

# The Role of Physical Environment on Molecular Electromechanical Switching

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**Abstract:** The influences of different physical environments on the thermodynamics associated with one key step in the switching mechanism for a pair of bistable catenanes and a pair of bistable rotaxanes have been investigated systematically. The two bistable catenanes are comprised of a cyclobis(paraquat-*p*-phenylene) (CBPQT<sup>4+</sup>) ring, or its diazapyrenium-containing analogue, that are interlocked with a macrocyclic polyether component that incorporates the strong tetrathiafulvalene (TTF) donor unit and the weaker 1,5-dioxy-naphthalene (DNP) donor unit. The two bistable rotaxanes are comprised of a CBPQT<sup>4+</sup> ring, interlocked with a dumbbell component in which one incorporates TTF and DNP units, whereas the other incorporates a monopyrrolotetrathiafulvalene (MPTTF) donor and a DNP unit. Two consecutive cycles of a variable scan rate cyclic voltammogram (10–1500 mV s<sup>-1</sup>) performed on all of the bistable switches (~1 mm) in MeCN electrolyte solutions (0.1 M tetrabutylammonium hexafluorophosphate) across a range of tempera-

tures (258–303 K) were recorded in a temperature-controlled electrochemical cell. The second cycle showed different intensities of the two features that were observed in the first cycle when the cyclic voltammetry was recorded at fast scan rates and low temperatures. The first oxidation peak increases in intensity, concomitant with a decrease in the intensity of the second oxidation peak. This variation changed systematically with scan rate and temperature and has been assigned to the molecular mechanical movements within the catenanes and rotaxanes of the CBPQT<sup>4+</sup> ring from the DNP to the TTF unit. The intensities of each peak were assigned to the populations of each conformation, and the scan-rate variation of each population was analyzed to obtain kinetic and thermodynamic data for the movement of the CBPQT<sup>4+</sup> ring. The Gibbs free energy

of activation at 298 K for the thermally activated movement was calculated to be 16.2 kcal mol<sup>-1</sup> for the rotaxane, and 16.7 and 19.2 kcal mol<sup>-1</sup> for the bipyridinium- and diazapyrenium-based bistable catenanes, respectively. These values differ from those obtained for the shuttling and circumrotational motions of degenerate rotaxanes and catenanes, respectively, indicating that the detailed chemical structure influences the rates of movement. In all cases, when the same bistable compounds were characterized in an electrolyte gel, the molecular mechanical motion slowed down significantly, concomitant with an increase in the activation barriers by more than 2 kcal mol<sup>-1</sup>. Irrespective of the environment—solution, self-assembled monolayer or solid-state polymer gel—and of the molecular structure—rotaxane or catenane—a single and generic switching mechanism is observed for all bistable molecules.

**Keywords:** bistability • catenanes • electrochemistry • metastability • NMR spectroscopy • rotaxanes

## Introduction

Very few molecular properties are amenable to investigation across a broad range of physical environments. One class of such properties are the electrochemically driven molecular mechanical motions<sup>[1]</sup> that characterize the switching bistability of certain [2]catenanes<sup>[2–6]</sup> and [2]rotaxanes.<sup>[7–11]</sup> These molecules, in fact, provide model systems for such investigations. Their synthetic modularity<sup>[12]</sup> and structural versatility<sup>[13]</sup> make them adaptable to a wide range of surroundings.<sup>[14]</sup> Furthermore, the relatively large geometrical and electronic changes that accompany their electrochemically

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driven internal molecular motions are accompanied by a variety of experimentally detectable signatures.<sup>[15]</sup>

The interlocked molecular compounds (Figure 1), whose switching and/or shuttling in the solution phase we are going to discuss in this paper, are two pairs<sup>[2–5]</sup> of [2]catenanes—**C1**<sup>4+</sup> and **C2**<sup>4+</sup> are bistable, **C3**<sup>4+</sup> and **C4**<sup>4+</sup> are degener-

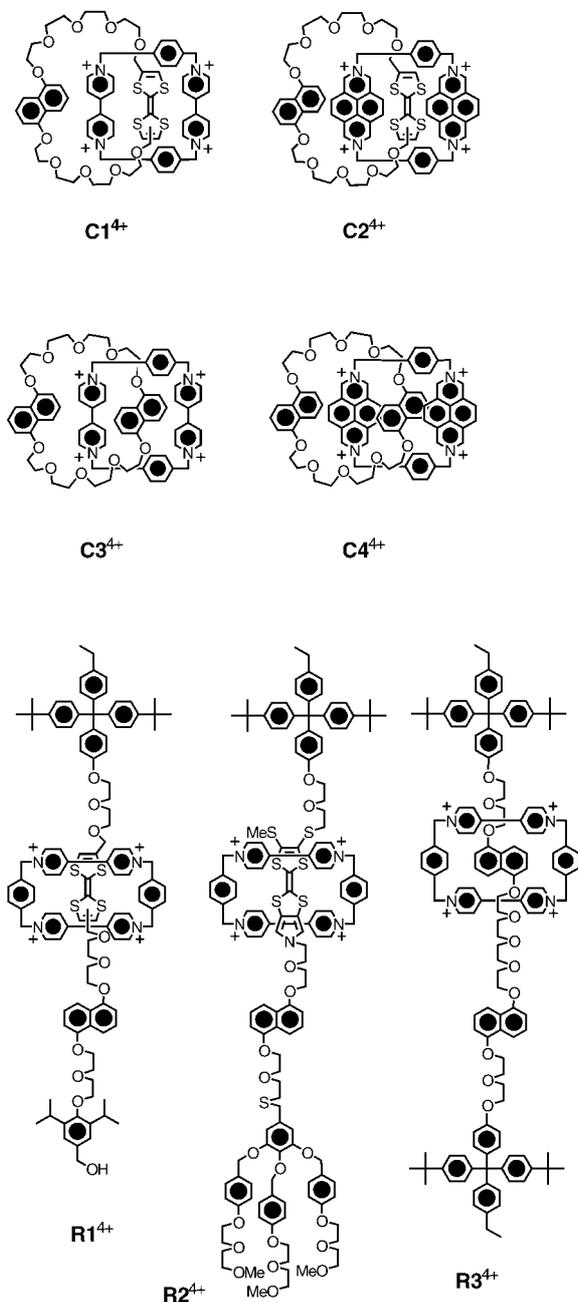


Figure 1. The structural formulas of two bistable [2]catenanes **C1**<sup>4+</sup> and **C2**<sup>4+</sup>, their degenerate [2]catenane analogues **C3**<sup>4+</sup> and **C4**<sup>4+</sup>, respectively, together with two bistable [2]rotaxanes **R1**<sup>4+</sup>, **R2**<sup>4+</sup>, and their degenerate analogue **R3**<sup>4+</sup>. The bistable catenanes and rotaxanes were characterized in solution by using electrochemical techniques and the degenerate analogues were investigated by dynamic <sup>1</sup>H NMR spectroscopy. Each bistable catenane and rotaxane is composed of a tetracationic cyclobis(paraquat-*p*-phenylene) (CBPQT<sup>4+</sup>) ring that is interlocked with either a polyether macrocycle or a dumbbell component, which incorporate a tetrathiafulvalene (TTF) unit and a 1,5-dioxynaphthalene (DNP) ring system.

ate—and three [2]rotaxanes, of which **R1**<sup>4+</sup> and **R2**<sup>4+</sup> are bistable<sup>[2,3]</sup> and **R3**<sup>4+</sup> is a degenerate shuttle.<sup>[16]</sup>

In a recent communication,<sup>[17]</sup> we discuss the electrochemical switching mechanism in a liquid polymer matrix for those interlocked molecules that are bistable. Briefly, for both the bistable [2]catenanes and [2]rotaxanes, there exists an equilibrium between the cyclobis(paraquat-*p*-phenylene) (CBPQT<sup>4+</sup>) ring encircling either the tetrathiafulvalene (TTF) unit, which is energetically favored and called the ground-state co-conformer (GSCC)<sup>[4,17]</sup>, or the dioxynaphthalene (DNP) site, referred to as the metastable-state co-conformer (MSCC).<sup>[4,17]</sup> The first oxidation for all of these systems corresponds to TTF→TTF<sup>•+</sup> and is accompanied by a rapid shuttling (for bistable [2]rotaxanes) or circumrotation (for bistable [2]catenanes) of the CBPQT<sup>4+</sup> ring so that it encircles the DNP site. At the moment when the TTF<sup>•+</sup> radical cation is reduced back to neutral TTF, the CBPQT<sup>4+</sup> ring still encircles the DNP site, and so the equilibrium is distorted toward the MSCC. Although this MSCC has not been observed previously for any of these bistable molecules in solution, it has been invoked<sup>[4,5,9]</sup> to account for the long (several minutes) retention times of the high-conductance states in the various molecular-switch tunnel junctions (MSTJs) fabricated from bistable [2]catenanes and [2]rotaxanes, including some of those discussed in this paper.

In a liquid polymer matrix,<sup>[17]</sup> the recovery of the GSCC from the MSCC for **C1**<sup>4+</sup>, **C2**<sup>4+</sup>, and **R2**<sup>4+</sup> may be detected optically, and the kinetics may be quantified by using time- and temperature-dependent cyclic voltammetry (CV). Furthermore, for a particular functionalized bistable [2]rotaxane that is organized as a self-assembled monolayer (SAM) on gold,<sup>[10]</sup> the same relaxation process can be characterized. This behavior results from the fact that the TTF→TTF<sup>•+</sup> oxidation potential is lowered by approximately 200 mV in the MSCC, relative to that in the GSCC. This lower potential for the MSCC is also consistent with that co-conformer being the one responsible for the switch-closed, high-conductance state in the MSTJ devices.<sup>[9]</sup>

The polymer matrix<sup>[17]</sup> may be viewed as a solvent, but with a viscosity approximately 10<sup>4</sup> times higher than that of a typical solvent, such as MeCN. The effect of solvent viscosity on unimolecular reaction rates for both small molecules<sup>[18]</sup> and for macromolecules<sup>[19]</sup> has been investigated by several research groups. While a detailed picture of how solvent viscosity and unimolecular reaction rates is not fully developed, the existing body of work suggests<sup>[18,19]</sup> that the polymer environment should slow down the rate of recovery of the GSCC from the MSCC by between 10<sup>2</sup> and 10<sup>3</sup> times. A general rule of thumb is that the rate of an activated process is reduced by an order of magnitude for every 10° reduction in temperature. These observations, taken together with the polymer matrix results,<sup>[17]</sup> suggest that the metastability for all the bistable [2]catenanes and [2]rotaxanes (Figure 1) should be readily detectable in common solvents by reduced-temperature CV measurements. In this paper, we report that we are, in fact, able to capture and quantify the metastability through a series of temperature- and time-dependent CV measurements in MeCN. We compare these

new results with 1) various control experiments; 2) results obtained by using variable-temperature  $^1\text{H}$  NMR spectroscopy on the degenerate systems  $\mathbf{C3}^{4+}$ ,  $\mathbf{C4}^{4+}$ , and  $\mathbf{R3}^{4+}$ ; and 3) those reported<sup>[17]</sup> for the polymer matrix, and find that the kinetics of bistable switching in these molecular mechanical systems can be correlated with both molecular structure<sup>[11c]</sup> and physical environment. In other words, although, relative to the solution state, the polymer environment slows down the MSCC  $\rightarrow$  GSCC relaxation kinetics for all the molecular switches by two or three orders of magnitude, the relative differences of the activation barriers in MeCN, for example, translate into similar relative differences in the polymer matrix. Most important, however, is the fact that these experiments, combined with the findings discussed in two previous publications,<sup>[10,17]</sup> provide compelling evidence for the robustness of a single molecular-switching mechanism across a wide range of physical environments. Furthermore, this mechanism applies to both bistable [2]catenanes and bistable [2]rotaxanes.

## Results and Discussion

**Cryoelectrochemistry on a bistable rotaxane:** In Figure 2a, we present two successive CVs of  $\mathbf{R1}^{4+}$  in MeCN (257 K,  $200\text{ mVs}^{-1}$ ) and compare them with those for the dumbbell component of  $\mathbf{R1}^{4+}$  (293 K,  $200\text{ mVs}^{-1}$ ). This bistable rotaxane exhibits an equilibrium GSCC:MSCC population of

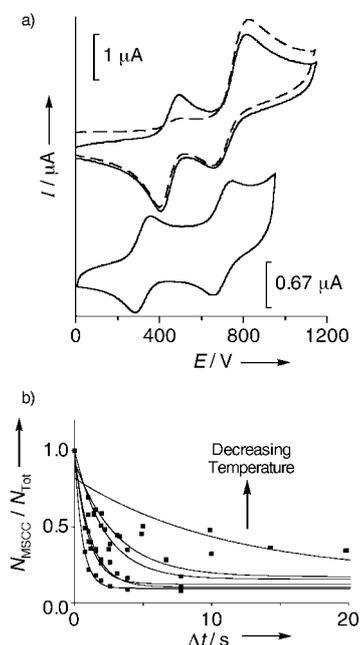


Figure 2. a) First (dashed line) and second (solid line) CVs of the bistable [2]rotaxane  $\mathbf{R1}^{4+}$ , displaying (above) the characteristic metastable peak in the second cycle recorded at 255 K and at a scan rate of  $200\text{ mVs}^{-1}$ . The CV of the rotaxane's corresponding dumbbell displays (below) the same CV for each cycle (293 K) under otherwise the same conditions (0.1 M TBAPF<sub>6</sub>/MeCN/versus SCE) used to obtain the CV of  $\mathbf{R1}^{4+}$ . b) Fitted first-order decay profiles for the relaxation of the MSCC to the GSCC of the bistable [2]rotaxane  $\mathbf{R1}^{4+}$  extracted from the CV data recorded over a range of different temperatures (249–278 K).

about 10:1 under ambient conditions. The first CV trace reflects this distribution; two oxidation features are recorded at 500 and 830 mV. The relatively weak feature at 500 mV corresponds to the TTF  $\rightarrow$  TTF<sup>+</sup> oxidation of the MSCC. The stronger peak at 830 mV is assigned to a combination of the mono-oxidation of the encircled TTF of the GSCC, superimposed on the feature that is assigned to the second oxidation (TTF<sup>+</sup>  $\rightarrow$  TTF<sup>2+</sup>) of  $\mathbf{R1}^{4+}$ . This oxidation step is independent of the co-conformer, since the CBPQT<sup>4+</sup> ring encircles the DNP site once the TTF unit is singly oxidized. It is observed that, although the peak position of the second oxidation is obscured by the first oxidation process of the GSCC, the subsequent reduction of the TTF<sup>2+</sup> ion occurs at the same potential as that of the dumbbell. In the second scan, the integrated current under the 500 mV feature, assigned to the MSCC, gains intensity at the expense of the 830 mV feature. The hysteretic response in the successive CV curves for  $\mathbf{R1}^{4+}$  at lower temperatures reflects the fast recovery of the ground-state equilibrium distribution, described by  $K_{(D/T)^{4+}}$ , and indicates that the recovery kinetics are much faster in the solution phase than they are in the polymer matrix<sup>[17]</sup> or for the “half-device” which employed a very similar bistable rotaxane that formed a SAM on gold.<sup>[10]</sup>

**Cryoelectrochemistry on a bistable catenane:** The bistable [2]catenane  $\mathbf{C2}^{4+}$  displays similar temperature-dependent CV behavior to that of the  $\mathbf{R1}^{4+}$ . There is, however, a negligible proportion of the MSCC present on the first cycle, and the single process at 1000 mV is assigned to the double oxidation of the encircled TTF unit. As the scan rate is increased, the second cycle displays the characteristic MSCC peak at 660 mV with increased intensity (Figure 3a) relative to the peak at 1000 mV. The MSCC peak is more visible at ambient temperature (295–303 K), revealing the slower kinetics associated with the thermal re-equilibration  $k_{D \rightarrow T}$

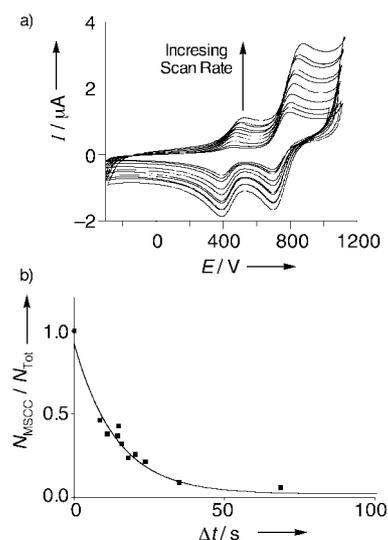


Figure 3. a) A series of second-cycle CVs for  $\mathbf{C2}^{4+}$  recorded at a variety of scan rates ( $60\text{--}500\text{ mVs}^{-1}$ ) at room temperature (298 K). b) The fitting of the population data extracted from a) to a first-order decay curve.

of the bistable catenane  $\mathbf{C2}^{4+}$  compared with the bistable rotaxane  $\mathbf{R1}^{4+}$ . By varying the time between the first and second CV scans of  $\mathbf{R1}^{4+}$  and  $\mathbf{C2}^{4+}$ , as well as the temperature of the experiment, the various kinetic parameters for relaxation from the MSCC to the GSCC can be determined, following the method<sup>[11b,20]</sup> outlined by us<sup>[17]</sup> previously. The first-order kinetics can be fitted<sup>[21]</sup> with exponential curves (Figure 2b) for the MSCC relaxing to the GSCC of  $\mathbf{R1}^{4+}$  over the temperature range 249–278 K. One single plot for  $\mathbf{C2}^{4+}$  at 298 K is shown in Figure 3b. An Eyring plot (Figure 4) reflects how the kinetics change with temperature for  $\mathbf{R1}^{4+}$ ,  $\mathbf{C1}^{4+}$  and  $\mathbf{C2}^{4+}$  in MeCN.

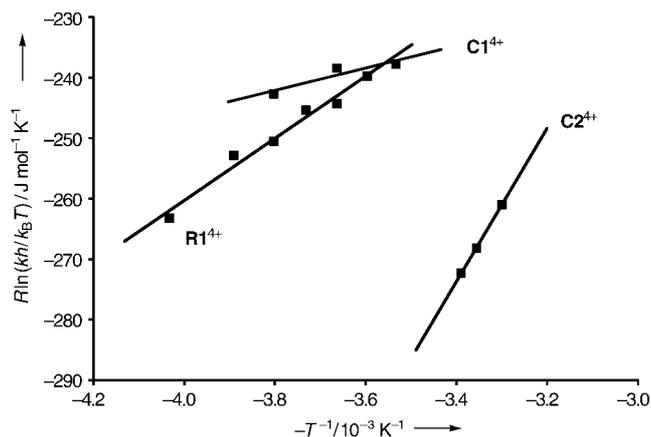


Figure 4. The Eyring plots for the bistable [2]rotaxane  $\mathbf{R1}^{4+}$  and the bistable [2]catenanes  $\mathbf{C1}^{4+}$  and  $\mathbf{C2}^{4+}$  in the liquid solution phase for the relaxation of the MSCC to the GSCC.

**Dynamic NMR on a degenerate catenane:** Observation of the switching process in bistable systems is too fast to be observed directly by dynamic  $^1\text{H}$  NMR spectroscopy, and to date it has not proved to be possible to observe the relaxation of the MSCC by  $^1\text{H}$  NMR spectroscopy. The kinetics for circumrotation and shuttling in degenerate catenanes and rotaxanes (Figure 5), however, can be studied. In a

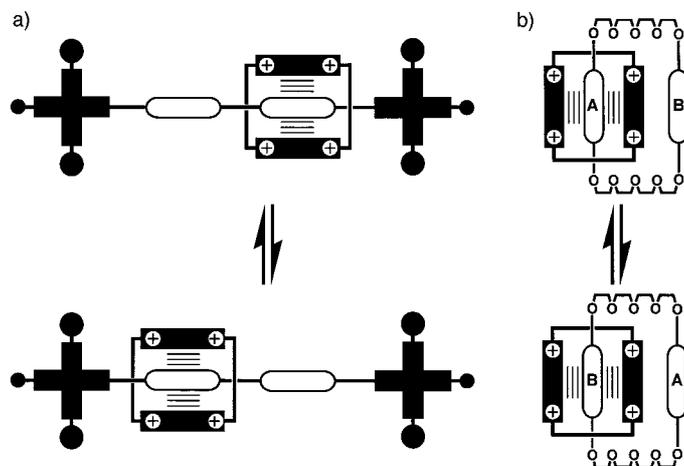


Figure 5. Graphical representations of a) shuttling and b) circumrotation in degenerate [2]rotaxanes and [2]catenanes, respectively.

recent report,<sup>[16]</sup> variable-temperature  $^1\text{H}$  NMR spectroscopy was employed to investigate shuttling in a series of degenerate [2]rotaxanes incorporating different spacers between the two recognition sites. The rotaxane  $\mathbf{R3}^{4+}$  incorporating two DNP recognition sites with a glycol chain spacer can be used as the model for relaxation of the MSCC in the bistable rotaxanes investigated in this report, and the barrier for shuttling ( $\Delta G^\ddagger$ ) in this rotaxane was determined<sup>[16]</sup> to be  $15.4 \text{ kcal mol}^{-1}$  at 293 K in  $\text{CD}_3\text{COCD}_3$ .

As models for relaxation of the MSCC in the bistable catenanes, two degenerate catenanes were chosen. The [2]catenane  $\mathbf{C3}^{4+}$  had been studied previously and the barrier for circumrotation determined<sup>[2,3]</sup> to be  $17.2 \text{ kcal mol}^{-1}$  at 361 K in  $\text{CD}_3\text{CN}$ . Although the synthesis of the other degenerate [2]catenane  $\mathbf{C4}^{4+}$  was reported in a previous paper,<sup>[5]</sup> kinetic and thermodynamic data for the circumrotation process was not presented. Here, we report relevant data for circumrotation in this compound obtained<sup>[22]</sup> by spin-saturation transfer at high temperature (388 K) in  $\text{CD}_3\text{SOCD}_3$ . The free energy of activation for the circumrotation of the macrocyclic polyether ring through the CBPQT $^{4+}$  ring in  $\mathbf{C4}^{4+}$  was determined at 388 K to be  $23.7 \text{ kcal mol}^{-1}$ . The data obtained for the degenerate compounds allow comparisons to be made with the  $\Delta G^\ddagger$  values determined for the relaxation of the MSCC in the bistable rotaxanes and catenanes.

**Influence of the physical environment on the switching:** In Table 1, we present a summary of the kinetic and thermodynamic data for all of the bistable [2]rotaxanes and [2]catenanes discussed here in solution and in the polymer matrix environment. We also include the data for the bistable [2]rotaxane SAM,<sup>[10]</sup> as well as that for the degenerate catenanes and rotaxanes.<sup>[22]</sup> There are several observations worth noting. First, the shuttling barriers obtained from the dynamic  $^1\text{H}$  NMR measurements on  $\mathbf{R3}^{4+}$  are very similar to those observed for  $\mathbf{R1}^{4+}$  in solution. By contrast, however, the parameters describing the circumrotational barrier for the degenerate  $\mathbf{C4}^{4+}$  are not similar to those for the corresponding bistable  $\mathbf{C2}^{4+}$ . For catenanes, the uncomplexed donor (DNP for the GSCC of  $\mathbf{C2}^{4+}$ ) has an “alongside” interaction with the CBPQT $^{4+}$  ring. This interaction is the major difference between the energetics of the degenerate ( $\mathbf{C4}^{4+}$ ) compared with the bistable ( $\mathbf{C2}^{4+}$ ) systems, and such an interaction is not nearly so important in the case of the rotaxanes.<sup>[23]</sup> This observation implies<sup>[11c]</sup> that the rates of relaxation are strongly influenced by the details of the chemical structure. The second observation from Table 1 is that the polymer environment does substantially slow down the MSCC→GSCC recovery kinetics for both the bistable [2]catenanes and [2]rotaxanes. For both  $\mathbf{R1}^{4+}$  and  $\mathbf{C2}^{4+}$ ,  $\Delta G_{298}^\ddagger$  increases by  $2 \text{ kcal mol}^{-1}$  on going from MeCN to the polymer environment. Moreover, the influence upon the free energy of activation within the polymer matrix is very similar to that observed<sup>[10]</sup> in the SAM “half-device”, and substantially different from that observed in solution (Figure 6). Note that,  $\mathbf{C2}^{4+}$  is a much slower switch in MeCN than  $\mathbf{R1}^{4+}$ , the effect of the polymer environment on the relaxation kinetics of both molecules is very similar. The

Table 1. Kinetic and thermodynamic data for relaxation of the metastable state or shuttling/circumrotation obtained from variable-temperature studies for a series of bistable and degenerate rotaxanes and catenanes in different environments.<sup>[a]</sup>

Compound (environment)	<i>T</i> range [K]	$\Delta G^\ddagger$ ( <i>T</i> [K]) [kcal mol <sup>-1</sup> ]	$\tau_{298}$ [s]	$k_{298}$ [s <sup>-1</sup> ]	$\Delta G_{298}^\ddagger$ [b] [kcal mol <sup>-1</sup> ]
<b>R1<sup>4+</sup></b> (solution)	249–278	15.9 ± 0.5(278)	0.123(±0.002)	8.11(±0.1)	16.2(±1.0)
<b>R1<sup>4+</sup></b> (polymer)	290–320	18.1 ± 0.5(298)	3.5(±0.25)	0.286(±0.02)	18.1(±0.5)
<b>RS<sup>4+</sup></b> (SAM) <sup>[c]</sup>	278–303	18.0 ± 0.2(293)	2.56(±0.01)	0.39(±0.2)	18.0(±0.5)
<b>C1<sup>4+</sup></b> (solution) <sup>[d]</sup>	263–283	16.1 ± 0.5(283)	0.24(±0.01)	4.1(±0.2)	16.7(±1.0)
<b>C1<sup>4+</sup></b> (polymer)	283–305	17.0 ± 0.4(298)	0.6(±0.1)	1.6(±0.4)	17.0(±0.4)
<b>C2<sup>4+</sup></b> (solution)	295–303	19.2 ± 0.5(298)	17.5(±1.2)	0.057(±0.004)	19.2(±0.5)
<b>C2<sup>4+</sup></b> (polymer)	298	21.0 ± 0.4(298)	800(±90)	0.0013(±0.0003)	21.0(±0.4)
<b>C3<sup>4+</sup></b> (CD <sub>3</sub> CN)	–	17.2(361)	–	–	–
<b>C4<sup>4+</sup></b> (CD <sub>3</sub> SOCD <sub>3</sub> )	–	23.7(388)	–	–	–
<b>R3<sup>4+</sup></b> (CD <sub>3</sub> COCD <sub>3</sub> )	247–305	15.4(293)	0.0358	27.9	15.5

[a] Solution data obtained on 1 mm samples in MeCN (0.1 M TBAPF<sub>6</sub>) by using a glassy carbon working electrode at a range of temperatures. Solid-state polymer data obtained from samples mixed within a polymer matrix (composition: w:w:w ratios 70:7:20:3 of MeCN/polymethylmethacrylate/propylene carbonate/LiClO<sub>4</sub>) at a Pt electrode over a range of temperatures. The thermodynamic data on **C3<sup>4+</sup>**, **C4<sup>4+</sup>**, and **R3<sup>4+</sup>** was obtained using variable-temperature <sup>1</sup>H NMR spectroscopy. [b] The  $\Delta G_{298}^\ddagger$ ,  $k_{298}$ , and  $\tau_{298}$  data on the bistable catenane and rotaxane were obtained from interpolation (**RS<sup>4+</sup>**) or extrapolation (**R1<sup>4+</sup>**, **C1<sup>4+</sup>**) by utilizing the Gibbs-Helmholtz relationship and the  $E_a$  from the Arrhenius relationship. [c] **RS<sup>4+</sup>** (SAM) was a self-assembled monolayer prepared on the surface of a gold working electrode, see reference [10]. This [2]rotaxane was identical to **R1<sup>4+</sup>** except that it bears a C<sub>8</sub>-based thiotic spacer instead of the –OH moiety. [d] The linear fit to the Arrhenius and Eyring plots for **C1<sup>4+</sup>** produced a low  $R^2$  value of 0.88.

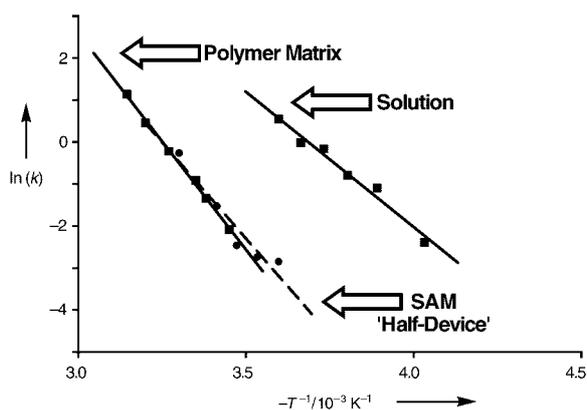
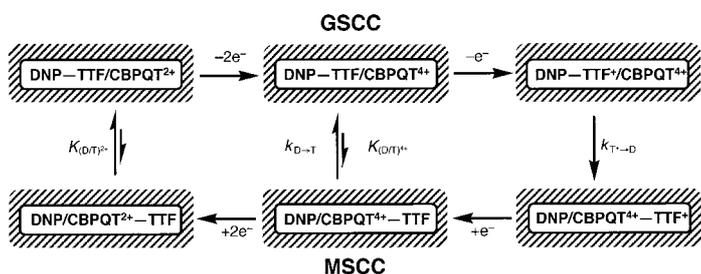


Figure 6. The Arrhenius plots for the bistable [2]rotaxane **R1<sup>4+</sup>** in solution and in a solid-state polymer electrolyte alongside the self-assembled monolayer of its disulfide-tethered analogue, **RS<sup>4+</sup>** (solid circles, dashed line).



Scheme 1. The generic molecular electromechanical mechanism for the switching cycle in both bistable [2]catenanes and [2]rotaxanes. The MSCC is formed from the GSCC by oxidizing and then reducing the TTF unit. The ground-state equilibrium is subsequently re-established either by relaxation over a barrier or stimulated by a redox cycle of CBPQT<sup>4+</sup>-based reduction and then oxidation. The hashed lines surrounding the switches represent either bistable catenanes or rotaxanes and also relates to any of the following environments—liquid solution phase, solid-state polymer electrolyte, and self-assembled monolayer.

final and most important observation from Table 1 is that, while the kinetics of the switching mechanism (Scheme 1) for bistable [2]rotaxanes and [2]catenanes exhibits a strong environmental dependence, a single, generic switching mechanism is observed for all the bistable molecules, regardless of whether they are in liquid solution, tethered to a solid support, or immobilized within a liquid polymer matrix.

## Conclusion

A single mechanism of switching displayed by bistable rotaxanes and catenanes has been verified by using kinetic and thermodynamic data obtained from variable-temperature electrochemistry. In fact, this

switching mechanism, and its environmental dependence, was first hypothesized<sup>[4,5,9]</sup> to explain the thermally activated switching process that occurs within molecular-switch tunnel junctions incorporating bistable [2]catenanes and [2]rotaxanes. The quantification of the switching mechanism in this and the previous reports<sup>[10,17]</sup> on a “half-device” and a polymer matrix go a long way toward validating the initial hypothesis. The precise molecular structure of the bistable molecule and the nature of the environment influences strongly the speeds at which the cycle of switching can be activated. In general, the rates of thermal relaxation of the metastable state co-conformation to the ground state co-conformation are slowed down when the molecules are transferred from solution to the more viscous polymer electrolyte gel. The same retardation of the relaxation step is achieved in the case of the rotaxane when it is organized as a self-assembled monolayer on a gold electrode. These investigations open up opportunities to study molecular mechanical processes that are normally too rapid at ambient temperatures in easily flowing solvents to be characterized quantitatively for the purposes of gaining more fundamental understanding and underpinning the possibilities for advancing technological applications.

## Experimental Section

**Electrochemistry:** Two custom-built electrochemical cells that cover the temperature ranges 260–303 K and 248–260 K were used, in conjunction with standard electrochemical apparatus, to record the variable-temperature CVs. One glass cell, based on a jacketed design for thermostatic control ( $T=260$ –303 K),<sup>[10]</sup> (Model 9000 refrigerated constant temperature bath and circulator, Allied Fisher Scientific) was modified to have four entry slots for the Pt coil counter electrode, a Ag wire pseudo-reference electrode, Teflon tubing carrying dry Ar gas for purging and the glassy

carbon working electrode. Another cell was designed to sit immersed in a liquid nitrogen slurry (*o*-xylene 249 K and 1,2-dichloroethane 257 K) held in a Dewar flask which incorporated a glass skirt to act as a thermal insulator, thus minimizing any temperature fluctuations. The cells were maintained under a positive pressure of Ar to ensure the exclusion of H<sub>2</sub>O condensation. The working electrode was cleaned with an alumina slurry (0.05 μm) on a felt pad and rinsed thoroughly between each CV to remove any absorbed material. Samples (1 mm) were prepared fresh from 0.1 M TBAPF<sub>6</sub> MeCN solutions (dried by passage through steel columns containing activated alumina under Ar using a solvent purification system (Anhydrous Engineering)) and thoroughly purged of O<sub>2</sub> vapor prior to experimentation. The CV experiments were conducted with the EG&G PAR263 A potentiostat under computer control across a range of scan rates 10–2200 mV s<sup>-1</sup>.

**Data analysis:** Exponential decay curves were obtained for each temperature by recording CVs over a range of different scan rates utilizing a modification of previously used methods.<sup>[11b,17,20]</sup> The time interval, Δt, was determined as the time between formation of the MSCC reduction to the TTF neutral redox state and its oxidation to the monocationic state, equivalent to the point of measurement of the proportion of MSCC remaining. The proportion of MSCC remaining  $N_{\text{MSCC}}/N_{\text{Tot}}$  was obtained by integrating the area under the peak of the MSCC in the second anodic scan,  $N_{\text{MSCC}}$ , and then normalized to a single electron ( $N_{\text{Tot}}, 1e^-$ ) by halving the total area ( $2e^-$ ) of the first or second anodic scan. The integrated areas were determined from baselined data. The accuracy of the baselining procedure was checked by comparing the integrated area from each of the anodic and cathodic scans and was found to vary by no more than ±5%. The integration regions were selected to include the contributions to the CV from the diffusional tail that follows the main peak. Two additional points were added to the decay curve that correspond to time zero, Δt=0 s,  $N_{\text{MSCC}}/N_{\text{Tot}}=1.0$  and, at long relaxation times, Δt=300 s, at which the value of  $N_{\text{MSCC}}/N_{\text{Tot}}$  was set equal to the steady-state value determined by the first anodic scan. The resulting decay curve was fitted to a single exponential curve in order to obtain the time constant, τ, and hence the rate constant,  $k_{\text{D-T}}$  at T.

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“alongside” interaction to the stabilization of the MSCC is expected to be small.

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