Communication

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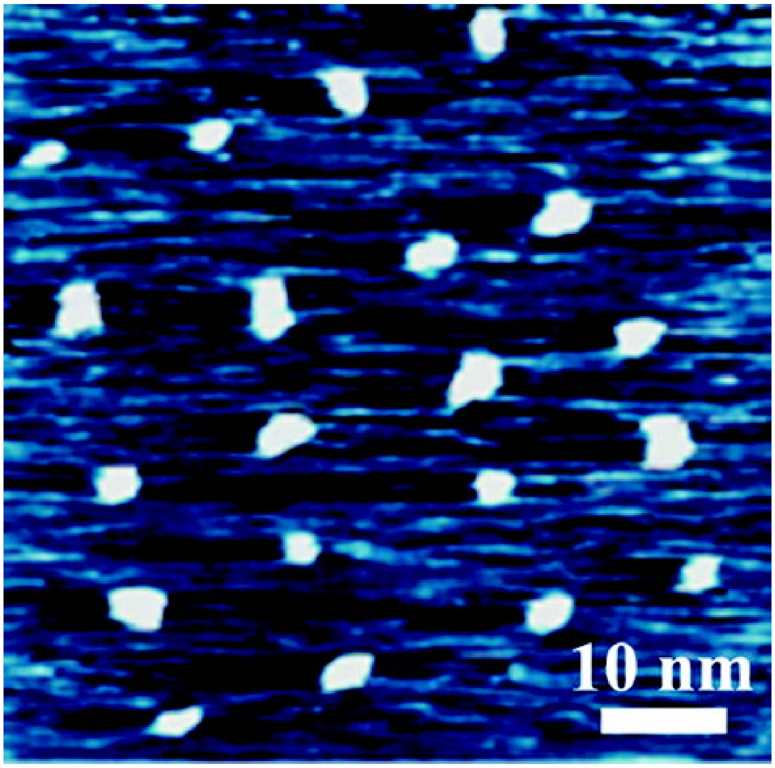

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Stable, Reproducible Nanorecording on Rotaxane Thin Films

Min Feng,[†] Xuefeng Guo,[‡,§] Xiao Lin,[†] Xiaobo He,[†] Wei Ji,[†] Shixuan Du,[†] Deqing Zhang,[‡]
Daoben Zhu,[‡] and Hongjun Gao*[,†]

Nanoscale Physics & Devices Laboratory, Institute of Physics, Chinese Academy of Sciences, and Organic Solids Laboratory, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

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Nanometer-scale recording on organic thin film media is a promising alternative to future ultrahigh-density information storage.[1] Scanning probe microscope (SPM) has been demonstrated to be an important tool in recording the nanometer patterns on functional organic thin films.[2] For practical applications, functional organics should possess stable switching properties in ambient conditions.[3] Rotaxanes represent a new class of the super molecules and show stability at various chemical states in solution.[4] The key structure of the molecules contains a π-electron-deficient macrocycle that is locked around a π-electron-rich component along the molecular "thread" with two bulky "stoppers". The macrocycle can move between different π-electron-rich components upon external stimuli, resulting in switching of electronic configuration.[4a] This makes rotaxane an interesting candidate for nanorecording. In this communication, we report on stable conductance transitions in solid-state rotaxane-based Langmuir−Blodgett (LB) thin films. Using scanning tunneling microscope (STM), we have achieved reproducible nanometer-scale recording on these films.

Figure 1a is the rotaxane $\mathbf{1}\cdot 4PF_6$ (H1) synthesized by our group.[5] This molecule has shown conclusive evidence of switching between two distinct configurations.[5] Such switching is originated from the reversible mechanical movement of the CBPQT^{4+} (macrocycle) between TTF and DNP components triggered by chemical stimuli. Theoretical calculations[6] have also revealed that a gain of 10−100 in conductivity can be expected when the CBPQT^{4+} moves from TTF to DNP.

We first prepared the H1 films on an ITO-coated glass substrate using common LB deposition technique. The substrate was dipped into the solution and lifted 50 times for multiple H1 coating. The average thickness of the films was about 70 nm. Using a two terminal junction, we observed a fast conductance-switching phenomenon with on/off ratio at about 100 in the H1 LB film. The $I-V$ characteristic of the film (Figure 1b) shows a reversible electrical bistability and the nonvolatile memory effect in the film. The first voltage scanning from 0 to 2 V, described by curve I, shows a sharp current increase starting at about 1.4 V, which indicates the transition from a low conductivity state (OFF state) to a high conductivity state (ON state). In curve II, the $I-V$ data measured after 12 h from the first measurement clearly show that the "ON" state in the sample is kept for a long time. The "OFF" state can be gradually recovered by applying reverse voltage scanning (curves III, IV, and V). Transient conductance measurement[11] (Figure 1c) performed on the same H1 sample shows a short transition time of about 60 ns.

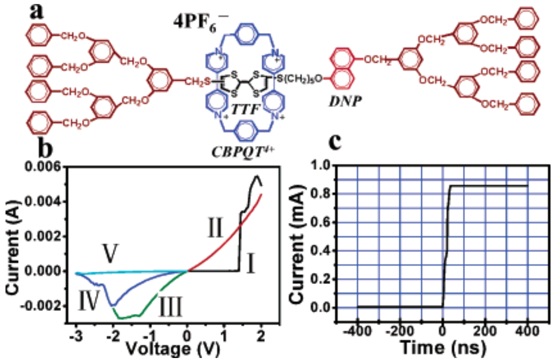

Figure 1. (a) Molecular structure of the rotaxane, H1. (b) $I-V$ characteristics of the thin H1 films on ITO glass, exhibiting the conductance transition from low- to high-conductivity state in curve I, the memory effect of the high-conductivity state in curve II, and the recovery of the low-conductivity state with reverse voltage scans in curves III to V. (c) Transition time measurement of the conductance switching, showing a very short transition time of about 60 ns.

To probe the origin of the reversible ON−OFF transition in the H1/ITO sample, we performed a series of comparative experiments. The $I-V$ measurements of the H1 films supported on highly oriented pyroletic graphite (HOPG) substrates gave the same "OFF", "ON", and "Recovery" behaviors under external voltage scans. Similar $I-V$ measurements on a layer of poly(methyl methacrylate) (PMMA) with thickness of about 100 nm revealed a sudden conductance transition from low- to high-conductance states, but no resumption of the OFF state could be obtained by applying reverse voltage scans. These experiments demonstrate that the reversible ON−OFF transition and nonvolatile memory effects of the H1 films originate from the rotaxane molecules. This stable conductance switching of the H1 films indicates that the film can be a good candidate for stable and reproducible nanorecording.

We utilized the conductance switching of the H1 thin films for STM-based nanorecording.[11] The film of about 20-nm thickness was deposited on an HOPG substrate (H1/HOPG). Figure 2a−c shows the formation of recording dots, which were written one by one by applying a positive voltage pulse of about 2 V and 5 ms from the STM tip. No recording dot was found if a negative voltage pulse was applied to the films, indicating that the recording is dependent on the voltage polarity. Additionally, no recording dots could be written on pure HOPG substrate when similar voltage pulse was applied. Figure 2d shows the $I-V$ measurements on the original film and on the dots formed. It clearly shows a conductivity increase at the dot. This $I-V$ characteristic is highly reproducible, suggesting that the voltage pulse causes a conductance transition of the H1 molecules and produces the recording dots. This voltage pulse-induced conductance transition at the dots on the films can be observed directly in conductive contact AFM experiments (see Supporting Information Figure 1S).[11] In addition, we tried to erase the bright marks by applying a negative voltage pulse on them. But it was not successful even though we changed the amplitude and the duration time of the pluses. With a large negative pulse,

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[†] Institute of Physics.
[‡] Institute of Chemistry.
[§] Current address: Department of Chemistry, Columbia University.

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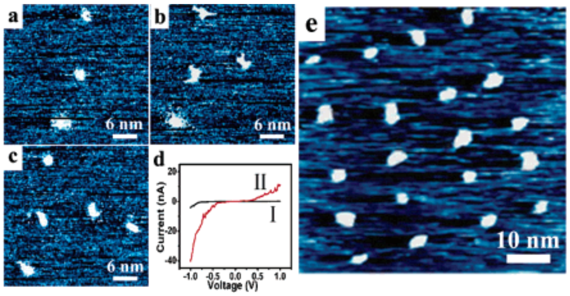

Figure 2. STM images of the recording dots written on the H1 thin films. (a−c) Recording dots written one by one through the application of the voltage pulses from the STM tip. (d) Typical $I-V$ characteristics measured on the original films (I) and on the induced recording dots (II). (e) STM images of a 5 × 4 recording dots array on the H1/HOPG sample. This film has been left exposed to air for about 2 months since its preparation. STM was performed in constant current mode with set points of $V_{\mathrm{bias}} = 0.65$ V and $I_{\mathrm{ref}} = 0.05$ nA.

the films were destroyed. This nonerasability might be due to the potential barrier of the molecule between the “off” and “on” states. Further modification of the molecule is probably needed to conduct the erasabilty of the recording.

Our further experimental results show that the H1/HOPG samples are very stable in ambient conditions. The conductance switching phenomena can be repeatedly observed on the same sample even after the sample has been left exposed in air for about 2 months. Figure 2e shows a 5 × 4 array of the recording dots written one by one by STM tip (about 2.2 V and 5 ms) on the two-month-old H1/HOPG sample. The writing is generally reproducible. If the writing occasionally fails for the first try, only little changes are needed to adjust the voltage pulse for a subsequent successful writing. The shape and size of the dots are not uniform, which may be due to the different configuration of local regions in the H1 films or some unexpected changes in external environment when the voltage pulses were applied. The combination of stable switching behavior and ease of control makes H1 quite applicable for nanorecording.

Similar conductance transition in rotaxane multilayers connected to two terminal junctions has been reported in the literature.[7] It is proposed that the switching comes from the transitions of the macrocycle. This hypothesis is supported by theoretical calculations.[6] Recently, people[8] have argued that this type of conductance transition comes from the formation of the metal filaments, rather than the movements of the macrocycle in the rotaxanes. Our experiments show no obvious evidence of the formation of the strong conducting filaments.[9] First, if the metallic filaments are formed, a very small resistance in the high conductive state and a very high ON/OFF ratio will be obtained. Our ON/OFF ratio of 10^2 is not consistent with the case where conducting filaments are formed (10^4-10^6). Second, the threshold voltage should increase linearly with the film thickness in the condition of metallic filaments formation. This is not in agreement with our results where the threshold voltage has no obvious relationship with the film thickness. Third, our comparative experiments performed on PMMA thin films suggest that the conductance transition depend on inherent properties of H1 molecules. Another possibility for this switching may come from the crystallinity change of the thin film.[2,10] However, from the Z-scale in Figure 1S,[11] the height difference on the site of the marks before and after recording is less than 0.3 nm, which suggests crystallinity change is not the main reason for the recording. Therefore, the conductance switching behaviors of H1 films in our experiment is believed to originate from the machine-like motion of the macrocycle between two recognizing sites. This resembles a transient “net oxidized” or “net reduced” state of the molecules when current flows through the asymmetric tunnel barriers in the two terminal junctions.[7a]

In summary, we have demonstrated the stable, reproducible nanorecording in the H1 films based on the unique structure property of H1 molecules. The thin films exhibit a reversible conductance switching and nonvolatile memory effect with an on/off ratio of about 100. Our results show that a rotaxane thin film may be a promising candidate for application in nanorecording.

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Supporting Information Available: Information about conductive contact AFM, $I-V$ measurement, nanorecording, and MM calculations of the orientation of the H1 on HOPG. This material is available free of charge via the Internet at http://pubs.acs.org.

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