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Quantifying the barrier for the movement of cyclobis(paraquat-p-phenylene) over the dication of monopyrrolo-tetrathiafulvalene†

Rikke Kristensen,‡a Mathias S. Neumann,‡a Sissel S. Andersen,a Paul C. Stein,a Amar H. Floodb and Jan O. Jeppesen*a

A bistable [2]pseudorotaxane 1⊂CBPQT•4PF6 and a bistable [2]rotaxane 2•4PF6 have been synthesised to measure the height of an electrostatic barrier produced by double molecular oxidation (0 to +2). Both systems have monopyrrolo-tetrathiafulvalene (MPTTF) and oxyphenylene (OP) as stations for cyclobis(paraquat-p-phenylene) (CBPQT•4+). They have a large stopper at one end while the second stopper in 2• is composed of a thiocellulose (SET) group and a thiodiethyleneglycol (TDEG) substituent, whereas in 1⊂, the SET group has been replaced with a less bulky thiomethyl (SMe) group. This seemingly small difference in the substituents on the MPTTF unit leads to profound changes when comparing the physical properties of the two systems allowing for the first measurement of the deslipping of the CBPQT•4+ ring over an MPTTF•4+ unit in the [2]pseudorotaxane. Cyclic voltammetry and 1H NMR spectroscopic was used to investigate the switching mechanism for 1⊂CBPQT•MPTTF•4+ and 2•MPTTF•4+, and it was found that CBPQT•4+ moves first to the OP station producing 1⊂CBPQT•OP6+ and 2•OP6+, respectively, upon oxidation of the MPTTF unit. The kinetics of the complexation/decomplexation process occurring in 1⊂CBPQT•MPTTF•4+ and in 1⊂CBPQT•OP6+ were studied, allowing the free energy of the transition state when CBPQT•4+ moves across a neutral MPTTF unit (17.0 kcal mol–1) or a di-oxidised MPTTF•4+ unit (24.0 kcal mol–1) to be determined. These results demonstrate that oxidation of the MPTTF unit to MPTTF•4+ increases the energy barrier that the CBPQT•4+ ring must overcome for decomplexation to occur with 7.0 kcal mol–1.

Introduction

Since the first syntheses1,2 of catenanes and rotaxanes were reported in the 1960s, scientists have been fascinated by these interlocked compounds. The advent of supramolecular chemistry3,4 has paved the way to much more efficient protocols for the synthesis of catenanes and rotaxanes compared to the early low-yielding statistical and demanding covalently templated approaches.2,8 The chemistry of the non-covalent bond has transformed these molecular systems from chemical curiosities into a flourishing field of modern research. Thus, it is now possible to prepare these kinds of ordered molecules by recognising the role that mechanical bonds9 can play alongside covalent and non-covalent bonds.

These interlocked compounds have been used extensively and successfully to create artificial molecular machines (AMMs)10 in an effort to mimic both biological processes (biomimetic11), such as pumps,15-19 cars,20 and elevators.21 These designs often rely on controlling15,22-24 the mechanisms of stimuli-driven motion, and thus motivate studies of kinetics25-29 and the underlying energy landscapes.30,31 We do this here by measuring the impact of double oxidation on the barrier to the motion of a mobile ring (Scheme 1).

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† Electronic Supplementary Information (ESI) available: 1H NMR and UV-Vis-NIR spectra, binding studies and kinetic studies. See DOI: 10.1039/x0xx00000x
‡ Both authors contributed equally to this work.

Scheme 1 Oxidation of the monopyrrolo-tetrathiafulvalene (MPTTF) unit in 1⊂CBPQT•MPTTF•4+ to produce 1⊂CBPQT•OP6+, which subsequently deslips in a slow and rate-limiting step (RLS) producing 12+ and CBPQT•4+.
The foundation for the success of switching is the TTF unit’s capability to be oxidised reversibly\(^{37-39}\) first to its radical cation (TTF\(^{+}\)) and secondly to the dication (TTF\(^{2+}\)), which creates an electrostatic repulsion between the positively charged TTF unit and the tetracationic CBPQT\(^{4+}\) ring forcing CBPQT\(^{4+}\) to move away from the oxidised TTF station to end up at another station (i.e. DNP or HQ).

In order to control the switching rate of the movement of CBPQT\(^{4+}\), different barriers, either steric or electrostatic\(^{40-45}\) as well as photo-switchable gates and dynamic foldameric linker regions\(^{43,46}\) have been incorporated in the dumbbell component between the stations. The kinetic data emerging from these systems have provided knowledge about the movement of CBPQT\(^{4+}\) away from the positively charged TTF unit (TTF\(^{+}\)/TTF\(^{2+}\)). Few studies, however, have been directed at examining whether the TTF\(^{2+}\) unit itself can act as an electrostatic barrier for CBPQT\(^{4+}\), i.e. is it possible for CBPQT\(^{4+}\) to cross a TTF\(^{2+}\) unit? To the best of our knowledge, only two studies have been directed toward this end. An exemplary study by Stoddart and co-workers\(^{47}\) made use of atomic force microscopy (AFM) to measure the force that was needed to pull the CBPQT\(^{4+}\) ring across the electrostatic barrier of a TTF\(^{2+}\) unit in a bistable [2]rotaxane attached to a silicon surface. It was concluded that the electrostatic barrier energy for the CBPQT\(^{4+}\) ring to cross the TTF\(^{2+}\) unit was 65 kcal mol\(^{-1}\), a value that does not allow the CBPQT\(^{4+}\) ring to cross TTF\(^{2+}\) under normal conditions unless it is forced to do so (by pulling with an AFM tip).\(^{43}\) However, in a recent study by some of us, it was reported that in a tetra-stable [2]rotaxane\(^{25}\) incorporating CBPQT\(^{4+}\) as the ring component and TTF, monopyrroloTTF (MPTTF), HQ and oxyphenylene (OP) as stations, the CBPQT\(^{4+}\) ring can cross both an MPTTF\(^{2+}\) and a TTF\(^{2+}\) unit under stress-free conditions (i.e. no pulling of CBPQT\(^{4+}\) is applied) at room temperature and in a time scale of less than 20 min. It was estimated that the free energy of activation required for CBPQT\(^{4+}\) to move across the MPTTF\(^{2+}\) unit is ca. 0.5 kcal mol\(^{-1}\) smaller compared to TTF\(^{2+}\). Although it was demonstrated qualitatively that the CBPQT\(^{4+}\) ring can move across both an MPTTF\(^{2+}\) and a TTF\(^{2+}\) unit under relatively mild conditions, the free energy of activation (\(\Delta G^\ddagger\) for the processes could not be determined.

In this paper, we describe the synthesis and characterisation of a bistable [2]pseudorotaxane\(^{54,55,58-51}\) 1⊂CBPQT•4PF\(_6\) (Fig. 1) and a model [2]rotaxane 2•4PF\(_6\), and the thermodynamic and kinetic characteristics of the [2]pseudorotaxane 1⊂CBPQT•4PF\(_6\), Both 1⊂CBPQT•4PF\(_6\) and 2•4PF\(_6\) contain two potential stations for CBPQT\(^{4+}\), namely a primary redox-active MPTTF station (green) and a secondary OP station (red). They are both constructed in such a way that the pyrrole moiety of the MPTTF unit point toward the OP station, which is directly connected to a conventional large triarylmethyl (SET) group and a thiodiethyleneglycol (TDEG) substituent. In the [2]rotaxane 2•4PF\(_6\), the second stopper is a smaller and more unconventional one that is composed of a thiethyl (SEt) group and a thiodiethyleneglycol (TDEG) substituent. By replacing the SET group with a less bulky thiomethyl (SMe) group, the CBPQT\(^{4+}\) ring (blue) possesses enough thermal energy at room temperature to permit its slow passage over the combi-
uncomplexed species $1^{2+}$ and CBPQT$^{4+}$, respectively. This observation allowed us not only to monitor the deslipping process but also to quantify the size of the electrostatic barrier when CBPQT$^{4+}$ moves across an MPTTF$^{2+}$ unit.

**Results and discussion**

**Synthesis**

The syntheses of the large triarylmethyl stopper $3$, the MPTTF derivatives $4$ and $5$, and CBPQT•4PF$_6$ have already been reported. Here, we describe the synthesis of the [2]pseudorotaxane $1$$\subset$CBPQT•4PF$_6$ and the [2]rotaxane $2$$\subset$4PF$_6$ as outlined in Schemes 2 and 3. Deprotonation of the pyrrole N-H proton in the MPTTF derivatives $4$ and $5$ using NaH in DMF followed by N-alkylation of the corresponding anions with the iodide $3$ carrying the large triarylmethyl stopper gave the semidumbbell $1$ and the dumbbell $6$ in 72 and 78% yields, respectively.

Mixing the yellow semidumbbell $1$ with equimolar amounts of the colourless CBPQT•4PF$_6$ ring in Me$_2$CO/CH$_2$Cl$_2$ (20:1) at 298 K gave a yellow solution, which slowly became green, an observation related to slow formation (Scheme 2) of the [2]pseudorotaxane $1$$\subset$CBPQT•4PF$_6$. Allowing the mixture to equilibrate for 16 h, followed by fast flash column chromatography, made it possible to separate the [2]pseudorotaxane $1$$\subset$CBPQT•4PF$_6$ from the uncomplexed semidumbbell $1$ and excess CBPQT•4PF$_6$, providing the [2]pseudorotaxane $1$$\subset$CBPQT•4PF$_6$ as a green residue/solid, which was redissolved in MeCN and stored cold at 232 K.

For the synthesis of the [2]rotaxane $2$$\subset$4PF$_6$, a high pressure reaction was carried out by using the dumbbell $6$ as the template for the formation (Scheme 3) of the encircling CBPQT$^{4+}$ ring. The [2]rotaxane $2$$\subset$4PF$_6$ was self-assembled by subjecting a mixture of the dumbbell $6$, 1"-([1,4-phenylenebis(methylene)]bis(4,4'-bipyridinium) bis(hexafluorophosphat)$^{34}$ (7$\cdot$2PF$_6$) and 1,4-bis(bromomethyl)benzene (8) in DMF/CH$_2$Cl$_2$ (11:1) to ultra-high pressure (10 kbar) for 3 d followed by counterion exchange affording $2$$\subset$4PF$_6$ as a green solid in 18% yield.

**Photophysical investigations**

The photophysical properties of the semidumbbell $1$, CBPQT$^{4+}$, the [2]pseudorotaxane $1$$\subset$CBPQT$^{4+}$, the dumbbell $6$ and the [2]rotaxane $2$$^{4+}$ were investigated in MeCN at 298 K. The UV-Vis-NIR absorption spectra of CBPQT$^{4+}$ (Fig. 2a) did not display any absorption bands in the visible spectral region and the solution appears colourless. The semidumbbell $1$ (Fig. 2a) and the dumbbell $6$ (Fig. 2b) only exhibit weak tails in the visible region at $\lambda \leq 500$ nm and these solutions, thus, appear yellow.

Mixing equimolar proportions of the semidumbbell $1$ and CBPQT$^{4+}$ in MeCN initially produced a yellow solution, which
upon standing slowly became green. This colour change was accompanied by the appearance of a charge-transfer (CT) band centered on 816 nm in the UV-Vis-NIR absorption spectrum (Fig. 2a), a situation which is characteristic of a superstructure in which the MPTTF unit is located inside the cavity of CBPQT4+. This sequence of events unambiguously reveals that the [2]pseudorotaxane 1⊂CBPQT•MPTTF4+ is formed upon mixing 1 and CBPQT4+ and that the combination of the SMe group and the TDEG substituent does not constitute a stopper group for the dumbbell components of the [2]pseudorotaxane. While UV-Vis-NIR spectroscopy indicates qualitatively the presence of CBPQT•MPTTF4+ and CBPQT4+, respectively, 1H NMR spectroscopy was used to provide more precise information about the interactions taking place between CBPQT4+ and the dumbbell/dumbbell.

From the 1H NMR spectrum (400 MHz) recorded (Fig. S1†) of the [2]rotaxane 24+ in CD3CN at 298 K, it is clearly evident that CBPQT4+ is present by the appearance of an AB system (JAB = 13.4 Hz) integrating for eight protons at δ = 5.69 and 5.72 ppm and three broad singlets at δ = 8.81 (4H), 8.97 (2H) and 9.05 (2H) ppm, which can be assigned to the 'NCH2 protons and the α-H protons, respectively, located in the CBPQT4+ ring. A comparison of the 1H NMR spectra (400 MHz, 298 K) of the dumbbell 6 and the [2]rotaxane 24+ recorded in CD3CN reveal significant chemical shift differences for the resonances associated with the protons located closest to the MPTTF unit, suggesting that the MPTTF unit is located inside the CBPQT4+ ring in the [2]rotaxane 24+. The most diagnostic evidence, which shows that the CBPQT4+ ring encircles the MPTTF unit, is the downfield shift of the resonance for the two methylene protons in the SET group and the upfield shift of the resonance for the two pyrrole-H protons. The SCH2CH3 protons resonate as a quartet (J = 7.4 Hz) at δ = 3.10 ppm and the pyrrole-H protons57 as an AB system (JAB= 2.0 Hz) at δ = 6.22 and 6.25 ppm in the [2]rotaxane 24+, compared with a quartet (J = 7.4 Hz) at δ = 2.84 ppm (SCH2CH3) and a singlet at δ = 6.63 ppm (pyrrole-H) in the dumbbell 6.

Because the [2]rotaxane 24+ contains two potential stations (i.e. MPTTF and OP) for CBPQT4+, it can, in principle, exist as a mixture of two translational isomers. One (i.e. 2•MPTTF4+) in which CBPQT4+ encircles the MPTTF station, and the other (i.e. 2•OP4+) in which CBPQT4+ encircles the OP station. Since the [2]rotaxane 24+ is constructed in such a way that the pyrrole moiety of the MPTTF unit point toward the OP station, the shutting of CBPQT4+ between the MPTTF and OP stations is expected to be fast on the 1H NMR timescale because the steric barrier exhibited from the planar pyrrole moiety is less than 15 kcal mol⁻¹.58 This is supported by the fact that only one set of signals are observed in the 1H NMR spectrum (400 MHz) recorded (Fig. S1†) of the [2]rotaxane 24+, which show that the exchange between the 2•MPTTF4+ and 2•OP4+ translational isomers occurs rapidly on the 1H NMR time scale (CD3CN, 400 MHz) at 298 K. Thus, the chemical shift values of the observed resonances are weighted average values between those for the 2•MPTTF4+ and 2•OP4+ translational isomers. Consequently, the population between the two isomers cannot be quantified from the 1H NMR spectrum. However, in a [2]rotaxane containing only an MPTTF station in the dumbbell component and CBPQT4+ as the ring component, it was observed that the SCH2CH3 protons resonate at δ = 3.03 ppm,53 which is very close to the value (3.10 ppm) observed for the same protons in the [2]rotaxane 24+, strongly suggesting that the [2]rotaxane 24+ mainly exists as 2•MPTTF4+. This is in full agreement with the fact that the binding affinity (vide infra) between the MPTTF derivative 9 (Fig. 3) and CBPQT4+ (DG° = −6.0 kcal mol⁻¹)27 is significantly larger as compared to the binding affinity between the OP derivative 10 (Fig. 3) and CBPQT4+ (DG° = −1.7 kcal mol⁻¹).27 Assuming that the relative populations between 2•MPTTF4+ and 2•OP4+ are related to the Gibbs free energy difference (ΔDG°) for the binding affinity between CBPQT4+ and the MPTTF derivative 9 and the OP derivative 10, respectively, it can be calculated77 that the relative populations of 2•MPTTF4+ and 2•OP4+ at equilibrium are 99.9% and 0.1%, respectively, in CD3CN at 298 K.

The UV-Vis-NIR absorption spectrum (Fig. 2b) recorded of a solution of the [2]rotaxane 24+ showed a broad absorption band at 811 nm and the colour of the solution appears green, indicating that the MPTTF unit is encircled by CBPQT4+. This is in line with the 1H NMR spectroscopic investigations taking place between CBPQT4+ and the dumbbell/dumbbell.

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Taken all together, these findings clearly indicate that the [2]rotaxane $2^{4+}$ almost exclusively exists as the translational isomer $2\cdot\text{MPTTF}^{4+}$ in which CBPQT $4^{+}$ resides around the MPTTF station in CD$_3$CN at 298 K.

Further support for the formation of the [2]pseudorotaxane $1\subset\text{CBPQT}^{4+}$ came from a comparison (Fig. 4) of the $^{1}$H NMR spectra (400 MHz, 298 K) of the semidumbbell $1$ and a 1:1 mixture of $1$ and CBPQT$^{4+}$ recorded in CD$_3$CN at 298 K.

The $^{1}$H NMR spectrum (400 MHz) of an equilibrated 1:1 mixture of the semidumbbell $1$ and CBPQT$^{4+}$ recorded in CD$_3$CN at 298 K revealed three sets of signals, because of slow exchange between the complexed (i.e. $1\subset\text{CBPQT}^{4+}$) and uncomplexed species (i.e. $1$ and CBPQT$^{4+}$) on the $^{1}$H NMR time scale. The uncomplexed semidumbbell $1$ (Fig. 4, black assignments) and CBPQT$^{4+}$ (Fig. 4, blue assignments) are easily identified in the $^{1}$H NMR spectrum, as all the protons in these two compounds were found to resonate at their original positions. The third set of signals observed in the $^{1}$H NMR spectrum (Fig. 4, green assignments) recorded of the equilibrated 1:1 mixture of the semidumbbell $1$ and CBPQT$^{4+}$ are all shifted relative to the signals for the uncomplexed $1$ and CBPQT$^{4+}$ and can be associated with the [2]pseudorotaxane $1\subset\text{CBPQT}^{4+}$. As for [2]rotaxane $2^{4+}$, exchange between the two [2]pseudorotaxanes $1\subset\text{CBPQT}\cdot\text{MPTTF}^{4+}$ and $1\subset\text{CBPQT}\cdot\text{OP}^{4+}$ take place rapidly on the $^{1}$H NMR time scale (CD$_3$CN, 400 MHz) at 298 K. Using the...
same analysis as carried out on the [2]rotaxane 2\textsuperscript{a}, it can be concluded that the [2]pseudorotaxane 1⊂CBPQT\textsuperscript{4+} almost exclusively exists as the translational isomer 1⊂CBPQT•MPTTF\textsuperscript{4+} in CD\textsubscript{3}CN at 298 K. The most diagnostic evidence which indicates that CBPQT\textsuperscript{4+} encircles the MPTTF station is the downfield shift of the resonance for the SMe protons. This signal is observed as a singlet at $\delta = 2.68$ ppm in 1⊂CBPQT\textsuperscript{4+}, compared with a singlet resonating at $\delta = 2.39$ ppm in the uncomplexed semidumbbell 1. The pyrrole-H protons also show significant shift upon complexation with CBPQT\textsuperscript{4+}. In the semidumbbell 1, the two pyrrole-H protons were found resonating as a singlet at $\delta = 6.63$ ppm, whereas in 1⊂CBPQT\textsuperscript{4+}, they were observed resonating as an AB system ($J_{AB} = 2.0$ Hz) at $\delta = 6.23$ and 6.27 ppm. This finding is in perfect agreement with the results obtained from the $^1$H NMR spectroscopic investigations (vide supra) of the [2]rotaxane 2\textsuperscript{a}, where the pyrrole-H protons were found as an AB system ($J_{AB} = 2.0$ Hz) resonating at $\delta = 6.22$ and 6.25 ppm.

### Binding studies

To estimate the distribution of translational isomers present in the [2]pseudorotaxane 1⊂CBPQT\textsuperscript{4+} and the [2]rotaxane 2•MPTTF\textsuperscript{4+}, binding affinities for the formation of 1⊂CBPQT\textsuperscript{4+} and two model host-guest systems 9⊂CBPQT\textsuperscript{4+} and 10⊂CBPQT\textsuperscript{4+} (Fig. 3) were compared. The MPTTF model compound 9 was synthesised as outlined in Scheme S1\textsuperscript{t}. Mixing 9 with equimolar amounts of CBPQT\textsuperscript{4+} in MeCN at 298 K leads to the production (Scheme S2\textsuperscript{t}) of the [2]pseudorotaxane 9⊂CBPQT\textsuperscript{4+}, as indicated by the immediate appearance of a green-coloured solution. The UV-Vis-NIR spectrum (Fig. S2\textsuperscript{t}) recorded of this solution showed a broad absorption band at 815 nm as a result of the CT interactions that occur when the MPTTF unit is located inside CBPQT\textsuperscript{4+}. The UV-Vis-NIR dilution method\textsuperscript{59} (see ESI) was used to determine (Table 1) the binding constants ($K_b$) and the Gibbs free energies ($\Delta G^\circ$) for the formation of the 1:1 complexes 1⊂CBPQT\textsuperscript{4+} and 9⊂CBPQT\textsuperscript{4+}, respectively, in MeCN at 298 K, while the $K_b$ and $\Delta G^\circ$ values for the formation of 10⊂CBPQT\textsuperscript{4+} were taken from the literature.\textsuperscript{22}

A comparison of the thermodynamic data obtained for the complexation between CBPQT\textsuperscript{4+} and the MPTTF derivative 9 and the OP derivative 10, respectively, reveals that the binding affinity between CBPQT\textsuperscript{4+} and the MPTTF station is four orders of magnitude higher relative to the binding affinity between CBPQT\textsuperscript{4+} and the OP station in MeCN at 298 K. This observation clearly suggest that both the [2]pseudorotaxane 1⊂CBPQT\textsuperscript{4+} and the [2]rotaxane 2•MPTTF\textsuperscript{4+} almost exclusively (vide supra) will exist as the translational isomers 1⊂CBPQT•MPTTF\textsuperscript{4+} and 2•MPTTF\textsuperscript{4+}, respectively, in which the MPTTF station is located inside the cavity of CBPQT\textsuperscript{4+}. Although the semidumbbell 1 contains two potential stations for CBPQT\textsuperscript{4+} to reside around, it was found that the binding constant for the formation of 1⊂CBPQT\textsuperscript{4+} was slightly lower as compared to the binding constant for the formation of 9⊂CBPQT\textsuperscript{4+}. This observation can most likely be accounted for by the fact that the large bulky stopper group present in 1 weakens the effect of stabilising [C–H···O] hydrogen bonding interactions between the a-H pyridinium protons of CBPQT\textsuperscript{4+} and the oxygen atoms present in the diethyleneglycol chain connecting the MPPTF and the OP units.\textsuperscript{58}

### Electrochemical investigations

The electrochemical properties of the semidumbbell 1, the dumbbell 6, a 1:2 mixture of 1 and CBPQT\textsuperscript{4+} and the [2]rotaxane 2\textsuperscript{a} were investigated using cyclic voltammetry (CV). The cyclic voltammograms (CVs) were all recorded (Fig. 5) in nitrogen-purged solutions 0.5 mM in MeCN with n-Bu\textsubscript{4}N•PF\textsubscript{6} as the electrolyte (0.1 M), a glassy carbon electrode as the working electrode and at a scan rate of 0.1 V s\textsuperscript{−1}.

![Fig. 5 Cyclic voltammograms of a) semidumbbell 1, b) dumbbell 6, c) a 1:2 mixture of 1 and CBPQT\textsuperscript{4+} and d) [2]rotaxane 2\textsuperscript{a}](image)

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![Fig. 5 Cyclic voltammograms of a) semidumbbell 1, b) dumbbell 6, c) a 1:2 mixture of 1 and CBPQT\textsuperscript{4+} and d) [2]rotaxane 2\textsuperscript{a}](image)
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Table 2 Electrochemical data for the semidumbbell 1, the dumbbell 6, a 1:2 mixture of 1 and CBPQT4+, and the [2]rotaxane 24a obtained by cyclic voltammetry (CV) at 298 K in MeCN (vs. Fc/Fc+).

<table>
<thead>
<tr>
<th>Compound</th>
<th>E_{ox1}</th>
<th>E_{ox2}</th>
<th>E_{ox3}</th>
<th>E_{red1}</th>
<th>E_{red2}</th>
<th>E_{red3}</th>
<th>E_{red4}</th>
<th>E_{red5}</th>
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<td>1</td>
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<td>–0.01</td>
<td>+0.02</td>
<td>+0.36</td>
<td>+0.29</td>
<td>+0.33</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>6</td>
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<td>+0.03</td>
<td>+0.36</td>
<td>+0.30</td>
<td>+0.33</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1 + CBPQT4+</td>
<td>+0.06</td>
<td>+0.00</td>
<td>+0.03</td>
<td>+0.27</td>
<td>+0.30</td>
<td>+0.37</td>
<td>+0.32</td>
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</tr>
<tr>
<td>24a</td>
<td>+0.31</td>
<td>+0.27</td>
<td>+0.29</td>
<td>+0.38</td>
<td>+0.34</td>
<td>+0.36</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

CV measurements of 1, 6, a mixture of 1 and CBPQT4+·4PF6 (1:2) and 2·4PF6 in nitrogen-purged solutions (0.5 mM in MeCN) were conducted with 0.1 M n-Bu4NPF6 as the electrolyte, a glassy carbon electrode as the working electrode, a Pt counter electrode and with a scan rate of 0.1 V s⁻¹; Eox1, Eox2, Eox3, Ered1, Ered2, Ered3, Ered4, and Ered5 values are ± 0.01 V. a Anodic oxidation peak. b Cathodic reduction peak. c Half-wave potential. d E1/2 = (Eox1 + Ered1)/2.

An SMe with an SEt group does not affect the redox properties of the MPTTF unit.

While the two mono-electronic redox-waves in the dumbbell 6 are well separated, they occur (Fig. 5d and Table 2) at two very close potentials (+0.29 and +0.36 V vs. Fc/Fc+) in the [2]rotaxane 24a. The shift of +0.26 V toward a more positive potential for the first redox-wave (E_{1/2}1) in the [2]rotaxane 24a relative to the dumbbell 6, clearly indicate that the MPTTF unit is encircled by CBPQT4+. The rather large anodically shifted first in the redox-waves can be explained based on electrostatic repulsion and the strong CT interaction taking place between the MPTTF unit and the two electron-accepting bipyrindium moieties in CBPQT4+.

A comparison between the second redox-wave (E_{1/2}2) of the dumbbell 6 and the [2]rotaxane 24a, reveals that the second oxidation process of the MPTTF unit in the [2]rotaxane 24a is not the same as that in the dumbbell 6. This indicates that upon oxidation of the MPTTF unit to MPTTF4+, the CBPQT4+ will leave the MPTTF unit and the CBPQT•MPTTF4+ ring will remain in the oxidation producing 1:2 CBPQT•MPTTF4+ in MeCN, MeCN being enough to isolate 1:2 CBPQT•MPTTF4+ as its PF6 salt, which immediately after its isolation was dissolved in MeCN and stored at 232 K.

The decomplexation of 1:2 CBPQT•MPTTF4+ is observed at 298 K and moves from the MPTTF unit over the SMe/TDEG barrier to form an uncomplexed 1 and CBPQT4+, as a unimolecular reaction and can accordingly be expected to follow first-order kinetics.

As the complexation/decomplexation between the semidumbbell 1 and CBPQT4+ was found (vide supra) to be in slow exchange on the ¹H NMR time scale at 298 K, it is evident that the combination of the SMe group and the TDEG substituent constitute a steric/kinetic barrier for CBPQT4+. This observation suggests that the [2]pseudorotaxane 1:2 CBPQT•MPTTF4+ may be isolated as a “rotaxane-like” complex. By applying flash column chromatography, it was possible to isolate 1:2 CBPQT•MPTTF4+ as its PF6 salt, which immediately after its isolation was dissolved in MeCN and stored at 232 K.

The decomplexation of 1:2 CBPQT•MPTTF4+ is a unimolecular reaction and can accordingly be expected to follow first-order kinetics.

Initially, the isolated sample of 1:2 CBPQT•MPTTF4+ in MeCN was heated from 232 K to room temperature, whereafter the decomplexation process (Fig. 6a) was monitored at 298 K using the decrease (Fig. S41) in the MPTTF/CBPQT4+ CT band (814 nm) as the probe. The data points were collected in the early stage of the experiment where the reverse process (i.e. complexation) is not yet occurring to any significant extent. After 100 s, a flattening of the curve was observed (Fig. 6b). Consequently, only the data from 0–100 s was used to determine the rate constant (k_d) for the decomplexation process. The selected experimental data were subjected to a first-order analysis, and the straight line obtained (Fig. 6b, red data) by plotting lnA against time (t) confirmed the first-order nature of the decomplexation process. The rate constant k_d and the corresponding free energy of activation (ΔG‡d) were obtained directly from the slope of this straight line providing a k_d value of 1.485 ± 0.013 × 10⁻⁴ s⁻¹ and a ΔG‡d value of 22.70 ± 0.02 kcal mol⁻¹ for the decomplexation process in MeCN at 298 K.
Since the free energy of complexation ($\Delta G^\circ$) between the semidumbbell 1 and CBPQT$^{4+}$ has been determined (Table 1), the corresponding free energy of activation for the complexation (i.e. $\Delta G^\ddagger$) can be calculated by subtracting $-\Delta G^\circ$ from $\Delta G^\ddagger$ to give a $\Delta G^\ddagger$ value of 17.0 kcal mol$^{-1}$ ((22.7$\pm$5.7) kcal mol$^{-1}$) for the complexation between the semidumbbell 1 and CBPQT$^{4+}$ in MeCN at 298 K (Fig. 6c). Consequently, it can be concluded that the energy of the transition state for the movement of CBPQT$^{4+}$ over the SMe/TDEG barrier is 17.0 kcal mol$^{-1}$ and it seems conceivable that the transition state structure (Fig. 6c) is a strained one in which the CBPQT$^{4+}$ ring is forced up against the SMe and TDEG groups.27

**Chemical oxidation of 2$^{4+}$ and 1$^{+}$CBPQT$^{4+}$**

While the electrochemical investigations indicate that 2$^{4+}$ and 1$^{+}$CBPQT•OP$^{6+}$ are produced upon di-oxidation of 2$^{4+}$MPTTF$^{4+}$ and 1$^{+}$CBPQT•MPTTF$^{4+}$, respectively, the NMR spectroscopy was used to confirm their formation.

Ten equiv. of the oxidising agent tris(p-bromophenyl)ammonium hexachloroantimonate (TBPASbCl$_6$) were added to either a solution of the [2]rotaxane 2$^{4+}$MPTTF$^{4+}$ in CD$_3$CN at 298 K or the [2]pseudorotaxane 1$^{+}$CBPQT•MPTTF$^{4+}$, produced by allowing a 1:2 mixture of 1 and CBPQT$^{4+}$ in CD$_3$CN to equilibrate for 10 h at 298 K, whereafter the NMR spectra were recorded as fast as possible (ca. 10-15 min) after adding TBPASbCl$_6$.

Following oxidation, the observations of significant shifts to all the protons in the NMR spectra are consistent with the formation of the MPTTF$^{2+}$ dication and the production of the translational isomers in which the CBPQT$^{4+}$ ring encircles the OP station. In the NMR spectrum (Fig. 7, top) of the oxidised [2]rotaxane 2$^{4+}$, the protons associated with the pyrrole-H protons are downfield shifted (δ = 8.21 ppm) relative to their position in which they are found resonating in the neutral [2]rotaxane 2$^{4+}$ (δ = 6.22 and 6.25 ppm, Fig. 7, bottom). In the case of the oxidised [2]pseudorotaxane 1$^{+}$CBPQT$^{6+}$, the protons associated with the pyrrole-H protons are downfield shifted (δ = 8.21 ppm, Fig. S6) compared to their position in which they are found resonating in the neutral [2]pseudorotaxane 1$^{+}$CBPQT$^{4+}$ (δ = 6.23 and 6.27 ppm, Fig. S7). Previous studies25 have shown that such behaviour is fully consistent with the formation of the MPTTF$^{2+}$ dication and, hence, the formation of the oxidised [2]rotaxane 2$^{4+}$ and [2]pseudorotaxane 1$^{+}$CBPQT$^{6+}$, respectively, upon addition of TBPASbCl$_6$.

Evidence for the movement of the CBPQT$^{4+}$ ring away from the oxidised MPTTF$^{2+}$ unit is made obvious from the dramatic shifts in the resonances associated with the OP-H protons (Schemes 2 and 3) in the oxidised [2]rotaxane 2$^{4+}$ and [2]pseudorotaxane 1$^{+}$CBPQT$^{6+}$, as compared to their positions in 2$^{4+}$MPTTF$^{4+}$ and 1$^{+}$CBPQT•MPTTF$^{4+}$, respectively.

In 2$^{4+}$MPTTF$^{4+}$ (Fig. 7, bottom) and 1$^{+}$CBPQT•MPTTF$^{4+}$ (Fig. S6), the OP-H protons appear as doublets (J = 8–9 Hz) resonating at δ = 6.68 and 6.67 ppm, respectively. Upon oxidation, the signals for the OP-H protons experience large upfield shifts to δ = 2.52 (2$^{4+}$) and 2.53 (1$^{+}$CBPQT$^{6+}$) ppm, respectively, on account of the anisotropic shielding effect that occurs when the OP station is positioned inside the CBPQT$^{4+}$ ring. Examination of the NMR correlation spectroscopy (COSY) spectra for 1$^{+}$CBPQT$^{6+}$ (Fig. S7) and 2$^{4+}$MPTTF$^{4+}$ (Fig. S8) and recorded in CD$_3$CN at 298 K in both cases clearly displays through-bond scalar coupling between the shielded OP-H$_6$ and OP-H$_7$ protons. Consistently, the protons associated with the methylene group (i.e. $-OCH(3)-$) attached directly to the encircled OP station in 2$^{4+}$ and 1$^{+}$CBPQT$^{6+}$ are also significantly shielded (Fig. 7 and Fig. S6) and appear both at δ = 1.52 ppm, and show through-bond scalar coupling to the neighbouring methylene group present in glycol chain.515 Overall, these observations unambiguously prove that 2$^{4+}$MPTTF$^{4+}$ and 1$^{+}$CBPQT•OP$^{6+}$ are produced upon di-oxidation of 2$^{4+}$MPTTF$^{4+}$ and 1$^{+}$CBPQT•MPTTF$^{4+}$, respectively.
After successful determination of the switching mechanism of $2 \cdot \text{MPTTF}^{4+}$ and $1 \subset \text{CBPQT} \cdot \text{MPTTF}^{4+}$, the next step was to probe the stability of $2 \cdot \text{OP}^{6+}$ and $1 \subset \text{CBPQT} \cdot \text{OP}^{6+}$ on a longer timescale.

Initially, experiments were carried out on $2 \cdot \text{OP}^{6+}$ in CD$_3$CN at 298 K. It was found that $2 \cdot \text{OP}^{6+}$ decomposes (Fig. S9†) over a period of 97 h without forming both $6^{2+}$ and CBPQT$^4+$ when $2 \cdot \text{MPTTF}^{4+}$ is oxidised with ten equiv. of TBPASbCl$_6$. To test whether it was the oxidised dumbbell $6^{2+}$ or CBPQT$^4+$ that decomposed over time, a 1:1 mixture of the dumbbell $6^{2+}$ and CBPQT$^4+$ was also oxidised (Fig. S9†) with ten equiv. of TBPASbCl$_6$. In this case, it was observed that the dumbbell $6^{2+}$ after 97 h was almost completely decomposed, while CBPQT$^4+$ was unaffected by the oxidising environment.

In order to improve the stability of $2 \cdot \text{OP}^{6+}$, it was discovered that the addition of 100 equiv. of NH$_4$PF$_6$ increases the stability of the oxidised $[2] \text{rotaxane}$ significantly. Therefore, ten equiv. of TBPASbCl$_6$ were added to a CD$_3$CN solution of $2 \cdot \text{MPTTF}^{4+}$ at 298 K containing 100 equiv. of NH$_4$PF$_6$. The $^1$H NMR spectra (Fig. S10†) recorded of this mixture after 1, 6, 23 and 48 h are almost identical, clearly indicating that the oxidised $[2] \text{rotaxane}$ $2^{6+}$ is stable for more than 48 h under these conditions and that the CBPQT$^4+$ ring was not affected by the oxidising environment.

Kinetic investigations of $1 \subset \text{CBPQT} \cdot \text{OP}^{6+}$

Having found appropriate conditions to stabilise the oxidised $[2] \text{rotaxane}$ $2 \cdot \text{OP}^{6+}$ and dumbbell $6^{2+}$, the next step was to investigate the oxidised $[2] \text{pseudorotaxane}$ $1 \subset \text{CBPQT} \cdot \text{OP}^{6+}$ under the same conditions. While $2 \cdot \text{OP}^{6+}$ was stable for more than 48 h and it was not observed that CBPQT$^4+$ could not escape from the oxidised dumbbell component (Scheme S6†), the situation is different for $1 \subset \text{CBPQT} \cdot \text{OP}^{6+}$. In this case, it is evident that $1 \subset \text{CBPQT} \cdot \text{OP}^{6+}$ is the kinetic product formed after oxidation of $1 \subset \text{CBPQT} \cdot \text{MPTTF}^{4+}$ and that the CBPQT$^4+$ ring subsequently deslips from the oxidised semidumbbell to produce the uncomplexed species $1^{2+}$ and CBPQT$^4+$, respectively (Fig. 8a).

The $[2] \text{pseudorotaxane}$ $1 \subset \text{CBPQT} \cdot \text{MPTTF}^{4+}$ was prepared by allowing a 1:2:100 mixture of the semidumbbell $1$ (2 mM), CBPQT$^4+$ (4 mM) and NH$_4$PF$_6$ (0.2 M) to equilibrate for 10 h in CD$_3$CN at 298 K before it was oxidised with ten equiv. of TBPASbCl$_6$. The $^1$H NMR spectrum (400 MHz, 298 K) recorded of this mixture reveals (Fig. S11†) that $1 \subset \text{CBPQT} \cdot \text{OP}^{6+}$ is produced initially. When the oxidised solution is monitored over a longer time, it is clearly evident from the $^1$H NMR spectra (Fig. S11†) that the signals arising from $1 \subset \text{CBPQT} \cdot \text{OP}^{6+}$ decrease in intensity, while new signals corresponding to $1^{2+}$ (black assignments) and CBPQT$^4+$ (blue assignments) simultaneously increase in intensity. For example, the signals associated with the OP-H$_S$ and CBPQT$^4+$-H protons in $1 \subset \text{CBPQT} \cdot \text{OP}^{6+}$ resonating at $\delta = 2.58$ and 7.46 ppm, respectively, decrease in intensity, while the same signals for the uncomplexed species $1^{2+}$ and CBPQT$^4+$ that resonate at $\delta = 6.80$ and 8.18 ppm, respectively, increase in intensity.

Fig. 7 Partial $^1$H NMR spectra (400 MHz, 298 K, CD$_3$CN, 2 mM) recorded of the $[2] \text{rotaxane}$ $2^{6+}$ (bottom) and the oxidised $[2] \text{rotaxane}$ $2^{6+}$ (top). $2^{6+}$ was generated by adding ten equiv. of TBPASbCl$_6$ to $2^{4+}$. The (CH$_3$)$_3$C, CD$_2$H$_2$CN and H$_2$O signals are not shown in their full height.
To quantify the size of the electrostatic barrier when CBPQT$^{4+}$ moves from the OP station across the combined MPTTF$^{2+}$/SMe/TDEG barrier, $^1$H NMR spectra (500 MHz) were recorded every hour for three days. An equilibrated mixture of 1CBPQT$^{4+}$ and 100 equiv. of NH$_4$PF$_6$ were examined in CD$_3$CN at five different temperatures (294, 303, 308, 313 and 323 K) following oxidation with ten equiv. of TBPASbCl$_6$. First-order kinetic analysis was conducted using the signals for the C(CH$_3$)$_3$ and OCH$_3$ protons in both 1CBPQT•OP$^{6+}$ and 1$^{2+}$ as well as the xylyl-$H$ protons in uncomplexed CBPQT$^{4+}$ as probes$^{57}$ with rate constants ($k_d$) obtained for the movement of CBPQT$^{4+}$ over the MPTTF$^{2+}$/SMe/TDEG barrier in CD$_3$CN at 294, 303, 308, 313 and 323 K. A representative example at 294 K is shown in Fig. 8b, where the signal at $\delta = 1.37$ ppm associated with the (CH$_3$)$_3$C protons in the oxidised [2]pseudorotaxane 1CBPQT$^{4+}$•OP$^{6+}$ is used as the probe. There is an initial lag period (black data points, Fig. 8b) before all 1CBPQT$^{4+}$•MPTTF$^{4+}$ is oxidised to 1CBPQT$^{4+}$•OP$^{6+}$ and the selected data points used to construct the linear plots (red data points, Fig. 8b and Fig. S12†) of ln$I$ against time ($t$) were therefore the ones measured after the onset of a clear decrease in the intensity of the signals associated with 1CBPQT$^{4+}$•OP$^{6+}$. Finally, the rate constant $k_d$ and the corresponding energy of activation $\Delta G_d$ at each temperature were obtained as an average of the values obtained for each of the five different probes (Table S8†), which gave averaged $\Delta G_d$ values of 25.53 ± 0.02, 25.80 ± 0.02, 26.07 ± 0.02, 26.14 ± 0.02 and 26.37 ± 0.02 kcal mol$^{-1}$ in CD$_3$CN at 294, 303, 308, 313 and 323 K, respectively. The enthalpic ($\Delta H_d$) and entropic ($\Delta S_d$) contributions (Table S9†) to the kinetic barrier were obtained by plotting (Fig. S13†) the barrier size ($\Delta G_d$) as a function of temperature ($T$). Interpolation of this plot gave a $\Delta G_d$ value of 25.7 ± 0.1 kcal mol$^{-1}$ for the movement of CBPQT$^{4+}$ from the OP station over the MPTTF$^{2+}$/SMe/TDEG barrier in CD$_3$CN at 298 K.

Providing that the binding affinity between the OP station and CBPQT$^{4+}$ is not affected to any significant degree by oxidation of the MPTTF unit, an energy diagram for the deslipping of 1CBPQT$^{4+}$•OP$^{6+}$ can be constructed (Fig. 8c). Thus, based on a $\Delta G_d$ value of $-1.7$ kcal mol$^{-1}$ (Table 1) for the binding of CBPQT$^{4+}$ to the OP station, it can be calculated that the energy of the transition state for the movement of CBPQT$^{4+}$ over the MPTTF$^{2+}$/SMe/TDEG barrier is 24.0 kcal mol$^{-1}$ ((25.7–1.7) kcal mol$^{-1}$) in CD$_3$CN at 298 K.

By comparing the energy of the transition state for the neutral [2]pseudorotaxane 1CBPQT$^{4+}$ (Fig. 6) and the oxidised [2]pseudorotaxane 1CBPQT$^{4+}$•OP$^{6+}$ (Fig. 8), it is evident that oxidation of the MPTTF unit to MPTTF$^{2+}$ increases the energy barrier that the CBPQT$^{4+}$ ring has to overcome in order for deslipping to occur with 7.0 kcal mol$^{-1}$ ((24.0–17.0) kcal mol$^{-1}$). This increase in energy is most likely caused by the Coulombic repulsion that arises between the positive charged MPTTF$^{2+}$ unit in 1$^{2+}$ and the four positive charges present in the tetracationic CBPQT$^{4+}$ ring. The magnitude of the electrostatic barrier (24.0 kcal mol$^{-1}$) for the movement of CBPQT$^{4+}$ ring over the MPTTF$^{2+}$ dication can be compared to the 2,6-dimethylpyridinium monocation (22.9 kcal mol$^{-1}$, CD$_3$CN, 298 K) determined in a CBPQT$^{4+}$-based rotaxane.$^{54}$

**Conclusions**

We have reported the first measurement of the electrostatic barrier arising from the installation of two positive charges, by oxidation of the MPTTF station to MPTTF$^{2+}$, in a CBPQT$^{4+}$-based rotaxane. To make this measurement, we described the design and synthesis of a bistable [2]pseudorotaxane 1CBPQT$^{4+}$•4PF$_6$...
located inside the CBPQT4+ ring to produce corresponding translational isomers in which the OP station is revealed that in the case of the [2]rotaxane 2•MPTTF4+, the switching process was confined and that the switched [2]rotaxane 2•OP6+ was stable for more than 48 h in CD3CN at 298 K if 100 equiv. of NH4PF6 was added. However, in the case of the oxidised [2]pseudorotaxane 1•CBPQT•OP6+, the CBPQT4+ ring possesses enough thermal energy at 298 K to escape from the oxidised semidumbbell producing the uncomplexed species 1• and CBPQT4+, respectively. From our kinetic studies, we were able to determine the free energy of the transition state when CBPQT4+ moves across either a neutral MPTTF unit (17.0 kcal mol–1) or a di-oxidised MPTTF2+ unit (24.0 kcal mol–1) when they are substituted with a thiomethyl (SMe) and a thiodiethyleneglycol (TDEG) group. Consequently, it can be concluded that oxidation of the MPTTF unit to MPTTF2+ increases the energy barrier that the CBPQT4+ ring must overcome for deslipping to occur with 7.0 kcal mol–1. This knowledge is believed to be important in the design of future systems, in which the movement of CBPQT4+ needs to be controlled by electrochemical stimuli.

Experimental section

General

All chemicals are commercially available and were used as received unless otherwise stated. 2-(2-(4-[Tris(4-tert-butylyphenyl)-methyl][phenoxo]ethoxy)ethylidio) (3), 2-(4-(methylthio)-5-(2-(methylene)ethoxy)ethylidio)-1,3-dithiol-2-yldene)-5-SH-[1,3]dithiolo[4,5-c]pyrrole (4), 2-(4-ethylythio)-5-(2-(methylene)ethoxy)ethylidio)-1,3-dithiol-2-yldene)-5-SH-[1,3]dithiolo[4,5-c]pyrrole (5), 1-hexyl-1,4-phenylene-bis(methylene)bis(4,4′-bipyridinium) bis(hexafluorophosphate) (7•2PF6)₄,₅,₆,₇ cyclobis(paraquat-p-phenylene) tetrakis(hexafluoroborate) (CBPQT•4PF6)₄,₅,₆,₇ and 1-iodo-2-(2-methoxy-ethoxy)ethane (11) were all prepared according to literature procedures. The reaction was carried out under an anhydrous nitrogen atmosphere. CH2Cl2 was distilled prior to use. DMF was dried over molecular sieves (4 Å) for at least 3 d prior to use. High pressure reactions were performed in a custom made teflon-tube, using a psika high pressure apparatus. Thin-layer chromatography (TLC) was carried out using aluminium sheets pre-coated with SiO2 (Merck 60 F254) and visualised with UV light (254 nm) or I2 vapor. Column chromatography was carried out using SiO2 (Merck 60 F 0.040–0.63 mm). ¹H NMR and ¹³C NMR spectra were recorded at 298 K (unless otherwise stated) at 400/500 MHz and 100 MHz, respectively, on a 400 MHz Bruker ADVANCED III spectrometer or on a 500 MHz Varian INOVA spectrometer using residual non-deuterated solvent as the internal standard. The solvent signals were assigned using Gottlieb et al. All chemical shifts are quoted on a δ scale. The following abbreviations are used in listing the NMR spectra: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Melting points (Mp) were determined on a Büchi 353 melting point apparatus and are uncorrected.

Semidumbbell 1. The MPTTF compound 4 (40.9 mg, 0.997 mmol) was dissolved in anhydrous DMF (10 mL) and gassed (N2, 20 min) before NaH (60% w/w dispersion in mineral oil, 31.6 mg, 0.792 mmol) was added in one portion. The resulting red reaction mixture was stirred at room temperature for 10 min prior to 2-(2-(4-[Tris(4-tert-butylyphenyl)methyl][phenoxo])ethoxy)ethylidio (3), (67.7 mg, 0.096 mmol) was added in one portion, whereafter it was stirred at room temperature for 3 h. The reaction mixture was concentrated in vacuo and the resulting residue was re-dissolved in CH2Cl2 (50 mL) and washed with H2O (3 × 25 mL). The combined aqueous phases were subsequently extracted with CH2Cl2 (25 mL) before the combined organic phases were dried (MgSO4). Removal of the solvent gave a brown residue which was purified by column chromatography (60 mL SiO2, 3 cm Ø, eluent: CH2Cl2:EtOAc, 9:1). The yellow band (Rf = 0.6 in CH2Cl2:EtOAc, 9:1) was collected and the solvent was evaporated affording 1 as a yellow solid. (69.0 mg, 72%). Mp 151–152.5 °C. ¹H NMR (400 MHz, CD3CN, 298 K): δ 1.28 (s, 27H), 2.39 (s, 3H), 2.96 (t, J = 6.3 Hz, 2H), 3.27 (s, 3H), 3.43–3.45 (m, 2H), 3.52–3.54 (m, 2H), 3.60 (t, J = 6.3 Hz, 2H), 3.70–3.72 (m, 4H), 3.99 (t, J = 4.9 Hz, 2H), 4.02–4.04 (m, 2H), 6.63 (s, 2H), 6.78 (d, J = 8.9 Hz, 2H), 7.13 (d, J = 8.9 Hz, 2H), 7.18 (d, J = 8.6 Hz, 6H), 7.31 ppm (d, J = 8.6 Hz, 6H). MS (ESI) of [z]997 [M]+. ¹³C NMR (100 MHz, CDCl3, 298 K): δ 19.2, 31.5, 34.5, 35.5, 50.9, 59.2, 63.3, 67.4, 70.1, 70.3, 70.6, 72.0, 77.4, 113.3, 119.1, 119.2, 124.2, 130.6, 130.9, 132.5, 140.2, 144.3, 148.5, 156.6 ppm.³₂O MS (Hères-FT ESI): calcd for C36H30N2O2S: 997.3389; found: 997.3350. Anal. calcd for C36H30N2O2S: C, 66.16; H, 6.76; N, 1.40; S, 19.27; found: C, 66.04; H, 6.79; N, 1.37; S, 19.00.
[2]Pseudorotaxane 1⊂CBPQT•4PF6. The yellow semidumbbell 1 (10 mg, 0.010 mmol) was dissolved in a minimum of CH2Cl2 (0.15 mL) and the colourless macrocycle CBPQT•4PF6 (11 mg, 0.010 mmol) was dissolved in a minimum of Me6CO (HPLC grade, 3.0 mL). Mixing the two solutions produced initially a yellow-coloured solution. Leaving the yellow solution to stand for 16 h at room temperature gave a green solution. The green solution was subjected to fast (<5 min) flash column chromatography (25 mL SiO2, 1.5 cm Ø) and the first yellow band (Rf = 0.4 in CH2Cl2) was collected, and the solvent evaporated affording 6 as a yellow/orange solid (144 mg, 78%). Mp 150–151 °C.

1H NMR (400 MHz, CD2CN, 298 K): δ 1.25 (6H, d, J = 7.3 Hz, 3H), 1.28 (s, 27H), 2.84 (q, J = 7.2 Hz, 2H), 2.98 (t, J = 6.3 Hz, 2H), 3.27 (s, 3 H), 3.43–3.45 (m, 2H), 3.52–3.54 (m, 2H), 3.60 (t, J = 6.3 Hz, 2H), 3.70–3.72 (m, 4H), 3.97–3.99 (m, 2H), 4.02–4.04 (m, 2H), 6.63 (s, 2H), 6.77 (d, J = 8.2 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 8.2 Hz, 6H), 7.31 ppm (d, J = 8.2 Hz, 6H). 13C NMR (100 MHz, CD2CN, 298 K): δ 15.2, 30.6, 31.5, 34.5, 35.5, 50.8, 59.2, 63.2, 67.4, 70.1, 70.3, 70.6, 72.0, 77.4, 113.3, 119.1, 124.2, 126.6, 128.7, 130.9, 132.5, 140.2, 144.3, 148.5, 156.6 ppm.305 MS (ESI) m/z: 1011 [M]+, 413. MS (HiRes-FT ESI): calcd for C92H101F12N5O4P2S6+: 1011.3546; found: 1011.3520. Anal. calcd for C92H101F12N5O4P2S6+: C, 66.43; H, 6.87; N, 1.38; S, 19.00; found: C, 66.68; H, 6.79; N, 1.48; S, 18.79.

[2]Rotaxane 2•4PF6, 1.1′-[4,4-bipyridinium]bis(hexafluorophosphate) (7•2PF6) (396 mg, 1.32 mmol) and 1,4-bis(bromomethyl)benzene (8) (350 mg, 1.33 mmol) was added to a solution of the dumbbell 6 (331 mg, 0.327 mmol) in CH2Cl2 (0.5 mL), whereupon anhydrous DMF (5.5 mL) were added. The reaction mixture was transferred to a Teflon tube and subjected to 10 kbar pressure for 3 d at room temperature. The resulting green dark solution was directly subjected to column chromatography (200 mL SiO2, 3 cm Ø) and unretracted dumbbell 6 was eluted with Me6CO, whereupon the eluent was changed to CH2Cl2 (100 mL), washed with H2O (~10 mL) followed by addition of cold H2O (0 °C, 3 × 3 mL), and Et2O (3 × 3 mL) before being dried affording the [2]rotaxane 2•4PF6 as a green solid (125 mg, 18%). Mp > 235 °C.

1H NMR (400 MHz, CD2CN, 298 K): δ 1.27 (s, 27H), 2.68 (s, 3H), 2.53 (t, J = 6.4 Hz, 2H), 3.30 (s, 3H), 3.61–3.63 (m, 2H), 3.73–3.77 (m, 2H), 3.89 (t, J = 6.4 Hz, 2H), 3.97–4.00 (m, 4H), 4.12–4.14 (m, 2H), 4.19–4.21 (m, 2H), 5.66 and 5.73 (AB, JAB = 13.6 Hz, 6H), 6.26 and 6.27 (AB, JAB = 2 Hz, 2H), 6.68 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 8.2 Hz, 6H), 7.29 (d, J = 8.8 Hz, 6H), 7.74 (bs, 4H), 7.76 (s, 8H), 7.97 (bs, 4H), 8.81 (bs, 4H), 9.00 ppm (bs, 4H).

Dumbbell 6. The MPTTF compound 5 (79.9 mg, 0.183 mmol) was dissolved in anhydrous DMF (12 mL) and degassed (N2, 15 min) before NaH (60% w/w dispersion in mineral oil, 57.5 mg, 1.44 mmol) was added in one portion. The resulting red reaction mixture was stirred at room temperature for 10 min before 2-(4-[tris(4-tertbutylyphenyl)ethyl]oxynoxy)ethoxy)ethylidiole (3) (132 mg, 0.188 mmol) was added in one portion, whereafter it was stirred at room temperature for 2.25 h. The reaction mixture was concentrated in vacuo before it was re-dissolved in CH2Cl2 (100 mL), washed with H2O (3 × 50 mL) and dried (MgSO4). Removal of the solvent gave a brown solid which was purified by column chromatography (60 mL SiO2, 3 cm Ø, eluent: CH2Cl2). The yellow band (Rf = 0.4 in CH2Cl2) was collected, and the solvent evaporated affording...
were subjected to a first-order analysis by plotting ln\(I_t\) against time for 10 min before 1-iodo-2-(2-methoxyethoxy)ethane (11) (38.5 mg, 0.167 mmol) dissolved in DMF (1 mL) was added in one portion. The resulting red reaction mixture was stirred at room temperature for 4.5 h. The reaction mixture was concentrated in vacuo and the resulting residue was re-dissolved in CH\(_2\)Cl\(_2\) (100 mL), washed with H\(_2\)O (3 × 50 mL), dried (MgSO\(_4\)) and concentrated in vacuo. The resulting yellow residue was purified by multiple gradient column chromatography (60 mL SiO\(_2\), 3 cm eluent: CH\(_2\)Cl\(_2\)/EtOAc, 9:1). The yellow band (\(R_t = 0.2\) in CH\(_2\)Cl\(_2\)/EtOAc, 9:1) was collected and the solvent was evaporated affording 9 as an orange oil. (61.0 mg, 69%). \(^1\)H NMR (400 MHz, CD\(_3\)CN, 298 K), \(\delta = 2.43\) (s, 3H), 2.99 (t, \(J = 6.3\) Hz, 2H), 3.27 (s, 3H), 3.28 (s, 3H), 3.41–3.48 (m, 4H), 3.49–3.53 (m, 2H), 3.53–3.57 (m, 2H), 3.62 (t, \(J = 6.3\) Hz, 2H), 3.65 (t, \(J = 5.2\) Hz, 2H), 3.99 (t, \(J = 5.2\) Hz, 2H), 6.65 ppm (s, 2H). \(^13\)C NMR (100 MHz, CD\(_3\)CN, 298 K); \(\delta = 19.3, 36.4, 51.3, 59.0, 70.6, 71.0, 71.1, 71.6, 72.6, 72.6, 109.4, 114.7, 118.7, 121.7, 125.2, 131.3 ppm.\(^{30}\) MS (ESI): \(m/z\) 526 [M+H\(^+\)]. MS (HiRes-FT ESI): calc for C\(_{19}\)H\(_{28}\)NO\(_4\)S\(_6\): 526.0337; found: 526.0331. Anal calc for C\(_{19}\)H\(_{28}\)NO\(_4\)S\(_6\): C, 43.40; H, 5.18; N, 2.66; S, 36.59; found: C, 43.45; H, 5.04; N, 2.69; S, 36.44.

Kinetic experiments. The rate constant for the decomposition of 1·CBPQT·MPTTF\(^{4+}\) into 1 and CBPQT\(^{4+}\) were measured at 30 K using UV-Vis-NIR spectroscopy. Initially, the isolated [2]pseudorotaxane 1·CBPQT·MPTTF\(^{4+}\) in a 232 K MeCN solution was transferred to a 3.0 mL cuvette (\(l = 1\) cm) and quickly heated to room temperature, before being placed in the thermostated cell compartment of the UV-Vis-NIR spectrophotometer at 298 K. The movement was monitored by using the MPTTF/CBPQT\(^{4+}\) CT band (814 nm) as the probe. The data points collected in the early stage of the experiment (100 s) where the reverse process is not yet occurring in any significant extent were subjected to a first-order analysis by plotting ln\(I_t\) against \(t\) and fitted by the best straight line, giving a correlation coefficient of 0.98. The slope of the line gives the rate constant \(k_d\) according to relationship ln\(I_t\) = –\(k_d\)\(t\).

The rate constants \(k_d\) for the decomposition of 1·CBPQT·MPTTF\(^{4+}\) into 1 and CBPQT\(^{4+}\) were measured at different temperatures (294, 303, 308, 313 and 323 K) using \(^1\)H NMR spectroscopy (500 MHz). The [2]pseudorotaxane 1·CBPQT·MPTTF\(^{4+}\) was prepared by allowing a 1:2:100 mixture of the semidumbbell 1 (2 mM), CBPQT\(^{4+}\) (4 mM), and NH\(_2\)PF\(_6\) (0.2 M) to equilibrate for 10 h in CD\(_3\)CN at 298 K before it was oxidised with ten equiv. of TB\(_3\)PdCl\(_2\) to give 1·CBPQT·OP\(^{6+}\). \(^1\)H NMR spectra (500 MHz) were recorded every hour for 3 d.

Initially, phase and baseline correction were performed on all spectra and each spectrum was normalised using the integral of TMS signal as internal standard. All signals that did not overlap with the H\(_2\)O/HDO signal or any other signals were integrated and used as probes. For each probe, a plot of ln\(I_t\) against \(t\), where \(I\) is the integral of the signal in question and \(t\) is the time, was made, and a number of data points, \(n\), after all 1·CBPQT·MPTTF\(^{4+}\) was oxidised were fitted by the best straight line, giving correlation coefficients of 0.87–1.00. The slope of the line gives the rate constant \(k_d\) according to relationship ln\(I_t\) = –\(k_d\)\(t\).

Conflicts of interest
There are no conflicts to declare.

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Notes and references
§1 A [2]catenane is a molecule composed of two interlocked macrocyclic components. The two macrocycles are not linked covalently to each other, rather, a mechanical bond holds them together and prevents their dissociation.\(^{30}\)

§2 A [2]rotaxane is a molecule composed of a ring component and a dumbbell-shaped component. The ring component encircles the linear rodlike portion of the dumbbell-shaped component and is trapped mechanically around it by two bulky stoppers. Thus, the two components cannot dissociate from one another, although they are not linked covalently to each other.

§3 In the experiments conducted by Stoddart and coworkers, the bistable [2]rotaxane was immobilised on a silicon surface a pulling force of 145 pN was required to allow the CBPQT\(^{4+}\) ring to move across the TTF\(^{2+}\) unit. By combining spectroscopic and computational data, it was concluded that that the electrostatic barrier energy for the CBPQT\(^{4+}\) ring to cross the TTF\(^{2+}\) unit is 65 kcal mol\(^{-1}\).\(^{47}\)

§4 In a [2]pseudorotaxane at least one of the stoppers on the dumbbell-shaped component is absent with the consequence that dissociation of the [2]pseudorotaxane into its two components can occur, and the equilibrium between the species is controlled by the free energy of complexation, i.e. a [2]pseudorotaxane is 1:1 complex.

§5 The distinction between rotaxanes and pseudorotaxanes is far from being a straightforward one. When size-complementarity between the stoppers and the macrocyclic component is achieved, certain “rotaxanes” behave as pseudorotaxanes and can dissociate into their components under appropriate conditions. Thus, a species which is a rotaxane at ambient temperature might well be a pseudorotaxane at elevated temperatures. Even a solvent change can turn a rotaxane into a pseudorotaxane at the same temperature.\(^{46-49}\)

§6 In the literature, this stopper is usually called the tetraarylme-thane stopper, however, it was found\(^{47}\) that the oxyphenylene-part

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The $K_a$ value for the equilibrium between 2-MPTTF and 2•OP$^+$ was calculated using the relationship $K_a = \exp(-\Delta G°/RT)$ where $\Delta G° = G°(10\text{-CBPQT}^+) - G°(9\text{-CBPQT}$), $R$ is the gas constant and $T$ is the absolute temperature.

It has previously been shown that attachment of glycol chains to the pyrrole moiety of the MPTTF unit stabilises the resulting [2]pseudorotaxanes with 0.3 kcal mol$^{-1}$ as a result of [C–H···O] hydrogen bonding interactions taking place between the α-H pyrromidine protons of CBPQT$^+$ and the first and in particular the second oxygen atoms present in the glycol chains.\(^57\)

In a single station [2]rotaxane, containing only an MPTTF station •OP$^+$ is stable for more than 48 h in CD$_3$CN at 298 K in the presence of TBPASbCl$_6$; it was observed, it can be concluded that the oxidised [2]rotaxane is not complexed to CBPQT$^+$ before the 1:2 mixture of 1 and CBPQT$^+$. By using a method described in Koumura and CBPQT$^+$(4 mM), it can be calculated that the fraction of the oxidised [2]pseudorotaxane 1\(\subset\)CBPQT•OP$^+$ is 6% at equilibrium under these conditions at 298 K.

These signals were found useful as probes since they do not take place because of the very low affinity between the oxidised semidumbbell 2$^+$ and CBPQT$^+$.

By using a $K_a$ value of 16 M$^{-1}$ (Table 1) for the complexation between the OP station and CBPQT$^+$ and the initial concentrations for the semidumbbell 1 (2 mM) and CBPQT$^+$ (4 mM), it can be calculated that the fraction of the oxidised [2]pseudorotaxane 1\(\subset\)CBPQT•OP$^+$ is 97%.

This outcome is a consequence of the fact that only deslipping can take place because of the very low affinity between the oxidised semidumbbell 2$^+$ and CBPQT$^+$.

This is due to the non-oxyphenylene part of the stopper as triarylmethyl.

$\Delta G° = \sqrt{\Delta H° + T \Delta S°}$

$\Delta H° = 0.2$ kJ mol$^{-1}$ and $\Delta S° = 9$ J K$^{-1}$ mol$^{-1}$.

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