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Charge Storage Behavior of Nanowire Transistors Functionalized with Bis(terpyridine)−Fe(II) Molecules: Dependence on Molecular Structure

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Redox-active molecules have potential as charge storage materials because of their ability to undergo facile electron-transfer reactions at low potentials.[1] To incorporate these molecules into CMOS technology platform presents an attractive route toward nanoscale memory devices with tailor-made characteristics.[2] For instance, when spin-coated onto the conduction channel of a field effect transistor (FET), the cobalt−phthalocyanine molecules can be brought into different redox states by gate voltage pulses; this chemical transformation then alters the conduction of the FET and renders the device an excellent bistability.[2d] The working principle is similar to that of the conventional silicon-based flash memories where a floating gate can be charged or discharged via electron tunneling through a thin oxide layer.[3] Replacing the insulating oxide layer with molecular components will further reduce device size and simplify fabrication. On the basis of this concept, we have built a multilevel molecular memory based on the self-assembly of a bis(terpyridine)−Fe(II) molecule on an indium oxide (In_2O_3) nanowire FET (NW-FET).[4] Here we report structural influences of a family of bis(terpyridine)−Fe(II) molecules on charge storage characteristics, including charge retention, width, and stability of the memory window.

Because of their octahedral configuration in coordination, bis(terpyridine)−transition metal complexes exhibit superior chemical and electronic stability toward redox reactions.[5,6] A model for application of these molecules in molecular electronics uses the metal atom as charge storage vehicle and the terpyridine ligands as insulating barriers for charge transfer.[7] The molecules shown in Figure 1a were synthesized according to literature methods[6,8] and were characterized with ^{1}H and ^{13}C NMR, mass (ES) spectroscopy, and elemental analysis. Cyclic voltammetric studies revealed that all three molecules exhibited pseudoreversible electron-transfer behavior with a pair of Fe(II)/Fe(III) redox peaks around 0.8 to 0.9 V (vs Ag/$AgNO_3$ in acetonitrile).

The left inset of Figure 1b shows an SEM image of a NW-FET, where a single-crystalline In_2O_3 nanowire was dispersed on a SiO_2-coated silicon wafer with patterned source/drain electrodes.[9] The devices exhibit typical *n*-type FET behavior and showed no hysteresis. Functionalization of the nanowire surface with molecules was carried out by literature methods using aqueous ammonium hydroxide/tetrahydrafuran solution (to convert the thioacetate groups into thiolate).[10] The formation of molecular monolayers was confirmed by ellipsometry.[4,11] The molecular coverage density was measured using a quartz crystal microbalance (QCM) to be 5.2, 5.1, and 6.5 molecules/nm^2 for molecule **1**, **2**, and **3**, respectively.[11]

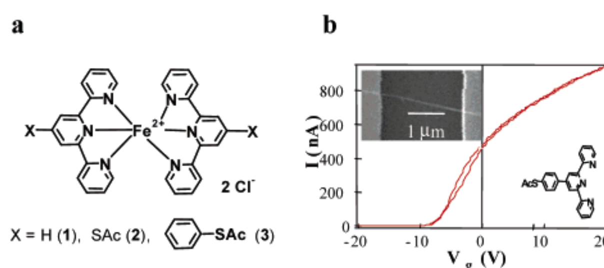

Figure 1. (a) Structure of the bis(terpyridine)−Fe(II) molecules used in this study. (b) $I-V_g$ curve of the device modified with the ligand of molecule **3** (V_{ds} = 0.1 V). Left inset: SEM image of the indium oxide NW-FET. Right inset: Structure of the ligand.

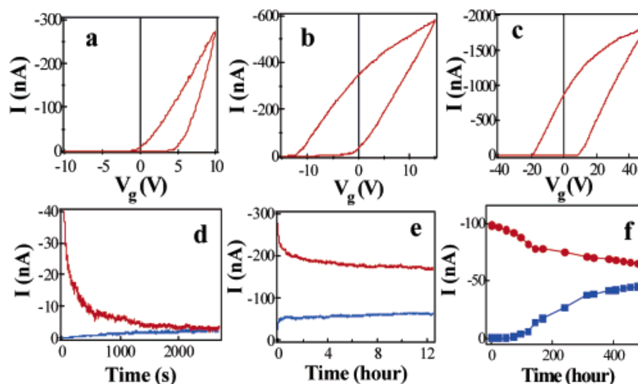

Figure 2. $I-V_g$ curves of devices with (a) molecule **1**, (b) molecule **2**, and (c) molecule **3** and current−time curves of devices with (d) molecule **1**, (e) molecule **2,** and (f) molecule **3** (V_{ds} = −0.1 V)

A negative voltage pulse on the silicon back gate injects positive charges into the nanowire and subsequently oxidizes the molecules; for an *n*-type In_2O_3 NW-FET, these oxidized molecules work as a chemical gate and lead to a high-conductance ("*on*") state. Conversely, a sufficiently large positive gate voltage pulse leads the device to low conductance ("*off*") state. These processes can be monitored by $I-V_g$ curves that show the drain current (I) as a function of gate voltage (V_g) at a small fixed drain voltage (V_{ds}). To ascertain the role of Fe(II) in charge storage, we obtained the $I-V_g$ curves of the NW-FETs assembled with the terpyridine ligand (lower right inset of Figure 1b) and with molecules **1**−**3**. As shown in Figure 1b and Figure 2a−c, the device with just the ligand showed very little hysteresis while devices with molecules **1**−**3** showed large hysteresis loops. A significant hysteresis indicates an electronic bistable system where the two states defined at V_g = 0 V can be used for data storage applications. These results confirm that the redox active Fe(II) center is responsible for the memory

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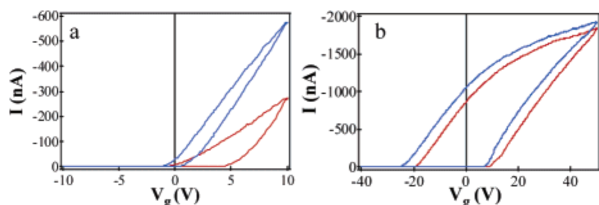

Figure 3. Dependence of $I-V_g$ curve on time for devices with molecule **1** (a) and molecule **3** (b). Red curve: $I-V_g$ curve of the device taken immediately after it was loaded in a vacuum. Blue curve: $I-V_g$ curve of the same device taken after it stayed in a vacuum for 2 days.

effect. Furthermore, the hysteresis becomes more pronounced within the series of molecules **1**−**3**, as is evident by the increasing gate voltage shift (ΔV_{th}) of 4.8, 10.0, and 28.0 V, showing a strong dependence of ΔV_{th} on molecular structure.

Charge retention was obtained by first writing (or erasing) the devices into "*on*" (or "*off*" state) using gate voltage pulses and then recording the source/drain conduction over time with fixed V_{ds} of −0.1 V. Figure 2d−f shows the dependence of drain current on time for devices with molecules **1**−**3** at both "*on*" (red curve) and "*off*" (blue curve) states. From these curves, retention time τ was estimated as $\tau_1 = 200$ s, $\tau_2 = 12$ h, and $\tau_3 = 287$ h.[11] The ratio τ_1:τ_2:τ_3 of 1:216:5166 indicates a strong dependence of charge retention on molecular structure. For electron-transfer reactions involving a single electron tunneling step, the exponential dependence of the electron-transfer constant on distance has been described by the super exchange model[12a,b] and has also observed in experiments.[12c,d] Compared with that of molecule **2**, the extra phenyl ring between the thiolate headgroup and the Fe(II) center in molecule **3** increases the charge tunneling distance by 5 to 6 Å, and thus could be responsible for the larger τ measured for molecule **3** ($\tau_3 = 24\ \tau_2$). It is less straightforward to comprehend the even greater difference in retention between molecules **1** and **2** ($\tau_2 = 216\ \tau_1$), since the two molecules only differ in a thiolate headgroup. However, it is known that molecules with thiolate groups can chemisorb on the In_2O_3 surface to form strong contact while those molecules without cannot; the latter may physisorb, i.e., trapped by weak van der Waals interaction, thus forming weaker and random contacts with the In_2O_3 surface.[9a] These weak and random contacts could result in poorly defined charge tunneling paths with low barriers, as is strongly indicated by the sharp current drop in a time scale of 100 s (Figure 2d) for molecule **1**. On the contrary, currents for devices with molecules **2** and **3** were nearly constant over a much longer time scale (Figure 2e,f). We believe this extremely slow leakage of charge indicates a uniform tunneling path with a high barrier, a possible result of the strong contact formed between the thiolate and In_2O_3 nanowire.

We further examined the influence of contact on device stability by monitoring the hysteresis of various devices in a vacuum for a prolonged period. Figure 3a shows two $I-V_g$ curves obtained with a NW-FET coated with molecule **1**, with the red curve taken immediately after the sample was loaded into vacuum and the blue curve taken 2 days later. A significant drift in hysteresis was observed; for example, the turn-on threshold voltage V_{th} shifted from −0.9 to −1.5 V, accompanied by a 3.1 V reduction in ΔV_{th}. In contrast, the device with molecule **3** showed much smaller drift in hysteresis (20% change in turn-on V_{th}) and no reduction in ΔV_{th} (Figure 3b). This striking difference suggests a difference in the chemical stability of the two devices. Since the two molecules have same bis(terpyridine)−Fe(II) core structure, we ascribe the larger stability for the device with molecule **3** to the ability of the thiolate headgroup to make stronger contact with the nanowire surface and vice versa.

In summary, we showed that both retention time (τ) and threshold voltage shift (ΔV_{th}) strongly depend on the structure of the bis(terpyridine)−Fe(II) molecule and both increase in the order of **1** < **2** < **3**. These results suggests that the presence of the thiolate headgroup and/or longer ligand length increases charge retention with a wider and more stable memory window, possibly due to the increasing tunneling barrier. The approach of using molecular components, i.e., ligand, to replace the inorganic oxide as insulating layer in memory devices, affords simple fabrication, ultra-small device size, and molecular level control.

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Supporting Information Available: Additional information on ellipsometry, QCM characterization of SAM, and retention time measurement. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Reed, M. A.; Chen, J.; Rawlett, A. M.; Price, D. W.; Tour, J. M. *App. Phys. Lett.* **2001**, *77*, 1224. (b) Bandyopadhyay, A.; Pal, A. J. *Chem. Phys. Lett.* **2003**, *371*, 86. (c) Roth, K. M.; Gryko, D. T.; Clausen, C.; Li, J.; Lindsey, J. S.; Kuhr, W. G.; Bocian, D. F. *J. Phys. Chem. B* **2002**, *106*, 8639.
(2) (a) Liu, Z.; Yasseri, A. A.; Lindsey, J. S.; Bocian, D. F. *Science* **2003**, *302*, 1543. (b) Li, C.; Zhang, D.; Liu, X.; Han, S.; Tang, T.; Zhou, C.; Fan, W.; Koehne, J.; Han J.; Meyyappan, M.; Rawlett, A. M.; Price, D. W.; Tour, J. M. *App. Phys. Lett.* **2003**, *82*, 645. (c) Pal, A. J. *Chem. Phys. Lett.* **2003**, *371*, 86. (d) Duan, X.; Huang, Y.; Lieber, C. M. *Nano Lett.* **2002**, *2*, 487.
(3) Ricco, B.; Torelli, G.; Lanzoni, M.; Manstretta, A.; Maes, H. E.; Montanari D.; Modelli, A. *Proc. IEEE* **1998**, *86*, 2399.
(4) Li, C.; Fan, W.; Lei, B.; Zhang, D.; Han, S.; Tang, T.; Liu, X.; Liu, Z.; Asano, S.; Meyyappan, M.; Han, J.; Zhou, C. *App. Phys. Lett.* **2004**, *84*, 1949.
(5) Sauvage, J.-P.; Collin, J.-P.; Chambron, J.-C.; Guillerez, S.; Coudret, C. Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigi, L. *Chem. Rev.* **1994**, *94*, 993 and references therein.
(6) (a) Maskus M.; Abruna; H. D. *Langmuir* **1996**, *12*, 4455. (b) Diaz, D. J.; Bernhard, S.; Storrier, G. D.; Abruna, H. D. *J. Phys. Chem. B* **2001**, *105*, 8746.
(7) Park, J.; Pasupathy, A. N.; Goldsmith, J. I.; Chang, C.; Yalsh, Y.; Petta, J. R.; Rinkoski, M.; Sethna, J. P.; Abruna, H. D.; McEuen, P. L.; Ralph, D. C. *Nature* **2002**, *417*, 722.
(8) (a) Collin, J.-P.; Guillerez, S.; Sauvage, J.-P.; Barigelletti, F.; De Cola, L.; Flamigni, L.; Balzani, V. *Inorg. Chem.* **1991**, *30*, 4230. (b) Potts, K. T.; Usifer, D. A.; Guadalupe, A.; Abruna, H. D. *J. Am. Chem. Soc.* **1987**, *109*, 3961.
(9) (a) Li, C.; Zhang, D.; Han, S.; Liu, X.; Tang, T.; Han, J.; Zhou, C. *Adv. Mater.* **2003**, *15*, 143 (b) Zhang, D.; Li, C.; Han, S.; Liu, X.; Tang, T.; Jin, W.; Zhou, C. *Appl. Phys. Lett.* **2003**, *82*, 112.
(10) (a) Yan, C.; Zharnikov, M.; Golzhauser, A.; Grunze, M. *Langmuir* **2000**, *16*, 6208. (b) Tour, J. M.; Jones, L.; Pearson, D. L.; Lamba, J. J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parikh, A. N.; Atre, A. J. *J. Am. Chem. Soc.* **1995**, *117*, 9529.
(11) See Supporting Information.
(12) (a) McConnell, H. M. *J. Chem. Phys.* **1961**, *35*, 508. (b) Miller, J. R.; Beitz, J. V. *J. Chem. Phys.* **1981**, *74*, 6746. (c) Sikes, H. D.; Smalley, J. F.; Dudek, S. P.; Cook, A. R.; Newton, M. D.; Chidsey, C. E. d.; Feldberg, S. W. *Science* **2001**, *291*, 1519−1523. (d) Wang, W.; Lee, T.; Reed, M. A. *Phys. Rev. B* **2003**, *68*, 035416.

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