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Self-Assembling Tetrathiafulvalene-Based Rotaxanes and Catenanes

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

Abstract: A general stepwise approach is described for the preparation of tetrathiafulvalene (TTF)-based linear and mono- and dimacrocylic compounds incorporating one or two 1,4-dioxyphenylene, 9,10-dioxanthrylene, or 1,5- or 2,6-dioxynaphthylene units from readily available starting materials. By utilizing the π - π stacking interactions of the TTF unit with the dipyrindinium 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 monomacrocylic compounds, respectively. From the dioxyphenylene-based dimacrocycle, three [3]pseudocatenanes (*trans*, *cis*, and a mixture of *cis/trans* iso-

mers) were obtained with the *trans* compound as the major product. From the dioxynaphthylene 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]pseudocatenane 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]pseudocate-

nane 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 ^1H 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 π - π 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 π - π 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.^[11a] 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 multimacrocylic 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

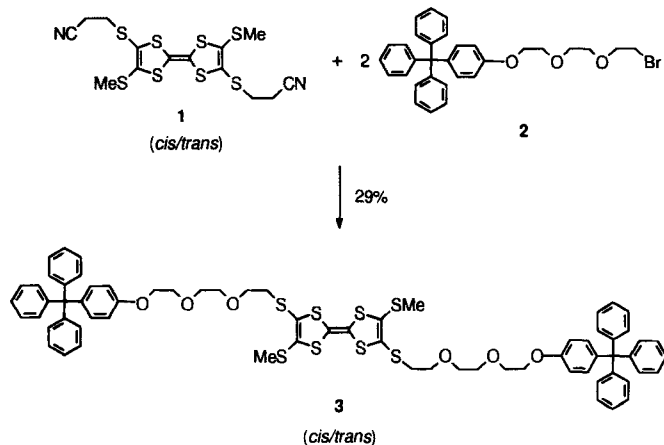
[*] Prof. Dr. J. Becher, Dr. Z.-T. Li, Dr. P. C. Stein, D. Jensen, P. Mørk, N. Svenstrup
Department of Chemistry, Odense University
Campusvej 55, DK-5230 Odense M (Denmark)
Fax: Int. code + (66) 15-8780

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.^[16] 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, diaminothiophene, 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 dimacrocylic 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 dimacrocylic 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 ¹H NMR spectroscopy; and 5) their electrochemical and spectroscopic properties.

Results and Discussion

Synthesis: Four types of TTF-containing compounds (the linear, TTF-planar monomacrocylic, and TTF-planar and TTF-nonplanar dimacrocylic 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 dimacrocylic 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 iso-



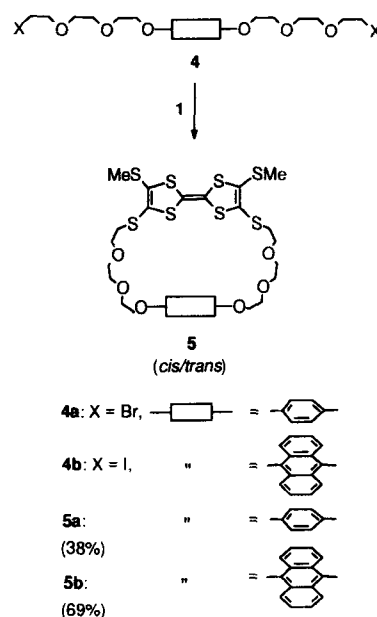
Scheme 1. Synthesis of **3**: N₂, 2 equiv CsOH·H₂O, DMF, RT, 16 h.

mers of **3** could be separated, but we were unable to assign their configuration from the ¹H 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 ¹H NMR spectra.

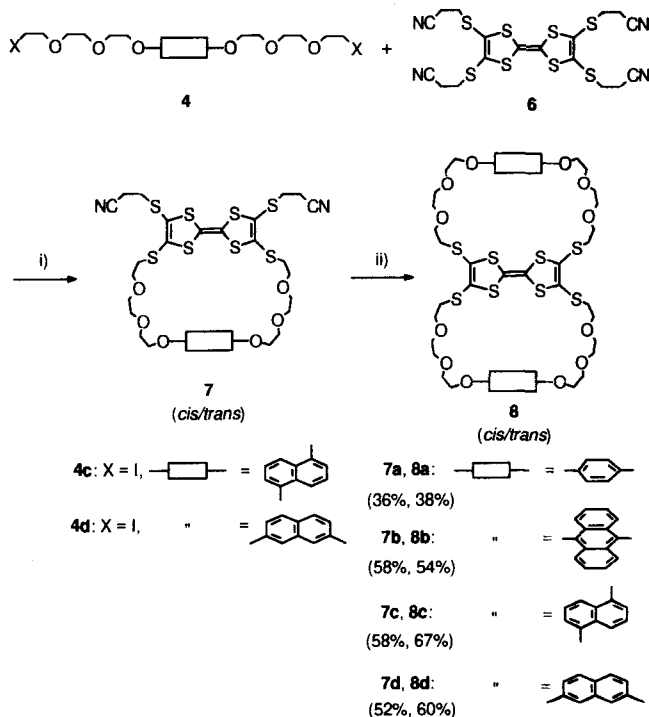
Under high-dilution conditions, monocyclic compounds **5a** and **5b** were prepared from **1** and **4a**^[18] or **4b**^[19] (Scheme 2). By two-step cyclization reactions, dimacrocylic compounds **8a–d** were prepared from **4a–d** and tetrathiafulvalene **6**^[20] with monocycles **7a–d** as intermediates (Scheme 3). The macro-

cylic compounds **5a–d**, **7a–d**, and **8a–d** are all inseparable mixtures of *cis* and *trans* isomers.^[21]

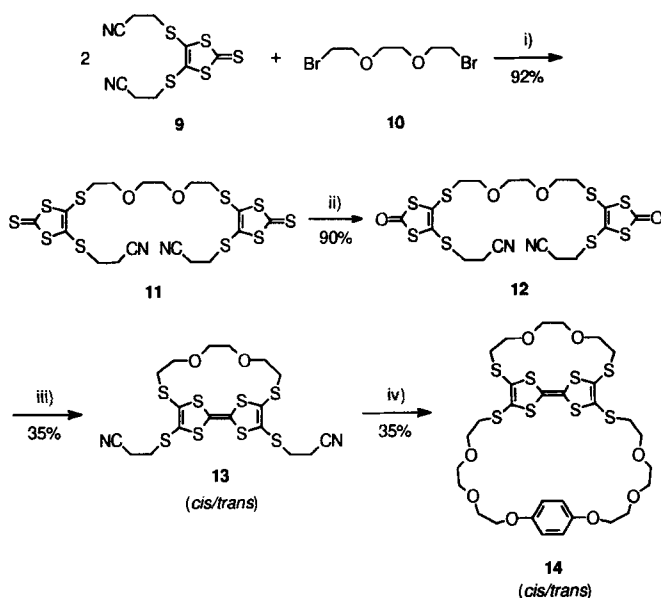
In order to study the influence of the distorted TTF unit on the self-assembly process, dimacrocylic compound **14** was synthesized. CPK models show that the TTF unit in **14** is slightly distorted as a result of the short triethylene glycol ether chain (distortions of about 6° for *cis* and 10° for *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 2. Synthesis of **5a** and **5b** using high-dilution techniques: N₂, 2 equiv CsOH·H₂O, DMF, RT, 17 h.



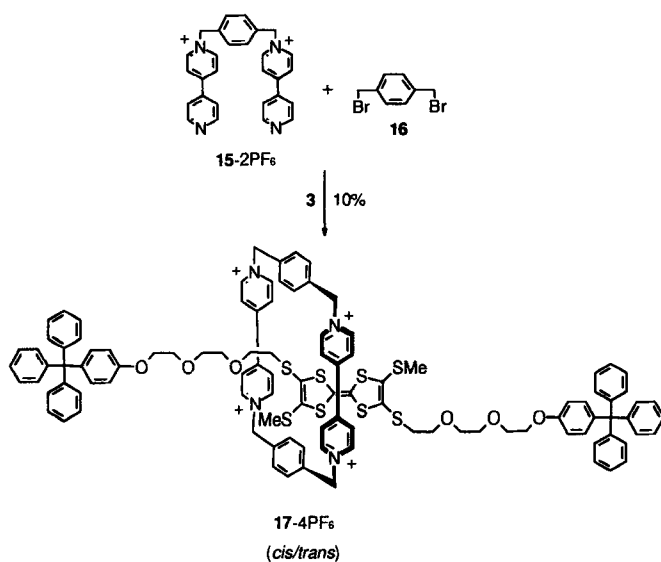
Scheme 3. Synthesis of **7a–d** and **8a–d**: i) and ii) N₂, 2 equiv CsOH·H₂O, DMF, RT, 17–25 h.



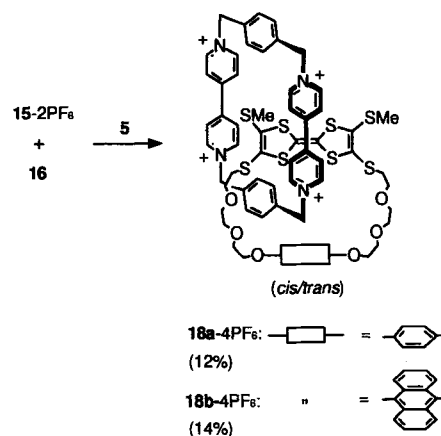
Scheme 4. Synthesis of **14** in four steps: i) N_2 , 2 equiv $CsOH \cdot H_2O$, DMF, RT, 16 h; ii) $Hg(OAc)_2$, $CHCl_3/AcOH$ (3:1), 24 h; iii) $P(OEt)_3$, toluene, reflux, 1 h; iv) **4a**, N_2 , 2 equiv $CsOH \cdot H_2O$, DMF, RT, 17 h.

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 dioxiphenylene-based rotaxanes,^[6b] rotaxane **17-4PF₆** was obtained as a mixture of *cis* and *trans* isomers in 10% yield from the reaction of **3**, dication **15-2PF₆**,^[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



Scheme 5. Synthesis of rotaxane **17-4PF₆**: N_2 , DMF, RT, 10 d.



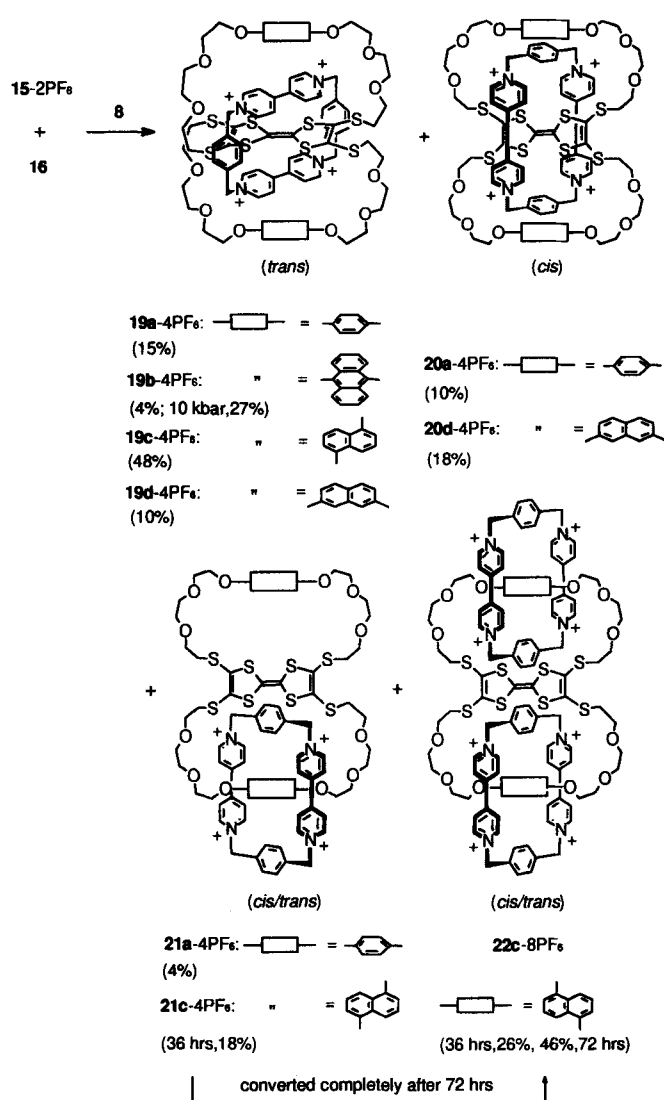
Scheme 6. Synthesis of [2]catenanes **18a-4PF₆** and **18b-4PF₆**: N_2 , DMF, RT, 10 d.

17-4PF₆ is not high, the reaction demonstrates that TTF can act as a template for the formation of the tetracationic macrocycle.

The reaction of monomacrocycle **5a** with **15-2PF₆** and **16** in DMF for seven days resulted in the formation of the [2]catenane **18a-4PF₆** in 12% yield. Similarly, another [2]catenane, **18b-4PF₆**, was prepared in 15% yield from the reaction of **5b**, **15-2PF₆**, 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**, **15-2PF₆**, 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-4PF₆**, *cis*-**20a-4PF₆**, and **21a-4PF₆** (a mixture of *cis* and *trans* isomers) were obtained in 15, 10, and 4% yields, respectively, after ten days. Similarly, *trans*-[3]pseudocatenane **19b-4PF₆** was obtained in 4% yield from the reaction of **8b**, **15-2PF₆**, and **16** after 21 days. No isomers similar to **20a-4PF₆** or **21a-4PF₆** were generated in this reaction. By using ultra-high pressure (10 kbar), **19b-4PF₆** could be prepared in 27% yield after three days.^[24] A [3]pseudocatenane, **19c-4PF₆**, a [3]catenane, **21c-4PF₆**, and a [4]catenane, **22c-8PF₆**, were obtained from the reaction of **8c**, **15-2PF₆**, and **16**. After 36 hours, TLC indicated that **8c** had been completely consumed—the dimacrocycle 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-4PF₆**, while **21c-4PF₆** and **22c-8PF₆** 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-4PF₆** was transformed completely to **22c-8PF₆** (monitored by TLC), and **22c-8PF₆** was then isolated in 46% yield, while the yield of **19c-4PF₆** remained unchanged. Under similar conditions, quite different results were obtained from the reaction of **8d**, a constitutional isomer of **8c**, with **15-2PF₆** and **16** over seven days: the *cis*-[3]pseudocatenane **20d-4PF₆** was isolated in 18% yield as the major product and the *trans*-[3]pseudocatenane **19d-4PF₆** in 10% yield as the minor product. No catenanes similar to **21c-4PF₆** or **22c-8PF₆** were detected in this reaction.

Stirring the solution of the dimacrocycle **14**, **15-2PF₆**, 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: N₂, DMF, RT, 7–21 d (2 equiv 15-2PF₆ and 16 in the cases of **8a** and **8b**; 3 equiv 15-2PF₆ and 16 in the cases of **8c** and **8d**).

mation of the tetracationic macrocycle around the dioxyphenylene unit.

The fact that rotaxane 17-4PF₆, and [2]catenanes 18a-4PF₆ and 18b-4PF₆ are mixtures of *cis* and *trans* isomers can readily be explained in terms of their structural features. The tetracationic macrocycle in 17-4PF₆ 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-4PF₆ has four possible translational isomers. Because the dioxyanthrylene unit is too big to be clamped by the tetracationic macrocycle, [2]catenane 18b-4PF₆ 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* isomerization. The fact that [3]catenanes 21a-4PF₆ and 21c-4PF₆ 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 dipyrindinium 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 15-2PF₆ 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-4PF₆ and *cis*-20a-4PF₆ 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-4PF₆ 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-dioxiphenylene 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 dipyrindinium unit. The CPK model shows that only *trans*-**8c** can adopt an energetically favorable conformation. Therefore, efficient self-assembly not only leads to 19c-4PF₆, but also to 21c-4PF₆ and 22c-8PF₆. 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 conformations are energetically unfavorable. As a result, self-assembly is not as efficient as with **8c**, and no catenane products similar to 21c-4PF₆ or 22c-8PF₆ are produced. The fact that *cis*-20d-4PF₆ 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-4PF₆ (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 PF₆[−] ions from three catenane species, reveal the complex fragmentation patterns of these supramolecular structures.^[30]

¹H NMR Spectroscopy: Because of their *cis/trans* isomerization, rotaxane 17-4PF₆, [2]catenanes 18a-4PF₆ and 18b-4PF₆, [3]pseudocatenane 21a-4PF₆, [3]catenane 21c-4PF₆, and [4]catenane 22c-8PF₆ have ¹H NMR spectra that cannot be completely assigned, whereas the configurations of [3]pseudo-

Table 1. ESMS data of rotaxane **17-4PF₆** and catenanes **18–22-4PF₆**.

	$[M - 4PF_6]^{4+}$	$[M - 3PF_6]^{3+}$	$[M - 2PF_6]^{2+}$	$[M - PF_6]^+$	$[2M - 3PF_6]^{3+}$	$[3M - 5PF_6]^{5+}$	$[3M - 4PF_6]^{4+}$
17-4PF₆	445	642	1035		1429	1272	1426
18a-4PF₆			1363 [a]				
18b-4PF₆	330	488	804	1754	1121	994	1280
19a-4PF₆	382	558	909		1261		1437
19b-4PF₆	432	625	1009		1395		1587
19c-4PF₆	407	591	960		1328		1512
19d-4PF₆		591	960				
20a-4PF₆	382	558	909	1964	1261		1437
20d-4PF₆		591	960				
21a-4PF₆	382	558	909	1964	1261		1437
21c-4PF₆	407	591	960		1328		1512
22c-4PF₆ [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-4PF₆**, **20a-4PF₆**, **19b-4PF₆**, **19c-4PF₆**, **19d-4PF₆**, and **20d-4PF₆** can easily be determined by their 1H NMR spectra. Because of their D_2 symmetry, both the α - and β -protons on the dipyrindinium 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 1H NMR spectra of **19d-4PF₆** and **20d-4PF₆** are shown in Figure 1 and Figure 2. The differences in the signals corresponding to the α - and β -protons on the dipyrindinium 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 ($\Delta\delta$) 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-4PF₆**; this indicates that the dioxanthyrene units interact most strongly with the dipyrindinium unit. The dynamic 1H NMR spectra of **19a-4PF₆**, **20a-4PF₆**, and **19b-4PF₆** were also examined. The 1H NMR spectra of **20a-4PF₆** are independent of temperature in the interval -35 to $75^\circ C$, whereas the aromatic resonances of **19a-4PF₆** and **19b-4PF₆** show a strong temperature dependence. NOESY (chemi-

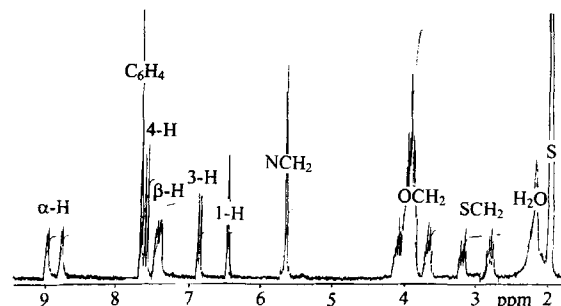


Fig. 1. 1H NMR spectrum (250 MHz) of *trans*-[3]pseudocatenane **19d-4PF₆** in CD_3CN at room temperature.

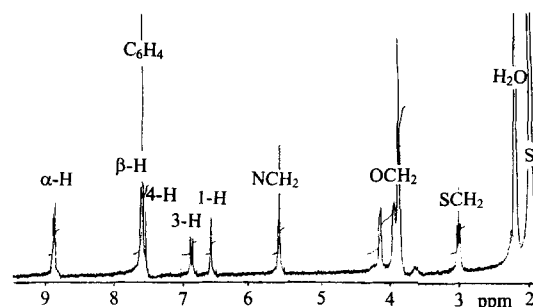


Fig. 2. 1H NMR spectrum (250 MHz) of *cis*-[3]pseudocatenane **20d-4PF₆** in CD_3CN at room temperature.

cal exchange) spectra prove that this temperature dependence is due to thermally activated exchange between sites on the aromatic rings. The rotational barrier in **19b-4PF₆** is higher than that in **19a-4PF₆**. All motions of the polyether chains of **20a-**

Table 2. Selected 1H 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_6H_4	NCH_2
free	8.93	8.23	7.60	5.78
<i>trans</i> - 19a-4PF₆	9.01 (d, 4H) (0.08)	8.82 (d, 4H) (-0.11)	7.80 (d, 4H) (-0.43)	7.63 (d, 4H) (-0.60)
<i>cis</i> - 20a-4PF₆	8.95 (d, 8H) (0.02)	8.13 (dd, 4H) (-0.41)	7.63 (s) (0.03)	5.66 (s) (-0.20)
<i>trans</i> - 19b-4PF₆	8.87 (dd, 4H) (-0.06)	8.50 (d, 4H) (-0.43)	7.86 (d, 4H) (-0.10)	7.60 (s) (-0.37)
<i>trans</i> - 19c-4PF₆	8.85 (d, 4H) (-0.08)	8.66 (d, 4H) (-0.27)	7.42 [b] (-0.61)	7.63 (s) (-0.96)
<i>trans</i> - 19d-4PF₆	8.95 (d, 4H) (0.02)	8.76 (d, 4H) (-0.17)	7.42 (d, 4H) (-0.61)	7.39 (d, 4H) (-0.84)
<i>cis</i> - 20d-4PF₆	8.84 (d, 8H) (-0.09)	7.62 (d, 8H) (-0.61)	7.60 (s) (0.00)	5.61 (s) (-0.21)

[a] In CD_3CN at room temperature. [b] Overlaps with the signal of the 4,8-protons of the naphthylene unit.

4PF₆ are frozen out on the NMR timescale, because its ¹H 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-4PF₆** and **19b-4PF₆**. 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-4PF₆** do not show any sign of such motion; this indicates that the benzene rings of the tetracationic macrocycle stabilize the hydroquinone rings by π - π 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 those three oxidation steps of **8b–d** are significantly lower than those of **8a**. We attribute this to the stronger electron-donating ability of the dioxanthrylene 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-4PF₆** are depicted in Figures 3 and 4, respectively, which illustrate the influence of the π - π donor-acceptor interaction on the redox behavior of the TTF unit. The fact that there is no significant difference between the values of **19a-4PF₆** and **20a-4PF₆** indicates that the configurational change does not greatly influence the redox process. The first two oxidation steps of **21a-4PF₆**, that is, the oxidation to the mono- and dications of the TTF unit, are apparently unaffected by the dipyrindinium macrocycle; this is indicative of a weaker interaction between the TTF unit and the dipyrindiniums within **21a-4PF₆**. The voltammograms of **19c-4PF₆** and **20d-4PF₆** display unresolved broad waves, probably due to the strong interaction between the dioxynaphthylene unit and dipyrindinium unit. In addition to the three processes corresponding to the oxidation of TTF and dioxanthrylene unit (the

Table 3. Half wave-potentials [a] for the oxidation by cyclic voltammetry, determined in CH₂Cl₂ [b] or CH₃CN [c]. For **19c-4PF₆** and **20d-4PF₆**, no accurate data are available [d].

	$E_{1/2}^1$	$E_{1/2}^2$	$E_{1/2}^3$
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
17-4PF₆	0.61	0.94	
18a-4PF₆	0.60	0.84	
18b-4PF₆	0.60 (irrev.)		
19a-4PF₆	0.63	0.94	1.34
20a-4PF₆	0.62 (irrev.)	0.92 (irrev.)	1.34
21a-4PF₆	0.58	0.82	1.28
19b-4PF₆	0.52 (irrev.)	0.87 (irrev.)	1.19
19d-4PF₆	0.46		1.01
21c-4PF₆	0.60	0.85	1.03
22c-8PF₆	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 mV s⁻¹; supporting electrolyte: *n*Bu₄NPF₆ 0.1 mol L⁻¹; conc. of compound: 5×10^{-4} L⁻¹.

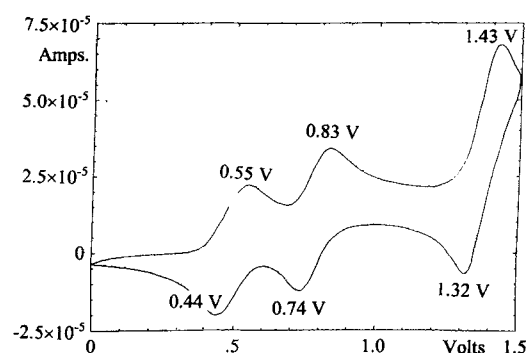


Fig. 3. The cyclic voltammogram of **8a** (for conditions, see Table 3).

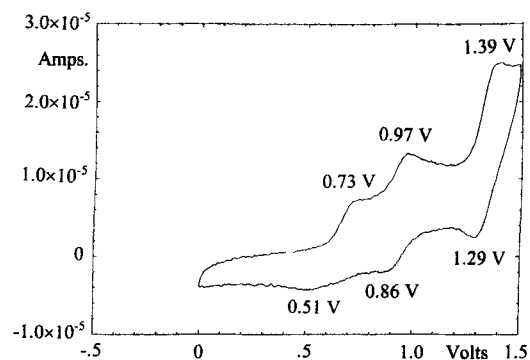


Fig. 4. The cyclic voltammogram of **19a-4PF₆** (for conditions, see Table 3).

three waves shown in Table 3), **19b-4PF₆** 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.

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 dipyrindinium units. The strongest absorptions are observed for **19b-4PF₆** and **19c-4PF₆**, as a result of the strong π -electron donating ability of the dioxanthrylene and 1,5-dioxynaphthylene units. Because of the movement of the tetracationic macrocycle along the glycol chains, rotaxane **17-4PF₆** and [2]catenanes **18a-4PF₆** and **18b-4PF₆** only exhibit weak CT absorption 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-4PF₆** is just the simple addition of that of two **21c-4PF₆**.

Table 4. Charge-transfer absorptions of rotaxane **17-4PF₆** 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)
17-4PF₆	660	745	19b-4PF₆	773	4200
18a-4PF₆	620	620	19c-4PF₆	790	4150
18b-4PF₆	665	820	21c-4PF₆	750	850
19a-4PF₆	785	3100	22c-4PF₆	780	1400
20a-4PF₆	807	2900	19d-4PF₆	760	2400
21a-4PF₆	770	900	20d-4PF₆	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 dimacrocylic 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 dimacrocylics, 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 dimacrocylic 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 π - π 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 dimacrocylics 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 60 F (Merck, 9385, 230–400 mesh). Melting points are uncorrected. ¹H 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 Biolon 10 K time-of-flight mass spectrometer (Biosystems, Uppsala, Sweden) over 5×10^5 fissions (²⁵²Cf). 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 $\mu\text{L min}^{-1}$, the capillary at 50 °C, and a coaxial flow of N₂ at 30–40 psi, and another source made in our laboratory, with a sample flow of 0.3–0.7 $\mu\text{L min}^{-1}$ 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 Bu₄NPF₆ as supporting electrolyte, with a sweep rate of 100 mV s⁻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 CH₂Cl₂ (200 mL). The organic phase was washed

with water and dried (MgSO₄). 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; ¹H NMR (250 MHz, CDCl₃): δ = 3.44 (t, 2H; BrCH₂), 3.65–3.86 (m, 8H; OCH₂), 4.10 (t, 2H; OCH₂), 6.79 (d, 2H; C₆H₄), 7.10 (d, 2H; C₆H₄), 7.20 (m, 15H; C₆H₅); MS (EI): m/z (%): 531 (100) [M]⁺. C₃₁H₃₁BrO₃ (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-(*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 (MgSO₄). The solvent was then removed in vacuo, and the residue was purified by column chromatography (CH₂Cl₂/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 ¹H NMR spectra. First isomer: M.p. 144–46 °C; ¹H NMR (CDCl₃): δ = 2.38 (s, 6H; SCH₃), 2.97 (t, 4H; SCH₂), 3.64–3.71 (m, 12H; OCH₂), 3.83 (m, 4H; OCH₂), 4.09 (m, 4H; OCH₂), 6.91 (dd, 8H; C₆H₄), 7.16–7.25 (m, 30H; C₆H₅); MS (PD): m/z : 1261.5 [M]⁺; C₇₀H₆₈O₆S₈ (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; ¹H NMR (250 MHz, CDCl₃): δ = 2.37 (s, 6H; SCH₃), 2.98 (t, 4H; SCH₂), 3.64–3.72 (m, 12H; OCH₂), 3.84 (m, 4H; OCH₂), 4.08 (m, 4H; OCH₂), 6.91 (d, d, 8H; C₆H₄), 7.16–7.26 (m, 30H; C₆H₅); MS (PD): m/z : 1259.9 [M]⁺; C₇₀H₆₈O₆S₈ (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 K₂CO₃ (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 CH₂Cl₂ (200 mL), and the organic phase washed with water and saturated aqueous NaCl solution. The solvent was dried over anhydrous MgSO₄ and removed in vacuo. The residue was subjected to column chromatography (silica gel) with CH₂Cl₂/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; ¹H NMR (CDCl₃): δ = 3.23 (t, 4H; ICH₂), 3.67 (t, 4H; OCH₂), 3.75 (m, 8H; OCH₂), 3.98 (t, 4H; OCH₂), 4.28 (t, 4H; OCH₂), 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); C₂₂H₃₀I₂O₆ (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 K₂CO₃ in acetone for 24 h. ¹H NMR (CDCl₃): δ = 3.25 (t, 4H; ICH₂), 3.73 (m, 12H; OCH₂), 3.92 (t, 4H; OCH₂), 4.24 (t, 4H; OCH₂), 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); C₂₂H₃₀I₂O₆ (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 perfluor pump. Stirring was continued for an additional 3 h, and the reaction mixture was then concentrated in vacuo. CH₂Cl₂ (100 mL) was added, and the organic solution washed with water, saturated aqueous NaCl solution, and dried (MgSO₄). The solvent was then removed and the oily residue purified by column chromatography (silica gel, CH₂Cl₂/EtOAc 8:1), affording **5a** (0.53 g, 38%) as an orange oil. ¹H NMR (CDCl₃): δ = 2.39 (ss, 4H; SCH₃), 2.95 (m, 4H; SCH₂), 3.69 (m, 12H; OCH₂), 3.80 (m, 4H; OCH₂), 4.12 (m, 4H; OCH₂), 6.87 (ss, 4H; C₆H₄); MS (EI): m/z (%): 698 (100) [M]⁺; C₂₆H₃₄O₆S₈ (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**. ¹H NMR (CDCl₃): δ = 2.72, 2.90 (ss, 4H; SCH₃), 3.04 (m, 4H; SCH₂), 3.79 (m, 12H; OCH₂), 3.91 (m, 4H; OCH₂), 4.43 (m, 4H; OCH₂), 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); C₃₄H₃₈O₆S₈ (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·H₂O (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, $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ 5:1). Compound **7c** (0.96 g, 58%) was obtained as an orange oil. $^1\text{H NMR}$ (CDCl_3): δ = 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] $^+$; $\text{C}_{34}\text{H}_{38}\text{N}_2\text{O}_6\text{S}_8$ (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-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**. $^1\text{H NMR}$ (CDCl_3): δ = 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); $\text{C}_{30}\text{H}_{36}\text{N}_2\text{O}_6\text{S}_8$ (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-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. $^1\text{H NMR}$ (CDCl_3): δ = 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); $\text{C}_{38}\text{H}_{46}\text{N}_2\text{O}_6\text{S}_8$ (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-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**. $^1\text{H NMR}$ (CDCl_3): δ = 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] $^+$; $\text{C}_{34}\text{H}_{38}\text{N}_2\text{O}_6\text{S}_8$ (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-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 $\text{CsOH} \cdot \text{H}_2\text{O}$ (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, $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ 4:1). **8c** (0.72 g, 67%) was obtained as an orange oil. $^1\text{H NMR}$ (CDCl_3): δ = 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] $^+$; $\text{C}_{50}\text{H}_{60}\text{O}_{12}\text{S}_8$ (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-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. $^1\text{H NMR}$ (CDCl_3): δ = 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); $\text{C}_{44}\text{H}_{56}\text{O}_{12}\text{S}_8$ (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-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. $^1\text{H NMR}$ (CDCl_3): δ = 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] $^+$; $\text{C}_{58}\text{H}_{64}\text{O}_{12}\text{S}_8$ (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-thioethoxy)ethoxy)ethoxy]naphthylene-1,4,5,8-tetrathiafulvalene (8d, cis/trans): was prepared in 60% yield as an orange oily solid from **4d** and **7d**. $^1\text{H NMR}$ (CDCl_3): δ = 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] $^+$; $\text{C}_{50}\text{H}_{60}\text{O}_{12}\text{S}_8$ (1109.6): calcd C 54.12, H 5.46; found: C 53.94, H 5.35.

1,2-Bis[2-(4-(2-cyanoethylthio)-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 $\text{CsOH} \cdot \text{H}_2\text{O}$ (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. $^1\text{H NMR}$ (CDCl_3):

δ = 2.79 (t, 4H; CH_2CN), 3.13 (m, 8H; SCH_2), 3.67 (s, 4H; $\text{OCH}_2\text{CH}_2\text{O}$), 3.75 (t, 4H; $\text{SCH}_2\text{CH}_2\text{O}$); MS (EI): m/z (%): 616 (100) [M] $^+$; $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_2\text{S}_{10}$ (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-cyanoethylthio)-1,3-dithiole-2-one-5-thio)ethoxy]ethane (12): A mixture of **11** (1.85 g, 3.0 mmol) and $\text{Hg}(\text{OAc})_2$ (5.0 g, 16 mmol) in $\text{CHCl}_3/\text{AcOH}$ (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, $\text{CH}_2\text{Cl}_2/\text{EtOAc}$, 15:1). **12** (1.58 g, 90%) was obtained as an orange oil. $^1\text{H NMR}$ (CDCl_3): δ = 2.78 (t, 4H; CH_2CN), 3.12 (m, 8H; SCH_2), 3.66 (s, 4H; $\text{OCH}_2\text{CH}_2\text{O}$), 3.74 (s, 4H; $\text{SCH}_2\text{CH}_2\text{O}$); MS (EI): m/z (%): 584 (100) [M] $^+$; $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_2\text{S}_8$ (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-dioxo-1,10-dithiadecane-1,10-diyl)-1,4,5,8-tetrathiafulvalene (13, cis/trans): A solution of **12** (1.17 g, 2.0 mmol), $\text{P}(\text{OEt})_3$ (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. $^1\text{H NMR}$ (CDCl_3): δ = 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] $^+$; $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_2\text{S}_8$ (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 $\text{P}(\text{OEt})_3$ 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-dioxo-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 $\text{CsOH} \cdot \text{H}_2\text{O}$ (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, $\text{EtOAc}/\text{cyclohexane}$ 1:1) to give **14** (0.14 g, 35%) as an orange oil. $^1\text{H NMR}$ (CDCl_3): δ = 3.02 (m, 8H; SCH_2), 3.32–3.74 (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] $^+$; $\text{C}_{30}\text{H}_{40}\text{O}_8\text{S}_8$ (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-(p-(triphenylmethyl)phenyl)ethoxy)ethoxy]ethylenedioxy]-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 $\text{MeOH}/\text{aqueous NH}_4\text{Cl}$ solution (2M)/ 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 $^1\text{H NMR}$ spectrum indicated this rotaxane to be a mixture of *cis* and *trans* isomers. M.p. 153 °C (decom.); $^1\text{H NMR}$ (CD_3CN): δ = 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 $_6$] $^{4+}$; $\text{C}_{106}\text{H}_{100}\text{N}_4\text{O}_6\text{F}_{24}\text{P}_4\text{S}_8$ (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 (decom.); $^1\text{H NMR}$ (CD_3CN): δ = 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 [5a] $^+$; $\text{C}_{62}\text{H}_{66}\text{N}_4\text{O}_6\text{F}_{24}\text{P}_4\text{S}_8$ (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-(thioethoxy)ethoxy)ethoxy)naphthylene]-1,4,5,8-tetrafulvalene (*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-4PF₆): This compound was prepared as described for 18a-4PF₆. 18b-4PF₆ was obtained as a blue solid in 14% yield from 5b, 15-2PF₆, and 16 in DMF after 12 d. M.p. 178 °C (decomp.); ¹H NMR (CD₃CN): δ = 2.68–3.25 (m, 10H; CH₃, SCH₂), 3.54–4.67 (m, 20H; OCH₂), 5.62–5.83 (m, 8H), 7.10–7.82 (m, 20H), 8.04–9.12 (m, 12H); MS (ES): *m/z*: 1754 [M – PF₆]⁺, 1280 [3M – 4PF₆]⁴⁺, 1121 [2M – 3PF₆]³⁺, 994 [3M – 5PF₆]⁵⁺, 804 [M – 2PF₆]²⁺, 488 [M – 3PF₆]³⁺, 330 [M – 4PF₆]⁴⁺; C₇₀H₇₀N₄O₆F₂₄P₄S₈ (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-(thioethoxy)ethoxy)ethoxy)naphthylene]-1,4,5,8-tetrafulvalene (*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-4PF₆), {1,4,5,8-Tetrahydro-2,7(6):3,6(7)-bis[1,5-bis(2-(2-(thioethoxy)ethoxy)ethoxy)naphthylene]-1,4,5,8-tetrafulvalene (*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-4PF₆), and {1,4,5,8-Tetrahydro-2,7(6):3,6(7)-bis[1,5-bis(2-(2-(thioethoxy)ethoxy)ethoxy)naphthylene]-1,4,5,8-tetrafulvalene (*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)} ([4]pseudocatenane 22c-8PF₆): Compounds 8c (222 mg, 0.2 mmol), 15-2PF₆ (425 mg, 0.6 mmol), and 16 (175 mg, 0.6 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/NH₄Cl solution (2M)/MeNO₂ (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/NH₄Cl 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 NH₄PF₆ solution added until precipitation was complete. After filtration and drying in vacuo, [3]pseudocatenane 19c-4PF₆ (213 mg, 48%) was obtained as a dark blue solid.

19c-4PF₆: M.p. 230 °C (decomp.); ¹H NMR (CD₃CN): δ = 2.81 (4H, m, SCH₂), 3.12 (m, 4H; SCH₂), 3.63 (m, 4H; OCH₂), 3.85–4.16 (m, 36H; OCH₂), 5.54 (s, 8H; C₆H₄CH₂), 6.58 (d, 4H; 2-H (naph)), 7.27 (dd, 4H; β-CH (py)), 7.40–7.55 (m, 12H; 3,4-H (naph), β-H (py)), 7.63 (s, 8H; CH₂C₆H₄), 8.66 (d, 4H; α-H (py)), 8.85 (d, 4H; α-H (py)); ¹³C NMR (CD₃CN): 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 – 4PF₆]⁴⁺, 1328 [2M – 3PF₆]³⁺, 1108 [8c]⁺, 960 [M – 2PF₆]²⁺, 591 [M – 3PF₆]³⁺, 407 [M – 4PF₆]⁴⁺; C₈₆H₉₂N₄O₁₂F₂₄P₄S₈ (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-4PF₆ (80 mg, 18%) and [4]pseudocatenane 22c-8PF₆ (172 mg, 26%) both as purple solids. The ¹H NMR spectra of 21c-4PF₆ and 22c-8PF₆ could not be assigned because they are mixtures of *cis* and *trans* isomers. 21c-4PF₆: M.p. 198 °C (decomp.); MS (ES): *m/z*: 1512 [3M – 4PF₆]⁴⁺, 1328 [2M – 3PF₆]³⁺, 1108 [8c]⁺, 960 [M – 2PF₆]²⁺, 591 [M – 3PF₆]³⁺, 407 [M – 4PF₆]⁴⁺; C₈₆H₉₂N₄O₁₂F₂₄P₄S₈ (2209.9): calcd C 46.74, H 4.20, N 2.54; found: C 46.42, H 4.09, N 2.49.

22c-8PF₆: M.p. 215 °C (decomp.); MS (ES): *m/z*: 1509 [M – 2PF₆]²⁺, 1179 [2M – 5PF₆]⁵⁺, 1108 [8c]⁺, 958 [M – 3PF₆]³⁺, 682 [M – 4PF₆]⁴⁺, 517 [M – 5PF₆]⁵⁺; C₁₂₂H₁₂₄N₈O₁₂F₄₈P₈S₈ (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-4PF₆ was transformed to 22c-8PF₆ completely, as detected by TLC. After workup as described above, 19c-4PF₆ and 22c-8PF₆ were isolated in 48 and 46% yields, respectively.

{1,4,5,8-Tetrahydro-2,6:3,7-bis[1,4-bis(2-(2-(thioethoxy)ethoxy)ethoxy)phenylene]-1,4,5,8-tetrafulvalene (*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-4PF₆), {1,4,5,8-Tetrahydro-2,7:3,6-bis[1,4-bis(2-(2-(thioethoxy)ethoxy)ethoxy)phenylene]-1,4,5,8-tetrafulvalene (*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-4PF₆), and {1,4,5,8-Tetrahydro-2,7(6):3,6(7)-bis[1,4-bis(2-(2-(thioethoxy)ethoxy)ethoxy)phenylene]-1,4,5,8-tetrafulvalene (*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-4PF₆) were prepared in 15, 10, and 4% yields, respectively, from 8a, 15-2PF₆, and 16 after 10 d.

19a-4PF₆: dark solid; m.p. 220 °C (decomp.); ¹H NMR (CD₃CN): δ = 2.80 (m, 4H; SCH₂), 3.21 (m, 4H; SCH₂), 3.71–4.12 (m, 40H; OCH₂), 5.66 (s, 8H; NCH₂), 6.32 (s, 8H; OC₆H₄), 7.63 (d, 4H; β-CH (py)), 7.68 (s, 8H; CH₂C₆H₄), 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 – 4PF₆]⁴⁺, 1261 [2M – 3PF₆]³⁺, 1008 [8a]⁺, 909 [M – 2PF₆]²⁺, 558 [M – 3PF₆]³⁺, 382 [M – 4PF₆]⁴⁺; C₇₈H₈₈N₄O₁₂F₂₄P₄S₈ (2109.8): C 44.40, H 4.21, N 2.66; found: C 43.74, H 4.51, N 3.05.

20a-4PF₆: dark blue solid; m.p. 185 °C (decomp.); ¹H NMR (CD₃CN): δ = 3.01 (t, 8H; SCH₂), 3.77–3.92 (m, 40H; OCH₂), 5.62 (s, 8H; NCH₂), 6.41 (s, 8H; OC₆H₄), 7.63 (s, 8H; C₆H₄CH₂), 7.82 (s, 8H, β-CH (py)), 8.95 (s, 4H; α-CH (py)); MS (ES): *m/z*: 1964 [M – PF₆]⁺, 1437 [3M – 4PF₆]⁴⁺, 1261 [2M – 3PF₆]³⁺, 909 [M – 2PF₆]²⁺, 558 [M – 3PF₆]³⁺, 382 [M – 4PF₆]⁴⁺; C₇₈H₈₈N₄O₁₂F₂₄P₄S₈ (2109.8): calcd C 44.40, H 4.21, N 2.66; found: C 43.88, H 4.19, N 2.67.

21a-4PF₆: brown solid; m.p. 200 °C (decomp.); MS (ES): *m/z*: 1964 [M – PF₆]⁺, 1437 [3M – 4PF₆]⁴⁺, 1261 [2M – 3PF₆]³⁺, 909 [M – 2PF₆]²⁺, 558 [M – 3PF₆]³⁺, 382 [M – 4PF₆]⁴⁺; C₇₈H₈₈N₄O₁₂F₂₄P₄S₈ (2109.8): C 44.40, H 4.21, N 2.66; found: C 44.42, H 4.52, N 2.73. 21a-4PF₆ is a mixture of *trans/cis* isomers and it is difficult to assign its ¹H NMR spectrum.

{1,4,5,8-Tetrahydro-2,6:3,7-bis[9,10-bis(2-(2-(thioethoxy)ethoxy)ethoxy)naphthylene]-1,4,5,8-tetrafulvalene (*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-4PF₆) and {1,4,5,8-Tetrahydro-2,7:3,6-bis[2,6-bis(2-(2-(thioethoxy)ethoxy)ethoxy)naphthylene]-1,4,5,8-tetrafulvalene (*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-4PF₆) were prepared in 10% and 18% yields, respectively, both as dark blue solids from 8d, 15-2PF₆, and 16 in DMF after 7 d. 19d-4PF₆: M.p. 205 °C (decomp.); ¹H NMR (CD₃CN): δ = 2.80 (m, 4H; SCH₂), 3.16 (m, 4H; SCH₂), 3.65 (m, 4H; OCH₂), 3.83–4.12 (m, 36H; OCH₂), 5.67 (s, 8H; C₆H₄CH₂), 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; CH₂C₆H₄), 8.76 (d, 4H; α-CH (py)), 8.95 (d, 4H; α-CH (py)); MS (ES): *m/z*: 1108 [8d]⁺, 960 [M – 2PF₆]²⁺, 591 [M – 3PF₆]³⁺; C₈₆H₉₂N₄O₁₂F₂₄P₄S₈ (2209.9): calcd C 46.74, H 4.20, N 2.54; found: C 46.58, H 4.64, N 2.63.

20d-4PF₆: M.p. 195 °C (decomp.); ¹H NMR (CD₃CN): δ = 3.02 (t, 8H; SCH₂), 3.89 (m, 24H; OCH₂), 3.96 (t, 8H; OCH₂), 4.14 (t, 8H; OCH₂), 5.61 (s, 8H; C₆H₄CH₂), 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; CH₂C₆H₄), 7.62 (d, 8H; β-CH (py)), 8.84 (d, 8H; α-CH (py)); MS (ES): *m/z*: 1108 [8d]⁺, 960 [M – 2PF₆]²⁺, 591 [M – 3PF₆]³⁺; C₈₆H₉₂N₄O₁₂F₂₄P₄S₈ (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 ¹H 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.
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- [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. [11 c] and [13]). The second approach involved one-electron oxidation of [12]- and [14]tetrathiafulvalenophanes (see ref. [11 d]). 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.
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- [30] Electrospray mass spectrometry (ESMS) has been used to characterize catenanes, and the fragmentation pattern corresponding to the loss of three PF₆[−] ions from a catenane dimer have been detected. However, more complex fragmentation patterns, e.g., the ion peaks [3M – 4PF₆]⁴⁺ and [3M – 5PF₆]³⁺, 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.