Self-Assembling Tetrathiafulvalene-Based Rotaxanes and Catenanes

Zhan-Ting Li, Paul C. Stein, Jan Becher,* Dorthe Jensen, Pernille Mørk, and Niels Svenstrup

Abstract: A general stepwise approach is described for the preparation of tetrathiafulvalene (TTF)-based linear and mono- and dimacrocyclic compounds incorporating one or two 1,4-dioxyphenylene, 9,10-dioxyanthrylene, or 1,5- or 2,6-dioxynaphthylene units from readily available starting materials. By utilizing the $\pi-\pi$ stacking interactions of the TTF unit with the dipyridinium dication of 1,1'-[1,4-phenylenebis (methylene)] bis-4,4'-bipyridinium bis(hexafluorophosphate), a rotaxane and two [2]catenanes were synthesized starting from the linear and monomacrocyclic compounds, respectively. From the dioxyphenylene-based dimacrocycle, three [3]pseudocatenanes (*trans*, *cis*, and a mixture of *cis*/*trans* isomers) were obtained with the *trans* compound as the major product. From the dioxyanthrylene dimacrocycle, only the *trans*-[3]pseudocatenane was obtained. Catenane products were formed quantitatively from the 1,5-dioxynaphthylene dimacrocycle in a template-directed reaction, affording a *trans*-[3]pseudo-catenane together with a [4]pseudocatenane (mixture of *cis*/*trans* isomers). From the 2,6-dioxynaphthylene dimacrocycle, a *cis*-[3]pseudocatenane was obtained as the major product and a *trans*-[3]pseudocatenane as the minor one. For the [3]pseudocatenanes (i.e., both the *cis* and *trans* catenanes), in which the TTF units were clamped by the tetracationic macrocycle, isomerizations were completely prevented even in the presence of trifluoroacetic acid. All new rotaxanes and catenanes were characterized by electrospray mass spectrometry, and the *cis*- and *trans*-[3]pseudocatenanes were additionally investigated by ^{1}H NMR spectroscopy. The electrochemical and spectral properties of the rotaxane and the catenanes are reported. Catenane formation increases the redox potentials of the TTF unit. The results demonstrate the versatility of TTF as a building block in the construction of supramolecular structures.

Keywords
catenanes · macrocycles · rotaxanes · self-assembly · tetrathiafulvalenes

Introduction

Interlocked molecular systems—rotaxanes and catenanes—were traditionally prepared by statistical methods and multistep directed synthesis.[1] The application of the concepts of supramolecular chemistry, especially the processes of self-assembly,[2] has made such topologically complex molecules relatively easily available, and several different synthetic methods have been developed during the past decade. For example, transition metals have been used as templates to construct a range of different rotaxanes, catenanes, and knots.[3] Two different methods of generating organometallic catenanes have also been reported. One of them involves Pd or Pt metal centers as part of the entangled macrocycles,[4] and the second utilizes the coordination of a metal center by the oxygen atoms of a crown ether.[5] The utilization of $\pi-\pi$ stacking and electrostatic interactions involving aromatic π donors and π acceptors has provided another efficient route to rotaxanes and catenanes.[6] The combination of hydrogen-bonding and $\pi-\pi$ stacking has led to the formation of several catenanes with identical rings.[7] By using the ability of naturally and chemically modified cyclodextrins to form inclusion complexes with various organic substrates, a range of cyclodextrin rotaxanes have been prepared, and more recently the synthesis of cyclodextrin catenanes has also been reported.[8] Nevertheless, developing new efficient methods for the synthesis of interlocked supramolecular structures of new topology currently remains one of the greatest challenges in modern preparative chemistry.

Although the synthesis of functionalized tetrathiafulvalenes has been stimulated by the search for new TTF-based organic metals,[9] there has been an increasing interest in incorporating the electroactive TTF unit into macrocyclic and supramolecular compounds.[10, 11] In recent years, using the readily available 1,3-dithiole-2-thione-4,5-dithiolate,[12] we have reported the preparation of a variety of TTF-containing macrocyclic systems.[13] We have recently developed a novel efficient method for the preparation of macrocyclic compounds incorporating TTF, based on the deprotection–alkylation of a dicyanoethylated TTF derivative such as 2,6-bis(2'-cyanoethylthio)-3,7-bis(methylthio)tetrathiafulvalene, in the presence of cesium hydroxide.[11a] Starting from 4,5-dibenzoylthio-1,3-dithiole-2-thione and related dibenzoyl derivatives, Olk et al. reported another convenient approach to the preparation of unsymmetrically substituted 1,3-dithiole-2-thione-4,5-dithiolates and, thus, novel unsymmetrical crown ethers.[11g] Further investigation showed that this method could be extended to 2,3,6,7-tetrakis(2'-cyanoethylthio)tetrathiafulvalene, a tetraprotected TTF derivative, which meant that it was possible to build TTF-based di- or even multimacrocyclic systems by stepwise cyclization reactions.[14] With the availability of these new methods, we became interested in the possibility of synthesizing TTF-containing rotaxanes and catenanes by using the self-assembly

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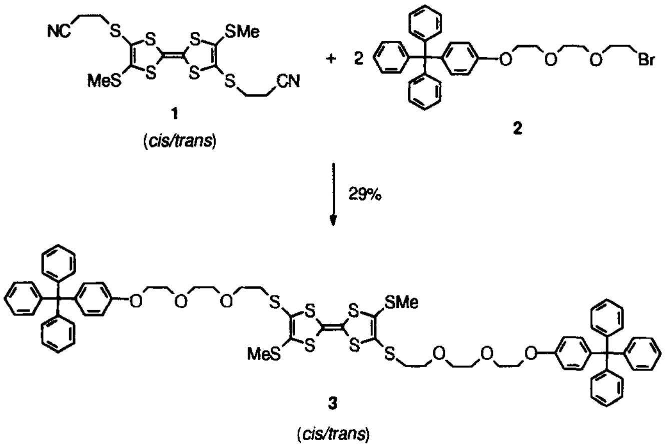
strategy developed by Stoddart et al:[6] TTF has been reported to form a 1:1 charge-transfer complex with the π-electron-accepting tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene),[15] and a rotaxane incorporating one TTF unit and two 1,4-dioxyphenylene units has also been synthesized.[6c] We expected that new types of TTF-based supramolecular systems could be constructed because the tetrathiafulvalene-2,3,6,7-tetrathiolate unit (TTFTT) could in principle function as a tetravalent building block, while most starting materials hitherto used to prepare macrocyclic and hence catenane systems, such as dihydroxyphenylene, diaminophenylene, benzidine, and bipyridine derivatives, are divalent species. In this paper,[16] we describe 1) the convenient synthesis of TTF-based linear, monocyclic, and dicyclic precursors; 2) how the π–π stacking interactions between the dipyridium unit and the linear and mono- and dimacrocyclic TTF systems incorporating different electron-rich aromatic units (e.g., 1,4-dioxyphenylene, 9,10-dioxyanthrylene, and 1,5- and 2,6-dioxynaphthylene) can be used to build a TTF-based rotaxane, [2]catenanes, [3]pseudocatenanes, and a [4]pseudocatenane; 3) how the information existing in the individual components, especially in the dimacrocyclic compounds, expresses itself through the different efficiencies of self-assembly and chemo- and configurational selectivities in the [3]pseudocatenanes systems; 4) the characterization of these molecular compounds by electrospray mass spectrometry (ESMS) and, in some cases, by ^{1}H NMR spectroscopy; and 5) their electrochemical and spectroscopic properties.

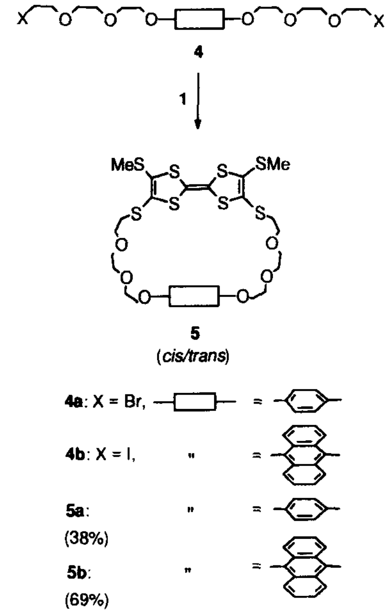
Results and Discussion

Synthesis: Four types of TTF-containing compounds (the linear, TTF-planar monomacrocyclic, and TTF-planar and TTF-nonplanar dimacrocyclic systems) were synthesized in order to investigate their different abilities to induce the formation of rotaxanes or catenanes. All the aromatic units are connected through diethylene glycol ether chains. For the linear compound, this chain is long enough that the stoppers do not prevent the formation of a rotaxane.[17] CPK (Corey–Pauling–Koltun) models of the mono- and dimacrocyclic compounds indicated that the separation between the TTF and the aromatic units is approximately 7 Å. This distance is optimal because it results in the preferred 3.5 Å separation between interacting rings for effective π–π charge-transfer stabilization.[6b]

The linear TTF compound **3** was prepared from tetrathiafulvalene **1**[11a] and (triphenylmethyl)benzene **2** in the presence of two equivalents of cesium hydroxide (Scheme 1). The two isomers of **3** could be separated, but we were unable to assign their configuration from the ^{1}H NMR spectra. Addition of a trace of trifluoroacetic acid to either one of the isomers immediately resulted in the formation of mixture of isomers in a 1:1 ratio, as indicated by the ^{1}H NMR spectra.



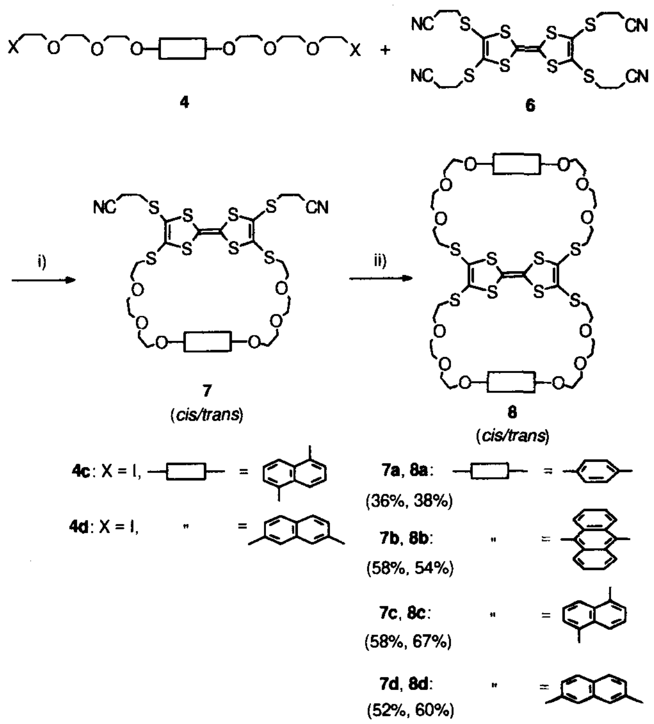
Scheme 1. Synthesis of **3**: N_2, 2 equiv $CsOH\cdot H_2O$, DMF, RT, 16 h.



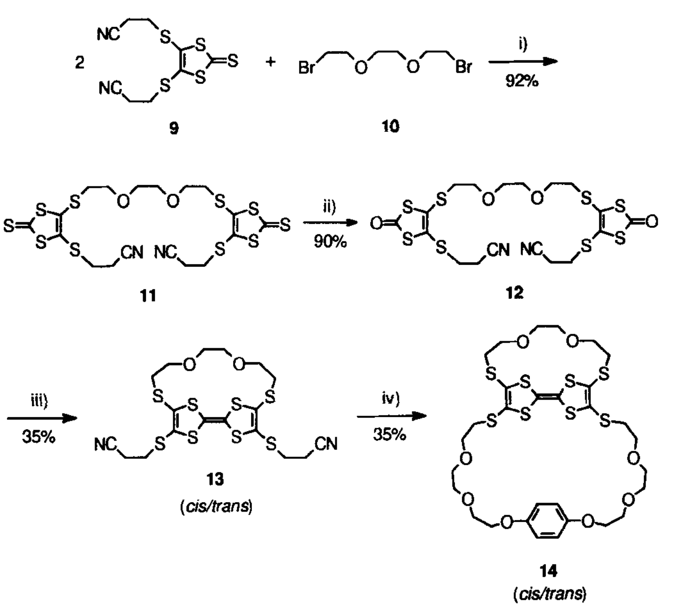
Scheme 2. Synthesis of **5a** and **5b** using high-dilution techniques: N_2, 2 equiv $CsOH\cdot H_2O$, DMF, RT, 17 h.

Under high-dilution conditions, monocyclic compounds **5a** and **5b** were prepared from **1** and **4a**[18] or **4b**[19] (Scheme 2). By two-step cyclization reactions, dimacrocycles **8a–d** were prepared from **4a–d** and tetrathiafulvalene **6**[20] with monocycles **7a–d** as intermediates (Scheme 3). The macrocyclic compounds **5a–d**, **7a–d**, and **8a–d** are all inseparable mixtures of *cis* and *trans* isomers.[21]

In order to study the influence of the distorted TTF unit on the self-assembly process, dimacrocyclic compound **14** was synthesized. CPK models show that the TTF unit in **14** is slightly distorted as a result of the short triethylene glycol ether chain (distortions of about 6° for *cis* and 10° for *trans* isomers). Starting from thione **9**[20] and dibromide **10**, **14** was prepared in four steps (Scheme 4). In the presence of cesium hydroxide, **9** reacted with **10** to give compound **11**, which was transformed to compound **12** by $Hg(OAc)_2$. The coupling reaction of **12** in the



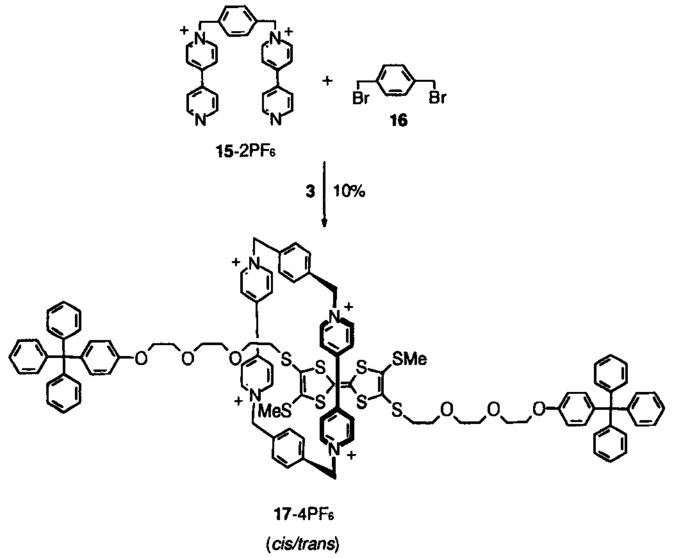
Scheme 3. Synthesis of **7a–d** and **8a–d**: i) and ii) N_2, 2 equiv $CsOH\cdot H_2O$, DMF, RT, 17–25 h.



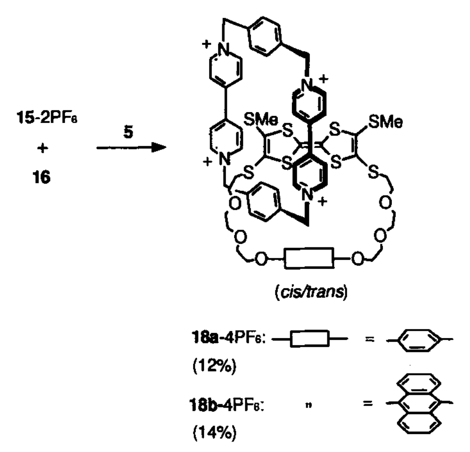
Scheme 4. Synthesis of **14** in four steps: i) N_2, 2 equiv CsOH·H_2O, DMF, RT, 16 h; ii) $Hg(OAc)_2$, $CHCl_3$/AcOH (3:1), 24 h; iii) $P(OEt)_3$, toluene, reflux, 1 h; iv) **4a**, N_2, 2 equiv CsOH·H_2O, DMF, RT, 17 h.

presence of $P(OEt)_3$ led to monocyclic compound **13** as a mixture of *cis* and *trans* isomers. The cyclization reaction of **13** with **4a** gave **14**, also as a *cis*/*trans* mixture.[22] Compound **13** was also prepared by direct coupling of **11** in the presence of $P(OEt)_3$, albeit in a lower yield. Because of their higher reactivity, all cyclization reactions using ω,ω'-diiodides gave better yields than those involving the corresponding dibromides.

Because there have been no reports on the ability of the TTF unit itself to act as a template for the formation of a tetracationic macrocycle, compound **3** was synthesized as a model compound to investigate the efficiency with which the TTF unit forms a rotaxane.[23] By a procedure similar to that for the synthesis of dioxyphenylene-based rotaxanes,[6b] rotaxane **17**-$4PF_6$ was obtained as a mixture of *cis* and *trans* isomers in 10% yield from the reaction of **3**, dication **15**-$2PF_6$,[6b] and 1,4-bis(bromomethyl)benzene (**16**) in DMF over ten days (Scheme 5). The isomers could not be separated. Although the yield of **17**-$4PF_6$ is not high, the reaction demonstrates that TTF can act as a template for the formation of the tetracationic macrocycle.



Scheme 5. Synthesis of rotaxane **17**-$4PF_6$: N_2, DMF, RT, 10 d.

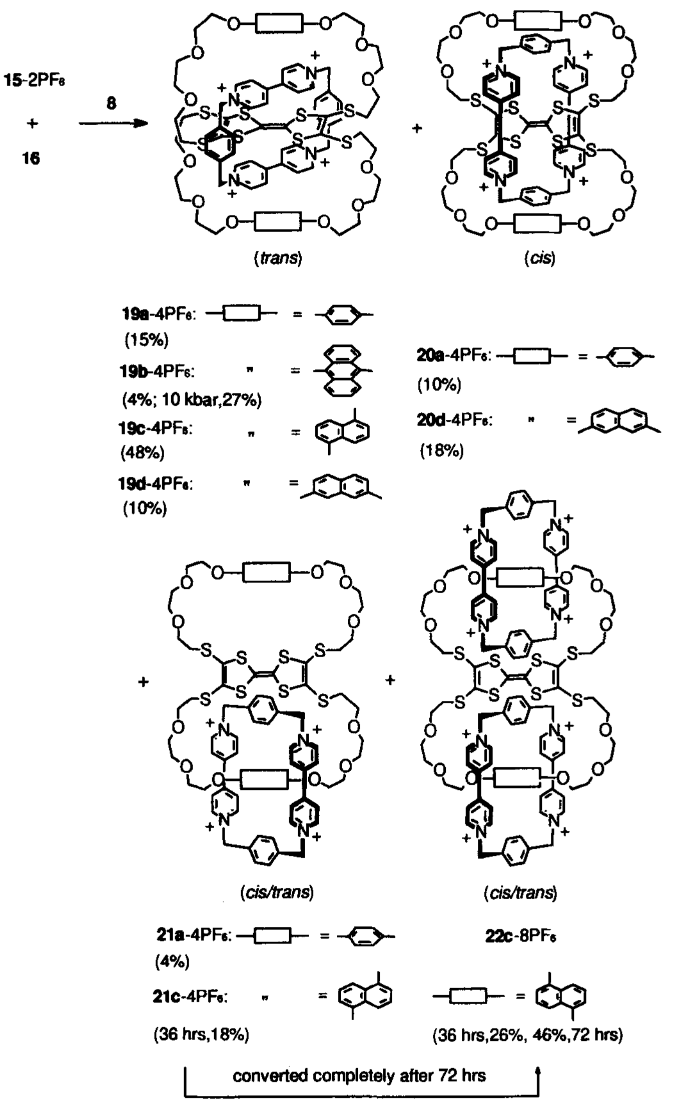


Scheme 6. Synthesis of [2]catenanes **18a**-$4PF_6$ and **18b**-$4PF_6$: N_2, DMF, RT, 10 d.

The reaction of monomacrocycle **5a** with **15**-$2PF_6$ and **16** in DMF for seven days resulted in the formation of the [2]catenane **18a**-$4PF_6$ in 12% yield. Similarly, another [2]catenane, **18b**-$4PF_6$, was prepared in 15% yield from the reaction of **5b**, **15**-$2PF_6$, and **16** over twelve days (Scheme 6). Both catenanes are mixtures of *cis* and *trans* isomers, which could not be separated.

Two new types of molecular compounds, namely, [3]pseudocatenane and [4]pseudocatenane, were obtained from the reactions of dimacrocycles **8a–d**, **15**-$2PF_6$, and **16** (Scheme 7). We name these compounds [3]- and [4]pseudocatenanes because compounds **8a–d** are systems combining two macrocyclic units while sharing one TTF group.[31] From the reaction of **8a**, the three [3]pseudocatenanes *trans*-**19a**-$4PF_6$, *cis*-**20a**-$4PF_6$, and **21a**-$4PF_6$ (a mixture of *cis* and *trans* isomers) were obtained in 15, 10, and 4% yields, respectively, after ten days. Similarly, *trans*-[3]pseudocatenane **19b**-$4PF_6$ was obtained in 4% yield from the reaction of **8b**, **15**-$2PF_6$, and **16** after 21 days. No isomers similar to **20a**-$4PF_6$ or **21a**-$4PF_6$ were generated in this reaction. By using ultra-high pressure (10 kbar), **19b**-$4PF_6$ could be prepared in 27% yield after three days.[24] A [3]pseudocatenane, **19c**-$4PF_6$, a [3]catenane, **21c**-$4PF_6$, and a [4]catenane, **22c**-$8PF_6$, were obtained from the reaction of **8c**, **15**-$2PF_6$, and **16**. After 36 hours, TLC indicated that **8c** had been completely consumed—the dimacrocyclic compound was transformed completely to the catenated products! To our knowledge, this is the first example of quantitative self-assembly of catenanes in a template-directed method.[25] The main product, isolated in 48% yield, was the *trans* isomer of **19c**-$4PF_6$, while **21c**-$4PF_6$ and **22c**-$8PF_6$ were isolated in 18 and 26% yields, respectively, both as mixtures of *cis*/*trans* isomers. When the reaction time was extended to three days, **21c**-$4PF_6$ was transformed completely to **22c**-$8PF_6$ (monitored by TLC), and **22c**-$8PF_6$ was then isolated in 46% yield, while the yield of **19c**-$4PF_6$ remained unchanged. Under similar conditions, quite different results were obtained from the reaction of **8d**, a constitutional isomer of **8c**, with **15**-$2PF_6$ and **16** over seven days: the *cis*-[3]pseudocatenane **20d**-$4PF_6$ was isolated in 18% yield as the major product and the *trans*-[3]pseudocatenane **19d**-$4PF_6$ in 10% yield as the minor product. No catenanes similar to **21c**-$4PF_6$ or **22c**-$8PF_6$ were detected in this reaction.

Stirring the solution of the dimacrocycle **14**, **15**-$2PF_6$, and **16** in DMF under similar conditions for 21 days did not afford any catenane products (monitored by TLC); this indicates that even a slight distortion of the TTF unit completely prevents the for-



Scheme 7. Synthesis of [3]pseudocatenanes and [4]catenane: N_2, DMF, RT, 7–21 d (2 equiv **15**-2PF_6 and **16** in the cases of **8a** and **8b**; 3 equiv **15**-2PF_6 and **16** in the cases of **8c** and **8d**).

mation of the tetracationic macrocycle around the dioxyphenylene unit.

The fact that rotaxane **17**-4PF_6, and [2]catenanes **18a**-4PF_6 and **18b**-4PF_6 are mixtures of *cis* and *trans* isomers can readily be explained in terms of their structural features. The tetracationic macrocycle in **17**-4PF_6 can easily move between the two triphenylmethylphenyl stoppers and is not fixed around the TTF unit. The *cis* and *trans* TTF units can therefore isomerize. Because of the configurational isomerization of the TTF unit and the two possible locations of the tetracationic macrocycle—around the TTF or dioxyphenylene unit—[2]catenane **18a**-4PF_6 has four possible translational isomers. Because the dioxyanthrylene unit is too big to clamped by the tetracationic macrocycle, [2]catenane **18b**-4PF_6 has only two possible configurational isomers. However, the facile rotation of the two component units along and around each other in both compounds makes it impossible to prevent *cis/trans* isomerisation. The fact that [3]catenanes **21a**-4PF_6 and **21c**-4PF_6 and even [4]catenane **22c** are still mixtures of *cis* and *trans* isomers indicates that the tetracationic macrocycles in these compounds can move easily and that the interactions between the TTF units and dipyridinium units have no significant influence on the isomerization of the TTF units.

All the [3]pseudocatenanes in which the TTF units are clamped by the tetracationic macrocycle are stable in solution. Addition of trifluoroacetic acid (0.1 M) to the solution of these catenanes in acetonitrile did not result in any change (monitored by TLC), indicating that no *cis/trans* isomerization took place. CPK models indicate that the movement of the tetracationic macrocycles in all these compounds is prevented by the four glycol chains. This surprising result therefore strongly suggests that the tetracationic macrocycle can only efficiently prevent the isomerization of a TTF unit when it is fixed around it.[26]

The different efficiencies and chemo- and configurational selectivities exhibited by the reactions of the dimacrocycles **8a–d** with **15**-2PF_6 and **16** suggest that the self-assembly of TTF-based supramolecular systems is strongly affected by electronic and structural features, especially by the π-electron-donating ability, size, and conformation of the aromatic units. Because of the relatively weak electron-donating ability of the dioxyphenylene unit, *trans*-**19a**-4PF_6 and *cis*-**20a**-4PF_6 are obtained in relatively low yields from the reaction of **8a**. Although the dioxyanthrylene unit has a much stronger electron-donating ability, its relatively large size significantly reduces the ability of **8b** to act as a template in the formation of the catenane, and low yields are thus obtained. The fact that, even under conditions of ultra-high pressure, no *cis* isomer of **19b**-4PF_6 is produced indicates that the *cis* isomer of **8b** cannot act as a template. The quantitative transformation of **8c** to a mixture of catenane products provides an excellent example of the efficiency of self-assembly. Actually, it has been reported that macrocyclic polyethers incorporating the 1,5-dioxynaphthylene unit are better templates in the self-assembly of catenanes than the similar 1,4-dioxyphenylene derivatives.[27] The great difference between the reactions of **8c** and **8d**, two constitutional isomers, can be explained in the following way:[28] In order to affect the self-assembly process, the dioxynaphthylene unit must form efficient π–π stacking interactions with the electron-deficient dipyridinium unit. The CPK model shows that only *trans*-**8c** can adopt an energetically favorable conformation. Therefore, efficient self-assembly not only leads to **19c**-4PF_6, but also to **21c**-4PF_6 and **22c**-8PF_6. In the case of **8d**, the dioxynaphthylene unit of the *trans* isomer must adopt a twisted conformation, while the dioxynaphthylene unit of its *cis* isomer can reach the spatial orientation necessary for the π–π stacking by twisting the glycol chains. However both confomations are energetically unfavorable. As a result, self-assembly is not as efficient as with **8c**, and no catenane products similar to **21c**-4PF_6 or **22c**-8PF_6 are produced. The fact that *cis*-**20d**-4PF_6 is the major product implies that *cis*-**8d** is a more effective template for self-assembly.[29]

Electrospray Mass Spectrometry (ESMS): The rotaxane and all the catenanes, except [2]catenane **18a**-4PF_6 (by FABMS), were characterized by ESMS spectrometry. Table 1 lists the ESMS data of the rotaxane and the catenanes. It can be seen that most compounds give peaks for $[M-4PF_6]^{4+}$, $[M-3PF_6]^{3+}$, $[M-2PF_6]^{2+}$, $[2M-3PF_6]^{3+}$, and $[3M-4PF_6]^{4+}$, and some compounds also generate peaks corresponding to $[M-PF_6]^{+}$ and $[3M-5PF_6]^{5+}$. The $[3M-4PF_6]^{4+}$ and $[3M-5PF_6]^{5+}$ peaks, corresponding to the loss of four and five PF_6^- ions from three catenane species, reveal the complex fragmentation patterns of these supramolecular structures.[30]

^{1}H NMR Spectroscopy: Because of their *cis/trans* isomerization, rotaxane **17**-4PF_6, [2]catenanes **18a**-4PF_6 and **18b**-4PF_6, [3]pseudocatenane **21a**-4PF_6, [3]catenane **21c**-4PF_6, and [4]catenane **22c**-8PF_6 have ^{1}H NMR spectra that cannot be completely assigned, whereas the configurations of [3]pseudo-

Table 1. ESMS data of rotaxane **17**-4PF$_6$ and catenanes **18**–**22**-4PF$_6$.

	$[M-4PF_6]^{4+}$	$[M-3PF_6]^{3+}$	$[M-2PF_6]^{2+}$	$[M-PF_6]^{+}$	$[2M-3PF_6]^{3+}$	$[3M-5PF_6]^{5+}$	$[3M-4PF_6]^{4+}$
17-4PF$_6$	445	642	1035		1429	1272	1426
18a-4PF$_6$			1363 [a]				
18b-4PF$_6$	330	488	804	1754	1121	994	1280
19a-4PF$_6$	382	558	909		1261		1437
19b-4PF$_6$	432	625	1009		1395		1587
19c-4PF$_6$	407	591	960		1328		1512
19d-4PF$_6$		591	960				
20a-4PF$_6$	382	558	909	1964	1261		1437
20d-4PF$_6$		591	960				
21a-4PF$_6$	382	558	909	1964	1261		1437
21c-4PF$_6$	407	591	960		1328		1512
22c-4PF$_6$ [b]	682	958	1509				

[a] FABMS value corresponding to the ion peak $[M-2PF_6]^+$. [b] Ion peaks corresponding to $[M-5PF_6]^{5+}$ and $[2M-5PF_6]^{5+}$ were also observed at m/z = 517 and 1179.

catenanes **19a**-4PF$_6$, **20a**-4PF$_6$, **19b**-4PF$_6$, **19c**-4PF$_6$, **19d**-4PF$_6$, and **20d**-4PF$_6$ can easily be determined by their ^{1}H NMR spectra. Because of their D_2 symmetry, both the α- and β-protons on the dipyridinium rings of all the *trans* compounds are split into two sets of signals. In contrast, the corresponding protons of the *cis* compounds give simple doublet signals as a result of their D_{2h} symmetry. The ^{1}H NMR spectra of **19d**-4PF$_6$ and **20d**-4PF$_6$ are shown in Figure 1 and Figure 2. The differences in the signals corresponding to the α- and β-protons on the dipyridinium unit between the *trans* and *cis* configurations can clearly be seen. The chemical shifts of the protons of the tetracationic macrocycles in the [3]pseudocatenanes **19** and **20** and the changes (Δδ) relative to the free tetracationic macrocycle are listed in Table 2. For both *cis* and *trans* structures, the greatest changes (all upfield shifts) are seen for the β-protons (−0.10 to −0.96 ppm). For the α-protons no general trends are observed; this probably indicates that it is the shielding action of the TTF units and not the charge-transfer interaction or the shielding action of the aromatic units that plays an important role, because the *cis* and *trans* isomers have very different conformations but display similar trends. Upfield shifts are also observed for the methylene protons (−0.12 to −0.26 ppm), but no significant changes are shown for the phenylene protons. Although the methylene protons of the *trans* compounds should in principle display two split doublets, such a signal pattern is observed only in the spectra of **19b**-4PF$_6$; this indicates that the dioxyanthrylene units interact most strongly with the dipyridinium unit. The dynamic ^{1}H NMR spectra of **19a**-4PF$_6$, **20a**-4PF$_6$, and **19b**-4PF$_6$ were also examined. The ^{1}H NMR spectra of **20a**-4PF$_6$ are independent of temperature in the interval −35 to 75 °C, whereas the aromatic resonances of **19a**-4PF$_6$ and **19b**-4PF$_6$ show a strong temperature dependence. NOESY (chemical exchange) spectra prove that this temperature dependence is due to thermally activated exchange between sites on the aromatic rings. The rotational barrier in **19b**-4PF$_6$ is higher than that in **19a**-4PF$_6$. All motions of the polyether chains of **20a**-

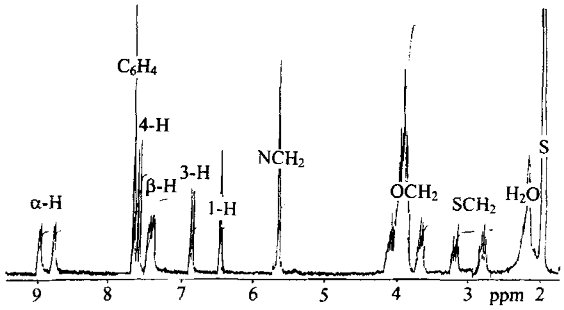


Fig. 1. ^{1}H NMR spectrum (250 MHz) of *trans*-[3]pseudocatenane **19d**-4PF$_6$ in CD$_3$CN at room temperature.

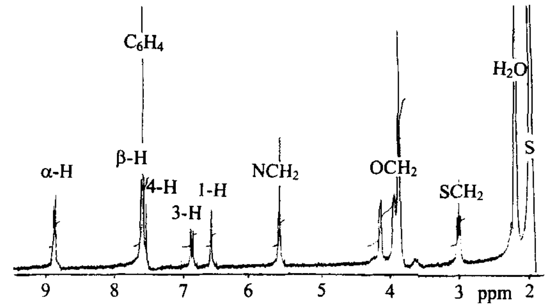


Fig. 2. ^{1}H NMR spectrum (250 MHz) of *cis*-[3]pseudocatenane **20d**-4PF$_6$ in CD$_3$CN at room temperature.

Table 2. Selected ^{1}H NMR resonances (δ) of the tetracationic macrocycles in the [3]pseudocatenanes **19** and **20** and chemical shift differences (given in parentheses, ppm) relative to the free tetracationic macrocycle [a].

	α-H		β-H		C$_6$H$_4$	NCH$_2$
free	8.93		8.23		7.60	5.78
trans-**19a**-4PF$_6$	9.01 (d, 4H)	8.82 (d, 4H)	7.80 (d, 4H)	7.63 (d, 4H)	7.68 (s)	5.66 (s)
	(0.08)	(−0.11)	(−0.43)	(−0.60)	(0.08)	(−0.12)
cis-**20a**-4PF$_6$	8.95 (d, 8H)		7.82 (d, 8H)		7.63 (s)	5.62 (s)
	(0.02)		(−0.41)		(0.03)	(−0.20)
trans-**19b**-4PF$_6$	8.87 (dd, 4H)	8.50 (d, 4H)	8.13 (dd, 4H)	7.86 (d, 4H)	7.60 (s)	5.59 (dd)
	(−0.06)	(−0.43)	(−0.10)	(−0.37)	(0.00)	(−0.23)
trans-**19c**-4PF$_6$	8.85 (d, 4H)	8.66 (d, 4H)	7.42 [b]	7.27 (dd, 4H)	7.63 (s)	5.54 (s)
	(−0.08)	(−0.27)	(−0.61)	(−0.96)	(0.03)	(−0.26)
trans-**19d**-4PF$_6$	8.95 (d, 4H)	8.76 (d, 4H)	7.42 (d, 4H)	7.39 (d, 4H)	7.66 (s)	5.67 (s)
	(0.02)	(−0.17)	(−0.61)	(−0.84)	(0.06)	(−0.15)
cis-**20d**-4PF$_6$	8.84 (d, 8H)		7.62 (d, 8H)		7.60 (s)	5.61 (s)
	(−0.09)		(−0.61)		(0.00)	(−0.21)

[a] In CD$_3$CN at room temperature. [b] Overlaps with the signal of the 4,8-protons of the naphthylene unit.

4PF$_6$ are frozen out on the NMR timescale, because its ^{1}H NMR spectra, especially the observed scalar couplings between the protons of the polyether moiety, are temperature independent. The pyridine and hydroquinone or hydroanthraquinone rings are highly mobile in the *trans* compounds **19a**-4PF$_6$ and **19b**-4PF$_6$. The polyether moieties are therefore arranged such that there is enough room for these ring systems to rotate around their axes. The hydroquinone rings of the *cis* compound **20a**-4PF$_6$ do not show any sign of such motion; this indicates that the benzene rings of the tetracationic macrocycle stabilize the hydroquinone rings by $\pi-\pi$ stacking interactions. Stacking of this type is impossible in a *trans* configuration.

Cyclic Voltammetry: The redox behavior of the rotaxane, the catenanes, and their TTF components were investigated by cyclic voltammetry (CV). The half-wave potentials are listed in Table 3. All the TTF components **3**, **5a–b**, and **8a–d** exhibit the typical redox behavior of TTF, that is, they display two reversible redox waves corresponding to the oxidation to the mono- and dications of the TTF units. The potentials for all three oxidation steps of **8b–d** are significantly lower than those of **8a**. We attribute this to the stronger electron-donating ability of the dioxyanthrylene and dioxynaphthylene units and hence their stronger interactions with the TTF unit. Because of the influence of the tetracationic macrocycle, the redox values of the TTF unit in the rotaxane and in the catenanes are all higher. The cyclic voltammograms of **8a** and **20a**-4PF$_6$ are depicted in Figures 3 and 4, respectively, which illustrate the influence of the $\pi-\pi$ donor–acceptor interaction on the redox behavior of the TTF unit. The fact that there is no significant difference between the values of **19a**-4PF$_6$ and **20a**-4PF$_6$ indicates that the configurational change does not greatly influence the redox process. The first two oxidation steps of **21a**-4PF$_6$, that is, the oxidation to the mono- and dications of the TTF unit, are apparently unaffected by the dipyridinium macrocycle; this is indicative of a weaker interaction between the TTF unit and the dipyridiniums within **21a**-4PF$_6$. The voltammograms of **19c**-4PF$_6$ and **20d**-4PF$_6$ display unresolved broad waves, probably due to the strong interaction between the dioxynaphthylene unit and dipyridinium unit. In addition to the three processes corresponding to the oxidation of TTF and dioxyanthrylene unit (the three waves shown in Table 3), **19b**-4PF$_6$ also exhibits another relatively low redox process at $E_{1/2} = 0.25$ V, which we speculate results from the intermolecular stacking interaction between the two hydroanthraquinone units.

Table 3. Half wave-potentials [a] for the oxidation by cyclic voltammetry, determined in CH$_2$Cl$_2$ [b] or CH$_3$CN [c]. For **19c**-4PF$_6$ and **20d**-4PF$_6$, no accurate data are available [d].

	$E^1_{1/2}$	$E^2_{1/2}$	$E^3_{1/2}$
3	0.54	0.87	
5a	0.53	0.83	1.41 (irrev.)
5b	0.43	0.77	1.06
8a	0.50	0.79	1.38 (irrev.)
8b	0.38	0.73	1.05 (irrev.)
8c	0.37	0.68	1.01
8d	0.40	0.70	1.06
17-4PF$_6$	0.61	0.94	
18a-4PF$_6$	0.60	0.84	
18b-4PF$_6$	0.60 (irrev.)		
19a-4PF$_6$	0.63	0.94	1.34
20a-4PF$_6$	0.62 (irrev.)	0.92 (irrev.)	1.34
21a-4PF$_6$	0.58	0.82	1.28
19b-4PF$_6$	0.52 (irrev.)	0.87 (irrev.)	1.19
19d-4PF$_6$	0.46		1.01
21c-4PF$_6$	0.60	0.85	1.03
22c-8PF$_6$	0.59		1.00

[a] Reversible redox process unless noted otherwise. [b] For free TTF components. [c] For the rotaxane and the catenanes. [d] Reference electrode: Ag/AgCl; working and counter-electrodes: Pt, sweep rate 100 mVs^{-1}; supporting electrolyte: nBu$_4$NPF$_6$ 0.1 mol L^{-1}; conc. of compound: 5×10^{-4} L^{-1}.

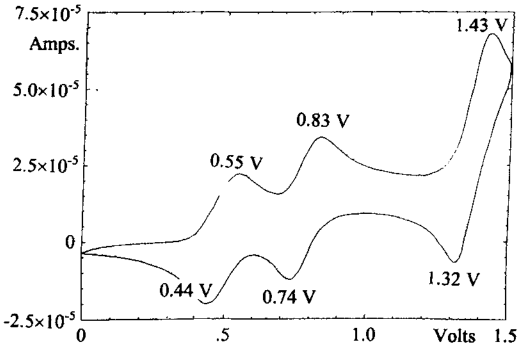


Fig. 3. The cyclic voltammogram of **8a** (for conditions, see Table 3).

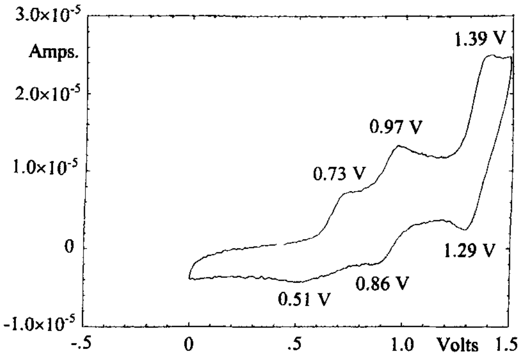


Fig. 4. The cyclic voltammogram of **19a**-4PF$_6$ (for conditions, see Table 3).

Charge-Transfer Absorption: UV/Vis spectra reveal charge-transfer absorption bands for the rotaxane and catenanes (Table 4). It can be seen that all the [3]pseudocatenanes in which the TTF units are locked by the tetracationic macrocycles have stronger absorptions than the other compounds. This indicates that fixing the TTF unit within the tetracationic macrocycle greatly increases the charge-transfer interaction between the TTF unit and the dipyridinium units. The strongest absorptions are observed for **19b**-4PF$_6$ and **19c**-4PF$_6$, as a result of the strong π-electron donating ability of the dioxyanthrylene and 1,5-dioxynaphthylene units. Because of the movement of the tetracationic macrocycle along the glycol chains, rotaxane **17**-4PF$_6$ and [2]catenanes **18a**-4PF$_6$ and **18b**-4PF$_6$ only exhibit weak CT aborption bands. This observation is in accordance with the fact that these molecular systems are mixtures of configurational isomers. According to their molar extinction coefficients, it seems that the charge-transfer interaction of **22c**-4PF$_6$ is just the simple addition of that of two **21c**-4PF$_6$.

Table 4. Charge-transfer absorptions of rotaxane **17**-4PF$_6$ and the catenanes **18–22**, recorded in MeCN at room temperature.

	λ_{max} (nm)	ε (M^{-1}cm^{-1})		λ_{max} (nm)	ε (M^{-1}cm^{-1})
17-4PF$_6$	660	745	**19b**-4PF$_6$	773	4200
18a-4PF$_6$	620	620	**19c**-4PF$_6$	790	4150
18b-4PF$_6$	665	820	**21c**-4PF$_6$	750	850
19a-4PF$_6$	785	3100	**22c**-4PF$_6$	780	1400
20a-4PF$_6$	807	2900	**19d**-4PF$_6$	760	2400
21a-4PF$_6$	770	900	**20d**-4PF$_6$	745	1900

Conclusion

In this paper we have established a methodology for the synthesis of TTF-containing rotaxanes and catenanes by utilizing the concept of self-assembly. From the reactions of TTF-based dimacrocyclic compounds incorporating two aromatic units, two new types of catenanes, namely, [3]pseudocatenanes and [4]pseudocatenanes, were synthesized, although the latter is a mixture of configurational isomers. The reactions of various dimacrocycles, containing aromatic units with different π-electron donating abilities and sizes, display different self-assembly patterns and hence lead to different regio- and configurational selectivities. In one example, the dimacrocyclic compound incorporating two 1,5-dioxynaphthylene units reacts quantitatively to form two catenanes, an example of quantitative self-assembly of catenanes in a template-directed method. The fixation of the TTF units within the tetracationic macrocycles provides a new approach to preventing the isomerization of unsymmetrical TTF compounds, which may be important for the future use of TTF-derived macrocycles in supramolecular chemistry.

Stoddart et al. originally developed the concept of $\pi-\pi$ donor–acceptor interactions in the synthesis of catenanes.[6] The successful synthesis, described in this paper, of a variety of TTF-containing rotaxane and catenane structures with a new topology represents a further development of this concept. The chemo- and configurational selectivities exhibited by the reactions of the dimacrocycles not only demonstrates the versatility of the electroactive TTF unit as a building block for large and highly ordered supramolecular structures, but also points towards the construction of controllable TTF-based catenanes.

Experimental Procedure

General Methods: Chemicals were purchased from Aldrich and Fluka and used as received. Solvents were purified according to standard procedure. Thin-layer chromatography (TLC) was carried out on aluminum sheets precoated with silica gel 60 F (Merck 5554) and inspected by UV light and/or developed with iodine vapour. Column chromatography was carried out using silica gel 60F (Merck, 9385, 230–400 mesh). Melting points are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AC250 or a Varian 500 spectrometer; all chemical shifts are referenced to TMS. Electron impact (EI) and fast atom bombardment (FAB) mass spectra were obtained on a VG 7070E or Varian MAT 311 A instrument. Plasma desorption mass spectra (PDMS) were carried out on BioIon 10 K time-of-flight mass spectrometer (Biosystems, Uppsala, Sweden) over 5×10^5 fissions (^{252}Cf). Electrospray (ES) mass spectra were recorded using a Finnigan MAT TSQ 700 triple quadrupole mass spectrometer. The catenanes were electrosprayed from methanol solution. The ions passed through a heated capillary into the first quadrupole from two different sources, the MAT electrospray ionization source with a sample flow of 5–10 µL min^{-1}, the capillary at 50 °C, and a coaxial flow of N_2 at 30–40 psi, and another source made in our laboratory, with a sample flow of 0.3–0.7 µL min^{-1} and a capillary at 150 °C. There was no overall difference in the spectra obtained with the two sources; the latter had the advantage of using less sample because of the lower flow rate. The electrospray needle was maintained at 4.5–5.2 kV and the instrument operated in positive ion mode. The exact appearance of the spectrum depended on the spray and instrument parameters. CV measurements were carried out with Bu_4NPF_6 as supporting electrolyte, with a sweep rate of 100 mVs^{-1}. Counter and working electrodes were made of Pt and the reference electrode was Ag/AgCl. UV/Vis spectra were recorded on a Shimadzu UV-160 instrument. Elemental analyses were carried out by Microanalytical Laboratory, Copenhagen University. All the reactions were carried out under the protection of nitrogen.

We use the name [3]pseudocatenane for the interlocked systems **19** and **20** in order to distinguish this type of catenane from a simple [3]catenane such as **21**. We are well aware that, strictly, compounds **19**, **20**, and **21** are all catenanes, and the prefix does not explain the actual structure. We have yet to come up with a good descriptive name for the type of catenane in which a bicyclic molecule is clamped by a ring around the central bond.

(2-(2-(2-Bromoethoxy)ethoxy)ethoxy)-4-(triphenylmethyl)benzene (2): A mixture of 2-(2-(2-(*p*-(triphenylmethyl)phenyl)ethoxy)ethoxy)ethyl tosylate [6n] (5.01 g, 8.05 mmol) and LiBr (1.42 g, 15.4 mmol) in acetone (100 mL) was refluxed for 16 h and then allowed to cool to room temperature. The solvent was removed in vacuo, and the residue extracted with CH_2Cl_2 (200 mL). The organic phase was washed with water and dried ($MgSO_4$). The solvent was removed to afford a residue, which was subjected to column chromatography (silica gel, EtOAc/light petroleum (60–80 °C) 1:5). **2** (2.51 g, 59%) was obtained as a solid. M.p. 102–104 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 3.44$ (t, 2H; BrCH_2), 3.65–3.86 (m, 8H; OCH_2), 4.10 (t, 2H; OCH_2), 6.79 (d, 2H; C_6H_4), 7.10 (d, 2H; C_6H_4), 7.20 (m, 15H; C_6H_5); MS (EI): *m*/*z* (%): 531 (100) $[M]^+$. $C_{31}H_{31}BrO_3$ (531.5): calcd C 70.05, H 5.89; found C 70.30, H 5.72.

1,4,5,8-Tetrahydro-2,7(6)-bis(methylthio)-3,6(7)-bis[2-(2-(2-(*p*-(triphenylmethyl)-phenyl)ethoxy)ethoxy)ethylthio]-1,4,5,8-tetrathiafulvalene (3, *cis*/*trans*): 2,7-Bis(2′-cyanoethylthio)-3,6-bis(methylthio)tetrathiafulvalene (**1**) (0.93 g, 2.0 mmol) was added to DMF (100 mL). Cesium hydroxide monohydrate (0.60 g, 4.0 mmol) in methanol (10 mL) was then added dropwise over 20 min with stirring. The mixture was stirred for 30 min, and then a solution of **2** (2.45 g, 4.61 mmol) in DMF (50 mL) was added. The solution was stirred overnight. After the solvent had been removed in vacuo, dichloromethane (100 mL) was added, and the organic phase washed with water, saturated aqueous NaCl solution, and dried ($MgSO_4$). The solvent was then removed in vacuo, and the residue was purified by column chromatography (CH_2Cl_2/cyclohexane 1:50). The two isomers of **3** (the first, 0.30 g (19%); the second, 0.24 g (10%)) were both obtained as orange solid. We could not assign the two compounds as *cis* or *trans* isomer on the basis of the ^{1}H NMR spectra. First isomer: M.p. 144–46 °C; ^{1}H NMR ($CDCl_3$): $\delta = 2.38$ (s, 6H; SCH_3), 2.97 (t, 4H; SCH_2), 3.64–3.71 (m, 12H; OCH_2), 3.83 (m, 4H; OCH_2), 4.09 (m, 4H; OCH_2), 6.91 (dd, 8H; C_6H_4), 7.16–7.25 (m, 30H; C_6H_5); MS (PD): *m*/*z*: 1261.5 $[M]^+$; $C_{70}H_{68}O_6S_8$ (1261.8): calcd C 66.63, H 5.44, S 20.33; found C 66.73, H 5.39, S 20.15. Second low-melting isomer: M.p. 83–85 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.37$ (s, 6H; SCH_3), 2.98 (t, 4H; SCH_2), 3.64–3.72 (m, 12H; OCH_2), 3.84 (m, 4H; OCH_2), 4.08 (m, 4H; OCH_2), 6.91 (d, d, 8H, C_6H_4), 7.16–7.26 (m, 30H; C_6H_5); MS (PD): *m*/*z*: 1259.9 $[M]^+$; $C_{70}H_{68}O_6S_8$ (1261.8): calcd C 66.63, H 5.44; found C 66.37, H 5.34.

1,5-Bis(2-(2-(2-iodoethoxy)ethoxy)ethoxy)naphthalene (4c): A mixture of 1,5-dihydroxynaphthalene (1.60 g, 10 mmol), 1,2-bis(2-iodoethoxy)ethane (30.0 g, 80 mmol), and K_2CO_3 (1.38 g, 10 mmol) in anhydrous acetone (100 mL) was refluxed with stirring for 16 h. The solvent was then removed in vacuo. The residue was extracted with CH_2Cl_2 (200 mL), and the organic phase washed with water and saturated aqueous NaCl solution. The solvent was dried over anhydrous $MgSO_4$ and removed in vacuo. The residue was subjected to column chromatography (silica gel) with CH_2Cl_2/EtOAc (20:1) as the eluent. **4c** (2.0 g) was obtained in 31% yield as a pale yellow solid. M.p. 58–60 °C; ^{1}H NMR ($CDCl_3$): $\delta = 3.23$ (t, 4H; ICH_2), 3.67 (t, 4H; OCH_2), 3.75 (m, 8H; OCH_2), 3.98 (t, 4H; OCH_2), 4.28 (t, 4H; OCH_2), 6.83 (d, 2H; 2-H (naph)), 7.34 (dd, 2H; 3-H (naph)), 7.86 (d, 2H; 4-H (naph)); MS (EI): *m*/*z* (%): 644 (55) $[M]^+$, 516 (24), 155 (100); $C_{22}H_{30}I_2O_6$ (644.3): calcd C 41.01, H 4.70; found C 40.96, H 4.77.

2,6-Bis(2-(2-(2-iodoethoxy)ethoxy)ethoxy)naphthalene (4d): was prepared similarly in 32% yield as a pale yellow oil by refluxing the mixture of 2,6-dihydroxynaphthalene, 1,2-bis(2-iodoethoxy)ethane, and K_2CO_3 in acetone for 24 h. ^{1}H NMR ($CDCl_3$): $\delta = 3.25$ (t, 4H; ICH_2), 3.73 (m, 12H; OCH_2), 3.92 (t, 4H; OCH_2), 4.24 (t, 4H; OCH_2), 7.02 (dd, 2H; 3-H (naph)), 7.05 (d, 2H; 1-H (naph)), 7.64 (d, 2H; 4-H (naph)); MS (EI): *m*/*z* (%): 644 (90) $[M]^+$, 402 (18), 155 (100); $C_{22}H_{30}I_2O_6$ (644.3): calcd C 41.01, H 4.70; found: C 40.96, H 4.50.

1,4,5,8-Tetrahydro-2,7(6)-[1,4-bis(2-(2-(2-thioethoxy)ethoxy)ethoxy)phenylene]-3,6(7)-bis(methylthio)-1,4,5,8-tetrathiafulvalene (5a, *cis*/*trans*): Compound **1** (0.93 g, 2.0 mmol) was dissolved in DMF (40 mL). A solution of cesium hydroxide monohydrate (0.74 g, 4.4 mmol) in methanol (10 mL) was added dropwise with stirring over 30 min. The solution was stirred for 1 h. Then this solution and a solution of **4a** (1.00 g, 2.0 mmol) in DMF (50 mL) were added simultaneously, during 17 h at room temperature, to DMF (200 mL) under high-dilution conditions by means of a perfusor pump. Stirring was continued for an additional 3 h, and the reaction mixture was then concentrated in vacuo. CH_2Cl_2 (100 mL) was added, and the organic solution washed with water, saturated aqueous NaCl solution, and dried ($MgSO_4$). The solvent was then removed and the oily residue purified by column chromatography (silica, gel, CH_2Cl_2/EtOAc 8:1), affording **5a** (0.53 g, 38%) as an orange oil. ^{1}H NMR ($CDCl_3$): $\delta = 2.39$ (ss, 4H; SCH_3), 2.95 (m, 4H; SCH_2), 3.69 (m, 12H; OCH_2), 3.80 (m, 4H; OCH_2), 4.12 (m, 4H; OCH_2), 6.87 (ss, 4H; C_6H_4); MS (EI): *m*/*z* (%): 698 (100) $[M]^+$; $C_{26}H_{34}O_6S_8$ (699.2): C 44.66, H 4.91; found C 44.50, H, 5.01.

1,4,5,8-Tetrahydro-2,7(6)-[9,10-bis(2-(2-(2-thioethoxy)ethoxy)ethoxy)anthrylene]-3,6(7)-bis(methylthio)-1,4,5,8-tetrathiafulvalene (5b, *cis*/*trans*) was prepared in 69% yield as an orange oil from **1** and **4b**. ^{1}H NMR ($CDCl_3$): $\delta = 2.72$, 2.90 (ss, 4H; SCH_3), 3.04 (m, 4H; SCH_2), 3.79 (m, 12H; OCH_2), 3.91 (m, 4H; OCH_2), 4.43 (m, 4H; OCH_2), 7.39–7.51 (m, 4H; 2-H (anth)), 8.51 (m, 4H; 1-H (anth)); MS (EI): *m*/*z* (%) = 798 (73) $[M]^+$, 209 (86), 45 (100); $C_{34}H_{38}O_6S_8$ (799.2): C 51.09, H 4.80; found C 50.95, H 4.73.

1,4,5,8-Tetrahydro-2,7(6)-bis(2′-cyanoethylthio)-3,6(7)-[1,5-bis(2-(2-(2-thioethoxy)-ethoxy)ethoxy)naphthylene]-1,4,5,8-tetrathiafulvalene (7c, *cis*/*trans*): 2,3,6,7-Tetrakis(2′-cyanoethylthio)tetrathiafulvalene (**6**) (1.09 g, 2.0 mmol) was added with stirring to DMF (40 mL). A solution of CsOH·H_2O (0.74 g, 4.4 mmol) in methanol (10 mL) was added dropwise with stirring over 20 min. The solution was stirred for

1 h. Then this solution and a solution of **4c** (1.30 g, 2.0 mmol) in DMF (50 mL) were added simultaneously, during 20 h at room temperature, to DMF (200 mL) under high-dilution conditions by means of a perfusor pump. Stirring was continued for an additional 5 h, and the reaction mixture then concentrated in vacuo. After workup, the oily residue was purified by column chromatography (silica gel, CH_2Cl_2/EtOAc 5:1). Compound **7c** (0.96 g, 58%) was obtained as an orange oil. ^{1}H NMR ($CDCl_3$): $\delta = 2.50-2.66$ (m, 4H; CH_2CN), 2.88–3.03 (m, 8H; SCH_2), 3.64 (m, 12H; OCH_2), 3.96 (m, 4H; OCH_2), 4.32 (m, 4H; OCH_2), 6.88 (m, 2H; 2-H (naph)), 7.35 (m, 2H; 3-H (naph)), 7.87 (m, 2H; 4-H (naph)); MS (FAB): *m/z*: 826 $[M]^+$; $C_{34}H_{38}N_2O_6S_8$ (827.2): calcd C 49.36, H 4.64, N 3.39; found: C 49.23, H 4.62, N 3.31.

1,4,5,8-Tetrahydro-2,7(6)-bis(2′-cyanoethylthio)-3,6(7)-[1,4-bis(2-(2-(2-thioethoxy)-ethoxy)ethoxy)phenylene]-1,4,5,8-tetrathiafulvalene (7a, *cis/trans*) was prepared in 36% yield as an orange oil from **4a** and **6**. ^{1}H NMR ($CDCl_3$): $\delta = 2.69$ (m, 4H; $CNCH_2$), 3.04 (m, 8H; SCH_2), 3.69 (m, 12H; OCH_2), 3.81 (m, 4H; OCH_2), 4.10 (m, 4H; OCH_2), 6.85, 6.88 (s, s, 4H; Ar-*H*); MS (EI): *m/z* (%): 776 (11) $[M]^+$, 436 (27), 404 (71), 172 (65), 54 (100), 32 (94); $C_{30}H_{36}N_2O_6S_8$ (777.2): calcd C 46.36, H 4.68, N 3.61; found: C 46.12, H 4.49, N 3.77.

1,4,5,8-Tetrahydro-2,7(6)-bis(2′-cyanoethylthio)-3,6(7)-[9,10-bis(2-(2-(2-thioethoxy)-ethoxy)ethoxy)anthrylene]-1,4,5,8-tetrathiafulvalene (7b, *cis/trans*) was prepared from **4b** and **6** in 58% yield as an orange oil. ^{1}H NMR ($CDCl_3$): $\delta = 2.39$, 2.68 (2t, 4H; $CNCH_2$), 2.81, 3.01 (2t, 4H; SCH_2), 3.09 (m, 4H; SCH_2), 3.72–3.90 (m, 12H; OCH_2), 3.97 (m, 4H; OCH_2), 4.36 (m, 4H; OCH_2), 7.38, 7.51 (2m, 4H; 1-H (anth)), 8.45 (m, 4H; 2-H (anth)); MS (EI): *m/z* (%) : 876 (8) $[M]^+$, 208 (87), 76 (100); $C_{38}H_{40}N_2O_6S_8$ (877.3): calcd C 52.02, H 4.61, N 3.19; found: C 52.14, H 4.60, N 3.40.

1,4,5,8-Tetrahydro-2,7(6)-bis(2′-cyanoethylthio)-3,6(7)-[2,6-bis(2-(2-(2-thioethoxy)-ethoxy)ethoxy)naphthylene]-1,4,5,8-tetrathiafulvalene (7d, *cis/trans*) was prepared in 52% yield as an orange oily solid from **4d** and **6**. ^{1}H NMR ($CDCl_3$): $\delta = 2.55-2.68$ (m, 4H; $CNCH_2$), 2.86–3.03 (m, 8H; SCH_2), 3.62–3.73 (m, 12H; OCH_2), 3.90 (m, 4H; OCH_2), 4.27 (m, 4H; OCH_2), 7.00 (dd, 2H; 3-H (naph)), 7.13 (d, 2H; 1-H (naph)), 7.63 (d, 2H; 4-H (naph)); MS (FAB): *m/z*: 826 $[M]^+$; $C_{34}H_{38}N_2O_6S_8$ (827.2): calcd C 49.36, H 4.64, N 3.39; found: C 49.23, H 4.62, N 3.48.

1,4,5,8-Tetrahydro-2,7(6):3,6(7)-bis[1,5-bis(2-(2-(2-thioethoxy)ethoxy)ethoxy)naphthylene]-1,4,5,8-tetrathiafulvalene (8c, *cis/trans*): Compound **7c** (0.83 g, 1 mmol) was added with stirring to DMF (45 mL). A solution of $CsOH\cdot H_2O$ (0.37 g, 2.2 mmol) in methanol (5 mL) was added dropwise with stirring over 30 min. The resulting solution was stirred for 1 h. Then this solution and a solution of **4d** (0.65 g, 1.0 mmol) in DMF (50 mL) were added simultaneously, during 20 h at room temperature, to 200 mL of DMF under high-dilution conditions. Stirring was continued for an additional 4 h. After workup, the oily residue was purified by column chromatography (silica gel, CH_2Cl_2/EtOAc 4:1). **8c** (0.72 g, 67%) was obtained as an orange oil. ^{1}H NMR ($CDCl_3$): $\delta = 2.86$ (m, 8H; SCH_2), 3.59 (m, 16H; OCH_2), 3.71 (m, 8H; OCH_2), 3.94 (m, 8H; OCH_2), 4.30 (m, 8H; OCH_2), 6.80–6.89 (m, 4H; 2-*H* (naph)), 7.26–7.40 (m, 4H; 3-H (naph)), 7.81–7.90 (d, 4H; 4-H (naph)); MS (FAB): *m/z*: 1108 $[M]^+$; $C_{50}H_{60}O_{12}S_8$ (1109.6): calcd C 54.12, H 5.46; found: C 54.27, H 5.67.

1,4,5,8-Tetrahydro-2,7(6):3,6(7)-bis[1,4-bis(2-(2-(2-thioethoxy)ethoxy)ethoxy)-phenylene]-1,4,5,8-tetrathiafulvalene (8a, *cis/trans*) was prepared from **4a** and **7a** in 38% yield as an orange oil. ^{1}H NMR ($CDCl_3$): $\delta = 2.95$ (m, 8H; SCH_2), 3.60 (m, 24H; OCH_2), 3.80 (s, 8H; OCH_2), 4.10 (m, 8H; OCH_2), 6.84, 6.88 (s, s, 4H; Ar-*H*); MS (EI): *m/z* (%): 1008 (18) $[M]^+$, 883 (10), 518 (28), 414 (40), 76 (100), 45 (77); $C_{42}H_{56}O_{12}S_8$ (1009.5): C 49.97, H 5.60; found: C 49.89, H 5.72.

1,4,5,8-Tetrahydro-2,7(6):3,6(7)-bis[9,10-bis(2-(2-(2-thioethoxy)ethoxy)ethoxy)-anthrylene]-1,4,5,8-tetrathiafulvalene (8b, *cis/trans*) was prepared from **4b** and **7b** in 54% yield as an orange oily solid. ^{1}H NMR ($CDCl_3$): $\delta = 2.84$, 2.92 (2m, 8H; SCH_2), 3.75 (m, 24H; OCH_2), 3.97 (m, 8H; OCH_2), 4.34 (m, 8H; OCH_2), 7.39, 7.49 (2m, 8H; 1-H (anth)), 8.39 (m, 8H; 2-H (anth)); MS (PD): *m/z*: 1209.4 $[M]^+$; $C_{58}H_{64}O_{12}S_8$ (1209.7): calcd C 57.58, H 5.34; found C 58.28, H 4.93. The compound was unstable and used immediately in the next step.

1,4,5,8-Tetrahydro-2,7(6):3,6(7)-bis[2,6-bis(2-(2-(2-thioethoxy)ethoxy)ethoxy)-naphthylene]-1,4,5,8-tetrathiafulvalene (8d, *cis/trans*) was prepared in 60% yield as as orange oily solid from **4d** and **7d**. ^{1}H NMR ($CDCl_3$): $\delta = 2.84-2.95$ (m, 8H; SCH_2), 3.56–3.68 (m, 24H; OCH_2), 3.84–3.88 (m, 8H; OCH_2), 4.24 (m, 8H; OCH_2), 7.00 (dd, 4H; 3-H (naph)), 7.18 (d, 4H; 1-H (naph)), 7.71 (d, 4H; 4-H (naph)); MS (FAB): *m/z*: 1108 $[M]^+$; $C_{50}H_{60}O_{12}S_8$ (1109.6): calcd C 54.12, H 5.46; found: C 53.94, H 5.35.

1,2-Bis[2-(4-(2-cyanoethyl)thio-1,3-dithiole-2-thione-5-thio)ethoxy]ethane (11): 4,5-Bis(2′-cyanoethylthio)-1,3-dithiole-2-thione (**9**) (3.04 g, 10.0 mmol) was dissolved in DMF (40 mL) at room temperature. A solution of $CsOH\cdot H_2O$ (3.35 g, 11.0 mmol) in methanol (20 mL) was added dropwise over 30 min. The solution was stirred for 1 h, and 1,2-bis(2-bromoethoxy)ethane (**10**) (1.38 g, 5.0 mmol) was then added. The solution was stirred for 15 h and then concentrated in vacuo. The oily residue was extracted with CH_2Cl_2 (200 mL), and the organic phase washed with water, saturated aqueous NaCl solution, and dried ($MgSO_4$). After the solvent was evaporated, the residue was purified by column chromatography (silica gel, tetrahydrofuran/cyclohexane 1:2). **11** (2.83 g, 92%) was obtained as an orange oil. ^{1}H NMR ($CDCl_3$): $\delta = 2.79$ (t, 4H; CH_2CN), 3.13 (m, 8H; SCH_2), 3.67 (s, 4H; OCH_2CH_2O), 3.75 (t, 4H; SCH_2CH_2O); MS (EI): *m/z* (%): 616 (100) $[M]^+$; $C_{18}H_{20}N_2O_2S_{10}$ (617.0): calcd C 35.04, H 3.27, N 4.54; found C 35.13, H 3.26, N 4.67.

1,2-Bis[2-(4-(2-cyanoethyl)thio-1,3-dithiole-2-one-5-thio)ethoxy]ethane (12): A mixture of **11** (1.85 g, 3.0 mmol) and $Hg(OAc)_2$ (5.0 g, 16 mmol) in $CHCl_3$/AcOH (3:1, 100 mL) was stirred at room temperature for 24 h. The resulting white precipitate was filtered through Celite and washed thoroughly with $CHCl_3$. The organic phase was then washed with aqueous $NaHCO_3$ solution (2%), water, saturated aqueous NaCl solution, and dried ($MgSO_4$). After removal of the solvent in vacuo, the oily residue was subjected to column chromatography (silica gel, CH_2Cl_2/EtOAc, 15:1). **12** (1.58 g, 90%) was obtained as an orange oil. ^{1}H NMR ($CDCl_3$): $\delta = 2.78$ (t, 4H; CH_2CN), 3.12 (m, 8H; SCH_2), 3.66 (s, 4H; OCH_2CH_2O), 3.74 (s, 4H; SCH_2CH_2O); MS (EI): *m/z* (%): 584 (100) $[M]^+$; $C_{18}H_{20}N_2O_4S_8$ (584.9): calcd C 36.96; H 3.45; N 4.79; found C 37.30; H 3.42; N 4.65.

1,4,5,8-Tetrahydro-2,7(6)-bis(2′-cyanoethylthio)-3,6(7)-(4,7-dioxa-1,10-dithiadecane-1,10-diyl)-1,4,5,8-tetrathiafulvalene (13, *cis/trans*): A solution of **12** (1.17 g, 2.0 mmol), $P(OEt)_3$ (freshly distilled, 2 mL) in toluene (30 mL) was refluxed with stirring for 30 min and then allowed to cool to room temperature. After removal of the solvent in vacuo, the oily residue was directly subjected to column chromatography (silica gel, petroleum ether (60–80 °C)/EtOAc, 2:1) to give **13** (0.39 g, 35%) as an orange oil. ^{1}H NMR ($CDCl_3$): $\delta = 2.65-2.86$ (m, 4H; CH_2CN), 2.89–3.23 (m, 8H; SCH_2), 3.43–4.00 (m, 8H; OCH_2); MS (EI): *m/z* (%): 552 (100) $[M]^+$; $C_{18}H_{20}N_2O_2S_8$ (552.9): Calcd C 39.10, H 3.65, N 5.07; found C 39.20·H, 3.52, N 4.76. Under similar conditions, refluxing a solution of **11** and $P(OEt)_3$ in toluene for 1 h afforded **13** in 22% yield.

1,4,5,8-Tetrahydro-2,7(6)-[1,4-bis(2-(2-(2-thioethoxy)ethoxy)ethoxy)phenylene]-3,6(7)-(4,7-dioxa-1,10-dithiadecane-1,10-diyl)-1,4,5,8-tetrathiafulvalene (14, *cis/trans*): Compound **13** (0.28 g, 0.5 mmol) was dissolved in DMF (45 mL). A solution of $CsOH\cdot H_2O$ (0.18 g, 1.1 mmol) in methanol (5 mL) was added dropwise with stirring over 20 min. The solution was stirred for 1 h. Then this solution and a solution of **4a** (0.25 g, 0.5 mmol) in DMF (50 mL) were added simultaneously, over 17 h at room temperature, to DMF (100 mL) under high-dilution conditions by means of a perfusor pump. Stirring was continued for an additional 5 h, and the reaction mixture was then concentrated in vacuo. CH_2Cl_2 (50 mL) was added. After filtration the organic solution was washed with water, saturated aqueous NaCl solution, and dried ($MgSO_4$). After the solvent was evaporated, the oily residue was purified by column chromatography (silica gel, EtOAc/cyclohexane 1:1) to give **14** (0.14 g, 35%) as an orange oil. ^{1}H NMR ($CDCl_3$): $\delta = 3.02$ (m, 8H; SCH_2), 33.52–3.74 (m, 24H; OCH_2), 3.80 (m, 4H; OCH_2), 4.07(m, 4H; OCH_2), 6.82, 6.90 (2s, 4H; Ar-*H*); MS (EI): *m/z* (%): 784 (100) $[M]^+$; $C_{30}H_{40}O_8S_8$ (785.2): Calcd C 45.89, H 5.15; found C 46.02, H 4.93.

{1,4,5,8-Tetrahydro-2,7(6)-bis(methylthio)-3,6(7)-bis[2-(2-(2-(*p*-(triphenylmethyl)-phenyl)ethoxy)ethoxy)ethylthio]-1,4,5,8-tetrathiafulvalene (*cis/trans*)}-{5,12,19,26-Tetraazoniaheptacyclo[24.2.2.2^{2,5}.2^{7,10}.2^{12,15}.2^{16,19}.2$^{21.24}$]tetraconta-2,4,7,9,12,14,16,18,21,23,26,28,29,31,33,35,37,39-octadecaene Tetrakis(hexa-fluorophosphate)} (rotaxane **17**-4PF_6): A solution of **3** (0.25 g, 0.2 mmol), **15**-2PF_6 (0.42 g, 0.6 mmol) [6b], and **16** (0.18 g, 0.66 mmol) in DMF (15 mL) was stirred at room temperature for 10 d. The solvent was then removed in vacuo without heating. The green residue was extracted with CH_2Cl_2 (100 mL). The organic solution, after workup, gave 0.21 g (85%) of unreacted **3**. The residue dissolved partly in methanol, and the undissolved solid was filtered off. The solution was concentrated in vacuo to give a residue, which was subjected to column chromatography on silica gel with MeOH/aqueous NH_4Cl solution (2 M)/$MeNO_2$ (7:2:1) as the eluent. Collection of the green fraction afforded a green solid after evaporation of the solvent in vacuo. The solid was partially dissolved in methanol and filtered, and the solvent evaporated in vacuo. The solid residue was then redissolved in a minimum amount of water (about 4 mL), and a saturated aqueous NH_4PF_6 solution was added until precipitation was complete. After filtration and drying in vacuo, rotaxane **17**-4PF_6 (48 mg, 10%) was obtained as a dark blue solid. The ^{1}H NMR spectrum indicated this rotaxane to be a mixture of *cis* and *trans* isomers. M.p. 153 °C (decom.); ^{1}H NMR (CD_3CN): $\delta = 2.64$ (s, 6H; SCH_3), 3.15 (t, 4H; SCH_2), 3.87–3.97 (m, 20H; OCH_2), 5.68 (m, 8H), 6.55 (d, 4H), 7.12 (d, 4H), 7.21 (m, 30H), 7.72 (m, 8H), 7.89 (d, 8H), 9.00 (m, 8H); MS (ES): *m/z*: 1429 $[2M - 3PF_6]^{3+}$, 1426 $[3M - 4PF_6]^{4+}$, 1272 $[3M - 5PF_6]^{5+}$, 1036 $[M - 2PF_6]^{2+}$, 642 $[M - 3PF_6]^{3+}$, 445 $[M - 4PF_6]^{4+}$; $C_{106}H_{100}N_4O_6F_{24}P_4S_8$ (2362.2): calcd C 53.89, H 4.28, N 2.37; found C 53.61, H 4.39, N 2.48. The reactions of the two isomers of **3** gave the same result.

{1,4,5,8-Tetrahydro-2,7(6)-bis(methylthio)-3,6(7)-[1,4-bis(2-(2-(2-thioethoxy)ethoxy)-ethoxy)phenylene]-1,4,5,8-tetrathiafulvalene (*cis/trans*)}-{5,12,19,26-Tetraazoniaheptacyclo[24.2.2.2^{2,5}.2^{7,10}.2^{12,15}.2^{16,19}.2$^{21.24}$]tetraconta-2,4,7,9,12,14,16,18,21,23,26,28,29,31,33,35,37,39-octadecaene Tetrakis(hexafluorophosphate)} ([2]catenane **18a**-4PF_6): A solution of **5a** (350 mg, 0.5 mmol), **15**-2PF_6 (106 mg, 0.15 mmol), and **16** (55 mg, 0.2 mmol) in DMF (10 mL) was stirred at room temperature for 7 d. After workup as described above, [2]catenane **18a**-4PF_6 (32 mg, 12%) was obtained as a brown solid. M.p. 146 °C (decomp.); ^{1}H NMR (CD_3CN): $\delta = 2.32-3.20$ (m, 10H; CH_3, SCH_2), 3.34–4.56 (m, 20H; OCH_2), 5.40–6.24 (m, 12H), 7.42–7.68 (m, 16H), 8.94–9.05 (m, 8H); MS (FAB): *m/z*: 1363 $[M - 3PF_6]^+$, 698 $[\mathbf{5a}]^+$; $C_{62}H_{66}N_4O_6F_{24}P_4S_8$ (1799.4): calcd C 41.38, H 3.70, N 3.11; found: C 41.09, H 3.52, N 2.90.

{1,4,5,8-Tetrahydro-2,7(6)-bis(methylthio)-3,6(7)-[9,10-bis(2-(2-(2-thioethoxy)-ethoxy)ethoxy)anthrylene]-1,4,5,8-tetrathiafulvalene (*cis/trans*)}-{5,12,19,26-Tetraazoniaheptacyclo[24.2.2.2^{2,5}.2^{7,10}.2^{12,15}.2^{16,19}.2$^{21.24}$]tetraconta-2,4,7,9,12,14,16,18,21,23,26,28,29,31,33,35,37,39-octadecaene Tetrakis(hexafluorophosphate)} ([2]catenane **18b**-4PF$_6$): This compond was prepared as described for **18a**-4PF$_6$. **18b**-4PF$_6$ was obtained as a blue solid in 14% yield from **5b**, **15**-2PF$_6$, and **16** in DMF after 12 d. M.p. 178 °C (decomp.); ^{1}H NMR (CD$_3$CN): δ = 2.68–3.25 (m, 10H; CH_3, SCH_2), 3.54–4.67 (m, 20H; OCH_2), 5.62–5.83 (m, 8H), 7.10–7.82 (m, 20H), 8.04–9.12 (m, 12H); MS (ES): m/z: 1754 $[M-\mathrm{PF_6}]^+$, 1280 $[3M-4\mathrm{PF_6}]^{4+}$, 1121 $[2M-3\mathrm{PF_6}]^{3+}$, 994 $[3M-5\mathrm{PF_6}]^{5+}$, 804 $[M-2\mathrm{PF_6}]^{2+}$, 488 $[M-3\mathrm{PF_6}]^{3+}$, 330 $[M-4\mathrm{PF_6}]^{4+}$; $\mathrm{C_{70}H_{70}N_4O_6F_{24}P_4S_8}$ (1899.5): calcd C 44.26, H 3.72, N 2.95; found: C 43.96, H 3.54, N 2.87.

{1,4,5,8-Tetrahydro-2,6:3,7-bis[1,5-bis(2-(2-(2-thioethoxy)ethoxy)ethoxy)naphthylene]-1,4,5,8-tetrathiafulvalene(*trans*)}-{5,12,19,26-Tetraazoniaheptacyclo-[24.2.2.2^{2,5}.2^{7,10}.2^{12,15}.2^{16,19}.2$^{21.24}$]tetraconta-2,4,7,9,12,14,16,18,21,23,26,28,29,31,33,35,37,39-octadecaene (*circum* TTF) Tetrakis-(hexafluorophosphate)} ([3]pseudocatenane 19c-4PF$_6$), {1,4,5,8-Tetrahydro-2,7(6):3,6(7)-bis[1,5-bis(2-(2-(2-thioethoxy)-ethoxy)ethoxy)naphthylene]-1,4,5,8-tetra-thiafulvalene (*cis/trans*)}-{5,12,19,26-Tetraazoniaheptacyclo-[24.2.2.2^{2,5}.2^{7,10}.2^{12,15}.2^{16,19}.2$^{21.24}$]tetraconta-2,4,7,9,12,14,16,18,21,23,26,28,29,31,33,35,37,39-octadecaene (*circum* naphthalene) Tetrakis-(hexafluorophosphate)} ([3]pseudocatenane 21c-4PF$_6$), and {1,4,5,8-Tetrahydro-2,7(6):3,6(7)-bis[1,5-bis(2-(2-(2-thioethoxy)ethoxy)ethoxy)naphthylene]-1,4,5,8-tetrathiafulvalene (*cis/trans*)}-2{5,12,19,26-Tetraazoniaheptacyclo-[24.2.2.2^{2,5}.2^{7,10}.2^{12,15}.2^{16,19}.2$^{21.24}$]tetraconta-2,4,7,9,12,14,16,18,21,23,26,28,29,31,33,35,37,39-octadecaene (*circum* naphthalene) Tetrakis(hexafluorophosphate)} ([4]pseudocatenane **22c**-8PF$_6$): Compounds **8c** (222 mg, 0.2 mmol), **15**-2PF$_6$ (425 mg, 0.6 mmol), and **16** (175 mg, 0.66 mmol) were dissolved in dry DMF (40 mL), and the solution was stirred at room temperature for 36 h. TLC indicated that all **8c** had been consumed. The solvent was then removed in vacuo without heating. The dark blue residue was dissolved partly in methanol, and the undissolved solid removed by filtration. The solution was concentrated in vacuo, giving a residue, which was subjected to column chromatography (silica gel, MeOH/NH$_4$Cl solution (2M)/MeNO$_2$ (7:2:1)). One blue and two purple bands were developed from the column. After the first two colored bands were washed down, the last band was eluted with MeOH/NH$_4$Cl solution (2M)/DMF (4:5:1). The first fraction afforded a dark blue solid after removal of the solvent in vacuo. This residue was partially dissolved in methanol and filtered, and the solvent was removed in vacuo. The residue was then dissolved in a minimum amount of water (about 20 mL), and saturated aqueous NH$_4$PF$_6$ solution added until precipitation was complete. After filtration and drying in vacuo, [3]pseudocatenane **19c**-4PF$_6$ (213 mg, 48%) was obtained as a dark blue solid.

19c-4PF$_6$: M.p. 230 °C (decomp.); ^{1}H NMR (CD$_3$CN): δ = 2.81 (4H, m, SCH_2), 3.12 (m, 4H; SCH_2), 3.63 (m, 4H; OCH_2), 3.85–4.16 (m, 36H; OCH_2), 5.54 (s, 8H; C$_6$H$_4$CH_2), 6.58 (d, 4H; 2-H (naph)), 7.27 (dd, 4H; β-H (py)), 7.40–7.55 (m, 12H; 3,4-H (naph), β-H (py)), 7.63 (s, 8H; CH$_2$C$_6$$H_4$), 8.66 (d, 4H; α-H (py)), 8.85 (d, 4H; α-H (py)); ^{13}C NMR (CD$_3$CN): δ = 36.02, 65.47, 68.44, 70.24, 70.56, 70.66, 106,85, 115.16, 118.33, 125.43, 126.58, 126.86, 130.72, 131.66, 136.95, 143.97, 144.92, 154.43; MS (ES): m/z: 1512 $[3M-4\mathrm{PF_6}]^{4+}$, 1328 $[2M-3\mathrm{PF_6}]^{3+}$, 1108 [**8c**]$^+$, 960 $[M-2\mathrm{PF_6}]^{2+}$, 591 $[M-3\mathrm{PF_6}]^{3+}$, 407 $[M-4\mathrm{PF_6}]^{4+}$; $\mathrm{C_{86}H_{92}N_4O_{12}F_{24}P_4S_8}$ (2209.9): calcd C 46.74, H 4.20, N 2.54; found: C 46.63, H 3.99, N 2.73.

After workup in a similar way, the second and third bands gave, after counterion exchange, [3]pseudocatenane **21c**-4PF$_6$ (80 mg, 18%) and [4]pseudocatenane **22c**-8PF$_6$ (172 mg, 26%) both as purple solids. The ^{1}H NMR spectra of **21c**-4PF$_6$ and **22c**-8PF$_6$ could not be assigned because they are mixtures of *cis* and *trans* isomers. **21c**-4PF$_6$: M.p. 198 °C (decomp.); MS (ES): m/z: 1512 $[3M-4\mathrm{PF_6}]^{4+}$, 1328 $[2M-3\mathrm{PF_6}]^{3+}$,1108 [**8c**]$^+$, 960 $[M-2\mathrm{PF_6}]^{2+}$, 591 $[M-3\mathrm{PF_6}]^{3+}$, 407 $[M-4\mathrm{PF_6}]^{4+}$; $\mathrm{C_{86}H_{92}N_4O_{12}F_{24}P_4S_8}$ (2209.9): calcd C 46.74, H 4.20, N 2.54; found: C 46.42, H 4.09, N 2.49.

22c-8PF$_6$: M.p. 215 °C (decomp.); MS (ES): m/z: 1509 $[M-2\mathrm{PF_6}]^{2+}$, 1179 $[2M-5\mathrm{PF_6}]^{5+}$, 1108 [**8c**]$^+$, 958 $[M-3\mathrm{PF_6}]^{3+}$, 682 $[M-4\mathrm{PF_6}]^{4+}$, 517 $[M-5\mathrm{PF_6}]^{5+}$; $\mathrm{C_{122}H_{124}N_8O_{12}F_{48}P_8S_8}$ (3310.2): calcd C 44.26, H 3.78, N 3.39; found: C 43.85, H 3.87, N 3.25.

When the reaction time was extended to 72 h, **21c**-4PF$_6$ was transformed to **22c**-8PF$_6$ completely, as detected by TLC. After workup as described above, **19c**-4PF$_6$ and **22c**-8PF$_6$ were isolated in 48 and 46% yields, respectivly.

{1,4,5,8-Tetrahydro-2,6:3,7-bis[1,4-bis(2-(2-(2-thioethoxy)ethoxy)ethoxy)phenylene]-1,4,5,8-tetrathiafulvalene(*trans*)}-{5,12,19,26-Tetraazoniaheptacyclo-[24.2.2.2^{2,5}.2^{7,10}.2^{12,15}.2^{16,19}.2$^{21.24}$]tetraconta-2,4,7,9,12,14,16,18,21,23,26,28,29,31,33,35,37,39-octadecaene (*circum* TTF) Tetrakis(hexafluorophosphate)} ([3]pseudocatenane **19a**-4PF$_6$), **{1,4,5,8-Tetrahydro-2,7:3,6-bis[1,4-bis(2-(2-(2-thioethoxy)ethoxy)ethoxy)-phenylene]-1,4,5,8-tetrathiafulvalene(*cis*)}-{5,12,19,26-Tetraazoniaheptacyclo-[24.2.2.2^{2,5}.2^{7,10}.2^{12,15}.2^{16,19}.2$^{21.24}$]tetraconta-2,4,7,9,12,14,16,18,21,23,26,28,29,31,33,35,37,39- octadecaene (*circum* TTF) Tetrakis(hexafluorophosphate)}** ([3]pseudocatenane **20a**-4PF$_6$), and **{1,4,5,8-Tetrahydro-2,7(6):3,6(7)-bis[1,4-bis(2-(2-(2-thioethoxy)ethoxy)-ethoxy)phenylene]-1,4,5,8-tetrathiafulvalene (*cis/trans*)}-{5,12,19,26-Tetraazoniaheptacyclo-[24.2.2.2^{2,5}.2^{7,10}.2^{12,15}.2^{16,19}.2$^{21.24}$]tetraconta-2,4,7,9,12,14,16,18,21, 23,26,28,29,31,33,35,37,39-octadecaene (*circum* benzene) Tetrakis(hexafluorophosphate)}** ([4]pseudocatenane **21a**-4PF$_6$) were prepared in 15, 10, and 4% yields, respectively, from **8a**, **15**-2PF$_6$, and **16** after 10 d.

19a-4PF$_6$: dark solid; m.p. 220 °C (decomp.); ^{1}H NMR (CD$_3$CN): δ = 2.80 (m, 4H; SCH_2), 3.21 (m, 4H; SCH_2), 3.71–4.12 (m, 40H; OCH_2), 5.66 (s, 8H; NCH_2), 6.32 (s, 8H; OC$_6$$H_4$), 7.63 (d, 4H; β-CH (py)), 7.68 (s, 8H; CH$_2$C$_6$$H_4$), 7.80 (d, 4H; β-CH (py)), 8.82 (d, 4H; α-CH (py)), 9.01 (d, 4H; α-CH (py)); MS (ES): m/z: 1437 $[3M-4\mathrm{PF_6}]^{4+}$, 1261 $[2M-3\mathrm{PF_6}]^{3+}$, 1008 [**8a**]$^+$, 909 $[M-2\mathrm{PF_6}]^{2+}$, 558 $[M-3\mathrm{PF_6}]^{3+}$, 382 $[M-4\mathrm{PF_6}]^{4+}$; $\mathrm{C_{78}H_{88}N_4O_{12}F_{24}P_4S_8}$ (2109.8): C 44.40, H 4.21, N 2.66; found: C 43.74, H 4.51, N 3.05.

20a-4PF$_6$: dark blue solid; m.p. 185 °C (decomp.); ^{1}H NMR (CD$_3$CN): δ = 3.01 (t, 8H; SCH_2), 3.77–3.92 (m, 40H; OCH_2), 5.62 (s, 8H; NCH_2), 6.41 (s, 8H; OC$_6$$H_4$), 7.63 (s, 8H; C$_6$$H_4CH_2$), 7.82 (s, 8H, β-CH (py)), 8.95 (s, 4H; α-CH (py)); MS (ES): m/z: 1964 $[M-\mathrm{PF_6}]^+$, 1437 $[3M-4\mathrm{PF_6}]^{4+}$, 1261 $[2M-3\mathrm{PF_6}]^{3+}$, 909 $[M-2\mathrm{PF_6}]^{2+}$, 558 $[M-3\mathrm{PF_6}]^{3+}$, 382 $[M-4\mathrm{PF_6}]^{4+}$; $\mathrm{C_{78}H_{88}N_4O_{12}F_{24}P_4S_8}$ (2109.8): calcd C 44.40, H 4.21, N 2.66; found: C 43.88, H 4.19, N 2.67.

21a-4PF$_6$: brown solid; m.p. 200 °C (decomp.); MS (ES): m/z: 1964 $[M-\mathrm{PF_6}]^+$, 1437 $[3M-4\mathrm{PF_6}]^{4+}$, 1261 $[2M-3\mathrm{PF_6}]^{3+}$, 909 $[M-2\mathrm{PF_6}]^{2+}$, 558 $[M-3\mathrm{PF_6}]^{3+}$, 382 $[M-4\mathrm{PF_6}]^{4+}$; $\mathrm{C_{78}H_{88}N_4O_{12}F_{24}P_4S_8}$ (2109.8): C 44.40, H 4.21, N 2.66; found: C 44.42, H 4.52, N 2.73. **21a**-4PF$_6$ is a mixture of *trans/cis* isomers and it is difficult to assign its ^{1}H NMR spectrum.

{1,4,5,8-Tetrahydro-2,6:3,7-bis[9,10-bis(2-(2-(2-thioethoxy)ethoxy)ethoxy)anthyl-ene]-1,4,5,8-tetrathiafulvalene(*trans*)}-{5,12,19,26-Tetraazoniaheptacyclo-[24.2.2.2^{2,5}.2^{7,10}.2^{12,15}.2^{16,19}.2$^{21.24}$]tetraconta-2,4,7,9,12,14,16,18,21,23,26,28,29,31,33,35,37,39-octadecaene (*circum* TTF) Tetrakis(hexafluorophosphate)} ([3]pseudocatenane **19b**-4PF$_6$) was prepared in 4% yield from **8b**, **15**-2PF$_6$, and **16** after 21 d. Under 10 kbar, **19b**-4PF$_6$ could be prepared in 27% yield after 3 d. Dark solid; m.p. 250 °C (decomp.); ^{1}H NMR (CD$_3$CN): δ = 2.70 (m, 4H; SCH_2), 3.13 (m, 4H; SCH_2), 3.55 (m, 8H; OCH_2), 4.04 (s, 8H; OCH_2), 4.13 (m, 4H; OCH_2), 3.82 (m, 16H; OCH_2), 4.47 (m, 4H; OCH_2), 5.59 (d, d, 8H; NCH_2), 6.95 (d, 4H; 1-H (anth)), 7.32 (d, 4H; 1-H (anth)), 7.35 (t, 4H; 2-H (anth)), 7.50 (t, 4H; 2-H (anth)), 7.60 (s, 8H; C$_6$$H_4CH_2$), 7.86 (d, 4H; β-CH (py)), 8.13 (d, 4H; β-CH (py)), 8.50 (d, d, 4H; α-CH (py)), 8.87 (d, d, 4H; α-CH (py)); MS (ES): m/z: 1587 $[3M-4\mathrm{PF_6}]^{4+}$, 1395 $[2M-3\mathrm{PF_6}]^{3+}$, 1009 $[M-2\mathrm{PF_6}]^{2+}$, 625 $[M-3\mathrm{PF_6}]^{3+}$, and 432 $[M-4\mathrm{PF_6}]^{4+}$; $\mathrm{C_{94}H_{96}N_4O_{12}F_{24}P_4S_8}$ (2310.0): calcd C 48.87, H 4.20, N 2.43; found: C 49.00, H 3.99, N 2.27.

{1,4,5,8-Tetrahydro-2,6:3,7-bis[2,6-bis(2-(2-(2-thioethoxy)ethoxy)ethoxy)naphthylene]-1,4,5,8-tetrathiafulvalene(*trans*)}-{5,12,19,26-Tetraazoniaheptacyclo-[24.2.2.2^{2,5}.2^{7,10}.2^{12,15}.2^{16,19}.2$^{21.24}$]tetraconta-2,4,7,9,12,14,16,18,21,23,26,28,29,31,33,35,37,39-octadecaene (*circum* TTF) Tetrakis(hexafluorophosphate)} ([3]pseudocatenane **19d**-4PF$_6$) and **{1,4,5,8-Tetrahydro-2,7:3,6-bis[2,6-bis(2-(2-(2-thioethoxy)ethoxy)ethoxy) naphthylene]-1,4,5,8-tetrathiafulvalene(*cis*)}-{5,12,19,26-Tetraazoniaheptacyclo-[24.2.2.2^{2,5}.2^{7,10}.2^{12,15}.2^{16,19}.2$^{21.24}$]tetraconta-2,4,7,9,12,14,16,18,21,23,26,28,29,31,33,35,37,39-octadecaene (*circum* TTF) Tetrakis(hexafluorophosphate)}** ([3]pseudocatenane **20d**-4PF$_6$) were prepared in 10% and 18% yields, respectively, both as dark blue solids from **8d**, **15**-2PF$_6$, and **16** in DMF after 7 d. **19d**-4PF$_6$: M.p. 205 °C (decomp.); ^{1}H NMR (CD$_3$CN): δ = 2.80 (m, 4H; SCH_2), 3.16 (m, 4H; SCH_2), 3.65 (m, 4H; OCH_2), 3.83–4.12 (m, 36H; OCH_2), 5.67 (s, 8H; C$_6$H$_4$CH_2), 6.47 (d, 4H; 1-H (naph)), 6.86 (dd, 4H; 3-H (naph)), 7.39 (d, 4H; β-CH (py)), 7.42 (d, 4H; β-CH (py)), 7.59 (d, 4H; 4-H (naph)), 7.66 (s, 8H; CH$_2$C$_6$$H_4$), 8.76 (d, 4H; α-CH (py)), 8.95 (d, 4H; α-CH (py)); MS (ES): m/z: 1108 [**8d**]$^+$, 960 $[M-2\mathrm{PF_6}]^{2+}$, 591 $[M-3\mathrm{PF_6}]^{3+}$; $\mathrm{C_{86}H_{92}N_4O_{12}F_{24}P_4S_8}$ (2209.9): calcd C 46.74, H 4.20, N 2.54; found: C 46.58, H 4.64, N 2.63.

20d-4PF$_6$: M.p. 195 °C (decomp.); ^{1}H NMR (CD$_3$CN): δ = 3.02 (t, 8H; SCH_2), 3.89 (m, 24H; OCH_2), 3.96 (t, 8H; OCH_2), 4.14 (t, 8H; OCH_2), 5.61 (s, 8H; C$_6$H$_4$CH_2), 6.61 (d, 4H; 1-H (naph)), 6.91(dd, 4H; 3-H (naph)), 7.56 (d, 4H; 4-H (naph)), 7.60 (s, 8H; CH$_2$C$_6$$H_4$), 7.62 (d, 8H; β-CH (py)), 8.84 (d, 8H; α-CH (py)); MS (ES): m/z: 1108 [**8d**]$^+$, 960 $[M-2\mathrm{PF_6}]^{2+}$, 591 $[M-3\mathrm{PF_6}]^{3+}$; $\mathrm{C_{86}H_{92}N_4O_{12}F_{24}P_4S_8}$ (2209.9): calcd C 46.74, H 4.20, N 2.54; found: C 46.56, H 4.53, N 2.69.

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[22] The ^{1}H NMR spectrum indicated that the ratio of the *cis* and *trans* isomers is about 5:1, based on the integration of the two phenylene proton signals.

[23] Recently, [2]catenanes incorporating a bis(2-oxy-1,3-propylenedithio)-tetrathiafulvalene unit and a 1,4-bis(oxymethyl)phenylene unit have been synthesized by Prof. Stoddart's group. We thank Dr. G. Mattersteig and Prof. J. F. Stoddart for providing the information.

[24] Ultra-high pressure has been used to promote the formation of catenanes; see D. B. Amabilino, P. R. Ashton, M. S. Tolley, J. F. Stoddart, D. J. Williams, *Angew. Chem.* **1993**, *105*, 1358; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1297.

[25] Quantitative synthesis of [2]catenanes has been reported recently by utilizing the labile nature of a palladium or platinum(II)–pyridine coordinate bond, in which Pd or Pt metal centers are part of the macrocycles but do not intervene during the catenation (see ref. [4a]).

[26] Unsymmetrical TTF compounds usually isomerize readily, catalyzed by trace amounts of acid. Two methods have been used to control the configurational isomerization of TTF macrocyclic compounds. The first utilized the difference between the ring strains of the *cis*/*trans* isomers (see ref. [11c] and [13]). The second approach involved one-electron oxidation of [12]- and [14]tetrathiafulvalenophanes (see ref. [11d]). However, in all these cases the planarity of the neutral TTF subunits was destroyed by the short chains linking the opposite ends of the TTF groups.

[27] a) P. R. Ashton, C. L. Brown, E. J. T. Chrystal, T. T. Goodnow, A. E. Kaifer, K. P. Parry, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, D. J. Williams, *Angew. Chem.* **1991**, *103*, 1055; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1039; b) D. B. Amabilino, P. R. Ashton, A. S. Reder, N. Spencer, J. F. Stoddart, *ibid.* **1994**, *106*, 1316 and **1994**, *33*, 1286; c) P. R. Ashton, L. Peres-Garcia, J. F. Stoddart, A. J. P. White, D. J. Williams, *ibid.* **1995**, *107*, 607 and **1995**, *34*, 571; d) M. J. Gunter, D. C. R. Hockless, M. R. Johnston, B. W. Skelton, A. H. White, *J. Am. Chem. Soc.* **1994**, *116*, 4810; e) P. R. Ashton, R. Ballardini, V. Balzani, M. T. Gandolfi, D. J.-F. Marquis, L. Peres-Garcia, L. Prodi, J. F. Stoddart, M. Venturi, *J. Chem. Soc. Chem. Commun.* **1994**, 177; f) D. B. Amabilino, P. R. Ashton, J. F. Stoddart, S. Menzer, D. J. Williams, *ibid.* **1994**, 2475.

[28] Constitutional changes may have great influence on the self-assembly of catenanes; see ref. [27a] and also D. B. Amabilino, P. R. Ashton, G. R. Brown, W. Hayes, J. F. Stoddart, M. S. Tolley, D. J. Williams, *J. Chem. Soc. Chem. Commun.* **1994**, 2479.

[29] The chemo- and configurational selectivity of the two reactions do not result from the ratio of the *cis* and *trans* isomers of the dimacrocycles **8a–d** because, for all these compounds, the ratio is about 1:1, as indicated by the ^{1}H NMR spectra (based on the integration of the two sets of aromatic proton signals).

[30] Electrospray mass spectrometry (ESMS) has been used to characterize catenanes, and the fragmentation pattern corresponding to the loss of three PF_6^- ions from a catenane dimer have been detected. However, more complex fragmentation patterns, e.g., the ion peaks $[3M - 4PF_6]^{4+}$ and $[3M - 5PF_6]^{5+}$, have apparently not been reported previously; see P. R. Ashton, C. L. Brown, J. R. Chapman, R. T. Gallagher, J. F. Stoddart, *Tetrahedron Lett*, **1992**, *33*, 7771.