A Single-Molecule Switch and Memory Element

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Abstract. The mechanically controllable break-junction technique enables us to investigate charge-carrier transport through an individually contacted and addressed molecule. Using a statistical measurement and analysis approach, we acquire simultaneously current–voltage curves during the repeated formation and breaking of a molecular junction. Thereby, a reversible and controllable switching between two distinct conductive states of a single-molecule system was investigated. Voltage pulses are used to switch from a low to a high conductive “on” state, and, furthermore, to reset the switch again to the “off” state. On this single-molecule level, collective phenomena can be excluded and therefore the observed switching mechanism has a truly molecular origin. Both conductive states are stable and accessible via non-destructive reading. Combined with the ability to reset the switch, this opens the way to employ this single-molecule as a memory element which is demonstrated by repeated write–read–erase–read cycles with non-destructive read-outs.

1. Introduction
Molecular electronics is aimed at the use of small ensembles or even individual molecules as functional building blocks in electronic circuits [1]. In recent years, devices applying thousands of molecules in parallel as functional elements have been presented [2, 3, 4, 5], revealing intriguing features such as negative differential resistance [3, 6], rectification behavior [7], Kondo effect [8, 9, 10], or conductance switching [4, 11]. For example, an unipolar voltage-triggered conductance switching of an ensemble of bipyridyl-dinitro oligophenylene-ethynylene dithiol molecules was reported previously using three different techniques [12]. Another type of switching often observed is stochastic switching [13]. It is caused by statistical fluctuations in the molecule itself or the molecule–metal contact. Recent experiments aiming to identify the fundamental mechanisms responsible for voltage-induced switching in sandwich-structures [11], indicate that the generic mechanism is dominated by the electrode properties or the molecule–metal interfaces, rather than the behavior inherent to the molecule [14, 15]. The investigation of intrinsic molecular functionality is difficult in these device architectures employing thousands of molecules in parallel, in particular because contact effects and collective phenomena cannot be excluded. In this paper, we demonstrate that a single molecule connected to two symmetric leads in a simple two terminal configuration can be reversibly and controllably switched between two stable states in response to an external voltage stimulus. In this geometry and under very controlled environment, we can exclude the formation of metal filaments and can conclude that the observed switching has truly a molecular origin.
2. Experimental

Charge-carrier transport studies are performed using the mechanically controllable break-junction (MCBJ) technique [16] (see Figure 1 and 2), an approach which has been proven to enable charge-carrier-transport measurements through an individual molecule [17]. Our MCBJ system is operated under ultra-high-vacuum (UHV) conditions in the temperature range between 5 and 300 K (see [18] for further experimental details). E-beam lithography is used to manufacture a freestanding metal bridge on top of a flexible substrate (Fig. 1). The initial cross-section of the bridge (typically 50 nm x 50 nm) is continuously reduced upon bending of the substrate in a three-point bending mechanism (Fig. 2(B)). Just before breaking, the cross-section of the bridge consists of a monoatomic chain, which is indicated by the appearance of quantized conductance. Further bending breaks the bridge and creates thereby two atomic-sized electrodes opposite to each other. The distance between the leads is then set to be longer than the length of the molecule to be studied. The molecules are deposited from a very diluted solution and can hereby adsorb to one of the two electrodes. Subsequently, the system is evacuated and measurements are performed when reaching UHV conditions. During the subsequent closing of the junction, molecules can bridge the gap between the electrodes by establishing the second chemical bond to the counter electrode, thus forming a molecular junction. This can be seen in resistance vs. electrode distance plots, when resistance plateaus are formed [19, 20]. In this regime, transport characteristics are acquired by measuring several hundreds of current–voltage (I–V) curves during formation and breaking of the molecular junction. The comprehensive data sets acquired are statistically analyzed, thereby, the most probable curves can be determined and single-molecule conductance values can be extracted. Voltages up to 2.5 V are typically applied to these single-molecule systems at low temperatures, thus accessing several electronic molecular levels. This enables us to monitor the characteristic signatures of the molecule under investigation [20].

![Figure 1](image1.png)

**Figure 1.** Scanning Electron Microscopy (SEM) picture of a freestanding metal bridge fabricated by electron-beam lithography on top of a flexible and insulating substrate. The electrical circuit is illustrated schematically. Reprinted from [18].

![Figure 2](image2.png)

**Figure 2.** The bending of the substrate in a three-point bending mechanism (A) stretches and finally breaks the bridge at its smallest constriction, creating thereby two separated electrodes (B). Reprinted from [18].
3. Single-Molecule Switch

Using the statistical measurement approach, we have investigated the transport properties of single bipyridyl-dinitro oligo-phenylene-ethynylene dithiol (BPDN-DT, Figure 3A)) molecules and bipyridyl oligophenylene-ethynylene dithiol (BP-DT, Figure 3B)) molecules connected to gold electrodes at 100 K. The BP-DT molecule acts as a reference molecule since it does not possess the functional nitro groups attached to the central bipyridil units. The $I-V$ sweeps for the two molecules exhibit the same conductance gap and an approximately six times lower current for BPDN-DT [18]. The lower conductance can be explained by the reduced conjugation of BPDN-DT due to its more twisted molecular structure caused by the steric hindrance of the nitro groups. Noticeable, in the $I-V$ curve of BPDN-DT is the appearance of a hysteresis at $\pm 0.9$ V as shown in Fig. 3. In contrast, the BP-DT exhibits no hysteresis and exclusively monotonic traces without any switching were measured. In addition, stochastic switching [13] is absent for both molecular systems. This can be explained by the low temperatures (100 K) where we typically do not observe statistical fluctuations in the molecule itself or the molecule–metal contact, in contrast to measurements at elevated temperatures ($T > 250$ K). Consequently, the mechanism causing the switching observed in BPDN-DT is not of a stochastic type but has truly a molecular origin, which is obviously caused by the functional nitro groups.

Figure 3. Molecular structures of A) BPDN-DT, and B) BP-DT molecules. C) Several repeated switching cycles of the BPDN-DT exhibiting a hysteresis. Reprinted from [18].

Figure 4. (A) Write, read and erase pulse pattern applied. (B) Current readings reveal a controlled switching between “off” and “on” state. Reprinted from [18].

Figure 3C) shows several $I-V$ curves taken for BPDN-DT at 100K revealing a hysteresis for positive and negative voltages. Starting the measurement from 0 V, the current signal increases monotonically until the voltage exceeds $V_{\text{Switch,pos}}$. The current signal suddenly jumps from a low conductive curve, called the “off” trace, at approximately +0.8 V to a high current curve, called “on” trace. Sweeping the voltage back, one observes a hysteresis. After this first switching sweep, when operating only at voltages above $V_{\text{Switch,neg}}$, the initial “off” state is no longer accessible and the metal-molecule-metal system remains in the higher conductive “on” state.
during all subsequent positive sweeps. Performing a negative voltage sweep, a similar switching behavior is observed. Sweeping back, the current signal follows again a monotonous trace. This negative sweep resets the system to the “off” state, which is verified by a subsequent positive sweep that again exhibits a lower current and a switching to the “on” state. In all our samples, the “off” state is always reconfigurable by applying a negative voltage pulse below a certain threshold voltage ($V_{\text{Switch, neg}}$). Both states of the system are remarkably stable: Even after several hours of measurement and performing more than 500 sweeps iteratively, the hysteresis effect is maintained and the system retains its ability to switch.

4. Memory Operation

As mentioned above, voltage pulses exceeding the threshold voltages can be applied to switch the system between the two discrete states in a very controlled and reversible manner. The “on” state is unaffected by successive read pulses at low positive voltages ($+0.5 \text{ V} < V_{\text{Read}} < V_{\text{Switch, pos}}$). This non-destructive reading in combination with the controlled switching in both directions makes it possible to use this single-molecule system as a memory element. We demonstrate memory operation by storing one bit in this molecular building block. A write pulse turns the system to “on”, which is controlled with a subsequent read-out of the bit-state by direct probing of the current. An erase pulse resets the memory element, which is again tested by another subsequent read-out. Fig. 4(A) displays the pulse pattern consisting of write ($+1.6 \text{ V}, 50 \text{ ms length}$) and erase ($-1.6 \text{ V}, 50 \text{ ms length}$) pulses with intermediate readings ($+1.1 \text{ V}, 3 \text{ s duration}$) which was applied to the metal–single-molecule–metal system. The inset of Figure 4(B) shows the $I–V$ curve for the specific sample used. The current through the molecule was directly probed (Figure 4(B)). During the reading times of three seconds, the current signals were constant and no decay of the state was observed. The currents measured for the “off” state vary between 0.05 and 0.13 nA, those for the “on” state between 0.9 and 3.6 nA, yielding a bit separation ($I_{\text{on}}/I_{\text{off}}$) ranging between 7 and 70. Furthermore, periodic reading of a stored bit (no voltage applied between readings) established that this single-molecule memory is non-volatile over a measurement time of several minutes at 100 K (see [18] for more details).

5. Conclusions

In conclusion, we have demonstrated that the metal–single-BPDN-DT–metal system can be controlled and reversibly switched between two distinct states. In our single-molecule measurements, collective phenomena and formations of metal filaments can be excluded, therefore the switching found in the BPDN-DT molecule has truly a molecular origin which we attribute to the functional nitro groups. In addition, we have demonstrated that the controlled switching behavior can be used to write, read and erase bits by simple voltage pulses and hence employ a single-molecule as a unimolecular memory element. Further experimental and theoretical research is required to fully elucidate the fundamental processes underlying the molecular switching mechanism.

6. Acknowledgments

We wish to acknowledge Walter Riess, Siegfried Karg and Paul F. Seidler for many helpful discussions. We are grateful to Charles T. Rettner and Daniel Secker for electron-beam lithography, and Meinrad Tschudy for technical support. The work at Rice University was supported by DARPA and AFOSR.
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