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Short Communication

The Conductance of Pyridine-Based Molecules Measured in Ambient Air and Electrolyte Solution: Effect of Surrounding

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In this work, we have investigated the single-molecule conductance of pyridine-based molecules using STM break junctions with new developed preamplifier constructed by four-out linear current-to-voltage converters. The influence of surrounding on the single-molecule conductance was carried out in ambient air and electrolyte solution. While $10^{-3.2}$ G_0 and $10^{-3.8}$ G_0 are found for BPY, BPY-EE gives out $10^{-3.4}$ G_0 and $10^{-4.2}$ G_0 in ambient air. In electrolyte solution, the single-molecule conductance is $10^{-3.0}$ G_0 and $10^{-3.7}$ G_0 for BPY, and $10^{-3.2}$ G_0 and $10^{-4.0}$ G_0 for BPY-EE. The conductance values of these molecules in electrolyte solution are larger than that in ambient air, which can be contributed to the different Fermi level of electrode in various surrounding.

Keywords: STM break junction, metal-molecule-metal junctions, surrounding, pyridine

1. INTRODUCTION

Single-molecule junctions has received lots of attentions, for its potential application in the molecular electronics [1-3]. While the intrinsic property of single-molecule junctions, such as molecular structure, contact between electrode and anchoring group, were improved to have the effect on the conductance [2,3], many attentions were also paid to the surrounding of single-molecule junctions [4]. The electron transport of such junctions may be altered by pH [5], photo [6-8], temperature [9], ion [10,11] and so on. However, the important role of electrolyte solution is less reported.

The existing of the solution may have effect on the Fermi level of the electrode, which may alter the energy coupling of the molecule and electrode [12]. In electrolyte solution, potential may applied on the electrode for there is bias between the two electrodes. This would have influence on the single-molecule conductance. Pyridine molecule can bind to the metal electrode (such as Au, Cu, Ag and Ni) through pyridine group [13-17], and is the most widely investigated molecule.

The single-molecule conductance can be measured by scanning tunneling microscopy break junctions (STM-BJ) [15,17-20], mechanically controlled break junctions (MCBJ) [15,21,22], conducting atomic fore microscopy [23], scanning tunneling microscopy trapping[24], and electromigration [25,26]. Among of them, STM-BJ can easy get the statistical result, which received the most attention in single-molecule conductance.

In this article, we measure the single molecule conductance of 4,4’-bipyridine (BPY), 1,2-di(pyridin-4-yl)ethene (BPY-EE) in air and electrolyte solution, by using new developed STM preamplifier with four channels. The influence of different surrounding on single-molecule junctions will be also discussed.

2. EXPERIMENTAL SECTION

4,4’-bipyridine (BPY) was purchased from Alfa Aesar, while 1,2-di(pyridin-4-yl)ethane (BPY-EE) and $NaClO_4$ were purchased from Sigma-Aldrich.

Au(111) is naturally formed on the single crystal beads through Clavilier’s method [27]. Prior to each experiment, the Au (111) substrate was electrochemically polished and annealed in a hydrogen flame, then cooled with protection of N_2. After that, Au(111) was immersed in aqueous solution containing 0.5 mM target molecules (BPY or BPY-EE) for 5 min and then in water for 5 min. Mechanical cut Au wire was used as STM tip, which was insulated in the electrolyte solution.

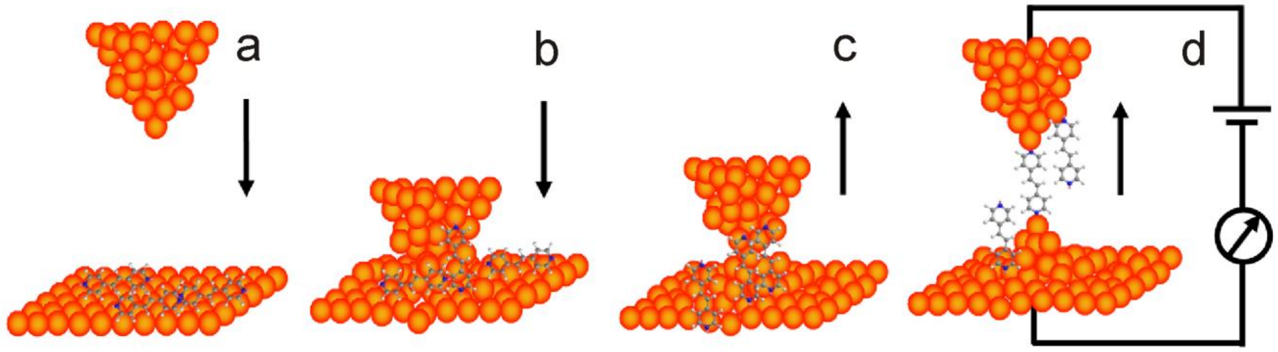

Figure 1. Schematic diagram of conductance measurement of single molecular junctions with Au electrode measured by the STM-BJ approach.

The conductance measurement was carried out on a modified Nanoscope IIIa STM (Veeco, U.S.A.) by using STM-BJ [19,28,29]. Comparing with the preamplifier with single-out linear current-to-voltage converter in our early studies [19,20,29], preamplifier with four-out linear current-to-voltage converters was designed and used in this work. The procedure of conductance measurement was as follows: Firstly, the Au(111) was imaged by normal STM mode, STM feedback was disabled till there was neglectable drift of STM image. Then, the Au tip was driven away from the Au(111) substrate for several tens nanometers and toward the substrate (Figure 1a), and the contact could be formed between tip and substrate (Figure 1b). The STM tip was pulled out of contact with speed of 20 nm s^{-1}, while the four channels of tip current were recorded at a sampling frequency of 20 kHz for per channel by AD card. This process was repeatedly performed to obtain a large number of conductance–distance curves. The four channels were multiplication by the gain factor, and then were combined in the linear scale. The histogram was constructed after the current curves were treated by the logarithm and binning.

3. RESULTS AND DISCUSSION

3.1. Single-molecule conductance of BPY and BPY-EE measured in air

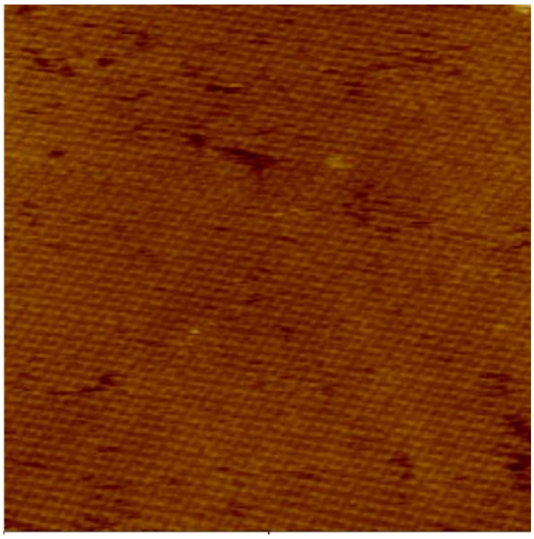

Figure 2. STM image (50 nm × 50 nm) of BPY-EE self-assembled on Au(111). The image was recorded in ambient air conditions under constant current with a setpoint of 1 nA and sample bias of 0.3 V.

The single-molecule conductance of BPY-EE was firstly carried out by the STM-BJ in ambient air. Au(111) with self-assembly monolayer was imaged, and order structure was observed (Figure 2). Those structure is completely different from the clean Au(111) substrate, and shows that BPY-EE has been assembled on the Au(111). We focus the conductance measurement of BPY-EE and will not discuss the detail of the ordered SAM.

The typical conductance curves show steps at multiplied 1 G_0, which is the Au quantized conductance (Figure 3a). After sharp decrease conductance upon the breaking off of the Au point contact, the plateaus at around $10^{-3.4}$ G_0 (31 nS) can be seen from Figure 3b, meanwhile the steps around $10^{-4.2}$ G_0 (4.9 nS) are also often seen. These features can be attributed to the formation of BPY-EE molecular junctions. We define $10^{-3.4}$ G_0 as high conductance value (HC), while $10^{-4.20}$ G_0 as low conductance value (LC).

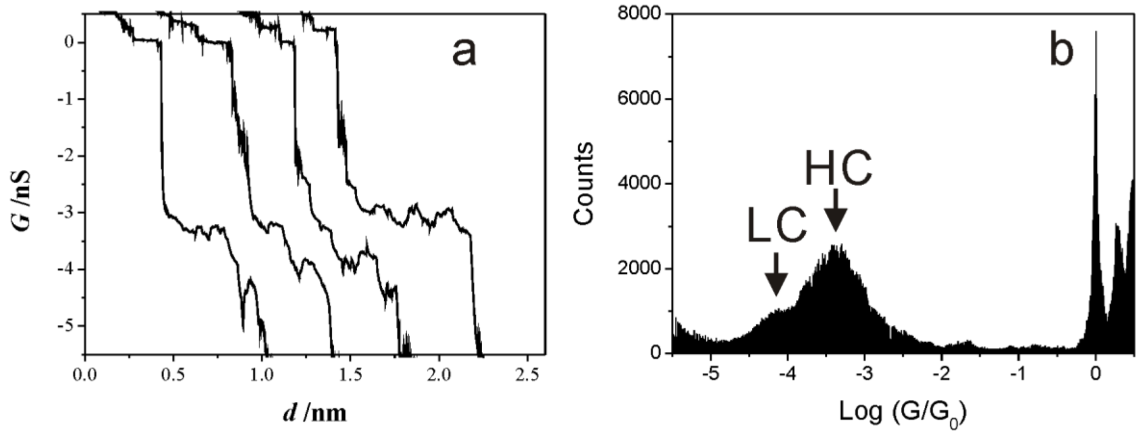

Figure 3. (a) Typical conductance curves and conductance histogram of Au-(BPY-EE)-Au junctions measured in ambient air conditions.

Those values are comparable with literature's reports with conductance values of $10^{-3.6}$ G_0 (19.4 nS) and $10^{-4.2}$ G_0 (4.9 nS) in 1,2,4-trichlorobenzene solution [14,30], which demonstrate the reliability of four-out linear current-to-voltage converters on the conductance measurement of single-molecule junctions. The two sets of conductance values are caused by the different contact conformation between pyridine and Au [15,31].

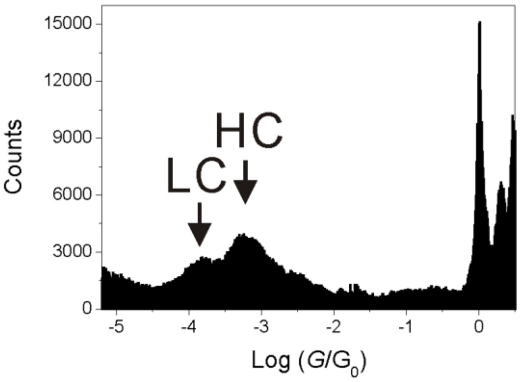

Figure 4. Conductance histogram of Au-BPY-Au junctions measured in ambient air condition.

The single-molecule conductance of Au-BPY-Au junctions was also carried out in ambient air. Figure 4 gives out the single-molecule conductance of $10^{-3.2}$ G_0 (HC, 49 nS) and $10^{-3.8}$ G_0 (LC, 12 nS) for BPY. Those values are also similar with those reported by Quek et al and Kamenetska (46 nS and

12 nS) [16,30], Wang et al (584 nS, 42 nS and 10 nS) [32], which is also consistent with our previously report (350 nS, 45 nS and 14 nS) [13]. The conductance ratio between BPY and BPY-EE is about 2.5, which is almost the same as our previously report [31]. Comparing the one order magnitude decrease conductance value upon insertion of C-C bond on BPY [13], the conductance value only decreases a little from BPY to BPY-EE (insertion of C=C bond). The reason is that the BPY-EE keeps good π coupling comparing with the BPY on the insertion of C=C bond, while the C-C bond destroys the π coupling [31].

3.2. Single-molecule conductance of BPY and BPY-EE measured in electrolyte solution

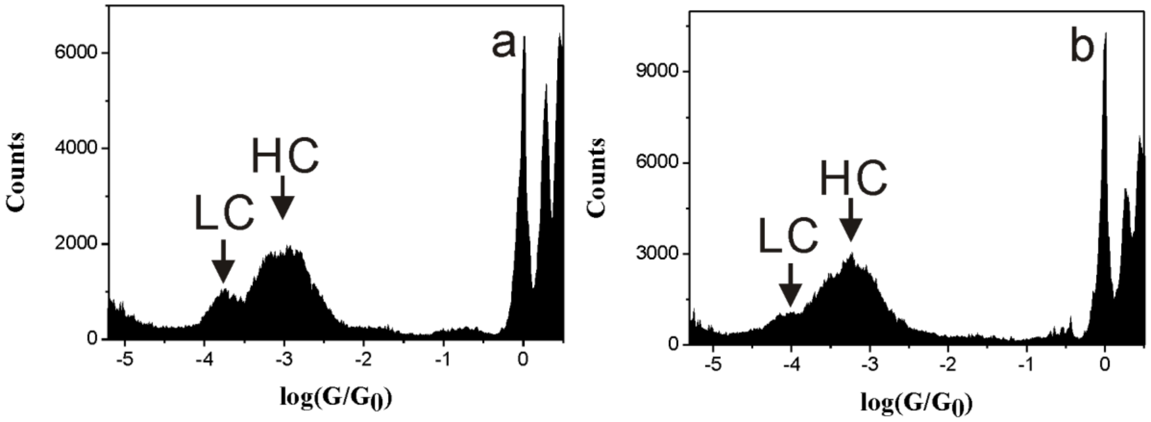

Figure 5. Conductance histogram of (a) Au-BPY-Au and (b) Au-(BPY-EE)-Au junctions measured in aqueous solution containing 50 mM $NaClO_4$.

In order to compare the influence of surrounding, the single-molecule conductance of BPY and BPY-EE molecules were also performed in aqueous solution containing 50 mM $NaClO_4$ and 0.5 mM BPY or BPY-EE. The STM tip was insulated to reduce the faradic current in electrolyte solution. Two sets of conductance values were also found in the solution. Figure 5 gives out the single-molecule conductance of $10^{-3.0}$ G_0 (77 nS) and $10^{-3.7}$ G_0 (15 nS) for BPY, and $10^{-3.2}$ G_0 (49 nS) and $10^{-4.0}$ G_0 (7.7 nS) for BPY-EE.

We studied the BPY and BPY-EE by using single-out linear current-to-voltage converter in the same solution [13]. The results gave out 350 nS, 45 nS and 14 nS for BPY and 163 nS, 20 nS and 6 nS for BPY-EE. Comparing the two sets of conductance values found in this study, three sets of single-molecule conductance values were found, the difference may caused by the different statistical method for constructing histogram. Those values are also different from BPY and BPY-EE molecules contacting to Ag electrode, which were investigated by an electrochemical jump-to-contact scanning tunneling microscopy break junction approach [33]. The reason is that there are different electronic coupling efficiencies between the molecule and electrodes in those experiments [33,34].

3.3. The influence of the surrounding on the single-molecule conductance

Now we will focus on the influence of surrounding on the single-molecule conductance. Taking Au-BPY-Au as example, the single-molecule conductance in electrolyte solution ($10^{-3.0}$ G_0 for HC and $10^{-3.7}$ G_0 for LC) is larger than that in ambient air ($10^{-3.2}$ G_0 for HC and $10^{-3.8}$ G_0 for LC) for both HC and LC. The situation is same for Au-(BPY-EE)-Au junctions.

It was reported that the single-molecule conductance of BPY and BPY-EE can be gated in electrochemistry [14,35,36]. The Fermi level of electrode can be changed by the potential, which can alter the energy coupling between Fermi level of electrode and forint energy level of molecule. Thus the Fermi level of Au in electrolyte solution should be different from that in ambient air for the applied bias between tip and substrate, which gives out the conductance values with little change. On the other hand, solvents, such as water, were also reported to change the transport resonances between molecule and electrode [37]. Those aspects may cause the different conductance value between air and electrolyte solution.

4. CONCLUSIONS

We have measured the single-molecule conductance of BPY and BPY-EE in ambient air and electrolyte solution. Two sets of conductance values were found for both molecules. The conductance values of these molecules in electrolyte solution are larger than that in ambient air, which can be contributed to the different Fermi level of electrode in different surrounding.

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