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# Electron transfer through coordination bond interaction between single molecules: conductance switching by metal ion

Phuc Tan Bui[a] and Tomoaki Nishino*[b]

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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**Molecular tips were used to investigate electron transfer through metal-coordination bonds between single molecules. Coordination of a single metal ion to two carboxylate-terminated thiolate molecules formed a sandwich-type single molecular junction. It was found that a favorable charge transfer is induced through such molecular junctions. The electron transfer facilitated by metal coordination was utilized to implement conductance switching in a molecular junction of a head-to-head pyridine dimer. The present research offers a method to control electronic functions required in the construction of functional electronic molecular devices.**

Measurements of single-molecule conductance have provided significant advances in understanding transport properties at the single-molecule level. The commonly employed techniques for such measurements include mechanically break junction and a related method based on scanning tunneling microscopy (STM). The rapidly growing progress brought by these techniques in the field of molecular electronics has revealed the influence of chemical and electronic structure on electron transmission in molecular electronic junctions.[1,2] In light of such development, deliberate control of the conductance of a single-molecule junction has attracted much attention.[3-5] For example, switching behavior between high- and low-conductance states has been studied using electrochemical gating. In this procedure, both the reference and counter electrodes act as gate electrodes.[6,7] Controllable electronic functions such as conductance switching effects are prerequisites for realizing functional electronic molecular devices.

The construction of such molecular devices also requires controlled organization via self-assembly processes, wherein individual molecules are organized through non-covalent interactions.[8] Therefore, understanding electron transfer between single molecules interacting with each other non-covalently is of great importance, although only little knowledge in this context is currently available.[9-11] We have developed molecular tips for STM, which were prepared by the chemical modification of conventional metal STM tips, typically via the chemisorption of organosulfur compounds.[12-14] Very recently, we utilized $\omega$-carboxy alkanethiol ($HS(CH_2)_nCOOH$, $C_nCOOH$; $n = 1–3$) molecular tips to quantify electron transfer through a hydrogen bond between single molecules (Fig. 1a), and revealed a notable difference in the transport properties of the hydrogen-bonded and covalent molecular junctions.[15] Furthermore, the electron transfer from a single electron donor to a single acceptor through the charge-transfer interaction was measured using a fullerene molecular tip, and the rectification property of the donor–acceptor assembly was quantitatively assessed.[16] Herein, molecular tips were utilized to examine electron transfer through a metal-coordination bond (Fig. 1b). It was revealed that the coordination bond further facilitates electron transfer compared to the transfer via hydrogen bond. Moreover, this phenomenon was shown to offer a novel means to implement a switching behavior in a molecular junction.

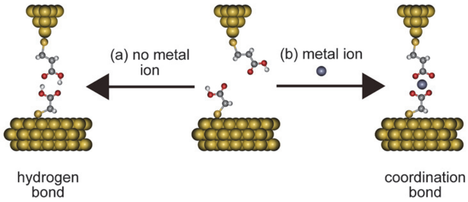

**Fig. 1** Schematic illustration of a molecular junction created using a molecular tip via (a) hydrogen bond and (b) metal-coordination bond interactions.

In the present study, $\omega$-carboxy alkanethiol was employed as a ligand to explore the effect of the metal coordination on the single-molecule conductance. Metal-carboxylate coordination is widely exploited, especially in metal-organic frameworks.[17-19] STM Au tips were modified with the self-assembled monolayers of $C_1COOH$ to prepare the molecular tips. A sample Au(111) surface was modified with $C_2COOH$ at low coverage, which is important for the quantification of electron transfer from a single molecule to its adjacent molecule. The electron transfer was directly measured by current–distance ($I$–$z$) traces. The molecular tip was first brought in close proximity to, but never in contact with, the $C_2COOH$-modified Au(111) substrate in pure 1,2,4-trichlorobenzene solvent. This was achieved by applying a relatively large set-point current (7.5 nA) under the STM feedback control. These conditions prevent the direct contact between the tip and substrate, unlike in the break-junction techniques, leaving the asymmetric experimental condition (different molecules on the tip and substrate) intact throughout the experiments.[15] The molecular tip was then raised with the feedback disabled, and the current flowing between the tip and substrate was recorded as a function of the tip–sample distance. We first obtained $I$–$z$ curves in the absence of metal species (Fig. 2a, blue). Without a metal ion, the molecular tip formed a hydrogen bond with the sample molecule through the carboxy groups (Fig. 1a), and facile electron transfer took place as demonstrated in our previous work.[15] Although the carboxyl or carboxylate group can act as a contact for the single molecule junction,[20,21] the single $C_nCOOH$ molecule on the tip (or the substrate) cannot form the molecular junction without involving another $C_nCOOH$ molecule on the substrate (the tip) under the present experimental conditions.[15] The facile electron transfer through the hydrogen bond is represented in Fig. 2a (blue) as plateaus at which current stayed constant despite the increasing separation. The current value at the plateau positions was statistically assessed by a current histogram constructed using the current value of each data point in thousands of $I$–$z$ curves (Fig. 2b, blue). Consequently, a single distinct peak appeared in the histogram. On the basis of the peak current of 1.1 nA, the conductance of the molecular junction formed from the hydrogen-bonded $C_1COOH$–$C_2COOH$ dimer was determined to be 5.6 nS (or $7.2 \times 10^{-5}$ $G_0$, where $G_0$ is the fundamental conductance quantum), agreeing well with our previous report.[15]

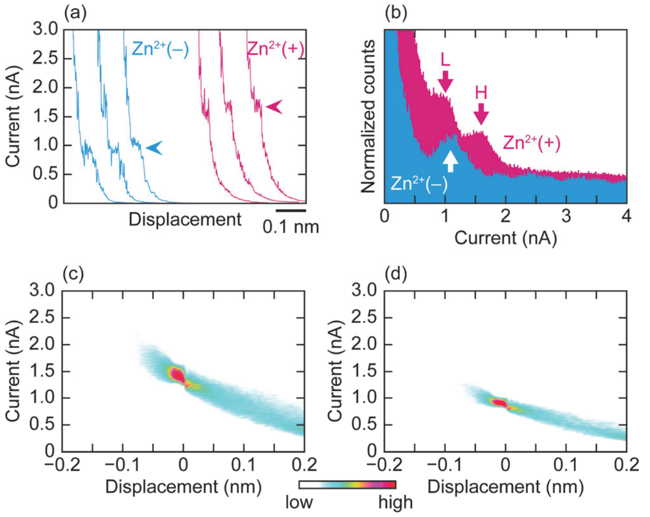

**Fig. 2** (a) Representative $I$–$z$ plots obtained using $C_2COOH$ tip and $C_1COOH$-modified substrate in the absence (blue) and presence (pink) of $Zn^{2+}$. Bias voltage: 0.2 V; initial set-point current: 7.5 nA. (b) Current histograms constructed from $I$–$z$ plots obtained in the absence (blue) and presence (pink) of $Zn^{2+}$. Bin size: 10 pA. (c) and (d) 2D current histograms for the high and low peaks, respectively. The origins in the displacement axes were set at the end of the plateaus.

Similar measurements were performed in the presence of $Zn^{2+}$ ion by using 10 mM $ZnBr_2$ solution in 1,2,4-trichlorobenzene. The resulting $I$–$z$ curves exhibited plateaus (Fig. 2a, pink), and the current histogram compiled from the curves exhibited two peaks (Fig. 2b, pink). Generally, multiple peaks can be observed in a current histogram obtained from $I$–$z$ curves for measuring single-molecule conductance. These peaks are interpreted as resulting from the formation of not single, but multiple, molecular junctions between the tip and the substrate.[22,23] These peaks may also result from different contact geometries between the anchoring groups of the molecule (such as thiol) and the gold surface.[3,24] However, in the present work, similar measurements carried out without the metal ion resulted in the histogram showing a single peak (Fig. 2b, blue). These results exclude the aforementioned interpretation (multiple junctions or different contact geometries); rather, they suggest that the multiple peaks in Fig. 2b (pink) arose from the effect of the metal ion on the single non-covalent molecular junction. By peak fitting, the current (conductance) values for the two peaks at high and low currents (labeled "$H$" and "$L$," respectively) were found to be 0.99 nA (4.9 nS or $6.4 \times 10^{-5}$ $G_0$) and 1.6 nA (7.9 nS or $1.0 \times 10^{-4}$ $G_0$), respectively. The $L$ peak agrees with the peak observed in Fig. 2b (blue); therefore, the $L$ peak originated from a hydrogen-bonded molecular junction that involved no metal ion (Fig. 1a). Concerning the $H$ peak, we attribute this higher peak to a sandwich coordination molecular junction where the molecules on the tip and substrate coordinate with the Zn ion (Fig. 1b).

It is usually difficult to gain structural information about the molecular junction.[3] We anticipate here that the coordination bond is formed by the deprotonated carboxylate groups of the sample and tip molecules (Fig. 1b), because such deprotonation proceeds during the substrate and tip modification in ethanolic solutions.[25] Consequently, some carboxyl groups of the molecules on both the tip and the substrate are in their deprotonated states, which enable the formation of the metal-coordination bond interaction, as shown in Fig. 1b. Although chelate-type coordination is illustrated in Fig. 1b, other coordination modes such as mono- and bidentate coordination are also possible.[26]

The $I$–$z$ curves were further analyzed by creating two-dimensional (2D) current histograms[27] according to the reported procedure.[28] First, $I$–$z$ traces exhibiting plateaus at the current value of either the $L$ or $H$ peak were selected using an automated algorithm (see ESI†). The origin in the displacement axis of the selected $I$–$z$ curve was set at the end of the plateaus, and the 2D histogram was constructed for the $H$ and $L$ peaks (Fig. 2c and 2d, respectively). Both histograms exhibited clear peaks, which extend over a displacement of approximately 0.4 Å. In contrast, the histograms for the $H$ ($L$) peak show no discernible peak at the current value of the $L$ ($H$) peak. These results mean that the $I$–$z$ curve contained a single plateau at a current value of either the $H$ or $L$ peak, and that both the plateaus did not appear simultaneously in a single measurement. This result supports our conclusion that the $H$ and $L$ peaks were caused by the molecular junctions formed by coordination bond interaction with the metal ion and hydrogen bond interaction without the metal ion, respectively. The 2D histogram analyses in Fig. 2c and 2d revealed a rupture of chemical interactions between single molecules, and the quantitative examination of the structural transition of non-covalent interactions by using 2D histogram analyses would be a subject for future research.

The electron transport through single metal complexes has been previously reported.[29-32] Unlike in these studies, the coordination bond was formed between single molecules *in situ* during current measurements in the present study. Nevertheless, the present results concur with the findings of these previous studies. For example, the conductance of a single oligopeptide has been found to increase upon metal-ion binding.[29] The increase in conductance observed in the present as well as in previous works are ascribed to the enhanced electron transport via redox levels of the metal ions; this interpretation has been confirmed by first-principle calculations.[30] The present study demonstrates that in-situ formation of the metal-coordination bond interaction induces facile electron transfer between single molecules. These observations deepen our understanding of electron transfer between single molecules.

The current measurements were performed in the presence of other metal salts, i.e., $CoBr_2$ and $MnBr_2$. Again, plateaus appeared in the resulting *I*–*z* curves, and the current histograms compiled from them exhibited two peaks (Fig. S1 in ESI†). In each case, the peak at lower current agreed well with the one in Fig. 1b (Table S1 in ESI†), and was thus assigned to the electron transfer through the hydrogen-bonded molecular junction without the metal ion. The peaks at higher current (1.5 nA for both $Co^{2+}$ and $Mn^{2+}$, Table S1) were attributed to the metal-ion bridged molecular junctions (Fig. 1b). We carried out the *I*–*z* measurements with 10 mM NaBr in solution. In this case, the same results as shown in Fig. 2a (blue) and 2b (blue) were obtained: the current histogram showed a single peak whose position agrees well with the peak position in Fig. 2b (blue; Table S1 in ESI†). These results demonstrate that a positive charge alone is not sufficient to increase the molecular conductance, and that the coordination bonding between the molecules on the tip and substrate and the metal ion plays an essential role. While previous studies on electron transport through single metal complexes reported moderate dependence of their conductance on the type of transition metal ion, no such dependence was noticed in the present measurements. Electron transport through a molecule primarily depends on the gap between the highest occupied and lowest unoccupied molecular orbitals of the sample molecule and on the alignment of these orbitals with respect to the Fermi energy of the metal electrodes. Detailed systematic theoretical calculations in these aspects might shed light on the metal dependence or independence of the junction conductance.

The conductance increase induced by metal coordination was further investigated by using aromatic molecules. 4-Mercaptobenzoic acid (4MBA) was employed as the molecular tip, and *I*–*z* measurements were performed using 4MBA-modified Au substrate in 0.1 M $NaClO_4$ aqueous solution. Plateaus were observed both in the absence and presence of $Zn^{2+}$ in the measurement solution, and the current histograms resulting from the *I*–*z* traces exhibited a single peak in each case (Fig. 3). However, the current values at the peak positions varied depending on the presence of the metal ion. In its absence, the peak was located at 3.6 nA (Fig. 3a), and the conductance value was calculated to be 18 nS (or $2.3 \times 10^{-4}\ G_0$). On the basis of the previous work,[15] this peak is attributed to electron transfer through a hydrogen bond interaction between the carboxy groups of the two 4MBA molecules on the tip and substrate. When $Zn^{2+}$ ion was present in the solution in the *I*–*z* measurements, the peak appeared at higher current; the peak current and conductance values were 5.7 nA and 29 nS (or $3.7 \times 10^{-4}\ G_0$), respectively (Fig. 3b). This result is in line with the observation for the aliphatic molecules (see above). The conductance increase is attributed to metal coordination bond formation, i.e., incorporation of the metal ion between 4MBA molecules on the tip and the substrate. To further substantiate this interpretation, similar measurements were carried out using the 4MBA tip and the sample in 0.1 M $NaClO_4$ solution containing 10 mM $ZnBr_2$ and ethylenediaminetetraacetic acid (EDTA). EDTA is a chelating agent capable of masking $Zn^{2+}$ ions. The resulting current histogram is characterized by a single peak located at 3.7 nA (Fig. S2 in ESI†). This peak coincides well with the one in Fig. 3a, demonstrating again the crucial role of the metal ion in the facilitation of the electron transfer. These results lead to the conclusion that coordination bond interaction within molecular junctions facilitates electron transfer between single molecules.

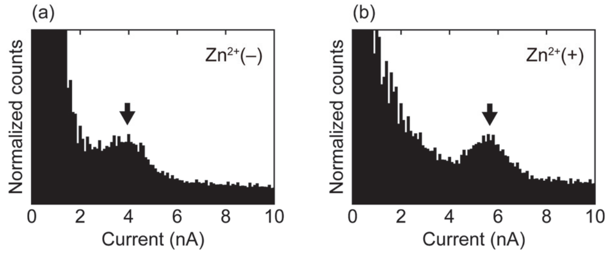

**Fig. 3** Current histograms constructed from *I*–*z* curves obtained by measurement with 4MBA tips over 4MBA-modified substrates in the (a) absence and (b) presence of $Zn^{2+}$. Bias voltage: 0.2 V; initial set-point current: 75 nA; bin size 100 pA.

When the current measurements were conducted using the $C_2COOH$ tip and $C_1COOH$-modified substrate, the current histogram exhibited the peak originating from a hydrogen-bonded $C_1COOH$–$C_2COOH$ dimer (Fig. 1a), even in the presence of $Zn^{2+}$ ion (Fig. 2b, pink). In contrast, in the case of the measurements using 4MBA tip and sample, no peak for the hydrogen-bonded 4MBA dimer appeared when $Zn^{2+}$ was present in the solution (Fig. 3b). These results were most probably caused by the difference in the solution: organic solvent (1,2,4-trichlorobenzene) was used for the former aliphatic case, whereas aqueous solution (0.1 M $NaClO_4$ aqueous solution) was used for the latter aromatic case. The aqueous solution facilitates deprotonation of the carboxy groups of the 4MBA molecules when compared to the organic solvent. Consequently, these molecules easily undergo coordination bond interaction with $Zn^{2+}$ ion; this interaction in turn suppresses the formation of the hydrogen-bonded molecular junction. Another difference between the aliphatic and aromatic systems was noticed in their conductance values. The 4MBA dimer is longer than the $C_1COOH$–$C_2COOH$ dimer: the distance between the terminal sulfur atoms was 10.5 Å (10.7 Å) and 16.0 Å (16.8 Å) for the hydrogen-bonded (coordination bonded) $C_1COOH$–$C_2COOH$ dimer and 4MBA dimer, respectively, based on DFT calculations using the B3LYP functional and the 6-31G(d) basis. Nevertheless, the 4MBA dimer exhibited larger conductance values both in the hydrogen- and coordination-bonded states. These observations agree with the results of previous measurements for single-molecule conductance. Aromatic molecules generally show higher conductance compared to their aliphatic counterparts because of the smaller gap between their highest occupied and lowest unoccupied molecular orbitals.[1,2]

Current measurements were also performed using a 4-mercaptopyridine (4MP) molecular tip over a 4MP-modified Au surface in a 0.1 M $NaClO_4$ solution. When no metal ion was added to the measurement solution, *I*–*z* curves exhibited no plateau and consequently simple exponential background current dominated the resulting current histogram (Fig. 4a, blue). Because the 4MP molecules do not carry protons under the present experimental condition, these molecules on the tip and substrate do not have chemical interactions such as hydrogen bonding. As a result, no molecular junction was formed, leading to the lack of plateaus and peaks in the *I*–*z* curves and the current histogram, respectively. In stark contrast, the presence of $Zn^{2+}$ ions in the solution caused plateaus in the *I*–*z* curves. On the basis of the peak that appeared in the current histogram (Fig. 4b, pink), the current (conductance) value was determined to be 0.88 nA (4.4 nS or $5.7 \times 10^{-5}$ $G_0$). By drawing analogy to the observations described above, we ascribe the peak in Fig. 4b (pink) to a molecular junction in which 4MP molecules on the tip and substrate are connected to each other through the central $Zn^{2+}$ ion via coordination. In the present case, the metal ion induces the formation of the molecular junction and subsequent electron transfer; these processes are totally suppressed in the absence of the metal species. Therefore, the 4MP system constitutes a potential bistate molecular switch operated by a single metal ion.

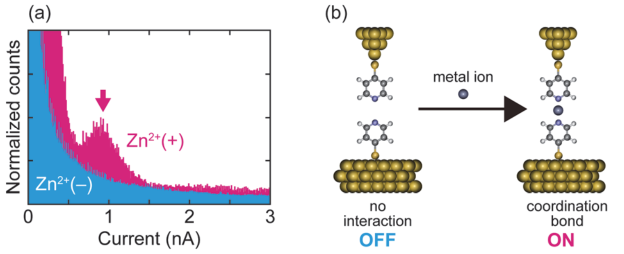

**Fig. 4** (a) Current histograms constructed from *I*–*z* curves obtained by measurements with 4MP tips over 4MP-modified substrates in the absence (blue) and presence (pink) of $Zn^{2+}$. Bias voltage: 0.2 V; initial set-point current: 7.5 nA; bin size 10 pA. (b) Schematic illustration of the molecular junction of 4MP dimer in non-interacting (left, “OFF”) and coordination-bonded (right, “ON”) states.

## Conclusions

In conclusion, we investigated the effect of a metal ion on the transport property between single molecules. We showed that a metal ion induces the formation of a molecular junction with carboxy-terminated molecules via a metal coordination bond. This sandwich coordination molecular junction significantly facilitates electron transfer between single molecules. These results provide essential knowledge for the construction of future bottom-up molecular devices. Moreover, the electron transfer induced by metal coordination was exploited in the construction of potential molecular switches activated by a single metal ion, using pyridine molecules. The next challenge in this context is reversible switching operation using various agents such as chelators.

## Acknowledgements

This work was supported by the Special Coordination Funds for Promoting Science and Technology commissioned by MEXT of Japan, and by JSPS KAKENHI Grant Number 23550103.

## Notes and references

[a] Department of Materials Science, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan.
[b] Department of Applied Chemistry, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan. E-mail: t-nishino@21c.osakafu-u.ac.jp

† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/b000000x/

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