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Origin of discrete current fluctuations in a single molecule junction†

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A series of fresh molecular junctions at a single molecule level were created and the current fluctuations were studied as electrons passed through them. Our results indicate that telegraph-like current fluctuations at room temperature neither originate from electron trapping/detrapping processes nor from molecule re-conformation. Our results will be helpful in better understanding the mechanism of current fluctuations.

With the rapid development of semiconductor technologies, the feature size of electronic devices is gradually approaching the miniaturization limits of silicon-based building blocks. Molecular electronic devices using single molecules as active electronic components are promising candidates in the ongoing miniaturization and integration of electronic devices.[1–4] However, the reliability of molecular devices can be severely affected by current fluctuation, a basic issue that may be an obstacle to realizing a functional single molecule-based device. Therefore, understanding the mechanism of conductance fluctuations is key to developing reproducible and reliable molecular electronic elements.

Recently, we and Weber's group have independently reported the observation of fast temporal telegraph-like conductance fluctuations in single molecule junctions, in which single molecules were sandwiched between two fresh nanoelectrodes.[5,6] The mechanism for the telegraph-like fluctuations has yet to be established, however, partly because of the absence of systematic experiments. Several possible mechanisms have been proposed, which can be mainly classified into three groups: (1) dynamic re-conformations of the molecular backbone structure;[7,8] (2) electron trapping/detrapping processes;[9,10] and (3) bond fluctuations of the metal–molecule contact.[11,12]

In this study, we investigate the current fluctuations of a series of molecules with varying numbers of phenyl rings along the molecular backbone. Interestingly, the rate of telegraph-like fluctuations was observed to decrease as the molecular re-conformational freedom increased, indicating that telegraph-like fluctuations of fresh molecular junctions are unlikely to be caused by molecular re-conformation. In contrast, the fluctuation event rate was observed to be strongly dependent on the density of molecules adsorbed onto the electrode surface, that is, when the mobility of metal atoms is suppressed by the local environment, the rate of conductance fluctuations decreases. Furthermore, the conductance fluctuation rate was observed to increase as the passing current increased, that is, fluctuations can be enhanced by the passing current as a result of thermal effects. Our results indicate that the conductance fluctuations in fresh single molecule junctions at room temperature originate mainly from a mechanism other than those previously discussed, that is the rearrangement of metal atoms on the fresh electrode surface.

Obtaining a single fresh molecule junction

We used the mechanically controllable break junction (MCBJ) technique to generate a fresh single molecule junction.[13,14] MCBJ has proven to be very useful for creating reliable single molecule junctions.[15–23] The main advantages of MCBJ are as follows: (1) fresh molecular junctions can be generated merely by mechanically breaking a nanostructure without any chemical treatment;[24] (2) the gap size between electrodes can be continuously adjusted with picometer accuracy and disturbing effects from the external environment can be strongly suppressed.[25–27] The chip used for MCBJ is shown in Fig. 1(a).[28,29] More details on the chip and setup fabrication can be found in the ESI.†

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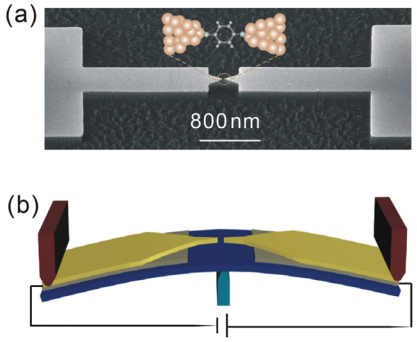

Fig. 1 Strategy to form a single molecule junction. (a) Scanning electron microscopy image of a nanofabricated MCBJ chip (top view). Insert: Schematic drawing of two nanoelectrodes bridged by a single molecule. (b) Schematic drawing of MCBJ sample mounted on a three-point bending apparatus. (Diagrams not drawn to scale or in proportion).

After establishing a self-assembling monolayer (1,4-benzenediamine, denoted as BDA) on the gold surface, the chip was mounted on a homemade three-point bending apparatus. All the following measurements were performed under vacuum ($<10^{-3}$ mbar) at room temperature. When the push rod exerts a bending force on the back side of the substrate, movement of the push rod in the Z direction elongates the constriction until the suspended metal bridge breaks, resulting in two fresh and separated tip-shape nanoelectrodes, as shown in Fig. 1(b). Precision control of the gap size is determined by the attenuation factor. An attenuation factor of $r \approx 5 \times 10^{-6}$ was achieved in our setup, see ESI† for detailed information. Thus, in theory, we can continuously adjust the gap size between electrodes with picometer accuracy.

After breaking the metal bridge, we formed a single molecule junction by reducing the gap size between two nanoelectrodes. As shown in Fig. 2(a), we continuously reduced the gap size by relaxing the substrate until a conductance jump appeared, followed by a conductance lock-in state. In the lock-in state, the conductance was insensitive to changes in gap size, and the conductance was found to be approximately $6.0 \times 10^{-3} G_0$ for the BDA molecule, which is comparable with a previously reported value.[30] Therefore, we claim that the single molecule junction is formed at the lock-in state as the first molecule reaches the opposite electrode.

Please note that we adopted a strategy of reducing the gap size, rather than separating two electrodes, to form the single molecule junction, although the separation approach provides a high probability of obtaining molecule junctions. The advantages of forming the molecule junction by reducing the gap size are: (1) we can easily find the exact single molecule junction state by identifying the current jump which indicates the first molecule reaching the opposite electrode. If employing the strategy of separating two electrodes, individual molecule junctions are usually obtained rather than a single molecule junction; that is, there may be several molecules simultaneously bridging two electrodes after breaking the Au–Au contact;[13] (2) we can avoid drastically changing the shape of

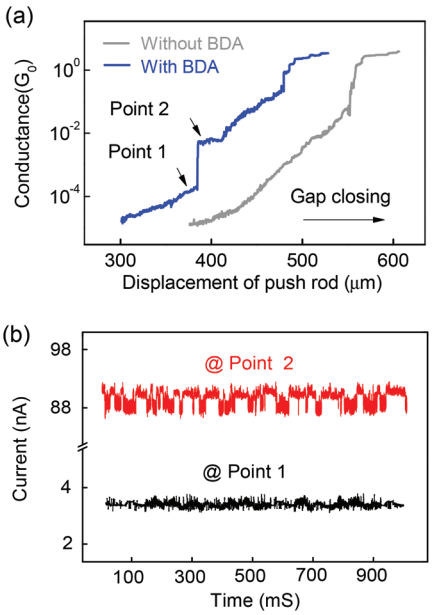

Fig. 2 Identification of a single molecule junction and current fluctuation characterization. (a) Junction conductance as a function of push rod displacement with a fixed bias of 0.2 V. For a molecule-containing junction (blue curve), the current sharply increased to a lock-in state, indicating the formation of a molecular junction. In contrast, the lock-in state was not present in the molecule-absent junction (gray curve). (b) The recorded real-time current fluctuations. Typically, two-level current fluctuations were observed when the nanogap was bridged by a single benzenediamine (measured @ point 2). In contrast, the two-level fluctuations were absent before formation of the molecular junction (measured @ point 1).

the electrode tips, which is impossible to avoid if one tries to obtain molecule junctions by separating two directly contacted electrodes.[28] Also, additional data show that this strategy is reproducible and reliable for generation of a single molecule junction, see ESI.†

Real-time conductance fluctuations

After the single molecule junction was obtained, the push rod was fixed and corresponding current fluctuation measurements were performed, as shown in Fig. 2(b). The current demonstrates telegram-like or discrete fluctuations at the fixed bias voltage (V_B = 0.2 V), indicating that telegram-like conductance fluctuation exists as the electrons pass through the molecular junction in the single molecule bridged junction. In contrast, only random conductance fluctuations were observed before the electrodes were bridged by a single molecule (measured at point 1), as shown in Fig. 2(b). Here, only those fluctuations where the amplitude difference between the two-level fluctuations was larger than 5% of the average value, were collected for further analysis.

Based on this observation, one may consider these telegram-like fluctuations to be a result of the breaking and reconnecting process of the molecular junction because of the weak

Au–N bonding energy. However, we note that the amplitude difference between the typical two-level fluctuations was only ~ 9% of the high current state. This indicates that such fluctuations cannot be simply attributed to the state transition between the breaking and reconnecting of the molecule at the bonding interface, because the breaking of a molecular junction usually results in a significant variation of the current amplitudes by more than one order of magnitude.[31] Moreover, additional experiments showed that the telegram-like fluctuations still existed even with a strong Au–S bond, see ESI.† Hence, we believe this observed telegram-like fluctuation does not originate from the breaking and reconnecting process.

Another potential explanation for the conductance fluctuation is that the telegram-like fluctuations are caused by conformational change of the molecular backbone. Additional current induced energy can trigger a conformational transition of the molecular backbone between several probable states when the tunneling current passes through the molecular junction. Donhauser *et al.* observed telegram-like conductance fluctuations of phenylene–ethynylene oligomers *via* a scanning tunneling microscopy (STM) experiment, and this conductance fluctuation behavior has been explained in terms of strong coupling between relative angular displacements or rotation of the phenyl rings.[7,8] However, we tentatively doubt this explanation, and have designed systematic experiments to verify its reliability.

We performed temporal conductance measurements with a series of molecule-bridged junctions. These molecules had the same binding groups (–NH_2), but each varied in length, with a different number of phenyl rings along the molecular backbone denoted as molecules 1–4, as shown in Fig. 3(a). To identify the single molecule junction state, we also determined the conductance amplitudes of each type of molecule using a statistical method. A statistical conductance histogram was built from 500 traces without data selection. Please note that because of the low yield of distinguished current plateau employing the approaching strategy, the presented statistical histogram was made based on current traces recorded during the electrode separation period. The conductance values of each type of molecule are indicated by the peaks of the histogram and were found to be $6.4 \times 10^{-3}G_0$, $1.4 \times 10^{-3}G_0$, $3.2 \times 10^{-4}G_0$, and $6.7 \times 10^{-5}G_0$ for molecules 1–4, respectively, which agree with a previous report.[30]

Using the conductance value as a reference, we can easily find the single molecule junction state using the approaching method. Subsequently, real-time current measurements at a fixed bias voltage were performed and the results are presented in Fig. 3(b). This figure demonstrates that with an increased number of phenyl rings along the molecular backbone, the rate of telegraph-like fluctuations is reduced. This observation indicates that the telegraph-like fluctuation is most likely not caused by molecular conformational changes. We know that the degrees of freedom for molecule re-conformation increased as the phenyl rings number increased. If the telegraph-like signals originate from the rotation of phenyl rings along the molecule backbone, then the rate of the switch

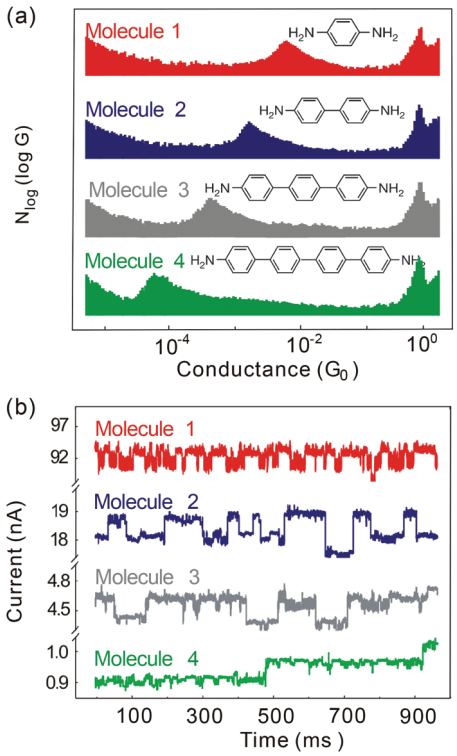

Fig. 3 Molecular conductance measurement and corresponding current fluctuation characterization. (a) Conductance histogram of the four types of molecules. The conductance values of the molecules were determined to be $6.4 \times 10^{-3}G_0$, $1.4 \times 10^{-3}G_0$, $3.2 \times 10^{-4}G_0$, and $6.7 \times 10^{-5}G_0$, respectively. (b) Real-time current measurements of the four types of studied molecules. Data were obtained at a fixed bias V_B = 0.2 V.

events would be expected to increase. Moreover, an obvious current fluctuation was observed with an octanedithiol bridged junction in which internal ring rotations are not possible, see ESI.† Therefore, the telegraph-like signal cannot be explained simply in terms of conformational changes of the molecular backbone.

Noise spectroscopy of a single molecule junction

To fully understand the mechanism for the conductance fluctuation, a statistical measurement is needed. Hence, we employed the noise spectroscopy method, which is a powerful tool to investigate the statistical features of the current fluctuation,[27,32–36] because traditional conductance temporal measurement shows only limited time fragments. Using this method, each noise spectrum was automatically obtained by averaging 100 individual spectra with a spectrum analyzer. Detailed information on the measurement system can be found in the ESI.†

Here, the noise power-spectral density of the single molecule junction was measured for both states (just before the lock-in plateau and exactly at the lock-in plateau). Only a domi-

nant 1/*f* noise component was observed when the gap distance between the nanoelectrodes was larger than the size of the molecule (measured @ point 1 in Fig. 2), as shown in Fig. 4(a). We also observed that such noise characterization is similar to the case of molecule-absent junctions, as shown in the ESI.† However, for a molecule-bridged junction, the noise spectroscopy showed a distinct feature. In addition to the 1/*f* noise characteristic, a new dominant noise component, $1/f^2$, was revealed in the high frequency regime, as illustrated in Fig. 4(b). The clearly observed single characteristic frequency indicated the existence of only a single or few Lorentz fluctuator(s) when current passes through it,[5] which is coherent with the observation of discrete temporal fluctuations.

For each of the molecule bridge junctions for molecule 1 to molecule 4, a $1/f^2$ noise component was found, as shown in Fig. 4(c). The arrow lines indicate the position of the characteristic frequency f_0 (to determine the position of f_0, one can plot $f S_V$ *vs.* f, and the vertex of each curve in this plot indicates the position of f_0, see the ESI†). As illustrated in Fig. 4, with an increased number of phenyl rings along the molecular backbone (increased rotational degrees of freedom along the backbone), the corresponding characteristic frequency f_0 decreased. Please note, for a simple telegraph-like fluctuation, the characteristic frequency f_0 is proportional to the fluctuation ratio.[5,6] Thereby, the order of magnitude of the characteristic frequency value agreed well with that of the temporal conductance fluctuation rate.

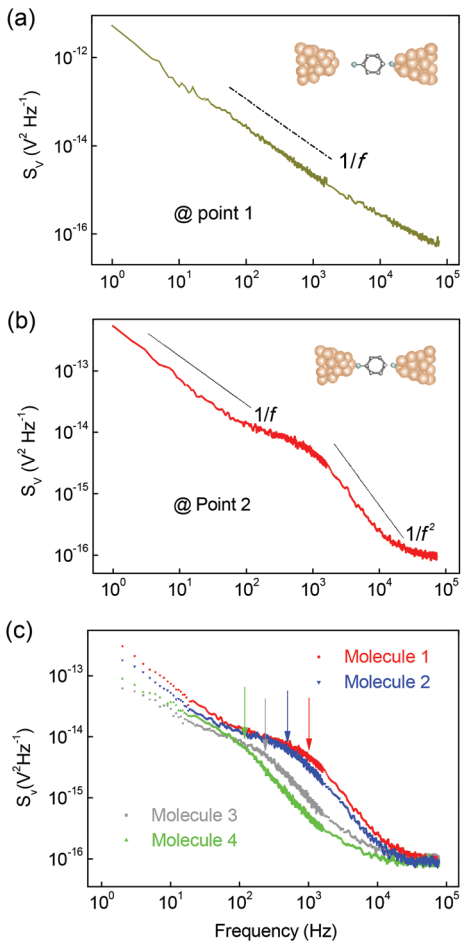

Fig. 4 Noise spectroscopy of the investigated junctions. (a) Measured power-spectral density of the molecule junction when the gap distance between the nanoelectrodes is larger than the molecular dimension (schematic). (b) The power-spectral density of the molecule in the lock-in state, corresponding to a single benzenediamine bridging two electrodes. (c) The voltage power-spectral density of the four types of molecule bridged junctions. Arrows indicate the positions of the respective characterization frequencies.

Fluctuations depend on bias voltage

We had previously reported discrete temporal fluctuations in monolayer molecular junctions, and the fluctuations were attributed to the processes of charge trapping/detrapping caused by unintentionally introduced defects. However, it is not likely that the fluctuations observed here were caused by this trapping/detrapping process. The reasons are as follows: (1) the defects are normally absent in a single molecule junction; (2) all the discrete fluctuations were observed with a small bias voltage (V_B = 0.2 V), which is not enough to trigger trapping/detrapping events.

Here, we attribute the discrete fluctuations to the movement of a gold atom tethered to the molecule junction. In fact, the rapid movement of a bare gold atom on electrode surface was directly observed by employing high resolution transmission electron microscopy (HTEM).[37,38] Maksymovych *et al.* proved that the reconstruction of the gold surface layer was lifted by the molecular self-assembly.[39] In our case, a fresh electrode surface was generated after physically breaking the nano gold bridge without annealing treatment or any further chemical treatment, such that the atoms on the gold surface may continuously rearrange to reach a new equilibrium with minimum total energy.[40] The discrete movement of gold atoms linked to the molecule has the probability of causing telegraph-like conductance fluctuations.

Please note that the observed fluctuation is faster than the speed of a bare gold atom movement observed with HTEM. We attribute this relatively fast fluctuation to the thermal effect induced by current. Fig. 5 clearly demonstrates that the average fluctuation rate increases as the applied voltage increases for each type of molecule junction. It is known that high local temperature can be induced by the current passing through the molecule junction.[41] Tsutsui *et al.* reported that the local temperature of nanoelectrodes of a BDT molecular junction can be raised up to 463 K by applying a bias voltage of up to 1 V at the external room temperature.[42] As a rule of thumb, the mobility of atoms can be promoted by high local temperature.[43] Hence, dependence of the fluctuation on the amplitude of the applied voltage is not surprising. At the same time, please note that the phenyl ring-absent molecule, octanedithiol, which has similar conductivity to molecule 3, also showed comparable current fluctuation and a similar characteristic frequency with the same bias voltage, see ESI.† This

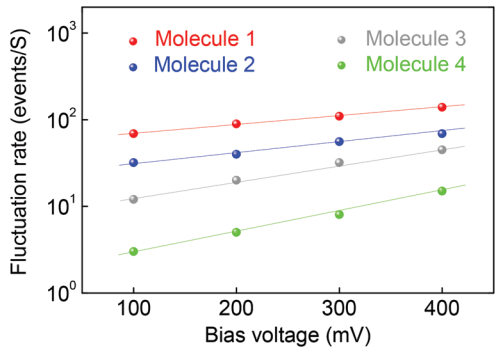

Fig. 5 The dependence of average fluctuation rate on applied bias voltage for four different molecule junctions. The fluctuation rate increases as the applied bias voltage is increased for each type of molecule junction, that is, when the passing current increases, the fluctuation rate is augmented.

finding could be used to further exclude the possibility of current fluctuations originating from molecule conformation change.

Furthermore, if the telegraph-like signal originates from the motion of a gold atom tethered to a molecule, the fluctuation events will presumably depend on the coverage density of the neighboring molecules because the mobility of the Au–NH_2 species can be reduced in a densely packed environment. To verify this hypothesis, we compared the switch ratio in different samples with varying molecular coverage densities. The incubation concentration of the molecules was varied from 0.1 to 10 mM in preparation of the SAM. We observed that for all four types of molecules the switch ratios were reduced as the incubation concentration increased, indicating that higher molecular coverage ratios hindered the motion of complex species and assisted gold atoms at being quieter, as shown in the ESI.† Thereby, our series of experimental approaches may conclude that the telegraph-like fluctuations mainly originate from the mobility of the metal atoms on the electrode surface tethered with the molecule.

Now we can further explain the dependence of fluctuation rate on molecule length. The current fluctuation mainly originated from the rearrangement of the Au atoms, and the atomic motion was affected by two factors: (1) the motion of the Au atom is thermally activated. Local heating is less pronounced with longer molecules under a fixed bias voltage[44] because longer molecules have poorer conductivity, resulting in a decrease of the fluctuation rate; (2) longer molecules tend to be packed more densely after the self-assembly process[45] and the densely packed environment will suspend the motion of the Au–NH_2 species, leading to a further decrease in fluctuations with longer molecules.

Conclusions

In summary, a combination of real-time conductance fluctuations and noise spectroscopy measurements were performed on single molecule junctions employing the MCBJ technique. We find that the characteristic frequency (f_0) and telegraph-like fluctuation events decrease as the degree of molecular re-conformation freedom increases. Furthermore, the dependence of the fluctuation ratio on both the incubation concentration of molecules and the amplitude of the current passing through the molecule junction was discerned. Our systematic investigation leads to the conclusion that telegraph-like conductance fluctuation is more likely associated with the rearrangement of metal atoms tethered with a molecule rather than molecular structural re-conformation. We believe the knowledge obtained from this study will be useful in improving the reliability of molecular electronic devices.

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