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The Influence of Conjugated Bond on Single Molecule Conductance of Carboxylic Acids Measured by Electrochemical Jump-To-Contact Scanning Tunneling Microscopy Break Junction

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In this article, we studied the conductance measurement of alkenedicarboxylic acid containing ethene contacting to the various metal electrodes by electrochemical jump-to-contact scanning tunneling microscopy break junction approach (ECSTM-BJ). The single molecule conductance values of fumaric acid show the order of Cu＞Ag＞Au, which is similar as conductance values of succinic acid. A consistent result is also found for trans-β-hydromuconic acid and adipinic acid. Those may attribute to the similar electronic coupling between the molecule and electrode.

Keywords: ECSTM-BJ, metal-molecule-metal junctions, carboxylic acid, Cu, Ag

1. INTRODUCTION

Understanding the charge transport of single metal-molecule-metal junctions is fundamental interest to the future molecular electronic devices [1-12]. Typically, the conductance of single molecule junctions is influenced by the intrinsic nature of the molecular structure and molecule-electrode contact [3,5]. The former aspect includes the conjugated or unconjugated backbone of molecule, molecular conformation and substitutional group besides backbone[3,4,13,14], and the latter aspect is influenced by the anchoring groups, electrodes, and contact configuration between them [1-3,15-20]. Generally, these can control the charge transport through changing the electronic coupling between the metal and molecule [15-20]. While the influence of insertion of unconjugated bond to the

π delocalization system on single molecule conductance has been received much attention [2,21], the replacing of saturated bond with the conjugated bond in satureated system is less reported.

Many kinds of methods have been used to measure the single molecule conductance, such as STM break junction (STM-BJ) [1,3,22-25] and mechanically controllable break junction (MCBJ) [22,26-28]. Specifically, electrochemical methods are proven to be a unique tool in this aspect, and can produce device with nanogap [29,30] or use the reference electrode as a gate to control the charge transport through the junctions [23,31-33]. Recently, an electrochemical jump-to-contact scanning tunneling microscopy break junction approach (ECSTM-BJ) was developed by us, and can be used for conductance measurement of the atomic-size nanowires [34,35] and single molecular junctions [36,37] with different metallic electrodes. In this approach, metal can be in-situ deposited on the tip from the solutions containing target metal ion.

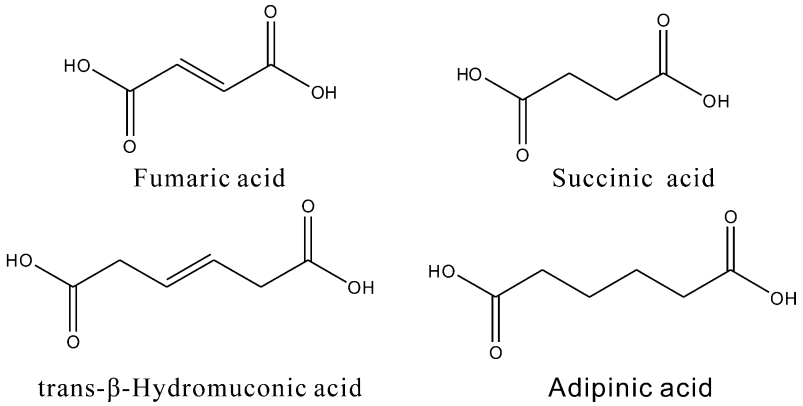


Figure 1. Molecular structures of the fumaric acid, succinic acid, trans-β-hydromuconic acid, adipinic acid.

Here, we report the conductance measurement of alkenedicarboxylic acid containing ethane (as shown in figure 1) contacting to the various metal electrodes by ECSTM-BJ. The carboxylic acid can bind to the metal through the carboxylate group ($-COO^-$) [38], and carboxylic acid based molecules are widely used in electrochemistry [39,40]. The comparison between the alkenedicarboxylic acid and alkanedicarboxylic acid is also discussed.

2. EXPERIMENTAL SECTION

Na_2SO_4 (99.9955%), $CuSO_4$ (99.999%), and Ag_2SO_4 (99.999%) were purchased from Alfa-Asia, trans-β-hydromuconic acid from Sigma-Aldrich and fumaric acid from Aladdin, all of them were used as received, without further purification. Ultrapure water (>18 MΩ cm) was used for preparing aqueous solutions.

The electrochemical jump-to-contact scanning tunneling microscopy break junction approach (ECSTM-BJ) was carried out on a modified Nanoscope IIIa STM (Veeco, US) as our previously

reports [34,36,37]. Au(111) and Pt-Ir wire were used as the substrate and tip, respectively. The substrate was annealed in a hydrogen flame before experiment and tip was insulated by the thermosetting polyethylene glue. Pt and Cu/Ag wire were used as the counter and reference electrode, respectively.

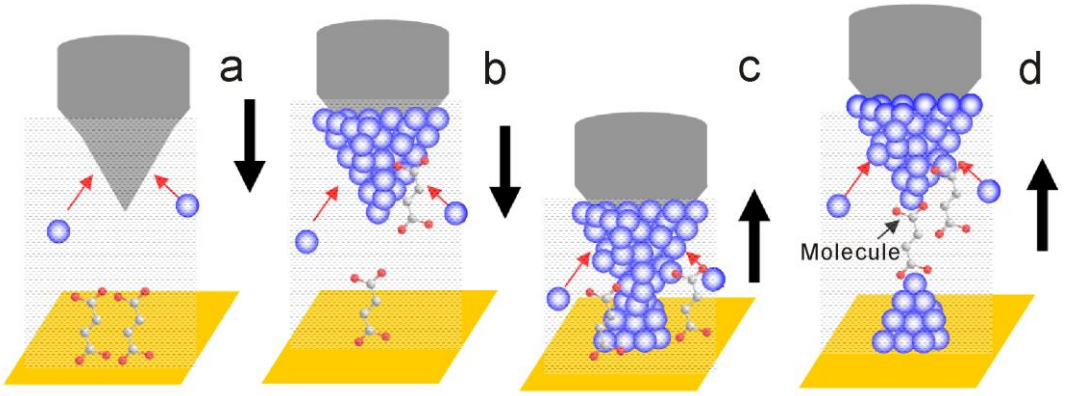


Figure 2. Schematic diagram of conductance measurement of single molecular junctions by the ECSTM-BJ approach. (a) deposition of metal onto tip, (b) pulling the tip far away from the substrate, (c) formation of nanoconstriction through jump-to-contact process, (d) formation of metal-molecule-metal junctions after broken of nanoconstriction.

Typically, the tip is controlled at potential of bulk deposition in aqueous solution containing target metal ion and target molecule, and can be continuously electrodeposited with the metal (Figure 2a), while the substrate is kept at slightly positive of Nernst equilibrium of metal to avoid metal bulk deposition. Then, the STM feedback is disabled and the tip is pulled far away from the substrate about several tens nanometers (Figure 2b). Next, the tip is driven towards the surface till a certain tip current is reached; a external voltage pulse is immediately applied onto the z-direction of piezo tube, atoms of deposited metal on the tip transferring to the substrate can happen, which is called a jump-to-contact process (Figure 2c). Then atomic-size wire of the deposited metal can be formed by pulling the tip out of the contact. At last, molecular junctions with deposited metal as electrodes can be formed after breaking of the metal contact (Figure 2d). The current vs. distance curves are recorded at the same time. The above process is repeated at different positions of the surface, and well-defined deposited metal contact can be realized. Large numbers of traces are collected to construct conductance histogram.

3. RESULTS AND DISCUSSION

3.1. Single molecule conductance measurement of carboxylic acids contacting with Cu, Ag and Au electrode

The conductance measurement of single molecule junctions fumaric acid were performed in aqueous solution containing 1 mM $CuSO_4$ + 1 mM fumaric acid + 50 mM Na_2SO_4. The typical

conductance traces of Cu-fumaric acid junctions are displayed in Figure 3a, and the conductance value of the step is nearly integer multiple of 18.4 nS.

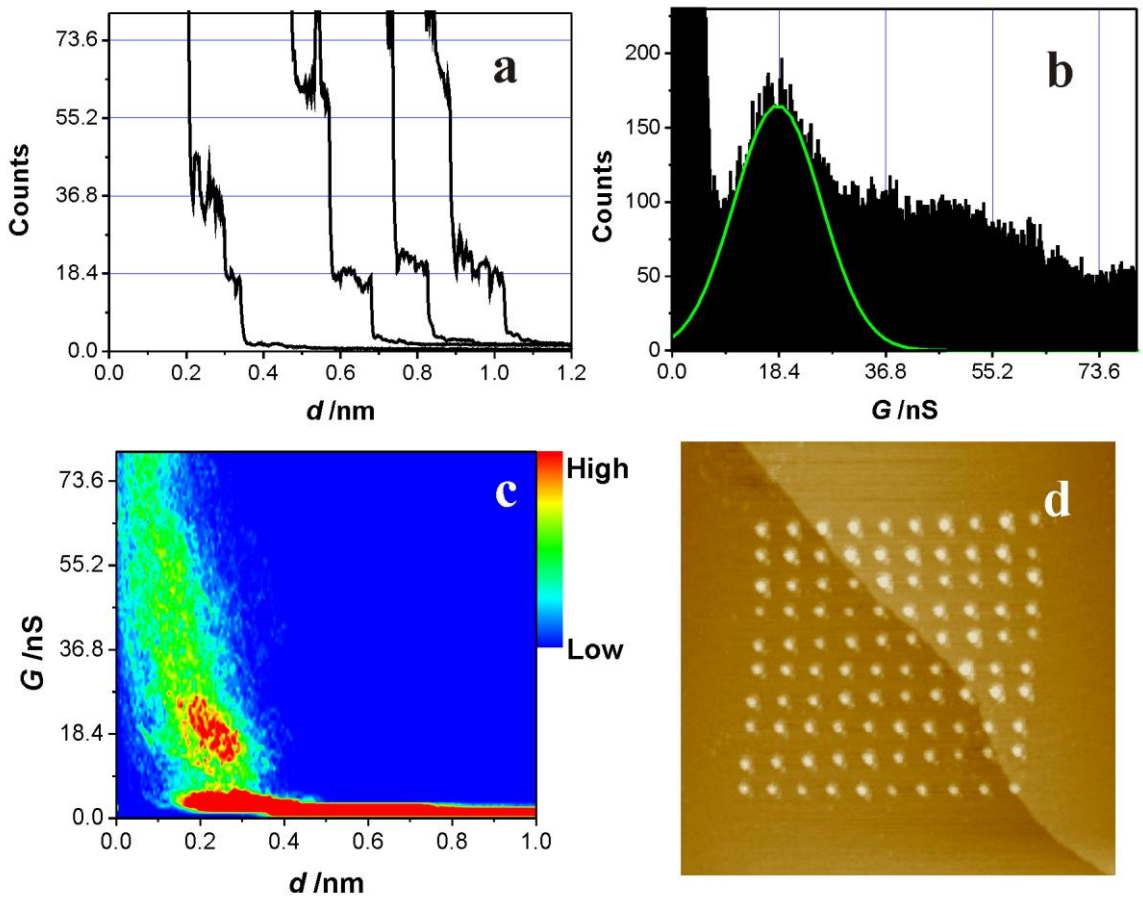


Figure 3. (a) Typical conductance curves of Cu-(fumairc acid)-Cu junctions measured at bias of 50 mV. (b) One-dimensional conductance histogram constructed from curves show in (a). (c) Two-dimensional conductance histogram of single molecule junctions. (c) The STM image (150 × 150 nm^2) of a 10 × 10 array of Cu clusters simultaneously generated with the conductance curves.

One dimensional conductance histogram constructed from hundreds of curves is shown in Figure 3b, and gaussian fit was also applied to determine the peak location yielding a peak of preferential occurrence of the steps at 18.4 nS. The peak position corresponds to the most frequently measured conductance of molecule. Figure 3c is the two-dimensional conductance histogram, which was constructed by counting the number of data at each conductance value with each stretching distance from conductance curves. Figure 3d shows 10 × 10 array of Cu clusters which was created on Au(111) substrate with tip potential of -25 mV, which demonstrates that the conductance of Cu-molecule-Cu junctions were measured.

By the same ECSTM-BJ approach, we also measured the single molecule conductance of Ag-fumaric acid junctions in aqueous solution containing 1 mM Ag_2SO_4 + 1 mM fumaric acid + 50 mM Na_2SO_4 and the Ag wire was used as the reference in experiment. And the potential was controlled at -

5 mV and 45 mV for the tip and the substrate, respectively. The conductance histogram gives a conductance peak at 14.3 nS as shown in Figure 4a.

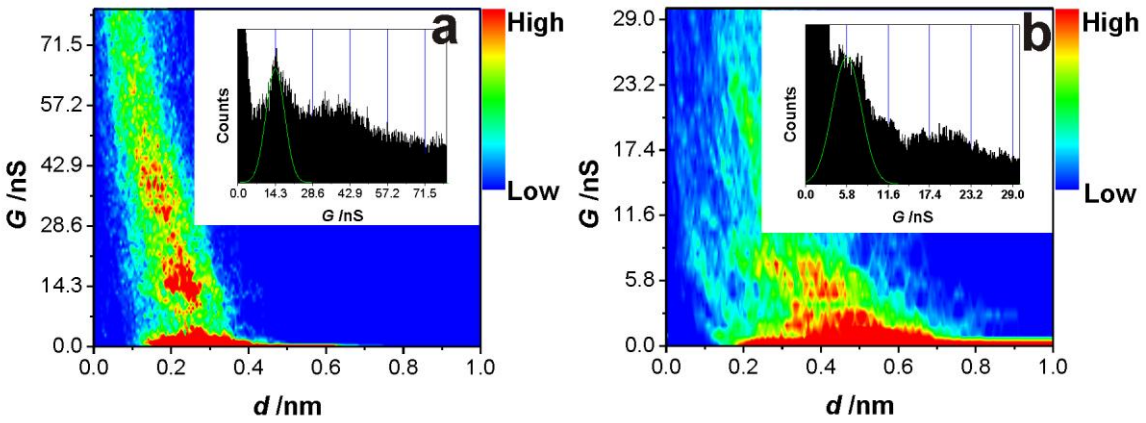


Figure 4. Two-dimensional conductance histograms of fumaric acid with contact of (a) Ag and (b) Au. Insets are the corresponding one-dimensional conductance histograms.

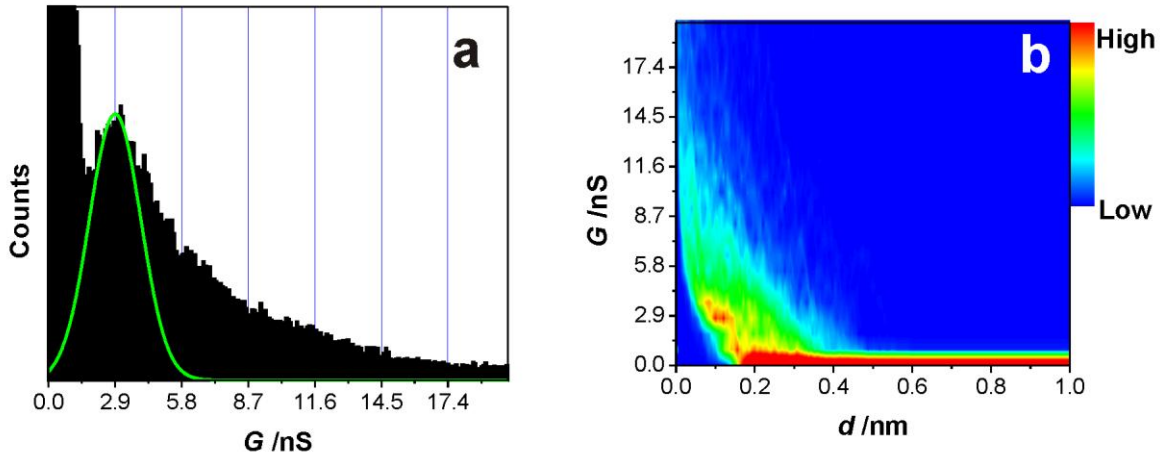


Figure 5. (a) One dimensional and (b) two-dimensional conductance histograms of trans-β-hydromuconic acid with contact of Cu.

The conductance of Au-fumaric acid junctions was measured by the traditional scanning tunneling microscopy break junction (STM-BJ) in 1 mM fumaric acid + 50 mM Na_2SO_4[1,2,22,41,42]. Au wire and Au(111) were used as tip and substrate, respectively. The conductance was measured at a fix bias voltage between tip and substrate, and gives value of 5.8 nS (Figure 4b).

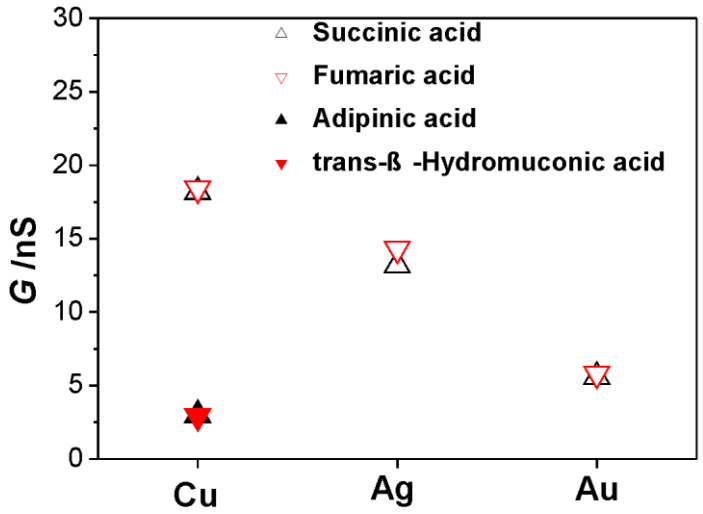
The conductance values of fumaric acid show the order of Cu＞Ag＞Au, which is the same as conductance of succinic acid junctions with Cu, Ag and Au electrodes. It can be attributed to the different electronic coupling efficiency between electrode and molecule. Interestingly, the conductance

of fumaric acid with ethene bond is almost the same as that of succinic acid with saturated ethane bond [36,37]. We will discuss it later.

We also measured the conductance of trans-β-hydromuconic acid with longer backbone contacting to Cu electrode. As shown in Figure 5, both 1D and 2D histograms give a single molecule conductance of 2.9 nS. This value is comparable with the adipinic acid.

3.2. The influence of saturated and unsaturated groups on conductance measurement of molecule

Our group have previously reported the conductance measurement of pyridyl sandwiching CH_2CH_2 or CH=CH group, named 1,2-di(pyridine-4-yl)ethane (BPY-EA) and 1,2-di(pyridine-4-yl)ethene (BPY-EE) [2]. Typically, the conductance of BPY-EE is about 5 times higher than that of BPY-EA. Sriharsha et al. also found that the ethane bridge at the center of the molecule backbone would reduce the communication between the aromatic rings [21]. Specifically, similar conductance values of molecule with ethane single bond and the ethene double bond are found in this study. Those values together with succinic acid and adipinic acid are shown in Figure 6.



Figue 6. Conductance of succinic acid (Black hollow triangle), fumaric acid (Read hollow triangle), adipinic acid (Black solid triangle) and trans-β-hydromuconic acid (Read solid triangle) binding to different metals. The values of succinic acid and adipinic acid are taken from reference [37].

The conductance of single molecule junction can be expressed by Landauer formula near zero bias [43], $G = (2e^2/h)T_{\text{left-contact}}T_{\text{molecule}}T_{\text{righ-contact}}$, where $T_{\text{left-contact}}$, T_{molecule} and $T_{\text{righ-contact}}$ are the efficiency of electron transmission through the left contact, molecule, and right contact, respectively. For the molecule with same anchoring group contacting to the same electrode, the $T_{\text{left-contact}}$ and $T_{\text{righ-contact}}$ can be regarded as the same. The big difference of the various conductance values upon the insertion of the conjugated ethane and nonconjugated ethane groups to the molecule should be caused the change of the T_{molecule}. For the electron transport efficiency of BPY-EE with conjugated backbone

is much higher than that of BPY-EA with unconjugated backbone destroyed by the CH_2CH_2 bond [4]. Hence, the conductance of BPY-EE is much larger than that of BPY-EA.

For trans-β-hydromuconic acid, the insertion of the CH=CH bond may have less influence on the unconjugated backbone (Figure 1), and it shows comparable conductance value with adipinic acid having CH_2CH_2 bond which may indicate that those two molecule have similar $T_{molecule}$.

Now we will focus on the fumaric acid and succinic acid. As shown in Figure 1, it seems that the fumaric acid molecule have a better conjugated backbone in comparison with the succinic acid. Conversely, similar conductance values are found for single molecular junctions of succinic acid and fumaric acid, which reveal similar electronic coupling between the molecule and electrode. One possible mechanism is that the coupling between carboxylate group ($-COO^-$) and π-system conjugated ethylene backbone is weak, thus leads to the similar $T_{molecule}$ for those molecules. Parameswaran et al. reported that the conductance of diphenylphosphine bridged with benzene are similar with diphenylphosphine bridged butane, and the conductance of trans-1,2-bis(diphenylphosphino)acetylene with C≡C is also similar with the 1,2-bis(diphenylphosphino)ethylane with CH_2CH_2 [44]. They proposed that the lone pair on the P is not coupling well to the π-system conjugated molecule backbone. Those results are consistent to our current experiment. Further theory calculation would be required to probe this aspect.

4. CONCLUSIONS

The single molecule conductance of alkenedicarboxylic acid binding to the Cu, Ag and Au electrodes were investigated. The conductance values are 18.4 nS, 14.3 nS and 5.8 nS for fumaric acid contacting with Cu, Ag and Au, respectively, while the conductance of Cu-(trans-β-hydromuconic acid)-Cu is 2.9 nS. Those values are similar as that molecule with saturated alkane in the backbone. Those may attribute to the similar electronic coupling between the molecule and electrode.

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