Measurement of the ground-state distributions in bistable mechanically interlocked molecules using slow scan rate cyclic voltammetry

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In donor–acceptor mechanically interlocked molecules that exhibit bistability, the relative populations of the translational isomers—present, for example, in a bistable [2]rotaxane, as well as in a couple of bistable [2]catenanes of the donor–acceptor vintage—can be elucidated by slow scan rate cyclic voltammetry. The practice of transitioning from a fast scan rate regime to a slow one permits the measurement of an intermediate redox couple that is a function of the equilibrium that exists between the two translational isomers in the case of all three mechanically interlocked molecules investigated. These intermediate redox potentials can be used to calculate the ground-state distribution constants, K . Whereas, (i) in the case of the bistable [2]rotaxane, composed of a dumbbell component containing π -electron-rich tetrathiafulvalene and dioxynaphthalene recognition sites for the ring component (namely, a tetracationic cyclophane, containing two π -electron-deficient bipyridinium units), a value for K of 10 ± 2 is calculated, (ii) in the case of the two bistable [2]catenanes—one containing a crown ether with tetrathiafulvalene and dioxynaphthalene recognition sites for the tetracationic cyclophane, and the other, tetrathiafulvalene and butadiyne recognition sites—the values for K are orders (one and three, respectively) of magnitude greater. This observation, which has also been probed by theoretical calculations, supports the hypothesis that the extra stability of one translational isomer over the other is because of the influence of the enforced side-on donor–acceptor interactions brought about by both π -electron-rich recognition sites being part of a macrocyclic polyether.

density functional theory | donor–acceptor molecules | electrochemistry | isomerism | switches

The ability to control the relative motions (1) of molecules is crucial for understanding many biological processes such as cell division and intracellular transport (2), muscle contraction (3), and ATP production (4). This control is essential to the development of potential applications as diverse as catalysis (5), drug delivery (6), elastic materials (7), molecular actuators (8), molecular transport (9), ion sensors (10), motors (11), and information storage (12). Supramolecular chemistry (13) has been one of the sources from which the inspiration and desire to build artificial molecular machines, as the counterpart to biological motors, has sprung. Understanding the mechanism by which intramolecular noncovalent bonding interactions occur—especially in those systems that can undergo reversible switching events—holds the key to how artificial molecular machines (14) can be engineered to fit the demands of a given function. Gaining intimate knowledge of the mechanisms (15–18) governing the relative molecular motions of their components is, therefore, a pursuit that yields crucial information for the design of artificial molecular machines. Bistable mechanically interlocked molecules (MIMs) [namely, bistable catenanes (19, 20) and rotaxanes (21), whose syntheses are often templated by noncovalent bond-

ing interactions that “live-on” in the MIMs] have experienced a frenzy of intense research activity in recent years. This attention is in part a consequence of the fact that bistable switchable MIMs possess the inherent ability to gain precise control over the relative motions of their mechanically interlocked components.

The use of donor–acceptor interactions for the preparation (22, 23) of switchable MIMs has been evolving now for well over two decades of thoroughgoing research effort. One of the most common and useful recognition motifs present in bistable catenanes and rotaxanes (Fig. 1) is of the donor–acceptor type that incorporates as one of its ring components the π -electron-poor tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene) (24–26) (CBPQT⁴⁺). The use of redox-active π -electron-rich units [e.g., tetrathiafulvalene (27, 28) (TTF)], along with another π -electron-rich donor [e.g., 1,5-dioxynaphthalene (DNP) in the other ring or dumbbell component], enables electrochemically induced molecular switching, which has been used in a whole variety of applications, such as molecular memory (29, 30), micro-scale mechanical actuation (31), and nanoscale systems that can store and release (32) molecular cargos.

Essential to the function of all of these applications is the mechanism of switching. In bistable MIMs involving TTF and another π -electron-rich recognition site, two co-conformations can be defined as one (i) where the CBPQT⁴⁺ ring resides around the TTF unit and the other (ii) where the CBPQT⁴⁺ ring resides around the other π -electron-rich unit. The much greater propensity in general for the TTF unit to be included inside the cavity of the CBPQT⁴⁺ ring in comparison with other π -electron donors has led to the naming (33) (Fig. 24) of this translational isomer as the ground-state co-conformation (GSCC), whereas, when the CBPQT⁴⁺ ring encircles the other π -electron-rich unit, the name metastable-state co-conformation (MSCC) is used. The ground-state distribution between the GSCC and the MSCC can be inverted through an oxidation–reduction cycle performed on the TTF unit. Oxidation of the TTF unit to its radical cation (or dicationic) form causes rapid movement of the CBPQT⁴⁺ ring onto the other π -electron-rich unit in order to relieve the Coulombic repulsion between the tetracationic CBPQT⁴⁺ ring and the TTF^{•+}/TTF²⁺ unit. Reduction of the oxidized TTF^{•+}/TTF²⁺

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Fig. 3. Experimental data showing the transition from the fast scan rate regime (blue traces) into the slow scan rate regime (red traces). The shifting of the anodic and cathodic peaks is illustrated by the colored arrows. All scans have been normalized to the square root of the scan rate, and IR compensation was applied. (A) The bistable rotaxane **R14+**: blue trace = 500 $\text{mV}\cdot\text{s}^{-1}$, red trace = 10 $\text{mV}\cdot\text{s}^{-1}$. (B) The bistable catenane **C14+**: blue trace = 500 $\text{mV}\cdot\text{s}^{-1}$, red trace = 10 $\text{mV}\cdot\text{s}^{-1}$. (C) The bistable catenane **C24+**: blue trace = 10 $\text{V}\cdot\text{s}^{-1}$, red trace = 200 $\text{mV}\cdot\text{s}^{-1}$; the scans were background subtracted.

In the case of **C14+** (Fig. 3B), which was first reported (19) in 1998, the ground-state distribution constant has never been measured carefully. CV experiments, however, suggest that the value must be significantly greater than approximately 10 as a consequence of the fact that the anodic peak corresponding to the MSCC of this bistable catenane could not be observed in the ground state at equilibrium. The technique reported herein offers, thereafter, a distinct advantage in being able to measure the ground-state distribution directly for this bistable catenane. By starting out using fast scan rates and scanning successively more slowly, we can see a new oxidation process emerge, whose redox potential was measured to be +0.58 V.

In order to demonstrate the full power of this electrochemical technique, we now turn our attention to **C24+** (Fig. 3C). Theoretical predictions suggest (20) that the distribution constant between the GSCC and the MSCC, where the CBPQT⁴⁺ encircles the butadiyne unit, is exceedingly large—indeed very much greater

than in the case of **R4+** or **C14+**. This prediction is rationalized by the fact that, although the butadiyne unit can be considered to be a π -electron-donating unit, its ability to act as such is extremely small compared to the donor strength of either the TTF or DNP units, most likely a consequence of the highest occupied molecular orbital–lowest unoccupied molecular orbital energy mismatch. The fact that the butadiyne unit serves as such a weak recognition site for the CBPQT⁴⁺ ring has further consequences in terms of the kinetics of the switching process. On scanning at progressively slower scan rates, we observe that the new redox potential is massively shifted toward positive potentials at +0.66 V—almost entirely overlapping with the second oxidation process ($\text{MSCC}^+ \rightarrow \text{MSCC}^{2+}$) to afford the TTF^{2+} dication.

In order to gain insight into the effect that scan rate has on the CVs observed for the bistable rotaxane and catenanes, we modeled a switching mechanism (39, 40) based on bistable MIMs incorporating TTF and an alternative binding site using an appropriate ladder-scheme mechanism (15) and began running simulations using Digisim. (For details regarding running the simulations, see *SI Text*. For an introduction on producing digitally simulated CV data based on a proposed mechanism, see ref. 40.) We first chose a ground-state distribution constant $K = 1,000$ and varied the scan rate (Fig. 4A) systematically in order to simulate the type of behavior to expect as the transition into the so-called “slow scan rate regime” begins to occur—where at every point in the (simulated) scan the redox-stimulated translational motion of the CBPQT⁴⁺ ring is allowed to come to an equilibrium. Starting out in the so-called “fast scan rate regime”—wherein the redox-stimulated translation of the CBPQT⁴⁺ ring is not given sufficient time to equilibrate as the potential is varied from point to point—we observe (33) what looks like a typical first-scan CV (blue trace) for MIMs of this type. As the scan rate is reduced progressively, we can witness quite clearly the transition into the slow scan rate regime take place. An anodic peak begins to emerge from the two-electron oxidation process observed around +0.8 V, and continues to shift toward more negative potentials. Likewise, the cathodic peak observed around +0.4 V begins to shift toward more positive potentials. We eventually reach a scan rate sufficiently slow (red trace) that these anodic and cathodic peaks shift in such a way as to form a “new” redox couple (E_{eq}), which is characterized by the expected approximately 60 mV separation between anodic and cathodic peaks expected for a totally reversible process. This simulation data provides further insight into the type of behavior we observe in the case of **R4+**, **C14+**, and **C24+** as the transition from the fast scan into the slow scan rate regime begins to occur.

Next, we investigated how, by employing digital simulations, the value of the ground-state distribution constant K affects (Fig. 4B) the CVs within the slow scan rate regime in order to develop a means to quantify the value of K . From the beginning, we chose a scan rate sufficiently slow that it placed us in the slow scan rate regime, and then systematically varied the distribution constant K by factors of 10. For every order of magnitude change in K , the redox potential, E_{eq} , shifts approximately 60 mV toward positive potentials. This trend agrees well with Eq. 5 (see below), which also predicts an order of magnitude change in K for every integer multiple of approximately 60 mV difference between E_{MSCC} and E_{eq} . [It is important to note that data from digital simulations reveals that at the redox potential, E_{eq} , the quantity $([\text{MSCC}^+])/([\text{GSCC}])$ is indeed equal to unity.]

In order to offer a rationalization of the simulated data that varying K has on the new redox potential E_{eq} , consider the following analysis. In each case (namely, **R14+**, **C14+**, and **C24+**), we can define the equilibrium based upon the ground-state distribution between the GSCC and the MSCC as

$$[\text{MSCC}] \stackrel{K}{\rightleftharpoons} [\text{GSCC}], \quad [1]$$

Fig. 4. Simulated CV data based on the proposed mechanism of switching. (A) Simulated data for a bistable rotaxane or catenane transitioning from the fast scan rate regime (blue trace) into the slow scan rate regime (red trace). The transition to the slow scan rate regime is characterized by the emergence of a new redox couple, E_{eq} . The shifting of the anodic and cathodic peaks associated with E_{eq} is illustrated by the colored arrows. The simulated scans have been normalized by the square root of the scan rate. (B) Simulated data showing the effect of varying the ground-state equilibrium constant (K) in the slow scan rate regime. For every order of magnitude change in K , an approximately 60 mV positive shift in the new redox potential is observed. Note: In order to arrive at a more accurate value of K obtained by least-squares fitting to simulated data, we relied upon a more sophisticated picture of the switching mechanism not represented by the ideal cases shown in this figure. See *SI Text*.

where K is the ground-state distribution constant governing the equilibrium of the GSCC, with the MSCC. It is well known (41) that there is a substantial difference in the oxidation potentials of TTF depending on whether or not it is encircled by the CBPQT⁴⁺ ring; indeed, the first oxidation potential of TTF becomes shifted by as much as approximately 400 mV. The first oxidation potential of TTF in the GSCC is, therefore, much higher than that of the MSCC. With this fact in hand, consider the following redox equilibrium:

From this relationship, we can invoke the use of the Nernst equation:

$$E_{Ap} = E_{\text{MSCC}} + \frac{RT}{nF} \ln \left(\frac{[\text{MSCC}^+]}{[\text{MSCC}]} \right), \quad [3]$$

where E_{MSCC} is the redox potential for the electron transfer process in Eq. 2, E_{Ap} is the applied potential, R is the gas constant, T is the temperature, n is the number of electrons transferred, and

F is Faraday's constant. Combining Eq. 1 with Eq. 3, we can derive an expression for $[\text{MSCC}]$ in terms of K and the $[\text{GSCC}]$:

$$E_{Ap} = E_{\text{MSCC}} + \frac{RT}{nF} \ln \left(\frac{K[\text{MSCC}^+]}{[\text{GSCC}]} \right). \quad [4]$$

Under the proper experimental conditions where the scan rate is sufficiently slow enough, such that at each point in the scan the redox-stimulated translational motion of the CBPQT⁴⁺ ring is allowed to reach an equilibrium as the potential is varied, there exists an applied potential E_{Ap} at which the quantity $\frac{[\text{MSCC}^+]}{[\text{GSCC}]}$ is equal to unity and effectively defines the new redox potential, E_{eq} . (To put it into more intuitive terms, if the scan rate is slow enough, as soon as the GSCC is oxidized to the GSCC⁺, it equilibrates immediately to the MSCC⁺; and conversely, as soon as the MSCC⁺ is reduced to the MSCC, it immediately equilibrates to the GSCC, at least on the time scale of the experiment.) Taking into consideration the fact that there is some applied potential, call it E_{eq} , at slow enough scan rates such that the expression $\frac{[\text{MSCC}^+]}{[\text{GSCC}]}$ is equal to one, solving Eq. 4 in terms of K leads us to the following expression:

$$K = \exp \left[(E_{eq} - E_{\text{MSCC}}) \frac{nF}{RT} \right]. \quad [5]$$

We now have a rationale for explaining why and how K varies as a function of the redox potential E_{eq} and E_{MSCC} . (It is possible to measure the redox potential E_{MSCC} directly by accessing the fast scan rate regime, and the new redox potential E_{eq} in the slow scan rate regime. See *SI Text*.) This analysis of redox potentials is an extension of similar analyses that have been reported previously on metal-ligand and supramolecular complexes in order to evaluate their binding affinities quantitatively. A discussion of these procedures can be found in refs. 39 and 40.

We use the fact that we can populate the MSCC through an oxidation/reduction cycle of the TTF unit, an experiment that allows the redox potential of which, E_{MSCC} , to be directly measured at relatively fast scan rates (8 V s⁻¹). We found E_{MSCC} to be equal to 0.42 V. In a similar manner as the rotaxane, **R**⁴⁺, we took advantage of the fact that the MSCC of the catenane **C1**⁴⁺ can be populated by an oxidation/reduction cycle of the TTF unit. The redox potential, E_{MSCC} , was then measured directly at relatively fast scan rates and was found to be once again 0.42 V. The relaxation process of the populated MSCC to the GSCC following an oxidation/reduction cycle of the TTF unit in the case of **C2**⁴⁺ is so rapid, it has not been possible to measure the oxidation of the MSCC directly with our current instrumentation. We have assumed therefore that the redox potential of the MSCC for **C2**⁴⁺ is the same as that for the case of the **R**⁴⁺ and **C1**⁴⁺.

By fitting the experimental data using simulation methods (see *SI Text*), we find that the value of the ground-state equilibrium constant for **R**⁴⁺ is equal to 10 ± 2 , an outcome that agrees well with that of the previously determined experimental value. The ground-state distribution constant in the case of **C1**⁴⁺ was measured by fitting the experimental data to the simulated curves: It was found to be $K = 150 \pm 20$, which is an order of magnitude higher than that for **R**⁴⁺. We hypothesize that this difference could be a result of several factors including solvation effects and enforced side-on interactions, which are not significantly active in the bistable rotaxane, but are present in the bistable catenane. By fitting the experimental to simulated data for **C2**⁴⁺, we determined a ground-state distribution constant of $K = 6,800 \pm 300$. Remarkably, the value of K is nearly three and two orders of magnitude higher (Fig. 5), respectively, when compared to the K values for **R**⁴⁺ and **C1**⁴⁺. We also used Eq. 5 to calculate K and found that the values determined from this mathematical

Fig. 5. Graphical summary of the ground-state equilibrium distribution (K) for the bistable rotaxane R^{4+} and bistable catenanes C1^{4+} and C2^{4+} . For each case, the value of K was determined either by χ^2 -fitting of the data to simulations or by Eq. 5. The catenane C2^{4+} with the weakly π -electron-donating butadiyne station was found to have the highest ground-state distribution, followed by C1^{4+} with the stronger π -electron-donating DNP unit. The smallest ground-state equilibrium distribution is exemplified by R^{4+} , which lacks any enforced side-on interactions with its DNP unit.

method are in good agreement (see Fig. 5 and *SI Text*) with those determined from the fitting of the data to simulations.

In order to elucidate the key factors responsible for the differences in the equilibrium between the GSCC and the MSCC for the bistable catenane C1^{4+} and bistable rotaxane R^{4+} , we performed a quantum mechanical study based on density functional theory (DFT)—using the M06 suite of functionals—which has been shown (42, 43) by us to be a good choice for the study of donor–acceptor bistable MIMs. Initially, we investigated the gas-phase and MeCN solvation energy differences between the GSCC and MSCC for catenane $\text{C1} \cdot 4\text{PF}_6$. Using the M06 functional (43, 44) and the 6-311++G** basis set, our results show that the energy difference (Fig. 6) between the GSCC and MSCC in the gas phase is 41.6 kcal/mol favoring the GSCC. This large energetic difference is not observed for the case of the rotaxane $\text{R} \cdot 4\text{PF}_6$, where the gas-phase energy difference is only 13.8 kcal/mol, also in favor of the GSCC. These relative gas-phase energies suggest that there are electronic effects in the catenane that are not present in the rotaxane, which cause the GSCC to be more stable by approximately 28 kcal/mol. The relative MeCN solvation energies act in the opposite direction, because the MSCC is solvated preferentially in both cases for the catenane and rotaxane. The increased solvation energy of the

Fig. 6. Graphical summary of results from theoretical calculations on the difference in energy between the GSCC and the MSCC for both the catenane C1^{4+} and the rotaxane R^{4+} . In both the gas phase and solution phase, the GSCC for C1^{4+} is substantially more favored than compared to the rotaxane R^{4+} . All calculations were based off of DFT using the M06 functional and the 6-311++G** basis set.

MSCC could be a consequence of the much higher accessibility of the more polar TTF recognition site (stronger solvation interactions) in the MSCC, when it is not encircled by the CBPQT $^{4+}$ ring. In addition, our calculations show that the relative MeCN solvation energy [$E_{\text{solv}}(\text{GSCC}) - E_{\text{solv}}(\text{MSCC})$] of the catenane (36.2 kcal/mol) is higher than for the rotaxane (11.0 kcal/mol). This observation suggests that the catenane's equilibrium constant may show a stronger dependence with solvent polarity as compared to the rotaxane. These computational data suggest that it is likely that side-on interactions in the MSCC of the catenane between the unencircled TTF unit and the periphery of the CBPQT $^{4+}$ ring may destabilize the recognition of the DNP unit, thus increasing the stability of the GSCC. This charge-transfer and polarization of the outside TTF unit in the MSCC also increases the solvation energy, a factor that reduces the switching free energy difference from the gas phase—or a less polar solvent. The computational results support our hypothesis that both solvation effects, as well as side-on interactions, are responsible for the difference in equilibrium constant for the GSCC and MSCC in a catenane and rotaxane, and serves to elucidate one of the fundamental physical differences between catenanes and rotaxanes. Side-on interactions present only in the catenane increase dramatically the difference in stability, whereas solvation effects mitigate this difference.

Conclusions

A method has been established whereby the ground-state distribution of co-conformations in bistable MIMs can be measured directly by using variable scan rate CV: The results can also be checked by a data simulation procedure. By way of examples, a two-station [2]rotaxane R^{4+} and a bistable [2]catenane C1^{4+} , comprised of the π -electron-rich units TTF and DNP, as well as a bistable [2]catenane C2^{4+} , consisting of TTF and butadiyne units, were investigated by CV in MeCN in the slow scan rate regime. At sufficiently slow scan rates, specific to each individual MIM, a new redox couple, E_{eq} , can be observed, the redox potential of which provides a means of answering the question—what is the value of K ? In other words, with a knowledge of the value of E_{eq} , it is possible to calculate the value of K for each bistable MIM. In the [2]rotaxane R^{4+} , the distribution of the CBPQT $^{4+}$ ring favors the TTF over the DNP unit by 10:1, whereas, in the analogous [2]catenane C1^{4+} , the distribution is even higher in favor of the TTF unit, namely 150:1. This difference in K , when comparing a bistable rotaxane with a bistable catenane with the same recognition units, can be rationalized by the geometrically enforced side-on interactions that are present in the catenane, but which are of much less significance in the rotaxane. When only one π -electron-rich recognition unit is present, as in the [2]catenane C2^{4+} , the distribution (6,800:1) favors the GSCC by almost three orders of magnitude over that observed for the bistable [2]rotaxane R^{4+} .

In designing bistable MIMs, it is important to understand the ground-state properties underlying each molecular compound. With an ever increasing knowledge of the GSCC, we envisage that it will become more and more possible to not only understand but also to predict (45) the behavior of MIMs in the more complex integrated systems found in device settings. Knowledge of the thermodynamic parameters, relating to bistable MIMs and their switching behavior, will most likely go a long way toward providing invaluable information to researchers when designing their experimental approaches toward the construction of devices where bistable MIMs are integrated with molecular electronic devices (MEDs). The approach we have described here for evaluating three bistable donor–acceptor MIMs is capable of being extended to other recognition motifs of this ilk. Equipped with this kind of intimate thermodynamic knowledge for a range of different molecules, chemists are now better able to design integrated systems ranging in diversity from—but not limited to—the

active binary components of MEDs, all the way through to artificial mechanical components of integrated nanobiomechanical and nanoelectromechanical systems.

Materials and Methods

All reagents were purchased from commercial suppliers (Aldrich or Fisher) and used without further purification. The catenanes **C1** • 4PF₆ (19) and **C2** • 4PF₆ (20) were prepared according to literature procedures. Both analytical and preparative HPLC were performed on reverse-phase (RP-HPLC) instruments, using C₁₈ columns and a binary solvent system (MeCN and H₂O with 0.1% CF₃CO₂H). CV experiments were carried out at room temperature in argon-purged solutions of MeCN with a Gamry Multipurpose instrument (Reference 600) interfaced to a PC. All CV experiments were performed using a glassy carbon working electrode (0.071 cm²). The electrode surface was polished routinely with 0.05 μm alumina-water slurry on a felt surface immediately before use. The counter electrode was a Pt coil and the reference electrode was a saturated calomel electrode unless otherwise noted. The concentration of the sample and supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAPF₆) were 1.0 mM and 0.1 M, respectively. The CV cell was dried in an oven immediately before use, and argon was continually flushed through the cell as it was cooled to room temperature to avoid condensation of water. Digital simulations of the CV experiments were performed using Digisim. The uncertainties in the ground-state distribution constants correspond to 3σ, where σ is standard deviation determined from least-squares fitting of the simulated data to the experimental data performed by the Digisim software. In the case of Eq. 5, error analysis was based on a ±10 mV uncertainty in measurement of *E*_{eq}.

R • 4PF₆: The diazido-functionalized thread **S2** (34) (500 mg, 0.69 mmol), the alkyne stopper **S1** (46) (596 mg, 2.76 mmol), and **CBPQT** • 4PF₆ (910 mg, 0.83 mmol) were dissolved in Me₂CO (100 mL). The solution was allowed to degas under argon for 30 min before adding Cu(MeCN)₄PF₆ (51 mg, 0.138 mmol) and tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (146 mg, 0.276 mmol) together as a solid. The reaction was allowed to stir for 1 d at room temperature under an inert atmosphere. A basic saturated solution of aqueous ethylenediaminetetraacetic acid was prepared using sodium bicarbonate and was added to the solution (20 mL) in order to remove the copper catalyst, followed by H₂O (200 mL), and excess NH₄PF₆ to induce precipitation of the crude product. The resulting green precipitate was collected by filtration, and washed with H₂O (200 mL). The filtered solid was further purified using RP-HPLC. The pure fractions were concentrated to a minimal volume before adding a saturated aqueous solution of NH₄PF₆, filtering, and washing the green solid with H₂O to remove any excess NH₄PF₆. We collected 550 mg (0.27 mmol, 39%) of a green solid, which was the target product **R** • 4PF₆ in pure form. For details of the characterization, see *SI Text*.

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