Redox-Controllable [2]Rotaxane

Toward Chemically Controlled Nanoscale Molecular Machinery**

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Richard Feynman, in his famous address[1] entitled "There is Plenty of Room at the Bottom" to the American Physical Society in December 1959, raised the fascinating question: "what are the possibilities of small but movable machines?" The rapid growth in supramolecular chemistry[2] provides a convincing answer to Feynman's question—namely, mechanically interlocked molecules, such as certain nondegenerate catenanes and rotaxanes,[3] which can be induced to switch between different ground-state geometries, thus creating substantial relative movement between their, at least, partially "asymmetrical" components and allowing these molecules to behave as nanoscale machines.[4,5] The ability to control the movement of components within these molecular machines, in response to either physical (light[6] or electrical[7]) or chemical (redox[8] or pH[9] changes) stimuli, is critical, because it relates directly to the performance of solid-state devices incorporating them.[7]

A [2]rotaxane consists of two components: a ring and a dumbbell-shaped one.[3] The ring component encircles the linear rodlike portion of the dumbbell and is trapped mechanically by two bulky stoppers at each end of the rod. When two constitutionally different recognition sites[10] are incorporated into the rodlike portion of the dumbbell, the [2]rotaxane can exist in two nondegenerate co-conformations[11] as translational isomers whose relative populations reflect the free energy difference for binding at these two sites. Thus, [2]rotaxanes of this ilk can be likened to a linear motor, since they possess two states between which the ring component can undergo translational motion along part of the rodlike portion of the dumbbell component. There are two fundamental requirements of a switchable [2]rotaxane for achieving the most efficient possible conversion of chemical, electrical, or optical energy into mechanical energy: one is the "complete" occupation of one of the two sites on the dumbbell by the ring component, and the other is the complete reversal of this occupation when the external stimulus is applied.

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Recently, we reported[12] the template-directed syntheses of an amphiphilic bistable [2]rotaxane composed of a ring component, cyclobis(paraquat-*p*-phenylene)[13] ($CBPQT^{4+}$), and a dumbbell-shaped component with two π-electron-rich aromatic sites, namely, a 1,5-dioxynaphthalene (DNP) one and a monopyrrolotetrathiafulvalene (MPTTF) one. Ideally, the $\pi\cdots\pi$ stacking interactions[14] between the π-electron-deficient $CBPQT^{4+}$ ring and the more π-electron-donating MPTTF site would result in this [2]rotaxane existing as a single co-conformation wherein the $CBPQT^{4+}$ ring encircles only the MPTTF site ($K_a = 1300\,M^{-1}$ in MeCN).[15] However, both UV/Vis and ^{1}H NMR spectroscopies have indicated[12] the presence, in Me_2CO (CD_3COCD_3) solution, of two stable translational isomers[16] in a 1:1 ratio at room temperature. Since the MPTTF site fails to entice the $CBPQT^{4+}$ ring to reside exclusively on it, its subsequent oxidation, and removal of its stabilizing interactions with the $CBPQT^{4+}$ ring, produces a switch that works no more than 50% of the time. This inherent lack of precise mechanical control compromises the utility of this [2]rotaxane when it comes to fabricating molecular electronic devices and construction of artificial motor-molecules. In an effort to produce a [2]rotaxane that will function as a prototypical linear molecular motor with 100% positional efficiency, we elected to employ a disubstituted TTF site in competition with the DNP site. After all, we know that TTF forms a strong, green 1:1 complex ($K_a = 8000\,M^{-1}$ in MeCN)[17] with $CBPQT^{4+}$ whereas 1,5-dihydroxy naphthalene forms a much weaker, red 1:1 complex with $CBPQT^{4+}$ ($K_a = 768\,M^{-1}$ in MeCN).[18] Moreover, a closely related nondegenerate [2]catenane based on the same TTF and DNP recognition sites has been demonstrated to behave as a "clean" switch, both in solution[19] and in a solid-state device.[19c,d] Here we describe 1) a [2]rotaxane (**1**·4PF$_6$) incorporating TTF and DNP recognition sites in its dumbbell component which is encircled exclusively on the TTF site by $CBPQT^{4+}$ and 2) the characterization by UV/Vis and ^{1}H NMR spectroscopies of its "clean" redox-switching action in solution, wherein the $CBPQT^{4+}$ component moves an estimated[20] 3.7 nm between the TTF and DNP recognition sites (Figure 1).

The UV/Vis spectrum (Figure 2, curve a) of **1**·4PF$_6$ reveals a charge-transfer (CT) absorption band, centered on 846 nm, which is characteristic[19a,b] of the translational isomer in which the TTF site is encircled by the $CBPQT^{4+}$ moiety. No absorption band is observed in the 500–600 nm region for a CT interaction which would result from the other translational isomer in which the DNP site is encircled by the $CBPQT^{4+}$ unit. Switching of **1**$^{4+}$ was observed in an $8 \times 10^{-4}\,M$ solution of the 4PF$_6^-$ salt in MeCN when Fe(ClO$_4$)$_3$ was added. Addition of the oxidant (1.0 equiv) led (Figure 2, curve b) to a decrease in the intensity of the CT band at 846 nm and the appearances of absorption bands centered on 450 and 600 nm that are characteristic[19a,b] of the TTF$^{+\cdot}$ radical cation. A new CT band was also observed at 515 nm as a hump between these two larger bands. The hump indicates[19a,b] the presence of a CT interaction between the DNP site and the $CBPQT^{4+}$ unit which now encircles it. Further addition (up to 2.0 equiv) of the oxidant caused the absorption bands for the TTF$^{+\cdot}$ radical cation to disappear and a new

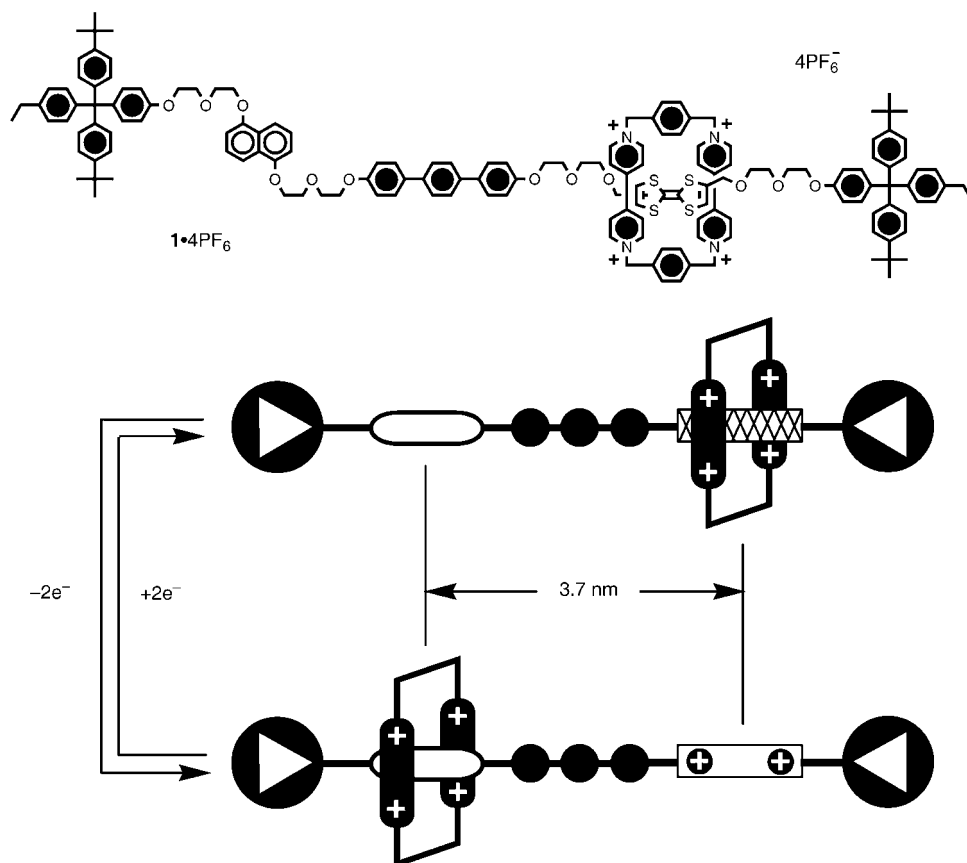1•4PF₆   4PF₆⁻

Figure 1. A [2]rotaxane with the TTF (hatched) and DNP (open) recognition units separated by a rigid terphenylene spacer (black circles) demonstrates a relative mechanical movement between the macrocyclic and dumbbell-shaped components of about 3.7 nm.

band to appear at 375 nm, which corresponds to the TTF^{2+} ion.[19a,b] The new CT band was now evident (Figure 2, curve c) at 530 nm. Addition of 2.0 equivalents of the reductant, ascorbic acid, led to the original spectrum being restored (Figure 2, curve d).

^{1}H NMR spectroscopy has established (Figure 3) the precise and quantitative nature[21] of the redox-controlled switching process undergone by the [2]rotaxane $\mathbf{1^{4+}}$. The
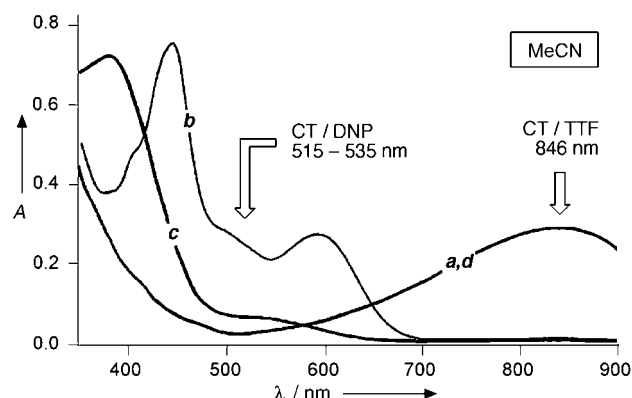

Figure 2. Absorption spectra (MeCN, 298 K) of a 8×10^{-4} M solution of [2]rotaxane 1·4PF₆ –(curve a) and of the same solution after addition of 1.0 and 2.0 equivalents of Fe(ClO₄)₃ (curves b and c). Addition of ascorbic acid (2 equiv) regenerates the original spectrum (curve d).

^{1}H NMR spectrum (Figure 3a) of $\mathbf{1 \cdot 4PF_6}$ was recorded in CD₃CN. The oxidant, tris(*p*-bromophenyl)aminium hexa-chloroantimonate,[22] was added (2.2 equiv) to the sample, the temperature was lowered[23] to 243 K, and the spectrum (Figure 3b) was recorded again. Prior to oxidation of the [2]rotaxane, two pairs of peaks of unequal intensities (47:53) at $\delta = 6.02$ and 6.12 ppm, and $\delta = 6.22$ and 6.28 ppm, respectively, can be assigned to the constitutionally heterotopic TTF methine protons in the *cis* and *trans* isomers (it is not clear from the data which peaks belong to which isomer) associated with the TTF unit in $\mathbf{1^{4+}}$. On oxidation, the signals for the constitutionally heterotopic methine protons on the TTF^{2+} ion resonate[24] at $\delta = 9.15$ and 9.25 ppm, while those for the methylene protons on the adjacent CH₂ groups resonate[25] at $\delta = 5.00$ and 5.16 ppm. In the case of the oxidized [2]rotaxane containing the TTF^{2+} ion, the presence of two isomers is no longer evident, presumably on account of the nonplanar geometry of the TTF^{2+} ion removing the possibility for *cis–trans* isomerism. Evidence for movement of the CBPQT^{4+} ring from the TTF to the DNP site upon oxidation of the [2]rotaxane is apparent from observation of upfield shifts of the peaks corresponding to the protons of the DNP site. The H-2/6 and H-3/7 protons resonate at $\delta = 6.28$ and 5.99 ppm, respectively (although H-2 and H-6 are non-equivalent protons, their signals in the ^{1}H NMR spectrum overlap and likewise for H-3/7), in the spectrum (Figure 3b)
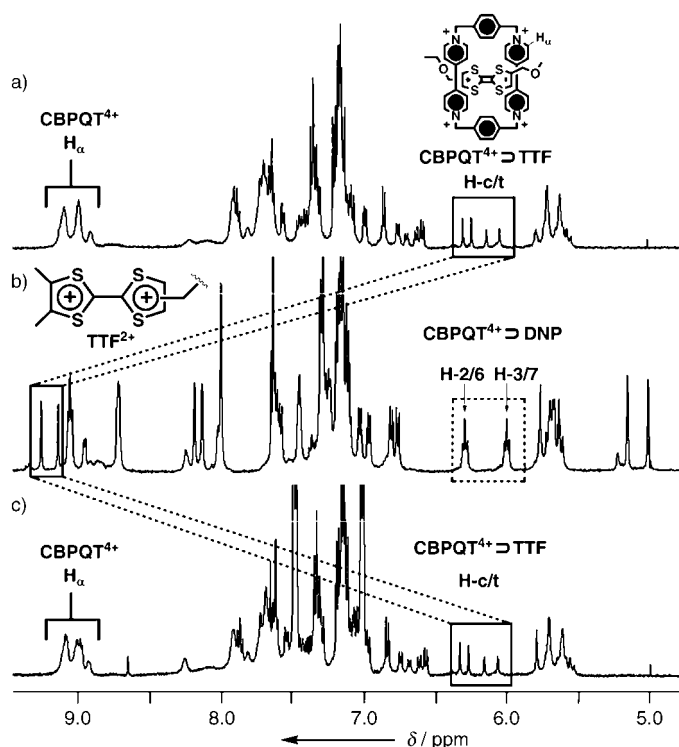
Figure 3. a) ¹H NMR spectrum of **1**·4 PF₆ in CD₃CN recorded at 500 MHz at room temperature. The solid box highlights the peaks for the H-c/t (*cis/trans*) protons in the neutral TTF unit. b) ¹H NMR spectrum of bis-oxidized **1**·4 PF₆ in CD₃CN recorded at 500 MHz at 243 K. The solid box highlights the peaks for the TTF²⁺ dicationic residues and the dotted box indicates the peaks for H-2/6 and H-3/7 of the "inside" DNP unit. (The peaks corresponding to H-4/8 appear at δ = 2.34 and 2.32 ppm and are not shown here.) c) ¹H NMR spectrum of reduced **1**·4 PF₆ in CD₃CN recorded at 500 MHz at room temperature. The solid box highlights the peaks for the neutral TTF unit.

Figure 4. ¹H DQF-COSY spectrum at 500 MHz of the bis-oxidized form of **1**·4 PF₆ in CD₃CN at 243 K. The solid lines indicate coupling between peaks corresponding to the protons of the DNP site encircled by a CBPQT⁴⁺ unit. Dotted lines show the weak long-range coupling between the protons on the TTF²⁺ unit and the adjacent CH₂ groups.

of oxidized **1**⁴⁺. The upfield shifts of about 1.5 ppm result from anisotropic shielding of the protons on the DNP site by the aromatic rings present in the encircling CBPQT⁴⁺ ring. Additionally, the H-4/8 protons of the encircled DNP site participate in C–H···π interactions with the paraphenylene bridges in the CBPQT⁴⁺ ring, which results in large upfield shifts of approximately 4.5 ppm to δ = 2.34 and 2.32 ppm. Examination of the ¹H DQF-COSY (double quantum filtered correlation spectroscopy) spectrum (Figure 4) for the oxidized [2]rotaxane shows clearly the scalar coupling between the protons of the DNP site. No observation of signals corresponding to the uncomplexed DNP site or the complexed TTF²⁺ ion are observed in the ¹H NMR spectrum of oxidized **1**⁴⁺, which indicates that all of the [2]rotaxane molecules have been switched within the limits of detection by ¹H NMR spectroscopy. Addition of Zn powder to the sample and vigorous shaking of the mixture led to reduction of the TTF²⁺ ion to its neutral form and movement of the CBPQT⁴⁺ ring away from the DNP site and back to the much stronger π-electron-donating TTF unit. The original ¹H NMR spectrum (Figure 3c) was restored.

While UV/Vis spectroscopy indicates the general nature of the redox-controlled switching process undergone by the
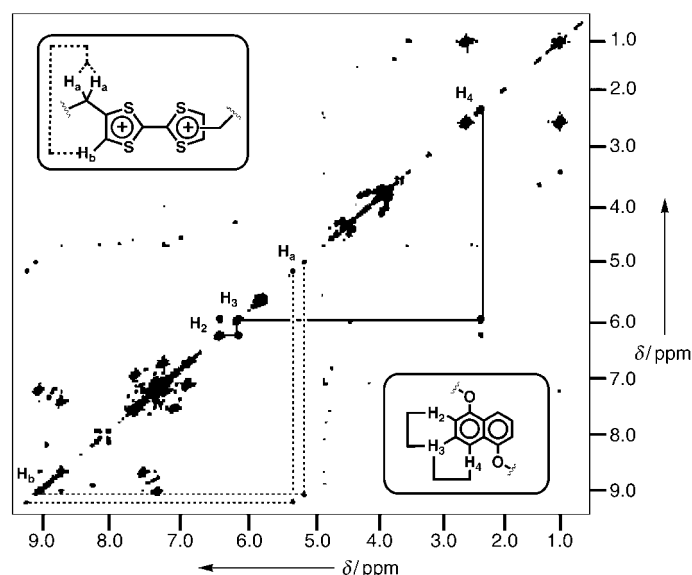
[2]rotaxane, ¹H NMR spectroscopy provides a precise and quantitative probe of the process, and yields fine, as well as gross, structural information. However, a further issue remains to be addressed in the near future. It relates to the incoherence associated with motor-molecules operating in solution, a deficiency which results in the dissipation of their mechanical energy during the switching process. Only by the mounting[26] of working motor-molecules at interfaces and on surfaces can we hope to harness their mechanical energy. In the wake of being able to monitor the redox-controlled switching of **1**⁴⁺ in solution, we are now exploring the potential of using nanoparticles as platforms for the self-assembly of motor-molecules, prior to their characterization by NMR spectroscopy. A link between solution-state molecular signatures, where incoherence is rife, and characterization of solid-state devices, where coherence occurs, is essential if further progress is to be made in the realization of small but movable machines.[1]

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[20] Molecular modeling studies were performed using the MM2 force-field as implemented in Chem3D version 7.0. The molecule was "stretched" and then minimized to give the most linear conformation possible. The distance of 3.7 nm was measured from the center of the TTF unit to the center of the DNP ring system and can be compared to an overall length of approximately 9 nm for the rotaxane.

[21] A variable temperature ^{1}H NMR spectroscopic investigation (H.-R. Tseng, S. Kang, S. A. Vignon, J. F. Stoddart, unpublished results) of a degenerate model [2]rotaxane, in which the DNP ring system is replaced by a TTF unit, reveals that shuttling of the CBPQT^{4+} ring between the two TTF units is slow at room temperature on the ^{1}H NMR timescale. An energy barrier in excess of 16 kcal mol^{-1} can be associated with this shuttling process. It follows that the ^{1}H NMR spectrum shown in Figure 3a is not an averaged one but a discrete one which indicates that the CBPQT^{4+} ring encircles the TTF unit exclusively.

[22] This oxidant was chosen for three reasons: 1) it has a high enough oxidative potential (0.7 V versus ferrocene) to oxidize

the TTF unit completely to TTF^{2+}, 2) the reduced form will give only two signals in the ^{1}H NMR spectrum and will not interfere with interpretation of the data, and 3) the solubilities of both the oxidant and its reduced form are good in the same solvents as the rotaxanes of interest. For details, see a) N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877–910; b) E. Steckhan, *Top. Curr. Chem.* **1987**, *142*, 1–69.

[23] It was necessary to lower the temperature to avoid decomposition of the oxidized [2]rotaxane during the accumulation of data for the ^{1}H DQF-COSY spectrum reproduced in Figure 4.

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[25] Peak assignments for the TTF^{2+} and adjacent CH$_2$ groups were made on the basis of an observed long-range coupling between the two, which led to the TTF^{2+} and TTF signals being triplets with a small splitting (ca. 1 Hz). This coupling can also be observed in the ^{1}H DQF-COSY spectrum (Figure 4) for the oxidized [2]rotaxane. Additional evidence to support the assignments was obtained by peak integrations, as well as by monitoring the peaks during titration with the oxidant. Similar dramatic chemical shift changes have been observed in our laboratory for other TTF-containing compounds upon oxidation.

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