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Single-Molecule Junctions with Strong Molecule−Electrode Coupling

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Forming molecule−electrode bonds is necessary for the development of nanoscale molecular devices because these bonds dominate the electrical conductance and device characteristics.[1,2] Strong molecular orbital interactions between π orbitals of the molecule and frontier orbitals of the electrode result in strong molecule−electrode coupling, yielding high electrical conductance, which is advantageous to device operations.[1] Therefore, the development of molecule−electrode bonds with strong molecule−electrode coupling is desired. We initially noticed that organic donor molecules in organic conductors are stacked in a face-to-face overlapping configuration, where p_z orbitals are stacked in a σ-type manner, resulting in strong π orbital interactions.[3] In organic conductors, large changes in electrical conductance can be obtained only by replacing S with Se in the donor molecules.[3] Thus, it is important to note when molecule−electrode bonds are stacked in a face-to-face type configuration because the single-molecule conductance in such a configuration can be adjusted only by atom substitution.

In this communication, we report the single-molecule conductances of tetrathiafulvalene (TTF) and tetraselenafulvalene (TSF). We found that the single-molecule conductance of Au−TTF−Au junctions is larger than that of Au−TSF−Au junctions and that Au−TTF−Au single-molecule junctions have two stable configurations. The relationship between single-molecule conductance and the properties of donor molecules indicates that TTF and TSF interact with electrodes in the face-to-face overlapping configuration. Thus, we demonstrated control of electrical conductance by atom substitution.

TTF and TSF were synthesized by conventional methods.[3] Molecular conductance measurements were performed at room temperature under vacuum using a nanofabricated mechanically controllable break junction (nano-MCBJ).[4] Typical conductance traces of Au−TTF−Au and Au−TSF−Au junctions are shown in Figure 1a; conductance plateaus were observed at less than 100 mG_0 and 10 mG_0, respectively, where G_0 is the conductance quantum. The measured substances were not crystals of the molecules because the typical conductance plateau length corresponding to the persistence length of the junctions was 1 nm. The results of 1000 conductance traces for Au−TTF−Au and Au−TSF−Au without any selection were expressed as conductance histograms (Figure 1b and 1c), which showed pronounced conductance peaks. In the histogram for Au−TSF−Au, the conductance peaks were obtained at integer multiples of ∼3.4 mG_0, and no peaks were obtained below 3.4 mG_0; therefore, the single-molecule conductance of Au−TSF−Au junctions was determined to be 3.4 mG_0. On the other hand, the conductance histogram of Au−TTF−Au junctions could not be analyzed using only one conductance state, so we assumed that these junctions have two conductance states. Two minimum peak conductances of 18 mG_0 and 28 mG_0 were assumed to correspond to single-molecule junction states A and B, respectively. Considering all combinations of the two conductance states, the two-molecule junction conductances were expected to be 36 mG_0 for A−A, 46 mG_0 for A−B, and 56 mG_0 for B−B. Further, three-molecule junction conductances were expected to be 54 mG_0 for A−A−A, 64 mG_0 for A−A−B, 74 mG_0 for A−B−B, and 84 mG_0 for B−B−B. When the conductance histogram of Au−TTF−Au junctions was analyzed using these conductances, the obtained histogram and peak conductances adequately corresponded to the expected results. Therefore, the two values of single-molecule conductance of Au−TTF−Au junctions were determined to be 18 mG_0 and 28 mG_0.

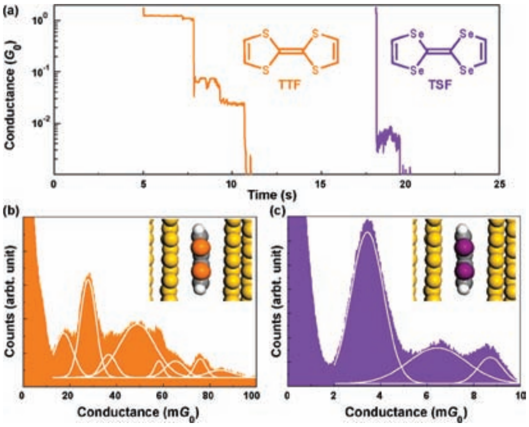

Figure 1. Conductance characteristics of Au−TTF−Au and Au−TSF−Au junctions. (a) Typical conductance traces of TTF and TSF junctions. Conductance histograms of (b) Au−TTF−Au and (c) Au−TSF−Au junctions. The white lines are Gaussian fits to peak profiles. The single-molecule conductance of Au−TSF−Au junctions is 3.4 mG_0, while those of Au−TTF−Au junctions are 18 mG_0 and 28 mG_0, which correspond to two configurations. Peak conductance of Au−TSF−Au junctions was obtained at integer multiples of ∼3.4 mG_0. Peak conductance of Au−TTF−Au junctions was obtained at all combinations of 18 mG_0 and 28 mG_0. The insets show proposed configurations of single-molecule junctions.

In an effort to study the single-molecule junction states in Au−TTF−Au and Au−TSF−Au, the voltage dependence of the conductance histograms was investigated. The histogram of Au−TSF−Au junctions was determined to be independent of voltage. This result shows that Au−TSF−Au single-molecule junctions are stabilized at one configuration because of strong Se−electrode bonds. On the other hand, the conductance histogram, constructed from 1000 traces for each voltage, of Au−TTF−Au junctions showed a large dependence on the voltage (Figure 2). In the low voltage range, counts of configuration B were larger than those of configuration A, while these counts were similar at high voltages. The growing signature of configuration A at high voltages indicates that configuration A is more stable and has stronger Au−S

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bonds compared with configuration B, when the voltage energy activates Au−S bond breaking.

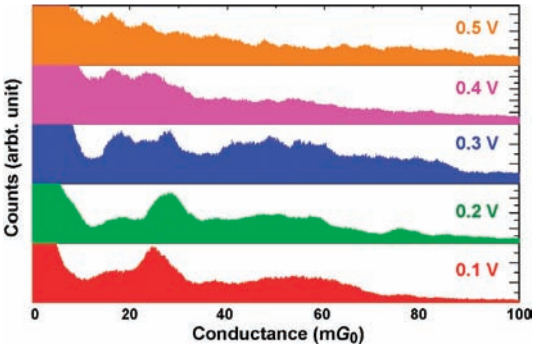

Figure 2. Voltage dependence of the conductance histogram (constructed from 1000 traces for each voltage) of Au−TTF−Au junctions.

The single-molecule conductance of Au−TTF−Au junctions is more than 6 times larger than that of Au−TSF−Au junctions. This difference in single-molecule conductance can originate from various factors: the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO−LUMO) gap, the degree of charge transfer from the molecule to the electrode, bond configuration, and the strength of molecule−electrode coupling.[1]

First, the HOMO−LUMO gaps of TTF and TSF were calculated to be 3.8 and 3.4 eV, respectively, using B3LYP density functional theory (DFT) calculations. This shows that there is little difference in the HOMO−LUMO gaps of the two molecules. Furthermore, the calculated HOMO energies of TTF and TSF are −4.6 and −4.7 eV, respectively. These results are supported by the fact that TTF and TSF have almost the same first oxidation potentials as obtained experimentally.[3] This means that the degree of charge transfer from molecule to electrode in the Au−TTF−Au junctions is the same as that in the Au−TSF−Au junctions.

On the other hand, the adsorption structure of molecules on Au substrates gives useful information about the bond configuration of Au−molecule−Au junctions. A TTF molecule is adsorbed on a Au substrate surface in a face-to-face overlapping configuration, where the molecular plane overlaps with and is parallel to the electrode surface.[5] The face-to-face overlapping configuration agreed with our calculated adsorption structure of TTF on the Au surface using DFT (See Supporting Information). The calculated adsorption structure of TSF was the same as that of TTF under the same conditions. It is, therefore, reasonable to assume that the bond configuration of Au−TTF−Au junctions is the same as that of Au−TSF−Au junctions.

Finally, the difference in strength of the molecule−electrode coupling between the two types of junctions must also be considered. When molecules are generally connected to the electrode by S−Au and Se−Au bonds, the p_z orbitals form an HOMO overlap with the 6s orbitals of the Au atoms in a π-type manner. Here, the strength of the Se−Au coupling is larger than that of the S−Au coupling.[6−8] On the other hand, when molecules are connected to electrodes in a face-to-face overlapping configuration, the p_z orbitals overlap with the 6s orbitals in a σ-type fashion. In this case as well, the strength of the Se−Au coupling is larger than that of the S−Au coupling. However, a face-to-face overlapping configuration provides much stronger molecule−electrode coupling since the σ-type manner has much stronger S−Au and Se−Au bonds compared with the π-type manner. Therefore, the π-type and σ-type molecule−electrode couplings exist in the weak and strong coupling regions, respectively.

A simple transport theory predicts that the single-molecule conductance increases with molecule−electrode coupling in the weak coupling region and conductance decreases with increasing coupling in the strong coupling region.[1,2] In fact, terthiophenediselenol has a larger conductance compared to terthiophenedithiol due to weak coupling originating from the π-type overlap.[8] In this study, stronger molecule−electrode coupling results in smaller single-molecule conductance; therefore, we speculate that the two molecules are connected to the electrode in a face-to-face overlapping configuration (insets of Figure 1b and 1c).

In summary, we measured the single-molecule conductance of Au−TTF−Au and Au−TSF−Au junctions using a nano-MCBJ. We found that the single-molecule conductance of Au−TTF−Au junctions is 6 times larger than that of Au−TSF−Au junctions and that Au−TTF−Au single-molecule junctions have two stable configurations. Considering the single-molecule conductances of the molecular junctions and the molecular properties of the molecules, it was hypothesized that the molecules are connected to the electrode in a face-to-face overlapping configuration. This overlapping fashion results in the Se−Au coupling being stronger than the S−Au coupling, leading to a difference in single-molecule conductances between the two types of molecular junctions. The face-to-face overlapping of a molecule with an electrode is a significant molecule−electrode bond type in which the single-molecule conductance can be controlled by substitution of one atom in the molecule. This property can be advantageous in the development of nanoscale molecular devices.

Supporting Information Available: Sample preparation and theoretical calculations. This material is available free of charge via Internet at http://pubs.acs.org.

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