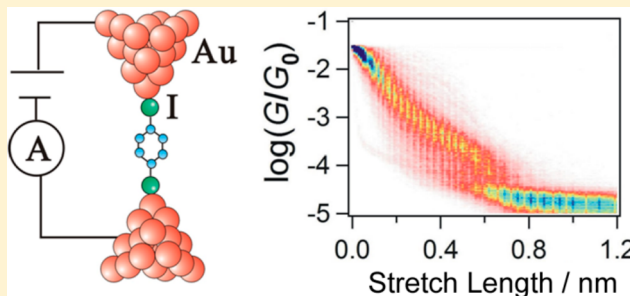


Single Molecular Bridging of Au Nanogap Using Aryl Halide Molecules

Yuki Komoto,[†] Shintaro Fujii,[†] Kenji Hara,[‡] and Manabu Kiguchi^{*,†}[†]Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 W4-10 Ookayama, Meguro-ku, Tokyo 152-8551, Japan[‡]Catalysis Research Center, Hokkaido University, Kita-21 Nishi-10, Kita-ku, Sapporo, 001-0021, Japan**S** Supporting Information

ABSTRACT: Single molecular junctions of benzene dihalide molecules (*para*-X-(C₆H₄)-X, X = Cl, Br, I) binding to Au electrodes were systematically studied by using the scanning tunneling microscopy break junction (STM-BJ) technique. The STM-BJ characterization revealed that the single molecular junction was formed only with 1,4-diiodobenzene, which was due to its ability to form particularly stable halogen bonds with Au electrodes for the iodide anchoring group. The conductance and strength of the metal–molecule bond of the single 1,4-diiodobenzene molecular junction were compared with that of 1,4-benzenediamine (*para*-H₂N-(C₆H₄)-NH₂). The conductance of a single 1,4-diiodobenzene molecular junction was $3.6 \times 10^{-4} G_0$ ($G_0 = 2e^2/h$), which was smaller than $1 \times 10^{-2} G_0$ measured for 1,4-benzenediamine. The distances to break single molecular junctions were 0.05 and 0.03 nm for single 1,4-diiodobenzene and 1,4-benzenediamine molecular junctions, respectively. The longer breakdown distance of the single 1,4-diiodobenzene molecular junctions indicated that the Au–I bond was stronger than that of the Au–NH₂ bond. The present work demonstrates that an iodide group can be utilized as an anchoring group for the single molecular junction.



1. INTRODUCTION

The investigation on electron transport through individual molecules is a central topic in molecular electronic devices.^{1–10} One of the current topics in the molecular electronics is the electrical contact between single and/or small ensembles of molecules and the metal electrodes. Various molecular anchoring groups have been investigated using the scanning tunneling microscope (STM) break junction technique, the mechanically controllable break junction technique, and other techniques.^{11–17} Amino (NH₂) and thiol (SH) groups are the most frequently used anchoring groups for the single molecular junctions.^{4–6,9,12,14–16} However, synthesis of molecules containing amino or thiol groups sometimes requires elaborate multistep procedures and/or consideration in accordance with regulation for hazardous chemicals.¹⁸ For example, 4,4'-diaminobiphenyl was registered as a carcinogenic compound.¹⁹ In contrast, molecules with halide functionality are relatively easily available, which enables both systematic fundamental studies and practical applications. If molecular conductance using halide molecules is established, significant contribution to molecular electronics is expected. We thus envisioned utilization of halide anchoring groups for the formation of single molecular junctions.

In the previous studies on single molecule conductance, halide groups have little attracted attention as anchoring groups for the single molecular junction. For example, trichlorobenzene has been utilized as the solvent,¹² because it is believed

that trichlorobenzene molecule does not bridge between Au electrodes. On the contrary, iodide can be regarded as reactive functionality, resulting in cleavage of the C–I bond via interaction with a metal electrode in metal-catalyzed reactions such as Ullmann-type reactions.¹⁸ Therefore, this study was aimed to find the applicability of the halide groups as anchoring groups in single molecular conductance.

We systematically investigate single molecular junction formation with 1,4-dichlorobenzene, 1,4-dibromobenzene, and 1,4-diiodobenzene. The single molecular junction was formed only with 1,4-diiodobenzene showing the conductance value of $3.6 (\pm 0.7) \times 10^{-4} G_0$ ($2e^2/h$). We revealed that an iodide group can be utilized as an anchoring group for the single molecular junction. The single molecular junction with 1,4-diiodobenzene was compared with that with 1,4-benzenediamine. The metal–molecule bond was stronger with 1,4-diiodobenzene, while the conductance was larger with 1,4-benzenediamine. The smaller conductance value of the 1,4-diiodobenzene was explained by the energy difference between the conduction orbital of the molecule and the Fermi level of the metal electrodes.

Received: May 17, 2013

Revised: October 22, 2013

Published: October 25, 2013

2. EXPERIMENTAL SECTION

Conductance measurements were performed using an electrochemical STM (Pico-SPM, Molecular Imaging Co.) with a Nano Scope IIIa controller (Digital Instruments Co.). Details of the experimental design used in this study have previously been reported by some of the present authors.¹⁷ Briefly, the STM tip was made of a Au wire (diameter ≈ 0.25 nm, purity $>99\%$). The Au(111) substrate was prepared by flame annealing, followed by quenching. The concentrations of solutions of 1,4-dichlorobenzene, 1,4-dibromobenzene, and 1,4-diiodobenzene in tetraethyleneglycol dimethyl ether (tetraglyme) were adjusted to 1 mM. The STM tip was repeatedly moved in and out of contact with the substrate in the solution at a rate of 50 nm/s at room temperature. Conductances were measured during the breaking process with an applied bias of 20 mV between the tip and the substrate. All statistical data were obtained using a large number (>2000) of individual conductance traces. The experiments were performed on three distinct samples.

3. RESULTS AND DISCUSSION

Figure 1 shows typical conductance traces when the Au contacts were broken in solutions containing 1,4-dichlorobenzene, 1,4-dibromobenzene, and 1,4-diiodobenzene. Most of the conductance traces showed a $1 G_0$ plateau, indicating the formation of Au atomic contacts before the Au contacts were broken (not shown in the figure).³ In a solution containing 1,4-diiodobenzene, the conductance decreased in a stepwise fashion (dotted lines in Figure 1c). The conductance value of the plateau was an integer multiple of $(3-4) \times 10^{-4} G_0$. Most of the steps showed a positive or negative slope, which originated from a slight structural change in the molecular junction during breaking of the junction. The corresponding conductance histograms (Figure 1g,k) showed distinctive features around $(3-4) \times 10^{-4} G_0$. Neither plateau nor features were observed below $(3-4) \times 10^{-4} G_0$ in the conductance traces and histograms. In the absence of halide molecules, neither plateaus nor peaks were observed below $1 G_0$ in both the conductance traces and histograms (Figure 1d,h,l). The plateau in the conductance traces and features in the conductance histograms, which occurred at $(3-4) \times 10^{-4} G_0$ and $2 \times (3-4) \times 10^{-4} G_0$ were (see Figure 1c,g), thus, due to the bridging of one and two 1,4-diiodobenzene molecules between the Au electrodes, respectively. The conductance of the single 1,4-diiodobenzene molecule junctions was determined to be $3.6 (\pm 0.7) \times 10^{-4} G_0$ by repeated measurements on three distinct samples. In addition to the assigned integer multiple peaks of the fundamental single molecular conductance as indicated by arrows in Figure 1g, we can recognize faint peaks in the conductance range from $3 \times 10^{-4} G_0$ to $15 \times 10^{-4} G_0$, which, we believe, is due to multiple compressed molecular junction formations with ill-defined metal–molecule contact configurations and molecular orientations before the stretching of the molecular junctions. It should be noted here that the faint conductance peaks above $(3-4) \times 10^{-4} G_0$ were not reproducible and the peak positions varied in the three sets of independent experiments. For a solution containing 1,4-dichlorobenzene or 1,4-dibromobenzene, no plateaus or peaks were observed in the conductance traces or histograms between $0.03 G_0$ and $5 \times 10^{-5} G_0$ and the measured conductance behavior was quite similar to that of the blank solution (Figure 1a,b,e,f,i,j).

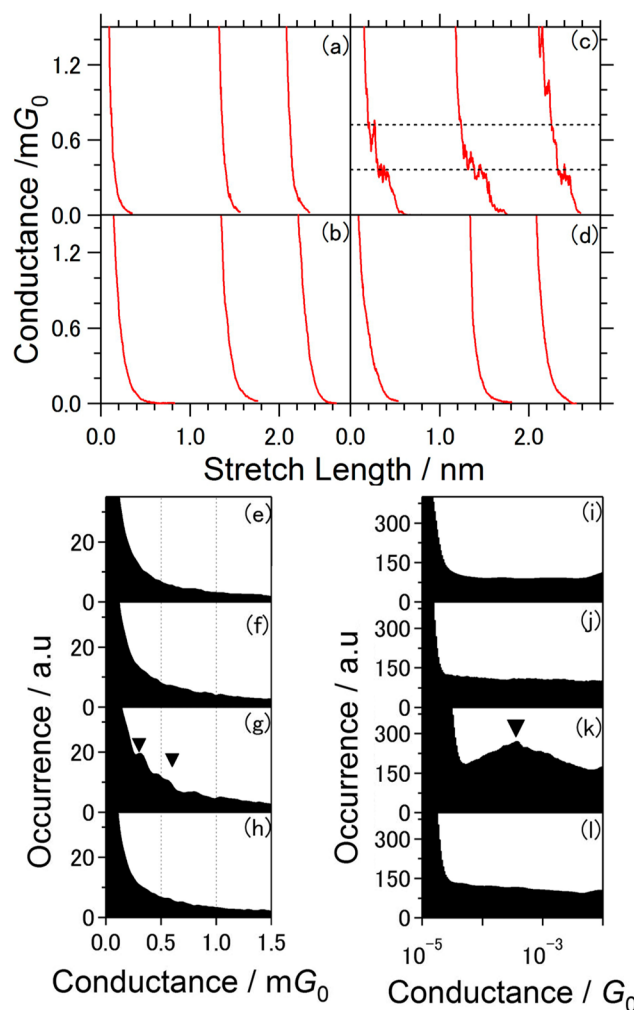


Figure 1. Conductance traces and conductance histograms of (a, e, i) 1,4-dichlorobenzene, (b, f, j) 1,4-dibromobenzene, (c, g, k) 1,4-diiodobenzene solution, and (d, h, l) blank. The conductance histograms (e–h, linear scale; i–l, linear (counts) vs log (conductance) scale) were obtained from 1000 conductance traces without data selection. The linear bin size was $1 \times 10^{-6} G_0$ for parts e–h. The logarithmic bin size of $\Delta \log(G/G_0)$ was 0.02 for parts i–l. The arrows in part g correspond to conductance peaks for one and two molecules in the junctions. The peak in part k indicated by the arrow is the fundamental single molecular conductance.

In the conductance range below the fundamental single molecular conductance of $3 \times 10^{-4} G_0$, we identified no preferable and reproducible conductance distribution, as shown in linear scale conductance traces and histograms in Figure 2. Such absence of the preferable conductance distribution can be seen in the log-scale conductance histograms in Figure 1k (see also Figure S2, Supporting Information).

The possible reasons for the absence of the features in the conductance traces and conductance histograms for 1,4-dichlorobenzene and 1,4-dibromobenzene are following: (1) The single molecular junction was not formed. (2) The conductance of the single molecular junction was under the detection limit. (3) The single molecular junction did not show a fixed conductance value. In order to clarify the origin of the absence of the conductance features, we obtained 2D conductance versus displacement histograms.²⁰ Figure 3 shows the 2D conductance histograms of 1,4-dichlorobenzene, 1,4-dibromobenzene, 1,4-diiodobenzene, and blank solution.

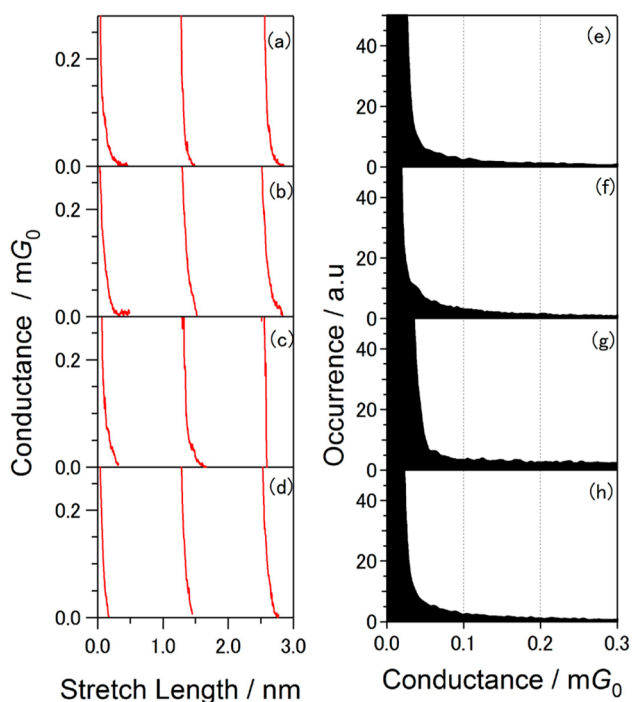


Figure 2. Conductance traces and conductance histograms of (a, e) 1,4-dichlorobenzene, (b, f) 1,4-dibromobenzene, (c, g) 1,4-diiodobenzene solution, and (d, h) blank. The conductance histograms were obtained from 1000 conductance traces without data selection. Below the fundamental single molecular conductance of $3 \times 10^{-4} G_0$, there are no preferable conductance distributions.

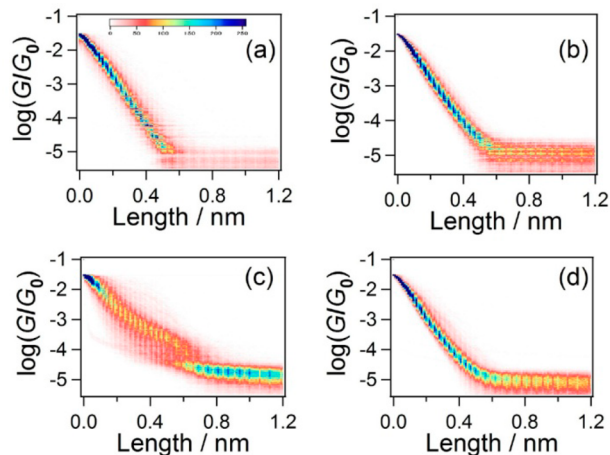


Figure 3. 2D conductance histograms of (a) 1,4-dichlorobenzene, (b) 1,4-dibromobenzene, (c) 1,4-diiodobenzene, and (d) blank solution. The 2D conductance histograms were obtained from the 2331 traces.

The 2D histograms were generated by identifying the first data point in every trace which had the conductance lower than $0.03 G_0$ as a relative zero distance $z = 0$ to overlap all individual traces in 2D space constructed from 2331 conductance traces without data selection. In the conductance range below $10^{-2} G_0$, the contribution of the background tunneling current is not negligible, which appears as monotonic conductance decay within the junction-stretch length of 0.5 nm for the 2D histograms in the 1,4-dichlorobenzene and 1,4-dibromobenzene solution as with the case of the blank solution. The results indicated that the single molecular junction was not formed in the 1,4-dichlorobenzene and 1,4-dibromobenzene solution.

In contrast, the conductance versus displacement curves for 1,4-diiodobenzene did not follow that for blank solution. Finite counts were observed at the upper right side of the blank solution. The conductance decreased from $3 \times 10^{-4} G_0$ to background level around 0.7 nm. The short plateaus in the diiodobenzene traces and the non-negligible contribution of the background tunneling current (Figure 1c) could be one of the main reasons for the spread and weak intensity of the single molecular conductance of 1,4-diiodobenzene in Figure 2c. We believe that, at the initial stage of the formation of the molecular junctions, 1,4-diiodobenzene molecules bridge a small gap between two metal electrodes in a tilted form with the iodide atoms attached to the metal surface. During the stretching process of the molecular junctions, the molecules are forced into an upright orientation until the junctions are broken. Stochastic breakdown events of the molecular junctions during the stretching process lead to the short plateaus in the conductance traces and spread intensity of the single molecular conductance of 1,4-diiodobenzene in Figure 2c.

The distance of 0.7 nm was close to the distances between the iodide atoms on the opposite sides of the 1,4-diiodobenzene molecule, supporting that the 1,4-diiodobenzene molecule bridged between Au electrodes with its molecular long axis parallel to the junction axis, and excludes the possibility of the dissociation of the 1,4-diiodobenzene molecule.²¹ The dissociation of the 1,4-diiodobenzene molecule could produce smaller molecules (cf. benzene, iodide), which could not bridge the 0.7 nm gap. Our X-ray photoelectron spectroscopy (XPS) results supported that 1,4-dichlorobenzene and 1,4-dibromobenzene did not adsorb on Au electrodes, while 1,4-diiodobenzene adsorbed on the Au electrode (see Figure S1, Supporting Information).

The preferential bridging of 1,4-diiodobenzene between the Au electrode could be explained by the higher ability of iodide groups to form halogen bonding, which is a non-covalent interaction electron acceptor of halogen and electron donor (i.e., Au in this study). Recently, Blakey et al. have investigated the particularly strong halogen bonding between iodoperfluoro benzene compounds and gold nanoparticles.²² The XPS results demonstrated that the aryl iodide molecules such as diiodobenzene and fluorinated diiodobenzene bound to gold nanoparticles via iodine atoms. It has been reported that halogen bonding is stronger, as the halogen is more polarizable.²³ Since polarizability increases from fluorine to iodine, the halogen-binding ability becomes higher in the order $\text{Cl} < \text{Br} < \text{I}$.²³ The polarizability of chlorobenzene, bromobenzene, and iodobenzene is $11.8, 12.9, 15.2 \times 10^{-24} \text{ cm}^3$, respectively.²⁴

The present study revealed that the iodide group can be utilized as an anchoring group for the single molecular junction. We then compared the performance of the iodide and amino groups as anchoring groups for the single molecular junction. The conductance behavior of the single 1,4-benzenediamine molecular junction was investigated under the same experimental condition. The conductance of the single 1,4-benzenediamine junction was determined to be ca. $1 \times 10^{-2} G_0$ (see the Supporting Information), which agreed with the previously reported value⁸ and was larger than that of the 1,4-diiodobenzene junction. The strength of the molecule–metal bond was investigated by statistical analysis of the conductance traces. Since the last plateau corresponds to a single molecular junction, the length of the last plateau is the distance over which the single molecular junction can be stretched before

breakdown (breakdown distance). The breakdown distances depend on the strength of the molecule–metal bond, molecular size, and mobility of the surface atoms on the electrodes.^{6,21,25} The molecular size and the mobility of the surface atoms on the electrodes for the single 1,4-diiodobenzene molecular junction were close to that for 1,4-benzenediamine. The breakdown distances, thus, reflected the strength of the molecule–metal bond when we compared the breakdown distance for the single 1,4-diiodobenzene and 1,4-benzenediamine molecular junctions. The breakdown distance was defined as the distance between the points (set points) at which the conductance dropped below $4.3 \times 10^{-4} G_0$ and $2.9 \times 10^{-4} G_0$ for the 1,4-diiodobenzene (see the Supporting Information in detail). The set points were $1.3 \times 10^{-2} G_0$ and $0.7 \times 10^{-2} G_0$ for the 1,4-benzenediamine. Figure 4 shows the distribution of the

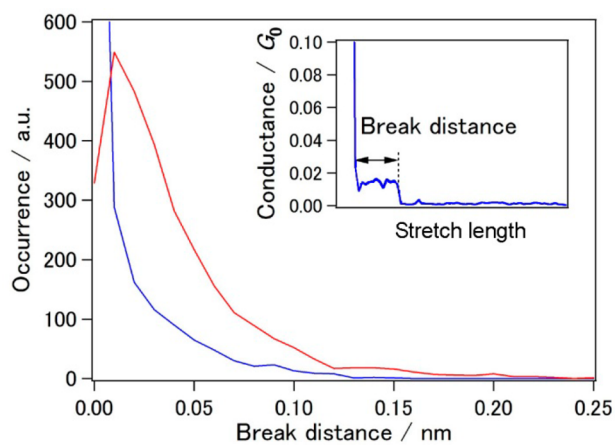


Figure 4. The distribution of breakdown distances for the 1,4-diiodobenzene (red) and 1,4-benzenediamine (blue) molecular junctions obtained by 2331 conductance traces. The inset shows the typical conductance trace for the 1,4-benzenediamine molecular junction. The break distance is shown by the arrow.

breakdown distances for the single 1,4-diiodobenzene and 1,4-benzenediamine molecular junctions. The histograms were obtained from the 2331 traces. The average lengths were 0.05 (± 0.01) and 0.03 (± 0.01) nm for the single 1,4-diiodobenzene and 1,4-benzenediamine molecular junctions, respectively. The longer breakdown distance for the single 1,4-diiodobenzene molecular junction indicated that the Au–I bond was stronger than the Au–NH₂ bond. The previously reported study for 1,4-benzenedithiol showed that the breakdown distance was 0.09 nm, which was longer than that for 1,4-diiodobenzene.²⁶ In the case of the single 1,4-benzenedithiol molecular junction, not the Au–S but the Au–Au bond breaks. Therefore, the Au–S bond was much stronger than the Au–I bond.

Here we comment on the difference in the observed conductance values between the single 1,4-benzenediamine and 1,4-diiodobenzene molecular junctions. In general, at the low bias tunneling regime, conductance of single molecule junctions is dependent on (i) alignment of the closest frontier molecular orbitals relative to the Fermi energy level of the electrodes and (ii) electronic coupling between the molecules and the metal electrodes. A smaller difference in the frontier molecular orbital and the Fermi level and stronger electronic coupling lead to higher conductance. The net effect of these two factors determines the conductance across the junction.²⁷ For weakly coupled molecule–metal systems, the frontier

molecular orbitals are not significantly altered by coupling to the surface.²⁸ Previous ultraviolet photoemission spectroscopy (UPS) studies on a variety of π -conjugated molecules adsorbed on Au have revealed that the change in the work function of the Au surface was 0.2–1 eV. The shift of the work function (i.e., change in molecular orbital levels) is due to electronic polarization at the molecule–metal interface, which is modeled by the image charge effect, charge transfer effect, etc.²⁹ In a similar fashion, the frontier orbital levels of 1,4-benzenediamine and 1,4-diiodobenzene can be shifted from the original upon relatively weak non-covalent bonding (i.e., donor–acceptor bonding) with Au electrodes. In the non-interacting limit, on the basis of the calculated ionization potential value (6.5 eV) that is close to the experimental value (6.9 eV),³⁰ the experimental Au work function value (5.1 eV),³¹ and calculated HOMO–LUMO gap values (5.0 eV), see the Supporting Information, HOMO and LUMO levels relative to the Fermi level of Au are calculated to be -1.4 and $+3.6$ eV for 1,4-benzenediamine. In a similar manner, HOMO and LUMO levels are calculated to be -3.2 and $+1.9$ eV for 1,4-diiodobenzene where the ionization potential, Au work function, and calculated HOMO–LUMO gap are 8.3 eV, which is close to the experimental value (8.6 eV),³² 5.1 eV,³¹ and 5.1 eV (see the Supporting Information), respectively. By neglecting the small shift of the molecular orbitals due to the polarization effect,²⁹ the frontier orbital closest to the Fermi level is most likely to be the HOMO and LUMO level for 1,4-benzenediamine and 1,4-diiodobenzene, respectively. The larger energy difference between the frontier orbital level and the Au Fermi level for 1,4-diiodobenzene (i.e., $+1.9$ eV at the non-interacting limit) than that for 1,4-benzenediamine (i.e., -1.4 eV) could explain the observed lower conductance values of 1,4-diiodobenzene. It should be noted here that Venkataraman and co-workers have reported in a recent UPS/XPS study of 1,4-benzenediamine on a Au surface that the HOMO level is located at 1.4–1.8 eV below the Au Fermi level,²⁸ suggesting that the frontier molecular orbitals are not significantly altered by coupling to the surface for the weakly coupled molecule–Au system.

As described above, stronger electronic coupling leads to higher conductance. Besides the electronic coupling, the binding strength of the anchoring group to metal electrodes has been reported to correlate well with the conductance of the molecular junctions.^{15,33} The anchoring group of a molecule is expected to affect the electronic coupling between the molecule and the electrode and thus the contact resistance.¹⁵ Chen et al. have demonstrated that stronger binding gives a lower contact resistance by investigating the conductance of single molecules using alkanes terminated with dithiol, diamine, and dicarboxylic-acid groups.²³ We have also found the correlation between the binding strength of the anchoring groups and the conductance for 1,4-disubstituted benzene bounded to metal electrodes such as Pt and Au,²⁶ in which the breakdown distances of the molecular junctions (i.e., binding strength) were largely associated with the single molecular conductance. Such correlation between the breakdown distance and the conductance was not evident for the 1,4-diiodobenzene–Au and 1,4-benzenediamine–Au junctions studied here. At the current stage, we believe that the lower charge transport property of the 1,4-diiodobenzene–Au junctions comes from the significant disadvantage in the energy level alignment between the molecular frontier orbital level and the Fermi level of the 1,4-diiodobenzene–Au junctions.

4. CONCLUSIONS

In summary, we demonstrate that 1,4-diiodobenzene bridges the gap between two Au electrodes to form the single molecular junctions via particularly strong halogen bonding between iodide and gold. The strength of the gold–molecule bonds and the single molecular conductance value of 1,4-diiodobenzene junctions were compared with those of 1,4-benzenediamine junctions. The single molecular junctions of 1,4-diiodobenzene exhibited stronger gold–molecule bonding but a lower conductance value than those of 1,4-benzenediamine. According to the single level tunneling model, a smaller difference between the conduction orbital and Fermi level as well as the stronger binding gives higher conductance. The observed smaller single molecular conductance value of the 1,4-diiodobenzene can be ascribed to the dominant effect of the relative alignment of the conduction orbital and Fermi level of the Au electrodes. The conduction orbital of 1,4-benzenediamine is expected to be closer to the Fermi level than that of 1,4-diiodobenzene. In principle, not only the conduction orbital level but also the strength of the halogen bond (i.e., Lewis acidity of the halogen bonding donor) can be controlled by introducing electron donating/withdrawing functional groups into the aryl moiety. Despite the observed relatively smaller conductance value, synthetically easy accessibility of the iodide anchoring group could provide an alternative design for constructing single molecular junctions.

■ ASSOCIATED CONTENT

Supporting Information

The XPS, conductance measurement of a single benzenediamine molecular junction, and analysis of the breakdown distance. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kiguti@chem.titech.ac.jp.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Grant-in-Aid for Scientific Research (A) (No. 24245027) and Scientific Research in Innovative Areas (No. 25104710), Challenging Exploratory Research (No. 25620055) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT).

■ REFERENCES

- (1) Cuevas, J. C.; Scheer, E. *Molecular Electronics: An Introduction to Theory and Experiment*; World Scientific Publishing Co. Pte. Ltd.: Singapore, 2010.
- (2) Cuniberti, G.; Fagas, G.; Richter, K. *Introducing Molecular Electronics*; Springer-Verlag: Berlin, Heidelberg, 2005.
- (3) Agrait, N.; Yeyati, A. L.; van Ruitenbeek, J. M. Quantum Properties of Atomic-Sized Conductors. *Phys. Rep.* **2003**, *377*, 81–279.
- (4) Song, H.; Reed, M. A.; Lee, T. Single Molecule Electronic Devices. *Adv. Mater.* **2011**, *23*, 1583–1608.
- (5) Tao, N. J. Electron Transport in Molecular Junctions. *Nat. Nanotechnol.* **2006**, *1*, 173–181.
- (6) (a) Kiguchi, M.; Kaneko, S. Single Molecule Bridging between Metal Electrodes. *Phys. Chem. Chem. Phys.* **2013**, *15*, 2253–2267. (b) Kiguchi, M.; Kaneko, S. Electron Transport through Single π -

Conjugated Molecules Bridging between Metal Electrodes. *Chem-PhysChem* **2012**, *13*, 1116–1126.

- (7) Joachim, C.; Gimzewski, J. K.; Aviram, A. Electronics Using Hybrid-Molecular and Mono-Molecular Devices. *Nature* **2000**, *408*, 541–548.

- (8) Hong, S.; Reifengerger, R.; Tian, R.; Datta, S.; Henderson, J. I.; Kubiak, C. P. Molecular Conductance Spectroscopy of Conjugated, Phenyl-Based Molecules on Au(111): the Effect of End Groups on Molecular Conduction. *Superlattices Microstruct.* **2000**, *28*, 289–303.

- (9) Wrochem, F.; Gao, D.; Scholz, F.; Nothofer, H.-G.; Nelles, G.; Wessels, J. M. Efficient Electronic Coupling and Improved Stability with Dithiocarbamate-Based Molecular Junctions. *Nat. Nanotechnol.* **2010**, *5*, 618–624.

- (10) Nature Nanotechnology Editorial. Does Molecular Electronics Compute? *Nat. Nanotechnol.* **2013**, *8*, 377.

- (11) Xu, B.; Tao, N. J. Measurement of Single-Molecule Resistance by Repeated Formation of Molecular Junctions. *Science* **2003**, *301*, 1221–1223.

- (12) Venkataraman, L.; Klare, J. E.; Tam, I. W.; Nuckolls, C.; Hybertsen, M. S.; Steigerwald, M. Single-Molecule Circuits with Well-Defined Molecular Conductance. *Nano Lett.* **2006**, *6*, 458–462.

- (13) Seminario, J. M.; De La Cruz, C. E.; Derosa, P. A. A Theoretical Analysis of Metal–Molecule Contacts. *J. Am. Chem. Soc.* **2001**, *123*, 5616–5617.

- (14) Hong, W.; D. Manrique, Z.; Moreno-Garcia, P.; Gulcur, M.; Mishchenko, A.; Lambert, C. J.; Bryce, M. R.; Wandlowski, T. Single Molecular Conductance of Tolanes: Experimental and Theoretical Study on the Junction Evolution Dependent on the Anchoring Group. *J. Am. Chem. Soc.* **2012**, *134*, 2292–2304.

- (15) Chen, F.; Li, X.; Hihath, J.; Huang, Z.; Tao, N. Effect of Anchoring Groups on Single-Molecule Conductance: Comparative Study of Thiol-, Amine-, and Carboxylic-Acid-Terminated Molecules. *J. Am. Chem. Soc.* **2006**, *128*, 15874–15881.

- (16) Haiss, W.; Wang, C.; Grace, I.; Batsanov, A. S.; Schiffrin, D. J.; Higgins, S. J.; Bryce, M. R.; Lambert, C. J.; Nichols, R. J. Precision Control of Single-Molecule Electrical Junctions. *Nat. Mater.* **2006**, *5*, 995–1002.

- (17) (a) Kiguchi, M.; Miura, S.; Hara, K.; Sawamura, M.; Murakoshi, K. Conductance of Single 1,4-Disubstituted Benzene Molecules Anchored to Pt Electrodes. *Appl. Phys. Lett.* **2007**, *91*, 53110. (b) Kiguchi, M.; Miura, S.; Hara, K.; Sawamura, M.; Murakoshi, M. Conductance of a Single Molecule Anchored by an Isocyanide Substituent to Gold Electrodes. *Appl. Phys. Lett.* **2006**, *89*, 213104. (c) Kiguchi, M.; Nakamura, H.; Takahashi, Y.; Takahashi, T.; Ohto, T. Effect of Anchoring Group Position on Formation and Conductance of a Single Disubstituted Benzene Molecule Bridging Au Electrodes: Change of Conductive Molecular Orbital and Electron Pathway. *J. Phys. Chem. C* **2010**, *114*, 22254–22261.

- (18) Jones, M. *Organic Chemistry*; W.W. Norton: New York, 1997.

- (19) See regulatory information (<https://scifinder.cas.org/>), CAS Registry Number: 92-87-5).

- (20) Perrin, M. L.; Prins, F.; Martin, C. A.; Shaikh, A. J.; Eelkema, R.; van Esch, J. H.; Briza, T.; Kaplanek, R.; Kral, V.; van Ruitenbeek, J. M.; J. van der Zant, H. S.; Dulic, D. Influence of the Chemical Structure on the Stability and Conductance of Porphyrin Single-Molecule Junctions. *Angew. Chem., Int. Ed.* **2011**, *50*, 11223–11226.

- (21) Kiguchi, M.; Takahashi, T.; Takahashi, Y.; Yamauchi, Y.; Murase, T.; Fujita, M.; Tada, T.; Watanabe, S. Electron Transport through Single Molecules Comprising Aromatic Stacks Enclosed in Self-Assembled Cages. *Angew. Chem., Int. Ed.* **2011**, *50*, 5708–5711.

- (22) Blakey, I.; Merican, Z.; Rintoul, L.; Chuang, Y.; Jack, K. S.; Micallef, A. S. Interactions of Iodoperfluorobenzene Compounds with Gold Nanoparticles. *Phys. Chem. Chem. Phys.* **2012**, *14*, 3604–3611.

- (23) Politzer, P.; Murray, J. S.; Clark, T. Halogen Bonding: an Electrostatically-Driven Highly Directional Noncovalent Interaction. *Phys. Chem. Chem. Phys.* **2010**, *12*, 7748–7757.

- (24) Bregman-Reisler, H.; Rosenberg, A.; Amiel, S. Molecular Charge Transfer Reactions of Monosubstituted Benzenes at Low Energies. *J. Chem. Phys.* **1973**, *59*, 5404–5410.

(25) Kamenetska, M.; Koentopp, M.; Whalley, A. C.; Park, Y. S.; Steigerwald, M. L.; Nuckolls, C.; Hybertsen, M. S. Formation and Evolution of Single-Molecule Junctions. *Phys. Rev. Lett.* **2009**, *102*, 126803.

(26) Kiguchi, M.; Miura, S.; Hara, K.; Sawamura, M.; Murakoshi, K. Conductance of Single 1,4-Disubstituted Benzene Molecules Anchored to Pt Electrodes. *Appl. Phys. Lett.* **2007**, *91*, 053110.

(27) Venkataraman, L.; Park, Y. S.; Whalley, A. C.; Nuckolls, C.; Hybertsen, M. S. Electronics and Chemistry: Varying Single-Molecule Junction Conductance Using Chemical Substituents. *Nano Lett.* **2007**, *7*, 502–506.

(28) Dell'Angela, M.; Kladnik, G.; Cossaro, A.; Verdini, A.; Kamenetska, M.; Tamblin, I.; Quek, S. Y.; Neaton, J. B.; Cvetko, D.; Morgante, A.; Venkataraman, L. Relating Energy Level Alignment and Amine-Linked Single Molecule Junction Conductance. *Nano Lett.* **2010**, *10*, 2470–2474.

(29) Ishii, H.; Sugiyama, K.; Ito, E.; Seki, K. Energy Level Alignment and Interfacial Electronic Structures at Organic/Metal and Organic/Organic Interfaces. *Adv. Mater.* **1999**, *11*, 605–625.

(30) Tsuji, K.; Saito, M.; Tani, T. Ionization Potentials of Phenylenediamines and Steric Effect in the Ortho Isomer. *Denki Kagaku oyobi Kogyo Butsuri Kagaku* **1973**, *41*, 688.

(31) Michaelson, H. B. The Work Function of the Elements and its Periodicity. *J. Appl. Phys.* **1977**, *48*, 4729–4733.

(32) Potts, A. W.; Lyus, M. L.; Lee, E. P. F.; Fattahallah, G. H. High Resolution Ultraviolet Photoelectron Spectra of C_6H_5X and $p-C_6H_4X_2$ where $X = Cl, Br$ or I . *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 556–570.

(33) Kiguchi, M.; Murakoshi, K. Conductance of Single C_{60} Molecule Bridging Metal Electrodes. *J. Phys. Chem. C* **2008**, *112*, 8140–8143.