

REDOX-INDUCED RING SHUTTLLING AND EVIDENCE FOR FOLDED STRUCTURES IN LONG AND FLEXIBLE TWO-STATION ROTAXANES

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Dedicated to Professor Sergio Roffia on the occasion of his retirement.

Two dumbbell-shaped components with tetraarylmethane-type stoppers – one hydrophobic and one hydrophilic – and a rod-like section containing a tetrathiafulvalene (TTF) unit and a 1,5-dioxynaphthalene (DNP) moiety as electron-donating units, and their [2]rotaxanes, incorporating the cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺) cyclophane as their electron-accepting ring component, have been synthesized, the latter using template-directed protocols. The two amphiphilic [2]rotaxanes, which differ from each other only in the lengths of the polyether chains associated with their hydrophilic stoppers, were designed in order (i) to have them exhibit enhanced amphiphilicities and, by altering the lengths of polyether chains, (ii) to improve the qualities of their Langmuir-Blodgett films, and by removing the phenolic residues, (iii) to increase the oxidative stabilities of these switchable molecules, and so extend the lifetimes of electronic devices fabricated from amphiphilic hysteretic molecular switches of this type. UV-VIS absorption and ¹H NMR spectra, as well as electrochemical measurements, show that both [2]rotaxanes exist to all intents and purposes in solution as the translational isomer in which the CBPQT⁴⁺ cyclophane surrounds the TTF unit. Evidence has also been obtained for the presence in solution of folded conformations of these [2]rotaxanes. While ox/red stimulation of the TTF unit causes shuttling of the CBPQT⁴⁺ cyclophane between the TTF and DNP stations, reduction of CBPQT⁴⁺ causes unfolding of the [2]rotaxane molecules.

Keywords: Molecular shuttles; Rotaxanes; Tetrathiafulvalene; Cyclophanes; Charge-transfer interactions; Bipyridinium ions; Photochemistry; Electrochemistry.

Two-station [2]rotaxanes are currently the subject of extensive investigations since controllable shuttling of the ring between the two stations can be exploited for mechanical and switching purposes^{1,2} in connection with the construction of molecular-level machinery and information processors³. In continuance of our studies in this field^{4,5}, we have synthesized two new [2]rotaxanes, consisting of the electron-accepting cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺) ring component and two novel dumbbell-shaped components. The precursor dumbbell compounds, which act as efficient templates for the formation of the encircling CBPQT⁴⁺ ring, comprise two tetraarylmethane-type stoppers (one hydrophobic and the other hydrophilic) and a rod-like section containing tetrathiafulvalene (TTF) and 1,5-dioxynaphthalene (DNP) derivatives as electron-donating units which act as recognition sites (stations) for the electron-accepting ring. The two dumbbells differ from each other as a result of the lengths of the polyether chains associated with their hydrophilic stoppers. They are also an approximately one-to-one mixture of *cis* and *trans* isomers as a result of rotation (fast on the laboratory timescale and slow on the NMR timescale) around the formal carbon-carbon double bond between the two five-membered rings in their TTF units^{5a,5c}. We will discover that this configurational isomerism is also expressed in the two [2]rotaxanes. The structural formulas for the rotaxanes **1**·4PF₆ and **2**·4PF₆ and of their respective dumbbell compounds **3** and **4** are shown in Fig. 1.

Presently, our design of amphiphilic, bistable rotaxanes is being driven (Fig. 2) by a desire to use compounds which are well characterized in solution, both with respect to their amphiphilic properties and their redox switching behaviors, and are anticipated to be robust and to act coherently in condensed phases and also in solid-state devices. To this end, we decided to remove the oxidatively sensitive phenolic residues from the hydrophilic stoppers from earlier generations⁷ of molecular switches and so impart improved stabilities upon electronic devices based on amphiphilic, bistable rotaxanes by giving them much longer lifetimes during their voltage-driven redox switching. Since it is of paramount importance to incorporate these molecules in an oriented and coherent fashion in such devices, they need to be self-organized, for example, in a two-dimensional fashion at the air-water interface as Langmuir-Blodgett (LB) films. With this objective in mind, we have varied the lengths of polyether chains associated with the hydrophilic stoppers. In contrast with previously investigated⁷ compounds of this family, the hydrophilic stoppers present in **1**⁴⁺ and **2**⁴⁺ should exhibit much weaker electron-donor properties on account of the fact that the four aromatic rings in the tetrasubstituted tetraarylmethane core of the



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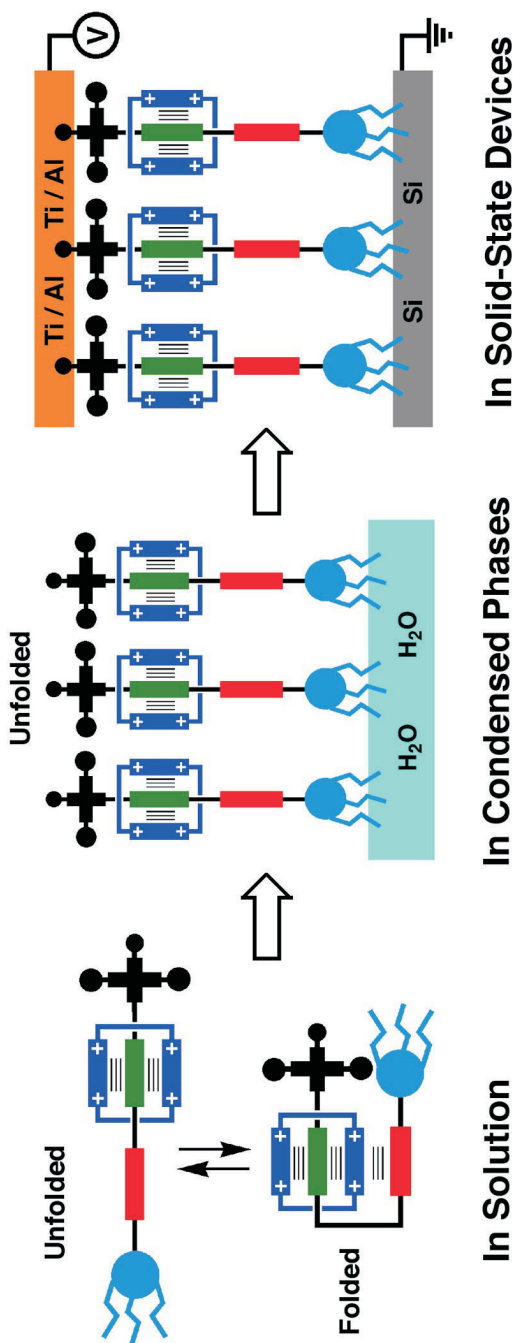


FIG. 2
Amphiphilic, bistable [2]rotaxanes in solution, condensed phases, and solid-state devices

hydrophilic stoppers are (i) not directly linked to oxygen atoms and (ii) are sterically inaccessible for efficient π - π stacking. The present investigation has been undertaken to establish whether this structural modification influences the redox-controlled shuttling and conformational folding observed in MeCN solutions of these two [2]rotaxanes. Earlier studies^{5b,5c,6} in solution have shown that, for related long and flexible pseudorotaxanes and rotaxanes, the folding-unfolding processes can be rendered considerably more complex since alongside interactions of the CBPQT⁴⁺ ring with the DNP unit are probably supplemented by π - π stacking interactions involving readily accessible electron-rich aromatic rings in their hydrophilic stoppers.

Previous investigations⁷ have shown that, in pseudorotaxanes, rotaxanes, and catenanes containing TTF- and DNP-type stations, one predominant translational isomer⁸ is present – namely, the one in which the CBPQT⁴⁺ ring encircles the TTF unit since it is the much stronger electron donor of the two. Here, we report our investigation on (i) the photophysical properties and (ii) the electrochemical behavior of the [2]rotaxanes **1**⁴⁺ and **2**⁴⁺, and of the related dumbbell compounds **3** and **4** in MeCN solution at room temperature. Model compounds for the hydrophobic and hydrophilic stoppers – namely, **5** and **6**, respectively – are portrayed in Fig. 3, along with the structural formulas for CBPQT·4PF₆[−], TTF, and 1,5-dimethoxynaphthalene (DMN). These compounds will be used as references in the photophysical and electrochemical investigations for the photo- and electroactive units

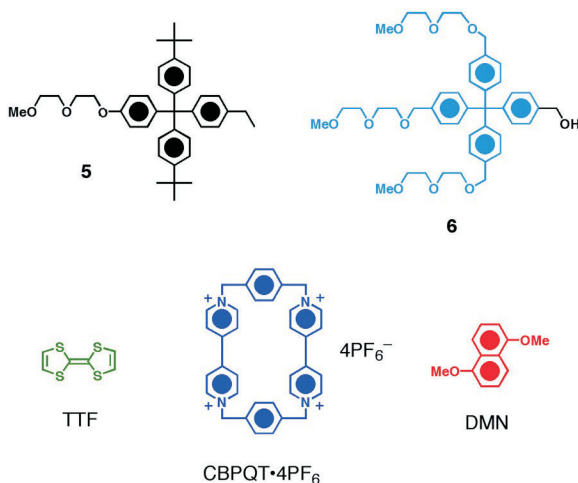


FIG. 3
Structural formulas of model compounds **5**, **6**, TTF, CBPQT·4PF₆[−], and DMN

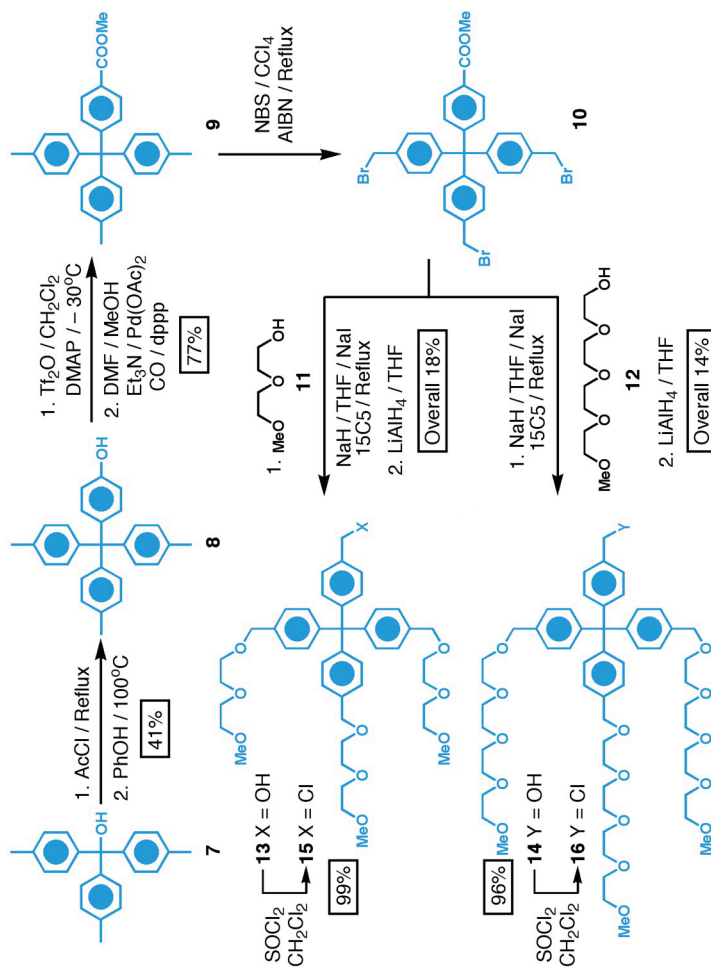
present in the rotaxanes and the free dumbbells. Although these investigations did bring some understanding to the issue of conformational isomerism between folded and unfolded conformations of 1^{4+} and 2^{4+} , they did not allow us to probe the configurational isomerism involving *cis* and *trans* isomers of 1^{4+} , 2^{4+} , **3**, and **4**. And so we record here (iii) how ^1H NMR spectroscopy has been used to probe the configurational isomerism present in all these compounds in solution. Finally, we describe (iv) the chemical ox/red stimulation conditions that promote “clean” mechanical switching between the different redox states of the two [2]rotaxanes.

RESULTS AND DISCUSSION

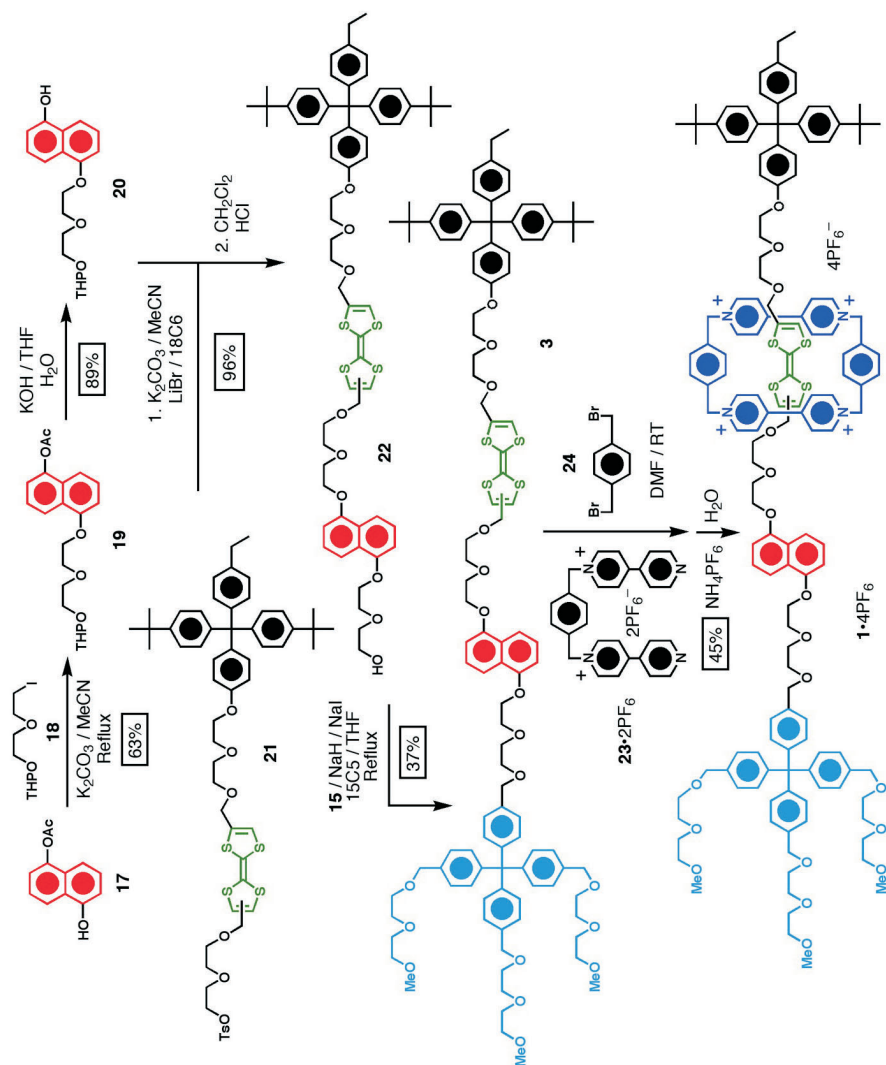
Synthesis

The procedures used in the synthesis of the amphiphilic [2]rotaxanes **1**·4PF₆ and **2**·4PF₆ are described in Schemes 1–3. The two hydrophilic stoppers **15** and **16** were obtained (Scheme 1) in 99 and 96% yields, respectively, by treating the alcohols **13** and **14** with SOCl₂ in CH₂Cl₂. The preparation of the alcohols **13** and **14** begins with chlorination of the tri-*p*-tolylmethanol⁹ (**7**) in acetyl chloride, followed by a Friedel–Craft reaction using an excess amount of phenol at 110 °C to afford compound **8** in 41% yield. Subsequent triflation and Pd-catalyzed CO insertion converts compound **8** to the ester **9** in 77% yield. The highly specific brominations of three aryl methyl groups in the ester **9** with NBS were carried out in CCl₄ using AIBN as catalyst. Without purification, the resulting tribromide **10** was reacted with diethyleneglycol monomethylether (**11**) in the presence of NaH and with NaI and [15]crown-5 (15C5) as catalysts. The resulting intermediate was then reduced with LiAlH₄ in THF to give the alcohol **13** in 18% yield overall for the three steps. Alcohol **14** was prepared in a similar yield (14%) by treating the tribromide **10** with tetraethyleneglycol monomethylether (**12**) under the same reaction conditions employed in the preparation of compound **13**.

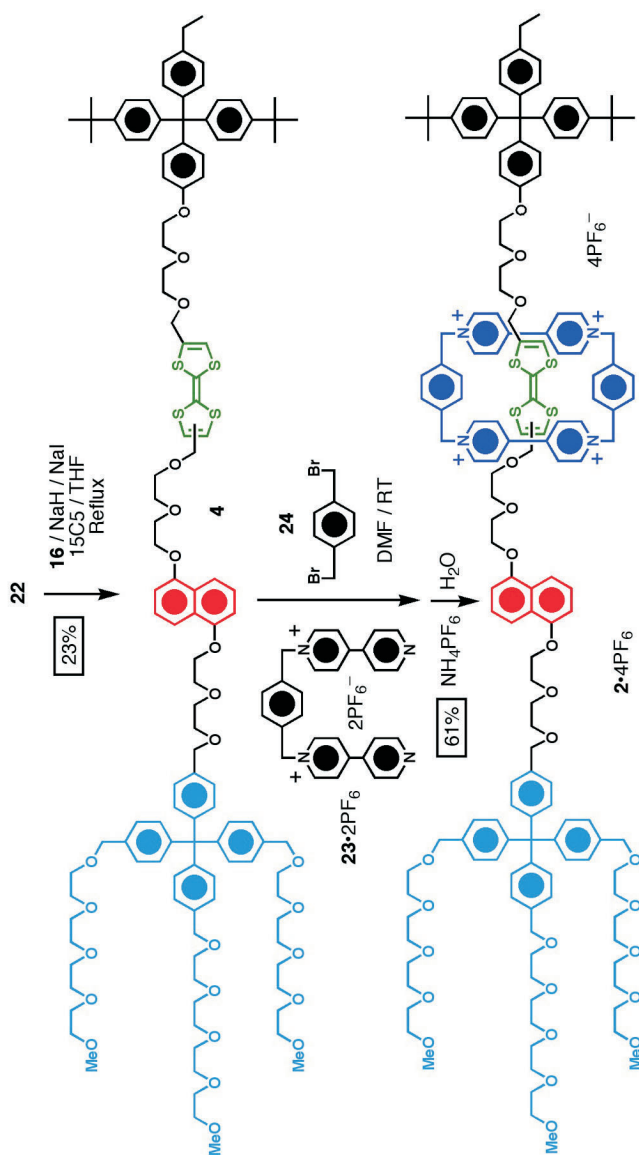
The sequence of reactions leading up to the template-directed synthesis¹⁰ of the rotaxane **1**·4PF₆ from its precursor dumbbell compound **2** are summarized in Scheme 2. Alkylation of the 1-acetoxy-5-hydroxynaphthalene¹¹ (**17**) with 2-[2-(2-iodoethoxy)ethoxy]tetrahydropyran¹² (**18**) in the presence of K₂CO₃ gave compound **19** (63%), which was subsequently reacted with KOH in a THF/H₂O mixture to obtain the deprotected alcohol **20** in 89% yield. The alcohol was reacted with compound^{5c} **21** under alkylation condi-



SCHEME 1
Synthesis of the hydrophilic stoppers **15** and **16**



SCHEME 2
 Synthesis of the amphiphilic, bistable [2]rotaxane **1·4PF₆**



SCHEME 3
 Synthesis of the amphiphilic, bistable [2]rotaxane 2·4PF₆

tions ($\text{K}_2\text{CO}_3/\text{NaI}/18\text{C}6/\text{THF}$) and the resulting intermediate was deprotected in the presence of HCl in CH_2Cl_2 to afford compound **22** in a yield of 96% overall. In the presence of NaH , the half-dumbbell compound **22** was reacted with the benzyl chloride **15** using NaI and $15\text{C}5$ as catalysts to produce the dumbbell compound **3** in 37% yield. The [2]rotaxane $1\cdot 4\text{PF}_6$ was obtained (Scheme 2) by a template-directed synthesis¹⁰, using the dumbbell compound **3** as the template, to form a CBPQT^{4+} ring from its dicationic precursor¹³ $23\cdot 2\text{PF}_6$ and 1,4-bis(bromomethyl)benzene (**24**). The [2]rotaxane $1\cdot 4\text{PF}_6$ was isolated in 45% yield as an analytically pure green solid after chromatography on silica gel using a 1% NH_4PF_6 solution in Me_2CO as the eluent. The template-directed synthesis¹⁰ of the rotaxane $2\cdot 4\text{PF}_6$ from its dumbbell-shaped precursor **4** is outlined in Scheme 3. The benzyl chloride **16** and the half-dumbbell **22** were reacted under alkylation conditions ($\text{NaH}/\text{NaI}/15\text{C}5/\text{THF}$) to afford the dumbbell compound **4** in 23% yield. The template-directed synthesis¹⁰ of the [2]rotaxane $2\cdot 4\text{PF}_6$ proceeded in 61% yield, when the reaction of the dumbbell compound **4**, the dicationic salt¹³ $23\cdot 2\text{PF}_6$ and the dibromide **24**, using exactly the same reaction and isolation conditions as those employed in the preparation of $1\cdot 4\text{PF}_6$, was carried out.

Photophysical Properties

The photophysical properties of the compounds shown in Figs. 1 and 3 have been studied in air-equilibrated MeCN solutions at room temperature. Each dumbbell, *i.e.*, compounds **3** and **4**, consists of four distinct chromophoric units – namely, a TTF unit and a DNP moiety, in addition to hydrophobic and hydrophilic stoppers. Both [2]rotaxanes (1^{4+} and 2^{4+}) contain the CBPQT^{4+} cyclophane which consists of two equivalent and non-interacting bipyridinium units. For comparison purposes, we have also investigated the properties of the model compounds **5** and **6** as well as TTF, CBPQT^{4+} and DMN shown in Fig. 3. Compound **6** is considered to be a good model for the hydrophilic stoppers present in both **3** and **4**.

The absorption spectra of the CBPQT^{4+} cyclophane and the four model compounds are shown in Fig. 4. The inset in this figure illustrates the fluorescence spectra of **5**, **6**, and DMN (TTF and CBPQT^{4+} do not exhibit any emission). The absorption spectra of the two dumbbells are practically the summation of the spectra of the component units. No emission is observed for the two dumbbells **3** and **4**, most likely because the fluorescent excited states of both the stoppers, and the DNP unit are quenched, as a result of energy transfer to the lower-lying, non-emitting excited states in the TTF

unit. On going from the dumbbells to the rotaxanes, broad and relatively weak absorption bands are expected to appear in the visible region as a consequence of charge-transfer (CT) interactions between the electron acceptor cyclophane and the electron-donor units of the dumbbell. Previous investigations have shown that such a CT band has a maximum around 850 nm when CBPQT⁴⁺ surrounds a TTF station^{5c,14,15} and around 520 nm when it encircles a DNP station¹⁶. The lower energy of the CT band involving the TTF unit is a consequence of the stronger electron-donor power of TTF compared with that of a DNP unit. The absorption spectra of the rotaxanes **1**⁴⁺ and **2**⁴⁺ in the UV region are similar, but not identical to the summation of the spectra of the dumbbell and ring components. They display (Fig. 5) a broad, relatively weak absorption band with a maximum around 840 nm ($\epsilon = 2700 \text{ l mol}^{-1} \text{ cm}^{-1}$ for **1**⁴⁺ and $3200 \text{ l mol}^{-1} \text{ cm}^{-1}$ for **2**⁴⁺) that is not present in the component spectra. The presence of this band and the absence of a band around 520 nm show that the predominant translational isomer of both **1**⁴⁺ and **2**⁴⁺ is by far the one in which the CBPQT⁴⁺ cyclophane surrounds the TTF unit. Furthermore, we propose that the slightly larger absorbances of the rotaxanes, compared with their molecular components in the 350–550 nm region, could arise from contributions from alongside CT interactions between the CBPQT⁴⁺ ring, surrounding the TTF unit, and either (i) the DNP moiety, or (ii) the stoppers, or (iii) both. These conclusions are in agreement with the fact that folded conformations are

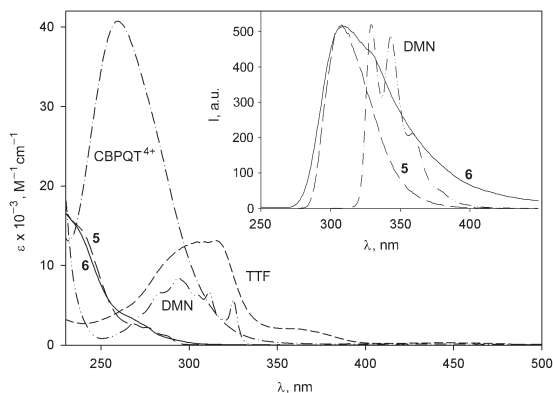


FIG. 4

Absorption spectra of the CBPQT⁴⁺ cyclophane and of the model compounds for the chromophoric units incorporated in the dumbbell-shaped compounds **3** and **4**. The emission spectra of the fluorescent model compounds are shown in the inset (air-equilibrated MeCN solution, room temperature)

required in order to be able to interpret the electrochemical results which are now about to be discussed.

Electrochemical Behavior

The electrochemical experiments were carried out in argon-purged MeCN solution at room temperature. The potential values are referred to SCE.

Since the rotaxanes 1^{4+} and 2^{4+} contain several electroactive units, they show rather complex electrochemical behavior. We have focused our investigation mainly on the oxidation processes of the TTF and DNP electron-donating units of the dumbbell components, and on the reduction of the electron-accepting bipyridinium units present in the CBPQT $^{4+}$ cyclophane component. For comparison purposes, the electrochemical properties of free dumbbells **3** and **4**, and of the model compound **6** have also been investigated. The behavior of the free CBPQT $^{4+}$ cyclophane^{16–18} and the model compounds TTF^{15,19}, DMN^{5b,5c,20}, and **5**^{5b,5c} is already known.

Before examining the results obtained for the rotaxanes 1^{4+} and 2^{4+} , let us consider the anticipated effect of mechanical interlocking on the redox processes of the cyclophane and of the dumbbell components. The oxidation of a TTF unit or a DNP moiety is strongly conditioned by the presence of a surrounding CBPQT $^{4+}$ cyclophane because of (i) the occurrence of donor-acceptor interactions, and (ii) the strong electrostatic repulsion, arising upon oxidation between the charged radical cation and the tetracationic cyclophane. By contrast, it is expected that reduction of the CBPQT $^{4+}$

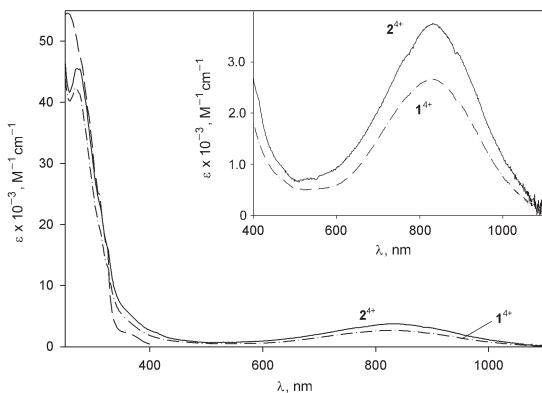


FIG. 5

Absorption spectra of [2]rotaxanes 1^{4+} and 2^{4+} and sum of the spectra of their molecular components (dashed line). The enlarged view of the CT bands of 1^{4+} and 2^{4+} is shown in the inset (MeCN solution, room temperature)

cyclophane is weakly influenced by the presence of a threaded, uncharged electron donor since no electrostatic effect will arise upon reduction. The reduction process should, however, be noticeably influenced by the presence of folded conformations since the highly charged cyclophane is strongly exposed to external interactions. It follows that the oxidation processes will reveal information on the nature of the translational isomers present in solution and also on the occurrence of any shuttling movements, whereas the reduction processes will be much more sensitive for exposing the existence of any folding/unfolding rearrangements in solution.

Oxidation processes. The data relating to the oxidation of the model compound **6**, the dumbbells **3** and **4**, and the rotaxanes **1**⁴⁺ and **2**⁴⁺ are gathered together in Table I along with the already available data for the other compounds. The most important results concern the oxidation processes associated with (Fig. 6) the TTF unit. In the dumbbell components, the TTF unit undergoes two well-separated, monoelectronic, and reversible processes, whereas, in the rotaxanes, the two processes merge at a potential almost equal to that observed for the second process in the dumbbells. In other words, in the rotaxanes, the first TTF oxidation process is shifted (410 mV) toward more positive potential values, compared with the corresponding dumbbells, whereas the second oxidation process is not displaced at all. Such behavior shows that, in the rotaxanes, the TTF unit is surrounded by

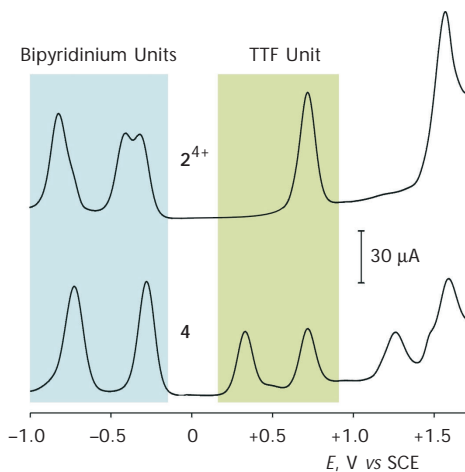


FIG. 6

DPV patterns of [2]rotaxane **2**⁴⁺ and its corresponding dumbbell-shaped component **4**. The current intensity has been corrected to take into account differences in concentrations and diffusion coefficients (argon-purged MeCN solution, room temperature, scan rate 20 mV s⁻¹, pulse height 75 mV)

TABLE I
Electrochemical data^a

Compound	Reduction, $E_{1/2}$ [n] ^b		Oxidation, $E_{1/2}$ [n] ^b		
	bipyridinium units		TTF unit	DNP unit ^c	stopper units ^c
1 ⁴⁺	-0.85 [2]	-0.42 [1]	-0.33 [1]	0.74 [2] ^d	1.62 ^e
3				0.33 [1]	0.75 [1]
2 ⁴⁺	-0.83 [2]	-0.41 [1]	-0.32 [1]	0.72 [2] ^d	1.60 ^e
4				0.33 [1]	0.74 [1]
DMN					1.25
TTF				0.35 [1]	0.71 [1]
5					1.13
6					1.25
CBPQT ⁴⁺	-0.71 [2]	-0.29 [2]			1.58 ^e
					1.55
					1.76
					1.86
					1.99

^a Room temperature argon-purged CH₃CN solution, halfwave potential values in V vs SCE; tetrabutylammonium hexafluorophosphate as supporting electrolyte, glassy carbon as working electrode. ^b Number of the exchanged electrons. ^c Irreversible process, potential value estimated by the DPV peak. ^d Process affected by kinetic complications, potential value estimated by the DPV peak. ^e Followed by overlapping processes.

(and engaged in CT interactions with) the CBPQT⁴⁺ cyclophane, and that, after the first oxidation, the cyclophane moves away from the TTF^{•+} unit. Such a mechanical movement takes place on the time-scale of milliseconds, as evidenced by the dependences of cyclic voltammograms on the sweep rates. This behavior has already been observed in TTF-containing pseudo-rotaxanes¹⁵.

The irreversible oxidation process of the dumbbells at about +1.2 V, assigned to the oxidation of the DNP unit – by comparison with the corresponding model compound (Table I) – is not observed (Fig. 6) in the rotaxanes, in keeping with the fact that it has been shifted to more positive potentials, thus merging with the oxidation processes (> +1.4 V) associated with the stoppers. Such a shift is consistent with the displacement of the CBPQT⁴⁺ cyclophane on the DNP moiety after oxidation of the TTF unit. It is indeed known²¹ that a DNP unit encircled by CBPQT⁴⁺ undergoes oxidation at +1.55 V.

Finally, it should also be noted that the behavior of the rotaxanes **1**⁴⁺ and **2**⁴⁺ is quite similar, an observation which suggests that the different lengths of the polyether chains associated with the hydrophilic stopper do not play a significant role, at least as far as the oxidation processes are concerned.

Reduction processes. The electrochemical properties of the CBPQT⁴⁺ cyclophane are known to change when it is engaged in electron donor-acceptor interaction. The first bielectronic reduction process is expected to move and, in fact, (i) does move slightly toward more negative potential values in pseudorotaxanes¹⁵ and rotaxanes^{6c}, and (ii) splits into two distinct processes in catenanes, in which the two bipyridinium units are topologically non-equivalent^{14,16,17}. Splitting, however, has also been observed for some pseudorotaxanes¹⁴ and rotaxanes^{2a,5c,22}.

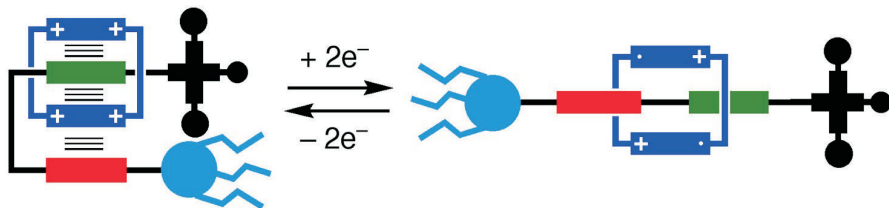


FIG. 7

Schematic representation of the folding/unfolding conformational rearrangements associated with the first reduction process of the two bipyridinium units in rotaxanes **1**⁴⁺ and **2**⁴⁺. The location of the doubly reduced ring along the dumbbell component cannot be clearly established from the voltammetric experiments

In the case of the rotaxanes **1**⁴⁺ and **2**⁴⁺, the first bielectronic reduction process of the CBPQT⁴⁺ component splits into two distinct processes (Table I), showing that the equivalence of the two bipyridinium units is lost. This result can be accounted for²³ by assuming that CBPQT⁴⁺, while encircling the TTF unit, is involved in nonsymmetric alongside interactions with the other donor units. Such behavior implies the presence of folded conformations – possibly of a “pseudocatenane” type (Fig. 7) – a suggestion which has been advanced previously to explain the results obtained in the case of other long and flexible pseudorotaxanes¹⁴ and rotaxanes^{5,6}. The somewhat similar behaviors exhibited by both **1**⁴⁺ and **2**⁴⁺ show that, in the case of the reduction processes as well, the different lengths of the polyether chains associated with the hydrophilic stoppers apparently do not play a significant role, at least in an electrochemical context.

The second reduction of the two bipyridinium units of the cyclophane takes place (Table I) simultaneously at a potential value more negative than that observed for the free cyclophane. This result shows that, after the first reduction process, the two bipyridinium units of the cyclophane (i) still interact with electron-donating units, and, more interestingly, (ii) they become equivalent. The latter observation strongly suggests that the first reduction of the two bipyridinium units causes unfolding (Fig. 7).

¹H NMR Spectroscopic Investigations

The ¹H NMR spectra of the [2]rotaxanes **1**·4PF₆ and **2**·4PF₆, recorded in CD₃CN solutions, display almost identical arrays of signals, with the exception of the tight package of resonances compressed into the region from δ 3.30 to 4.70 ppm for the *O*-methylene protons present in four different portions of the dumbbell component of the rotaxanes. Clearly, the rotaxane **2**⁴⁺ contains 12 more *O*-methylene portions than does its lower homolog **1**⁴⁺. The ¹H NMR spectrum of the [2]rotaxane **1**·4PF₆ is shown in Fig. 8. When all said and done, however, the difference in the lengths of the polyether chains, associated with the hydrophilic stoppers in the two compounds, has little or no influence on how the remainders of the molecules behave in solution. It would not be unreasonable to assume that they exist in folded conformations – as indicated by both photophysical and electrochemical investigations – involving alongside π–π stacking interactions between the DNP unit and the CBPQT⁴⁺ ring. Such an interaction has already been detected^{5c} by ¹H NMR spectroscopy in bistable rotaxanes with closely related structures, particularly with respect to the rod portions of their dumbbells.

In agreement with the results of the electrochemical investigations, only *one* translational isomer – the one in which the CBPQT⁴⁺ ring encircles the TTF unit – is detected by ¹H NMR spectroscopy to be present in the intensely green solutions of each of the two rotaxanes **1**·4PF₆ and **2**·4PF₆. The ¹H NMR spectra of both of these compounds in CD₃CN at 500 MHz exhibit similar spectra – *i.e.*, in each case, two pairs of singlets of unequal intensities, resonating at δ 5.98 and 6.06 ppm, and 6.17 and 6.27 ppm for **1**·4PF₆ (Fig. 8) and at δ 5.96 and 6.06 ppm, and 6.16 and 6.22 ppm for **2**·4PF₆ – for the constitutionally heterotopic methine protons on the TTF units encircled by CBPQT⁴⁺ rings. The fact that there is also an equilibrating mixture of *cis* and *trans* isomers as a result of slow rotation on the ¹H NMR timescale around the formal carbon–carbon double bond between the two substituted five-membered rings of the TTF units accounts²⁴ for the signal pat-

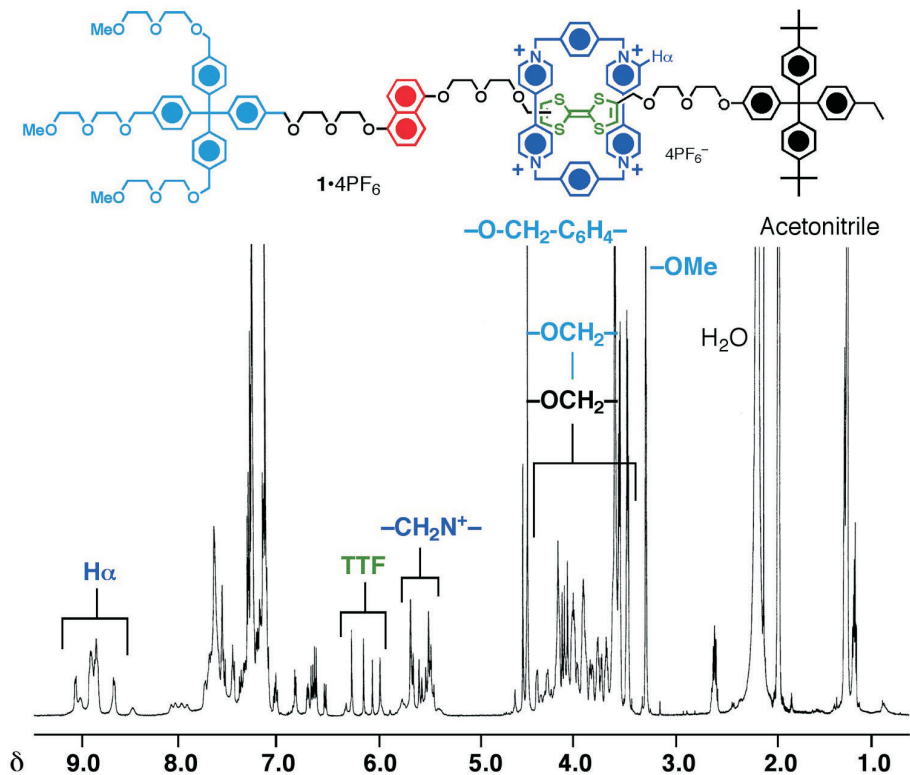


FIG. 8

¹H NMR spectrum of the rotaxane **1**·4PF₆ recorded in CD₃CN at 500 MHz

terns of their two methine protons associated with these units which are externally diastereotopic, in addition to being internally constitutionally heterotopic. So far, we have been unable to establish which of the isomers, the *cis* or the *trans*, is the major one in CD₃CN solution at room temperature. It is interesting that, in the case of the **1**⁴⁺ and **2**⁴⁺, heavily skewed translational isomerism is accompanied by finely balanced configurational isomerism. It is, however, always possible that, when the progression (Fig. 2) from the solution phase to the condensed phase on into solid-state devices is made, the supramolecular forces associated with the self-organization of the amphiphilic, bistable rotaxanes will shift the equilibrium in favor of one of the two configurational isomers. Or the equilibrium proportions of the *cis* and *trans* isomers could persist, leading to the formation of domains rich in one or other of the two isomers. On the basis of what we know at this stage about the inter-relationships between molecular and supramolecular structures as we cross phase boundaries, anything is possible, it has to be said.

Mechanical Switching by Chemical Ox/Red Stimulation

It is known that TTF and its derivatives can be mono- and di-oxidized by stoichiometric amounts of Fe(III) perchlorate. Such oxidation processes can be followed by changes²⁵ in absorption spectra (TTF^{•+}: $\lambda = 434$ nm, $\epsilon = 15\,000$ l mol⁻¹ cm⁻¹; $\lambda = 577$ nm, $\epsilon = 4000$ l mol⁻¹ cm⁻¹; TTF²⁺: $\lambda = 348$ nm,

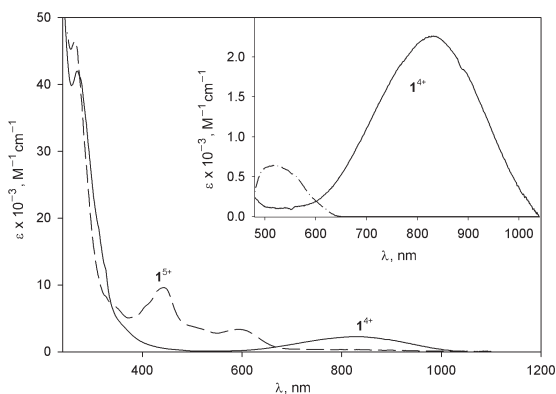


FIG. 9

Absorption spectra of [2]rotaxane **1**⁴⁺ and its mono-oxidized form. The enlarged view of the CT band of **1**⁴⁺ and of the difference between the spectra of **1**⁵⁺ and **3**⁺ (dotted and dashed line) is shown in the inset (for details, see the text)

$\epsilon = 9000 \text{ l mol}^{-1} \text{ cm}^{-1}$). We have found that this observation is also borne out for the TTF unit in the dumbbells **3** and **4**. In both rotaxanes, the absorption bands with maxima around 840 nm – related to the CT interactions between TTF and CBPQT⁴⁺ – disappear (Fig. 9) upon addition of one equivalent of Fe(III) perchlorate. When the spectrum of the mono-oxidized dumbbell component is subtracted from the spectrum of the corresponding mono-oxidized rotaxane, a weak absorption band with a maximum of around 520 nm appears (inset in Fig. 9), confirming that the CBPQT⁴⁺ cyclophane moves from the TTF to the DNP station upon mono-electron oxidation. Successive reduction of TTF^{•+}, performed by adding a stoichiometric amount of the 1,1'-dimethyl-4,4'-bipyridinium dication in its mono-reduced form, moves the ring back to the TTF station, thereby restoring the original starting state of the chemically ox/red system.

CONCLUSIONS

The absorption spectra and the results obtained from electrochemical oxidation show that the [2]rotaxanes **1**⁴⁺ and **2**⁴⁺ exist to all intents and purposes as the translational isomer in which the CBPQT⁴⁺ cyclophane surrounds the TTF unit. The electrochemical reduction studies indicate that the two bipyridinium units of the cyclophane are non-equivalent, implying the presence of asymmetric alongside interactions. It can thus be inferred that the rotaxane structure is not stretched out, but folded up in some manner (Fig. 1) in solution. Upon ox/red (electrochemical or chemical) TTF-localized stimulation, the CBPQT⁴⁺ cyclophane shuttles between the TTF and DNP stations. Upon red/ox (electrochemical) bipyridinium-localized stimulation, some kind of unfolding/folding conformational change takes place in solution. The different lengths of the polyether chains appended to the hydrophilic stopper in **1**⁴⁺ and **2**⁴⁺ apparently do not play a significant role in controlling this conformational change in solution. Until now, most of the interest in rotaxanes has been focused on controlled ring-shuttling. The evidence found from redox-induced unfolding/folding conformations²⁶ in long and flexible rotaxanes is yet another reason for making every effort to examine the structural arrangements of amphiphilic, bistable rotaxanes in different phases and settings. So too is the observation of the configurational isomerism within the dumbbell components of the two rotaxanes. It is quite challenging to achieve all the control you might wish to have in functioning exotic molecules. It is also humbling to note that, while conformational isomerism in **1**⁴⁺ and **2**⁴⁺ is exposed by photophysical and electrochemical studies, it is hard to detect by ¹H NMR spectroscopy,

whereas configurational isomerism, which is so evident from a cursory inspection of the ^1H NMR spectra of **1**· 4PF_6 and **2**· 4PF_6 , is not at all transparent in the information provided by photophysical and electrochemical measurements. The lesson to be learnt is a familiar one – keep all eyes open, for, what one set of eyes finds difficult to see and even misses altogether, another set of eyes sees very clearly indeed.

EXPERIMENTAL

Synthesis

General methods. Chemicals were purchased from Aldrich and used as received. The compounds tri-*p*-tolylmethanol⁹ (**7**), 1-acetoxy-5-hydroxynaphthalene¹¹ (**17**), 2-[2-(2-iodoethoxy)-ethoxy]tetrahydropyran¹² (**18**), compound^{5c} **21** and 1,1'-(1,4-phenylenedimethylene)di-(4,4'-bipyridin-1-ium) bis(hexafluorophosphate)¹³ (**23**· 2PF_6) were all prepared according to literature procedures. Solvents were dried following methods described in the literature²⁷. All reactions were carried out under an anhydrous argon atmosphere. Thin layer chromatography (TLC) was performed on aluminum sheets, coated with silica gel 60F (Merck 5554). The plates were inspected by UV light and, if required, developed in I_2 vapor. Column chromatography was carried out by using silica gel 60 (Merck 9385, 230–400 mesh). Melting points were determined on an Electrothermal 9100 melting point apparatus and are uncorrected. All ^1H and ^{13}C NMR spectra were recorded on either (i) a Bruker ARX400 (400 and 100 MHz, respectively), (ii) a Bruker ARX500 (500 and 125 MHz, respectively) or (iii) a Bruker Avance500 (500 and 125 MHz, respectively), using residual solvent as the internal standard. Samples were prepared using CDCl_3 , CD_3COCD_3 or CD_3CN purchased from Cambridge Isotope Laboratories. All chemical shifts (in ppm) are quoted using the δ -scale, and all coupling constants (*J*) are expressed in Hz. Fast atom bombardment (FAB) mass spectra were obtained using a ZAB-SE mass spectrometer, equipped with a krypton primary atom beam utilizing a *m*-nitrobenzyl alcohol matrix. Cesium iodide or poly(ethylene glycol) were employed as reference compounds. Electrospray mass spectra (ESMS) were measured on a VG ProSpec triple focusing mass spectrometer with MeCN as the mobile phase. Microanalyses were performed by Quantitative Technologies, Inc.

Compound 8. A mixture of tri-*p*-tolylmethanol (**7**) (20 g, 66 mmol) and AcCl (103 g, 1.32 mol) was heated under reflux for 24 h. After cooling down to room temperature, acetyl chloride was removed in vacuo to give a yellow oil, which was then mixed with phenol (80 g, 0.85 mol) to obtain a reddish-black mixture. The reaction mixture was then stirred at 100 °C for 18 h. PhMe (200 ml) was added and the mixture was washed with an aqueous solution of NaOH (1.0 mol l^{-1} , 7 × 150 ml) and dried (MgSO_4). After removal of the solvent, the residue was purified by column chromatography (SiO_2 : CH_2Cl_2) to give compound **8** (10.2 g, 41%) as an off-white solid. ^1H NMR (400 MHz, CDCl_3): 2.34 (s, 9 H), 4.71 (s, 1 H), 6.70 (d, *J* = 8.5, 2 H), 7.06–7.12 (m, 14 H). ^{13}C NMR (100 MHz, CDCl_3): 21.0, 63.3, 114.2, 128.1, 131.0, 132.3, 135.2, 139.8, 144.4, 153.3. MS (FAB), *m/z* (%): 378 (83) [M]⁺. For $\text{C}_{28}\text{H}_{26}\text{O}$ calculated: 88.85% C, 6.92% H; found: 88.51% C, 6.97% H.

Compound 9. Trifluoromethanesulfonic anhydride (12.5 g, 44 mmol) was added dropwise to a solution of compound **8** (10 g, 26 mmol), 2,6-dimethylpyridine (5.3 ml, 6.0 mmol) and DMAP (0.72 g, 45 mmol) in anhydrous CH_2Cl_2 (100 ml) at –30 °C. The reaction mixture was

then stirred at $-30\text{ }^{\circ}\text{C}$ for 30 min and at room temperature for 1 h. H_2O (100 ml) was added and the mixture was extracted with CH_2Cl_2 (3×100 ml) and dried (MgSO_4). The combined organic layers were concentrated and the residue was then purified in a short-path column (SiO_2 : CH_2Cl_2 /hexane, 1:2) to give a yellow oil, which was dissolved in a mixture of anhydrous DMF (100 ml), anhydrous MeOH (40 ml) and Et_3N (6.4 g, 63 mmol). $\text{Pd}(\text{OAc})_2$ acetate (0.65 g, 3.0 mmol) and 1,3-bis(diphenylphosphino)propane (1.2 g, 3.0 mmol) were added and the reaction mixture was stirred at $70\text{ }^{\circ}\text{C}$ under an atmosphere of CO for 7 h. After cooling down to room temperature, H_2O (200 ml) was added and the mixture was extracted with CH_2Cl_2 (3×50 ml) and dried (MgSO_4). The combined organic layers were concentrated and the residue was subjected to column chromatography (SiO_2 : CH_2Cl_2 /hexane, 1:1) to yield compound **9** (14.2 g, 77%) as a pale yellow solid. ^1H NMR (400 MHz, CDCl_3): 2.32 (s, 9 H), 3.90 (s, 3 H), 7.05–7.11 (m, 12 H), 7.34 (d, $J = 8.5$, 2 H), 7.91 (d, $J = 8.5$, 2 H). ^{13}C NMR (100 MHz, CDCl_3): 20.9, 52.0, 64.2, 127.6, 128.4, 128.7, 130.9, 131.1, 135.6, 143.6, 152.8, 167.1. MS (FAB), m/z (%): 421 (95) $[\text{M}]^+$. For $\text{C}_{30}\text{H}_{28}\text{O}_2$ calculated: 85.68% C, 6.71% H; found: 85.50% C, 6.68% H.

Compound 13. A mixture of compound **9** (6.26 g, 15 mmol), NBS (8.21 g, 46 mmol) and AIBN (50 mg, catalytic amount) in anhydrous CCl_4 (100 ml) was heated under reflux for 6 h. After cooling down to room temperature, the reaction mixture was filtered and the solid was washed with CCl_4 (20 ml). The combined organic filtrate was concentrated and purified by column chromatography (SiO_2 : CH_2Cl_2) to give compound **10** as an off-white solid. Compound **10** was dissolved in THF (20 ml) and added to a solution of diethyleneglycol monomethylether (**11**) (18 g, 150 mmol), 15-crown-5 (10 mg, catalytic amount), NaI (10 mg, catalytic amount) and NaH (3.0 g, 120 mmol) in THF (200 ml). The reaction mixture was heated under reflux for 20 h. After cooling down to room temperature, H_2O (200 ml) was added and the mixture was extracted by CH_2Cl_2 (3×150 ml) and dried (MgSO_4). The combined organic layers were concentrated to give a brown oil, which was then dissolved in THF (200 ml). LiAlH_4 (0.5 g, 13 mmol) was added in small portions over a period of 15 min and the reaction mixture was stirred at room temperature for 24 h. H_2O (10 ml) was slowly added and the mixture was extracted by CH_2Cl_2 (3×100 ml) and dried (MgSO_4). After removal of the solvent, the residue was subjected to column chromatography (SiO_2 : EtOAc/MeOH , 95:5) to give compound **13** (2.05 g, 18%) as a pale-yellow oil. ^1H NMR (500 MHz, CDCl_3): 3.35 (s, 9 H), 3.52–3.54 (m, 6 H), 3.63–3.68 (m, 18 H), 4.51 (s, 6 H), 4.62 (s, 2 H), 7.16–7.23 (m, 16 H). ^{13}C NMR (125 MHz, CDCl_3): 58.9, 64.1, 64.7, 69.6, 70.4, 70.5, 71.8, 72.9, 126.1, 126.9, 130.8, 130.9, 131.0, 135.7, 138.4, 146.0. MS (FAB), m/z (%): 747 (100) $[\text{M}]^+$. For $\text{C}_{44}\text{H}_{58}\text{O}_{10}$ calculated: 70.75% C, 7.83% H; found: 70.58% C, 7.72% H.

Compound 14. A mixture of compound **9** (2.5 g, 5.9 mmol), NBS (3.40 g, 19 mmol) and AIBN (15 mg, catalytic amount) in anhydrous CCl_4 (30 ml) was heated under reflux for 7 h. After cooling down to room temperature, the reaction mixture was filtered and the solid was washed with CCl_4 (20 ml). The combined organic filtrate was concentrated and purified by a short-path column (SiO_2 : CH_2Cl_2) to give compound **10** as a off-white solid. Compound **10** was dissolved in THF (10 ml) then added dropwise to a solution of tetraethyleneglycol monomethylether (**12**) (8.0 g, 38 mmol), 15-crown-5 (10 mg, catalytic amount), NaI (10 mg, catalytic amount) and NaH (1.26 g, 50 mmol) in THF (100 ml). The reaction mixture was heated under reflux for 48 h. After cooling down to room temperature, the mixture was filtered and the solid was washed with THF (50 ml). The combined filtrate was concentrated to obtain a brown oil, which was then dissolved in THF (100 ml). LiAlH_4 (0.5 g, 13 mmol) was added in small portions over a period of 15 min and the reaction mixture was stirred at

room temperature for 48 h. H_2O (10 ml) was added and the mixture was extracted by CH_2Cl_2 (100 ml) and dried (MgSO_4). After removal of the solvent, the residue was subjected to column chromatography (SiO_2 : EtOAc/MeOH, 90:10) to give compound **14** (0.85 g, 14%) as a colorless oil. ^1H NMR (500 MHz, CDCl_3): 3.14 (s, 9 H), 3.32–3.45 (m, 48 H), 4.33 (s, 6 H), 4.38 (s, 2 H), 6.99–7.03 (m, 16 H). ^{13}C NMR (125 MHz, CDCl_3): 58.6, 60.0, 61.2, 63.9, 64.0, 69.4, 70.2, 70.3, 70.4, 71.0, 71.6, 72.6, 125.9, 126.6, 130.7, 130.9, 135.6, 139.0, 145.4, 145.9. MS (MALDI), m/z : 1033.5455 $[\text{M} + \text{Na}]^+$. For $\text{C}_{56}\text{H}_{82}\text{O}_{16}$ calculated: 66.51% C, 8.17% H; found: 66.66% C, 8.26% H.

Compound 15. Thionyl chloride (1.8 g, 15 mmol) was added dropwise to the solution of compound **13** (0.75 g, 1.5 mmol) in anhydrous CH_2Cl_2 (10 ml). After stirring at room temperature for 2 h, the reaction mixture was concentrated and the residue was purified by column chromatography (SiO_2 : CH_2Cl_2) to give compound **15** (0.76 g, 99%) as a colorless oil. ^1H NMR (500 MHz, CDCl_3): 3.37 (s, 9 H), 3.54–3.56 (m, 6 H), 3.64–3.68 (m, 18 H), 4.53 (s, 6 H), 4.56 (s, 2 H), 7.07–7.24 (m, 16 H). ^{13}C NMR (125 MHz, CDCl_3): 45.9, 60.2, 64.2, 69.8, 70.6, 70.7, 72.1, 73.0, 126.9, 127.6, 130.9, 131.2, 134.9, 135.9, 145.8, 147.0. MS (FAB), m/z (%): 765.32 (40) $[\text{M} + \text{H}]^+$.

Compound 16. Thionyl chloride (290 g, 1.9 mmol) was added dropwise to a solution of compound **14** (190 mg, 0.19 mmol) in anhydrous CH_2Cl_2 (10 ml). After stirring at room temperature for 2 h, the reaction mixture was concentrated and the residue was purified by column chromatography (SiO_2 : CH_2Cl_2) to give compound **15** (186 mg, 96%) as a colorless oil. Without further characterization, compound **15** was used directly to alkylate compound **22** and so form the dumbbell compound **4**.

Compound 19. A solution of 1-acetoxy-5-hydroxynaphthalene (**17**) (1.58 g, 7.88 mmol), 2-[2-(2-iodoethoxy)ethoxy]tetrahydropyran (**18**) (3.55 g, 12 mmol), K_2CO_3 (3.0 g, 22 mmol), and 18-crown-6 (10 mg, catalytic amount) in anhydrous MeCN (50 ml) was stirred under reflux for 48 h. After cooling down to room temperature, the reaction mixture was filtered and the solid was washed with MeCN (50 ml). The combined organic filtrate was concentrated and the residue was subjected to column chromatography (SiO_2 : CH_2Cl_2 /MeOH, 95:5) to give compound **19** (1.84 g, 63%) as a pale-yellow oil. ^1H NMR (500 MHz, CD_3CN): 1.48–1.90 (m, 6 H), 2.56 (s, 3 H), 3.50–4.41 (m, 10 H), 4.72 (t, $J = 3.2$, 1 H), 7.09 (d, $J = 8.5$, 1 H), 7.42 (d, $J = 8.5$, 1 H), 7.53–7.65 (m, 3 H), 8.31 (d, $J = 8.5$, 1 H). ^{13}C NMR (125 MHz, CD_3CN): 20.3, 21.1, 26.2, 31.4, 62.7, 67.4, 69.1, 70.2, 71.4, 99.7, 106.8, 114.3, 118.2, 120.0, 120.8, 125.8, 127.8, 129.0, 147.7, 155.5, 170.6. MS (FAB), m/z (%): 374 (100) $[\text{M}]^+$. For $\text{C}_{21}\text{H}_{26}\text{O}_6$ calculated: 67.36% C, 7.00% H; found: 67.40% C, 7.02% H.

Compound 20. A solution of compound **19** (0.50 g, 1.34 mmol) and KOH (0.4 g, 6.7 mmol), in THF (10 ml) and H_2O (10 ml) was heated under reflux for 3 h. After cooling down to room temperature, H_2O (20 ml) was added, and the mixture was extracted with CH_2Cl_2 (3×20 ml) and dried (MgSO_4). The combined organic layers were concentrated to give a brown oil, which was purified by column chromatography (SiO_2 : EtOAc/hexane, 9:1) to give compound **20** (0.40 g, 89%) as a reddish-brown oil. ^1H NMR (400 MHz, CDCl_3): 1.50–1.58 (m, 6 H), 3.48–3.50 (m, 1 H), 3.71–3.82 (m, 6 H), 4.00–4.03 (m, 2 H), 4.30–4.32 (m, 2 H), 4.66 (t, $J = 3.2$, 3 H), 6.84 (d, $J = 8.5$, 1 H), 7.25–7.36 (m, 2 H), 7.72–7.74 (m, 1 H), 7.86–7.88 (m, 1 H). ^{13}C NMR (100 MHz, CDCl_3): 19.4, 25.4, 30.6, 62.3, 66.7, 67.9, 69.8, 70.9, 99.0, 105.5, 109.3, 114.2, 114.4, 125.0, 125.2, 125.6, 127.1, 152.8, 154.5. MS (FAB), m/z (%): 332.04 (100) $[\text{M}]^+$.

Compound 22. A solution of compound **20** (0.27 g, 0.81 mmol), compound **21** (0.87 g, 0.82 mmol), K_2CO_3 (0.45 g, 3.25 mmol), LiBr (20 mg, catalytic amount) and 18-crown-6

(20 mg, catalytic amount) in MeCN (50 ml) was heated under reflux for 36 h. After cooling down to room temperature, the reaction mixture was filtered and the solid was washed with MeCN (20 ml). The combined filtrate was concentrated and the residue was purified by column chromatography (SiO_2 : $\text{CH}_2\text{Cl}_2/\text{EtOH}$, 100:3) to give compound **22** (0.88 g, 96%) as an orange oil. ^1H NMR (500 MHz, CD_3COCD_3): 1.21 (t, $J = 7.6$, 3 H), 1.31 (s, 18 H), 2.62 (q, $J = 7.6$, 2 H), 2.70 (s, 1 H), 3.54–3.81 (m, 14 H), 3.97–3.99 (m, 4 H), 4.09–4.12 (m, 2 H), 4.30–4.33 (m, 8 H), 6.47–6.52 ($4 \times$ s, 2 H), 6.83–6.85 (m, 2 H), 6.96–6.99 (m, 2 H), 7.10–7.16 (m, 10 H), 7.30–7.32 (m, 4 H), 7.34–7.40 (m, 2 H), 7.85–7.88 (m, 2 H). ^{13}C NMR (125 MHz, CD_3CN): 14.8, 25.1, 27.7, 30.5, 33.8, 60.9, 63.0, 67.3, 67.4, 69.1, 69.2, 69.8, 70.0, 70.1, 70.2, 71.4, 72.2, 106.8, 113.3, 114.3, 116.5, 116.6, 118.2, 120.0, 120.8, 124.3, 125.8, 126.7, 127.8, 129.0, 130.2, 130.4, 131.6, 134.5, 134.6, 139.5, 141.5, 144.4, 144.7, 147.7, 148.3, 155.5, 156.6. MS (FAB), m/z (%): 1128 (55) $[\text{M}]^+$.

Dumbbell compound 3. A solution of compound **15** (0.19 g, 0.25 mmol) in THF (5 ml) was added dropwise to a suspension of compound **22** (0.20 g, 0.177 mmol), 15-crown-5 (10 mg, catalytic amount), NaI (10 mg, catalytic amount), NaH (0.05 g, 2.0 mmol) in THF (20 ml). The reaction mixture was heated under reflux for 24 h. After cooling down to room temperature, the mixture was filtered and the solid was washed with THF (10 ml). The combined organic filtrate was concentrated and purified by column chromatography (SiO_2 : EtOAc) to give dumbbell compound **3** (0.125 g, 37%) as a yellow oil. ^1H NMR (500 MHz, CD_3COCD_3): 1.21 (t, $J = 7.6$, 3 H), 1.31 (s, 18 H), 2.62 (q, $J = 7.6$, 2 H), 3.30 (s, 9 H), 3.47–3.62 (m, 38 H), 3.94–3.96 (m, 4 H), 4.05–4.12 (m, 2 H), 4.25–4.26 (m, 8 H), 4.48–4.49 (m, 8 H), 6.26–6.29 ($4 \times$ s, 2 H), 6.78–6.80 (m, 2 H), 6.90–6.93 (m, 2 H), 7.05–7.28 (m, 32 H), 7.79 (d, $J = 8.5$, 2 H). ^{13}C NMR (125 MHz, CD_3CN): 14.8, 25.1, 27.7, 30.5, 33.8, 58.9, 60.9, 63.0, 64.1, 64.7, 67.3, 67.4, 69.1, 69.2, 69.6, 69.8, 70.0, 70.1, 70.2, 70.4, 70.5, 71.4, 71.8, 72.2, 72.9, 106.8, 113.3, 114.3, 116.5, 116.6, 118.2, 120.0, 120.8, 124.3, 125.8, 126.1, 126.7, 126.9, 127.8, 129.0, 130.2, 130.4, 130.8, 130.9, 131.0, 131.6, 134.5, 134.6, 135.7, 138.4, 139.5, 141.5, 144.4, 144.7, 146.0, 147.7, 148.3, 155.5, 156.6. MS (FAB), m/z (%): 1857.84 (100) $[\text{M} + \text{H}]^+$. For $\text{C}_{109}\text{H}_{132}\text{O}_{18}\text{S}_4$ calculated: 70.44% C, 7.16% H, 6.90% S; found: 70.42% C, 7.12% H, 6.86% S.

Dumbbell compound 4. A solution of compound **16** (186 mg, 0.181 mmol) in THF (5 ml) was added dropwise to a suspension of compound **22** (200 mg, 0.177 mmol), 15-crown-5 (10 mg, catalytic amount), NaI (10 mg, catalytic amount), NaH (50 mg, 2.0 mmol) in THF (20 ml). The reaction mixture was heated under reflux for 2 days. After cooling down to room temperature, the mixture was filtered and the solid was washed with THF (10 ml). The combined organic filtrate was concentrated and purified by column chromatography (SiO_2 : EtOAc/MeOH, 9:1) to give the dumbbell compound **4** (85 mg, 23%) as a yellow oil. ^1H NMR (500 MHz, CD_3COCD_3): 1.21 (t, $J = 7.6$, 3 H), 1.31 (s, 18 H), 2.61 (q, $J = 7.6$, 2 H), 3.28 (s, 9 H), 3.45–3.79 (m, 64 H), 3.95–4.03 (m, 6 H), 4.29–4.31 (m, 6 H), 4.52–4.55 (m, 8 H), 6.45–6.50 ($4 \times$ s, 2 H), 6.81–6.82 (m, 2 H), 6.93–6.95 (m, 2 H), 7.15–7.35 (m, 32 H), 7.85 (d, $J = 8.5$, 2 H). ^{13}C NMR (125 MHz, CD_3COCD_3): 14.9, 25.2, 27.6, 30.6, 33.8, 59.0, 60.9, 63.1, 64.1, 64.7, 67.3, 67.4, 69.1, 69.2, 69.6, 69.8, 69.9, 70.0, 70.1, 70.2, 70.3, 70.4, 70.5, 71.4, 71.9, 72.4, 73.1, 105.9, 113.1, 114.2, 116.5, 116.6, 118.4, 120.1, 120.8, 124.3, 125.8, 126.1, 126.7, 126.8, 127.9, 129.1, 130.2, 130.3, 130.8, 130.9, 131.0, 131.6, 134.6, 134.6, 135.7, 138.4, 139.5, 141.5, 144.3, 144.7, 145.9, 147.7, 148.1, 154.3, 156.8. MS (FAB), m/z (%): 2122.00 (100) $[\text{M} + \text{H}]^+$. For $\text{C}_{121}\text{H}_{156}\text{O}_{24}\text{S}_4$ calculated: 68.46% C, 7.41% H, 6.04% S; found: 68.19% C, 7.36% H, 6.06% S.

[2]Rotaxane 1-4PF₆. A solution of dumbbell compound **3** (0.125 g, 0.067 mmol), **23-2PF₆** (0.143 g, 0.205 mmol) and 1,4-bis(bromomethyl)benzene (**24**) (0.053 g, 0.202 mmol) in anhydrous DMF (5 ml) was stirred at room temperature for 10 days. The reaction mixture was directly subjected to column chromatography (SiO₂) and unreacted compound **3** was recovered with Me₂CO, whereupon the eluent was changed to Me₂CO/NH₄PF₆ (1.0 g NH₄PF₆ in 100 ml Me₂CO) and the green band containing [2]rotaxane 1-4PF₆ was collected. After removal of solvent, H₂O (50 ml) was added and the resulting precipitate was collected by filtration to afford the [2]rotaxane 1-4PF₆ (90 mg, 45%) as a green solid. ¹H NMR (500 MHz, CD₃CN): 1.13–1.19 (m, 3 H), 1.23–1.26 (m, 18 H), 2.55–2.60 (m, 2 H), 3.25 (s, 9 H), 3.42–4.13 (m, 52 H), 4.44 (s, 6 H), 4.48 (s, 2 H), 5.38–5.71 (m, 8 H), 5.91, 5.99, 6.08, 6.19 (4 × s, 2 H), 6.47 (d, *J* = 8.5, 1 H), 6.56–6.65 (m, 3 H), 6.76 (d, *J* = 8.5, 1 H), 6.95–6.98 (m, 1 H), 7.03–8.02 (m, 48 H), 8.38–8.97 (m, 8 H). MS (FAB), *m/z* (%): 2814 (8) [M – PF₆]⁺, 2668 (13) [M – 2PF₆]⁺, 2523 (8) [M – 3PF₆]⁺. For C₁₄₅H₁₆₄F₂₄N₄O₁₈P₄S₄ calculated: 58.86% C, 5.59% H, 1.89% N; found: 58.79% C, 5.54% H, 1.86% N.

[2]Rotaxane 2-4PF₆. A solution of dumbbell compound **4** (81 mg, 0.038 mmol), **23-2PF₆** (81 mg, 0.114 mmol) and 1,4-bis(bromomethyl)benzene (**24**) (30 mg, 0.114 mmol) in DMF (5 ml) was stirred at room temperature for 10 days. The reaction mixture was directly subjected to column chromatography (SiO₂) and unreacted compound **4** was recovered with Me₂CO, whereupon the eluent was changed to Me₂CO/NH₄PF₆ (1.0 g NH₄PF₆ in 100 ml Me₂CO) and the green band containing [2]rotaxane 2-4PF₆ was collected. After removal of solvent, H₂O (50 ml) was added, forming a precipitate, which was collected by filtration to give the [2]rotaxane 2-4PF₆ (0.074 mg, 61%) as a green solid. ¹H NMR (500 MHz, CD₃CN): 1.15–1.17 (m, 3 H), 1.91–1.93 (m, 18 H), 2.55–2.58 (m, 2 H), 3.25 (s, 9 H), 3.42–4.35 (m, 76 H), 4.44–4.48 (m, 8 H), 5.43–5.66 (m, 8 H), 5.93, 6.00, 6.09, 6.19 (4 × s, 2 H), 6.46–6.80 (m, 2 H), 6.99–7.65 (m, 52 H), 8.59–8.97 (m, 8 H). MS (FAB), *m/z* (%): 3078.29 (57) [M – PF₆]⁺, 2934.05 (100) [M – 2PF₆]⁺, 2788.29 (57) [M – 3PF₆]⁺. For C₁₅₇H₁₈₈F₂₄N₄O₂₄P₄S₄ calculated: 58.50% C, 5.88% H, 1.74% N; found: 58.20% C, 5.81% H, 1.69% N.

Photophysical Experiments

All the measurements were performed at room temperature in air-equilibrated MeCN solutions (2×10^{-5} – 1×10^{-4} mol l⁻¹). UV-Vis absorption spectra were recorded with a Perkin-Elmer Lambda 40 spectrophotometer. Uncorrected fluorescence spectra were obtained with a Perkin-Elmer LS-50 spectrofluorimeter equipped with a Hamamatsu R928 phototube. The estimated experimental errors are: 2 nm on band maxima, ±5% on the molar absorption coefficients and fluorescence intensity.

Electrochemical Experiments

Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) experiments were carried out in argon-purged MeCN solution at room temperature with an Autolab 30 multipurpose instrument interfaced to a personal computer. The working electrode was a glassy carbon electrode (0.08 cm², Amel); its surface was routinely polished with 0.3 μm alumina-water slurry on a felt surface, immediately prior to use. In all cases, the counter electrode was a Pt spiral, separated from the bulk solution with a fine glass frit, and an Ag wire was used as a quasi-reference electrode. Decamethylferrocene²⁸ (*E*_{1/2} = -0.11 V vs SCE) was present as internal standard. In all the electrochemical experiments the compound concentrations were in the range 5×10^{-4} – 1×10^{-3} mol l⁻¹ and tetrabutylammonium hexafluoro-

phosphate with 100 times higher concentration was added as supporting electrolyte. Cyclic voltammograms were obtained with sweep rates in the range 0.02–1.0 V s⁻¹; the DPV experiments were performed with a scan rate of 20 or 4 mV s⁻¹ (pulse height 75 and 10 mV, respectively) and a duration of 40 ms. The reversibility of the observed processes was established by using the criteria of (i) separation of 60 mV between cathodic and anodic peaks, (ii) the close to unity ratio of the intensities of the cathodic and anodic currents, and (iii) the constancy of the peak potential on changing sweep rate in the cyclic voltammograms. The same halfwave potential values were obtained from the DPV peaks and from an average of the cathodic and anodic CV peaks, as expected for reversible processes. For irreversible processes the potential values were estimated from the DPV peaks. The number of exchanged electrons in the redox processes of the investigated dumbbells and rotaxanes was measured by comparing the current intensity of the CV waves and the area of the DPV peaks with those found for the two reversible and bielectronic reduction processes of the CBPQT⁴⁺ cyclophane^{16–18}, after correction for differences in the diffusion coefficients and concentrations²⁹. The experimental error on the potential values was estimated to be ±10 mV and ±20 mV for reversible and irreversible processes, respectively.

Chemical Ox/Red Experiments

A standardized Fe(ClO₄)₃ solution in MeCN at room temperature was used to perform the mono-oxidation of the TTF unit contained in the dumbbells and rotaxanes. The concentrations of the dumbbell and rotaxane solutions were 2.0 × 10⁻⁵ mol l⁻¹. The reduction of the TTF⁺⁺ species was performed by using a MeCN solution of the 1,1'-dimethyl-4,4'-bipyridinium radical cation, obtained by reducing with zinc powder the 1,1'-dimethyl-4,4'-bipyridinium dication.

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