J|A|C|S
COMMUNICATIONS

Self-Organized Interconnect Method for Molecular Devices

Masateru Taniguchi,*,† Yoshihiro Nojima,† Kazumichi Yokota,† Jun Terao,‡ Kimihiko Sato,‡
Nobuaki Kambe,*,‡ and Tomoji Kawai*,†

*The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka, Japan, and
Department of Molecular Chemistry & Science and Technology Center for Atoms, Molecules and Ions Control,
Graduate School of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka, Japan*

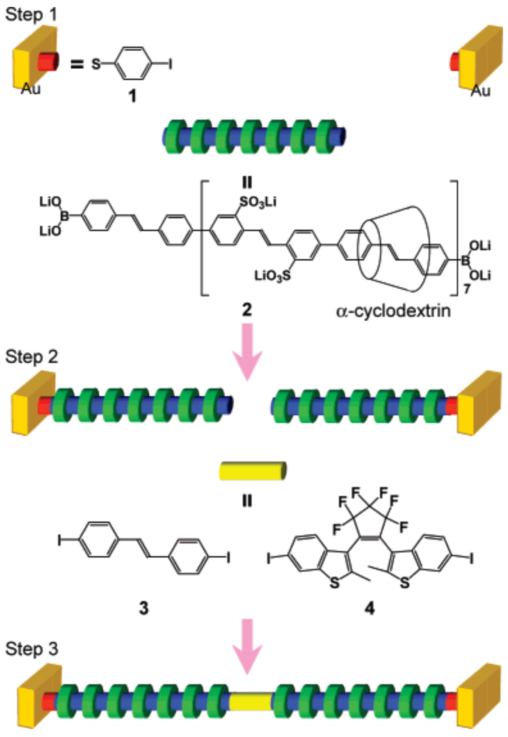
Received August 10, 2006; E-mail: tanigut@sanken.osaka-u.ac.jp; kambe@chem.eng.osaka-u.ac.jp; kawai@sanken.osaka-u.ac.jp

As the miniaturization of silicon semiconductors reaches its physical and economic limits, pressure has increased on device innovation. Since molecules can now be synthesized uniformly in large quantities with changed or added functions by chemical techniques, interest has focused particularly on molecular electronics.[1−4] However, the development of nanosized molecular electronics has been precluded by the difficulty in wiring molecules between nanoelectrodes. Many researches have already reported synthesized molecules with thiols on both ends and bridged nanoelectrodes with the molecules.[1−4] However, it is difficult to synthesize a molecule with thiols on both ends because of the low stability of such conjugated system molecules. Also, long molecular wires have a strong aggregation tendency and are difficult to wire between electrodes. Therefore, a new molecular interconnect method needs to be developed to produce a molecular device from a long molecule.

Here we report an interconnect method for molecular devices that can control electrode-molecule binding, molecular orientation, and device functions. The interconnect method is a self-organized method in which three types of molecules are programmed to have different functions and are connected sequentially between the nanoscale electrodes. By using this method we demonstrate a conduction wire and optical switching device. The self-organized interconnect method is an innovative method allowing the easy control of molecular device functions and has the potential to significantly promote the development of nanoscale molecular electronics.

The self-organized interconnect method consists of three steps with three kinds of molecules: interface control molecule (4-iodobenzenethiol **1**[5]), orientation control molecule (polyrotaxane **2**[6]), and function control molecule (stilbene **3**[7], diarylethene **4**[8]) (Scheme 1). The interconnect method is a simple liquid solution process in which nanoelectrodes that are placed with a nanoscale spacing are dipped into three kinds of solutions sequentially. In the first step, the electrodes and interface control molecules **1** are bound to each other. The interface control molecules **1** bound to the electrodes are the π-electron molecules that have chemical reaction points to bind to the orientation control molecules **2**. In the second step, a chemical reaction binds the orientation control molecules **2** with the interface control molecules **1**. The orientation control molecules **2** are π-electron molecules that have two chemical reaction points at their ends to bind to interface control molecules **1** and function control molecules **3**,**4**. The π electrons are covered with α-cyclodextrin to keep the molecular structure almost straight[9−11] and control the growth direction of the molecules along the electrode spacing. In the third step, a chemical reaction binds function control molecules **3**,**4** with orientation control molecules **2**. The function control molecules **3**,**4** have chemical reaction points at both ends to bind to the orientation control molecules **2**.

Scheme 1. Self-Organized Interconnect Method for Molecular Devices[a]



[a] The interface control molecule **1**, orientation control molecule **2**, and function control molecules (**3**,**4**). **3** and **4** function as a conduction wire and as an optical switching device, respectively. Molecule **2** is a π-conjugated molecule covered with α-cyclodextrin.

After the first step, we used X-ray photoelectron spectroscopy to measure the self-assembled monolayer of **1** and found a strong peak at 161 eV, which is the S2p binding energy in the gold−sulfur bond.[12]

As in the first step, we conducted a reflective UV−vis spectroscopy measurement on the gold electrode after binding orientation control molecules **2** with interface control molecules **1** and found an absorption peak at 400 nm, which corresponds to the absorption peak of 397 nm for orientation control molecules **2** in solutions. This indicates that the chemical bonding of **1** and **2** molecules extended the π-conjugated system.

In the third step, the function control molecules **3**,**4** and orientation control molecules **2** are bound to each other. We used **3** and **4** as the function control molecules. The molecular wire is conductive because **3** is a π-electron molecule. **4** is in a ring-opening state under visible light, but in a closed-ring state under UV

---

† The Institute of Scientific and Industrial Research.
‡ Graduate School of Engineering.

10.1021/ja065806z CCC: $33.50

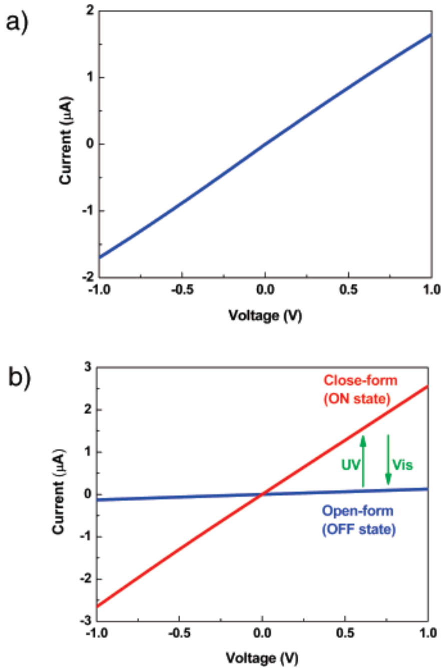


Figure 1. Device characteristics of the molecular wires between the nanogap electrodes, whose spacing was 30 nm: current−voltage curves of (a) the conductive wire and (b) the optical switching device for which we used **3** and **4** as the functional molecule, respectively.

radiation.[13,14] That is, the molecular structure switches in response to light and the molecular wire containing **4** works as an optical switching device.

The interelectrode spacing was 30 nm. The width and height of the electrode were about 40 and 20 nm, respectively. Hence, if we assume that the two molecular wires are cylindrical with a diameter of about 1.5 nm (the diameter of α-CD)[15] and are wired in parallel between the electrodes, there are up to 450 molecules wired between the electrodes.

After the second and third steps, we measured electric conduction in molecular wires possessing either **3** or **4** at room temperature with no light in a vacuum condition below 10^{-5} Torr. The molecular wire with **3** was a conductive wire having Ohmic contact (Figure 1a). Its electric resistance was 5.9×10^5 Ω. It showed no electric conduction after the second step, but showed conduction after the third step, which implies that the electrodes are wired with the molecular wire in the third step. We measured the temperature dependence of the electric conductance and found the conductance decreased as the temperature decreased, indicating that the molecule is of the thermal activation type. The activation energy in a high-temperature range was 109 meV.

On the other hand, we placed the optical switching device in ultraviolet light or visible light and shielded them from light to measure the current−voltage characteristic of the device (Figure 1b). We applied ultraviolet radiation to the molecules to drive them into the closed-ring state (ON state, 3.9×10^5 Ω), and then applied visible light to switch them into the ring-opening state (OFF state, 7.6×10^6 Ω). The electric current in the molecular wire with **4** increased under ultraviolet radiation by 20-fold, but it was reduced under visible light, indicating a reversible switching property with light. The optical switching property was not observed after the second step, indicating that the switching molecules were bound chemically to the orientation control molecules **2** at both ends in the third step, and that the electrodes were wired with the optical switching molecule.

In the measurement of the temperature characteristics of the molecule in the ON state, we found that the molecule has the thermal activation type conduction mechanism, just like the molecular wire with stilbene **3**, and that the activation energy in the high-temperature range was 117 meV. The long length of the orientational control molecule **2** indicates that the orientational control molecule **2** has a hopping conduction mechanism and the conduction mechanism of the entire molecular wire is dominated by the hopping conduction of the orientational control molecule **2**. This could explain why both the molecule with stilbene **3** and the molecule with diarylethene **4** have the hopping conduction mechanism with comparable activation energies. These results show that the function control molecules can control the device functions of the molecular wires.

In conclusion, we have developed an interconnect method to program three kinds of component molecules with their own functions and to wire a molecular device between nanoscale electrodes in a self-organized manner. By using the interconnect method we developed, we produced conductive wires and optical switching devices and have demonstrated their device functions. Combining these three control molecules allows us to produce molecular wires with various device properties that can be controlled.

Acknowledgment. This work was partially supported by the Japan Science and Technology Corporation (JST) and Nanotechnology Process Foundry of Osaka University.

Supporting Information Available: Materials, spectra, temperature dependence of conductivity of the molecular devices, and expanded discussion and interpretation of the optical switching device. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Aviram, A.; Ratner, M. A. *Molecular Electronics*: *Science and Technology*; New York Academy of Sciences: New York, 1998.
(2) Tour, J. M. *Molecular Electronics*: *Commercial Insights, Chemistry, Devices, Architecture and Programming*; World Scientific: Singapore, 2003.
(3) McCreery, R. L. *Chem. Mater.* **2004**, *16*, 4477−4496.
(4) Nitzan, A.; Ratner, M. A. *Science* **2003**, *300*, 1384−1389.
(5) Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376−1387.
(6) (a) Michels, J. J.; O'Connell, M. J.; Taylor, P. N.; Wilson, J. S.; Cacialli, F.; Anderson, H. L. *Chem.*−*Eur. J.* **2003**, *9*, 6167−6176. (b) Stanier, C. A.; Alderman, S. J.; Claridge, T. D. W.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2002**, *41*, 1769−1772. (c) Taylor, P. N.; O'Connell, M. J.; McNeill, L. A.; Hall, M. J.; Aplin, R. T.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 3456−3460.
(7) Lucas, N. T.; Noaras, E. G. A.; Cifuentes, M. P.; Humphrey, M. G. *Organometallics* **2003**, *22*, 284−301.
(8) Matsuda, K.; Irie, M. *Chem.*−*Eur. J.* **2001**, *7*, 3466−3473.
(9) Cacialli, F.; Wilson, J. S.; Michels, J. J.; Daniel, C.; Silva, C.; Friend, R. H.; Severin, N.; Samorì, P.; Rabe, J.; O'Connell, M. J.; Taylor, P. N.; Anderson, H. L. *Nat. Mater.* **2002**, *1*, 160−164.
(10) Yoshida, K.-I.; Shimomura, T.; Ito, K.; Hayakawa, R. *Langmuir* **1999**, *15*, 910−913.
(11) Harada, A.; Li, J.; Kamachi, M. *Nature* **1992**, *356*, 325−327.
(12) Ulman, A. *An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self-Assembly*; Academic Press: San Diego, CA, 1991.
(13) Dulić, D.; van der Molen, S. J.; Kudernac, T.; Jonkman, H. T.; de Jong, J. J. D.; Bowden, T. N.; van Esch, J.; Feringa, B. L.; van Wees, B. J. *Phys. Rev. Lett.* **2003**, *91*, 207402−207405.
(14) Irie, M.; Fukaminato, T.; Sasaki, T.; Tamai, N.; Kawai, T. *Nature* **2002**, *420*, 759−760.
(15) Saenger, W. *Angew. Chem., Int. Ed.* **1980**, *19*, 344−362.

JA065806Z