for the Pt/1,4-benzenedithiol/Pt junction. For the Pt/1,4-diisocyanobenzene/Pt junction, isocyanide coordination via C atoms may contribute to the junction formation. In the following, these molecular junctions are referred to as the molecular junction with the Pt-CN bond and the molecular junction with the Pt-S bond, respectively. In our previous study, the conductance of the molecular junction was determined to be  $4 \times 10^{-3} (\pm 1 \times 10^{-3}) G_0$  for the junction with the Au-S bond and  $3 \times 10^{-3} (\pm 1 \times 10^{-3}) G_0$  for the junction with the Au-CN bond. Present results prove that the conductance of the single molecule junction with the Pt electrodes is one order higher than that with the Au electrode.

Before discussing the conductance of the single molecular junction in detail, the metal-anchoring group bond strength is discussed by statistical analysis of the conductance trace. Since the last plateau corresponds to a single molecular junction,<sup>5,14</sup> the length of the last plateau should be the distance over which the single molecular junction can be stretched before breakdown (breakdown distance). The breakdown distance reflects the stability of the molecular junction and the strength of the metal-anchoring group bond.<sup>5</sup> To evaluate characteristics of the breakdown distance quantitatively, the distribution of the breakdown distance of the molecular junction was investigated (Fig. 3). For comparison, the results obtained by the Au-S and Au-CN bonds in our previous reports<sup>5</sup> are also shown in the figure. The average length of the molecular junction was 0.16 ( $\pm 0.02$ ) nm for the junction with the Pt-S bond, 0.11 ( $\pm 0.01$ ) nm for the Pt-CN bond, 0.090 ( $\pm 0.009$ ) for the Au-S bond, and 0.064 ( $\pm 0.006$ ) nm for the Au-CN bond. Since the stretching length reflects the bond strength of the molecular junctions,<sup>5</sup> the present results suggest that the strength of the metal-anchoring group bond decreased in the order of Pt-S, Pt-CN, Au-S, and Au-CN.

Based on the above experimental results, the conductance of the single molecular junction will now be discussed. The experimentally obtained conductance values of a single molecular junction can differ by two orders of magnitude among various reports, even for the same molecule, due to different experimental conditions.<sup>2,15</sup> Generally, it is difficult to compare the conductance of single molecular junction of

different molecules measured under different conditions. On the other hand, statistical analysis of the present data showed that the conductance values of a single molecular junction measured under the same conditions could be determined to a precision of 30%.<sup>5</sup> Thus, the comparison of the conductance values of the single molecular junction with Au and Pt using our results measured under the same condition may provide information on the metal dependence. Our series of recent studies<sup>5</sup> show that the conductance of the molecules anchored to the Pt electrodes was one order higher than those of the Au electrodes, while the conductance showed little dependence on the choice of the anchoring groups. Recently, the conductance of single benzene molecule anchored by S or NC anchoring groups to Au and Pt electrodes has been calculated, considering the tunneling model<sup>10,11</sup> Similar tendencies in the conductance differences among the single molecular junctions with the Au-S, Au-CN, Pt-S, and Pt-CN bonds were observed for both calculations and in our experimental results, although the calculated conductance values are about ten times higher than the experimental ones. Observed conductance differences in the systems of the 1,4-disubstituted (-CN or -SH) benzene molecules anchored to two Pt or Au electrodes can be discussed, considering the tunneling model.

In a simple tunneling model,<sup>4</sup> the conductance [ $G(E)$ ] of the single molecular junction is given by  $T(E) = A((\beta^2 \rho / E - \varepsilon_i))^2$ , where  $A$ ,  $\beta$ ,  $\rho$ , and  $\varepsilon_i$  are the constant, hopping integral between the molecule and metal orbitals, local density of states value of the contact metal atom at the  $E_F$ , and the energy of the  $i$ th molecular orbital, respectively. Here,  $\beta$  increases with the bond strength.<sup>5</sup> Large  $\rho$ ,  $\beta$ , and small  $E_F - \varepsilon_i$  are essential for molecular junctions showing high conductivity. The  $\rho$  of Pt is much larger than the  $\rho$  of Au at the  $E_F$ .<sup>8,16</sup> Statistical analysis of the stretching length of the molecular junction showed that the binding energy of Pt-S and Pt-CN bonds was larger than that of Au-S and Au-CN bonds, suggesting that the  $\beta$  of the junction with the Pt electrode is larger than that with the Au electrode. Due to relatively large  $\rho$  and  $\beta$  for the junction with the Pt electrode, the conductance of the molecular junction with the Pt electrode would be one order higher than that with the Au electrode. Higher conductivity in the Pt electrode than that of the Au observed in the present experiment can be explained by these contributions of  $\rho$  and  $\beta$ .

Here, we briefly comment on the fact that the conductance of the molecular junction with the Pt-S bond was close to that with the Pt-CN bond. The value of  $E_F - \varepsilon_i$  varies with the choice of the anchoring group, and it would also affect the difference in the conductance between the molecular junction with the Pt electrode and Au electrode. The stretching length of the molecular junction showed that the binding energy ( $\beta$ ) of the Pt-S bond was larger than that of the Pt-CN bond. Since the conductance is obtained as the product of  $\beta^2$  and  $1/(E_F - \varepsilon_i)$ , the close agreement between the conductance of the molecular junction with the Pt-S and Pt-CN bonds indicates that energy difference between molecular and metal orbitals would be larger for the junction with the Pt-S bond than for the Pt-CN bond.

The present experimental study clearly showed that  $\rho$ ,  $\beta$ , and  $E_F - \varepsilon_i$  play the decisive role in determining the conductance of the single molecule. In developing an electronic device with a single molecule, it is becoming important to study electron transport through a single molecule with a high degree of functionality.<sup>1</sup> The three factors depend on the choice of the molecules and the electrode metals. By considering these three factors in choosing the best electrode metal for the individual molecules, the conductance of the single molecule junction would be drastically improved, which leads to a higher performance for the molecular devices. Finally, the effect of the catalytic behavior of Pt on the single molecular junction is briefly discussed. Various catalytic reactions occur on the Pt surface due to its high catalytic reactivity.<sup>17</sup> If an organic molecule is adsorbed strongly in uncontrolled manner on the Pt electrode, the molecule cannot be used for the single molecular junction. On the other hand, by introducing the anchoring groups to the target molecule, the molecule is bound to the metal surface via the anchoring group. The molecule is in contact with the metal surface having well-defined adsorbed structure. Choosing appropriate anchoring group should be very important to control the adsorption of the molecule for the single molecular junctions.

In conclusion, we fabricated well-defined molecular junctions with Pt-S and Pt-CN bonds. The conductance of the molecular junctions with the Pt electrodes was one order higher than that with the Au electrodes. A Pt metal is a promising choice for a single molecular junction.

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