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Room-temperature single molecular memory
Shinya Kano, Yasuyuki Yamada, Kentaro Tanaka, and Yutaka Majima

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Room-temperature single molecular memory

Molecular switching behaviors have attracted much attention because of their potential application for molecular solid-state devices. Various molecular switching phenomena have been reported, for example, in catenane-rotaxane interlocked molecules, oligo(phenylene-ethynylene) (OPE), and fullerenes. Molecular switching behaviors by porphyrin derivatives have been especially studied toward the realization of molecular switches. The origin of the switching behaviors has been attributed to, for example, adsorption geometry, conformational changes of molecules, and reduction-oxidation reactions. 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. 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. 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. 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 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 \( \sim 10^{-8} \) 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. This molecule has four substituents, consisting of four disulfide groups oriented downward and tert-butoxycalbonyl 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 \( \approx 0.6 \) nm from the Au(111) surface. Therefore, the coupling between the \( \pi \)-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-butylyphenyl-porphyrin (H\(_2\)-TBPP) sandwiched between two SiO\(_2\) insulative layers works as a Coulomb island in double-barrier tunneling junctions.

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

\[
C = 4\pi \varepsilon_0 \varepsilon_r F,
\]

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with

$$F = 1 + \frac{1}{2r} + \frac{1}{4s^2 - 1} + \frac{1}{8s^3 - 4s} + \frac{1}{16s^4 - 12s^2 + 1} + \frac{1}{32s^5 - 32s^3 + 6s} + \ldots,$$

where \(\varepsilon_r\) is the relative dielectric constant (1.0 for vacuum), \(\varepsilon_0\) is the vacuum dielectric constant \((8.85 \times 10^{-12} \text{ F/m})\), \(r\) is the radius of the porphyrin ring of Boc-Por-SS1(Cu) \((0.5 \text{ nm})\), \(d\) is the distance between the porphyrin ring plane and the Au(111) surface \((0.6 \text{ nm})\), and \(s\) is defined as \(s = dr + 1\).\(^{16,17}\) 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 \(0.072 \text{ aF}\). The electrostatic charging energy of the Coulomb island is \(U = e^2/2C_\text{s}\), where \(C_\text{s}\) is the sum of the capacitances of the double-barrier tunneling junctions. Here, \(C_\text{s}\) is assumed to be \(2C\). The charging energy of Boc-Por-SS1(Cu) is calculated to be \(0.56 \text{ eV}\), and this value is 20 times larger than the thermal fluctuation \(kBT\) at RT \((\sim 0.026 \text{ eV})\). 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) \((\text{represented as bright points of diameter around } 3 \text{ nm})\). Figure 2(b) shows the typical \(I-V\) characteristics of a single Boc-Por-SS1(Cu) with bidirectional voltage sweep between \(-2.5\) and \(+2.5 \text{ V}\) at RT by STS. The suppression of current near zero sample bias voltage is clearly observed in the log \(I-V\) curves \((\text{semilog plots})\), 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 \((\text{not shown})\). 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.
Consequently, these results suggest that memory by STM not only under RT but also under cryogenic conditions is of the same order as those of previous reports of single molecular memory devices. Voltage-triggered memory operation has also been demonstrated for a molecular switching behavior by a programmed 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 voltages. The high conductive state (on state) and low conductive state (off state) were controlled by writing and erasing voltages. 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 voltages. 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).

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 for a molecular switching behavior by a programmed 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.

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References

14. See supplementary material at http://dx.doi.org/10.1063/1.3679127 for the detail of synthetic procedure of Boc-Por-SS1(Cu).
15. M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford, CT, 2009.