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The Metastability of an Electrochemically Controlled Nanoscale Machine on Gold Surfaces

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The advent of supramolecular chemistry^[1] has provided chemists with the wherewithal to construct molecule-level machines^[2, 3] in an efficient manner using the protocol of template-direction.^[4] Synthetically accessible, linear motor molecules come in the

guise of bistable [2]rotaxanes in which the ring component can be induced^[5] to move relative to the dumbbell-shaped one by altering the redox characteristics of the molecules. Such precisely controllable nanoscale molecular machines and switches have attracted a lot of attention^[2, 3] because of their potential to meet the expectations of a visionary^[6] and to act as some of the smallest components for the engineering of nanoelectromechanical systems (NEMS) and the fabrication of nanoelectronic devices.^[7]

Although the redox-switching properties of numerous bistable [2]rotaxanes^[8] have been demonstrated in solution, the lack of coherence of the switches in this phase makes it difficult to harness the potential envisaged by Feynman.^[6] It is essential that we establish how to self-assemble these tiny switches in an orderly manner at surfaces^[9–12] and to investigate their switching properties in conjunction with their introduction into solid-state devices that have been shown^[7] to function as two-dimensional molecular electronic circuits. The fabrication of such devices required the design and synthesis^[13] of bistable [2]rotaxanes that are amphiphilic, so that they can be transferred^[7, 14–16] as molecular monolayers using the Langmuir–Blodgett (LB) technique into a device setting. A molecular switch tunnel junction (MSTJ) has been fabricated^[7] by sandwiching such self-organized LB monolayers between a bottom Si electrode and a top Ti/Al electrode in a crossbar device architecture. The switch-on (high conductance) and switch-off (low conductance) states of each junction can be addressed respectively upon applying a +2 V or a –2 V bias. The proposed electromechanical switching mechanism (Figure 1) suggests that the ground state, where the cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺, blue) ring initially encircles the tetrathiafulvalene (TTF, green) unit, represents^[17] the switch-off state. When a +2 V bias is applied, the CBPQT⁴⁺ ring moves mechanically to the 1,5-dioxynaphthalene (DNP, red) ring system as a result of oxidation of the TTF unit to its radical cation. Although, when the bias is removed, neutrality is restored to the TTF unit, the CBPQT⁴⁺ ring continues to reside on the DNP ring system, forming the metastable state. The observation of a switch-on state can be attributed to this slow-decaying metastable state that can be erased by applying a –2 V bias for a fleeting moment during the switching cycle. Since the mechanical motion associated with this decay is an activated process, these devices exhibit a hysteretic current–voltage response.

Herein, we describe how we have utilized a custom-designed variable temperature (VT) electrochemical apparatus to investigate the redox-switching behavior of an Au surface-confined^[18] linear motor-molecule, that is, a disulfide-tethered bistable [2]rotaxane **SSR**·4PF₆, together with the corresponding dumbbell-shaped control compound **SSD**. In both cases, the appended disulfide function is used to immobilize the redox-active [2]rotaxane and dumbbell control onto gold surfaces as self-assembled monolayers (SAMs). The [2]rotaxane **SSR**·4PF₆ was obtained (Figure 2) by a template-directed protocol^[4] wherein a CBPQT⁴⁺ ring was clipped around the TTF unit of the dumbbell-shaped precursor **SSD**. Here, we report i) the results of a semiquantitative electrochemical investigation^[19] carried out on the surface-confined **SSR**⁴⁺ and the control (**SSD**) at room temperature in MeCN, leading to the identification^[20] of a

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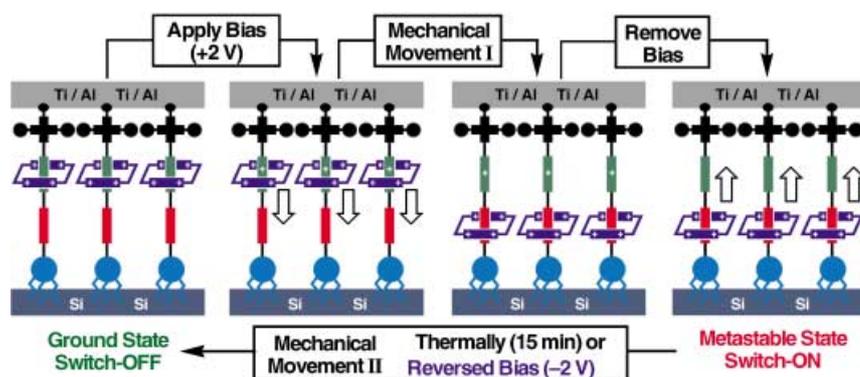


Figure 1. Proposed electromechanical mechanism which accounts for the hysteretic current-voltage response by an amphiphilic, bistable [2]rotaxane monolayer in an MSTJ device, where the bottom electrode is Si and the top electrode is Ti/Au. The devices are described in ref. [7] and the rotaxane molecules consist of i) an amphiphilic dumbbell component containing two recognition sites—a tetrathiafulvalene (TTF, green) unit and a 1,5-dioxynaphthalene (DNP, red) ring system, and two stoppers, one (upper) hydrophilic (black) and the other (lower) hydrophilic (blue) and ii) a ring component, the tetracationic cyclophane (blue), cyclobis(paraquat-p-phenylene). See ref. [7] for the structures of rotaxanes that give hysteretic current-voltage responses in the

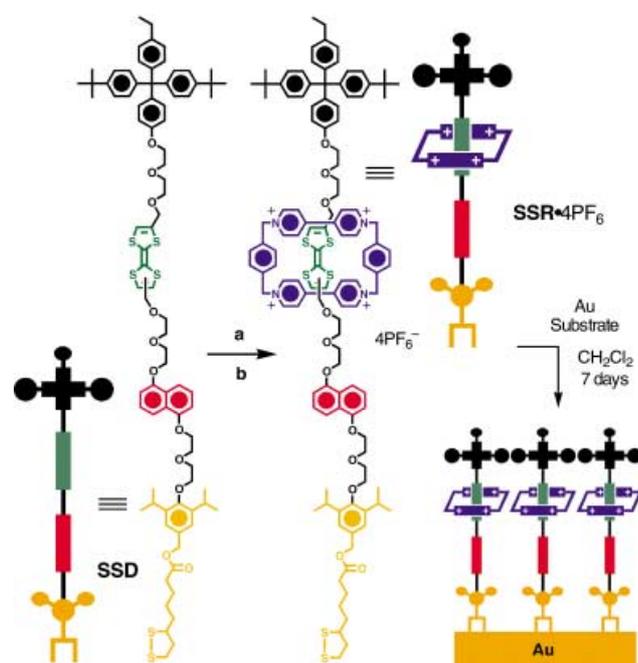


Figure 2. Template-directed synthesis of the disulfide-tethered, bistable [2]rotaxane $\text{SSR} \cdot 4\text{PF}_6$ from its dumbbell-shaped precursor SSD and their self-organization on gold as SAMs. Reagents and conditions: a) α, α' -[1,4-phenylenebis(methylene)]bis(4,4'-bipyridium) bis(hexafluorophosphate), 1,4-bis(bromo-methyl)benzene, *N,N*-dimethylformamide, RT, 10 days; b) chromatography on SiO_2 : $\text{Me}_2\text{CO}/\text{NH}_4\text{PF}_6$, followed by addition of H_2O to the eluent.

metastable state, translationally isomeric with its ground state, ii) the kinetics associated with the first-order decay of the metastable state back to its ground state, in SAMs of SSR^{4+} at 288 K, and iii) a variable-temperature analysis of the kinetics over the range from 278 to 303 K, leading to an estimate of the activation energy for the relaxation of the metastable state of the surface-confined SSR^{4+} back to its ground state. Finally, we demonstrate how iv) the metastable state is quelled when the

bipyridinium units in the CBPQT^{4+} ring are reduced to radical cations.

SAMs of SSR^{4+} and SSD were prepared by immersing a coiled gold wire (99.9%/length, 105 mm/diameter, 0.5 mm) into their solutions (0.1 mM) in CH_2Cl_2 for seven days. After washing the substrate with CH_2Cl_2 and drying under an air-flow, the SAM-modified gold wire was placed into the custom-built electrochemical cell for cyclic voltammetry (CV) measurements, which were carried out in an electrolyte solution of LiClO_4 (0.05 M) in MeCN over a range of temperatures (263 to 303 K) under an Ar atmosphere. All potentials are referenced to an Ag/AgCl reference electrode. In the investigations of the TTF-centered oxidation processes, namely $\text{TTF} \rightarrow \text{TTF}^{+\cdot}$ and then $\text{TTF}^{+\cdot} \rightarrow \text{TTF}^{2+}$, three oxidation peaks were observed (Figure 3a) for

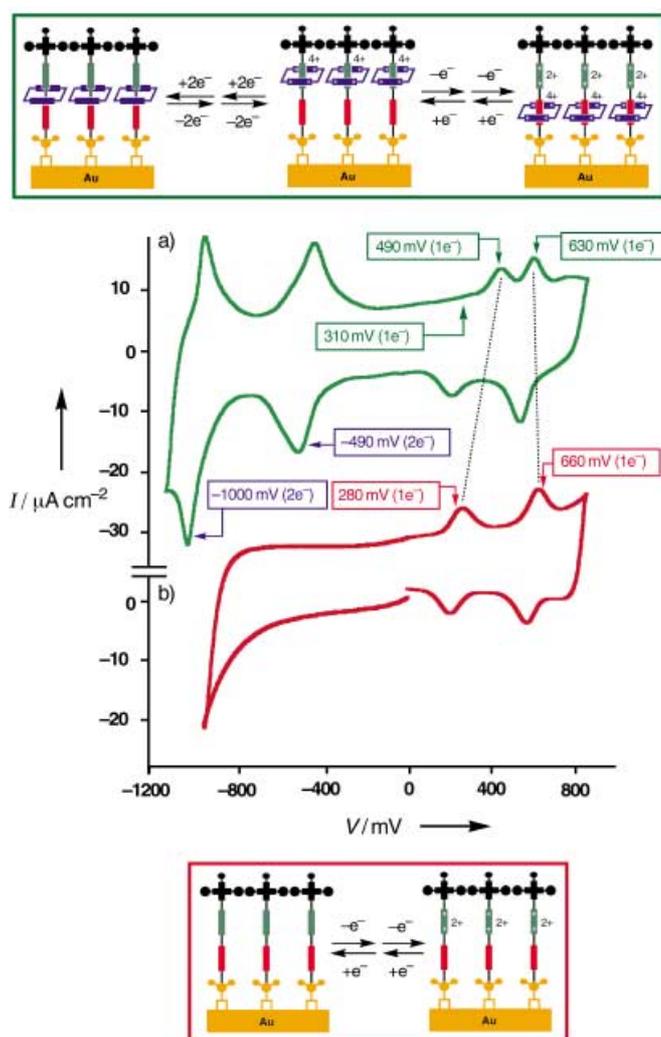


Figure 3. a) The CV (green) of the surface-confined, bistable [2]rotaxane SSR^{4+} . b) The CV (red) of the surface-confined dumbbell compound SSD . The associated redox and/or mechanical changes for SSR^{4+} are shown inside the green box. The associated redox changes for SSD are shown inside the red box.

SSR^{4+} at +310, +490, and +630 mV in the ratio of 1:9:10, respectively. This observation indicates^[21] the presence of two unequally populated (ca. 1:9) translational isomers—the minor one, in which the CBPQT⁴⁺ ring encircles the DNP ring system, can be associated with peaks centered at +310 and +630 mV, but only one-tenth of the latter. These two peaks can be assigned to rotaxane structures with free TTF units, since they have oxidation potentials very similar to those for SSD , where two mono-electronic processes were observed (Figure 3b) at +280 and +660 mV. The major translational isomer, where the CBPQT⁴⁺ ring encircles the TTF unit is responsible for the peaks located^[22] at +490 and +630 mV, or at least nine-tenths of the latter peak. In this case, the high first oxidation potential indicates that CBPQT⁴⁺ encircles the TTF unit. On the other hand, considering the reduction processes associated with SSR^{4+} , the two peaks centered on –490 and –1000 mV can be assigned, respectively, to the first and second bielectronic processes of the threaded CBPQT⁴⁺ ring. By contrast, no reduction process was observed in the case of the control, that is, SSD . In addition, the CV data of these SAMs displayed a linear increase in current with scan rate, an observation^[23] which is characteristic of surface-confined redox systems. Furthermore, such SAMs have proved to be extremely stable, displaying the same current response for more than 100 scan cycles. The samples also retained their electrochemical robustness over the course of several days in the electrolyte. Based on the integration of the current to the time

associated with each peak, the surface coverage by the rotaxane^[24] was found to be 0.25 molecule nm^{-2} , that is, SSR^{4+} has a footprint on gold of the order of 4 nm^2 .

To achieve a better understanding of the electromechanical mechanism associated with the switching process in the rotaxane-based SAMs, further electrochemical investigations were performed in the oxidation “window”, namely –100 to +900 mV. Figure 4a portrays the first and second cycles of continuous CV measurement, recorded at a scan rate of 300 mV s^{-1} at 288 K. The first CV cycle (green curve), which exhibits the same features as the oxidative portions of the CV shown in Figure 3a, corresponds to a SAM of the [2]rotaxanes SSR^{4+} in its ground-state. The second CV cycle (red curve), however, signals a dramatic change. In fact, all of the CV cycles, except the first one, showed exactly the same features as those observed in the second CV cycle. In the second and subsequent cycles, the peak (+490 mV) associated with the first oxidation of the CBPQT⁴⁺-encircled TTF unit decreased, and, as a direct consequence, the peak associated with the first oxidation process of the free TTF unit increased. This result provides incontrovertible evidence for the direct observation of the continuously decaying metastable state, which is generated during the previous CV cycle, and then “captured” by the following CV cycle at relatively high scan rates. Although the presence of such a metastable state was previously proposed^[7] to rationalize the hysteretic behavior of the voltage-driven

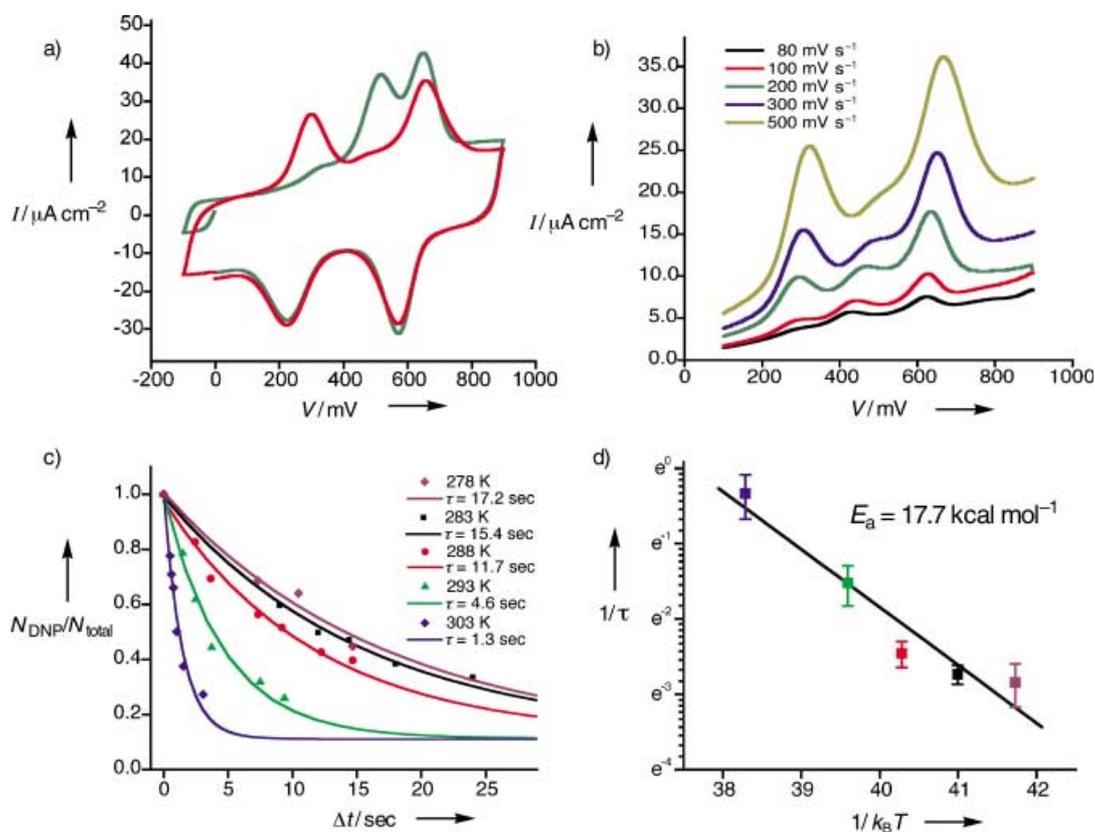


Figure 4. a) The first (green) and second (red) CV cycles of the surface-confined, bistable [2]rotaxane SSR^{4+} measured at 300 mV s^{-1} at 288 K. b) The cathodic peaks of the second CV cycles measured at different scan rates, ranging from 80–500 mV s^{-1} at 288 K. c) The population ratios of the less stable translational isomer ($N_{\text{DNP}}/N_{\text{total}}$) and the relaxation times (Δt) fitted to a first-order decay model, which allows the lifetimes (τ) of the metastable states to be obtained at different temperatures, ranging from 278–303 K. d) An Arrhenius plot of $(1/\tau)$ against $(1/k_{\text{B}}T)$ from which an activation energy (E_{a}) of $17.7 \pm 2.8 \text{ kcal mol}^{-1}$ has been obtained for the relaxation process.

switching process of a related bistable [2]rotaxane-based MSTJ in a solid-state device, the proposal was a phenomenologically inspired one. The electrochemical studies reported herein on the surface-confined bistable rotaxane, which may be regarded as a good model for solid-state MSTJs, add credence to the notion that the metastability observed for these electromechanical switches in an electrochemical cell translates to their hysteretic switching behavior in solid-state devices.^[7, 25]

When continuous CV measurements were made at different scan rates from 80 to 500 mV s⁻¹ at 288 K, the ratios (Figure 4b) between the two different translational isomers in the SAM in the second CV cycle changed accordingly because of the instability of the metastable state. When the scan rate is slower, there is sufficient time between the first and second CV cycles to allow a substantial number of the rotaxane molecules to return to their ground state. The ratio of the two different isomers in the second CV cycle can be obtained by integrating the first and second oxidation peaks. While the first peak area (N_{DNP}) is proportional to the thermodynamically less-stable translational isomer (the metastable one) where the CBPQT⁴⁺ ring encircles the DNP ring system, the second peak area (N_{TTF}) is proportional to the more stable isomer (the ground state) in which the CBPQT⁴⁺ ring encircles the TTF unit. The third peak area ($N_{\text{DNP}} + N_{\text{TTF}} = N_{\text{total}}$) corresponds to the total number of rotaxane molecules on the gold substrate. Ideally, when the CV scan reaches the second cathodic peak (+230 mV) of the reversible oxidation processes, the SAM will be "primed" in its metastable state, wherein 100% of the bistable rotaxane molecules reside as the thermodynamically less-stable translational isomer. At the same time, neutrality will be restored to the TTF unit and the relaxation of the SAM will begin. The average relaxation time (Δt) was defined as the period between the second cathodic peak (+230 mV) of the first CV cycle and the first anodic peak (+310 mV) of the second CV cycle. Different scan rates changed the relaxation times correspondingly. Ideally, a first-order kinetic model should explain the decay process. Thus, we fitted the population ratio of the less stable translational isomer ($N_{\text{DNP}}/N_{\text{total}}$) and the relaxation time (Δt) according to a first-order decay model.^[26] The lifetime (τ) of the metastable state at 288 K was found (red curve in Figure 4c) to be 11.7 s. Another four sets of scan-rate-dependent CV experiments were carried out at 278, 283, 293, and 303 K. The corresponding lifetimes are summarized in Figure 4-c. Since the lifetimes (τ) of the metastable state are dependent on the temperature (T) and the activation energy (E_a) of the relaxation process, we fitted (Figure 4d) the values of τ from the VT scan-rate-dependent CV experiments to the Arrhenius equation^[27] to obtain an E_a of 17.7 ± 2.8 kcal mol⁻¹.^[28, 29] We have also carried out the scan-rate dependent CV experiments at temperatures lower than 278 K. However, the relaxation of the metastable state becomes too slow for our CV equipment to collect reliable enough data to be fitted into the first-order decay model. It is important to note, however, that, when the CV experiment is carried out at 263 K, the metastable state has a lifetime of approximately 5 min. Such a long-lived situation is significant, and could find applications in memory devices.

It will be recalled that two bielectronic reduction processes in the rotaxane-based SAMs have been observed, wherein both of

the two bipyridinium units in the CBPQT⁴⁺ ring become reduced to their radical cations. According to previous investigations,^[13b,c] this bi-electronically reduced CBPQT⁴⁺ ring loses its affinity for the electron-donating recognition sites in the dumbbell-shaped components and no longer encircles them. Thus, we argued that it might be possible to use this reduction process to erase the metastable state in the oxidation loop. This idea was tested on SSR⁴⁺ at 263 K in MeCN. The metastable state was generated and probed by CV cycles between 0 and +900 mV. This state was found to be stable for 5 min and could be probed by subsequent CV cycles. However, immediately upon implementing a CV cycle in the reduction mode (0 to -600 mV), this metastable state was erased completely (Figure 5) and replaced by the ground state, that is, the reduction of two bipyridinium units in the CBPQT⁴⁺ ring destabilizes the metastable state and accelerates the relaxation process, thus erasing any previous information which has been stored in the molecule.

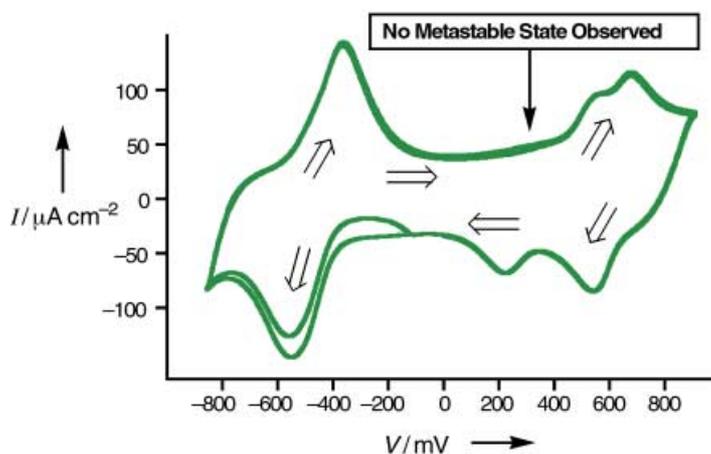


Figure 5. The first and second CV cycles (both green) of the surface-confined, bistable [2]rotaxane SSR⁴⁺ measured at 1500 mV s⁻¹ at 263 K. The metastable state was erased completely and replaced by the ground state when the CV cycle in the reduction mode (0 to -600 mV) was applied.

The redox-controlled electromechanical switching mechanism exhibited by the surface-confined [2]rotaxane SSR⁴⁺ at the solution-solid interface is summarized in Figure 6. While the mechanical movement I is too rapid to be detected by CV, the kinetics for the mechanical movement II can be studied precisely by VT scan-rate-dependent CV experiments – from which the lifetime and activation energy of the metastable state can be deduced. These data not only provide important feedback into the molecular design and synthesis of bistable rotaxane-based nanoelectronic devices, but they also tell us that we can now self-assemble these tiny linear motor-molecules on surfaces and operate them in a coherent and cooperative manner. The results augur well for the design and production of nanomachinery that can be driven electrochemically in the context, for example, of nano-electromechanical systems that alter the surface properties of the channels in microfluidic systems.

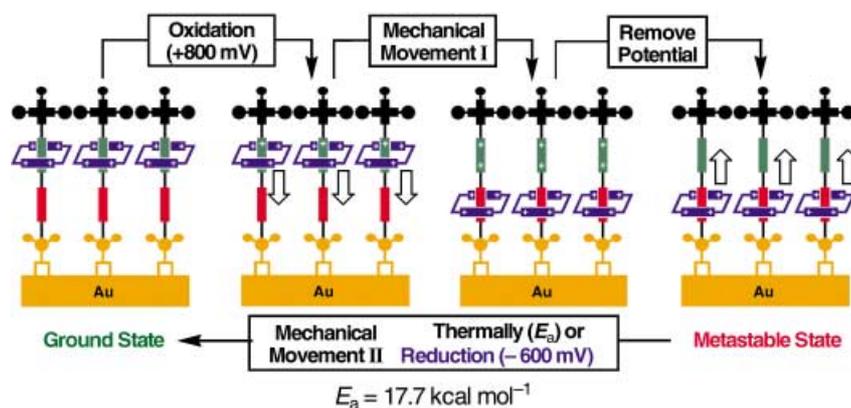


Figure 6. Proposed electromechanical mechanism for the redox switching of the surface-confined, bistable [2]rotaxane SSR^{4+} on the gold surface. This mechanism should be compared with that presented in Figure 1. Note that the graphical representations of the amphiphilic bistable [2]rotaxane molecules are highly idealized.

For the present, however, it is the identikit match between the details of the switching mechanism (Figure 6) exhibited by the disulfide-tethered, bistable [2]rotaxane SSR^{4+} on gold, as revealed by the electrochemical experiments described in this communication and the proposed^[7] switching mechanism (Figure 1) for a very closely related amphiphilic bistable [2]rotaxane in a device setting, as demonstrated by current-voltage measurements, that we wish to report.

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Keywords: electrochemistry · kinetics · metastable states · molecular switches · self-assembled monolayers · surfaces

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- where N_{DNP}^0 is the equilibrium population (10%) of the ground state at the beginning of the experiment.
- [27] The E_a value was obtained from the Arrhenius equation by plotting $(1/\tau)$ against $(1/k_B T)$.
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for protons in the DNP ring systems. The energy barriers of around 14.5 kcal mol⁻¹, which were obtained using a spin saturation transfer method in solution, can be compared with the E_a value of 17.7 kcal mol⁻¹ found for the relaxation of the metastable state of a related bistable [2]rotaxane SSR⁴⁺ confined on a gold surface.

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Enhanced Biomacromolecule Encapsulation by Swelling and Shrinking Procedures

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The layer-by-layer (LBL) self-assembly technique has been diversely applied to fabricate multilayer ultrathin organic or hybrid films with various properties since it was introduced by Decher et al.^[1] Oppositely charged polyelectrolytes from dilute aqueous solution are deposited consecutively onto solid substrates by utilizing electrostatic attraction and complex formation between polyanions and polycations. Recently, LBL assembly of oppositely charged polyelectrolytes onto removable colloidal particles has been utilized to create novel hollow nano- and microcapsules with customized physicochemical properties.^[2] These nano- and micron-sized capsules are of both scientific and technological interest because of their potential applications as new colloidal structures in areas such as medicine, drug delivery, artificial cells (viruses), and catalysis.

Many efforts have been devoted to the nanoscale encapsulation of drugs, minerals, dyes, proteins, enzymes and genes.^[3] Materials such as enzymes or drugs can be transformed into a core template or can be attached to core template particles prior to core decomposition so as to trap them inside hollow capsules.^[4] Hollow polyelectrolyte capsules have been filled with low molecular weight dyes such as 6-carboxyfluorescein (6-CF) and rhodamine 6G (Rd6G) by modifying the solubility of a compound by variation of the pH value.^[5] Macromolecules such

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