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Direct Measurement of Electron Transfer through a Hydrogen Bond between Single Molecules

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Supporting Information

ABSTRACT: Understanding electron transfer (ET) from a single molecule to another single molecule holds essential importance to realize bottom-up molecular devices in which constituent molecules are self-assembled via noncovalent interactions between each other. However, rather little is currently known about the ET properties at the single-molecule interface. Here we employ molecular tips to quantify the ET through a H-bond between single molecules. We found that a H-bond conducts electrons better than a covalent σ bond at short-range. Its conductance, however, decays steeply as the chain length of the H-bonded molecules increases. First-principle calculations were performed to reveal the electronic origin of the facile ET through the H-bond. Our results demonstrate that H-bonding in a molecular junction significantly affects its transport property.

Understanding electron transport at the single molecule level is of primary importance in utilizing a single molecule as an electronic component.[1,2] Recently, there have been significant advances in the measurement of electron transport through a single molecule, and a large variety of molecules with unique electronic functions, e.g., wires,[3,4] diodes,[5−7] switches,[8,9] and transistors,[10,11] have been reported.[12] Functional nanoelectronic devices can be realized by controlled organization via self-assembly processes, where individual molecules are organized through noncovalent interactions between each other.[13] These chemical interactions should allow not only the structural robustness of the molecular assemblies but also a suitable electrical connection between the constituent molecules. Thus, the next challenge lies in measuring ET between single molecules interacting with each other noncovalently. Among the possible noncovalent interactions, H-bonding is ubiquitous in molecular interactions in both artificial and biological systems. However, rather little is currently known about the ET properties through the noncovalent interactions, including H-bonding, at the single-molecule interface,[14−18] and even at the macroscopic scale.[19−21]

We have developed molecular tips for scanning tunneling microscopy (STM). The molecular tips are prepared by chemical modification, typically via chemisorption of organosulfur compounds, of conventional metal STM tips. We demonstrated that such functionalization enables recognition of chemical identities of a single molecule.[22] Moreover, the molecular tips offer a unique means to detect the ET between single molecules. We previously proved rectified ET within a single electron donor−acceptor complex with a fullerene molecular tip.[6] Recently, molecular tips were further used to quantify electron transport induced by covalent bond formation between single molecules.[23] In the present study, we show quantification of the ET through a H-bond between single molecules. Although ET though a H-bond in a single DNA base pair has been reported,[14−16] we employed a simpler carboxylated alkanethiol, which allows a more direct investigation of the effect of the H-bond. We found that a H-bond conducts electrons better than a covalent σ bond at short range. Its conductance, however, decays steeply as the ET pathway becomes longer. First-principle calculations were performed to reveal the electronic origin of the facile ET through the H-bond. Our results demonstrate that H-bonding in a molecular junction significantly affects its transport property.

In the present work, STM tips were modified with self-assembled monolayers of ω-carboxyl alkanethiols (HS-$(CH_2)_nCOOH$, C_nCOOH) to prepare the molecular tips (see Supporting Information, SI, for the experimental details). A gold substrate was modified with C_nCOOH, and the molecular tip was brought into proximity with this sample surface. The current flowing between the tip and surface was measured in 1,2,4-trichlorobenzene. Carboxylic acids readily undergo H-bond interactions in such nonprotic solvents. During the measurements, the tip position and tip−sample distance were held constant by freezing the feedback loop of STM (Figure 1). Figure 2a shows representative current−time (I−t) plots measured using C_2COOH molecular tips over C_2COOH-covered Au(111) substrates. In addition to the background current, which is equal to the set-point value, current jumps and

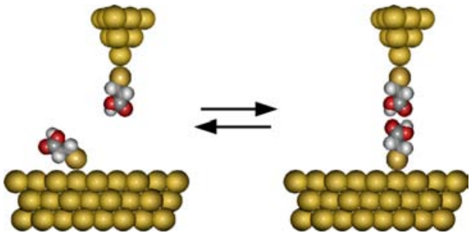

Figure 1. Schematic of tunneling current measurements. The ET through a H-bond was measured via spontaneous formation of a chemical interaction between the tip and sample molecules.

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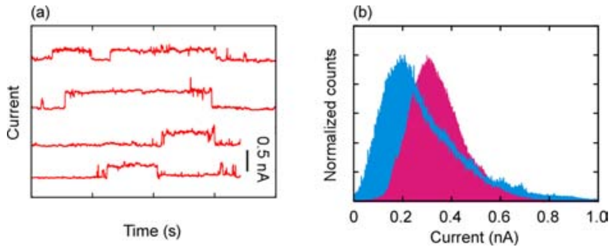

Figure 2. ET between a single H-bonded C_2COOH dimer. (a) Representative $I-t$ plots showing jump−plateau signals measured using C_2COOH tips over C_2COOH-covered surfaces. Each plot is vertically shifted for clarity. Bias voltage: 0.2 V; set-point current: 0.5 nA. (b) Current histograms constructed from $I-t$ plots. Pink: measurements made using C_2COOH tips over C_2COOH-covered surfaces. fwhm = 0.23. Blue: measurements made using Au tips and C_8DT-covered surfaces. fwhm = 0.26.

consecutive plateaus were observed in the $I-t$ plots. We previously reported such jump−plateau signals, which result from the formation of a single covalent linkage between the thiol groups of the molecular tip and the sample molecules.[23] In the present case, the tip and sample molecules have carboxyl groups at their free ends, and we attribute the current jumps to H-bond formation between these terminal carboxyl groups (Figure 1, right). The current increase brought on by the current jump, therefore, reflects ET through the H-bond interaction between the two single molecules. A histogram of the (increased) current caused by the H-bond formation was constructed from hundreds of individual current jumps (Figure 2b, pink; see also SI). For comparison, we performed $I-t$ experiments for the electron transport through a single octanedithiol (C_8DT) molecular junction, which contains 8 carbon atoms (Figure 2b, blue).[24] The length of the H-bonded C_2COOH dimer, composed of 6 carbon atoms in total (see Figure 1, right), is almost the same (1.21 nm between terminal S-atoms) as that of C_8DT (1.19 nm), allowing a direct comparison. Each histogram in Figure 2b exhibits a single distinct peak; the conductance of the molecular junction was calculated using the peak current value. Despite the fact that the Au tip and substrate were connected by σ bonds in the case of C_8DT, the conductance of the H-bonded C_2COOH dimer (1.5 nS) was larger than that of the C_8DT (0.99 nS).

The conductance of the H-bonded molecular junctions was further investigated by current measurements as a function of tip displacement from the substrate. After being brought into close proximity to the C_2COOH-covered Au(111) substrate in 1,2,4-trichlorobenzene, the molecular tip was raised. Figure 3a illustrates representative current−displacement ($I-z$) curves measured with the C_2COOH tip and C_2COOH-covered surface. Besides smooth exponential decay due to the electron tunneling, the $I-z$ curves showed clear steps or plateaus. These steps are ascribed to the H-bond interaction between the C_2COOH molecules on the tip and sample surface. A current histogram was constructed using the current value of each data point in the $I-z$ curves (Figure 3b, yellow). A single pronounced peak is found in the histogram; the conductance of the H-bonded C_2COOH dimer was calculated to be 1.4 nS, which is in agreement with the conductance determined using the $I-t$ measurements. Generally, multiple peaks are seen in the histogram obtained from the $I-z$ measurements, such as STM break-junction experiments. These peaks are interpreted as resulting from the formation of multiple, not single, molecular junctions between the tip and the substrate[4,25] or different contact geometries between the anchoring groups of the molecule, such as thiol, and the gold surface.[24,26] In contrast, only one single peak appeared in the histogram in Figure 3b, demonstrating that electrons are transferred through the single H-bonded molecular junction. Although the carboxyl group was shown to be an effective contact group for the single molecule junction,[27,28] the control experiments using either a clean Au substrate or unmodified Au tip exclude the possibility that the C_2COOH tip formed a molecular junction directly on the Au surface without involving the sample molecule on the substrate (see SI). The molecular junction in the present study was created by spontaneous association between the molecule freely diffusing on the substrate and the tip molecule. We, therefore, expect that the intermolecular geometry was optimized so as to form a favorable H-bond in-between. The most probable structure of the H-bond interaction between the tip and substrate is the well-known cyclic structure in which the two carboxyl groups form two very strong H-bonds (Figure 1, right) since such a structure is shown to be most stable in both the gas phase and weakly polar to nonpolar solutions.[29] The observation of only a single peak in Figure 2b (pink) indicates that no H-bond configuration other than the cyclic structure was detected in the present experiments. Although the tilt angles of the sample and tip molecules were not controlled in the present experiments, it has been demonstrated that the tilt angle has little, if any, effects on the junction conductance unless particularly strong electronic coupling exists between the molecule in the junction and the substrate.[30,31]

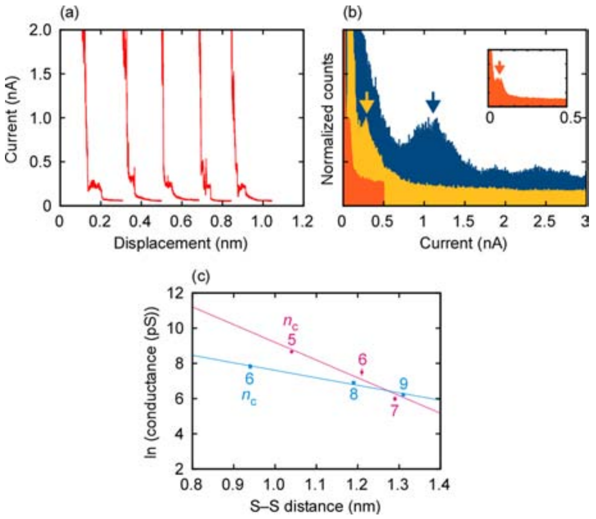

Figure 3. Distance dependence of ET through H-bond. (a) Representative $I-z$ plots measured using C_2COOH tips over C_2COOH-covered surfaces. Each plot is horizontally shifted for clarity. Bias voltage: 0.2 V; set-point current: 7.5 nA. (b) Current histograms constructed from $I-z$ plots measured using C_2COOH tips over Au substrates modified with C_1COOH (blue), C_2COOH (yellow), and C_3COOH (orange). A highly sensitive preamplifier (0.1 nA/V) was used for the measurements of the C_3COOH-covered surface (Inset). Larger currents cannot be measured in this case. (c) Distance dependence of conductance of molecular junction consisting of H-bonded C_nCOOH dimer (pink) and alkanedithiolate (blue). Number of C-atoms (n_c) in the molecular junction, including those in carboxyl groups, is indicated for each data point.

Next, the distance dependence of the ET was investigated for ω-carboxyl alkanethiols with different molecular lengths for the tip and sample molecules. $I-z$ measurements were performed, and current histograms were constructed using the C_2COOH tip over the Au(111) substrates modified with C_1COOH (Figure 3b, blue), C_2COOH (Figure 3b, yellow), and C_3COOH (Figure 3b, orange). In all cases, current steps appeared in the $I-z$ curves, and each histogram exhibited a single distinct maximum (arrow in Figure 3b). The preamplifier used for the measurement of the C_3COOH-covered surface has higher sensitivity (0.1 nA/V) but a narrower measurable current range than the preamplifier for the other measurements. The conductance values for the single H-bonded molecular pair were determined by the peak currents of the histograms. Figure 3c shows the conductance as a function of the length of the molecular pair (pink); the plot reveals that the conductance value depends exponentially upon the length. The slope of this logarithmic plot is referred to as the β decay constant and found to be 10 nm^{-1}. The conductance values for single alkanedithiol molecular junctions (hexanedithiol, C_8DT, nonanedithiol) are also shown in Figure 3c (blue); the conductance exhibits an exponential dependence upon the molecular length. The β value in this case was 4.2 nm^{-1}, being consistent with reported values.[24,32] The higher β values for the same alkanedithiol junctions (approximately 8.5 nm^{-1}) were also reported,[26,33] and these results are attributed to the differences in the surface concentrations of the sample molecules on the substrate[26] or in the degree of surface flatness of the substrate at the atomic scale.[34] As shown in the $I-t$ measurements, the conductance of the molecular pair interacting with each other via the H-bond interaction was larger than that of the alkanedithiol molecular junction (where the Au tip and substrate were fully connected by σ covalent bonds) for the shorter cases. The conductance of the hydrogen-bonded junction, however, decays more quickly than that of the covalent junction as the molecular length increases because of the larger β value of the H-bonded junction. The H-bonded molecular pair consequently becomes less conductive than its covalent counterpart for the larger case. A similarly large β value has previously been reported for a H-bonded molecular pair.[15]

We performed control experiments to confirm that the H-bond between the tip and sample molecules mediates the ET. The $I-z$ measurements were performed in the presence of urea in the solvent. Urea possesses excellent H-bond capabilities[35] and, thus, can disrupt H-bonding between the C_2COOH molecules on the tip and sample. With the urea addition, the plateaus as shown in Figure 3a were observed on only 0.1% of the $I-z$ curves out of 14 000 measurements. In an additional experiment, we employed a methyl ester of C_2COOH, methyl 3-mercaptopropionate, as a molecular tip, and again, essentially no plateaus were observed in the $I-z$ curves. These results demonstrate that H-bond interaction between the tip and sample molecules plays an essential role in ET.

The first-principle calculations were carried out to qualitatively examine the origin of the superior conductivity of the short H-bonded junctions. We investigated the electronic structures of the molecular junctions by projected density of states (PDOS). Transmission spectra based on nonequilibrium Green's function in conjunction with density functional theory, rather than PDOS, are often utilized to investigate molecular conductivity. It was demonstrated that PDOS peaks correlates well with transmission peaks.[36] Moreover, PDOS analyses allow for evaluating contributions of each atom or moiety of the molecular junction to the current.[37,38] We considered either the C_2COOH dimer or the single C_8DT molecule connected to the Au electrodes at their terminals (Figure 4a). Figure 4b shows the PDOS onto terminal S-atoms, methylene groups, and the central parts of the molecular junctions of the C_2COOH dimer (pink) and C_8DT (blue). The PDOS on the S-atoms and the first two methylene groups nearest to the electrodes exhibited similar peaks for these two junctions (see also Figure S1 in SI). However, a significant difference was found in the PDOS in the central regions. There exist prominent peaks centered at approximately −2.1 eV in the PDOS on the two carboxyl groups interacting with each other via the H-bond in the case of the C_2COOH dimer junction (pink in Figure 4b). In contrast, these peaks are totally absent in the PDOS on the four central methylene groups of the C_8DT junction (blue in Figure 4b). Because valence band structures affect the tunneling current through molecular junctions,[38] we attribute the higher conductivity of the short H-bonded junctions to the occupied states at −2.1 eV. Development of a theoretical framework that extends beyond the currently available ones is required before one can make quantitative arguments about the facilitated ET.

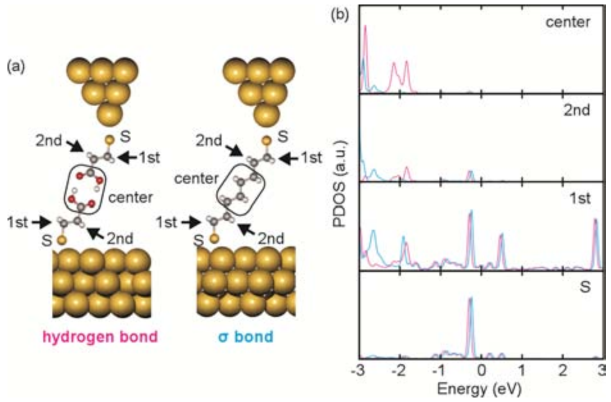

Figure 4. PDOS of molecular junctions. (a) Schematic illustration of molecular junctions consisting of H-bonded C_2COOH dimer (left) and C_8DT (right). (b) PDOS of C_2COOH dimer (pink) and C_8DT (blue). Cutoff energy, 400 eV. The central regions include two carboxy and four methylene groups in the case of the C_2COOH dimer and the C_8DT, respectively. The PDOS values of the symmetrically equivalent atoms or groups (S, first CH_2, and second CH_2) were added up together.

In summary, it is shown here that a H-bond interaction facilitates electron transfer between single molecules. We revealed the superior conductivity of the H-bonded molecular junction compared to the junctions connected by the covalent σ bonds. The property of the electron transfer through the H-bond exhibited pronounced dependence on the junction length. These results indicate that the electrical connection between single molecules can be deliberately controlled by adjusting the length of H-bond linkers between each other. Furthermore, we anticipate the facilitated electron transfer can be switched on and off by changing the solution's pH, since (de)protonation of a functional group can cause the formation or destruction of a H-bond interaction. Our results suggest that H-bonding can be utilized not only merely for structural connection but also for implementing electronic functions, including electrical connections and switching, in molecular nanoelectronic devices.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Control experiments using an unmodified Au substrate or tip, additional PDOS data for the H-bonded molecular junction (Figure S1), and experimental procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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