Review

Studies on single-molecule bridging metal electrodes: development of new characterization technique and functionalities

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Abstract: A single molecular junction is a nanoscale structure prepared by bridging a single molecule between macroscopic metal electrodes. It has attracted significant attention due to its unique structure and potential applications in ultra-small single molecular electronic devices. It has two metal-molecule interfaces, and thus the electronic structure of the molecule can be significantly modulated from its original one. The single molecular junction can be regarded as a new material that includes metal electrodes, a so-called “double interface material”. Therefore, we can expect unconventional physical and chemical properties. To develop a better understanding of the properties and functionalities of single molecular junctions, their atomic and electronic structures should be characterized. In this review, we describe the development of these characterization techniques, such as inelastic electron tunneling spectroscopy, surface-enhanced Raman scattering, as well as shot noise and thermopower measurements. We have also described some unique properties and functionalities of single molecular junctions, such as switching and diode properties.

Keywords: single molecular junction, molecular electronics, electron transport, metal-molecule interface, atomic and electronic structures

1. Introduction

The single molecular junction is a molecule-metal hybrid system, where a single molecule forms a bridge between two metal electrodes. Single molecular junctions have attracted attention recently because of their unique properties and potential applications in ultra-small electronic devices.1),2) Currently, the minimum line width of an electronic device is about 10 nm, using silicon-based technology. Since the size of a molecule is around 1 nm, device size can be decreased further by realizing single-molecular devices. The single molecular junction is a key component of a single molecular device. In terms of fundamental science, a single molecular junction is expected to have novel properties and functionalities because of its unique structure.3) The single molecular junction is a one-dimensional nanomaterial with two metal-molecule interfaces. Due to the reduced dimensionality and size, quantum effects and surface effects are significant. The molecule-metal interaction also affects the device properties. Catalytic reactions can proceed on the metal surface. The catalytic reactivity originates from the metal-molecule interaction. Even one metal-molecule interface can cause new functionalities to arise. Since the single molecular junction has two metal-molecule interfaces, we can expect unconventional properties and/or functionalities from single molecular junctions.4)

Due to these interesting properties, single molecular junctions have been both theoretically and experimentally studied. Research into single molecular junctions started in 1972. Aviram and Ratner theoretically proposed a single molecular diode consisting of a donor π unit and an acceptor π unit separated by alkane units.5) In 1997, Reed et al. first measured the electron-transport properties of a benzene dithiol (BDT) single molecular junction.6) Single molecular junction can be fabricated by
breaking the metal atomic contact covered with target molecules using a scanning tunneling microscope (STM) or a mechanically controllable break junction (MCBJ). Figure 1 shows a schematic image of the single molecular junction fabrication process. By pulling the metal contact, the diameter of the metal contact decreases. An atomic metal contact is formed just before breaking the metal contact. Further pulling the junction breaks the metal contact, and a nanoscale gap is formed. Several molecules bridge the gap between the metal electrodes, and form molecular junctions. The number of bridging molecules decreases one by one. And just before breaking the molecular junction entirely, a single molecular junction can be formed. Using break junction techniques, a variety of single molecular junctions have been investigated. Diode, switch, and transistor properties as well as other functionalities have been reported for single molecular junctions.

Although various properties and functionalities have been reported for single molecular junctions, there are two main research subjects. First, the reproducibility of the experimental results is quite low. For example, the reported conductance values of BDT single molecular junctions differ among groups by several orders of magnitude. Second, there are few studies reporting new properties and functionalities that are characteristic of single molecular junctions. The functionalities of the molecule, itself, are often lost in the studies of single molecular junctions. For example, ring-closing reactions of diarylethene were not observed in the single molecular junction, while the ring-opening and closing reactions are known to proceed in the bulk state.

One of the reasons for low the reproducibility is a lack of characterization techniques to directly observe the single molecule bridging metal electrodes. The conductance of a single molecular junction has often been discussed, without any identification of the atomic and electronic structures of the single molecular junction. To improve our understanding of the single molecular junction, new characterization techniques are essential. Finding new properties and functionalities characteristic of the single molecular junction is also crucial.

2. Characterization techniques for single molecular junctions

The most direct way to observe the bridging
molecule of a single molecular junction is to take atomic images of the junction. Transmission electron microscopy (TEM) is one of the most promising techniques to obtain atomic images, and it has been applied to a Gd metallofullerene (Gd@C$_{82}$) single molecular junction by Kasumov et al.\textsuperscript{14) Figure 2 shows a high-resolution TEM (HRTEM) image of a Gd@C$_{82}$ molecular dimer between superconducting metal electrodes. The existence and number of bridging molecules can be clearly identified from the atomic image. The TEM is a powerful tool to observe single molecular and atomic junctions. Furthermore, metal atomic junctions, the formation process, and atomic structures of the atomic chain and helical multi shell wire have been successfully imaged using HRTEM.\textsuperscript{15,16) However, high-energy electrons can damage single molecules, and thus there have been few TEM studies of the single molecular junctions up to now.

The number of bridging molecules can be evaluated based on shot-noise measurements together with conductance measurements.\textsuperscript{17) Here, we briefly describe the shot noise. The electrical current through a conductor exhibits temporal fluctuation, because of the discreteness of the electron charge. If individual electrons are transmitted randomly through the conductor, the transfer of an electron is described by Poisson statistics. The noise power, $P$, which is the Fourier transform of the current-current correlation function, has its maximum value as $P = 2eI = P_{\text{Poisson}}$, where $I$ is the average current and $e$ is the electron charge. If electrons are correlated, the correlation suppresses the noise below $P_{\text{Poisson}}$. Because the size of the single molecule junction is comparable to the typical length that determines the level of correlation between the electrons, the noise is suppressed and it is represented by

$$P = S = 2eV \coth\left(\frac{eV}{2kT}\right) \frac{2e^2}{h} \Sigma \tau_i (1 - \tau_i) + 4kT \frac{2e^2}{h} \Sigma \tau_i^2,$$

where $V$, $k$, $T$, $h$ are the applied voltage, the Boltzmann constant, the junction temperature, and Planck’s constant, respectively. Here, $\tau_i$ is the transmission probability of the $i$-th transmission channel. Meanwhile, the conductance is represented by

$$G = \frac{2e^2}{h} \Sigma \tau_i.$$ \textsuperscript{[2]}

Here, $2e^2/h$ is the quantum unit. In the case of a single molecular junction and an atomic junction, their diameter and length are small (sub nm). Reflecting the small diameter and the lateral confinement of electrons, the conductance is quantized and it is represented by the Landauer equation \textsuperscript{[2]. By solving these two equations, the number of transmission channels and the transmission probability of each channel could be precisely obtained for up to two transmission channels. Figure 3(a) shows a schematic image of the shot noise measurement.\textsuperscript{17) Since the shot noise is very weak, special care is needed to distinguish the shot noise from other noise. The signal is thus measured by two different amplifiers. By taking the cross spectra, the intrinsic shot noise can be extracted from the signal. Figure 3(b) shows the noise power as a function of the bias current of benzene molecular junctions from three distinct samples.\textsuperscript{18) The noise power increases with the bias current. By analyzing the shot noise and the conductance of the benzene molecular junction, the transmission probabilities can be determined for each sample. The number of transmission channels generally increases with the conductance of the junction. The number of transmission channels for the benzene molecular junction with a conductance value of 0.20 $G_0$ is one, which clearly shows that the number of bridging molecules is strictly one. Here, the number of bridging molecules is 0.20.\textsuperscript{17)

The chemical species of the bridging molecule can be determined by vibrational spectroscopy. Inelastic electron tunneling spectroscopy (IETS) is the first type of vibrational spectroscopy to be applied to single molecular junctions. When the applied bias voltage increases, the differential con-

![Fig. 2. High resolution transmission electron microscopy image of a Gd@C$_{82}$ molecular dimer between electrodes.\textsuperscript{14}](image-url)
ductance changes at a certain voltage due to electron-phonon interactions. This threshold voltage provides the energy of the vibration mode. Figure 4(a) shows an example the IETS spectrum from a benzene single molecular junction using Pt electrodes. At a bias voltage of around 40 meV, symmetric upward steps are observed in the $dI/dV$ curve, and we can see corresponding peaks in the $d^2I/dV^2$ curve (IETS). The steps and peaks in the $dI/dV$ curve and the $d^2I/dV^2$ curve correspond to a vibrational mode (40 meV). The isotope shift of the vibrational mode proves that the benzene molecule bridges the Pt electrodes. Figure 4(b) shows histograms of the vibrational energy for $^{12}$C$_6$H$_6$ and $^{13}$C$_6$H$_6$ single molecular junctions.

Surface-enhanced Raman scattering (SERS) is a vibrational spectroscopy appropriate for studying single molecular devices. In the single molecular junction, an enhanced field is formed at the gap between the metal electrodes. The SERS signal from the bridging molecule can be selectively detected. Figure 5(a) illustrates the experimental setup used to obtain the SERS spectra from single molecular junctions. The formation of a single molecular junction is examined by monitoring the conductance of the junction. Figure 5(c) shows Raman imaging of the ring breathing mode of 4,4'-bipyridine (BPY) for the BPY single molecular junction. An intense SERS signal is detected only at the gap. Figure 5(c) shows the SERS spectrum of a BDT single molecular junction. The SERS spectrum shows three vibrational modes, which are assigned to the C=C stretching mode ($\sim$1560 cm$^{-1}$, $\nu_{8a}$), the ring breathing mode ($\sim$1070 cm$^{-1}$, $\nu_1$), and the deformation-coupled C–S stretching mode ($\sim$330 cm$^{-1}$, $\nu_{6a}$), respectively. Currently, single molecule dynamics can be revealed by time-resolved SERS, and site-specific SERS has been reported for single molecular junctions.

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**Fig. 3.** (a) Experimental setup to measure the shot noise of a single molecular junction. (b) Bias current-shot noise curves for three distinct benzene molecular junctions with Pt electrodes. The conductances of the benzene molecular junctions are 1.08 $G_0$ (filled square), 0.71 $G_0$ (triangle), and 0.20 $G_0$ (filled circle). The transmission probabilities are shown in the inset.

**Fig. 4.** (a) $dI/dV$ curve (top) and $d^2I/dV^2$ curve (bottom) of a benzene single molecular junction with Pt electrodes. (b) Histograms of the vibrational energy from $^{12}$C$_6$H$_6$ and $^{13}$C$_6$H$_6$ single molecular junctions.
The interface structure of a single molecular junction can be revealed by the $I$-$V$ curve. The $I$-$V$ curve from a single molecular junction is given by the equation:

$$I(V) = \frac{8e}{\hbar} \left\{ \tan^{-1} \left( \frac{\Gamma_R}{\Gamma_L + \Gamma_R} eV - \varepsilon_0 \right) \right\} \left( \frac{\Gamma_R}{\Gamma_L + \Gamma_R} eV + \varepsilon_0 \right)$$

where $\Gamma_L$, $\Gamma_R$, and $\varepsilon_0$ are the molecule-metal coupling strength at the left and right electrodes and the energy difference between the Fermi level and the conduction orbital, respectively. Here, we assume a single-level tunneling model. The values of $\varepsilon_0$, $\Gamma_L$, and $\Gamma_R$ depend on the metal-molecule interface of the single-molecule junction. By analyzing these parameters, we can determine the interface structure. Figure 6 shows a histogram of $I$-$V$ curves from BDT single molecular junctions. Three distinct conductance states (high (H), medium (M), low (L)) are visible. By fitting the experimentally obtained $I$-$V$ curves to eq. [3], the values of $\varepsilon_0$ and $\Gamma (= \Gamma_L + \Gamma_R)$ can be determined for the BDT single molecular junction with three distinct states. By comparing the experimental results with theoretical calculations, the L, M, and H states are assigned to the atop, hollow and bridge states, respectively (Fig. 6).
The electronic structure of the single molecular junction can be resolved by simultaneous measurements of the $I$-$V$ curve and the thermopower.\textsuperscript{27} The sign of the thermopower of a material depends on the type of carrier (hole or electron).\textsuperscript{28} If the carriers are holes, the HOMO stays close to the Fermi level of the single molecular junction. Meanwhile, the $I$-$V$ curve measurement fixes the energy difference between the Fermi level and the conduction orbital, although it does not indicate whether the conduction orbital is below or above the Fermi level. Therefore, by combing the $I$-$V$ curve measurement with the thermopower measurement, we can determine the energy alignment of the conduction orbital. Figure 7(a) shows $I$-$V$ curves from the C$_{60}$ single molecular junction at temperature differences of 10 K and 0 K.\textsuperscript{29} The thermoelectric voltage was observed as an offset voltage in the $I$-$V$ curves. A positive thermoelectric voltage corresponds to a negative thermopower, indicating that the LUMO stays close to the Fermi level. The $I$-$V$ curve measurement reveals that the energy difference between the Fermi level and the conduction orbital is 0.5–0.6 eV. A combined analysis reveals that LUMO is 0.5–0.6 eV above the Fermi level (Fig. 7(b)).

3. Innovation of new functionalities

There have been many studies of single molecular junctions that report on various device functionalities, such as diodes, switches, and transistors.\textsuperscript{9,11,30} But, the functional properties of the molecule, itself, are often lost in the single molecular junction,\textsuperscript{13} as discussed in Introduction. This is because the metal-molecule interaction changes the electronic structure of the molecule. One of the approaches used to overcome this problem is to decrease the amount of metal-molecule interactions. Jia et al. successfully fabricated a fully reversible diarylethene single molecular switch with high accuracy, stability, and reproducibility using this strategy.\textsuperscript{31} They incorporated three methylene groups into each side of the molecular backbone to decrease the molecule-metal interaction. Here, we introduce another strategy by which new properties and functionalities can be produced by taking advantage of strong metal-molecule interactions.

The first example is an enhancement of the conductance by effective hybridization of the molecular orbital and the metal orbital. In 2008, our group reported that the conductance of the benzene single molecule bridging Pt electrodes was 1 G\textsubscript{0} (2e\textsuperscript{2}/h).\textsuperscript{18,32} This conductance value agrees with that of the Au atomic junction. In the bulk, benzene is an insulator. By bridging Pt electrodes, its conductance is drastically improved. This high conductivity is achieved by effective hybridization of the $\pi$ orbital of benzene with the Pt orbital. Our newly developed direct $\pi$-binding techniques have been applied to various molecules, such as C$_{60}$,\textsuperscript{21,22,32–34} Ce@C$_{82}$,\textsuperscript{33} acetylene, ethylene, and pyrazine.\textsuperscript{35}

Diode behavior can be induced by preparing asymmetric interfaces. Batra et al. reported diode behavior from a single molecular junction of the stilbene derivative (Fig. 8(a)).\textsuperscript{36} The stilbene molecular backbone binds to the Au electrode via a Au–S bond, and via a Au–C bond. Figure 8(b) shows the $I$-$V$ curve of the stilbene derivative single molecular junction. A larger current flows at a positive bias voltage, indicating the behavior of a diode. The electric coupling of the Au–C bond is larger than that of the Au–S bond. In the stilbene derivative single molecular junction, the conduction orbital is the HOMO. Owing to strong coupling at the Au–C side, the conduction orbital primarily follows the Fermi level of the Au electrode at the left side. The HOMO is moved into the bias window when a positive bias voltage is applied to the right electrode.\textsuperscript{37,38} Electrons can be easily transported via the HOMO, which leads to a large current. However, at negative bias voltages, the HOMO is pushed away from the bias window, leading to a small current.

One of the problems with single molecular junctions is fluctuation of the conductance, depending on the interface structure. This disadvantage can become an advantage if we can control the interface...
structure. Conductance switching can be realized by dynamically controlling the interface structure of the single molecular junction. Figure 9(a) shows the time dependence of the conductance of a pyrazine single molecular junction with Pt electrodes. The dotted line in the figure shows the distance between the Pt electrodes. The conductance reversibly switches between two conductance states (high (H) and low (L)). The conductance, IETS, and theoretical calculations show that the H and L conductance states correspond to the tilted and parallel configurations, respectively (see Figs. 9(b) and (c)). In the H state (Fig. 9(b)), the metal-molecule coupling is large because the pyrazine molecule connects with the Pt electrode via both direct π-bonding and Pt–N bonding. Effective hybridization of the π-orbital with the metal orbital results in high conductivity. In contrast, in the L state, the pyrazine molecule connects with the Pt electrodes only via a Pt–N bond, leading to low conductivity. The interface structure affects the conductance of the pyrazine single molecular junction, as in the case of the BDT single molecular junction showing three distinct conductance states. In the bulk phase, the conductivity of pyrazine cannot be drastically modulated by mechanical force. In a single molecular junction, the conductance can be easily tuned by a controlling the interface structure with a tiny mechanical force.

Fig. 8. (a) Single molecular junction of a stilbene derivative. The Au–C bond is formed at the left electrode (L) and the Au–S bond is formed at the right electrode (R). (b) $I-V$ curve for the stilbene derivative single molecular junction. (c) Energy diagram of the stilbene derivative single molecular junction. The shaded regions represent the bias windows at positive and negative bias voltages.

Fig. 9. (a) Time dependence of the conductance of the pyrazine single molecular junction. The gap distance is represented by the dashed line. The H and L states are highlighted as a circle with a solid line and a dotted line, respectively. Structural model of (b) high (H) and (c) low (L) conductance states. The Pt atom and N atoms of pyrazine are represented with a large ball and a small ball, respectively.
(~1 nN). This functionality is a consequence of the intrinsic characteristics of the single molecular junction. Similar mechanical switches have been reported using bipyridine, BDT, C₆₀, ScN@C₈₀, oligothiophene and Au atomic junctions.²⁸),³⁰),⁴⁰)

Using covered oligothiophene (QT), we first developed a single molecular switch showing multiple conductance states.⁴¹) The QT molecule has four thiophene rings, which can bind to metal electrodes. By changing the gap distance, the QT single molecular junction shows three distinct conductance states. The anchoring positions in the QT molecule can be changed by controlling the gap size. The effective tunneling length can be changed, and thus the conductance changes, depending on the gap size.

Finally, we discuss the chemical reactivity of single molecular junctions. We observed the enhancement of a chemical reaction on a single molecular junction with a bowl-shaped molecule, sumanene. Figure 10(a) shows two types of STM images of sumanene molecules on Au (111).⁴²) We can observe bright and dark spots, as shown in Fig. 10(a). From a comparison of the experimentally obtained STM image and the theoretical one, the bright and dark spots are found to correspond to the bowl-down and bowl-up conformations, respectively. In the case of a bowl-shaped molecule, the bowl inversion reaction is one of its characteristics. We found that the bowl inversion reaction was enhanced when the STM tip approached the molecule to form a single molecular junction. The inversion rate was between 0.3 and 0.5 Hz, which was two orders of magnitude larger than the stochastic inversion rate (0.005 Hz). Figures 10(b) and (c) show the calculated activation barriers for the bowl inversion reaction as a function of the distance between the molecule and the electrode. The activation barrier for the bowl inversion reaction decreases with decreasing distance. The increase in the metal-molecule interaction modulates the activation barrier of the chemical reaction. This indicates that a novel chemical reaction can proceed on the single molecular junction.⁴³),⁴⁴)

**Conclusion**

In this review, we discussed the characterization techniques as well as the properties and functionalities of the single molecular junction. The number of bridging molecules, their chemical species, and the electronic structure can be determined from measurements of the shot noise, IETS or SERS, and thermopower, respectively. Since the atomic structure of a single molecular junction can vary with the sample, its atomic and electronic structures and its chemical and physical properties should be determined at the same time. Therefore, simultaneous measurements using several techniques are crucial for obtaining a full understanding of the single molecular junction. With regard to the properties and functionalities of single molecular junctions, there have been few studies revealing the unconventional chemical and physical properties, which are characteristic of single molecular junctions, up to now. Since single molecular junctions have a unique structure, we can expect them to exhibit interesting and useful properties and functionalities. In this review, we commented on some examples, where the diode and switch behavior as well as chemical reactivity appear in single molecular junctions. Although these phenomena arise due to the unique structure, the properties and functionalities are not so excellent. However, further research into single molecular junctions should result in drastic improve-
ments if single molecular junctions with truly unconventional properties and functionalities can be obtained.

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References

1) Joachim, C., Gimzewski, J.K. and Aviram, A. (2000) Electronics using hybrid-molecular and mono-molecular devices. Nature 408, 541–548.

2) Kiguchi, M. and Fujii, S. (2017) Governing the metal–molecule interface: towards new functionality in single-molecule junctions. Bull. Chem. Soc. Jpn. 90, 1–11.

3) Komoto, Y., Fujii, S., Iwane, M. and Kiguchi, M. (2016) Single-molecule junctions for molecular electronics. J. Mate. Chem. C 4, 8842–8858.

4) Komoto, Y., Fujii, S. and Kiguchi, M. (2018) Single-molecule junctions of π molecules. Mater. Chem. Front. 2, 214–218.

5) Aviram, A. and Ratner, M.A. (1974) Molecular rectifiers. Chem. Phys. Lett. 29, 277–283.

6) Reed, M.A., Zhou, C., Muller, C.J., Burgin, T.P. and Tour, J.M. (1997) Conductance of a molecular junction. Science 278, 252–254.

7) Kiguchi, M., Konishi, T. and Murakoshi, K. (2005) Hydrogen-assisted stabilization of Ni nanowires in solution. Appl. Phys. Lett. 87, 043104.

8) Kiguchi, M. and Murakoshi, K. (2008) Conductance of single C60 molecule bridging metal electrodes. J. Phys. Chem. C 112, 8140–8143.

9) Song, H., Kim, Y., Jang, Y.H., Jeong, H., Reed, M.A. and Lee, T. (2009) Observation of molecular orbital gating. Nature 462, 1039–1043.

10) Fujii, S., Marques-Gonzalez, S., Shin, J.Y., Shinokubo, H., Masuda, T., Nishino, T. et al. (2017) Highly-conducting molecular circuits based on antiaromaticity. Nat. Commun. 8, 15984.

11) Diez-Perez, I., Hihath, J., Lee, Y., Yu, L., Adamska, L., Kozlowski, M.A. et al. (2009) Rectification and stability of a single molecular diode with controlled orientation. Nat. Chem. 1, 635–641.

12) Perrin, M.L., Verzijl, C.J., Martin, C.A., Shaikh, A.J., Eelkema, R., van Esch, J.H. et al. (2013) Large tunable image-charge effects in single-molecule junctions. Nat. Nanotechnol. 8, 282–287.

13) Dulić, D., van der Molen, S.J., Kudernac, T., Jonkman, H.T., de Jong, J.J., Bowden, T.N. et al. (2003) One-way optoelectronic switching of photophysical molecules on gold. Phys. Rev. Lett. 91, 207402.

14) Kasumov, A.Y., Tsukagoshi, K., Kawamura, M., Kobayashi, T., Aoyagi, Y., Senba, K. et al. (2005) Proximity effect in a superconductor-metallofullerene-superconductor molecular junction. Phys. Rev. B 72, 033414.

15) Ohnishi, H., Kondo, Y. and Takayanagi, K. (1998) Quantized conductance through individual rows of suspended gold atoms. Nature 395, 780–783.

16) Oshima, Y., Ono, A. and Takayanagi, K. (2003) Helical gold nanotube synthesized at 150 K. Phys. Rev. Lett. 91, 205503.

17) Dijkic, D. and van Ruitenbeek, J.M. (2006) Shot noise measurements on a single molecule. Nano Lett. 6, 789–793.

18) Kiguchi, M., Tal, O., Wohlthatt, S., Pauly, F., Krieger, M., Dijkic, D. et al. (2008) Highly conductive molecular junctions based on direct binding of benzene to platinum electrodes. Phys. Rev. Lett. 101, 046801.

19) Hihath, J., Arroyo, C.R., Rubio-Bollinger, G., Tao, N. and Agrait, N. (2008) Study of electron-phonon interactions in a single molecule covalently connected to two electrodes. Nano Lett. 8, 1673–1678.

20) Kiguchi, M., Stadler, R., Kristensen, I.S., Dijkic, D. and van Ruitenbeek, J.M. (2007) Evidence for a single hydrogen molecule connected by an atomic chain. Phys. Rev. Lett. 98, 146802.

21) Nie, S. (1997) Probing single molecules and single nanoparticles by surface-enhanced raman scattering. Science 275, 1102–1106.

22) Iwane, M., Fujii, S. and Kiguchi, M. (2017) Surface-enhanced raman scattering in molecular junctions. Sensors (Basel) 17, 1901.

23) Konishi, T., Kiguchi, M., Takase, M., Nagasawa, F., Nabika, H., Ieeda, K. et al. (2013) Single molecule dynamics at a mechanically controllable break junction in solution at room temperature. J. Am. Chem. Soc. 135, 1009–1014.

24) Kaneko, S., Murai, D., Marques-Gonzalez, S., Nakamura, H., Komoto, Y., Fujii, S. et al. (2016) Site-selection in single-molecule junction for highly reproducible molecular electronics. J. Am. Chem. Soc. 138, 1294–1300.

25) Komoto, Y., Fujii, S., Nakamura, H., Tada, T., Nishino, T. and Kiguchi, M. (2016) Resolving metal-molecule interfaces at single-molecule junctions. Sci. Rep. 6, 26606.

26) Matsuhiita, R., Horikawa, M., Naitoh, Y., Nakamura, H. and Kiguchi, M. (2013) Conductance and SERS measurement of benzenedithiol molecules bridging between Au electrodes. J. Phys. Chem. C 117, 1791–1795.

27) Reddy, P., Jang, S.Y., Segalman, R.A. and Majumdar, A. (2007) Thermoelectricity in molecular junctions. Science 315, 1568–1571.

28) Aiba, A., Demir, F., Kaneko, S., Fujii, S., Nishino, T., Tsukagoshi, K. et al. (2017) Controlling the thermoelectric effect by mechanical manipulation
of the electron’s quantum phase in atomic junctions. Sci. Rep. 7, 7949.

29) Komoto, Y., Ishiki, Y., Fujii, S., Nishino, T. and Kiguchi, M. (2017) Evaluation of the electronic structure of single-molecule junctions based on current-voltage and thermopower measurements: application to C₆₀ single-molecule junction. Chem. Asian J. 12, 440–445.

30) Quek, S.Y., Kamenetska, M., Steigerwald, M.L., Choi, H.J., Louie, S.G., Hybertsen, M.S. et al. (2009) Mechanically controlled binary conductance switching of a single-molecule junction. Nano Lett. 9, 2474–2478.

31) Jia, C., Migliore, A., Xin, N., Huang, S., Wang, J., Yang, Q. et al. (2016) Covalently bonded single-molecule junctions with stable and irreversible photoswitched conductivity. Science 352, 1443–1445.

32) Kiguchi, M., Inatomi, J., Takahashi, Y., Tanaka, R., Osuga, T., Murase, T. et al. (2013) Highly conductive [3xn] gold-ion clusters enclosed within self-assembled cages. Angew. Chem. Int. Ed. Engl. 52, 6202–6205.

33) Kaneko, S., Wang, L., Luo, G., Lu, J., Nagase, S., Sato, S. et al. (2012) Electron transport through single endohedral Ce@C₈₂ metallofullerenes. Phys. Rev. B 86, 155406.

34) Kiguchi, M. (2009) Electrical conductance of single C₆₀ and benzene molecules bridging between Pt electrode. Appl. Phys. Lett. 95, 073301.

35) Nakazumi, T., Kaneko, S., Matsushima, R. and Kiguchi, M. (2012) Electric conductance of single ethylene and acetylene molecules bridging between Pt electrodes. J. Phys. Chem. C 116, 18250–18255.

36) Batra, A., Darancet, P., Chen, Q., Meisner, J.S., Widawsky, J.R., Neaton, J.B. et al. (2013) Tuning rectification in single-molecular diodes. Nano Lett. 13, 6233–6237.

37) Fujii, S., Tada, T., Komoto, Y., Osuga, T., Murase, T., Fujita, M. et al. (2015) Rectifying electron-transport properties through stacks of aromatic molecules inserted into a self-assembled cage. J. Am. Chem. Soc. 137, 5939–5947.

38) Iwane, M., Fujii, S. and Kiguchi, M. (2017) Molecular diode studies based on a highly sensitive molecular measurement technique. Sensors (Basel) 17, 956.

39) Kaneko, S., Motta, C., Brivio, G.P. and Kiguchi, M. (2013) Mechanically controllable bi-stable states in a highly conductive single pyrazine molecular junction. Nanotechnology 24, 315201.

40) Rincon-Garcia, L., Ismael, A.K., Evangelie, C., Grace, I., Rubio-Bollinger, G., Porfyakis, K. et al. (2016) Molecular design and control of fullerene-based bi-thermoelectric materials. Nat. Mater. 15, 289–293.

41) Kiguchi, M., Ohto, T., Fujii, S., Sugiyasu, K., Nakajima, S., Takeuchi, M. et al. (2014) Single molecular resistive switch obtained via sliding multiple anchoring points and varying effective wire length. J. Am. Chem. Soc. 136, 7327–7332.

42) Fujii, S., Ziatdinov, M., Higashibayashi, S., Sakurai, H. and Kiguchi, M. (2016) Bowl inversion and electronic switching of buckybowls on gold. J. Am. Chem. Soc. 138, 12142–12149.

43) Kiguchi, M., Konishi, T., Hasegawa, K., Shidara, S. and Murakoshi, K. (2008) Three reversible states controlled on a gold monatomic contact by the electrochemical potential. Phys. Rev. B 77, 245421.

44) Kiguchi, M., Konishi, T. and Murakoshi, K. (2006) Conductance bistability of gold nanowires at room temperature. Phys. Rev. B 73, 125406.

Profile

Manabu Kiguchi was born in Tokyo, Japan in 1972. He received a B.Sc. degree in Chemistry from The University of Tokyo in 1994. In 2000, he obtained his Ph.D. from the same university, working under the supervision of Prof. Toshiaki Ohta. In 1999, he joined Prof. Kojiro Saiki’s group as a research associate at The University of Tokyo. In 2004, he joined Prof. Kei Murakoshi’s group as a lecturer at Hokkaido University. In 2009, he moved to the Department of Chemistry at Tokyo Institute of Technology as an associate professor, and in 2013 he was appointed to the position of Professor. He was awarded the 14th JSPS PRIZE in 2017.