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Binding Studies between Triethylene Glycol-Substituted Monopyrrolotetrathiafulvalene Derivatives and Cyclobis(paraquat-*p*-phenylene)

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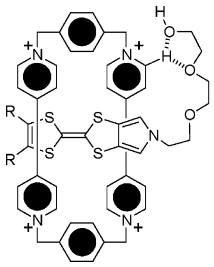

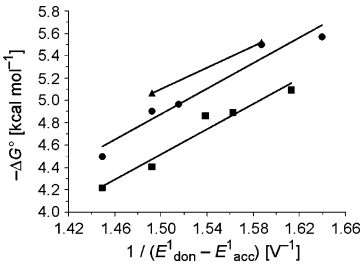

The synthesis of several π-electron-donating monopyrrolotetrathiafulvalene (MPTTF) derivatives, which conceptually can be divided into three classes containing none, one, or two triethylene glycol (TEG) substituents, is described. In all cases, the complexation between the π-electron donating MPTTF unit and the π-electron-deficient tetracationic cyclophane cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) has been investigated using UV−vis dilution techniques. The results reveal that the strength of the binding between MPTTF derivatives and $CBPQT^{4+}$ is directly correlated to the π-electron donating properties of the MPTTF derivatives. However, the π-electron-donating properties of the MPTTF derivatives is not the only factor of importance. The results enclosed in the present studies demonstrate that the TEG substituents assist the complexation process most likely on account of their capacity to participate in [C−H···O] hydrogen bonding interactions with some of the α-CH protons in the bipyridinium units of $CBPQT^{4+}$ and the stabilizing effect that attachment of one or two TEG substituents to the MPTTF unit exerts upon complexation with $CBPQT^{4+}$ has been quantified to approximately 0.3 and 0.5 kcal mol^{-1}, respectively. These results serve to lay an extended foundation for the understanding of which buttons to push when it comes to improve the design of bistable molecular switches based on (MP)TTF and $CBPQT^{4+}$.

Introduction

The advent of supramolecular chemistry[1] and its precise delicate noncovalent bonding interactions has stimulated the interest of chemists of many different persuasions in mechanically interlocked compounds such as catenanes and rotaxanes.[2] The internal guidance, provided by their intercomponent noncovalent bonding interactions, has transformed these interlocked molecular compounds from chemical curiosities into the centerpieces of a vibrant area of modern-day research. They are now prime candidates for the construction of artificial molecular machines[3,4] and the fabrication of nanoelectronic devices.[5] The redox-active tetrathiafulvalene[6] (TTF) unit serve[7] as an excellent recognition site for the tetracationic cyclophane,[8] cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$), as a result of stabilizing noncovalent interactions. TTF's unique π-electron donor properties and its ability to form a stable inclusion complex with $CBPQT^{4+}$ has made it and its derivatives prime candidates for the construction of molecular switches in the shape of bistable [2]catenanes[9,10] and [2]rotaxanes.[10,11] However, it is known experimentally that even subtle changes in the design of bistable [2]catenanes and [2]rotaxanes—in which one of the π-electron-donating sites is a TTF unit and the ring component is $CBPQT^{4+}$—can induce rather large changes in their physically behavior. Consequently, it is of paramount importance to understand and ultimately quantify the strength of the nonco-

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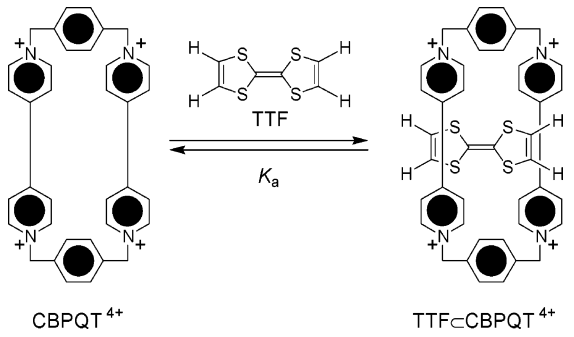
valent interactions that take place between the different components in bistable [2]catenanes and [2]rotaxanes in order to improve future design. The inclusion of TTF derivatives inside the cavity of $CBPQT^{4+}$ is well documented[7] and leads to the formation of pseudorotaxanes[12] under thermodynamic control upon mixing of their acyclic and cyclic components in solution and several research groups has investigated the green 1:1 complex formed (Scheme 1) between $CBPQT^{4+}$ and different

SCHEME 1. Complexation of TTF by $CBPQT^{4+}$



TTF derivatives.[13,14] It has been concluded[7e] that the strength of the binding between TTF derivatives and $CBPQT^{4+}$ is strongly dependent on the π-electron-donating ability of the TTF derivatives. Thus, the better is the π-electron donor, the stronger is the complex formed with $CBPQT^{4+}$. Other studies[5g,15,16] have shown that addition of ethylene glycol substituents to the TTF unit enhance the binding constant with the $CBPQT^{4+}$ host by up to 2 orders of magnitude by virtue of their entering into [C−H···O] hydrogen bonding interactions with some of the α-CH hydrogen atoms in the bipyridinium units of $CBPQT^{4+}$. Consequently, there seems to be two major sets of noncovalent interactions one needs to take into account when the strength of the binding between $CBPQT^{4+}$ and a TTF unit bearing ethylene glycol substituents is considered, namely (i) $\pi-\pi$ and

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charge-transfer (CT) interactions between the electron donor (TTF) and electron acceptor ($CBPQT^{4+}$) and (ii) [C−H···O] interactions taking place between the α-CH hydrogen atoms in the bipyridinium units of $CBPQT^{4+}$ and some of the oxygen atoms in the ethylene glycol substituents.[17] However, a comparison of the strength of these two different sets of noncovalent interactions has to the best of our knowledge not been undertaken. Therefore, we decided to design and synthesize series of different triethylene glycol (TEG) substituted monopyrrolotetrathiafulvalene (MPTTF) derivatives in which both the donor strength of the MPTTF unit and the number of TEG substituents attached to it is being systematically varied in order to quantify the effect that TEG substituents exerts upon complexation between MPTTF derivatives and $CBPQT^{4+}$.

Results and Discussion

Attachment of electron-donating substituents, such as alkyl groups, to the MPTTF unit is known to increase its donor strength, whereas attachment of electron-withdrawing substituents, such as thioalkyl groups, is known to decrease its donor strength.[18] Therefore, the donor strength of MPTTF derivatives can be efficiently controlled by attachment of appropriate substituents to the MPTTF unit. The MPTTF derivatives, investigated in this work, are shown in Figure 1. These derivatives can conceptually be divided into three different categories, containing (i) none (**1**−**5**), (ii) one (**6**−**10**), or (iii) two (**11** and **12**) TEG substituents capable of entering into [C−H···O] hydrogen-bonding interactions with $CBPQT^{4+}$.

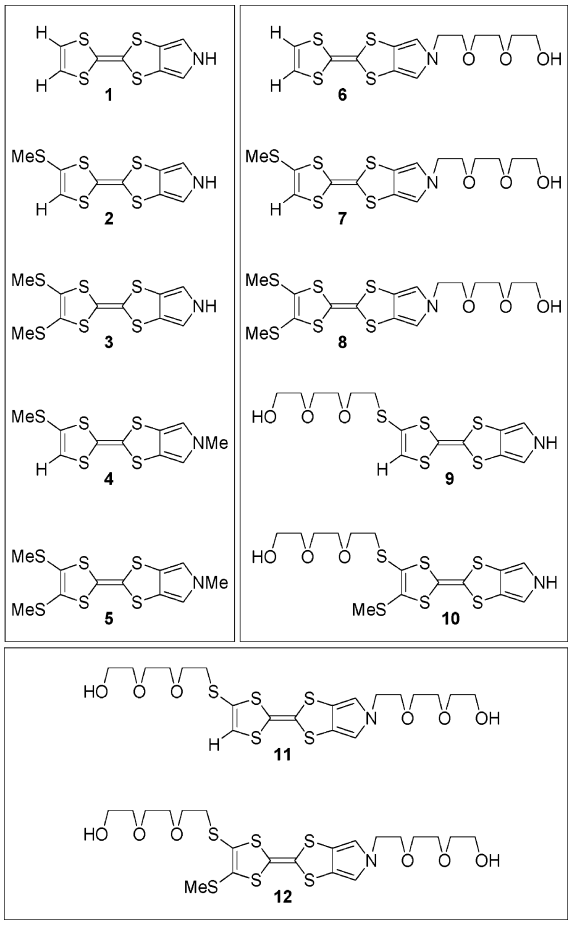
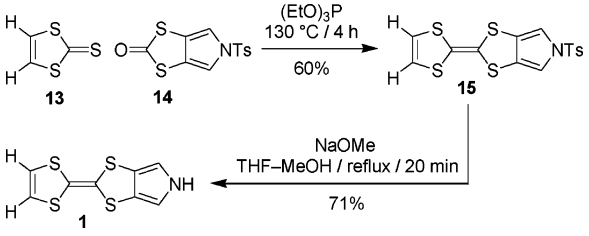


FIGURE 1. Molecular formulas of the different MPTTF derivatives **1**−**12** investigated in the present work. The twelve MPTTF derivatives can be divided into three classes containing none (**1**−**5**), one (**6**−**10**), or two (**11** and **12**) TEG substituents as indicated by the boxes.

Synthesis. The syntheses of compounds **2**,[11i] **3**,[18b] and **5**[18b] have already been reported. Here, we describe the syntheses of compounds **1**, **4**, and **6**−**12** as illustrated in Schemes 2−5.

The synthesis of compound **1** was carried out as outlined in Scheme 2. Cross coupling of 1,3-dithiole-2-thione (**13**) with 5-tosyl-(1,3)-dithiolo[4,5-*c*]pyrrole-2-one[18b] (**14**) using triethyl phosphite ($(EtO)_3P$) as the coupling reagent gave the MPTTF derivative **15** in 60% yield. Removal of the tosyl protecting group was accomplished in 71% yield by heating **15** under reflux in a 1:1 mixture of THF and MeOH in the presence of an excess of NaOMe.

SCHEME 2. Synthesis of the MPTTF Derivative 1



(12) A [2]rotaxane is an interlocked molecule composed of a ring and dumbbell-shaped component between which there are no covalent bonds—only a mechanical and noncovalent bonds are present. The ring encircles the linear portion of the dumbbell-shaped component and is trapped mechanically around it by two bulky stoppers. By contrast, in a [2]pseudorotaxane, at least one of the stoppers on the dumbbell-shaped component is absent with the consequence that dissociation into its two components can occur spontaneously (see ref 2b).

(13) Originally, in a communication (see: Philp, D.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1991**, 1584−1586), a K_a value of 51 M^{-1} for the 1:1 complex in MeCN at 300 K was reported. Subsequently, it was found that this K_a value was in error. After numerous experiments had been carried out by both the Stoddart group (see ref 7a) and Bryce (see ref 7b), a consistent conclusion was reached, that is, that the K_a value is ca. 10000 M^{-1} in MeCN at 298 K, while in Me_2CO at 298 K it is ca. 2600 M^{-1}.

(14) Besides $CBPQT^{4+}$ being able to host TTF and its derivatives, it has been demonstrated that TTF can be used as an efficient template for the synthesis of $CBPQT^{4+}$. See: Doddi, G.; Ercolani, G.; Mencarelli, P.; Piermattei, A. J. *Org. Chem.* **2005**, *70*, 3761−3764.

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(17) Although the existence of other noncovalent interactions, such as [N^+···O] ion−dipole interactions, taking place between the bipyridinium units of $CBPQT^{4+}$ and some of the oxygen atoms in the ethylene glycol substituents, can not be ruled out. Previous studies (see: Castro, R.; Nixon, K. R.; Evanseck, J. D.; Kaifer, A. E. *J. Org. Chem.* **1996**, *61*, 9591−9595, refs 3e and 15) indicate that the host $CBPQT^{4+}$ binds a number of different guests through complementary $\pi-\pi$, CT, [C−H···O], and [C−H···π] interactions. In addition, calculations (see ref 16) have shown that ethylene glycol groups are of paramount importance in assisting the complexation process by virtue of their entering into [C−H···O] interactions with some of the α-CH hydrogen atoms in the bipyridinium units of $CBPQT^{4+}$. Consequently, $\pi-\pi$, CT, and [C−H···O] interactions are probably the most important interactions to be considered when the strength of the binding between $CBPQT^{4+}$ and ethylene glycol substituted TTF derivatives are compared, since [C−H···π] interactions do not exist (see ref 13) in TTF⊂$CBPQT^{4+}$ complexes.

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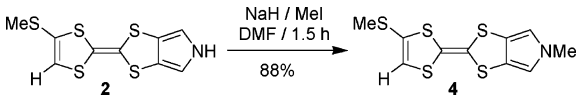
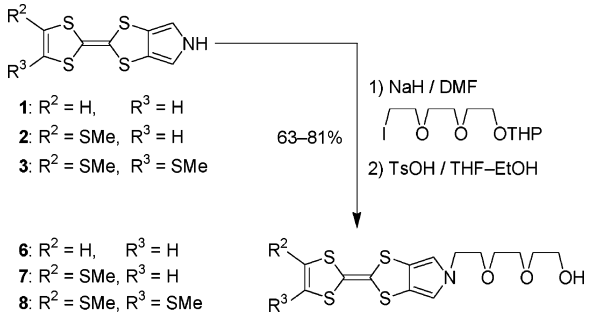
SCHEME 3. Synthesis of the MPTTF Derivative 4



The *N*-methylated MPTTF derivative **4** was obtained (Scheme 3) in 88% yield following N-alkylation (NaH/DMF) of the pyrrole unit in **2** with MeI.

The three *N*-alkylated MPTTF derivatives **6**−**8** were obtained as shown in Scheme 4. Alkylation (NaH/DMF) of the pyrrole nitrogen in compounds **1**−**3** with 2-{2-[2-(tetrahydropyranyl-2-oxy)ethoxy]ethoxy}ethyl iodide[19] followed by removal of the THP protecting groups with *p*-toluenesulfonic acid (TsOH) in THF−EtOH afforded the MPTTF derivatives **6**−**8** in overall yields of 63−81%.

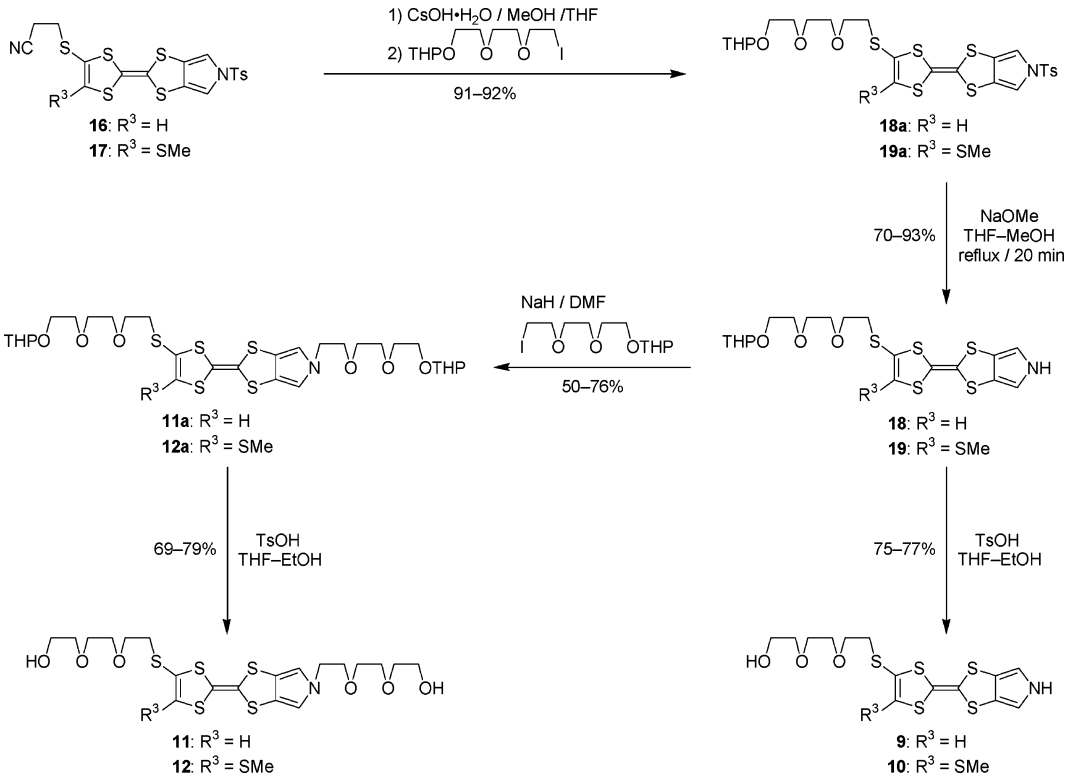
SCHEME 4. Syntheses of MPTTF Derivatives 6−8



The MPTTF derivatives **9**−**12** were synthesized from the MPTTF building blocks **16**[11i] and **17**,[11c] according to the routes outlined in Scheme 5. Coupling of 2-{2-[2-(tetrahydropyranyl-2-oxy)ethoxy]ethoxy}ethyl iodide[19] with **16** and **17**, following their in situ deprotection with 1.05 equiv of $CsOH{\cdot}H_2O$ in a 7:1 mixture of THF and MeOH, gave the MPTTF derivatives **18a** and **19a** in yields of 91% and 92%, respectively. Removal of the tosyl protecting groups in **18a** and **19a** was carried out in 70% and 93% yields, respectively, using NaOMe in a 1:1 mixture of THF and MeOH affording the MPTTF derivatives **18** and **19**. Subsequently, treatment of the THP ethers **18** and **19** with TsOH in THF−EtOH gave the desired alcohols **9** and **10** in 77% and 75% yields, respectively. To obtain compound **11** and **12**, the pyrrole units of the MPTTF derivatives **18** and **19** were N-alkylated (NaH/DMF) with 2-{2-[2-(tetrahydropyranyl-2-oxy)ethoxy]ethoxy}ethyl iodide[19] obtaining **11a** and **12a** in yields of 50% and 76%, respectively. Finally, removal of the THP protecting groups in **11a** and **12a** with TsOH in THF−EtOH provided **11** and **12** in 69% and 79% yields.

Binding Studies between the MPTTF Derivatives 1−12 and $CBPQT^{4+}$. Mixing the MPTTF derivatives **1**−**12** with equimolar amounts of the tetracationic macrocycle $CBPQT^{4+}$ at 296 K in Me_2CO leads to the formation of the [2]pseudorotaxanes **1**−**12**⊂$CBPQT^{4+}$ as indicated by the immediate[20] formation of green solutions and the concomitant appearance of CT bands in the 750−900 nm region of the absorption spectra. These observations are characteristic[7] for superstructures in which MPTTF derivatives are being complexed inside the cavity of $CBPQT^{4+}$. By employing the UV−vis dilution method,[7e] the associated binding constants (K_a values) at 296 K in Me_2CO were determined by correlating the maximum absorptions of the MPTTF/$CBPQT^{4+}$ CT bands with the concentration of the components in a 1:1 mixture of the MPTTF derivatives **1**−**12** and $CBPQT^{4+}$. In each particular case, the absorbance (A) was measured at λ_{max} for the CT absorption band in Me_2CO at various absolute concentrations (c) between 10^{-5} and 10^{-4} M. Plotting c/A against $1/A^{1/2}$ affords a straight line, with a slope of $\alpha = (1/K_a\epsilon l)^{1/2}$, and the y intercept can be defined as $y_0 = 1/\epsilon l$, where ϵ is the molar extinction

SCHEME 5. Syntheses of MPTTF Derivatives 9−12



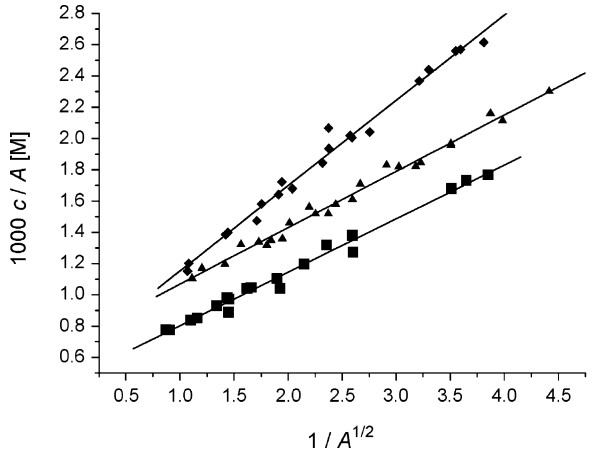


FIGURE 2. Linear plots of c/A against $1/A^{1/2}$ for 1:1 mixtures of $CBPQT^{4+}$ and the MPTTF derivatives **2** (■), **10** (◆), and **12** (▲). The absorbance A was in each particular case measured at several different absolute concentrations (c) obtained from dilution of at least two independent stock solutions. The obtained data points [$1/A^{1/2}$, c/A] were fitted to best straight lines, giving correlation coefficients of 0.986, 0.987, and 0.988, respectively.

coefficient for the CT absorption band of the MPTTF/$CBPQT^{4+}$ complex and l is the optical path length. By combining these two expressions, it transpires[7e] that $K_a = y_0/\alpha$.[2] In each case, the data points [$1/A^{1/2}$, c/A] were fitted to a best straight line and correlations coefficients of 0.919 to 0.988 were obtained confirming the linear relationship between $1/A^{1/2}$ and c/A. Representative examples are shown in Figure 2. The K_a values determined from these 12 dilution experiments were used to derive the free energies of complexation[21] ($-\Delta G°$), which are summarized in Table 1, together with number of data points and associated correlation coefficients.

Electrochemistry of MPTTF Derivatives 1−12. The π-electron donor strength of the MPTTF derivatives **1−12** was determined by measuring the first redox potential ($E_{1/2}{}^1$) using cyclic voltammetry (CV). The cyclic voltammograms (CVs) of all 12 MPTFF derivatives recorded at 296 K in MeCN revealed two reversible redox waves which can be associated with the first (MPTTF → $MPTTF^{+\bullet}$) and second ($MPTTF^{+\bullet}$ → $MPTTF^{2+}$) oxidation process of the MPTTF unit. The $E_{1/2}{}^1$ values obtained from these experiments are recorded in Table 1.

The data summarized in Table 1 reveal several significant trends. First of all, they support the general finding[7e] that the noncovalent binding interactions between $CBPQT^{4+}$ and TTF derivatives is directly correlated to the π-electron-donating properties of the TTF derivatives. For example, a comparison between similar structures, such as **3** and **5**, reveal that increasing the π-electron donor strength by substituting a hydrogen atom on the pyrrole nitrogen by an electron-donating methyl group favors the complexation process. On the other hand, increasing the number of electron-withdrawing thiomethyl substituents by going from **1** → **2** → **3** greatly disfavors the complexation process by decreasing the π-electron donor strength of the MPTTF derivative. Another important trend transpires when a comparison between MPTTF derivatives with the same π-electron donor strength, but different numbers of attached TEG substituents, is carried out. For instance, the $CBPQT^{4+}$ binding affinity of **8** ($K_a = 4200\ M^{-1}$) is roughly two times higher than that of **5** ($K_a = 1800\ M^{-1}$) when studied under identical conditions. A more detailed analysis of the data collected in Table 1 was carried out by employing the following relationship[22] for donor−acceptor interactions

$$-\Delta G° = k_1 + T\Delta S° + \frac{k_2\beta^2}{E^1_{\text{don}} - E^1_{\text{acc}}} \qquad (1)$$

where β expresses the value of the overlap integral between the donor and acceptor, k_1 and k_2 are constants, while E^1_{don} and E^1_{acc} are the first redox potential of the donor and acceptor, respectively. In this particular case, the MPTTF in question is the donor and $CBPQT^{4+}$ is the acceptor. Using for the cyclic acceptor[23] $CBPQT^{4+}$, $E^1_{\text{acc}} = -0.25$ V vs (Ag/AgCl in MeCN) and for E^1_{don} the $E_{1/2}{}^1$ values listed in Table 1, a plot (Figure 3) of $-\Delta G°$ in Me_2CO vs the reciprocal difference $1/(E^1_{\text{don}} - E^1_{\text{acc}})$ in redox potentials for the MPTTF derivatives **1−12** can be constructed. It is evident from Figure 3 that the data points originating from the MPTTF derivatives without TEG substituents (**1−5**) can be fitted to a straight line and that the data points originating from the MPTTF derivatives with one TEG substituent (**6−10**) can be fitted to another straight line almost parallel to the first one. This finding indicates that attachment of a single TEG substituent to an MPTTF unit results in a stabilizing effect of approximately 0.3 kcal mol^{-1} on the complex between the tetracationic cyclophane $CBPQT^{4+}$ and the MPTTF derivative. Note that the two lines are not

TABLE 1. Comparison of Binding Constants (K_a Values) and Derived Free Energies of Complexation[21] ($-\Delta G°$) between $CBPQT^{4+}$ and the MPTTF Derivatives 1−12 Determined by Absorption Spectroscopy at 296 K in Me_2CO Using the MPTTF/$CBPQT^{4+}$ CT Band as Probes with the First Redox Potentials ($E_{1/2}{}^1$) for the MPTTF Derivatives 1−12 Obtained by Cyclic Voltammetry (CV) at 296 K in MeCN

compd	λ_{max} (nm)	data points	correlation coefficient	K_a[a,b] (M^{-1})	$-\Delta G°$ [b] (kcal mol^{-1})	$E_{1/2}{}^1$ [c−e] (V)
1	855	20	0.983	5800 ± 750	5.09 ± 0.08	+0.37
2	830	19	0.986	3900 ± 450	4.86 ± 0.07	+0.40
3	805	16	0.980	1300 ± 150	4.21 ± 0.07	+0.44
4	815	19	0.978	4100 ± 450	4.89 ± 0.07	+0.39
5	815	16	0.940	1800 ± 200	4.41 ± 0.07	+0.42
6	845	21	0.961	13000 ± 2200	5.57 ± 0.10	+0.36
7	820	32	0.970	11600 ± 1700	5.50 ± 0.09	+0.38
8	805	16	0.983	4200 ± 700	4.90 ± 0.10	+0.42
9	815	27	0.919	4700 ± 600	4.97 ± 0.08	+0.41
10	800	20	0.987	2100 ± 250	4.50 ± 0.07	+0.44
11	810	22	0.984	12000 ± 1800	5.52 ± 0.09	+0.38
12	795	24	0.988	5500 ± 700	5.06 ± 0.08	+0.42

[a] The K_a values reported are for the tetrakis(hexafluorophosphate) ($4PF_6^-$) salt of $CBPQT^{4+}$. [b] The errors were obtained as described in the Supporting Information. [c] CV measurements were carried out in nitrogen-purged MeCN solutions (1.0 mM) with tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) as supporting electrolyte (0.1 M) and a platinum disk as working electrode at a scan rate of 100 mV s^{-1}. [d] Potential values in V vs Ag/AgCl. [e] The estimated errors on the $E_{1/2}{}^1$ values are ±5 mV.

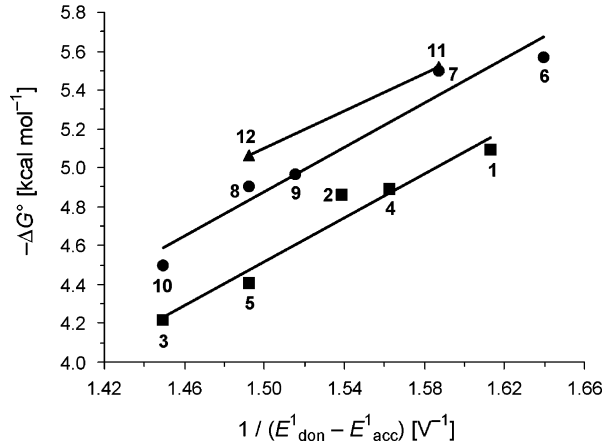


FIGURE 3. Linear plots of $-\Delta G°$ in Me_2CO vs $1/(E^1_{don} - E^1_{acc})$ for the MPTTF derivatives **1**−**12**. The $-\Delta G°$ values were obtained as described in Tables 1. Best straight lines, with correlation coefficients of 0.954, 0.950, and 1.000 respectively, have been fitted to the data points corresponding to the MPTTF derivatives containing none (i.e., **1**−**5**, ■), one (i.e., **6**−**10**, ●), and two (i.e., **11** and **12**, ▲) TEG substituents.

completely parallel, an observation which most likely can attributed to experimental uncertainties. Analogous, it can be deduced from Figure 3 that adding an additional TEG substituent, as in the case of **11** and **12**, leads to a further increase of $-\Delta G°$ of roughly 0.2 kcal mol^{-1}. However, on account of the limited data available it is obviously more difficult to quantify the stabilizing effect that attachment of two TEG substituents to an MPTTF unit exert upon complexation with CBPQT^{4+}, but a value of approximately 0.5 kcal mol^{-1} seems to be reasonable. Although these effects seems to be small they are nevertheless important to take into account when designing new molecular and supramolecular systems based on (MP)TTF and CBPQT^{4+}, since even very small changes in the degree of interaction between an (MP)TTF unit and CBPQT^{4+} in, for example, bistable rotaxanes[11i] might have a huge effect on the distribution of translational isomers.

Variable-Temperature Binding Constant Measurements. The increase in the binding affinity toward CBPQT^{4+} being observed upon attaching TEG substituents to the MPTTF unit is expected to arise from [C−H···O] hydrogen-bonding interactions taking place between the acidic α-CH protons in the tetracationic cyclophane and some of the oxygen atoms in the TEG substituent.[17] To support this hypothesis, additional binding studies between the tetracationic cyclophane CBPQT^{4+} and the MPTTF derivatives **1** and **6** containing none and one TEG substituent, respectively, were carried out at different temperatures to compare the enthalpic ($\Delta H°$) and entropic ($\Delta S°$) contributions to the formation of **1**⊂CBPQT^{4+} and **6**⊂CBPQT^{4+}, respectively. UV−vis dilution experiments were carried out at several different temperatures[24] to determine the temperature dependence of the binding constants for the 1:1 complexation of CBPQT^{4+} with the MPTTF derivatives **1** and **6**, respectively, in Me_2CO. The K_a and derived $-\Delta G°$ values, obtained from these UV−vis dilution experiments, are recorded in Tables 2 and 3.

The outcome of these binding studies reveals that the complexation between CBPQT^{4+} and the MPTTF derivatives **1** and **6** is strongly temperature dependent. An increase in the temperature results in a lower degree of complexation, whereas a decrease in the temperature results in a higher degree of

TABLE 2. Binding Constants (K_a Values) and Derived Free Energies of Complexation[21] ($-\Delta G°$) between CBPQT^{4+} and the MPTTF Derivative 1 Determined by Absorption Spectroscopy in Me_2CO at Different Temperatures Using the MPTTF/CBPQT^{4+} CT Band as Probe

T (K)	λ_{max} (nm)	data points	correlation coefficient	K_a[a] (M^{-1})	$-\Delta G°$[a] (kcal mol^{-1})
289	855	11	0.988	11900 ± 2000	5.38 ± 0.10
294	855	11	0.994	7300 ± 1000	5.19 ± 0.08
298	850	11	0.999	5100 ± 600	5.06 ± 0.07
304	855	11	0.992	3900 ± 450	4.98 ± 0.07
308	855	11	0.998	2500 ± 250	4.79 ± 0.06
313	850	10	0.999	1900 ± 200	4.70 ± 0.07

[a] The errors were obtained as described in the Supporting Information.

TABLE 3. Binding Constants (K_a Values) and Derived Free Energies of Complexation[21] ($-\Delta G°$) between CBPQT^{4+} and the MPTTF Derivative 6 Determined by Absorption Spectroscopy in Me_2CO at Different Temperatures Using the MPTTF/CBPQT^{4+} CT Band as Probe

T (K)	λ_{max} (nm)	data points	correlation coefficient	K_a[a] (M^{-1})	$-\Delta G°$[a] (kcal mol^{-1})
288	840	12	0.995	21000 ± 4500	5.70 ± 0.12
293	840	12	0.997	13100 ± 2300	5.52 ± 0.10
298	845	12	0.995	8000 ± 1150	5.33 ± 0.09
303	845	12	0.985	5500 ± 700	5.19 ± 0.08
308	845	11	0.986	4200 ± 500	5.11 ± 0.07
313	845	12	0.991	2300 ± 250	4.82 ± 0.07

[a] The errors were obtained as described in the Supporting Information.

complexation. Since, the K_a values have been determined at different temperatures, the enthalpic ($\Delta H°$) and entropic ($\Delta S°$) contributions to the formation of **1**⊂CBPQT^{4+} and **6**⊂CBPQT^{4+} can be determined by constructing plots (Figure 4) of ln K_a against T^{-1}. Straight lines, each with a good fit, can be approximated to the experimental data, and the thermodynamic parameters obtained are presented in Table 4.

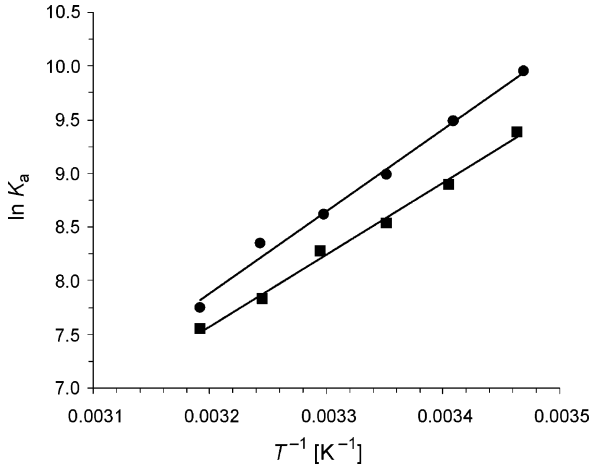


FIGURE 4. Linear plots of l nK_a against T^{-1} for the complexation of the MPTTF derivatives **1** (■) and **6** (●) by CBPQT^{4+} in Me_2CO. The K_a values were obtained as described in Tables 2 and 3. The data points have been fitted to best straight lines, giving correlation coefficients of 0.994 and 0.992, respectively. The slope and intercept of each line of best fit give the values $-\Delta H°/R$ and $\Delta S°/R$ (see Table 4), respectively, from the equation $\ln K_a = (-\Delta H°/R)(1/T) + \Delta S°/R$.

As can be seen from an inspection of Table 4, formation of both **1**⊂CBPQT^{4+} and **6**⊂CBPQT^{4+} are as expected favored enthalpically and disfavored entropically. Taking the obtained

TABLE 4. Thermodynamic Parameters for the Complexation between CBPQT^{4+} and the MPTTF Derivatives 1 and 6 Me_2CO at 298 K

complex	$-\Delta G°$ [a] (kcal mol^{-1})	$-\Delta H°$ [b,c] (kcal mol^{-1})	$-\Delta S°$ [b,c] (cal mol^{-1} K^{-1})
1⊂CBPQT^{4+}	5.06 ± 0.07	13.3 ± 1.8	27.4 ± 6.0
6⊂CBPQT^{4+}	5.33 ± 0.09	15.2 ± 2.1	33.0 ± 7.0

[a] The $\Delta G°$ values were obtained as described in Tables 2 and 3. [b] The $\Delta H°$ and $\Delta S°$ values were obtained from the intercept and slope of the straight line in the plot of $\ln K_a$ against T^{-1}, using the relationship $\ln K_a = (-\Delta H°/R)(1/T) + \Delta S°/R$, where T is the absolute temperature and K_a is the binding constant obtained as described in Tables 2 and 3. [c] The errors on the $\Delta H°$ and $\Delta S°$ values were obtained as described in the Supporting Information.

errors on the enthalpic and entropic contribution to the formation of **1**⊂CBPQT^{4+} and **6**⊂CBPQT^{4+} into account, it transpire that no unambiguous conclusion can be obtained upon a comparison of the thermodynamic parameters for the complexes **1**⊂CBPQT^{4+} and **6**⊂CBPQT^{4+}. However, the data listed in Table 4 seems to reveal that the formation of **6**⊂CBPQT^{4+} is more enthalpically favorable (2 kcal mol^{-1}) than the assembly of **1**⊂CBPQT^{4+}, indicating that the noncovalent bonding interactions between **6** and CBPQT^{4+} is stronger than those occurring between **1** and CBPQT^{4+}. This observation can probably be ascribed to the presence of [C−H···O] hydrogen-bonding interactions[17] (Figure 5) between the acidic α-CH protons in

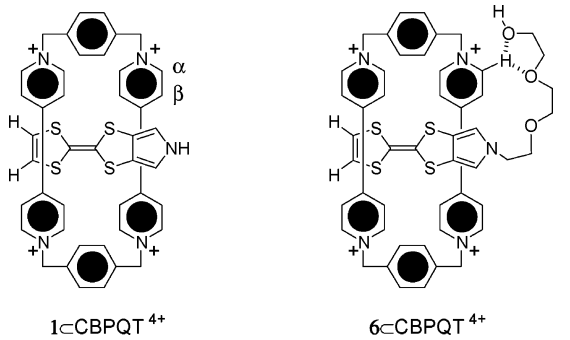


FIGURE 5. Illustrations of the complexes **1**⊂CBPQT^{4+} and **6**⊂CBPQT^{4+}. Both complexes are stabilized by CT and $\pi-\pi$ stacking interactions between their respective donor units and the electron-accepting bipyridinium moieties present in CBPQT^{4+}. The complex **6**⊂CBPQT^{4+} is most likely stabilized further by the presence of [C−H···O] hydrogen-bonding interactions (shown by the dashed lines) between the acidic α-CH protons in the bipyridinium moieties of CBPQT^{4+} and some of the oxygen atoms in the TEG substituent of the MPTTF derivative **6**.

the bipyridinium moieties of CBPQT^{4+} and some of the oxygen atoms in the TEG substituent of the MPTTF derivative **6**.

Conclusion

In conclusion, we have synthesized and characterized three series of MPTTF derivatives containing none (**1**−**5**), one (**6**−**10**), or two (**11** and **12**) TEG substituents. The complexation between these 12 π-electron-donating MPTTF derivatives and the π-electron-accepting tetracationic cyclophane CBPQT^{4+} has been investigated by UV−vis spectroscopy, and the resulting thermodynamic parameters were correlated with the donor strength (measured by the first redox potentials $E_{1/2}^1$) of the MPTTF derivatives. In the case of the MPTTF derivatives **1** and **6** containing none and one TEG substituent, respectively, the enthalpic ($\Delta H°$) and entropic ($\Delta S°$) contributions to the formation of **1**⊂CBPQT^{4+} and **6**⊂CBPQT^{4+} were obtained by variable-temperature binding constant measurements. The thermodynamic data demonstrated clearly that (i) the degree of complexation between the MPTTF derivatives and CBPQT^{4+} is highly dependent on the π-electron-donor strength of the MPTTF unit, (ii) introduction of TEG substituents on the MPTTF units significantly increases the strength of complexation with CBPQT^{4+} and it has been quantified that attachment of one or two TEG substituents to the MPTTF units stabilize the assembly process with CBPQT^{4+} by approximately 0.3 and 0.5 kcal mol^{-1}, respectively, and (iii) the stronger binding of the TEG-substituted MPTTF derivatives toward CBPQT^{4+} can most likely be associated with the presence of [C−H···O] hydrogen-bonding interactions between the acidic α-CH protons in the bipyridinium moieties of CBPQT^{4+} and some of the oxygen atoms in the TEG substituent. The finding reported in this paper are undoubtedly not unimportant when it comes to the future design of bistable [2]rotaxanes based on TTF and the tetracationic cyclophane CBPQT^{4+}.

Experimental Section

2-{1,3-Dithiol-2-ylidene}-5-tosyl-(1,3)-dithiolo[4,5-*c*]pyrrole (15). A solution of thione **13** (0.57 g, 4.25 mmol) and ketone **14** (0.88 g, 2.83 mmol) in $(EtO)_3P$ (30 mL) was heated to 130 °C. After the mixture was stirred for 5 min, additional thione **13** (0.38 g, 2.83 mmol) was added in one portion. The brown solution was stirred for 20 min, whereupon another portion of thione **13** (0.57 g, 4.25 mmol) was added. The reaction mixture was then stirred for 2 h, followed by cooling to room temperature. Addition of MeOH (75 mL) gave a yellow solid which was filtered and washed with MeOH to give the product **15** (0.68 g, 60%) containing traces of bispyrrolotetrathiafulvalene: mp > 250 °C; ^{1}H NMR (CD_3SOCD_3) δ 2.38 (s, 3H), 6.74 (s, 2H), 7.37 (s, 2H), 7.45 (d, J = 8.2 Hz, 2H), 7.82 (d, J = 8.2 Hz, 2H); ^{13}C NMR (CD_3SOCD_3) δ 21.1, 112.4, 112.7, 118.7, 119.6, 126.7, 126.8, 130.4, 134.5, 145.8; MS (EI) m/z 397 (M^+, 42), 242 (M^+ − Ts, 100); MS (HiResMALDI) calcd for $C_{15}H_{11}NO_2S_5$ 396.9393, found 396.9405.

2-{1,3-Dithiol-2-ylidene}-(1,3)-dithiolo[4,5-*c*]pyrrole (1). A suspension of **15** (0.53 g, 1.33 mmol) in anhydrous THF−MeOH (1:1 v/v, 50 mL) was degassed (N_2, 15 min) before sodium methoxide (25% solution in MeOH, 1.5 mL, 1.44 g, 26.6 mmol) was added in one portion. The yellow reaction mixture was refluxed for 20 min, leaving a brown, clear solution. The reaction mixture was cooled to room temperature and concentrated to approximately 20 mL, whereupon H_2O (50 mL) was added. The resulting yellow precipitate was filtered and purified by column chromatography (deactivated silica gel:[25] CH_2Cl_2/MeOH 49:1 v/v). The yellow band

(19) Fuchter. M. J.; Beall, L. S.; Baum, S. M.; Montalban, A. G.; Sakellariou, E. G.; Mani, N. S.; Miller, T.; Vesper, B. J.; White, A. J. P.; Williams, D. J.; Barrett, A. G. M.; Hoffman, B. M. *Tetrathedron* **2005**, *61*, 6115−6130.

(20) As expected, the exchange between the complexed and uncomplexed species in a 1:1 mixture of the MPTTF derivatives **1**−**12** and CBPQT^{4+} occurs rapidly on the ^{1}H NMR time scale (CD_3COCD_3, 300 MHz) at 300 K.

(21) The $\Delta G°$ values were calculated using the relationship $\Delta G° = -RT \ln K_a$ where R is the gas constant and T is the absolute temperature.

(22) *Donor-Acceptor Bond*; Gur'yanova, E. N., Gol'dshtein, I. P., Romm, I. P., Eds.; (translated from Russian by R. Kondor, translation edited by D. Slutzkin); Koterpress Enterprises: Jerusalem, Israel, 1975.

(23) Amabilino, D. B.; Anelli, P.-L.; Ashton, P. R.; Brown, G. R.; Córdova, E.; Godínez, L. A.; Hayes, W.; Kaifer, A. E.; Philp, D.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Tolley, M. S.; Williams, D. J. *J. Am. Chem. Soc.* **1995**, *117*, 11142−11170.

(24) See the Experimental Section for further details.

(25) The SiO_2 was deactivated by suspending it in 4% Et_3N in CH_2Cl_2, followed by removal of the solvents and washing with CH_2Cl_2 to remove traces of Et_3N, and finally resuspended in the desired eluent.

(R_f = 0.6) was collected and concentrated to give **1** as a yellow powder (0.23 g, 71%): mp 190−191 °C; ^{1}H NMR (CD_3SOCD_3) δ 6.72 (s, 2H), 6.78 (d, J = 2.7 Hz, 2H), 11.07 (s, 1H); ^{13}C NMR (CD_3SOCD_3) δ 110.5, 113.5, 115.3, 117.6, 119.5; MS (EI) m/z 243 (M^+, 100), 141 (25); CV (MeCN vs Ag/AgCl) $E_{1/2}^1$ +0.37 V, $E_{1/2}^2$ +0.72 V. Anal. Calcd for $C_8H_5NS_4$: C, 39.48; H, 2.07; N, 5.75; S, 52.70. Found: C, 39.61; H, 2.12; N, 5.69; S, 52.56.

2-{4-Methylthio-1,3-dithiol-2-ylidene}-5-methyl-(1,3)-dithiolo-[4,5-*c*]pyrrole (4). Compound **2** (100 mg, 0.35 mmol) was dissolved in anhydrous DMF (15 mL) and degassed (N_2, 15 min) before the alkylating agent MeI (0.32 mL, 0.75 g, 5.25 mmol) was added. NaH (55% suspension in mineral oil, 91 mg, 2.07 mmol) was added in one portion, resulting in an immediate color change from yellow to brown. The reaction mixture was stirred for 1.5 h. Brine (100 mL) was added followed by extraction of the aqueous phase with CH_2Cl_2 (3 × 50 mL). The combined organic phases were dried ($MgSO_4$), and the solvent was removed in vacuo. The resulting brown oil was purified by column chromatography (silica gel: CH_2Cl_2). Collection and concentration of the broad yellow band (R_f = 0.7) gave **4** as a dark-yellow oil (93 mg, 88%): ^{1}H NMR (CD_3SOCD_3) δ 2.43 (s, 3H), 3.60 (s, 3H), 6.73 (s, 1H), 6.76 (s, 2H); ^{13}C NMR (CD_3SOCD_3) δ 18.5, 36.9, 111.6, 114.4, 116.9, 117.0, 117.0, 118.9, 127.0; MS (HiResMALDI) calcd for $C_{10}H_9NS_5$ 302.9338, found 302.9351; CV (MeCN vs Ag/AgCl) $E_{1/2}^1$ +0.39 V, $E_{1/2}^2$ +0.75 V.

General Procedure for *N*-Alkylation of MPTTF Derivatives with 2-{2-[2-(Tetrahydropyranyl-2-oxy)ethoxy]ethoxy}ethyl Iodide Followed by THP Deprotection. The appropriate MPTTF compound **1**, **2**, or **3** was dissolved in anhydrous DMF and degassed (N_2, 15 min) before the alkylating agent 2-{2-[2-(tetrahydropyranyl-2-oxy)ethoxy]ethoxy}ethyl iodide (1.05 equiv) was added. NaH (55% suspension of mineral oil, 5 equiv) was added in one portion, resulting in an immediate color change from yellow to brown. The reaction mixture was stirred for 2 h, or until the reaction was complete. Brine (60 mL) was added followed by extraction of the aqueous phase with CH_2Cl_2 (3 × 50 mL). The combined organic phases were dried ($MgSO_4$) and the solvent removed in vacuo. The resulting brown oil was purified by column chromatography (silica gel) affording the THP protected products **6a**−**8a**. Removal of the THP protection group was facilitated by dissolving the MPTTF derivative **6a**−**8a** in anhydrous THF−EtOH (1:1 v/v). After degassing (N_2, 15 min), TsOH (catalytic amount) was added. The reaction mixture changed color from yellow to green and was stirred for 4 h or until complete. The reaction was terminated by addition of CH_2Cl_2 followed by washing of the organic phase with a saturated aqueous solution of $NaHCO_3$ (50 mL) and H_2O (50 mL). The organic phase was dried ($MgSO_4$) and the solvent removed yielding a yellow oil which was purified by column chromatography (silica gel) affording the analytically pure products **6**−**8** as yellow oils.

2-{1,3-Dithiol-2-ylidene}-5-{2-[2-(hydroxyethoxy)ethoxy]ethyl}-(1,3)-dithiolo[4,5-*c*]pyrrole (6). *N*-Alkylation using **1** (155 mg, 0.64 mmol) in DMF (6 mL): column chromatography R_f = 0.25 (CH_2Cl_2/EtOAc 1:1) afforded **6a** as a brown oil (265 mg, 90%); THP deprotection using **6a** (250 mg, 0.54 mmol) in THF−EtOH (1:1 v/v, 10 mL); R_f = 0.25 (CH_2Cl_2/MeOH 19:1); yellow oil; yield (142 mg, 70%); ^{1}H NMR (CD_3SOCD_3) δ 3.38−3.51 (m, 8H), 3.64 (t, J = 5.4 Hz, 2H), 3.99 (t, J = 5.4 Hz, 2H), 4.55 (bs, 1H), 6.72 (s, 2H), 6.81 (s, 2H); ^{13}C NMR (CD_3SOCD_3) δ 49.7, 60.2, 69.6, 69.7, 70.2, 72.3, 113.7 (two lines overlapping), 114.6, 117.2, 119.6; MS (EI) m/z 375 (M^+, 100), 242 (20), 146 (35); CV (MeCN vs Ag/AgCl) $E_{1/2}^1$ +0.36 V, $E_{1/2}^2$ +0.75 V. Anal. Calcd for $C_{14}H_{17}NO_3S_4$: C, 44.77; H, 4.56; N, 3.73; S, 34.15. Found: C, 44.39; H, 4.71; N, 3.70; S, 33.46.

2-{4-Methylthio-1,3-dithiol-2-ylidene}-5-{2-[2-(hydroxyethoxy)-ethoxy]ethyl}-(1,3)-dithiolo[4,5-*c*]pyrrole (7). *N*-Alkylation using **2** (0.15 g, 0.52 mmol) in DMF (8 mL): column chromatography R_f = 0.2 (CH_2Cl_2/MeOH 49:1) afforded **7a** as a yellow brown oil (210 mg, 80%); THP deprotection using **7a** (0.21 g, 0.42 mmol) in THF−EtOH (1:1 v/v, 20 mL); R_f = 0.15 (CH_2Cl_2/MeOH 24:1); yellow oil; yield (0.15 g, 86%); ^{1}H NMR (CD_3SOCD_3) δ 2.43 (s, 3H), 3.36−3.53 (m, 8H), 3.64 (t, J = 5.2 Hz, 2H), 4.00 (t, J = 5.2 Hz, 2H), 4.57 (s, 1H), 6.73 (s, 1H), 6.83 (s, 2H); ^{13}C NMR (CD_3SOCD_3) δ 18.5, 49.7, 60.2, 69.6, 69.7, 70.2, 72.3, 111.8, 113.8, 113.8, 116.9, 116.9, 118.1, 118.8, 126.9; MS (EI) m/z 421 (M^+, 100), 317 (20), 149 (37); CV (MeCN vs Ag/AgCl) $E_{1/2}^1$ +0.38 V, $E_{1/2}^2$ +0.75 V. Anal. Calcd for $C_{15}H_{19}NO_3S_5$: C, 42.73; H, 4.54; N, 3.32; S, 38.02. Found: C, 42.68; H, 4.76; N, 3.36; S, 37.75.

2-{4,5-Bis(methylthio)-1,3-dithiol-2-ylidene}-5-{2-[2-(hydroxyethoxy)ethoxy]ethyl}-(1,3)-dithiolo[4,5-*c*]pyrrole (8). *N*-Alkylation using **3** (0.50 g, 1.49 mmol) in DMF (20 mL): column chromatography R_f = 0.3 (CH_2Cl_2/MeOH 49:1) afforded **8a** as a yellow brown oil (0.71 g, 87%); THP deprotection using **8a** (0.56 g, 1.01 mmol) in THF−EtOH (1:1 v/v, 50 mL); R_f = 0.2 (CH_2Cl_2/MeOH 24:1); yellow oil; yield (0.44 g, 93%); ^{1}H NMR (CD_3COCD_3) δ 2.45 (s, 6H), 3.49−3.61 (m, 9H), 3.73 (t, J = 5.1 Hz, 2H), 4.07 (t, J = 5.1 Hz, 2H), 6.79 (s, 2H); ^{13}C NMR (CD_3SOCD_3) δ 18.3, 49.6, 60.1, 69.5, 69.5, 70.0, 72.2, 107.2, 113.8, 116.5, 121.0, 125.9; MS (EI) m/z 467 (M^+, 100); CV (MeCN vs Ag/AgCl) $E_{1/2}^1$ +0.42 V, $E_{1/2}^2$ +0.75 V. Anal. Calcd for $C_{16}H_{21}NO_3S_6$: C, 41.09; H, 4.53; N, 2.99; S, 41.13. Found: C, 41.34; H, 4.53; N, 2.97; S, 40.95.

General Procedure for *S*-Alkylation. The appropriate MPTTF derivative **16** or **17** (1.0 mmol) was dissolved in anhydrous THF (70 mL) and degassed (N_2, 15 min) before a solution of CsOH·H_2O (1.05 equiv) in anhydrous MeOH (8 mL) was added dropwise by means of a syringe over a period of 1 h. 2-{2-[2-(Tetrahydropyranyl-2-oxy)ethoxy]ethoxy}ethyl iodide (1.07 equiv) in anhydrous THF (10 mL) was added in one portion. The yellow reaction mixture was stirred for 24 h, whereupon the solvent was evaporated. The yellow residue was redissolved in CH_2Cl_2 (100 mL), washed with H_2O (2 × 100 mL), and dried ($MgSO_4$). Removal of the solvent gave a yellow residue, which was purified by column chromatography (silica gel) to yield compounds **18a** or **19a**.

2-{4-(2-{2-[2-(Tetrahydropyranyl-2-oxy)ethoxy]ethoxy}-ethylthio)-1,3-dithiol-2-ylidene}-5-tosyl-(1,3)-dithiolo[4,5-*c*]pyrrole (18a). *S*-Alkylation using **16** (0.48 g, 1.0 mmol); R_f = 0.6 (CH_2Cl_2/MeOH 49:1); yellow oil; yield (0.64 g, 92%); ^{1}H NMR (CD_3COCD_3) δ 1.35−1.60 (m, 6H), 2.42 (s, 3H), 2.99 (t, J = 6.3 Hz, 2H), 3.40−3.70 (m, 12H), 4.59 (s, 1H), 6.76 (s, 1H), 7.28 (s, 2H), 7.45 (d, J = 8.5 Hz, 2H), 7.86 (d, J = 8.5 Hz, 2H); ^{13}C NMR (CD_3SOCD_3) δ 19.1, 21.1, 25.0, 30.2, 34.9, 61.2, 66.1, 68.9, 69.4, 69.7, 69.8, 98.1, 112.6 (two lines overlapping), 114.3, 117.1, 123.1, 124.8, 126.26, 126.31, 126.8, 130.4, 134.5, 145.8; MS (MALDI) m/z 645 (M^+, 15), 491 (M^+ − Ts, 60).

2-{4-(2-{2-[2-(Tetrahydropyranyl-2-oxy)ethoxy]ethoxy}ethylthio)-5-methylthio-1,3-dithiol-2-ylidene}-5-tosyl-(1,3)-dithiol[4,5-*c*]pyrrole (19a). *S*-Alkylation using **17** (0.53 g, 1.0 mmol); R_f = 0.6 (CH_2Cl_2/MeOH 49:1); yellow oil; yield (0.59 g, 91%); ^{1}H NMR (CD_3COCD_3) δ 1.30−1.50 (m, 6H), 2.29 (s, 3H), 2.33 (s, 3H), 2.89 (t, J = 6.4 Hz, 2H), 3.45−3.55 (m, 12 H), 4.46 (s, 1H), 7.16 (s, 2H), 7.31 (d, J = 7.8 Hz, 2H), 7.71 (d, J = 7.8 Hz, 2H); ^{13}C NMR (CD_3SOCD_3) δ 18.5, 19.1, 21.1, 25.0, 30.2, 35.1, 61.2, 66.0, 69.2, 69.7, 69.8, 69.8, 98.0, 112.4, 112.7 (two lines overlapping), 117.5; MS (MALDI) m/z 714 (M^+ + Na, 4), 691 (M^+, 13), 537 (M^+ − Ts, 100), 453 (20). Anal. Calcd for $C_{27}H_{33}NO_6S_7$; C, 46.86; H, 4.81; N, 2.02; S, 32.44. Found: C, 47.01; H, 4.99; N, 2.01; S, 32.23.

General Procedure for Detosylation. The appropriate MPTTF derivative **18a** or **19a** (0.85 mmol) in anhydrous THF−MeOH (1:1 v/v, 140 mL) was degassed (N_2, 15 min) before sodium methoxide (30% solution in MeOH, 2.4 mL, 0.68 g, 12.6 mmol) was added in one portion. The yellow reaction mixture was heated under reflux for 20 min, leaving a brown clear solution. The reaction mixture was cooled to room temperature and concentrated in vacuo. The resulting yellow oil was redissolved in CH_2Cl_2 (150 mL), washed with H_2O (3 × 100 mL), and dried ($MgSO_4$). Removal of the solvent gave a yellow oil, which was purified by column chroma-

tography (silica gel: CH_2Cl_2/MeOH 49:1). The yellow band (R_f = 0.3) was collected and concentrated to give compounds **18** or **19**.

2-{4-(2-{2-[2-(Tetrahydropyranyl-2-oxy)ethoxy]ethoxy}-ethylthio)-1,3-dithiol-2-ylidene}-(1,3)-dithiolo[4,5-*c*]pyrrole (18). Detosylation using **18a** (0.55 g, 0.85 mmol): R_f = 0.3 (CH_2Cl_2/MeOH 49:1); yellow oil; yield (0.29 g, 70%); ^{1}H NMR (CD_3COCD_3) δ 1.35−1.60 (m, 6H), 2.99 (t, J = 7.4 Hz, 2H), 3.50−3.70 (m, 12H), 4.62 (s, 1H), 6.74 (s, 1H), 6.79 (s, 2H), 10.45 (bs, 1H); ^{13}C NMR (CD_3SOCD_3) δ 19.1, 25.0, 30.2, 34.8, 61.3, 66.1, 68.9, 69.3, 69.7, 69.8, 98.1, 110.7, (two lines overlapping), 111.9, 117.2, 117.3, 118.5, 123.1, 124.8; MS (MALDI) *m*/*z* 514 (M^+ + Na, 10), 491 (M^+, 100), 407 (M^+ − THP, 10). Anal. Calcd for $C_{19}H_{25}NO_4S_5$: C, 46.41; H, 5.12; N, 2.85. Found: C, 46.12; H, 5.34; N, 2.54.

2-{4-(2-{2-[2-(Tetrahydropyranyl-2-oxy)ethoxy]ethoxy}-ethylthio)-5-methylthio-1,3-dithiol-2-ylidene}-(1,3)-dithiolo[4,5-*c*]pyrrole (19). Detosylation using **19a** (0.58 g, 0.84 mmol): R_f = 0.3 (CH_2Cl_2/MeOH 49:1); yellow oil; yield (0.42 g, 93%); ^{1}H NMR (CD_3SOCD_3) δ 1.35−1.59 (m, 6H), 2.43 (s, 3H), 2.98 (t, J = 6.4 Hz, 2H), 3.55−3.75 (m, 12H), 4,55 (s, 1H), 6.76 (s, 2H), 10.35 (s, 1H); ^{13}C NMR (CD_3SOCD_3) δ 19.0, 19.7, 25.6, 30.8, 35.5, 61.8, 66.6, 69.8, 70.3, 70.3, 70.3, 98.6, 107.8, 111.3 (two lines overlapping), 117.55, 117.58, 122.2, 123.7; MS (MALDI) *m*/*z* 564 (10), 537 (M^+, 30), 177 (30), 138 (20). Anal. Calcd for $C_{20}H_{27}NO_4S_6$: C, 44.66; H, 5.06; N, 2.60; S, 35.77. Found: C, 45.07; H, 5.32; N, 2.58; S, 35.16.

General Procedure for THP Deprotection of 18 and 19. Removal of the THP protection group was facilitated by dissolving the appropriate MPTTF derivative **18** or **19** (∼0.5 mmol) in anhydrous THF−EtOH (1:1 v/v). After degassing (N_2, 15 min), TsOH (catalytic amount) was added. The reaction mixture change color from yellow to green and was stirred for 20 h. The reaction was terminated by addition of CH_2Cl_2 (100 mL) followed by washing of the organic phase with a saturated aqueous solution of $NaHCO_3$ (100 mL) and H_2O (100 mL). The organic phase was dried ($MgSO_4$) and the solvent removed yielding a yellow oil which was purified by column chromatography (silica gel: CH_2Cl_2/MeOH 19:1). Collection and concentration in vacuo of a yellow band afforded the analytically pure products **9** or **10**.

2-{4-(2-[2-(Hydroxyethoxy)ethoxy]ethylthio)-1,3-dithiol-2-ylidene}-(1,3)-dithiolo[4,5-*c*]pyrrole (9). Deprotection using the MPTTF derivative **18** (0.25 g, 0.51 mmol) in anhydrous THF−EtOH (1:1 v/v, 30 mL); R_f = 0.2 (CH_2Cl_2/MeOH 19:1); sticky yellow oil; yield (0.16 g, 77%); ^{1}H NMR (CD_3COCD_3) δ 3.00 (t, J = 6.4 Hz, 2H), 3.52−3.72 (m, 11H), 6.75 (s, 1H), 6.80 (s, 2H), 10.42 (s, 1H); ^{13}C NMR (CD_3SOCD_3) δ 34.8, 60.2, 68.8, 69.7 (two lines overlapping), 72.4, 110.7 (two lines overlapping), 101.9, 117.2, 117.3, 118.5, 123.2, 124.7; MS (MALDI) *m*/*z* 430 (M^+ + Na, 3), 407 (M^+, 70); CV (MeCN vs Ag/AgCl) $E_{1/2}^1$ +0.41 V, $E_{1/2}^2$ +0.73 V. Anal. Calcd for $C_{14}H_{17}NO_3S_5$: C, 41.25; H, 4.20; N, 3.44. Found: C, 39.89; H, 4.23; N, 3.12.

2-{4-(2-[2-(Hydroxyethoxy)ethoxy]ethylthio)-5-methylthio-1,3-dithiol-2-ylidene}-(1,3)-dithiolo[4,5-*c*]pyrrole (10). Deprotection using the MPTTF derivative **19** (0.19 g, 0.35 mmol) in anhydrous THF−EtOH (1:1 v/v, 20 mL): R_f = 0.25 (CH_2Cl_2/MeOH 19:1); brown oil; yield (0.12 g, 75%); ^{1}H NMR (CD_3COCD_3) δ 2.43 (s, 3H), 3.00 (t, J = 6.2 Hz, 2H), 3.55−3.70 (m, 11H), 6.76 (s, 2H), 10.33 (s, 1H); ^{13}C NMR (CD_3SOCD_3) δ 17.9, 34.5, 59.7, 68.7, 69.2, 69.2, 71.9, 106.7, 110.2 (two lines overlapping), 116.5, 116.5, 121.2, 122.6, 129.1; MS (MALDI) *m*/*z* 492 (M^+ + K, 2), 455 (M^+ + 2, 35) 453 (M^+, 100), 178 (25), 138 (35); CV (MeCN vs Ag/AgCl) $E_{1/2}^1$ +0.44 V, $E_{1/2}^2$ +0.75 V. Anal. Calcd for $C_{15}H_{19}NO_3S_6$: C, 39.71; H, 4.02; N, 3.09; S, 42.40. Found: C, 39.83; H, 4.36; N, 3.08; S, 42.59.

General Procedure for *N*-Alkylation of MPTTF Derivatives 18 and 19. The appropriate MPTTF derivative **18** or **19** (∼0.5 mmol) was dissolved in anhydrous DMF and degassed (N_2, 15 min) before the alkylating agent 2-{2-[2-(tetrahydropyranyl-2-oxy)-ethoxy]ethoxy}ethyl iodide (1.05 equiv) was added. NaH (60% suspension of in mineral oil, 2.5 equiv) was added in one portion, resulting in an immediate color change from yellow to reddish brown. The reaction mixture was stirred for 2 h. Brine (100 mL) was added followed by extraction of the aqueous phase with CH_2Cl_2 (3 × 75 mL). The combined organic phases were dried ($MgSO_4$), and the solvent removed in vacuo. The resulting brown oil was purified by column chromatography (silica gel: CH_2Cl_2/EtOAc 1:1). Collection and concentration in vacuo of a yellow band provided the doubly THP-protected products **11a** or **12a**.

2-{4-(2-{2-[2-(Tetrahydropyranyl-2-oxy)ethoxy]ethoxy}-ethylthio)-1,3-dithiol-2-ylidene}-5-{2-(2-[2-(tetrahydropyranyl-2-oxy)ethoxy]ethoxy)ethyl}-(1,3)-dithiolo[4,5-*c*]pyrrole (11a). *N*-Alkylation using compound **18** (0.36 g, 0.73 mmol) in anhydrous DMF (30 mL): R_f = 0.35 (CH_2Cl_2/EtOAc 1:1); yellow oil; yield (0.27 g, 50%); ^{1}H NMR (CD_3COCD_3) δ 1.30−1.60 (m, 12H), 3.05 (t, J = 6.7 Hz 2H), 3.50−3.80 (m, 24H), 4.11 (t, J = 5.1 Hz, 2H), 4.56 (bs, 2H), 6.75 (s, 1H), 6.80 (s, 2H); ^{13}C NMR (CD_3SOCD_3) δ 18.6, 24.5, 29.7, 34.3, 49.2, 60.7, 60.8, 65.6, 65.6, 68.3, 69.2 (two lines overlapping), 69.3 (two lines overlapping), 69.7, 97.5, 97.6, 111.6, 113.3 (two lines overlapping), 116.3, 116.3, 117.3, 122.6, 124.3; MS (MALDI) *m*/*z* 707 (M^+, 15). Anal. Calcd for $C_{30}H_{45}NO_8S_5$: C, 50.89; H, 6.41; N, 1.98; S, 22.65. Found: C, 51.12; H, 6.51; N, 2.01; S, 22.52.

2-{4-(2-{2-[2-(Tetrahydropyranyl-2-oxy)ethoxy]ethoxy}-ethylthio)-5-methylthio-1,3-dithiol-2-ylidene}-5-{2-(2-[2-(tetrahydropyranyl-2-oxy)ethoxy]ethoxy)ethyl}-(1,3)-dithiolo[4,5-*c*]pyrrole (12a). *N*-Alkylation using compound **19** (0.19 g, 0.35 mmol) in anhydrous DMF (10 mL): R_f = 0.35 (CH_2Cl_2/EtOAc 1:1); brown oil; yield (0.20 g, 76%); ^{1}H NMR (CD_3COCD_3) δ 1.35−1.55 (m, 12H), 2,43 (s, 3H), 2.99 (t, J = 6.7 Hz, 2H), 3.40−3.70 (m, 24H), 4.04 (t, J = 5.2 Hz, 2H), 4.56 (bs, 2H), 6.75 (s, 2H); MS (MALDI) *m*/*z* 775 (M^+ + Na, 10), 753 (M^+, 100), 356 (15). Anal. Calcd for $C_{31}H_{47}NO_8S_6$: C, 49.37; H, 6.28; N, 1.86; S, 25.51. Found: C, 49.49; H, 6.33; N, 1.93; S, 25.39.

General Procedure for THP Deprotection of 11a and 12a. Removal of the THP protection group was facilitated by dissolving the appropriate MPTTF derivative **11a** or **12a** (∼0.3 mmol) in anhydrous THF−EtOH (1:1 v/v). After degassing (N_2, 15 min), TsOH (catalytic amount) was added. The reaction mixture changed color from yellow to green and was stirred for 24 h. The reaction was terminated by addition of CH_2Cl_2 (100 mL) followed by washing of the organic phase with a saturated aqueous solution of $NaHCO_3$ (100 mL) and H_2O (100 mL). The organic phase was dried ($MgSO_4$) and the solvent removed yielding a yellow oil which was purified by column chromatography (silica gel: EtOAc/MeOH 23:2). Collection and concentration in vacuo of a yellow band afforded the analytically pure products **11** and **12**.

2-{4-(2-[2-(Hydroxyethoxy)ethoxy]ethylthio)-1,3-dithiol-2-ylidene}-5-{2-[2-(hydroxyethoxy)ethoxy]ethyl}-(1,3)-dithiolo-[4,5-*c*]pyrrole (11). Deprotection using the MPTTF derivative **11a** (0.25 g, 0.35 mmol) in anhydrous THF−EtOH (1:1 v/v, 30 mL): R_f = 0.15 (EtOAc/MeOH 23:2); yellow oil; yield (0.13 g, 69%); ^{1}H NMR (CD_3COCD_3) δ 2.99 (t, J = 6.3 Hz, 2H), 3.50−3.75 (m, 22H), 4.08 (t, J = 5.3 Hz, 2H), 6.74 (s, 1H), 6.79 (s, 2H); ^{13}C NMR (CD_3SOCD_3) δ 34.8, 49.7, 60.3, 68.9, 69.7, 69.7, 69.7 (two lines overlapping), 70.2, 72.4, 72.4, 112.2, 113.9 (two lines overlapping), 116.9, 116.9, 117.9, 123.2, 124.8; MS (MALDI) *m*/*z* 539 (M^+, 100); CV (MeCN vs Ag/AgCl) $E_{1/2}^1$ +0.38 V, $E_{1/2}^2$ +0.71 V. Anal. Calcd for $C_{20}H_{29}NO_6S_5$: C, 44.50; H, 5.42; N, 2.59; S, 29.70. Found: C, 44.75; H, 5.46; N, 2.67; S, 29.53.

2-{4-(2-[2-(Hydroxyethoxy)ethoxy]ethylthio)-5-methylthio-1,3-dithiol-2-ylidene}-5-{2-[2-(hydroxyethoxy)ethoxy]ethyl}-(1,3)-dithiolo[4,5-*c*]pyrrole (12). Deprotection using the MPTTF derivative **12a** (0.18 g, 0.24 mmol) in anhydrous THF−EtOH (1:1 v/v, 20 mL): R_f = 0.2 (EtOAc/MeOH 23:2); yield (0.11 g, 79%); ^{1}H NMR (CD_3COCD_3) δ 2.43 (s, 3H), 2.99 (t, J = 6.3 Hz, 2H), 3.40−3.70 (m, 22H), 4.05 (t, J = 5.3 Hz, 2H), 6.78 (s, 2H); ^{13}C NMR (CD_3SOCD_3) δ 18.4, 34.9, 49.6, 60.1, 60.1, 69.1, 69.5, 69.6, 69.6, 69.7, 70.1, 72.3, 72.4, 107.3, 113.9 (two lines overlapping),

116.5, 116.5, 121.0, 123.0, 129.6; MS (MALDI) *m/z* 585 (M^+, 100); CV (MeCN vs Ag/AgCl) $E_{1/2}^1$ +0.42 V, $E_{1/2}^2$ +0.73 V. Anal. Calcd for $C_{21}H_{31}NO_6S_6$: C, 43.05; H, 5.33; N, 2.39; S, 32.84. Found: C, 43.34; H, 5.50; N, 2.43; S, 32.57.

Photophysical Experiments. All the measurements were performed in air-equilibrated Me_2CO solutions, and hexafluorophosphate (PF_6^-) ions were the counterions in the case of all the cationic complexes. Absorption spectra were recorded on a UV−vis spectrometer and the temperature was controlled using an electronic thermostat. The estimated experimental errors are: 5 nm on band maxima ($\Delta\lambda$), ±2% on the absorbances (ΔA), ±1% on the concentrations (Δc), and ±1 K on the temparetures (ΔT) unless otherwise stated.

Determination of Binding Constants (K_a Values) Using the UV−vis Dilution Method: [2]Pseudorotaxanes 1−12⊂CBPQT·4PF$_6$. The UV−vis dilution method was employed to determine the binding constant (K_a) at 296 K. Mixing the colorless cyclophane CBPQT·4PF$_6$ and the yellow MPTTF derivatives **1**−**12** in equimolar proportions in Me_2CO immediately produced green-colored solutions. Appropriate dilutions of at least two independent stock solutions produced solutions with absolute concentrations (c) in the range of $10^{-4}-10^{-5}$ M. These were subsequently placed in the thermostatted cell compartment of the UV−vis spectrophotometer and then allowed to equilibrate to 296 K, before the absorbance A was measured at a specific wavelength in the region between 795 and 855 nm (λ_{max}). This resulted in 20, 19, 16, 19, 16, 21, 32, 16, 27, 20, 22, and 24 data points [$1/A^{1/2}$, c/A] for **1**−**12**⊂CBPQT·4PF$_6$, respectively. For each particular [2]pseudorotaxane **1**−**12**⊂CBPQT·4PF$_6$, a plot of c/A against $1/A_{1/2}$ afforded a straight line with slope α of $(1/K_a\epsilon\ l)^{1/2}$ and a y-intercept y_0 of $1/\epsilon\ l$, where ϵ is the molar extinction coefficient for the CT band of the complex and l is the optical path length, according to the Equation $c/A = [(1/K_a\epsilon l)^{1/2}\text{-}(1/A^{1/2})] + 1/\epsilon\ l$. The linear relationship between c/A and $1/A^{1/2}$ at 296 K was demonstrated by calculation of the correlation coefficient, and values (Table 1) of 0.919−0.988 were obtained. The K_a and ϵ values were obtained from the relationship $K_a = y_0/\alpha^2$, where α and $y_0 = 1/\epsilon\ l$ is the slope and y-intercept of the line, respectively.

Determination of Binding Constants (K_a values) at Variable Temperatures Using the UV−vis Dilution Method: [2]Pseudorotaxane 1⊂CBPQT·4PF$_6$. Mixing the colorless cyclophane CBPQT·4PF$_6$ and the yellow MPTTF derivative **1** in equimolar proportions in Me_2CO immediately produced a green-colored solution. Appropriate dilutions produced solutions with absolute concentrations (c) in the range of $10^{-4}-10^{-5}$ M. These were subsequently placed in the thermostated cell compartment of the UV−vis spectrophotometer and then allowed to equilibrate to a constant temperature, before the absorbance A was measured at 850/855 nm (λ_{max}). Measurements were carried out at 288.7, 293.7, 298.4, 303.5, 308.1, and 313.3 K, where the temperature T was measured in the cuvette before and after each experiment and readings of equal to or less than ± 0.1 K (ΔT) were obtained. This resulted in 11, 11, 11, 11, 11, and 10 data points [$1/A^{1/2}$, c/A] for **1**⊂CBPQT·4PF$_6$. For each particular temperature a plot of c/A against $1/A_{1/2}$ afforded a straight line with slope α of $(1/K_a\epsilon\ l)^{1/2}$ and a y-intercept y_0 of $1/\epsilon\ l$, where ϵ is the molar extinction coefficient for the CT band of the complex and l is the optical path length, according to the Equation $c/A = [(1/K_a\epsilon l)^{1/2}(1/A^{1/2})] + 1/\epsilon\ l$. The linear relationship between c/A and $1/A^{1/2}$ at each particular temperature was demonstrated by calculation of the correlation coefficient, and values (Table 2) of 0.988−0.999 were obtained. The K_a and ϵ values were obtained from the relationship $K_a = y_0/\alpha^2$, where α and $y_0 = 1/\epsilon\ l$ is the slope and y-intercept of the line, respectively.

[2]Pseudorotaxane 6⊂CBPQT·4PF$_6$. Mixing the colorless cyclophane CBPQT·4PF$_6$ and the yellow MPTTF derivative **6** in equimolar proportions in Me_2CO immediately produced a green-colored solution. Appropriate dilutions produced solutions with absolute concentrations (c) in the range of $10^{-4}-10^{-5}$ M. These were subsequently placed in the thermostatted cell compartment of the UV−vis spectrophotometer and then allowed to equilibrate to a constant temperature, before the absorbance A was measured at 840/845 nm (λ_{max}). Measurements were carried out at 288.2, 293.3, 298.4, 303.2, 308.3, and 313.3 K, where the temperature T was measured in the cuvette before and after each experiment and readings of equal to or less than ±0.1 K (ΔT) were obtained. This resulted in 12, 12, 12, 12, 11, and 12 data points [$1/A^{1/2}$, c/A] for **6**⊂CBPQT·4PF$_6$. For each particular temperature a plot of c/A against $1/A_{1/2}$ afforded a straight line with slope α of $(1/K_a\epsilon\ l)^{1/2}$ and a y-intercept y_0 of $1/\epsilon\ l$, where ϵ is the molar extinction coefficient for the CT band of the complex and l is the optical path length, according to the equation $c/A = [(1/K_a\epsilon l)^{1/2}(1/A^{1/2})] + 1/\epsilon\ l$. The linear relationship between c/A and $1/A^{1/2}$ at each particular temperature was demonstrated by calculation of the correlation coefficient, and values (Table 3) of 0.985−0.997 were obtained. The K_a and ϵ values were obtained from the relationship $K_a = y_0/\alpha^2$, where α and $y_0 = 1/\epsilon\ l$ is the slope and y-intercept of the line, respectively.

Electrochemical Experiments. Cyclic voltammetric (CV) experiments were carried out in nitrogen-purged MeCN solutions in a classical three-electrode, single-compartment cell at room temperature. The electrochemical cell was connected to a computerized potentiostat controlled by a personal computer. The working electrode was a platinum disk electrode and its surface was polished immediately prior to use. The counter electrode was a platinum wire and the reference electrode was a $Ag/AgNO_3$ electrode. Before and after each experiment, the first redox potential of tetrathiafulvalene (+0.34 V vs Ag/AgCl)[18b] was measured and all potentials are referenced to the Ag/AgCl electrode. The concentration of the examined compounds was 1.0 mM and tetrabutylammonium hexafluorophosphate (0.1 M) was added as the supporting electrolyte. All MPTTF derivatives exhibited two pairs of reversible redox waves corresponding to two one-electron processes. 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 first half-wave potentials ($E_{1/2}^1$), reported in Table 1, were obtained from an average of the cathodic and anodic cyclic voltammetric peaks. Based on repetitive measurements, absolute errors on potentials have been found to be less than ±5 mV.

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Supporting Information Available: General experimental methods together with details on the calculations of binding constants and thermodynamic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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