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Functionally Rigid Bistable [2]Rotaxanes

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Abstract: Two-station [2]rotaxanes in the shape of a degenerate naphthalene (NP) shuttle and a nondegenerate monopyrrolotetrathiafulvalene (MPTTF)/NP redox-controllable switch have been synthesized and characterized in solution. Their dumbbell-shaped components are composed of polyether chains interrupted along their lengths by (i) two π-electron-rich stations—two NP moieties or a MPTTF unit and a NP moiety—with (ii) a rigid arylethynyl or butadiynyl spacer situated between the two stations and terminated by (iii) flexibly tethered hydrophobic stoppers at each end of the dumbbells. This modification was investigated as a means to simplify both molecular structure and switching function previously observed in related bistable [2]rotaxanes with flexible spacers between their stations and incorporating a cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) ring. The nondegenerate MPTTF-NP switch was isolated as near isomer-free bistable [2]rotaxane. Utilization of MPTTF removes the cis/trans isomerization that characterizes the tetrathiafulvalene (TTF) parent core structure. Furthermore, only one translational isomer is observed (> 95 < 5), surprisingly across a wide temperature range (198−323 K), meaning that the $CBPQT^{4+}$ ring component resides, to all intents and purposes, predominantly on the MPTTF unit in the ground state. As a consequence of these two effects, the assignment of NMR and UV−vis data is more simplified as compared to previous donor−acceptor bistable [2]rotaxanes. This development has not only allowed for much better control over the position of the ring component in the ground state but also for control over the location of the $CBPQT^{4+}$ ring during solution-state switching experiments, triggered either chemically (^{1}H NMR) or electrochemically (cyclic voltammetry). In this instance, the use of the rigid spacer defines an unambiguous distance of 1.5 nm over which the ring moves between the MPTTF and NP units. The degenerate NP/NP [2]rotaxane was used to investigate the shuttling barrier by dynamic ^{1}H NMR spectroscopy for the movement of the $CBPQT^{4+}$ ring across the new rigid spacer. It is evident from these measurements that the rigid spacer poses a much lower barrier to the 1.0 nm movement of the $CBPQT^{4+}$ ring from one station to another as compared with previous systems—a finding that is thought to be a result of the combination of fewer favorable interactions between the spacer and the $CBPQT^{4+}$ ring and a relatively unimpeded path between the two NP stations. This example augers well for exploiting rigidity during the development of well-defined bistable [2]rotaxanes, which are unencumbered by the excesses of structural conformations that have characterized the first generations of molecular switches based on the donor−acceptor recognition motif.

Introduction

Since their first inception, bistable [2]rotaxanes,[1] comprising two different recognition sites, have attracted considerable attention as molecular switches[2] and as potential candidates for applications in molecular electronics.[3,4] Rotaxanes are mechanically interlocked molecules, which consist of a linear rod component, stoppered at each end by bulky substituents (dumbbell) and encircled by a macrocyclic ring component. Most bistable [2]rotaxanes are constructed in such a way that the dumbbell component contains two different recognition sites (stations) for the macrocyclic ring to reside upon at equilibrium. This design creates two different translational isomers, which are populated in a particular ratio depending mainly on the relative strengths of the weak interactions stabilizing the ring component when it encircles either one of the two stations.[2i] A well-known class of bistable [2]rotaxanes have been designed such that the dumbbell component incorporates the π-electron-rich unit, tetrathiafulvalene[2d,e,f] (TTF), or one of its derivatives—either monopyrrolotetrathiafulvalene[2b,c,i] (MPTTF) or bispyrrolotetrathiafulvalene[3i,5] (BPTTF)—together with a second, much less π-electron-rich naphthalene (NP) moiety. The bista-

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bility is achieved as a result of the dumbbell being encircled by a π-electron-deficient tetracationic macrocyclic ring[6]—cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$). It has been shown[7] that the $CBPQT^{4+}$ ring interacts much more strongly with the TTF unit than it does with the NP moiety. The reversible oxidation of TTF[8] to a mono- and dication, sequentially, can be used to create a positive charge on the TTF unit in the bistable [2]rotaxane, producing a Columbic charge−charge repulsion between the oxidized $TTF^{+\bullet/2+}$ unit and the $CBPQT^{4+}$ ring, thereby inducing the ring component to move to and reside on the only remaining π-electron-rich station of the dumbbell, namely, the NP moiety. In an ideal system, the $CBPQT^{4+}$ ring would only encircle the strongest π-electron donor, that is the TTF unit, thereby creating the possibility for perfect control over the location of the tetracationic cyclophane (ring) using electrical impulses. The use of the core TTF unit in the dumbbell component, however, suffers from the major drawback that the facile cis/trans isomerization[9] of TTF creates a dumbbell that exists as two inseparable isomers,[10] thereby significantly complicating the NMR spectroscopic assignments of both the dumbbells and the [2]rotaxanes. To overcome this shortcoming, the isomer-free MPTTF unit[11] has already found widespread use in the construction of bistable [2]rotaxanes, although it is known experimentally[2b,c,i] that, in MPTTF-based bistable [2]-rotaxanes, the $CBPQT^{4+}$ ring does not encircle the MPTTF unit exclusively but also resides on the NP station to some significant extent. This observation has been attributed mainly to the fact that $\pi-\pi$ interactions, and hence the relative donor strengths of the TTF and MPTTF stations, are not the only interactions to consider when determining the translational isomeric distribution. Previous investigations and the analysis of experimental data have revealed that a wide range of weak interactions, such as [C−H$\cdots\pi$] ones and hydrogen bonding, influence the position the tetracationic ring occupies along the dumbbell component in solution. Moreover, the use of polyethyleneglycols (PEGs) as spacers between the stations in the bistable [2]-rotaxanes introduces additional weak noncovalent interactions between them and the $CBPQT^{4+}$ ring, a situation that affects the isomeric distribution in donor−acceptor bistable [2]rotaxanes in a unpredictable manner. Such a situation leaves the molecular structures and hence the desired switching properties less well-defined. It follows that a greater level of structural control is required to remedy these issues, and for this reason, we decided to explore of introducing rigidity into the backbones of bistable [2]rotaxanes.

The inherent flexibility of the PEG linkers employed in the first generation of MPTTF-based bistable [2]rotaxanes allows the molecules to adopt many different conformations in solution as well as in more confined and condensed media, such as monolayers[12] and devices.[3f,i] The outcome is that precise

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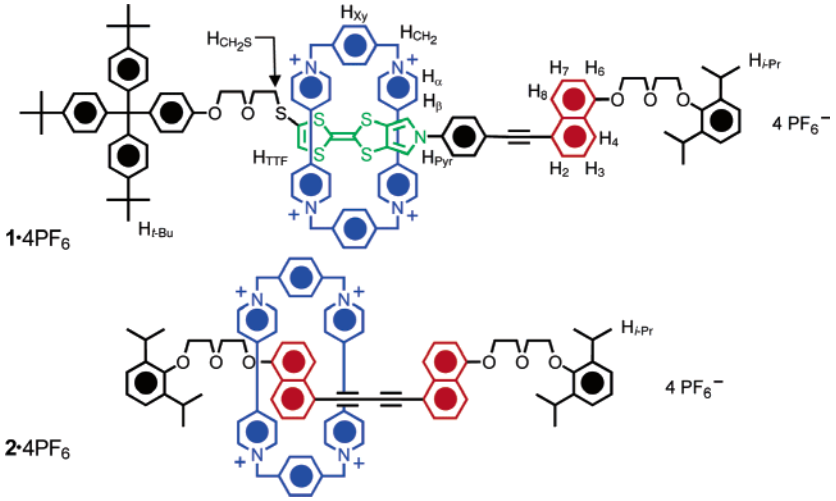

Figure 1. Structural formulas of the bistable MPTTF/NP-containing [2]rotaxane **1**·4PF_6 and the degenerate NP/NP-containing [2]rotaxane **2**·4PF_6.

structures are not at all well-defined. For instance, back-folding phenomena[13] can occur when the $CBPQT^{4+}$ ring encircles the MPTTF or NP station and the dumbbell component of the bistable [2]rotaxane folds back in such a way that the ring can interact in an alongside manner with the unoccupied station. This back-folding could be prevented if the PEG linkers between the MPTTF and NP units were replaced with a linear and rigid linker. Such a modification might well favor a situation where the π-electron-deficient $CBPQT^{4+}$ ring encircles only the more π-electron-rich MPTTF unit, to all intents and purposes, rather than the NP moiety, since a rigid system would minimize the influence of the weak interactions caused by the PEG linkers. Thus, creating rigidified MPTTF- and NP-containing [2]-rotaxanes constitutes the first step toward bistable [2]rotaxane systems with precisely defined structures.

Notwithstanding the advantages of structural rigidity in the context of molecular switches, the replacement of the PEG spacers for rigid ones has obvious rewards in the design of machine-like actuators.[14] In addition, it is undoubtedly less efficient to harvest[3g,h] the mechanical energy of the *movement* of the $CBPQT^{4+}$ ring along the dumbbell of bistable [2]-rotaxanes from station to station when using the PEG linkers because some energy must inevitably be spent on the loss of conformational freedom when the $CBQPT^{4+}$ ring passes across the PEG spacers. Moreover, the evaluation of such an entropic contribution to the switching rates would be challenging to determine both experimentally[3f,i,4b,15] and computationally.[16] For physical understanding[17] and mechanical applications,[3g] the distance over which a force is exerted in order to perform work would be much better defined with a linear rigid spacer present in the dumbbell component of such rigidified bistable [2]-rotaxanes. The mechanochemical analyses would be greatly simplified and consequently offer a far greater opportunity to harness the performance of molecular machines by a rational design approach rather than being at the mercy of rampant disorder when highly flexible bistable [2]rotaxanes are bound to surfaces for technological applications.[18] It is likely that the linear rigid spacers have potential returns as functional units as well as the structural ones. Linear-rigid bistable [2]rotaxanes could herald a significant advance over previous systems by providing the bistable [2]rotaxanes with well-defined conformations and motions.

In the first part of this paper, we report on the preparation of two [2]rotaxanes (**1**·4PF_6 and **2**·4PF_6, in Figure 1) having rigid spacers in between their two stations—MPTTF and NP or both NP.

We employed the arylethynyl and butadiynyl units as the rigid spacers to act as bridges between the two stations on account of the ease of their preparation and the fact that their lengths are both similar to those of the PEG chains frequently used in previous[2] bistable [2]rotaxanes. In the present case, however, the rigidity dictates inter-station distances of 1.5 and 1.0 nm. The second part of the paper focuses on the characterization of **1**·4PF_6 and **2**·4PF_6 by (i) ^{1}H NMR spectroscopy in order to (a) investigate the effect of the spacer on the isomeric distribution of the bistable [2]rotaxane **1**·4PF_6, and (b) to analyze magnitude of the shuttling barrier of the $CBPQT^{4+}$ ring in the degenerate [2]rotaxane **2**·4PF_6, and by (ii) UV−vis absorption spectroscopy and (iii) electrochemistry to determine the switching of the MPTTF-NP [2]rotaxane **1**·4PF_6 as a result of applying either chemical or electrochemical stimuli.

Results and Discussions

Design and Synthetic Strategy. Retrosynthetic analysis of the bistable MPTTF/NP-containing [2]rotaxane **1**·4PF_6 and the

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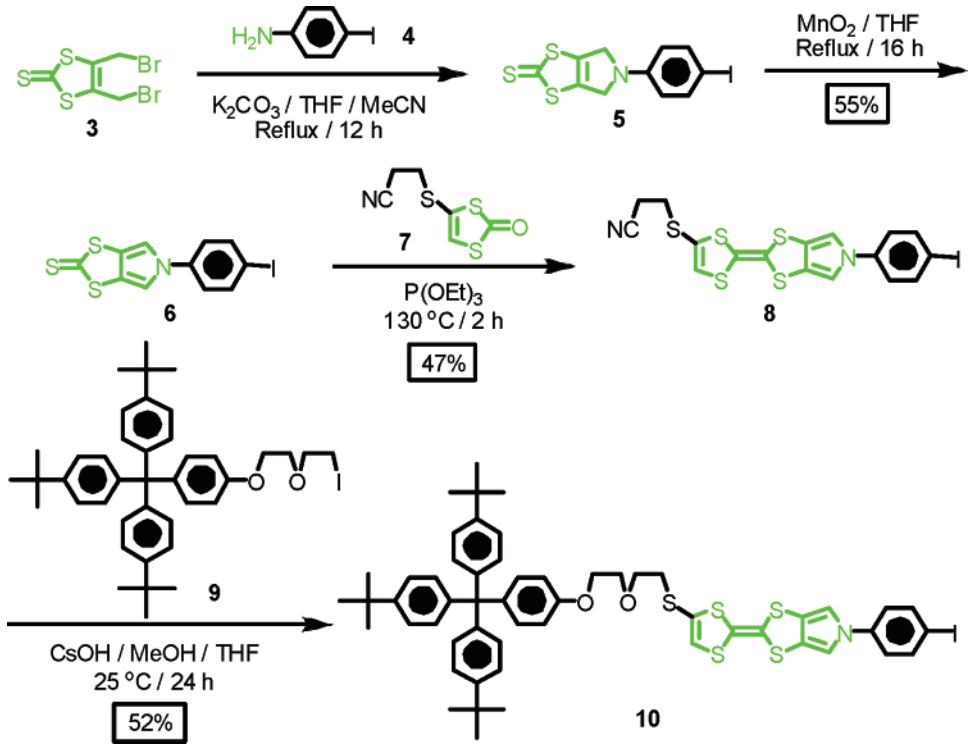
Scheme 1. Synthesis of the MPTTF-Containing (Green) Half-Dumbbell **10**



degenerate NP/NP-containing [2]rotaxane **2**·4PF_6 revealed that a modular strategy, similar to those employed in the past,[2,3i,5] would be the most sensible and efficient. This feeling is evident from the fact that the two dumbbell compounds **18** and **19** can be prepared from a combination of two building blocks, namely, the MPTTF unit **10** and the NP unit **17**. These two units can be cross-coupled using a Pd-catalyzed Sonogashira[19] type reaction, which ensures that the linkage between the two π-electron-rich moieties is a rigid and linear one. Common to preparation of both **1**·4PF_6 and **2**·4PF_6 is the template-directed clipping reaction at ultrahigh pressure to form the $CBPQT^{4+}$ ring around the respective dumbbell-shaped compounds **18** and **19**. The modular approach to the syntheses of the dumbbell compounds relies on the progressive assembly of four different fragments, namely (i) the iodine-terminated hydrophobic tetraarylmethane stopper[20] **9**, which is employed as the stopper on (ii) the new MPTTF unit **10**, and (iii) the hydrophobic diisopropylaryl stopper **14**, which is subsequently used on (iv) the new NP unit **17**.

Synthesis. The synthetic routes employed in the fabrication of the rigid, two-station [2]rotaxane **1**·4PF_6 as well as the degenerate [2]rotaxane **2**·4PF_6 are outlined in Schemes 1−4. The preparation of the MPTTF-containing half-dumbbell **10** began with the reaction of dibromide[21] **3** with *p*-iodoaniline (**4**) in the presence of K_2CO_3 in MeCN, affording the crude ring-closed product **5**, which was resuspended in anhydrous THF and subsequently oxidized with activated MnO_2 to yield the desired thione building block **6** in an overall yield of 55% for the two steps.

A cross-coupling reaction in neat $(EtO)_3P$ between the thione building block **6** and the ketone building block[22] **7** gave the MPTTF derivative **8** in 47% yield. The iodide-terminated tetraarylmethane stopper[20] **9** was coupled to the MPTTF unit **8**—following the in situ deprotection of the cyanoethyl protection group to form the *S*-nucleophile with 1.1 equiv of CsOH·H_2O—to give the MPTTF-containing half-dumbbell **10** in 52% yield.

Similarly, a modular approach was employed in the synthesis of half-dumbbell **17**. Initially, the amino functionality of 5-aminonaphthalen-1-ol (**11**) was converted into an iodo group to afford 5-iodonaphthalen-1-ol (**12**), employing the intermediacy of diazonium salt formation, in an acceptable 40% yield. Second, 2,6-diisopropylphenol (**13**) was treated with 2-(2-chloroethoxy)ethanol in the presence of K_2CO_3 and LiBr to give the alcohol **14** in 65% yield.

Subsequently, the naphthol **12** was coupled with the alcohol **14** to afford **15** in 73% yield by employing a Mitsunobu reaction in the presence of diisopropylazodicarboxylate (DIAD) and triphenylphosphine (Ph_3P). Finally, a Pd-catalyzed Sonogashira cross-coupling reaction of the iodide **15** with trimethylsilyl (TMS) acetylene gave the TMS-protected compound **16** in 90% yield, and subsequent deprotection of the TMS group with K_2CO_3/MeOH provided the acetylene-teminated NP half-dumbbell compound **17** in 60% yield.

In order to accomplish the synthesis of the desired rigid MPTTF/NP- and NP/NP-containing dumbbell compounds **18** and **19**, two different coupling reactions were carried out. A Pd-catalyzed cross-coupling reaction with the two-half-dumbbell compounds **10** and **17**, afforded the desired rigid MPTTF/NP-containing dumbbell compound **18** in 94% yield, whereas the rigid, degenerate NP/NP-containing dumbbell compound **19** was obtained in 76% yield by a homo-coupling reaction of the NP-

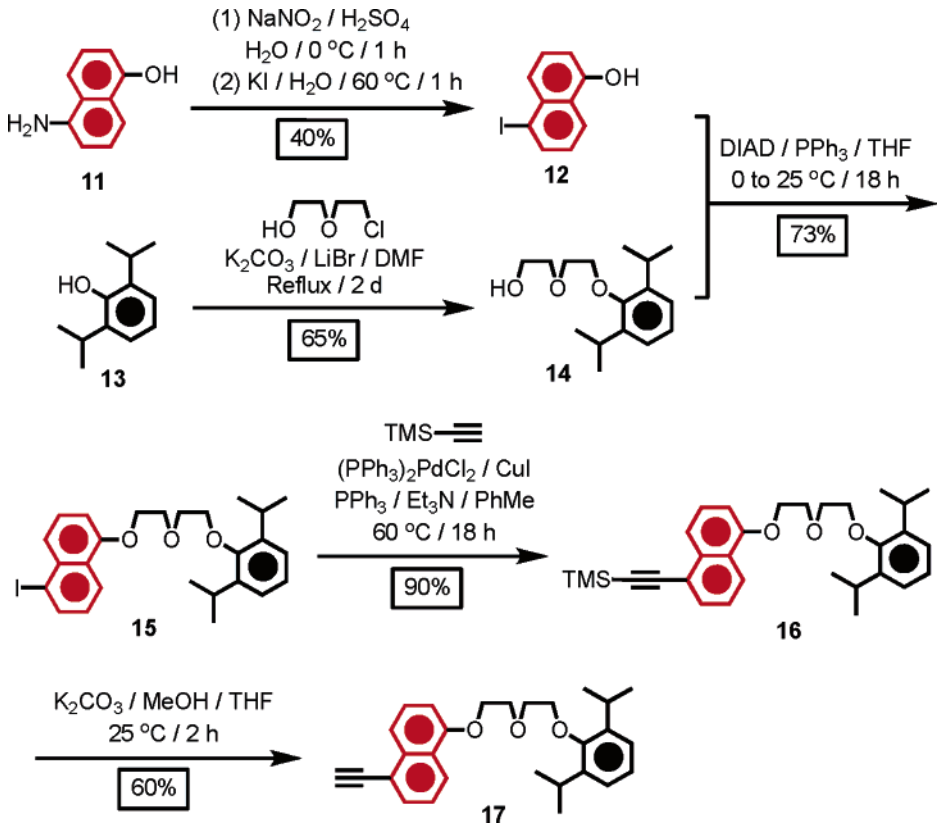
(19) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *50*, 4467−4470. (b) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627−630.

(20) The iodide-stoppered compound **9** was prepared by a Finkelstein reaction (see Supporting Information) of the bromide-stoppered compound **9a** (see Supporting Information), previously reported by Raehm, L.; Kern, J.-M.; Sauvage, J.-P. *Chem. Eur. J.* **1999**, *5*, 3310−3317.

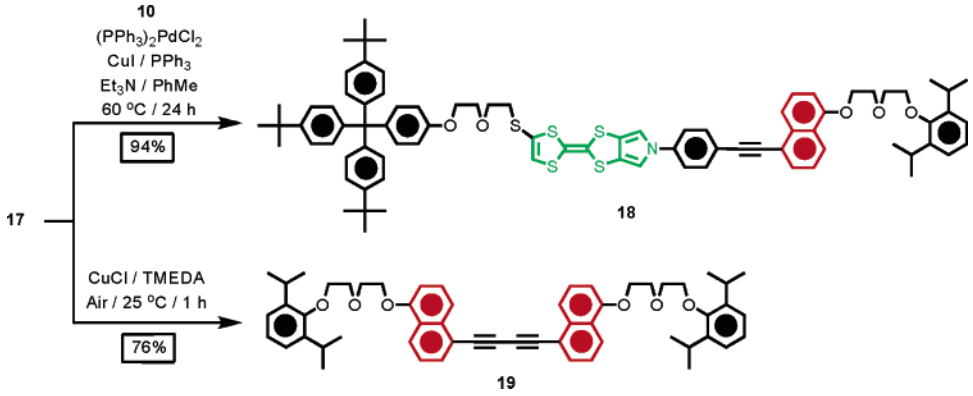
(21) (a) Jeppesen, J. O.; Takimiya, K.; Jensen, F.; Becher, J. *Org. Lett.* **1999**, *1*, 1291−1294. (b) Jeppesen, J. O.; Takimiya, K.; Jensen, F.; Brimert, T.; Nielsen, K.; Thorup, N.; Becher, J. *J. Org. Chem.* **2000**, *65*, 5794−5805.

(22) Jia, C.; Zhang, D.; Guo, K.; Wan, S.; Zhu, D. *Synthesis* **2002**, 2177−2182.

Scheme 2. Synthesis of the NP-Containing (Red) Half-Dumbbell **17**



Scheme 3. Synthesis of the Rigid MPTTF/NP-Containing Two-Station Dumbbell Compound **18** and the Degenerate NP/NP-Containing Dumbbell Compound **19**



containing half-dumbbell compound **17** using Cu(I)-promoted Hay oxidative coupling conditions.[23]

Generally, the two dumbbell compounds **18** and **19** underwent template-directed clipping reactions (Scheme 4) at high pressure[24] (10 kBar) with the dicationic precursor[6a] **20**·2PF_6 and 1,4-bis(bromomethyl)benzene (**21**) to give the corresponding [2]rotaxanes **1**·4PF_6 and **2**·4PF_6, respectively. The rigid MPTTF/NP-containing [2]rotaxane **1**·4PF_6 was obtained after counterion exchange from the template-directed high-pressure reaction in DMF, where the dumbbell compound **18** functions as a template around which the $CBPQT^{4+}$ ring forms from precursors **20**·2PF_6 and **21**. The [2]rotaxane **1**·4PF_6 was isolated in 23% yield as a green solid with a [3]rotaxane as a byproduct in 21% yield by preparative thin-layer chromatography (PTLC) using Me_2CO/NH_4PF_6 (100:1 v/w) as the eluent. Similarly, the degenerate NP/NP-containing [2]rotaxane **2**·4PF_6 was obtained following counterion exchange from the template-directed high-pressure reaction in DMF from the dumbbell compound **19**, with the precursors **20**·2PF_6 and **21**. The [2]rotaxane **2**·4PF_6 was isolated as a purple solid in 8% yield after column chromatography on silica gel using Me_2CO/NH_4PF_6 (100:1 v/w) as the eluent: once again, a [3]rotaxane was a byproduct in 6% yield.

Structural Characterization of [2]Rotaxanes by Mass Spectrometry. The [2]rotaxane structures were characterized unambiguously by electrospray ionization mass spectrometry (ESI-MS). A set of peaks (Table 1) corresponding to the consecutive loss of two, three, and four PF_6^- counterions were observed for both [2]rotaxanes **1**·4PF_6 and **2**·4PF_6. The ESI-MS of **1**·4PF_6 reveals a doubly charged peak at *m*/*z* of 1075.0 ($[M - 2PF_6]^{2+}$), a triply positively charged ($[M - 3PF_6]^{3+}$) signal at *m*/*z* of 668.3, and a quadruply positively charged ion

(23) Siemsen, P.; Livingston, R. C.; Diederich, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 2632−2657.
(24) Klärner, F.-G.; Wurche, F. *J. Prakt. Chem.* **2000**, *7*, 609−636.

Table 1. ESI-MS Data of the [2]Rotaxanes **1**·4PF_6 and **2**·4PF_6

	m/z				
[2]rotaxane	M^+ *A*	$[M - PF_6]^{+}$ [a]	$[M - 2PF_6]^{2+}$	$[M - 3PF_6]^{3+}$	$[M - 4PF_6]^{4+}$
1·4PF_6	(2440.7)	(2295.7)	1075.0	668.3	465.0
2·4PF_6	(1930.6)	(1785.6)	820.2	498.5	337.6

[a] Peaks corresponding to the molecular ions (M^+) and the loss of one PF_6^- counterion ($[M - PF_6]^+$) were not observed. These molecular weights are shown in parentheses however.

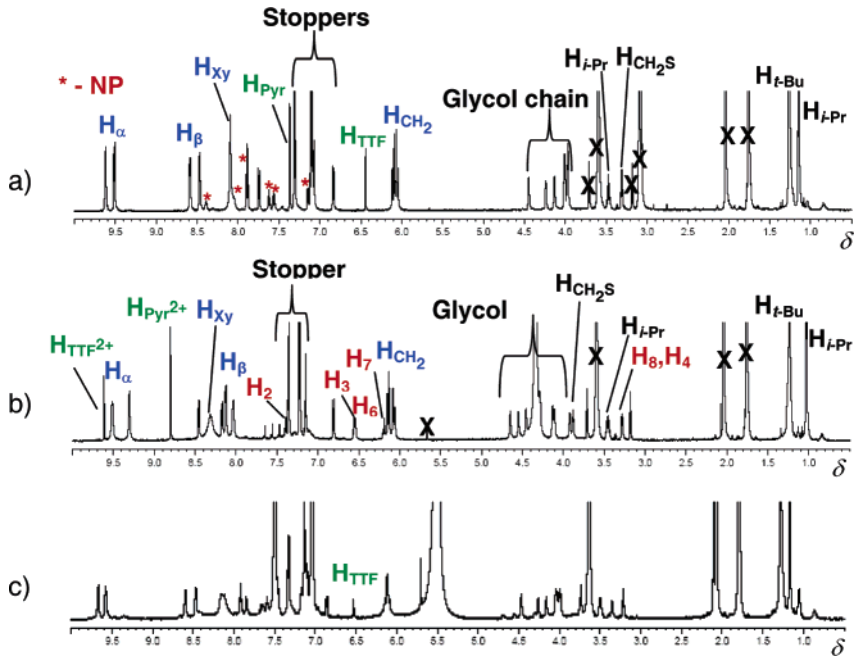
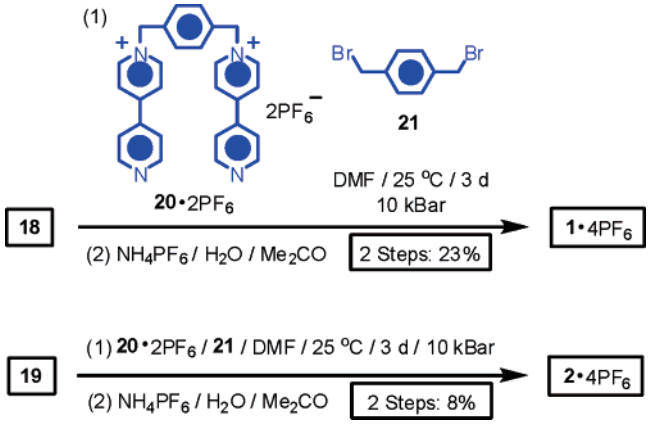


Figure 2. ^{1}H NMR spectra (600 MHz, $(CD_3)_2CO$) of **1**·4PF_6: (a) at 273 K, the solution is green; (b) after the addition of 2.0−2.5 equiv of the oxidant, the solution becomes red; (c) after the addition of Zn powder, the solution is green.

($[M - 4PF_6]^{4+}$) at *m*/*z* of 465.0. Besides these ions originating from the loss of PF_6^- counterions from the bistable [2]rotaxane, a singly charged positively signal at *m*/*z* of 561.2 is also observed, corresponding to the fragmentation of $CBPQT^{4+}$ ring into the **20**·2PF_6 fragment minus a PF_6^- counterion. The same pattern was observed in the ESI-MS of the degenerate [2]-rotaxane **2**·4PF_6, where doubly, triply, and quadruply positively charged peaks were observed at *m*/*z* of 820.2, 498.5, and 337.6, respectively.

Structural Characterization of [2]Rotaxanes by ^{1}H NMR Spectroscopy. An analysis of the ^{1}H NMR spectrum of **1**·4PF_6 recorded in $(CD_3)_2CO$ at various temperatures (198−298 K), reveals that the $CBPQT^{4+}$ ring predominantly encircles the MPTTF unit. This observation is quite surprising, as previous bistable [2]rotaxanes in which the two recognition units—MPTTF and (D)NP—are connected by flexible PEG linkers have been isolated as mixtures of the two possible translational isomers at room temperature.[2i] An inspection of the ^{1}H NMR spectrum (Figure 2a) reveals that all resonances are present only once in the case of **1**·4PF_6, whereas all the signals would be present twice and in various ratios, if the isolated [2]rotaxane **1**·4PF_6 had been a mixture of the two possible translational isomers.[25] To the limits of ^{1}H NMR spectroscopy, this represents a > 95 < 5 Boltzmann-weighted ratio, in which **1**·4PF_6 exists preferentially as a single translational isomer at room temperature in $(CD_3)_2CO$.

Scheme 4. Synthesis of [2]Rotaxanes **1**·4PF_6 and **2**·4PF_6



The most diagnostic evidence in favor of the assignment that **1**·4PF_6 exists as a single translational isomer predominantly, and hence that the $CBPQT^{4+}$ ring does not encircle the NP unit,

(25) This statement is only true, of course, if the equilibration between the two translational isomers is slow on the ^{1}H NMR timescale in $(CD_3)_2CO$ at room temperature. Since there was no evidence for a second set of signals at low temperatures, we are prepared to accept that equilibration is fast on the ^{1}H NMR timescale at room temperature and, if it does slow down at lower temperatures, then the extent to which the minor isomer is populated must be miniscule. If we assume fast exchange between the signals at room temperature for major and minor translational isomers, then the chemical shifts we observe for the signals associated with the six NP protons should differ in the bistable [2]rotaxane **1**·4PF_6 from those observed for its dumbbell precursor **18** where there is no $CBPQT^{4+}$ ring present. A comparison of the chemical shifts of these six protons in **18** (δ = 6.94, 7.46, 7.50, 7.80, 8.01, 8.35 in $CDCl_3$) with the chemical shifts for the same six protons in **1**·4PF_6 (δ = 7.14, 7.57, 7.62, 7.89, 8.09, 8.39 in $(CD_3)_2CO$) is good evidence, despite the running of the two spectra in different solvents, for the NP unit in **1**·4PF_6 being "free" from encirclement by $CBPQT^{4+}$ rings at room temperature in solution.

can be found by observing the NP proton resonances H_4 and H_8. Previous ^{1}H NMR studies on NP containing [2]rotaxanes as well as those performed on the degenerate NP-based [2]rotaxane **2**·4PF_6 reveal that the encirclement by the CBPQT^{4+} ring of the NP moiety results in a very significant upfield shift of the resonances of the NP H_4 and H_8 protons in the order of ~5 ppm. This upfield shift is not observed in the case of **1**·4PF_6 at either 198 K (see Supporting Information) or 298 K as the NP H_4 and H_8 protons resonate in the aromatic part of the spectrum supporting the interpretation that only a single-translational isomer is found primarily in solution over the sampled temperature range. This assignment is substantiated further by the ^{1}H DQ-COSY (double quantum correlation spectroscopy) spectrum for **1**·4PF_6, where all the scalar couplings for the NP protons are clearly evident in the low-field part of the spectrum (see Supporting Information). If an appreciable amount of NP units had been encircled, an easily recognizable scalar coupling from the low-field region to the high-field region would have been present.

Cooling down the sample of **1**·4PF_6 to 198 K in $(CD_3)_2CO$ does not significantly change the translational isomeric distribution. This inherent lack of temperature dependence has, to the best of our knowledge, never been observed before in any TTF/MPTTF-containing two-station [2]rotaxanes. Previously, it has been noted[2c,i] that lowering the temperature has a considerable influence on which station CBPQT^{4+} encircles. More specifically all previously isolated systems of this type have shown that lowering the temperature favors the situation where the NP station is encircled. It is thus evident that a temperature-independent "all-or-nothing" two-station [2]rotaxane system based on a TTF derivative has been created that presents the appearance of a single isomer > 95 < 5 in solution.

Chemical Switching of the Bistable [2]Rotaxane Monitored by ^{1}H NMR Spectroscopy. The switching properties of **1**·4PF_6 in solution have been invesitgated using ^{1}H NMR spectroscopy. Chemical switching can be achieved by oxidizing the MPTTF derivative using tris(*p*-bromophenyl)ammonium hexafluoroantimonate to its dicationic state (MPTTF^{2+}) and then reducing the MPTTF^{2+} dication back to its neutral state with Zn powder.[2e,f,i,3h]

The ^{1}H NMR spectrum (Figure 2a) of **1**·4PF_6 in $(CD_3)_2CO$ was recorded at 273 K first of all for comparison and then the MPTTF was oxidized to MPTTF^{2+} by adding 2.0−2.5 equiv of the oxidant, followed by running the ^{1}H NMR spectrum (Figure 2b). As a result of the oxidation process, the color of the solution changes from green to red as is expected from such a system on account of the generation of the MPTTF dication. A comparison between the ^{1}H NMR spectra[26] of the neutral and oxidized bistable [2]rotaxane reveals that the resonances associated with the H_{TTF}, H_{Pyr}, and H_{SCH2} protons are all shifted to lower fields (δ = 9.62, 8.80, and 3.88 ppm, respectively) relative to the neutral system (δ = 6.44, 7.37, and 3.31 ppm, respectively). Previously investigations[2i,27] have shown that this behavior is entirely consistent with the formation of a MPTTF^{2+} dication. Moreover, the resonances associated with the NP protons, H_4 and H_8, are shifted to a higher field (δ = 3.28 ppm) as a consequence of the NP moiety being encircled by the CBPQT^{4+} ring. These observations support the proposed switching mechanism of the MPTTF/NP-containing [2]rotaxane.

The addition of a small amount of Zn powder followed by vigorous shaking returns the MPTTF^{2+} to its neutral form. The resulting ^{1}H NMR spectrum (Figure 2c) correlates well with the original spectrum (Figure 2a) before oxidation. One notable difference is the presence of two large signals at δ = 7.50 and 7.04 ppm, corresponding to tris(*p*-bromophenyl)amine, the reduced form of the oxidant. Thus, the chemically induced switching of this bistable [2]rotaxane was shown to adopt the switched state in which the NP station is encircled by the CBPQT^{4+} ring upon oxidation and return to the stable ground state upon reduction.

Dynamic ^{1}H NMR Spectroscopy of Degenerate [2]Rotaxane. Since the switching rates of bistable [2]rotaxanes play an important role in relation to their performance in device settings, it was crucial for us to study the effect of rigidifying the linker between the recognition sites on the rate of return from the metastable state to the ground state in **2**·4PF_6. For this purpose variable temperature (VT) NMR spectroscopic studies were performed on the structurally related and degenerate [2]rotaxane **2**·4PF_6.

As both recognition sites are identical in **2**·4PF_6, the shuttling process will be between two isoenergetic co-conformers. In the absence of the ring, the dumbbell component of this rotaxane possesses an axis of symmetry normal to its long axis that bisects it affording two equivalent halves. Localization of the CBPQT^{4+} ring on one of the two possible recognition sites breaks this symmetry, resulting in two nonequivalent halves. If the ring shuttles between the two sites rapidly on the ^{1}H NMR timescale, then it will appear as though the axial symmetry has been restored as is the case for **2**·4PF_6 at high temperatures (Figure 3). As the temperature is decreased, the shuttling rate slows down and eventually, at a low enough temperature, the symmetry will be broken and two sets of signals will be observed for the protons of the two stoppers. One set corresponds to the stopper close to the recognition site where the CBPQT^{4+} ring resides and the other for the more distant stopper.

The temperature dependence of the ^{1}H NMR spectrum (Figure 3) of **2**·4PF_6 was studied by varying the temperature of the sample from 270 down to 185 K.

An estimation of the symmetry-averaging shuttling process was obtained using the coalescence method[28] and it was found[29] that the free energy of activation ($\Delta G_c^{\ddagger}$) for this process is 9.6 ± 0.1 kcal/mol at 199 K. This activation barrier is relatively low compared with those obtained from previous studies[2g] on similar degenerate [2]rotaxanes ($\Delta G_c^{\ddagger} \approx 15.0$ kcal/mol at ~240 K), which have more flexible PEG linkers between the two NP stations. The difference most likely stems from two factors, namely, (i) the interaction between the NP units and the CPBQT^{4+} ring in **2**·4PF_6 is substantially weaker in this system since the stabilizing intramolecular [C−H···O] interactions are severely curtailed by the absence of enough and appropriate oxygen atoms and (ii) the rigid hydrocarbon linker does not

(26) The ^{1}H NMR spectrum of oxidized **1**·4PF_6 was recorded at various temperatures and since the best spectrum was obtained at 265 K, this spectrum was used as a comparison.

(27) Vignon, S. A.; Stoddart, J. F. *Collect. Czech. Chem. Commun.* **2005**, *10*, 1493−1576.

(28) In the coalescence method, the rate of exchange at the point of coalescence is calculated from the separation, $\Delta\upsilon$, between the two peaks at minimum exchange (low temperature) using the equation, $k_{ex} = (\pi\Delta\upsilon)/\sqrt{2}$. The rate constant, k_{ex}, is then entered into the Eyring equation, $\Delta G_c^{\ddagger} = -RT_c \ln(k_{ex}h/k_bT_c)$, along with the coalescence temperature, T_c, in order to calculate the free energy of activation, $\Delta G_c^{\ddagger}$. See *Dynamic NMR Spectroscopy*; Sandstrom, J., Ed.; Academic Press: New York, 1982.

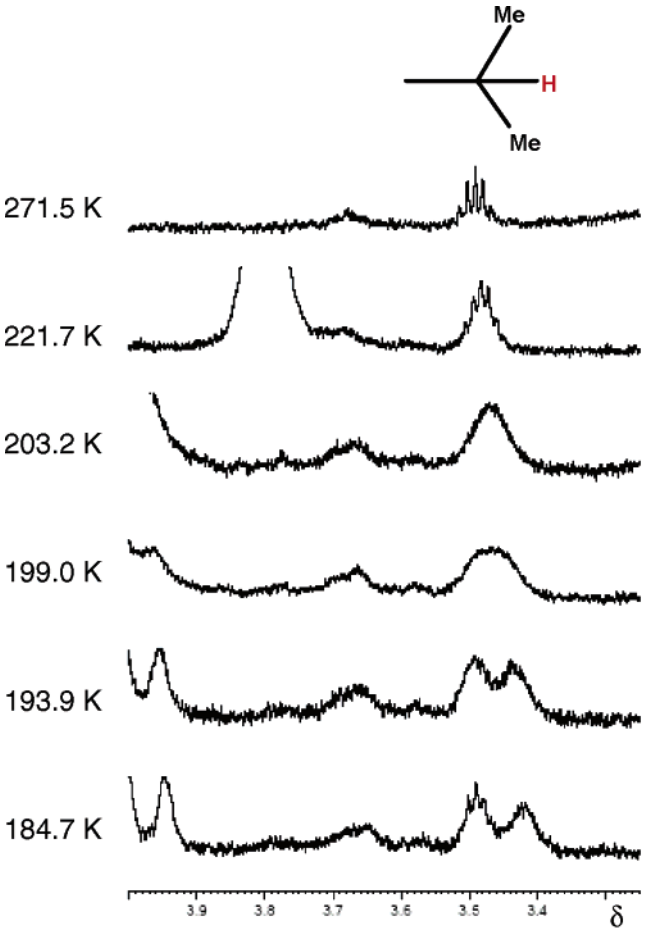


Figure 3. Section of the temperature-dependent ^{1}H NMR spectrum (600 MHz, $(CD_3)_2CO$) of **2**·4PF$_6$. The splitting of the resonances associated with the methine protons of the isopropyl groups was used to probe the shuttling process and the coalescence data were used to calculate $\Delta G_c^{\ddagger}$.

interact with the CBPQT^{4+} ring in the same manner as do the PEG chains. It is expected that entropic and enthalpic contributions to the barrier will be simpler to interpret in the case of the rigid [2]rotaxanes and will lead us to the view that the shuttling process has less friction and consequently is faster. This investigation shows that the shuttling rates in [2]rotaxanes can be tuned by using appropriate linkers between the recognition sites.

Photophysical Properties. In order to understand the behavior and physical properties of the ground state systems, as well as the oxidized systems, a series of UV−visible (UV−vis) spectroscopic investigations have been carried out.

(a) Half-Dumbbells and Dumbbells. The two half-dumbbell compounds **10** and **17** serve as reference compounds for the chromophore units present in the full dumbbell compounds **18** and **19**. The UV−vis spectrum (Figure 4) of the MPTTF-containing half-dumbbell derivative **10** can be attributed to the absorption of the MPTTF unit, whereas in **17**, the spectrum results from the incorporated NP unit. The UV−vis spectrum of the two-station dumbbell compound **18** is very similar to the sum of the spectra of the model compounds **10** and **17**, as indicated by the broad absorption around 335 nm. Notably, the observed continuous absorption stretching from 335 nm to approximately 530 nm in **18** might result from the internal transition of the conjugated backbone, linking the MPTTF and the NP stations. As expected, **19** has an intense absorption situated around 370 nm arising from the two NP units in the dumbbells backbone.

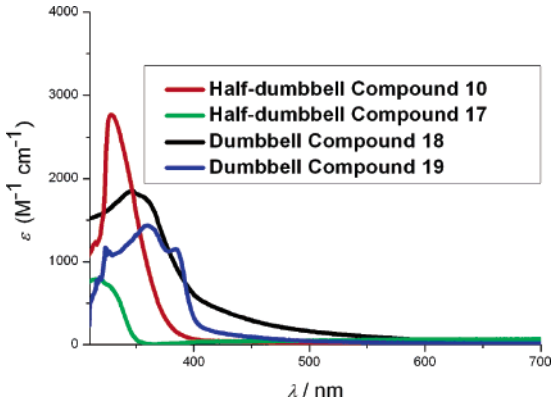


Figure 4. Comparison of the absorption spectra of **18** and **19** as well as **10** and **17**. The spectra for **17** and **18** were recorded in MeCN at 298 K, whereas those for **10** and **19** were recorded in Me_2CO at 298 K.

(b) Rotaxanes. A comparison of the UV−vis spectra recorded for **1**·4PF$_6$ and **2**·4PF$_6$ reveals, as expected, major differences. A broad and relatively intense charge transfer (CT) band is observed (Figure 5) at 810 nm for **1**·4PF$_6$. This absorption band reflects the encirclement of the MPTTF unit by the CBPQT^{4+} ring in **1**·4PF$_6$, which gives the solution its green color. On the other hand, the CT band in **2**·4PF$_6$ is observed at 470 nm, corresponding to the encirclement of the NP unit by the CBPQT^{4+} ring, which gives the solution its red color. The absorption spectrum of **1**·4PF$_6$ in MeCN indicates that the CT band is fully symmetric and centered around 810 nm, whereas

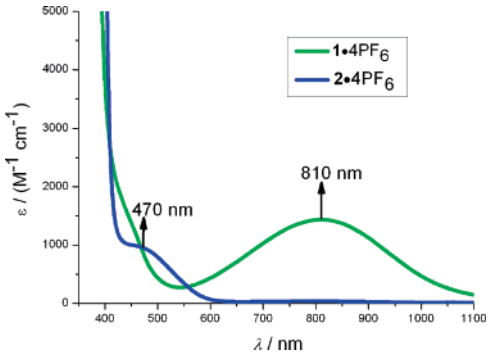


Figure 5. Comparison of the absorption spectra of **1**·4PF$_6$ and **2**·4PF$_6$ recorded in MeCN at 298 K.

there is no CT band observed around 470 nm as in **2**·4PF$_6$. Such symmetric CT bands have also been observed[2c] in previously studied two-station (pseudo) [2]rotaxanes. In the case of two-station MPTTF-containing [2]rotaxanes, two different observations regarding the UV−vis behavior have been made in the past. First of all, the CT band has not been fully symmetric around the 800 nm band originating from the MPTTF-CBPQT^{4+} interaction, as a consequence of either the fact that the NP unit is encircled by the CBPQT^{4+} ring, giving rise to a 470 nm CT band. There has been some evidence of the existence of alongside CT interactions between the CBPQT^{4+} ring, which is positioned on the NP station, and the MPTTF unit giving

(29) The methine proton in the isopropyl group on the stoppers was used in variable temperature NMR spectroscopy to probe the dynamic process. The investigation was performed on a 600 MHz NMR spectrometer as this high field instrument enabled the observation of the unsymmetrical [2]rotaxane.

rise to an asymmetry in the CT band.[2c] Therefore, the preserved symmetry of the MPTTF/CBPQT^{4+} CT band in this case supports the assignment that the CBPQT^{4+} ring encircles the MPTTF unit predominantly, as no back-folding effect is possible in this molecule on account of the inherent rigidity of the linker between the NP and MPTTF units.

The assignment of the exact position of the CT band, originating from the interaction between the NP unit and the CBPQT^{4+} ring in the degenerate [2]rotaxane **2**·4PF$_6$, correlates with the ^{1}H NMR spectroscopy results, which show that the CBPQT^{4+} ring predominantly encircles the MPTTF unit in the two-station [2]rotaxane **1**·4PF$_6$. A series of experiments were carried out to investigate whether or not the translational isomeric distribution is affected by varying the temperature. The temperature dependence that is observed (see Supporting Information) on heating a solution of **1**·4PF$_6$ in MeCN, arises solely from the trivial effect of thermal dilution, meaning that the CT band situated at 810 nm dominates at all temperatures ranging from 283 to 323 K, but a decrease is observed in the CT band intensity at higher temperatures as a result of the expansion of the solvent. No significant effect of the fluctuating temperature is observed in the region around 470 nm, again indicating that the CBPQT^{4+} ring predominantly encircles the MPTTF unit from 283 to 323 K (see Supporting Information). The lack of temperature dependence on the translational isomeric distribution in **1**·4PF$_6$ confirms the assumption that the CBPQT^{4+} ring encircles the MPTTF unit and that this conformation constitutes the energetic ground-state at a wide range of temperatures, not only from 198 to 298 K as determined by ^{1}H NMR but also up to 323 K. This finding suggests that the PEG spacer has played a significant role in previous bistable [2]rotaxanes, wherein significant temperature effects have been the basis for a thorough review of the underlying thermodynamics controlling translational isomerism,[30] as well as for a correlation[3i] with the temperature effects of molecular switch tunnel junction devices that arise from the concomitant effect of temperature on the translational isomerism of bistable [2]-rotaxanes.

The effect of the solvent on the absorption spectrum (Figure 6) of **1**·4PF$_6$ was investigated in Me_2CO, $CHCl_3$, and MeCN. Since the CT bands represent a charge redistribution going from the ground state to the excited state, one would expect that changing the solvent would greatly affect the chromophoric properties of the system as well as possibly changing the translational isomeric distribution. Comparatively, the variation of absorption spectra, recorded in Me_2CO and MeCN is small, as both solvents yields clear green solutions with a distinct CT band at approximately 800 nm. Another feature, assumed to be the local transition of the MPTTF unit, is also observed around 365 nm. Changing the solvent from Me_2CO to the less polar solvent $CHCl_3$, influences the absorption spectra, as the CT interaction is red-shifted by 135 nm out of the visible area and into the near-infrared (NIR) area, yielding an orange solution, which at first might be taken as an indication of a change in the isomeric distribution. However, inspection of the absorption spectra show that the observed color change is caused by the CT band being red-shifted by 135 nm out of the visible area and into the near-infrared (NIR) region. Also the local MPTTF transition is red-shifted to 390 nm because of the solvent's polarities. Thus, it appears that in $CHCl_3$ the entire spectrum is red-shifted by approximately 135 nm relative to the more polar solvents MeCN and Me_2CO.

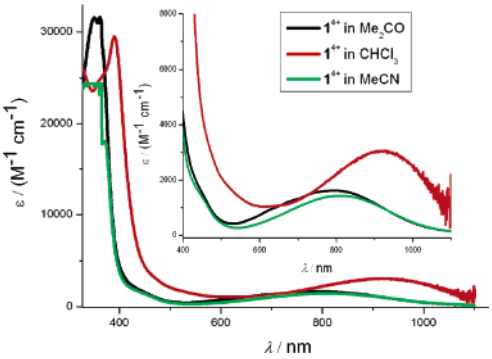


Figure 6. Absorption spectra of **1**·4PF$_6$ recorded in Me_2CO, $CHCl_3$, and MeCN displaying the significant red-shift in the absorption maxima in going from Me_2CO/MeCN to $CHCl_3$. Inserted is a magnification of the CT band in the visible to NIR area.

Chemical Switching of the Bistable [2]Rotaxane Monitored by Absorption Spectroscopy. The chemical oxidant Fe(ClO$_4$)$_3$ has been employed to oxidize the MPTTF unit of the [2]rotaxane **1**·4PF$_6$ and the associated spectroscopic changes were followed by absorption spectroscopy. The titration of 1.0 equiv of Fe(ClO$_4$)$_3$ with **1**·4PF$_6$ (see Supporting Information) resulted in the formation of three dominant absorptions centered around 725, 441, and 350 nm. These absorptions, originating from the mono-oxidized MPTTF$^{\bullet+}$ unit are very intense, compared to the initial CT band at 810 nm; hence, it is not possible to follow the position of the CBPQT^{4+} ring along the dumbbell. Addition of another equivalent of Fe(ClO$_4$)$_3$ results in a bleach of the three absorption bands attributed to the MPTTF$^{\bullet+}$ and the appearance of a new broad absorption centered around 575 nm, resulting from the formation of the doubly oxidized MPTTF^{2+} unit. Again, the much more intense absorption from the MPTTF^{2+} unit dominates the CT band originating from the NP unit encircled by the CBPQT^{4+} ring, making it impossible to speculate about the position of the CBPQT^{4+} ring from this experiment.

Electrochemical Switching Investigated by CV, DPV, and SEC. The electrochemically induced switching behavior of the rigid rotaxane **1**·4PF$_6$ was investigated using cyclic voltammetry (CV), differential pulse voltammetry (DPV), and UV−vis spectroelectrochemistry (SEC). The half-dumbbell compounds **10** and **17**, the rigid MPTTF/NP-containing dumbbell compound **18**, and the free cyclophane CBPQT^{4+} were studied as references. The CV traces for these compounds are shown in Figure 7. The half-dumbbell compound **10** shows (Figure 7a) two reversible and monoelectronic oxidization waves, which are the signatures of the stepwise oxidation process of the MPTTF unit.[11] The half-wave potentials (see Supporting Information) of the first and second oxidization of MPTTF half-dumbbell compound **10** at +0.55 and +0.75 V (vs SCE) were determined by the DPV measurement. The oxidation (Figure 7b) of the NP half-dumbbell compound **17** is irreversible, and its anodic peak lies at +1.47 V (vs SCE). The rigid dumbbell compound **18** showed two reversible and one irreversible oxidation processes associated with the MPTTF and NP unit, respectively (Figure 7c). The half-wave potentials of the MPTTF unit in the rigid

(30) Moonen, N. N. P.; Flood, A. H.; Fernandez, J. M.; Stoddart, J. F. *Top. Curr. Chem.* **2005**, *262*, 99−132.

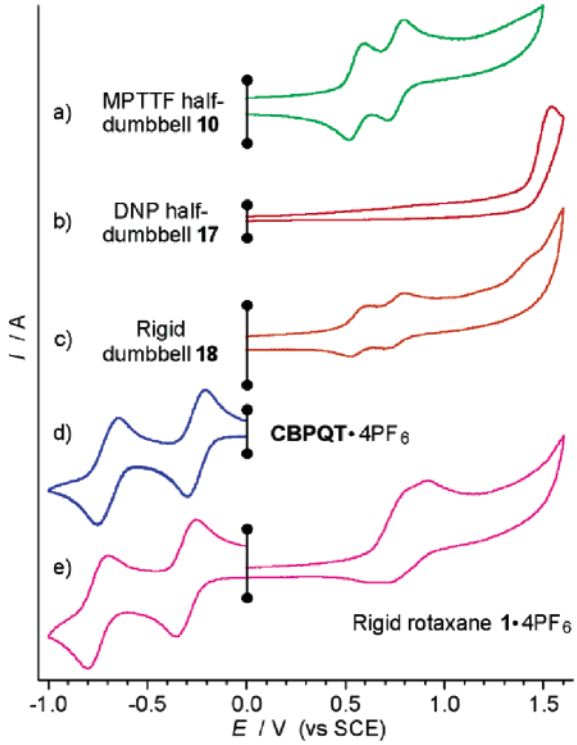


Figure 7. Cyclic voltammetry of the (a) MPTTF half-dumbbell compound **10**, (b) NP half-dumbbell compound **17**, (c) rigid dumbbell component **18**, (d) CBPQT^{4+}, and (e) rigid rotaxane **1**·4PF$_6$. The data have been scaled for ease of comparison of the CVs, and the scale bars at 0.0 V correspond to 5 μA. All data presented were recorded at 200 mV s^{-1} in argon-purged DMF. 1.0 mM of the sample in 0.1 M TBA·PF$_6$ solution, 298 K, working electrode: glassy carbon electrode (0.0178 cm^2).

dumbbell compound **18** (+0.55 and +0.76 V vs SCE) are almost the same as those of the precursor half-dumbbell compound **10**. Although redox potentials are strictly thermodynamic properties that relate to the stabilities of both neutral reactant and oxidized product, the fact that the oxidation (+1.41 V vs SCE) of the NP unit in **18** occurs at a slightly lower potential than that for **17** (+1.47 V vs SCE) is consistent with the extension of π-conjugation observed in the UV−vis spectroscopic data. The cyclophane CBPQT^{4+} shows the two characteristic,[6a] reversible two-electron reduction processes at −0.29 V and −0.72 V (vs SCE) (Figure 7d).

The electrochemical properties of the rigid [2]rotaxane **1**·4PF$_6$ are distinctly different from (Figure 7e) that of its rigid dumbbell component **18**. In the oxidation region (V > 0 V), two close anodic peaks were observed between +0.80 and +0.90 V (vs SCE). The integral of the whole process corresponds to a two-electron oxidation, suggesting that the first and second oxidation of the MPTTF unit occur at almost the same potential. The more positive first oxidation potential of the MPTTF (or TTF) unit—when encircled by the CBPQT^{4+} ring—has been reported previous studies on bistable [2]rotaxanes[2,3i] and [2]catenanes.[31] This phenomenon suggests that CBPQT^{4+} ring encircles MPTTF in the ground state. The oxidation of the NP unit does not occur until +1.6 V (vs SCE), a potential that is higher than is required for the oxidation of the bare NP unit. This result suggests that the CBPQT^{4+} ring is translocated from the MPTTF to NP unit after the oxidation of the MPTTF unit and thus hinders the oxidation of the NP unit through CT interaction. The cathodic peaks for the first and second reduction of the MPTTF unit (MPTTF^{2+} → MPTTF$^{\bullet+}$ → MPTTF) are not separated well in the CV measurement.

The anodic sweep of the CV indicates that the MPTTF station is oxidized 250 mV more anodic than the dumbbell component, suggesting that it is tightly encircled by the CBPQT^{4+} ring[3h] (i.e., it is not in equilibrium with the NP station). At ~800 mV, the monocation is formed and the CBPQT^{4+} ring is typically repelled away, allowing the second oxidation generating the dication MPTTF^{2+} to occur at the same potential as that observed in the dumbbell. In the present case, however, the dication is formed at a potential greater than that for the dumbbell by ~100 mV. This observation is consistent with the movement of the ring to the NP unit but that the electrostatic effect[13] of the tetracationic CBPQT^{4+} ring on the cationic MPTTF$^{+\bullet/2+}$ unit is still being felt through space across the length of the rigid spacer. The return sweep of the CV shows the anodic shift for the dication's reduction to the monocation. The anodic shift for the reformation of the neutral MPTTF unit is larger than that observed in previous systems and is consistent with the rapid and unhindered return of the CBPQT^{4+} ring to the neutral MPTTF unit. In summary, the electrochemistry data confirm that the CBPQT^{4+} is switched reversibly between the MPTTF and NP units during a cycle of two-electron oxidation and reduction and potentially only after one-electron oxidation.

The reduction behavior of the CBPQT^{4+} ring in the rigid rotaxane **1**·4PF$_6$ is similar to that in the simple one-station [2]-rotaxanes. The half-wave potentials of the CBPQT^{4+} ring were determined to be −0.25 and −0.70 V (vs SCE). These values are both more negative than those for the free CBPQT^{4+}, suggesting that the effect of the dumbbell component on the electrochemical behavior of the CBPQT^{4+} is consistent with a MPTTF−CBPQT^{4+} CT interaction. The cathodic shift of the second reduction peak has not been observed all that often. It suggests that there is an interaction between the reduced forms of the ring and dumbbell component. The first reduction peak of the CBPQT^{4+} ring in rotaxanes and catenanes often shows separations[2d,g,i, 27, 31] on account of the nonequivalent environment for the two bipyridinium units. In the case of rotaxanes, the back-folding phenomena may be the cause of why the two bipyridinium units have nonequivalent electrochemical environments. Although there is an absence of direct separation in the first reduction peak of CBPQT^{4+} in the rigid rotaxane **1**·4PF$_6$ there is a peak broadening when compared to CBPQT^{4+} as illustrated in Figure 7, panels e and d, respectively. This result suggests that back-folding phenomena is much reduced and that its contribution to previous peak separations may be larger than has been otherwise considered.

The UV−vis spectroscopic changes associated with the electrochemical oxidation process of the rigid rotaxane **1**·4PF$_6$ were recorded in order to shed some light on the mechanical movement of the CBPQT^{4+} ring between the two electron-rich units MPTTF and NP (Figure 8).

The ground state UV−vis spectrum of **1**·4PF$_6$ displays (Figure 8a) the characteristic CT band at 820 nm, corresponding to the MPTTF−CBPQT^{4+} CT interaction. By applying a potential of +0.75 V (V_{ap}), the ground-state bands bleach and are replaced by bands in the visible region at 441 and 725 nm,

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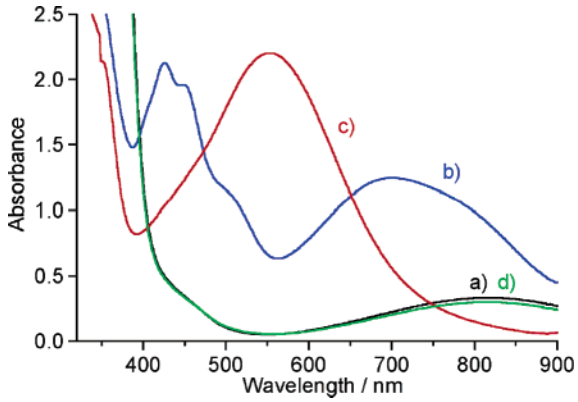

Figure 8. UV−vis spectroelectrochemistry of the rigid rotaxane **1**·4PF_6 (1.0 mM **1**·4PF_6 in 0.1 M TBA·PF_6/MeCN) recorded at applied voltage (V_{ap}): (a) ground-state $V_{ap} = 0$ V; (b) $V_{ap} = +0.75$ V (vs Ag) to generate $MPTTF^{\bullet+}$ radical cation; (c) $V_{ap} = +0.95$ V (vs Ag) to generate $MPTTF^{2+}$ dication; and (d) $V_{ap} = 0$ V to regenerate the ground state.

which are associated with the absorption of the $MPTTF^{\bullet+}$ radical cation (Figure 8b). After switching the applied potential from +0.75 to +0.95 V, the spectrum displays a bleaching of the $MPTTF^{\bullet+}$ bands, which is concomitant with the formation of a large broad band at 555 nm, characteristic of the $MPTTF^{2+}$ dication absorption (Figure 8c). These observations mirror those obtained for the chemical oxidation of **1**·4PF_6 in which the chromophores of the MPTTF cations dominate the visible region. The original spectrum at the ground state was fully reproduced by leaving the solution at room temperature for overnight at 0 V (Figure 8d). The electrochemical reaction is fully reversible.

Conclusion

In conclusion, the syntheses and characterization of a pair of rigid, two-station [2]rotaxanes, the bistable MPTTF/NP-containing [2]rotaxane **1**·4PF_6 and the degenerate NP/NP-containing [2]rotaxane **2**·4PF_6, have been reported. The incorporation of a rigid spacer into the two-station [2]rotaxane **1**·4PF_6 results in a very favorable and temperature-independent isomeric distribution of the isolated compound, > 95 < 5, in favor of the translational isomer where the $CBPQT^{4+}$ ring encircles the MPTTF unit. This finding is quite surprising as all other MPTTF-containing two-station [2]rotaxanes investigated so far have been mixtures of the two possible translational isomers whose ratios vary significantly with temperature implicating the role of the spacer in modulating the effect of temperature on each isomer. It is believed that the rigid backbone linking the two stations in **1**·4PF_6 effectively minimizes the back-folding effect associated with the dumbbell, thereby favoring the translational isomer where the $CBPQT^{4+}$ ring encircles the stronger donor, namely, the MPTTF unit. By employing dynamic ^{1}H NMR measurements on the degenerate [2]rotaxane **2**·4PF_6, it was found that the shuttling barrier over the 1.0 nm distance is significantly lower—indeed, by more than 5 kcal/mol—than that found previously in other non-rigid rotaxanes, implying that this barrier can be fine-tuned by changing the molecular architecture. In order for these molecules to work as molecular switches, one has to be able to switch the position of the $CBPQT^{4+}$ ring from the ground-state position around the MPTTF unit to the NP station by applying an appropriate stimulus. We have shown here that the two-station [2]rotaxane **1**·4PF_6 is addressable in solution by electrochemical, as well as by chemical stimuli. Cyclic voltammetry suggests that oxidation to the dication and reduction back to the neutral form results in a complete switch of 1.5 nm between two close to "all-or-nothing" states. The range of favorable properties introduced with the rigid linker make this molecular design an interesting candidate for the construction of molecular switches that could be expected to display strong on−off ratios that are temperature-independent and exhibit rapid kinetics in suitably designed devices. Finally, these functional rigid bistable [2]-rotaxanes will serve as an important starting point for the utilization of rigidity when well-defined structures and functions are of the outmost importance, such as in molecular pistons and simple motor molecules.

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Supporting Information Available: Synthetic procedure of all compounds as well as the relevant NMR and UV−vis spectroscopic data. Complete ref 6a. This material is available free of charge via the Internet at http://pubs.acs.org.

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