

論文 / 著書情報
Article / Book Information

Title	ROOM-TEMPERATURE SINGLE MOLECULAR MEMORY
Authors	Shinya Kano,Yasuyuki Yamada,kentaro Tanaka,YUTAKA MAJIMA
Citation	Applied Physics Letter, Vol. 100, ,
Pub. date	2012, 1
URL	http://scitation.aip.org/content/aip/journal/apl
Copyright	Copyright (c) 2012 American Institute of Physics

Room-temperature single molecular memory

Shinya Kano, Yasuyuki Yamada, Kentaro Tanaka, and Yutaka Majima

Citation: *Appl. Phys. Lett.* **100**, 053101 (2012); doi: 10.1063/1.3679127

View online: <http://dx.doi.org/10.1063/1.3679127>

View Table of Contents: <http://apl.aip.org/resource/1/APPLAB/v100/i5>

Published by the American Institute of Physics.

Related Articles

Computational study of graphene-based vertical field effect transistor
J. Appl. Phys. **113**, 094507 (2013)

Spin filtering in molecular junction: Magnetoresistance evaluation from wave-function calculations
J. Chem. Phys. **138**, 094105 (2013)

Vibrational spectroscopy of single-molecule junctions by direct current measurements
J. Appl. Phys. **113**, 084301 (2013)

Spin polarized current through Cu-DNA modulated by a gate voltage
Appl. Phys. Lett. **102**, 072410 (2013)

High capacity reversible hydrogen storage by metallo-carbohedrenes: An ab initio molecular dynamics simulation study
Appl. Phys. Lett. **102**, 073901 (2013)

Additional information on *Appl. Phys. Lett.*


Journal Homepage: <http://apl.aip.org/>

Journal Information: http://apl.aip.org/about/about_the_journal


Top downloads: http://apl.aip.org/features/most_downloaded

Information for Authors: <http://apl.aip.org/authors>

ADVERTISEMENT



Does your research require low temperatures? Contact Janis today.
Our engineers will assist you in choosing the best system for your application.



10 mK to 800 K
Cryocoolers
Dilution Refrigerator Systems
Micro-manipulated Probe Stations

LHe/LN₂ Cryostats
Magnet Systems

sales@janis.com www.janis.com
Click to view our product web page.

Room-temperature single molecular memory

Shinya Kano,^{1,2} Yasuyuki Yamada,^{2,3} Kentaro Tanaka,^{2,4} and Yutaka Majima^{1,2,5,a)}

¹Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan

²CREST, Japan Science and Technology Agency, Yokohama 226-8503, Japan

³Research Center for Materials Science, Nagoya University, Nagoya 464-8602, Japan

⁴Department of Chemistry, Graduate School of Science, Nagoya University, Nagoya 464-8602, Japan

⁵Department of Printed Electronics Engineering, Sunchon National University, Sunchon 540-742, South Korea

(Received 21 October 2011; accepted 7 November 2011; published online 30 January 2012)

Single molecular memory operation was observed on a porphyrin derivative by scanning tunneling microscopy at room temperature. A porphyrin derivative with four disulfide groups was chemically synthesized and chemisorbed on a Au(111) surface. Coulomb blockade behaviors and switching behaviors in current-voltage (*I*-*V*) characteristics were observed on a single porphyrin derivative by scanning tunneling spectroscopy. Based on the switching behaviors, the memory operation of electrical conductance in the porphyrin derivative was demonstrated by applying a programmed pulse sequence with an on/off ratio of 2.9 at room temperature. © 2012 American Institute of Physics. [doi:10.1063/1.3679127]

Molecular switching behaviors have attracted much attention because of their potential application for molecular solid-state devices.¹ Various molecular switching phenomena have been reported, for example, in catenane-rotaxane interlocked molecules,² oligo(phenylene-ethynylene) (OPE),^{3,4} and fullerene.^{5,6} Molecular switching behaviors by porphyrin derivatives have been especially studied toward the realization of molecular switches.⁷ The origin of the switching behaviors has been attributed to, for example, adsorption geometry,⁸ conformational changes of molecules,⁹ and reduction-oxidation reactions.^{10,11} For practical applications of a single molecular switch in solid-state devices, observation of single molecular switching behaviors under room temperature (RT) conditions is one of the most important issues; however, almost all single molecular switches have been demonstrated at low temperature. Porphyrin derivatives with multiple thiol groups as a clip to the Au surface have been reported.^{12,13} Thiol-derivatized porphyrins have a covalent immobilization with the Au surface, and they are expected to apply to molecular devices.

Here, we report the single molecular switching properties of a single porphyrin derivative at room temperature. We synthesized a Cu(II) complex of porphyrin derivatives, Boc-Por-SS1(Cu), which have disulfide groups in four substituents as four clips to the Au(111) substrate. The detail of synthetic procedure is shown in supplementary material.¹⁴ We demonstrate the conductance switching properties of a single Boc-Por-SS1(Cu) molecule on Au(111) by ultra-high-vacuum scanning tunneling microscopy (UHV-STM) and scanning tunneling spectroscopy (STS) at RT. This phenomenon is discussed on the basis of the fractional residual charge (*Q*₀) on the molecule with Coulomb blockade behavior. We also demonstrate the memory effect of Boc-Por-SS1(Cu) in a two-terminal electrode between the STM tip and the Au(111) surface by application of a programmed pulse sequence.

The sample preparation methods are as follows. The Au substrates were formed on a freshly cleaved mica surface by

vacuum thermal evaporation. The Au substrates were flame-annealed and quenched in ethanol before use to form a Au(111) surface on mica. Boc-Por-SS1(Cu) were deposited onto the Au(111) surface by immersion in an ethanol solution for 2 h. After molecular deposition onto the Au surface, the substrates were introduced into the UHV-STM (JEOL: JSTM-4500). The tungsten (W) STM tips were electrochemically etched in potassium hydroxide (KOH) water solution and were cleaned by electron beam bombardments in the UHV-STM chamber before use. The STM images were obtained at sample bias voltages in the constant-current mode. During STS measurements, the STM tip was held at a fixed position above the sample surface without feedback control. All measurements in this paper were carried out under RT, and the vacuum pressure was maintained at ~10⁻⁸ Pa.

Figure 1(a) shows the schematic molecular structure of the Boc-Por-SS1(Cu) and Fig. 1(b) shows the schematic STM images of the sample structure with a single Boc-Por-SS1(Cu). The structural compatibility of the molecule to the surface was confirmed via Gaussian 09 calculation.¹⁵ This molecule has four substituents, consisting of four disulfide groups oriented downward and *tert*-butoxycarbonyl groups oriented upward relative to a porphyrin ring plane. Because of the interaction between the disulfide groups and the Au atoms, Boc-Por-SS1(Cu) is expected to be chemisorbed coplanar onto Au(111) via four gold-thiol bonds and the porphyrin ring plane of Boc-Por-SS1(Cu) has a gap of ~0.6 nm from the Au(111) surface. Therefore, the coupling between the π -conjugated molecular orbital and the Au(111) surface is expected to be less than that of the typical porphyrin molecule on the Au(111) surface, and there exists a tunneling barrier between Boc-Por-SS1(Cu) and the Au(111) surface. According to a previous report, tetrakis-3,5-di-*t*-butylphenyl-porphyrin (H₂-TBPP) sandwiched between two SiO₂ insulative layers works as a Coulomb island in double-barrier tunneling junctions.¹⁶

Here, the capacitance of the organic molecules for Coulomb islands was regarded as the capacitance between a sphere conductor and a planar electrode,

$$C = 4\pi\epsilon_r\epsilon_0rF, \quad (1)$$

^{a)} Author to whom correspondence should be addressed. Electronic mail: majima@msl.titech.ac.jp.

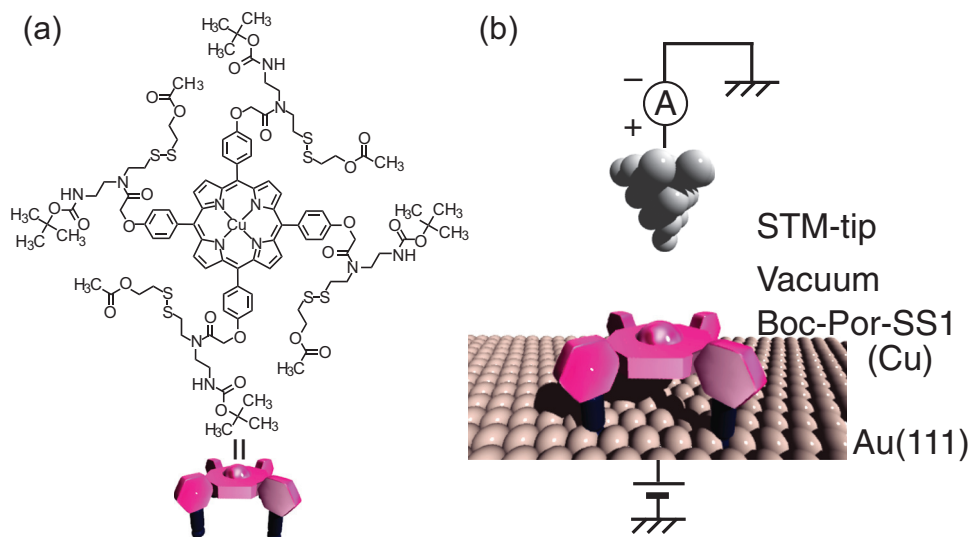


FIG. 1. (Color online) (a) Molecular structure of Boc-Por-SS1(Cu). (b) Schematic image of single molecular double-barrier tunneling junctions, which consist of the W STM tip/vacuum/Boc-Por-SS1(Cu)/Au(111) surface.

with

$$F = 1 + \frac{1}{2s} + \frac{1}{4s^2 - 1} + \frac{1}{8s^3 - 4s} + \frac{1}{16s^4 - 12s^2 + 1} + \frac{1}{32s^5 - 32s^3 + 6s} + \cdots, \quad (2)$$

where ϵ_r is the relative dielectric constant (1.0 for vacuum), ϵ_0 is the vacuum dielectric constant (8.85×10^{-12} F/m), r is the radius of the porphyrin ring of Boc-Por-SS1(Cu) (0.5 nm), d is the distance between the porphyrin ring plane and the Au(111) surface (0.6 nm), and s is defined as $s = d/r + 1$.^{16,17} Both r and d values are estimated from the optimized molecular structure. By using this equation, the capacitance of the Boc-Por-SS1(Cu) as a Coulomb island is estimated to be 0.072 aF. The electrostatic charging energy of the Coulomb island is $U = e^2/2C_\Sigma$, where C_Σ is the sum of the capacitances of the double-barrier tunneling junctions. Here, C_Σ is assumed to be $2C$. The charging energy of Boc-Por-SS1(Cu) is calculated to be 0.56 eV, and this value is 20 times larger than the thermal fluctuation $k_B T$ at RT (≈ 0.026 eV). Therefore, Boc-Por-SS1(Cu) has potential to work as a Coulomb island in this system even at RT.

Figure 2(a) shows a three-dimensional STM topographic image of Boc-Por-SS1(Cu) chemisorbed onto Au(111). Though some bundles exist, a single Boc-Por-SS1(Cu) is stably observed on Au(111) (represented as bright points of diameter around 3 nm). Figure 2(b) shows the typical I - V characteristics of a single Boc-Por-SS1(Cu) with bidirectional voltage sweep between -2.5 and $+2.5$ V at RT by STS. The suppression of current near zero sample bias voltage is clearly observed in the log I - V curves (semilog plots), similar to RT Coulomb blockade behaviors using 1.8-nm Au nanoparticles.¹⁸ Moreover, switching phenomena have been observed in the I - V characteristics of a single Boc-Por-SS1(Cu) on a Au(111) structure during a continuous voltage sweep. STS measurements over Au(111) did not show any Coulomb gap or switching characteristics (not shown). These results strongly support that Boc-Por-SS1(Cu) can work as a Coulomb island of a double-barrier tunneling junction at RT.

The switching phenomena can be interpreted as a change in the fractional residual charge Q_0 in the double-

barrier tunneling junctions. In previous papers, it was reported that Q_0 affects the I - V curves, shifting them quasi-continuously along the voltage axis in the middle of a voltage sweep.^{18–20} In Fig. 2(b), the theoretical fitting curves derived from the “orthodox” theory for the double-barrier tunneling junction system are shown as two curves.^{18,19,21} The theoretical fitting curves agree well with each experimental curve, and the I - V curves change with the shift in Q_0 . These results indicate that the change in Q_0 affects I - V characteristics in double-barrier tunneling junctions and Q_0 can be the origin of switching phenomena in I - V curves.

Q_0 on the Coulomb island can be modulated by the gate voltage in SETs with three-terminal electrodes.²² When Q_0 is modulated on the molecule between two-terminal electrodes by a certain applied electrode voltage, this device can operate as a rewritable single molecular memory.

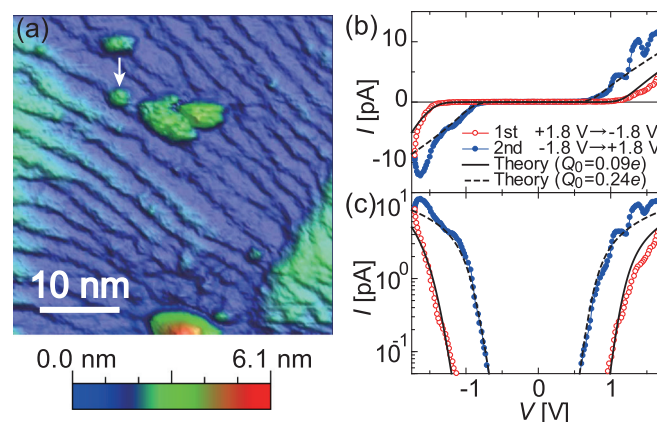


FIG. 2. (Color online) (a) STM image of individual Boc-Por-SS1(Cu) chemisorbed on a Au(111) surface. The scan size is 40×40 nm². The set-point current is 40 pA at a sample bias voltage of -1.8 V. STS measurements in (b) were carried out at the position indicated by the arrow. (b) I - V characteristics measured over single a Boc-Por-SS1(Cu) by STS. (c) Semilogarithmic plots of (b). In (b) and (c), the open circles represent I - V characteristics of the voltage sweep direction from positive to negative, and the closed circles represent I - V characteristics of the voltage sweep direction from negative to positive. Both theoretical curves are calculated by using the parameter values $C_1 = 0.046$ aF, $C_2 = 0.057$ aF, and $R_1/R_2 = 1.7$. Solid lines ($Q_0 = 0.09e$) and broken lines ($Q_0 = 0.24e$) are the theoretical fitting curves derived from orthodox theory for first sweep and second sweep, respectively, where e is an unit charge.

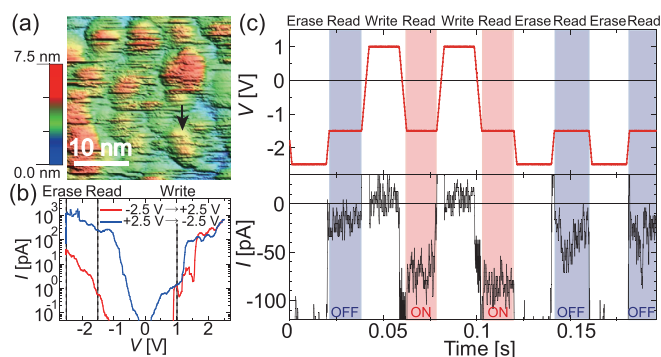


FIG. 3. (Color online) Memory operation of a single Boc-Por-SS1(Cu) by STM. (a) STM image of Boc-Por-SS1(Cu). The scan size is $40 \times 40 \text{ nm}^2$. The set-point current is 30 pA at a sample bias voltage of -2.5 V . All measurements in (b) and (c) were carried out at the location indicated by the arrow. (b) Semilogarithmic plots of I - V characteristics measured over a single Boc-Por-SS1(Cu) in (a). (c) Top: Write, read, and erase voltage pulse sequence applied to a single Boc-Por-SS1(Cu). Writing, reading, and erasing voltages are $+1.0$, -1.5 , and -2.5 V , respectively. Bottom: Tunneling current response following the voltage pulse sequence.

Figures 3(a) and 3(b) show the STM image and the I - V characteristics by STS measurements of other single Boc-Por-SS1(Cu). The size of Boc-Por-SS1(Cu) looks larger than that of Fig. 2(a) because the STM image strongly depends on the STM tip condition and the STM tip conditions differed. The switching behavior is different from that of Fig. 2(b) because Q_0 changed during the sample bias voltage sweeping. Figure 3(c) shows the memory operation of Boc-Por-SS1(Cu) triggered by a programmed pulse sequence, which was applied to the STM tip over a single Boc-Por-SS1(Cu) without feedback control. The voltages of writing, erasing, and reading are $+1.0$, -2.5 , and -1.5 V , respectively, as determined from the I - V characteristics in Fig. 3(b). Single molecular switching behavior by a programmed pulse sequence using STM has been observed in the response of tunneling current between the STM tip and the Au(111) surface. The high conductive state (on state) and low conductive state (off state) were controlled by writing and erasing voltage pulses, respectively. By applying certain voltages, we can modulate the Coulomb blockade by changing Q_0 . The average values of the on-state current and the off-state current are -77 and -27 pA , respectively. Therefore, the current on/off ratio is estimated to be 2.9; this value is of the same order as those of previous reports of single molecular memory by STM not only under RT but also under cryogenic temperature.^{8,9,23,24} Consequently, these results suggest that single molecular memory can work by using a porphyrin derivative placed between two-terminal electrodes at RT.

In conclusion, we have demonstrated that a synthesized porphyrin derivative shows Coulomb blockade behaviors and switching behaviors of electrical conductance by STM at RT. Voltage-triggered memory operation has also been demonstrated by monitoring tunneling current. These behaviors can be attributed to a change in the fractional residual charge Q_0 on the molecules. These results show that an organic molecule that works as a Coulomb island is one possible candi-

date for application of two-terminal molecular memory devices.

The numerical calculations of Gaussian 09 were carried out on TSUBAME2.0 at the Global Scientific Information and Computing Center of Tokyo Institute of Technology. This work was partially supported by a Grant-in-Aid for Scientific Research on Innovative Areas (No. 20108011, “ π -space”) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan; a Grant-in-Aid for Japan Society for the Promotion of Science (JSPS) Fellows, MEXT, Japan (S.K.); the Global Centers of Excellence (COE) Program of “Photonics Integration-Core Electronics,” MEXT, Japan; the Collaborative Research Project of Materials and Structures Laboratory, Tokyo Institute of Technology, Japan; and the World Class University (WCU) Program through the Ministry of Education, Science and Technology of Korea (R31-10022), Korea.

- ¹S. J. van der Molen and P. Liljeroth, *J. Phys.: Condens. Matter* **22**, 133001 (2010).
- ²C. P. Collier, G. Mattersteig, E. W. Wong, Y. Luo, K. Beverly, J. Sampaio, F. M. Raymo, J. F. Stoddart, and J. R. Heath, *Science* **289**, 1172 (2000).
- ³Z. J. Donhauser, B. A. Mantooth, K. F. Kelly, L. A. Bumm, J. D. Monnell, J. J. Stapleton, D. W. Price Jr., A. M. Rawlett, D. L. Allara, J. M. Tour, and P. S. Weiss, *Science* **292**, 2303 (2001).
- ⁴K.-H. Jung, E. Hase, Y. Yasutake, H.-K. Shin, Y.-S. Kwon, and Y. Majima, *Jpn. J. Appl. Phys.* **45**, L840 (2006).
- ⁵Y. Yasutake, Z. Shi, T. Okazaki, H. Shinohara, and Y. Majima, *Nano Lett.* **5**, 1057 (2005).
- ⁶M. Iwamoto, D. Ogawa, Y. Yasutake, Y. Azuma, H. Umemoto, K. Ohashi, N. Izumi, H. Shinohara, and Y. Majima, *J. Phys. Chem. C* **114**, 14704 (2010).
- ⁷M. Jurow, A. E. Schuckman, J. D. Batteas, and C. M. Drain, *Coord. Chem. Rev.* **254**, 2297 (2010).
- ⁸S. W. Wu, N. Ogawa, G. V. Nazin, and W. Ho, *J. Phys. Chem. C* **112**, 5241 (2008).
- ⁹F. Moresco, G. Meyer, K.-H. Rieder, H. Tang, A. Gourdon, and C. Joachim, *Phys. Rev. Lett.* **86**, 672 (2001).
- ¹⁰J.-R. Koo, H.-S. Lee, Y. Ha, Y.-H. Choi, and Y. K. Kim, *Thin Solid Films* **438**, 123 (2003).
- ¹¹C. Li, J. Ly, B. Lei, W. Fan, D. Zhang, J. Han, M. Meyyappan, M. Thompson, and C. Zhou, *J. Phys. Chem. B* **108**, 9646 (2004).
- ¹²M. Kanehara, H. Takahashi, and T. Teranishi, *Angew. Chem. Int. Ed.* **47**, 307 (2008).
- ¹³K. Shimazu, M. Takechi, H. Fujii, M. Suzuki, H. Saiki, T. Yoshimura, and K. Uosaki, *Thin Solid Films* **273**, 250 (1996).
- ¹⁴See supplementary material at <http://dx.doi.org/10.1063/1.3679127> for the detail of synthetic procedure of Boc-Por-SS1(Cu).
- ¹⁵M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford, CT, 2009.
- ¹⁶Y. Wakayama, T. Kubota, H. Suzuki, T. Kamikado, and S. Mashiko, *J. Appl. Phys.* **94**, 4711 (2003).
- ¹⁷Y. Oyama, Y. Majima, and M. Iwamoto, *J. Appl. Phys.* **86**, 7087 (1999).
- ¹⁸S. Kano, Y. Azuma, M. Kanehara, T. Teranishi, and Y. Majima, *Appl. Phys. Express* **3**, 105003 (2010).
- ¹⁹A. E. Hanna and M. Tinkham, *Phys. Rev. B* **44**, 5919 (1991).
- ²⁰C. T. Black, M. T. Tuominen, and M. Tinkham, *Phys. Rev. B* **50**, 7888 (1994).
- ²¹H. Zhang, Y. Yasutake, Y. Shichibu, T. Teranishi, and Y. Majima, *Phys. Rev. B* **72**, 205441 (2005).
- ²²Y. Azuma, Y. Yasutake, K. Kono, M. Kanehara, T. Teranishi, and Y. Majima, *Jpn. J. Appl. Phys.* **49**, 090206 (2010).
- ²³S. Yasuda, T. Nakamura, M. Matsumoto, and H. Shigekawa, *J. Am. Chem. Soc.* **125**, 16430 (2003).
- ²⁴P. Liljeroth, J. Repp, and G. Meyer, *Science* **317**, 1203 (2007).