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Locking down the Electronic Structure of (Monopyrrolo)tetrathiafulvalene in [2]Rotaxanes

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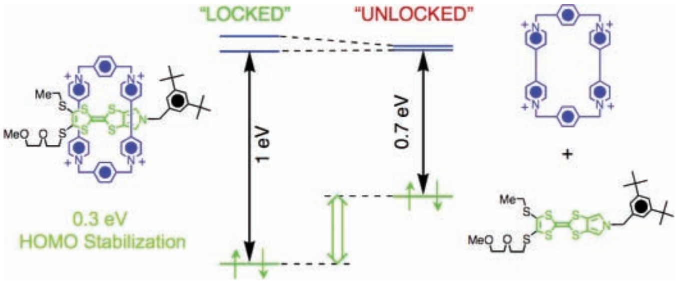
ABSTRACT



The redox potentials of a highly constrained [2]rotaxane have been measured and used to model the energy of the HOMO of tetrathiafulvalene-based bistable [2]rotaxanes in their two co-conformationally isomeric states. Restrained from co-conformational movements, the measured oxidation and reduction potentials provide insights into the orbital energies and electronic structure of a (monopyrrolo)tetrathiafulvalene unit when encircled by a tetracationic cyclobis(paraquat-*p*-phenylene) ring.

Redox-active bistable [2]rotaxanes[1,2] and their [2]catenane cousins[3] have been utilized[4] in molecular electronics to demonstrate binary switching in molecular memory devices.[4b] The bistable[5] rotaxanes are characterized structurally by a π-electron-deficient cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) ring that is interlocked around a dumbbell-shaped component incorporating two π-donor units, monopyrrolotetrathiafulvalene (MPTTF, green)[6] and the weaker π-donor, 1,5-dioxynaphthalene (DNP, red). In the rotaxane's ground-state co-conformation (GSCC), the ring preferentially encircles the MPTTF unit. Switching occurs (Figure 1) through an oxidation−reduction cycle[7] of the MPTTF unit that drives the movement of the $CBPQT^{4+}$ ring to the DNP

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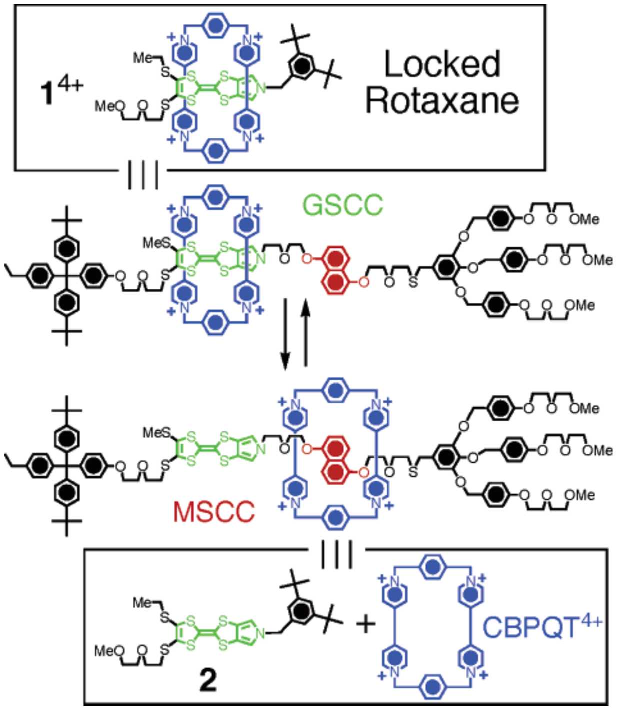

Figure 1. Molecular structures (boxes) of the highly constrained [2]rotaxane **1**$^{4+}$ together with the dumbbell **2** plus the **CBPQT**$^{4+}$ ring that emulate, respectively, the GSCC and MSCC of bistable [2]rotaxanes.

unit, thereby generating a metastable state co-conformation (MSCC). Significant differences exist between the electronic structures of the two co-conformations based upon electrochemical studies conducted on rotaxanes[1,7] and catenanes.[3] In particular, the oxidation potential of the MPTTF-based donor appears to shift anodically between the MSCC and GSCC. This shift is believed[4] to play a key role in the binary switching of conductivity displayed in the memory devices. However, the degree of the anodic shift has never been confirmed unambiguously because the oxidation of the MPTTF unit in all other rotaxanes and catenanes is also coupled to a molecular movement of the CBPQT^{4+} ring. Consequently, we have verified this potential shift and its magnitude by utilizing an appropriate control rotaxane **1**$^{4+}$, which does not display gross mechanical movement, and by comparing the redox properties to those of its dumbbell component **2** and the **CBPQT**$^{4+}$ ring.

The change in conductivity across the rotaxane in memory devices is proposed[4] to rely directly or indirectly[8] upon the change in the energy gap (ΔE) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). In the bistable rotaxanes, the LUMO is localized on the CBPQT^{4+} ring and the HOMO on the MPTTF unit. These localizations hold irrespective of the location of the ring, i.e., for both the MSCC and the GSCC. In the MSCC (ON state of the memory device), the MPTTF unit is bare and the CBPQT^{4+} ring is away on the DNP unit, resulting in a relatively small energy gap, whereas for the GSCC (OFF state), the ring encircles the MPTTF unit and ΔE is larger. The stabilization of the MPTTF-based HOMO in the GSCC is believed to be a result of an electrostatic interaction[1] with the surrounding tetracationic ring. A secondary effect on the orbital energies is a charge-transfer (CT) interaction that leads to the solution-phase optical transition observed at 812 nm (MeCN) for **1**$^{4+}$.

This energy gap hypothesis is supported[9] by quantum chemical simulations. However, verifying experimentally the electronic structure of bistable [2]rotaxanes based on solution-phase electrochemistry has not been straightforward on account of the mobility of the CBPQT^{4+} ring. For example, the act of oxidation converts the GSCC into the oxidized form of the MSCC on a millisecond time scale, rather than forming the oxidized form of the GSCC. Consequently, we have prepared[10] and investigated the redox properties of a highly constrained [2]rotaxane **1**$^{4+}$ that retains the basic structure of the GSCC (also when oxidized) while the linear combination of its dumbbell **2** plus the **CBPQT**$^{4+}$ ring serves (Figure 1) as a model of the MSCC. The DNP unit is believed to be less important[9b] on account of the fact that its oxidation potential is always more positive[1,3,7] than that of the MPTTF unit by at least 400 mV. The bulky and spatially close steric barriers on either side of the MPTTF unit are introduced in order to reinforce the mechanical

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(5) Different classes of bistable molecular switches can be found in: (a) Feringa B. L., Ed. *Molecular Switches*; Wiley-VCH: New York, 2001. (b) de Silva, A. P.; McClenaghan, N. D. *Chem. Eur. J.* **2004**, *10*, 574. (c) He, J.; Chen, F.; Liddell, P. A.; Andreasson, J.; Straight, S. D.; Gust, D.; Moore, T. A.; Moore, A. L.; Li, J.; Sankey, O. F.; Lindsay, S. M. *Nanotechnology* **2005**, *16*, 695. (d) Tomasulo, M.; Giordani, S.; Raymo, F. M. *Adv. Funct. Mater.* **2005**, *15*, 787. For electrochemically active switches, see: (e) Li, Q. L.; Mathur, G.; Gowda, S.; Surthi, S.; Zhao, Q.; Yu, L. H.; Lindsey, J. S.; Bocian, D. F.; Misra, V. *Adv. Mater.* **2004**, *16*, 133. (f) Gorodetsky, B.; Samachetty, H. D.; Donkers, R. L.; Workentin, M. S.; Branda, N. R. *Angew Chem., Int. Ed.* **2004**, *43*, 2812. (g) Morales, G. M.; Jiang, P.; Yuan, S.; Lee, Y.; Sanchez, A.; You, W.; Yu, L. *J. Am. Chem. Soc.* **2005**, *127*, 10456.

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bonding, thereby removing the influence of significant mechanical movements on the oxidation and reduction potentials.[11]

The energy levels in molecular systems can be evaluated[12] by different methods, including the gas-phase measurements of ionization potential and electron affinity, or in the solution phase, relative to a reference electrode, using electrochemical techniques. In solution-phase investigations[13] used to characterize the HOMO and LUMO energies of CT compounds that are based on metal−ligand bonding, the oxidized donor unit does not dissociate from the site of complexation on account of overriding metal−ligand σ bonding. This situation does not pertain, however, for bistable rotaxanes. For this reason, we needed to verify the energy shifts in the MPTTF-based HOMO using the model system in which the overriding mechanical bonding prevented the compound from dissociating during the time frame of the measurement.

The cyclic voltammetry (CV) of the highly constrained rotaxane **1**$^{4+}$, its dumbbell **2**, and the **CBPQT**$^{4+}$ ring were recorded[14] and compared (Table 1 and Figure 2). The dumbbell displays a pair of characteristic one-electron oxidation processes at $E_{1/2} = +411$ and $+720$ mV assigned to the MPTTF unit's first and second oxidations, respectively. Similarly, the **CBPQT**$^{4+}$ ring displays a standard pair[1,3,7] of two-electron reduction processes at −307 and −733 mV. By contrast to all other related bistable [2]rotaxanes,[1,3,7] the CV of **1**$^{4+}$ reveals a dumbbell-looking two-wave pattern, indicating that the CBPQT^{4+} ring is stationary for the time period of the experiment.[15] Both processes are assigned to the MPTTF unit's oxidation, and they shift anodically by +325 and +408 mV to +737 and +1130 mV, respectively, compared to **2**. Typically, however, the MPTTF unit's second oxidation peak in bistable [2]rotaxanes is located[1] at exactly the same potential as that for the bare MPTTF unit in the corresponding dumbbell on account of the CBPQT^{4+} ring's switching (as a result of the first oxidation)—this is an effect that is locked out in **1**$^{4+}$. In addition, each reduction process of the mechanically constrained ring in **1**$^{4+}$ displays a small splitting of 80 mV. Although the splitting of the first reduction peaks of the CBPQT^{4+} ring is a common feature of rotaxanes,[1,3,7] the shift of the first reduction of the split peak (−283 mV) to less negative potentials than for free **CBPQT**$^{4+}$ (−307 mV) is not. These features support the idea[3,16] that the CT interactions, which mix the MPTTF HOMO and the bipyridinium LUMOs together, are also responsible[17] for splitting the degeneracy of the bipyridinium-based LUMOs. Typically in bistable rotaxanes, the diradical dicationic CBPQT$^{2\bullet/2+}$ ring lowers the affinity[18] between the ring and the MPTTF unit, thus allowing the donor−acceptor pair to behave independently of each other. In this particular highly constrained [2]rotaxane, however, the CBPQT$^{2\bullet/2+}$ ring is now restrained in place, such that the electronic splitting (−855 and −946 mV) is preserved[19] even in the second reduction process that forms the neutral CBPQT^0 ring. In summary, the shift in the second oxidation peak and the splitting of the second reduction process at ca. −900 mV confirm that the ring remains encircled (Scheme 1) around the MPTTF unit over the voltage range of +1.6 to −2.0 V in MeCN at a scan rate[15] of 200 mV s^{-1}.

Table 1. Half-Wave Potentials ($E_{1/2}$ versus SCE in mV) for **1**$^{4+}$ and Its Components in MeCN[a]

	ox1	ox2	red1	red2	red3	red4
1^{4+}	+737	+1130	−283	−365	−855	−946
2	+411	+720				
CBPQT^{4+}			−307		−733	

[a] 0.1 M TBAPF$_6$/200 mV s^{-1}.

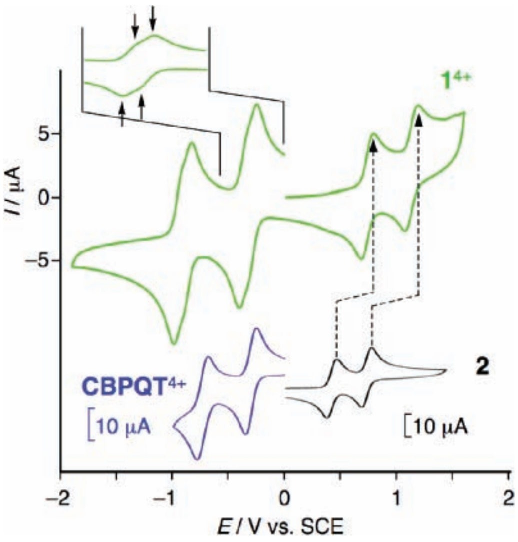

Figure 2. Cyclic voltammetry (MeCN/0.1 M TBAPF$_6$/200 mV s^{-1}) of the highly constrained rotaxane **1**$^{4+}$ and its components, the dumbbell **2** and the **CBPQT**$^{4+}$ ring (current scaled by 0.3 and 0.5, respectively, to account for the differences in sample concentrations).

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[11] The mechanical mobility of the CBPQT^{4+} rings in [2]rotaxanes and [2]catenanes is responsible for imparting the appearance of quasireversible electrochemistry (see refs 1 and 3).

[12] Loutfy, R. O.; Loutfy, R. O. *Can. J. Chem.* **1976**, *54*, 1454.

[13] Balzani, V. *Tetrahedron* **1992**, *48*, 10443.

[14] Electrochemical experiments were carried out at room temperature in argon-purged MeCN solutions, with a Princeton Applied Research 263A interfaced to a PC. CV experiments were performed using a glassy-carbon working electrode (0.018 cm^2) polished with an alumina−water slurry immediately before use. The counter electrode was a Pt wire and the reference electrode was an SCE. Tetrabutylammonium hexafluorophosphate (0.1 M) was added as supporting electrolyte. $E_{1/2}$ was calculated from an average of the cathodic and anodic CV peaks. Experimental errors: potential values, ±5 mV.

[15] The barriers for deslipping have been measured for **1**$^{4+}$ (PhCN), mono-oxidized **1**$^{5+}$ (MeCN), and doubly oxidized **1**$^{6+}$ (MeCN) and correspond to time constants of 11 y, 25 h, and 147 s, respectively, at 298 K; see citation in ref 10.

[16] Cordova, E.; Bissell, K. A.; Kaifer, A. E. *J. Org. Chem.* **1995**, *60*, 1033.

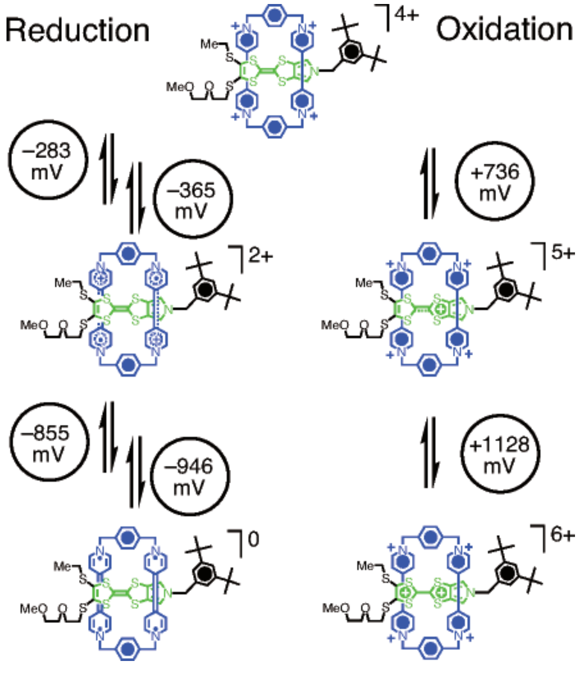
[17] No evidence for slow interconversion between near equi-energetic conformations on the time scale of the CV was observed.

[18] Tseng, H.-R.; Wu, D.; Fang, N. X.; Zhang, X.; Stoddart, J. F. *ChemPhysChem* **2004**, *5*, 111.

[19] Chemical inequivalence following the first 2e$^-$ reduction has been observed[3] in the diradical dication of catenanes but is typically absent for rotaxanes.[1c]

These electrochemical data are related[20] to the HOMO and LUMO energies of the mechanically interlocked molecule. Referenced to the standard calomel electrode, the MPTTF-based HOMO lies at +737 mV and a CBPQT^{4+}-based LUMO at −283 mV, defining an experimental energy gap ΔE_e of 1020 mV for the GSCC. By contrast, the band gap of the MSCC (ON state)—calculated as the difference between the oxidation potential of the isolated dumbbell **2** and the reduction potential of the isolated **CBPQT**$^{4+}$ ring—decreases markedly to 720 mV. An energy level diagram (Figure 3) representing the orbital energies of the two co-conformations based on the CV data agrees semiquantitatively with the simulations on a related host−guest complex.[9b] There is a significant change in the energy gap, and most of this change arises from the stabilization of the MPTTF-based HOMO. The degree of stabilization of the HOMO and splitting of the LUMO energy levels are greater for the calculated structures, presumably because of the absence of solvation in the simulation. Furthermore, the calculated MO representations of the split CBPQT^{4+}-based LUMOs displays[9b] CT mixing with the TTF-based HOMO.

Scheme 1. Mechanism of Electrochemical Oxidation (Top) and Reduction (Bottom) for **1**$^{4+}$ That Occurs during a CV recorded at 200 mV s^{-1} [a]



[a] $E_{1/2}$ values are reported versus the SCE.

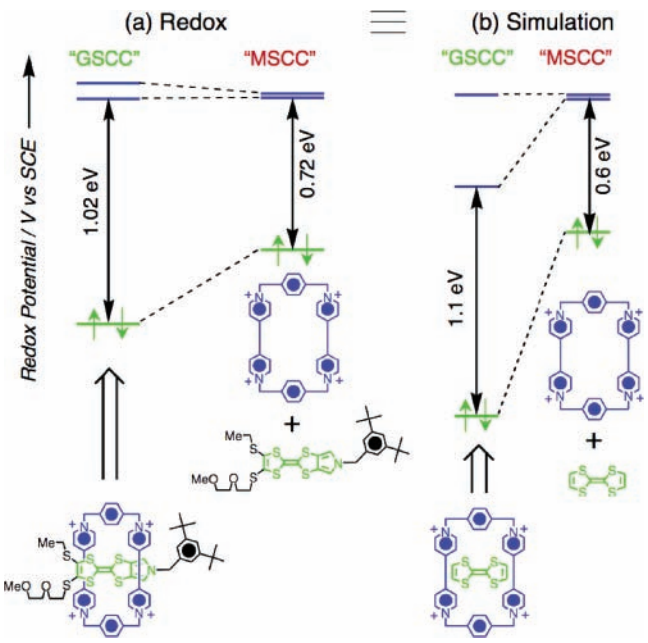


Figure 3. Energy level diagrams illustrating how the HOMOs (green, MPTTF) and the LUMOs (blue, CBPQT^{4+}) shift based on (a) electrochemical studies and (b) simulation, together with the molecular formulas of the model compounds representing the GSCC and MSCC.

In conclusion electrochemical data obtained for a highly constrained rotaxane have verified that the change in the energy gap based on the stabilization of the MPTTF unit's HOMO by the tetracationic CBPQT^{4+} ring amounts to a significant difference between the MSCC and GSCC. These studies provide evidence for changes that occur within the frontier molecular orbitals of solution-phase switches, changes which may also be present in electronic devices.

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Supporting Information Available: Electrochemistry data and analysis of the effect of solvation. This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] Little change in ΔE and the redox potentials was observed when the CVs were recorded in different solvation environments provided by Me_2CO, PhCN, and H_2O; see the Supporting Information.