Tetrathiafulvalenophanes and their catenanes†

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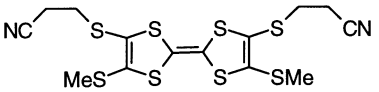
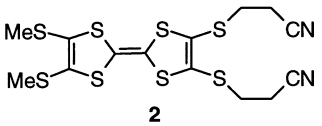
Monomacrocycles of the two electron donors tetrathiafulvalene (TTF) and 1,5-dioxynaphthalene have been prepared, together with three symmetric TTF-containing bismacrocycles, two of which have been prepared by a two-step deprotection–cyclization approach. By utilizing the donor–acceptor interactions of these donors with the dipyridinium dication of 1,1′-[1,4-phenylenebis(methylene)]bis-4,4′-bipyridinium bis(hexafluorophosphate), [2]catenanes were synthesized. In the case of one of the bismacrocycles it was possible to isolate a minor amount of a bis[2]catenane. The catenanes were characterized by ^{1}H NMR spectroscopy, electrospray mass spectroscopy (ESMS) and their fragmentation in the gas phase was also analysed by collisional activation (ESMS/MS).

Also, one tetramacrocyclic compound, the first TTF-based ribbon compound, has been synthesized. This compound shows complex electrochemical properties.

In recent years, there has been increasing interest in incorporating the tetrathiafulvalene unit into macrocyclic and supramolecular compounds due to its reversible redox characteristics.[1,2] By using the self-assembly strategy developed by Stoddart *et al.*[3] several TTF-containing catenanes and rotaxanes have been prepared from macrocyclic and linear compounds, respectively.[4] Traditionally, TTF-based macrocyclic molecules have been synthesized mainly by coupling of the corresponding 1,3-dithiole derivatives, 1,3-dithiole-2-thiones or 1,3-dithiolium salts, forming the central fulvene double bond in the last step.[5] This route involves multistep reactions for preparations of the starting materials and a number of substituents cannot withstand the coupling reaction conditions usually required. We have previously reported that dicyanoethylated TTFs can be used to synthesize a variety of TTF derivatives *via* conversion to the corresponding mono- or di-caesium salts with caesium hydroxide and the subsequent reaction of the di-caesium salts with a,v-ditosylates to produce monomacrocyclic compounds.[2a,b] This route has provided a novel and efficient approach to TTF containing macrocycles. Recently, we have also utilized the similar deprotection–cyclization reaction of tetracyanoethylated TTF to construct TTF containing bismacrocycles incorporating two phenylene, anthrylene or naphthylene units, which were used to build a novel type of catenanes.[6] A subsequent objective was to explore the construction of more topologically complex macrocyclic systems containing multiple TTF units. In this paper, we report the synthesis of four monomacrocyclic compounds and three bismacrocyclic compounds, in order to investigate their abilities to form catenanes. Also, one tetramacrocyclic compound, the first TTF-based ribbon compound,[7] has been synthesized. The electrochemical redox properties of these compounds are also discussed.

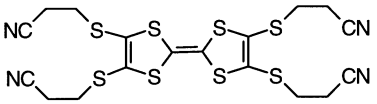


1
(*cis/trans*)



2

† Note added in proof: TTF macrocycles similar to **13** and **22** have recently been published: S.-I. Yunoki, K. Takimiya, Y. Aso and T. Otsubo, *Tetrahedron Lett.*, 1997, **17**, 3017.



3

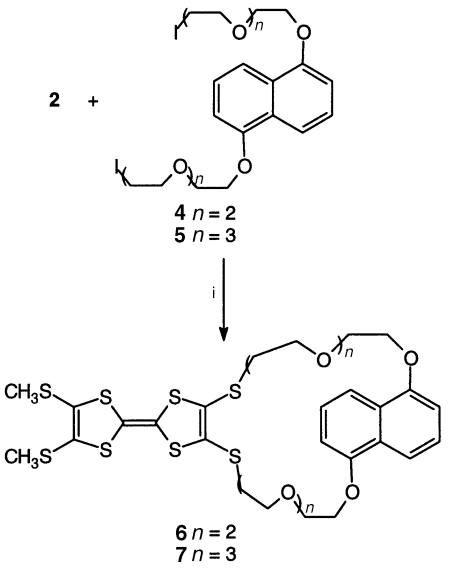
The key starting materials in our synthesis are 2,7(6)-bis(2-cyanoethylthio)-3,6(7)-bis(methylthio)tetrathiafulvalene **1** (*cis/trans*), 2,3-bis(2-cyanoethylthio)-6,7-bis(methylthio)-tetrathiafulvalene **2**, and 2,3,6,7-tetrakis(2-cyanoethylthio)tetrathiafulvalene **3**, which are readily prepared from 4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-thione.[8] Compounds **1** and **2** are used to prepare TTF-incorporating linear diiodides in one-step deprotection–alkylation reactions.

Results and Discussion

Preparation of monomacrocycles

Monocyclic compounds **6** and **7** consisting of TTF and 1,5-dihydroxynaphthalene units connected through diethylene glycol ether chains were prepared from tetrathiafulvalene **2** and bis-alkylating reagents **4** and **5**, respectively (Scheme 1). Under high dilution conditions using a perfusor pump, **4** (**5**) was reacted with the di-caesium salt produced *in situ* from **2** by treating with 2 equiv. of caesium hydroxide monohydrate in dimethylformamide (DMF) to generate **6** (**7**) in a yield of 42% (51%).

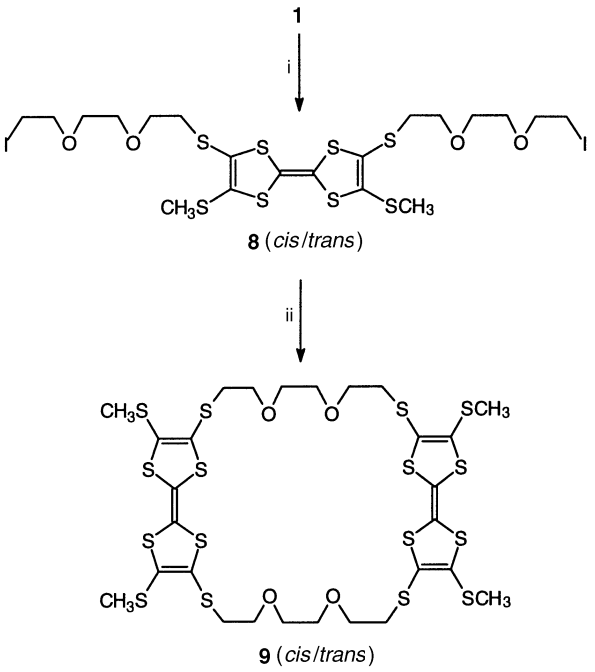
Treatment of **1** with 2 equiv. of caesium hydroxide mono-



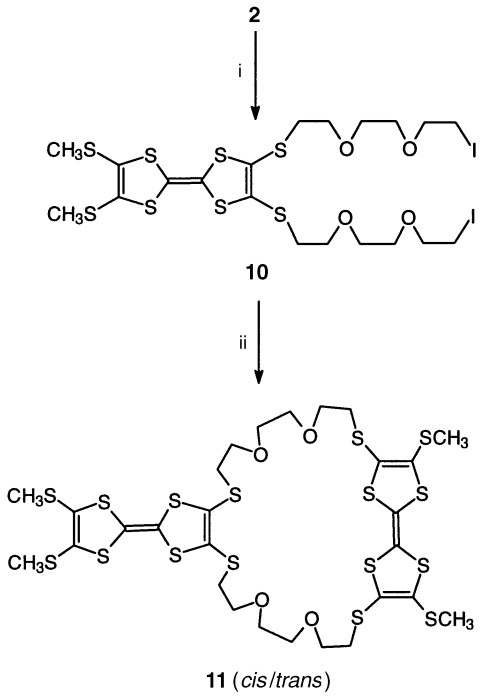
Scheme 1 *Reagents and conditions*: i, $CsOH{\cdot}H_2O$ (2 equiv.), MeOH, DMF, room temp., 16 h, 42% (for $n=2$) and 51% (for $n=3$)

hydrate and excess of 1,2-bis(2-iodoethoxy)ethane in DMF generated compound **8** in 79% yield (Scheme 2). No cyclization products were detected in this reaction. The reaction of **8** with **1** in the presence of 2 equiv. of caesium hydroxide under high dilution conditions resulted in the formation of monomacrocycle **9** as an inseparable mixture of *cis*/*trans* configurational isomers in 80% yield.

Treatment of **2** with 2 equiv. of caesium hydroxide monohydrate and excess of 1,2-bis(2-iodoethoxy)ethane in DMF generated compound **10** in 60% yield (Scheme 3). From **10** and **1** the monocycle **11** was prepared as a mixture of *cis*/*trans* isomers in 68% yield.



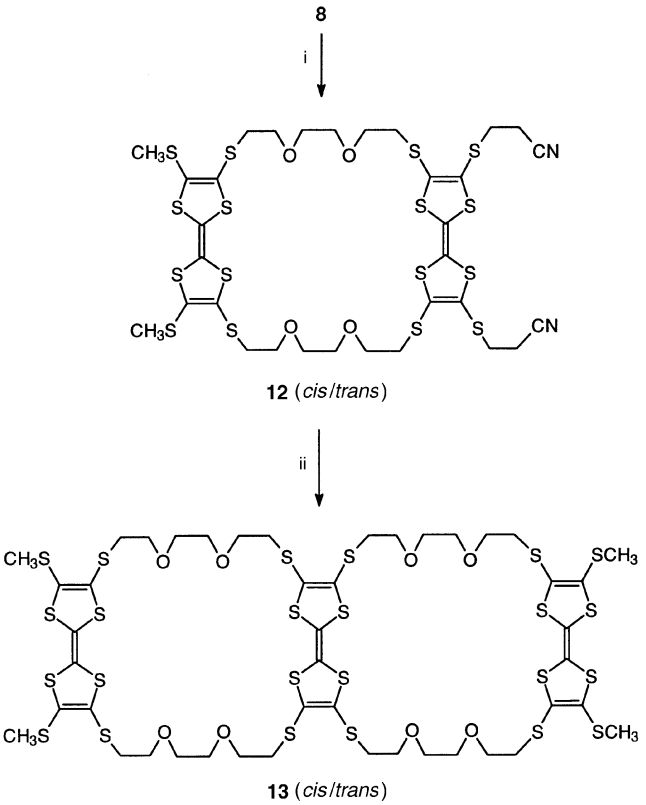
Scheme 2 *Reagents and conditions*: i, $CsOH{\cdot}H_2O$ (2 equiv.), MeOH, $I(CH_2CH_2O)_2CH_2CH_2I$ (8 equiv.), DMF, room temp., 12 h, 79%; ii, **1**, $CsOH{\cdot}H_2O$ (2 equiv.), MeOH, DMF, room temp., 20 h, 80%



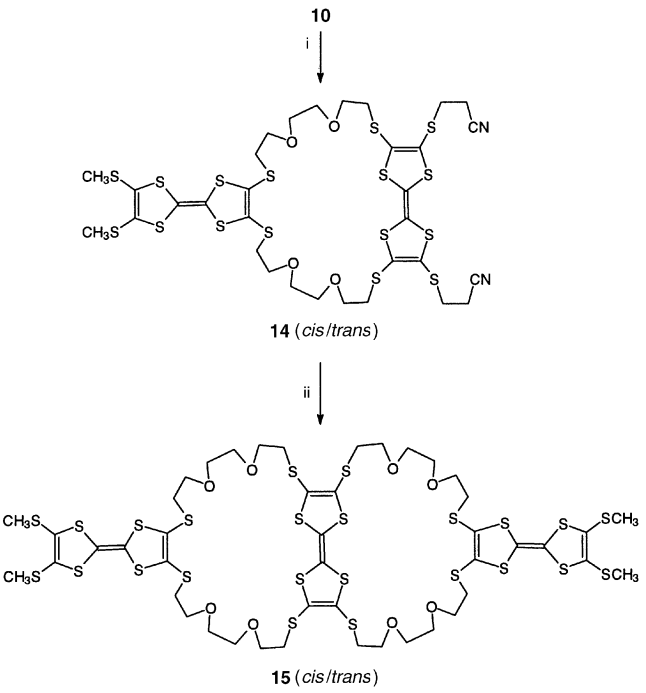
Scheme 3 *Reagents and conditions*: i, $CsOH{\cdot}H_2O$ (2 equiv.), MeOH, $I(CH_2CH_2O)_2CH_2CH_2I$ (8 equiv.), DMF, room temp., 14 h, 60%; ii, **1**, $CsOH{\cdot}H_2O$ (2 equiv.), MeOH, DMF, room temp., 20 h, 68%

Preparation of bismacrocycles

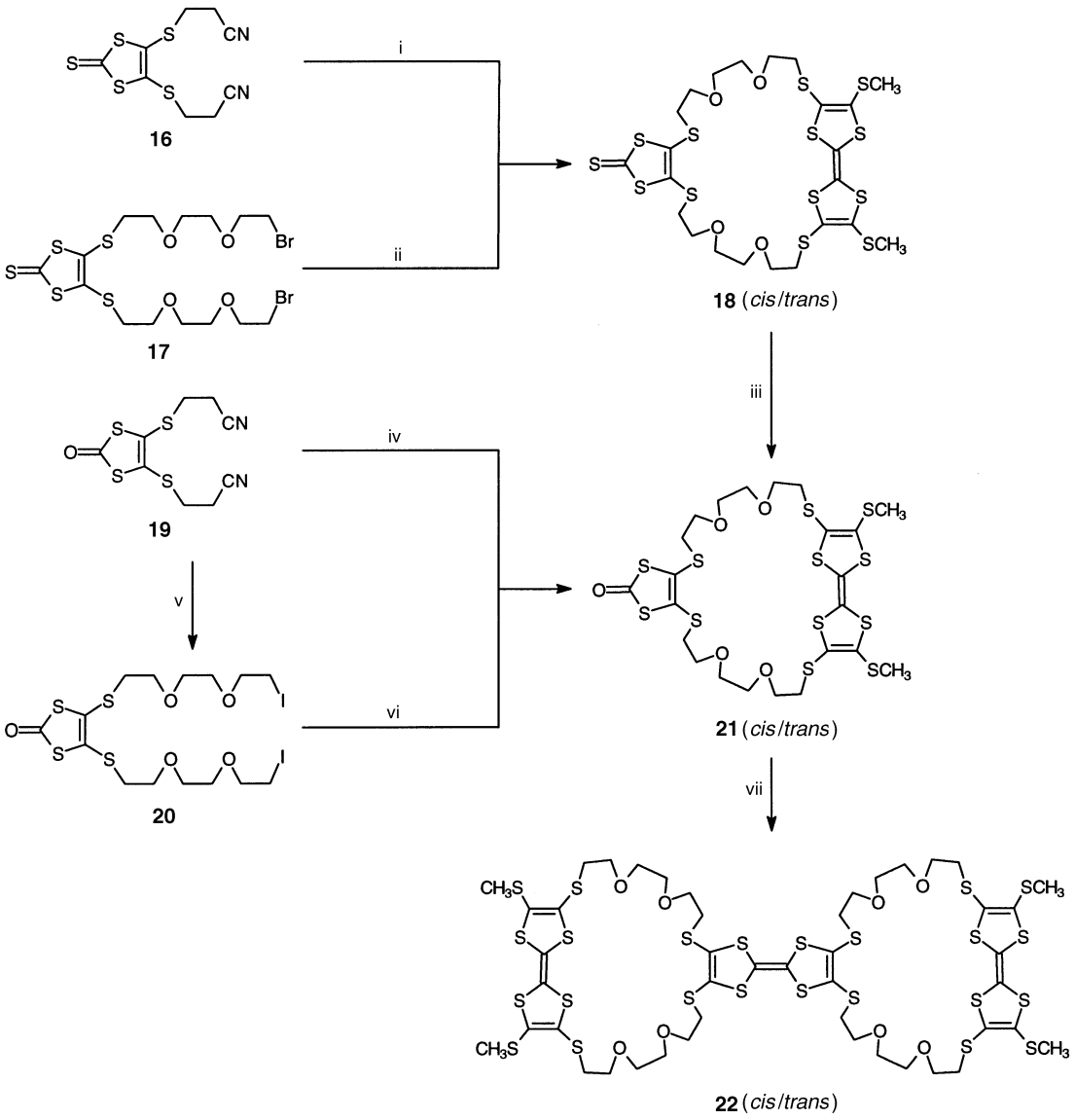
Bismacrocycles **13** and **15** were prepared by a two-step deprotection–cyclization approach (Scheme 4 and 5). Reaction of **8**



Scheme 4 *Reagents and conditions*: i, **3**, $CsOH{\cdot}H_2O$ (2 equiv.), MeOH, DMF, room temp., 20 h, 53%; ii, **8**, $CsOH{\cdot}H_2O$ (2 equiv.), MeOH, DMF, room temp., 20 h, 50%



Scheme 5 *Reagents and conditions*: i, **3**, $CsOH{\cdot}H_2O$ (2 equiv.), MeOH, DMF, room temp., 20 h, 63%; ii, **10**, $CsOH{\cdot}H_2O$ (2 equiv.), MeOH, DMF, room temp., 20 h, 55%



Scheme 6 *Reagents and conditions*: i, **8**, $CsOH{\cdot}H_2O$ (2 equiv.), MeOH, DMF, room temp., 11 h, 40%; ii, **1**, $CsOH{\cdot}H_2O$ (2 equiv.), MeOH, DMF, room temp., 15 h, 31%; iii, $Hg(OAc)_2$, $CHCl_3$–CH_3CO_2H, room temp., 2 h, 95%; iv, **8**, $CsOH{\cdot}H_2O$ (2 equiv.), MeOH, DMF, room temp., 11 h, 16%; v, $CsOH{\cdot}H_2O$ (2 equiv.), MeOH, $I(CH_2CH_2O)_2CH_2CH_2I$ (8 equiv.), DMF, room temp., 1 d, 16%; vi, **1**, $CsOH{\cdot}H_2O$ (2 equiv.), MeOH, DMF, room temp., 15 h, 44% vii, $P(OEt)_3$, PhMe, 120 °C, 4.5 h, 57%

(**10**) and **3** in the presence of 2 equiv. of caesium hydroxide generated monomacrocyclic compound **12** (**14**) in 53% (63%) yield. No 2,3-deprotection–cyclization products were generated since thin-layer chromatography (TLC) indicated that no other important products were formed except for a small amount of insoluble linear oligomers. The reaction of **12** (**14**) with **8** (**10**) resulted in the formation of bismacrocycle **13** (**15**) in 50% (55%) yield.

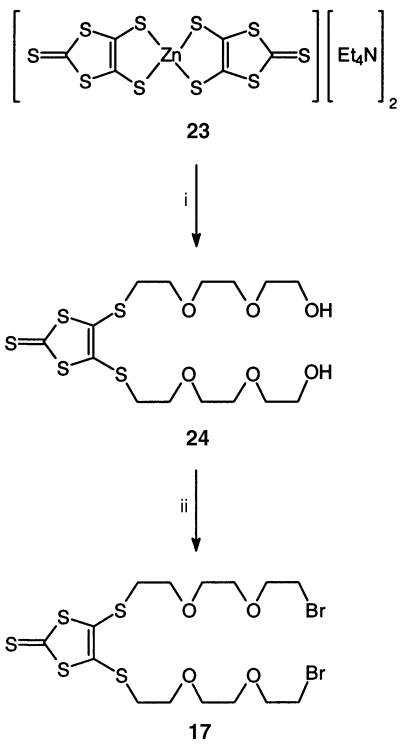
Since it is not possible to selectively deprotect only the 2 and 3 positions of **3,** bismacrocycle **22** had to be prepared from a coupling of the 1,3-dithiole-2-one macrocycle **21** by triethyl phosphite in toluene (Scheme 6). Macrocycle **21** could be prepared by transchalcogenation of the thione **18** using mercury(II) acetate. The instability of the dithiolate of **19** probably causes the low yield in the reaction between **19** and **8**. Dibromide **17** was prepared according to Scheme 7 from the dihydroxy compound **24** by the action of Ph_3P–CBr_4 in 74% yield.

Preparation of a TTF-based ribbon system

Because of its tetravalency, the TTF unit represents an attractive building block for preparation of ribbon type systems. By the repeated deprotection–cyclization protocol, the first TTF-based ribbon compound **28**, having four rings, was prepared (Scheme 8). 2,7-Bis(2-cyanoethylthio)-3,6-[9,10-bis{2-[2-(2-thioethoxy)ethoxy]ethoxy}anthrylene]-1,4,5,8-tetrathiafulvalene **25** was chosen as the starting material because a TTF-based bismacrocyclic compound incorporating two 9,10-dioxyanthracene units was used successfully for preparation of TTF-catenanes.[6] Thus, the reaction of **25** with excess of 1,2-bis(2-iodoethoxy)ethane in DMF at room temperature afforded compound **26**, the key intermediate, in 75% yield. Under high dilution conditions, **26** reacted with **3** affording bismacrocycle **27** in 59% yield. Similarly, the reaction of **27** and **26** resulted in the formation of tetracyclic compound **28** in 38% yield.

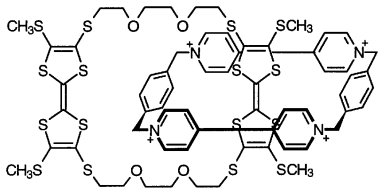
Preparation of catenanes

Catenanes were prepared by treating the macrocycle with 1,1′-[1,4-phenylenebis(methylene)]bis-4,4′-bipyridinium bis(hexafluorophosphate) **29**–$2PF_6$ and 1,4-bis(bromomethyl)benzene **30** in DMF and subjecting the mixture to 10 kbar for 4 d.[9] The catenation of macrocycles **6** and **7** is shown in Scheme 9, affording [2]catenanes **31**-$4PF_6$ and **32**-$4PF_6$, respectively. The small cavity catenane **31**-$4PF_6$ is less flexible than **32**-$4PF_6$ as evidenced

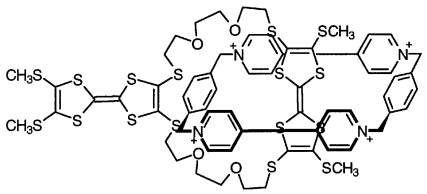


Scheme 7 *Reagents and conditions*: i, $I(CH_2CH_2O)_2CH_2CH_2OH$ (6 equiv.), MeCN, reflux, 1.5 h, 56%; ii, CBr_4, PPh_3, CH_2Cl_2, room temp., 1 d, 74%

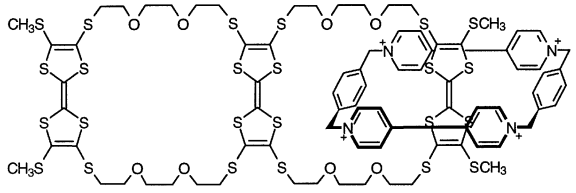
by ^{1}H NMR and UV spectroscopy. The products of catenation of macrocycles **9**, **11**, **13** and **22** are shown below and the yields are given in Table 1. The positions of the tetracationic cyclophane cyclobis(paraquat-*p*-phenylene) (*blue box*) in the catenanes produced from the bismacrocycles have been concluded from the ^{1}H NMR spectra. Any selection of a *cis*/*trans* isomer in the complexation process is not observed for any of these macrocycles. The bis[2]catenane **36**–$8PF_6$ was only isolated as an impure minor product and assigned by its ES mass spectrum. Bismacrocycle **15** exclusively gives a *cis*-catenane in 20% yield under ultra-high pressure.[4c] Thus, two peripheral TTFs and not only one as in the monomacrocycle **11** are necessary for the selection of a single isomer. As has previously been shown, the yields of catenation are strongly affected by electronic and structural features,[4d] and the formation of the precatenane problably occurs with different yields depending on the conformation of the isomers.



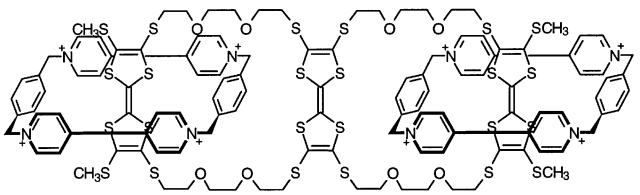
33-$4PF_6$ (*cis/trans*)



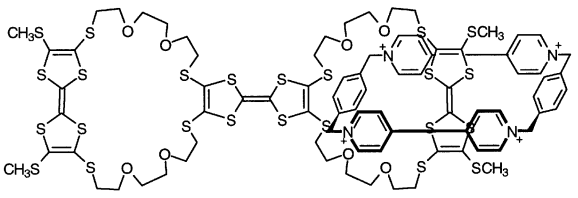
34-$4PF_6$ (*cis/trans*)



35-$4PF_6$ (*cis/trans*)



36-$8PF_6$ (*cis/trans*)



37-$4PF_6$ (*cis/trans*)

Table 1 Product yields

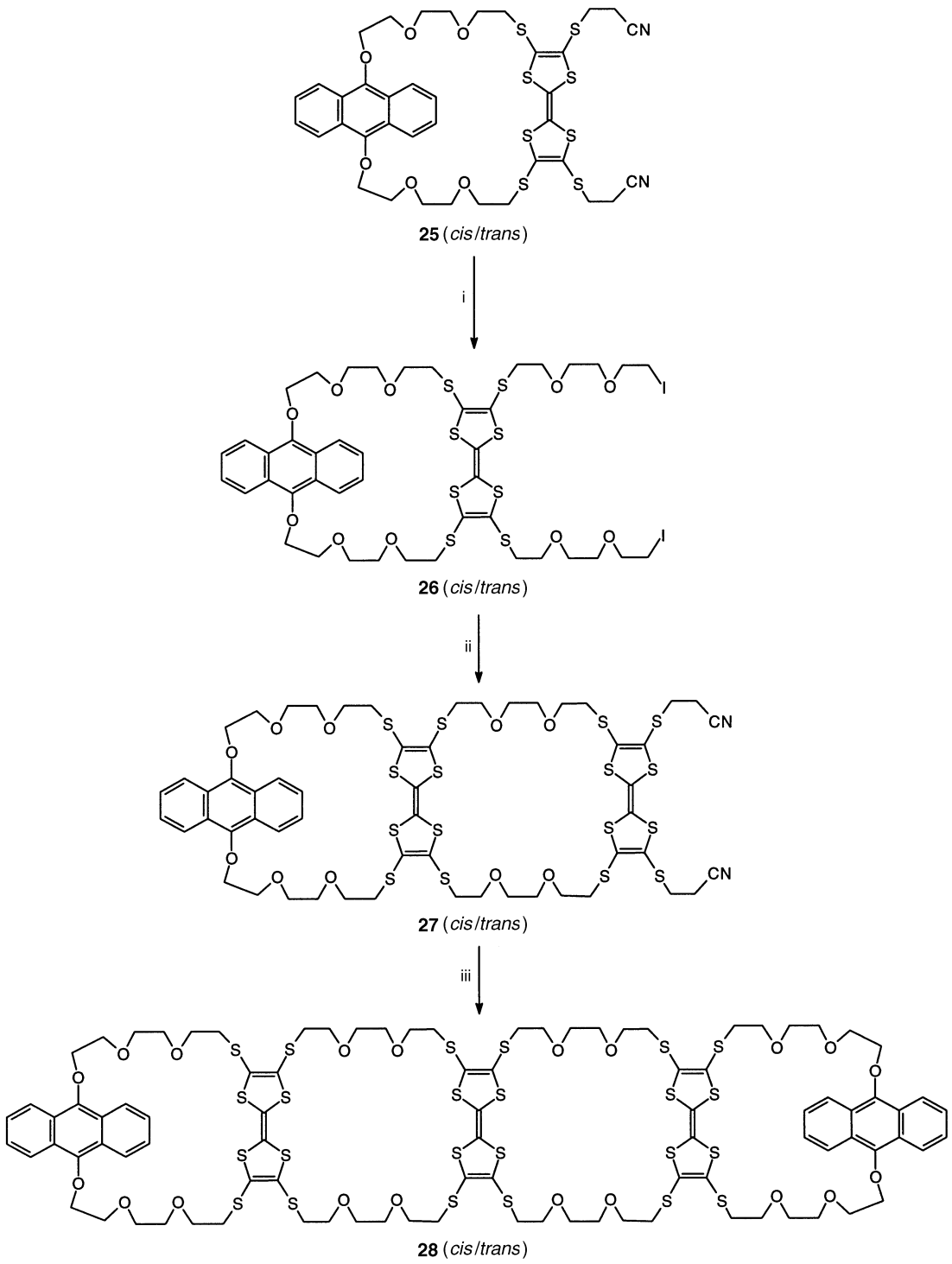
	Yield (%)
31-$4PF_6$	50
32-$4PF_6$	45
33-$4PF_6$	16
34-$4PF_6$	7
35-$4PF_6$	9
36–$8PF_6$	<3
37-$4PF_6$	9

Electrospray mass spectrometry (ESMS)

The catenanes were characterized by ESMS, and the data are listed in Table 2. It can be seen that the compounds give peaks for $[M-4PF_6]^{4+}$, $[M-3PF_6]^{3+}$ and $[M-2PF_6]^{2+}$. Small peaks due to fragmentation of the catenane structure can also be seen in the spectra. These peaks are more evident in the daughter ion spectra (ESMS/MS) of selected parent ions (Table 3). Collisional activation of $[M-nPF_6]^{n+}$ by argon results in fragmentation of the supramolecular structure. For **34**-$4PF_6$ the ESMS and ESMS/MS spectra are shown in Fig. 1. The peaks can be explained by the mechanisms in Scheme 10. The breakdown of the tetracationic cyclophane is accompanied by one or two electron transfers from the macrocycle to the cyclophane. A similar fragmentation pattern is observed for all the catenanes. Thus, ESMS/MS presents a very powerful tool for analysing catenanes of this type.

^{1}H NMR Spectroscopy

The chemical shifts of the a- and b-protons of the tetracationic cyclophanes are listed in Table 4. Catenanes **31**-$4PF_6$ and **32**-$4PF_6$ both show different inner and outer a- and b-protons, but the inner protons of the small cavity catenane **31**-$4PF_6$ are also different due to decreased flexibility. The b-protons show large upfield shifts, but the most dramatic shifts are seen for the 4-H naphthalene protons, which move upfield to *ca.* 2.4 ppm. This large shift is in accordance with published results.[10] When the tetracationic cyclophane is locked around the TTF unit the SCH_3 groups move *ca.* 0.2 ppm downfield. For both catenanes **35**-$4PF_6$ and **37**-$4PF_6$ it is therefore possible to conclude that the tetracationic macrocycle is interlocked around one of the peripheral TTF units and not around the central TTF unit. When recorded in CD_3CN the SCH_3 protons of the uncomplexed TTF unit in **37**-$4PF_6$ are hidden

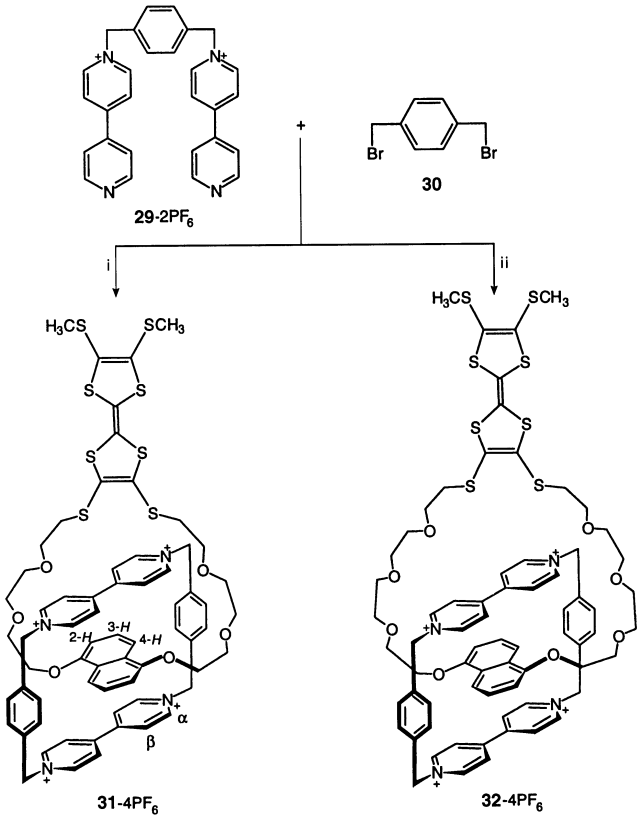


Scheme 8 *Reagents and conditions*: i, $CsOH{\cdot}H_2O$ (2 equiv.), MeOH, $I(CH_2CH_2O)_2CH_2CH_2I$ (8 equiv.), DMF, room temp., 1 h, 75%; ii, **3**, $CsOH{\cdot}H_2O$ (2 equiv.), MeOH, DMF, room temp., 20 h, 59%; iii, **26**, $CsOH{\cdot}H_2O$ (2 equiv.), MeOH, DMF, room temp., 25 h, 38%

under solvent peaks or are very broad peaks. However, in dimethyl sulfoxide (DMSO) the SCH_3 protons of **37**-$4PF_6$ are seen as singlets at *ca.* 2.44 ppm. All the catenanes **33-**, **34-**, **35-**, **37**-$4PF_6$ and **36**–$8PF_6$ are mixtures of *cis*/*trans* isomers.[11] In comparison, catenation of **15** results selectively in the formation of a *cis*-catenane.[4c]

Cyclic voltammetry

The redox behaviour of the compounds is shown in Table 5. Compound **15** exhibits two reversible redox couples ($E_{\frac{1}{2}} = 0.57$ and 0.92 V in CH_2Cl_2), which are typical of the TTF system. This result indicates that there is no interaction between the peripheral and central TTF units of **15**. Although in principle there may be aromatic p–p interactions between the peripheral and central TTF units of compound **13** when they adopt *trans* configurations, **13** also reveals two reversible redox couples at $E_{\frac{1}{2}} = 0.55$ and 0.91 V, respectively. However, a change of solvent to CH_2Cl_2–MeCN (10% v/v) causes a splitting of the first wave. Compound **22** and the monocycles all exhibit two reversible couples. In contrast, compound **28** exhibits more complex electrochemical properties as seen from its cyclic voltammogram shown in Fig. 3. The first two oxidative waves are consistent with the loss of an electron from the peripheral and central TTFs. The third and fourth oxidative waves arise from their second oxidations, whereas the last oxidative wave corresponds to the anthracene giving off one electron. The fact



Scheme 9 *Reagents and conditions*: i, **6**, DMF, room temp., 10 kbar; ii, **7**, DMF, room temp., 10 kbar

that compound **28** shows two reductive waves seems to indicate that the first and second electron reception processes of the peripheral and central TTFs take place simultaneously.

The first oxidation peaks for the TTFs in the catenanes **31**-$4PF_6$ and **32**-$4PF_6$ are increased relative to the free macrocycles. This may be explained by an interaction (electrostatically or by folding) between the TTF moiety and the tetracationic cyclophane. For the other catenanes the first oxidation potential is more or less increased, but the peaks from complexed and uncomplexed TTFs are unresolved.

Charge-transfer absorption

UV–VIS spectra reveal charge-transfer (CT) absorption bands for the catenanes (Table 6). For **31**-$4PF_6$ and **32**-$4PF_6$ CT bands are seen in the naphthalene donor region at a wavelength l_{max} of *ca.* 460–500 nm. For **32**-$4PF_6$ a shoulder at *ca.* 670 nm is seen, which can be ascribed to an interaction between TTF and *blue box*. For **31**-$4PF_6$ only a tail is seen in this region. A reasonable explanation is that **32**-$4PF_6$ has a higher degree of flexibility for such an interaction to be established. For catenanes **33-, 34-, 35-** and **37**-$4PF_6$ the absorptions are much stronger. This can be ascribed to the better donating abilities of TTF compared to naphthalene.

Conclusions

We have demonstrated that a variety of tetrathiafulvalenophanes will form mono[2]catenanes with the cyclic acceptor *blue box*. In most cases the catenanes are obtained as inseparable mixtures of *cis*/*trans* isomers. This problem may be solved by the use of an alternative TTF-type donor without geometrical isomers, or alternatively by using sterically constrained TTF-donors.

Experimental

General methods

All reactions were carried out under an atmosphere of dry N_2. MeOH was distilled from Mg. DMF was allowed to stand over molecular sieves (4 Å) for at least 3 days before use. All reagents were standard grade and used as received. Analytical TLC was performed on Merck DC-Alufolien Kieselgel 60 F_{254} 0.2 mm thickness. Column chromatography was carried out using silica gel 60F (Merck, 9385, 230–400 mesh). Melting points were determined on a Büchi melting point apparatus

Table 2 ESMS data of catenanes

	$[M-nPF_6]^{n+}$ (*n*: 8, 6, 5)	$[M-4PF_6]^{4+}$	$[M-3PF_6]^{3+}$	$[M-2PF_6]^{2+}$	$[M-PF_6]^{+}$
31-$4PF_6$		317	471	779	1703
32-$4PF_6$		339	500	823	
33-$4PF_6$		367	538	879	
34-$4PF_6$		367	538	879	
35-$4PF_6$		507	724	1159	
36–$8PF_6$	319 473 597	782	1091		
37-$4PF_6$		507	724	1159	

Table 3 ESMS/MS data of catenanes

		daughter ions					
		blue box fragment ions					
	parent ion	$[C_8H_8]^{?+}$	$[(C_{18}H_{16}N_2)_n]^{2n+}$ (*n*: 1, 2)	$[C_{28}H_{24}N_4]^{2+}$	$[C_{18}H_{16}N_2]^{\cdot+}$	[macrocycle]$^{2+}$	[macrocycle]$^{?+}$
31-$4PF_6$	317	104	130	208	260	374	748
	471	104		208, 561[a]			748
32-$4PF_6$	339	104	130	208	260	418	836
33-$4PF_6$	367	104	130	208	260	474	948
34-$4PF_6$	367	104	130	208	260	474	948
	538	104	130	208, 561[a]	260		948
35-$4PF_6$	507	104	130	208	260	754	1508
37-$4PF_6$	507			208		754	

[a] $[C_{28}H_{24}N_4, PF_6]^{+}$.

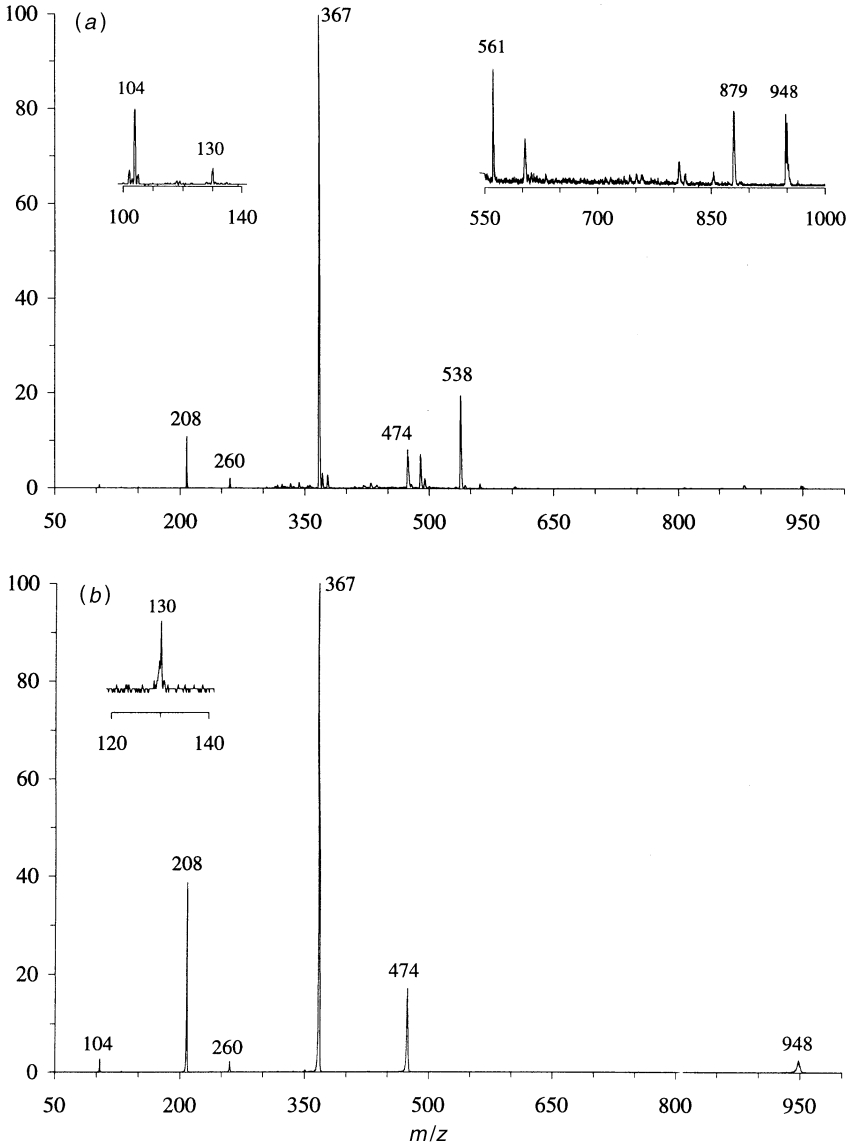
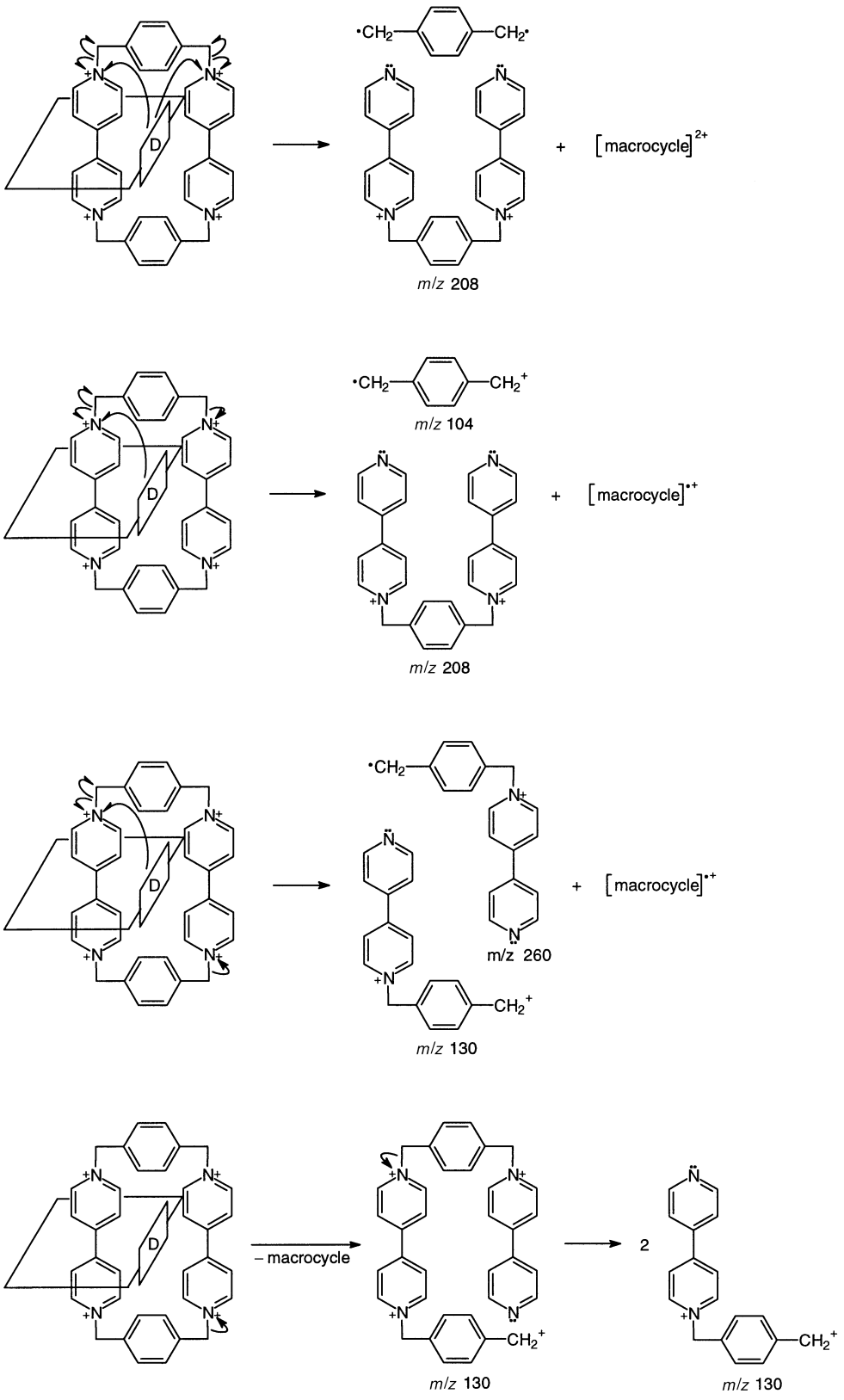


Fig. 1 (*a*) ESMS and (*b*) ESMS/MS selected spectra for **34**-4PF_6 (parent ion *m/z* 367)

and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AC250, a Varian 300 or a Varian 500 spectrometer; all chemical shifts are referenced to Me_4Si; *J* values are in Hz. Electron impact (EI) and fast atom bombardment (FAB) mass spectra were obtained on a Varian MAT 311A instrument and a Kratos MS 60 TC, respectively. Plasma desorption (PD) mass spectra were carried out on a 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 acetonitrile solution. The typical conditions were: flow rate: 10 ml min^{-1}, capillary potential: 5.1 kV, heated capillary: 50–100 °C, sheath gas pressure: 30 psi. ESMS/MS experiments were performed using argon at a typically pressure of 0.7 mTorr. The ion of interest was selected by the first quadrupole, collisionally activated in the second (actually an octapole), and the products analysed by the third quadrupole. CV measurements were carried out with Bu_4NPF_6 as supporting electrolyte, with a sweep rate of 100 mV^{-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 performed at the Microanalytical Laboratory, University of Copenhagen.

1,5-Bis(2-{2-[2-(2-iodoethoxy)ethoxy]ethoxy}ethoxy)-naphthalene 5

A mixture of 1,5-dihydroxynaphthalene (2.04 g, 13 mmol), bis-[2-(2-iodoethoxy)ethyl] ether (47.5 g, 115 mmol), and K_2CO_3 (1.76 g, 13 mmol) in anhydrous acetone (150 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 (10 : 1) as the eluent. **5** (3.40 g, 36%) was obtained as a pale-yellow solid. Mp 36–38 °C; d_H ($CDCl_3$) 3.22 (t, 4 H, *J* 6.9; ICH_2), 3.61–3.82 (m, 20 H; OCH_2), 3.99 (t, 4 H, *J* 4.9; OCH_2), 4.30 (t, 4 H, *J* 4.9; OCH_2), 6.84 [d, 2 H, *J* 7.6; 2-H (naph)], 7.34 [t, 2 H, *J* 8.0; 3-H (naph)], 7.86 [d, 2 H, *J* 8.5; 4-H (naph)]; d_C ($CDCl_3$) 67.92, 69.81, 70.19, 70.63, 70.75, 70.99, 71.94, 105.66, 114.60, 125.03, 126.76, 154.32; MS (EI): *m/z* (%): 732 (M^+, 26), 199



Scheme 10

(26), 155 (100), 45 (10); Found: C, 42.87; H, 5.22; $C_{26}H_{38}I_2O_8$ requires C, 42.64; H, 5.23%.

2,3-Bis(methylthio)-6,7-[naphthalene-1,5-diyldioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)-bisthio]tetrathiafulvalene 6

To a solution of **2** (0.40 g, 0.9 mmol) in DMF (40 ml) was dropwise added a solution of $CsOH{\cdot}H_2O$ (0.32 g, 1.9 mmol) in methanol (10 ml) with stirring over 10 min. The solution was stirred for 1 h. Then this solution and a solution of 1,5-bis{2-[2-(2-iodoethoxy)ethoxy]ethoxy}naphthalene **4**[4d] (0.55 g, 0.9 mmol) in DMF (50 ml) were added simultaneously, during 16 h at room temp., to DMF (100 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

Table 4 Selected ^{1}H NMR resonances (d) of the tetracationic cyclophanes in the catenanes compared to the free tetracationic cyclophane

	a-H			b-H		
free	8.93			8.23		
31-4PF$_6$	8.55 (d, 2H)	8.71 (d, 4H)	8.95 (d, 2H)	7.23 (d, 4H)	7.44 (d, 2H)	7.66 (d, 2H)
32-4PF$_6$	8.64 (d, 4H)	9.08 (d, 4H)		7.24 (d, 4H)	7.37 (d, 4H)	
33-4PF$_6$	9.07–9.16 (8H)			8.08 (m, 8H)[a]		
34-4PF$_6$	9.08 (d, 4H)	9.16 (d, 4H)		7.96–8.28 (8H)[a]		
35-4PF$_6$	9.07–9.14 (8H)			8.07 (m, 8H)		
37-4PF$_6$	9.07 (d, 4H)	9.17 (d, 4H)		7.96–8.28 (8H)		

[a]See Fig. 2

Table 5 Half-wave potentials for the oxidation by cyclic voltammetry

	$E_{\frac{1}{2}}^{1a}$	$E_{\frac{1}{2}}^{2a}$	$E_{\frac{1}{2}}^{1b}$	$E_{\frac{1}{2}}^{2b}$
6	0.52	0.86	0.48	0.74
7	0.53	0.86	0.48	0.75
9	0.55	0.92	0.50[c]	0.86
11	0.55	0.91	0.51	0.85
13	0.55	0.91	0.49 0.58	0.85
15	0.57	0.92	0.53	0.85
22	0.54	0.88	0.51	0.85
31-4PF$_6$			0.56	0.79
32-4PF$_6$			0.57	0.81
33-4PF$_6$			0.57	0.85
34-4PF$_6$			0.54	0.81
35-4PF$_6$			0.54	0.81
36–8PF$_6$			0.55 (*br*)	0.84 (*br*)
37-4PF$_6$			0.52	0.84

[a]Solvent: CH_2Cl_2. [b]Solvent: CH_2Cl_2–MeCN (10% v/v) for macrocycles and MeCN for catenanes. [c]A minor shoulder was seen at $E_{\frac{1}{2}}$ 0.69 V. *br* = broad. Reference electrode: Ag/AgCl; working and counter electrodes: Pt; sweep rate 100 mV s^{-1}; supporting electrolyte: Bu_4NPF_6 0.1 M; conc. of compound: 3×10^{-4} M.

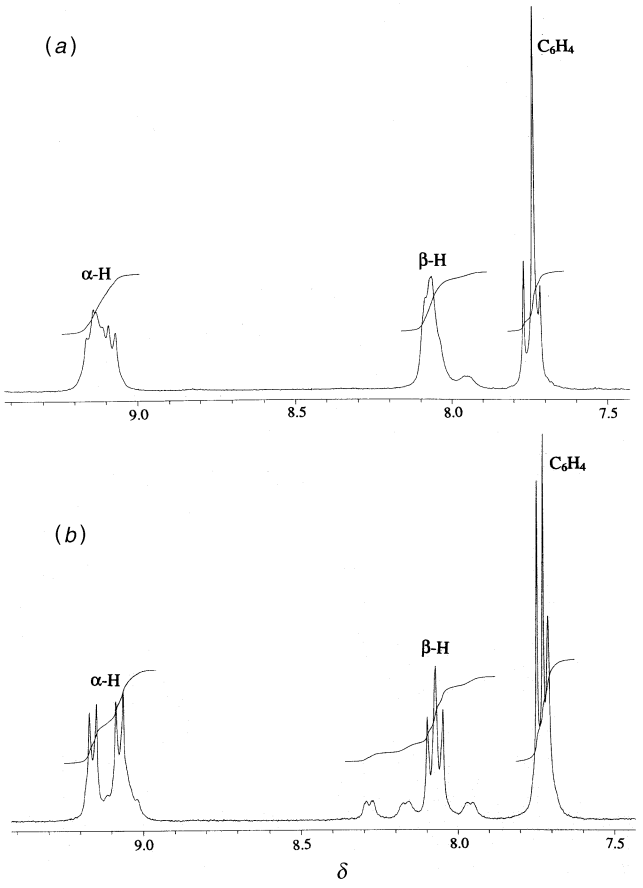


Fig. 2 Selected proton NMR spectra for (*a*) **33**-4PF$_6$ and (*b*) **34**-4PF$_6$

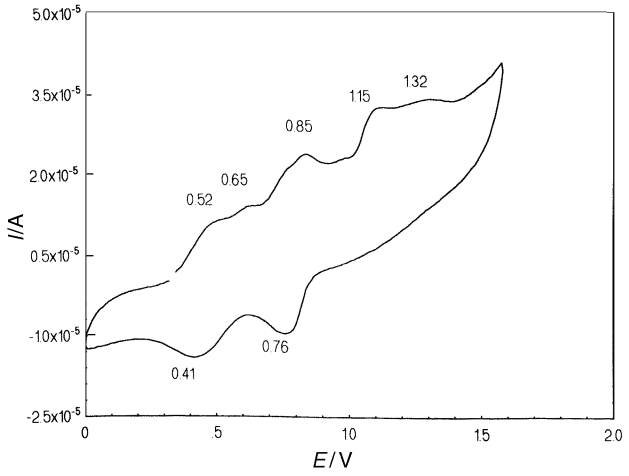


Fig. 3 Cyclic voltammogram of compound **28**

Table 6 Charge-transfer absorptions recorded in MeCN at room temperature

	l_{max}/nm	e/dm^3 mol^{-1} cm^{-1}	l_{max}/nm	e/dm^3 mol^{-1} cm^{-1}
31-4PF$_6$	460 (*sh*)[a]	1500	>650 (*t*)[b]	
32-4PF$_6$	495	1100	670 (*sh*)	620
33-4PF$_6$			799	3500
34-4PF$_6$			786	3300
35-4PF$_6$			801	3700
37-4PF$_6$			786	3400

[a]*sh* = shoulder, [b]*t* = tail.

the organic solution washed with water, saturated aqueous NaCl, and dried ($MgSO_4$). The solvent was then removed and the residue purified by column chromatography (silica gel, CH_2Cl_2–EtOAc 10:1), affording **6** (0.27 g, 42%) as an orange solid. Mp 93.5–95 °C (from ethanol); d_H ($CDCl_3$) 2.41 (s, 6 H; SCH_3), 2.63 (t, 4 H, *J* 6.8; SCH_2), 3.43 (t, 4 H, *J* 6.8; OCH_2), 3.55 (m, 4 H; OCH_2), 3.72 (m, 4 H; OCH_2), 3.96 (m, 4 H; OCH_2), 4.39 (m, 4 H; OCH_2), 6.92 [d, 2 H, *J* 7.6; 2-H (naph)], 7.36 [t, 2 H, *J* 8.0; 3-H (naph)], 7.89 [d, 2 H, *J* 8.4; 4-H (naph)]; MS (FAB): *m*/*z*: 748 (M^+); Found: C, 47.89; H 4.65; $C_{30}H_{36}O_6S_8$ requires C, 48.10; H, 4.84%.

2,3-Bis(methylthio)-6,7-[naphthalene-1,5-diyldioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)bisthio]tetrathiafulvalene 7

Compound **7** was prepared from **2** and **5** in 51% yield as an orange oil. d_H ($CDCl_3$) 2.41 (s, 6 H; SCH_3), 2.81 (t, 4 H, *J* 6.8; SCH_2), 3.43–3.52 (m, 8 H; OCH_2), 3.56–3.60 (m, 4 H; OCH_2), 3.64–3.69 (m, 4 H; OCH_2), 3.76–3.80 (m, 4 H; OCH_2), 3.99 (t, 4 H, *J* 4.5; OCH_2), 4.35 (t, 4 H, *J* 4.5; OCH_2), 6.89 [d, 2 H, *J* 7.6; 2-H (naph)], 7.35 [t, 2 H, *J* 8.1; 3-H (naph)], 7.88 [d, 2 H, *J* 8.4; 4-H (naph)]; d_C ($CDCl_3$) 18.84, 35.03, 67.90, 69.50, 69.60, 70.15, 70.30, 70.49, 70.86, 105.77, 110.43, 110.75, 114.44, 124.93, 126.69, 127.23, 127.43, 154.22; MS (FAB): *m*/*z*: 836 (M^+);

Found: C, 48.67; H, 5.08; $C_{34}H_{44}O_8S_8$ requires C, 48.78; H, 5.30%.

2,7(6)-Bis(methylthio)-3,6(7)-bis{2-[2-(2-iodoethoxy)ethoxy]-ethylthio}tetrathiafulvalene 8, *cis/trans*

A solution of $CsOH·H_2O$ (1.48 g, 8.8 mmol) in methanol (10 ml) was added to a solution of **1** (1.86 g, 4.0 mmol) in DMF (100 ml) with stirring at room temp. in 10 min. After 1 h, 1,2-bis(2-iodoethoxy)ethane (29.6 g, 80 mmol) was added and the mixture was stirred for 12 h. The reaction mixture was concentrated *in vacuo*. CH_2Cl_2 (200 ml) was added, and the organic phase was washed with water, saturated aqueous NaCl, and dried ($MgSO_4$). Concentration *in vacuo* gave an oil which was chromatographed on silica gel using CH_2Cl_2–AcOEt (40:1) as an eluent. Isolation of the main fraction gave compound **5** (2.66 g, 79%) as an orange oil. d_H ($CDCl_3$) 2.44 (s, 6 H; SCH_3), 3.01 (t, 4 H, *J* 6.7; SCH_2), 3.27 (t, 4 H, *J* 6.8; ICH_2), 3.66 (m, 8 H; OCH_2), 3.70 (t, 4 H, *J* 6.7; OCH_2), 3.77 (t, 4 H, *J* 6.8; OCH_2); d_C ($CDCl_3$) 2.72, 2.82, 19.00, 29.51, 33.94, 35.36, 68.57, 69.48, 70.06, 70.38, 71.88, 110.48, 110.51, 124.28, 124.43, 130.59, 130.74; MS (EI): *m/z* (%): 844 (M^+, 83), 474 (18), 199 (26), 155 (100), 142 (80), 127 (26); Found: C, 28.76; H, 3.69; $C_{20}H_{30}I_2O_4S_8$ requires C, 28.44; H, 3.59%.

2,3-Bis(methylthio)-6,7-bis{2-[2-(2-iodoethoxy)ethoxy]ethylthio}tetrathiafulvalene 10

Compound **10** was prepared in a similar way from **2** and 1,2-bis(2-iodoethoxy)ethane in 60% yield as an orange oil. d_H ($CDCl_3$) 2.42 (s, 6 H; SCH_3), 3.04 (t, 4 H, *J* 6.7; SCH_2), 3.25 (t, 4 H, *J* 6.8; ICH_2), 3.64 (m, 12 H; OCH_2), 3.68 (t, 4 H, *J* 5.1; OCH_2); d_C ($CDCl_3$) 2.96, 19.16, 35.41, 70.04, 70.11, 70.43, 71.92, 110.38, 110.90, 127.36, 127.81; MS (EI): *m/z* (%): 844 (M^+, 55), 570 (19), 474 (70), 386 (33), 155 (100), 142 (75); Found: C, 28.60; H, 3.55; $C_{20}H_{30}I_2O_4S_8$ requires C, 28.43; H, 3.59%.

2,7(6)-Bis{2-[2-(2-iodoethoxy)ethoxy]ethylthio}-3,6(7)-[anthracene-9,10-diyldioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)bisthio]tetrathiafulvalene 26, *cis/trans*

Compound **26** was prepared in a similar way from **25**[6] and 1,2-bis(2-iodoethoxy)ethane in 75% yield as a semicrystalline orange solid. d_H ($CDCl_3$) 2.82–3.20 (m, 12 H; ICH_2, SCH_2), 3.23–3.50 (m, 4 H; OCH_2), 3.52–4.00 (m, 28 H; OCH_2), 4.32–4.40 (m, 4 H; OCH_2), 7.39–7.53 [m, 4 H; 1-H (anth)], 8.40–8.47 [m, 4 H; 2-H (anth)]; d_C ($CDCl_3$) 2.93, 2.98, 35.38, 35.42, 35.56, 35.65, 69.69, 69.81, 70.01, 70.06, 70.17, 70.31, 70.42, 70.60, 70.69, 70.83, 71.39, 71.58, 71.76, 71.88, 74.86, 74.99, 109.71, 109.89, 122.71, 122.78, 125.03, 125.07, 125.27, 125.31, 127.19, 127.29, 128.27, 128.69, 146.96, 146.99; MS (FAB): *m/z*: 1254 (M^+); Found: C, 42.25; H; 4.59; $C_{44}H_{56}I_2O_{10}S_8$ requires C, 42.10; H, 4.51%.

2,7(6)-Bis(methylthio)-3,6(7)-[2,7(6)-bis(methylthio)-tetrathiafulvalene-3,6(7)-diylbisthiobis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)bisthio]tetrathiafulvalene 9, *cis/trans*

Compound **9** was prepared from **1** and **8** in 80% yield as an orange oil. d_H ($CDCl_3$) 2.44 (m, 12 H; SCH_3), 2.96–3.03 (m, 8 H; SCH_2), 3.65–3.73 (m, 16 H; OCH_2); d_C ($CDCl_3$) 19.04, 19.08, 19.12, 35.09, 35.16, 35.30, 35.39, 68.64, 69.53, 70.09, 70.20, 70.46, 70.53, 70.58, 110.77, 110.80, 111.11, 124.22, 124.48, 124.95, 124.99, 130.20, 131.13, 131.55; MS (FAB): *m/z*: 948 (M^+); Found: C, 35.73, H; 3.83; $C_{28}H_{36}O_4S_{16}$ requires C, 35.42; H, 3.82%.

2,3-Bis(methylthio)-6,7-[2,7(6)-bis(methylthio)-tetrathiafulvalene-3,6(7)-diylbisthiobis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)bisthio]tetrathiafulvalene 11, *cis/trans*

Compound **11** was prepared from **1** and **10** in 68% yield as an orange oil. d_H ($CDCl_3$) 2.43 (s, 6 H; SCH_3), 2.45 (m, 6 H; SCH_3), 2.97–3.06 (m, 8 H; SCH_2), 3.63–3.74 (m, 16 H; OCH_2); d_C($CDCl_3$) 19.07, 19.11, 35.04, 35.51, 35.55, 35.66, 69.94, 69.99, 70.16, 70.34, 70.38, 70.48, 70.60, 70.62, 110.57, 111.20, 111.30, 124.12, 124.81, 127.48, 127.89, 128.15, 130.46, 131.87; MS (FAB): *m/z*: 948 (M^+); Found: C, 35.65; H, 3.82; $C_{28}H_{36}O_4S_{16}$ requires C, 35.42; H, 3.82%.

2,7(6)-Bis(2-cyanoethylthio)-3,6(7)-[2,7(6)-bis(methylthio)-tetrathiafulvalene-3,6(7)-diylbisthiobis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)bisthio]tetrathiafulvalene 12, *cis/trans*

Compound **12** was prepared from **3** and **8** in 53% yield as an orange oil. d_H ($CDCl_3$) 2.45 (m, 6 H; SCH_3), 2.69–2.76 (m, 4 H; CH_2CN), 2.97–3.10 (m, 12 H; SCH_2), 3.65 (m, 8 H; OCH_2), 3.69–3.76 (m, 8 H; OCH_2); d_C ($CDCl_3$) 14.12, 18.48, 18.72, 19.08, 19.14, 19.17, 20.94, 25.89, 29.59, 31.28, 31.36, 35.19, 35.29, 35.49, 35.61, 35.70, 51.10, 60.26, 70.06, 70.10, 70.48, 70.57, 70.62, 110.43, 110.59, 117.50, 117.59, 122.90, 123.01, 123.35, 124.29, 124.60, 124.68, 130.77, 131.22, 132.78, 133.10; MS (FAB): *m/z*: 1026 (M^+); Found: C, 37.25; H, 3.72; N, 2.88; $C_{32}H_{38}N_2O_4S_{16}$ requires C, 37.40; H, 3.73; N, 2.73%.

2,7(6):3,6(7)-Bis[2,7(6)-bis(methylthio)tetrathiafulvalene-3,6(7)-diylbisthiobis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)bisthio]tetrathiafulvalene 13, *cis/trans*

Compound **13** was prepared from **8** and **12** in 50% yield as a semicrystalline orange oil. d_H ($CDCl_3$) 2.44 (m, 12 H; SCH_3), 2.97–3.02 (m, 16 H; SCH_2), 3.60–3.74 (m, 32 H; OCH_2); MS (PD): *m/z*: 1509.2 (M^+); Found: C, 36.74; H, 4.12; $C_{46}H_{60}O_8S_{24}$ requires C, 36.57; H, 4.01%.

2,7(6)-Bis(2-cyanoethylthio)-3,6(7)-[2,3-bis(methylthio)tetrathiafulvalene-6,7-diylbisthiobis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)bisthio]tetrathiafulvalene 14, *cis/trans*

Compound **14** was prepared from **3** and **10** in 63% yield as an orange oil. d_H ($CDCl_3$) 2.43 (s, 6 H; SCH_3), 2.74 (m, 4 H; CH_2CN), 3.07 (m, 12 H; SCH_2), 3.64 (m, 12 H; OCH_2), 3.71 (m, 4 H; OCH_2); d_C($CDCl_3$) 14.11, 18.71, 18.85, 19.09, 20.91, 29.57, 31.31, 31.42, 35.40, 35.47, 35.68, 60.23, 69.95, 70.12, 70.40, 70.57, 70.60, 70.66, 110.96, 111.29, 117.47, 117.64, 123.17, 124.11, 127.39, 127.74, 127.99, 128.71, 130.77, 132.53, 132.59; MS (PD): *m/z*: 1027.5 (M^+); Found: C, 37.48; H, 3.71; N, 3.01; $C_{32}H_{38}N_2O_4S_{16}$ requires C, 37.40; H, 3.73; N, 2.73%.

2,7(6):3,6(7)-Bis[2,3-bis(methylthio)tetrathiafulvalene-6,7-diylbisthiobis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)bisthio]tetrathiafulvalene 15, *cis/trans*

Compound **15** was prepared from **10** and **14** in 55% yield as a semicrystalline orange oil. d_H ($CDCl_3$) 2.43 (s, 12 H; SCH_3), 3.02 (m, 16 H; SCH_2), 3.63–3.73 (m, 32 H; OCH_2); d_C ($CDCl_3$) 19.09, 26.79, 29.55, 30.07, 35.20, 35.41, 35.64, 69.97, 70.10, 70.37, 70.55, 70.66, 110.40, 110.78, 111.40, 127.36, 127.58, 127.77, 127.00, 128.62; MS (PD): *m/z*: 1509.2 (M^+); Found: C, 36.33; H, 3.74; $C_{46}H_{60}O_8S_{24}$ requires C, 36.57; H, 4.01.

4,5-Bis{2-[2-(2-hydroxyethoxy)ethoxy]ethylthio}-1,3-dithiole-2-thione 24

To a solution of bis(tetraethylammonium) bis(2-thioxo-1,3-dithiole-4,5-dithiolato)zincate **23** (2.76 g, 3.8 mmol) in MeCN (100 ml) was added 2-[2-(2-iodoethoxy)ethoxy]ethanol (6.0 g, 23 mmol) and the mixture was refluxed for 90 min. The resulting solution was cooled to room temp. and concentrated *in vacuo*. The product was redissolved in CH_2Cl_2 (500 ml), washed with water, and dried ($MgSO_4$). The solvent was then removed and the residue purified by column chromatography (silica gel, CH_2Cl_2–MeOH 9:1), affording **24** (2.00 g, 56%) as an orange oil. d_H ($CDCl_3$) 2.63 (t, 2 H, *J* 5.7; O*H*), 3.09 (t, 4 H, *J* 6.3; SCH_2), 3.59–3.76 (m, 20 H; OCH_2); d_C ($CDCl_3$) 36.08, 61.71, 69.82, 70.32, 70.58, 72.57, 136.61, 211.01; MS (EI): *m*/*z* (%): 462 (M^+, 100), 429 (81), 198 (38), 121 (36), 89 (75); Found: C, 38.69; H, 5.25; $C_{15}H_{26}O_6S_5$ requires C, 38.94; H, 5.66%.

4,5-Bis{2-[2-(2-bromoethoxy)ethoxy]ethylthio}-1,3-dithiole-2-thione 17

To a solution of **24** (1.94 g, 4.2 mmol) in CH_2Cl_2 (100 ml) was added CBr_4 (2.92 g, 8.8 mmol). Then PPh_3 (2.85 g, 10.9 mmol) was added during 2 h. The reaction mixture was left overnight with stirring, whereupon it was concentrated *in vacuo* and the residue subjected to column chromatography (silica gel, CH_2Cl_2–MeOH 9:1), affording **17** (1.82 g, 74%) as an orange oil. d_H ($CDCl_3$) 3.09 (t, 4 H, *J* 6.3; SCH_2), 3.48 (t, 4 H, *J* 6.2; BrCH_2), 3.64–3.84 (m, 16 H; OCH_2); MS (EI): *m*/*z* (%): 588 (M^+, 25), 393 (65), 223 (23), 147 (29), 121 (32), 107 (100), 88 (24); Found: C, 30.64; H 3.97; $C_{15}H_{24}Br_2O_4S_5$ requires C, 30.62; H, 4.11%.

4,5-Bis{2-[2-(2-iodoethoxy)ethoxy]ethylthio}-1,3-dithiole-2-one 20

To a solution of 4,5-bis(2′-cyanoethylthio)-1,3-dithiole-2-one **19** (1.24 g, 4.3 mmol) in DMF (50 ml) was dropwise added a solution of $CsOH{\cdot}H_2O$ (1.52 g, 9.1 mmol) in methanol (10 ml) under stirring in 30 min. After stirring for 30 min 1,2-bis(2-iodoethoxy)ethane (15.9 g, 43 mmol) was added. The reaction mixture was left overnight with stirring, whereupon it was concentrated *in vacuo*. CH_2Cl_2 (200 ml) was added, and the organic solution washed with water, saturated aqueous NaCl, and dried ($MgSO_4$). The solvent was then removed and the residue purified by column chromatography (silica gel, CH_2Cl_2–EtOAc 10:1), affording **20** (0.46 g, 16%) as an orange oil. d_H ($CDCl_3$) 3.07 (t, 4 H, *J* 6.5; SCH_2), 3.27 (t, 4 H, *J* 6.8; ICH_2), 3.65–3.79 (m, 16 H; OCH_2); MS (FAB): *m*/*z*: 666 (M^+); Found: C, 27.12; H, 3.11; $C_{15}H_{24}I_2O_5S_4$ requires C, 27.04; H 3.63%.

2,7(6)-Bis(methylthio)-3,6(7)-[2-thioxo-1,3-dithiole-4,5-diyl-bisthiobis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)bisthio]tetrathiafulvalene 18, *cis*/*trans*

Method 1: **18** was prepared from **8** and **16** in 40% yield as an orange oil. d_H ($CDCl_3$) 2.44 (m, 6 H; SCH_3) 2.95–3.11 (m, 8 H, *J* 7.0; SCH_2), 3.62–3.76 (m, 16 H; OCH_2); MS (FAB): *m*/*z*: 786 (M^+); Found: C, 34.83; H, 3.57; $C_{23}H_{30}O_4S_{13}$ requires C, 35.09; H, 3.84%.
Method 2: **18** was prepared from **1** and **17** in 31% yield.

2,7(6)-Bis(methylthio)-3,6(7)-[2-oxo-1,3-dithiole-4,5-diyl-bisthiobis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)bisthio]tetrathiafulvalene 21, *cis*/*trans*

Method 1: **21** was prepared from **8** and **19** in 16% yield as an orange oil. d_H ($CDCl_3$) 2.45 (m, 6 H; SCH_3) 2.94–3.10 (m, 8 H; SCH_2), 3.61–3.76 (m, 16 H; OCH_2); MS (FAB): *m*/*z*: 770 (M^+); Found: C, 35.93; H, 3.65; $C_{23}H_{30}O_5S_{12}$ requires C, 35.82; H, 3.92%.
Method 2: **21** was prepared from **1** and **20** in 44% yield.

Method 3: $Hg(OAc)_2$ (0.31 g, 1.0 mmol) was added to a solution of **18** (0.31 g, 0.4 mmol) in chloroform (50 ml) and glacial acetic acid (20 ml). The solution was stirred for 2 h, whereupon it was filtered on Celite. The filtrate was washed with $NaHCO_3$ (aq), water, and dried ($MgSO_4$). The solvent was then removed to afford **21** (0.29 g, 95%).

2,3:6,7-Bis[2,7(6)-bis(methylthio)tetrathiafulvalene-3,6(7)-diylbisthiobis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)bisthio]tetrathiafulvalene 22, *cis*/*trans*

A solution of **21** (0.32 g, 0.4 mmol) in toluene (4 ml) and freshly distilled $P(OEt)_3$ (7 ml) was heated to 120 °C. The mixture was stirred for 4.5 h and then allowed to cool to room temp., whereupon it was concentrated *in vacuo*. The oily residue was subjected to column chromatography (silica gel, CH_2Cl_2–EtOAc 10:1), affording **22** (0.18 g, 57%) as an orange oil. d_H ($CDCl_3$) 2.45 (m, 12 H; SCH_3), 2.95–3.06 (m, 16 H; SCH_2), 3.62–3.74 (m, 32 H; OCH_2); d_C($CDCl_3$) 19.10, 19.14, 34.76, 34.90, 35.08, 35.58, 35.62, 69.83, 69.96, 70.00, 70.19, 70.38, 70.42, 70.51, 70.65, 111.20, 111.27, 124.18, 124.85, 127.92, 128.17, 130.48, 131.88; MS (PD): *m*/*z*: 1510.3 (M^+); MS (FAB): *m*/*z*: 1508 (M^+); Found: C, 37.03; H, 4.06; $C_{46}H_{60}O_8S_{24}$ requires C, 36.58; H, 4.00%.

2,7(6)-[Anthracene-9,10-diyldioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)bisthio]-3,6(7)-[2,7(6)-bis(2-cyanoethylthio)tetrathiafulvalene-3,6(7)-diylbisthiobis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)-dioxybis(ethane-1,2-diyl)bisthio]tetrathiafulvalene 27, *cis*/*trans*

Compound **27** was prepared from **3** and **26** in 59% yield as a dark-orange oil. d_H ($CDCl_3$) 2.65–2.72 (m, 4 H; CH_2CN), 2.98–3.04 (m, 16 H; SCH_2), 3.43–3.87 (m, 28 H; OCH_2), 3.93–3.99 (m, 4 H; OCH_2), 4.33–4.39 (m, 4 H; OCH_2), 7.41–7.53 [m, 4 H; 1-H (anth)], 8.38–8.47 [m, 4 H; 2-H (anth)]; MS (FAB): *m*/*z*: 1436 (M^+); Found: C, 46.80; H, 4.32; N, 1.99; $C_{56}H_{64}N_2O_{10}S_{16}$ requires C, 46.76; H, 4.49; N, 1.95%.

2,7(6):3,6(7)-Bis{3,6(7)-[anthracene-9,10-diyldioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)-bisthio]tetrathiafulvalene-2,7(6)-diylbisthiobis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)-bisthio}tetrathiafulvalene 28, *cis*/*trans*

Compound **28** was prepared in 38% yield from **26** and **27** as a dark-orange semicrystalline oil. d_H ($CDCl_3$) 2.83–3.12 (m, 24 H; SCH_2), 3.43–3.86 (m, 72 H; OCH_2), 3.96 (m, 8 H; OCH_2), 4.37 (m, 8 H; OCH_2), 7.26–7.53 [m, 8 H; 1-H (anth)], 8.39 [m, 8 H; 2-H (anth)]; MS (FAB): *m*/*z*: 2328 (M^+); Found: C, 48.66; H, 5.33; $C_{94}H_{112}O_{20}S_{24}$ requires C, 48.42; H, 4.85%.

{2,3-Bis(methylthio)-6,7-[naphthalene-1,5-diyldioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)-bisthio]tetrathiafulvalene}–{5,12,19,26-tetraazoniaheptacyclo-[24.2.2.2.$2^{2,5}$.$2^{7,10}$.$2^{12,15}$.$2^{16,19}$.$2^{21,24}$]tetraconta-2,4,7,9,12,14,16,18,21,23,26,28,29,31,33,35,37,39-octadecaene tetrakis(hexafluorophosphate)} (31-4PF_6)

A solution of **6** (0.120 g, 0.16 mmol), **29**–2PF_6 (0.340 g, 0.48 mmol), and **30** (0.148 g, 0.56 mmol) in DMF (12 ml) was transferred to a high-pressure-reaction Teflon tube, which was then compressed (10 kbar) at room temp. for 4 d. The solvent was then removed *in vacuo* to give a residue, which was subjected to column chromatography on silica gel with MeOH–aqueous NH_4Cl (2 M)–$MeNO_2$ (7:2:1) as the eluent. Collection of the violet fraction afforded a violet 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 methanol, and saturated aqueous NH_4PF_6 was added until precipitation was complete. The solid product was removed by filtration (Celite), washed with water, pumped dry, and then extracted with acetonitrile. After the solvent was removed *in vacuo*, **31**-4PF_6 (0.148 g, 50%) was obtained as a dark violet solid. Mp 213–215 °C (decomp.); d_H (CD_3CN) 2.34 (s, 6 H; SCH_3), 2.37 [d, 2 H, *J* 8.5; 4-H (naph)], 2.42–2.63 (m, 4 H; SCH_2), 3.48–3.65 (m, 4 H; OCH_2), 3.74–4.03 (m, 10 H; OCH_2), 4.18–4.26 (m, 2 H; OCH_2), 4.38–4.44 (m, 2 H; OCH_2), 4.61–4.69 (m, 2 H; OCH_2), 5.60–5.80 (m, 8 H; NCH_2), 5.96 [t, 2 H, *J* 8.1; 3-H (naph)], 6.40 [d, 2 H, *J* 7.8; 2-H (naph)], 7.23 [d, 4 H, *J* 6.4; b-H), 7.44 [d, 2 H, *J* 7.0; b-H), 7.66 [d, 2 H, *J* 6.6; b-H), 7.95–8.04 (m, 8 H; C_6H_4), 8.55 [d, 2 H, *J* 6.5; a-H), 8.71 [d, 4 H, *J* 6.2; a-H), 8.95 [d, 2 H, *J* 6.0; a-H); MS (ES): *m/z*: 130, 317 $[M-4PF_6]^{4+}$, 471 $[M-3PF_6]^{3+}$, 748 [macrocycle]$^{?+}$, 779 $[M-2PF_6]^{2+}$, 1703 $[M-PF_6]^{+}$; MS/MS (ES): parent ion: *m/z*: 317, daughter ions: *m/z*: 104, 130, 208, 260, 374, 748; parent ion: *m/z*: 471, daughter ions: *m/z*: 104, 208, 561, 748; Found: C, 41.94; H, 3.66; N, 2.95; $C_{66}H_{68}F_{24}N_4O_6P_4S_8$,$2H_2O$ requires C, 42.04; H, 3.85; N, 2.97%.

{2,3-Bis(methylthio)-6,7-[naphthalene-1,5-diyldioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)-dioxybis(ethane-1,2-diyl)bisthio]tetrathiafulvalene}{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)} (32-4PF_6)

A solution of **7** (0.120 g, 0.14 mmol), **29**–2PF_6 (0.304 g, 0.43 mmol) and **30** (0.132 g, 0.50 mmol) in DMF (12 ml) was subjected to 10 kbar at room temp. for 4 d. The solvent was then removed *in vacuo* to give a residue, which was subjected to column chromatography on silica gel with MeOH–aqueous NH_4Cl (2 M)–$MeNO_2$ (7:2:1) as the eluent. Collection of the brown fraction afforded a brown solid after evaporation of the solvent *in vacuo*. The solid was washed with water, whereupon it was dissolved in $MeNO_2$ (20 ml). Then it was washed with saturated aqueous NH_4PF_6 and finally with water. Evaporation of the solvent afforded **32**-4PF_6 (0.126 g, 45%) as a brown solid; Mp > 250 °C; d_H (CD_3CN) 2.42 [m, 10 H; SCH_3, 4-*H* (naph), SCH_2], 2.77 (s, 1 H; SCH_2), 2.89 (s, 1 H; SCH_2), 3.16 (m, 4 H; OCH_2), 3.47 (m, 4 H; OCH_2),), 3.70 (m, 4 H; OCH_2), 3.89 (m, 4 H; OCH_2), 4.03 (m, 4 H; OCH_2), 4.21 (m, 4 H; OCH_2), 4.32 (m, 4 H; OCH_2), 5.68–5.76 (m, 8 H; NCH_2), 5.99 [t, 2 H, *J* 7.9; 3-*H* (naph)], 6.27 [d, 2 H, *J* 7.8; 2-*H* (naph)], 7.24 [d, 4 H, *J* 5.2; b-H), 7.37 [d, 4 H, *J* 5.2; b-H), 7.95 (s, 4 H; C_6H_4), 8.04 (s, 4 H; C_6H_4), 8.64 [d, 4 H, *J* 6.3; a-H), 9.08 [d, 4 H, *J* 5.0; a-H); MS (FAB): *m/z*: 665 [*blue box*, $PF_6]^{+}$, 836 [macrocycle]$^{+}$, 1501 $[M-3PF_6]^{+}$, 1646 $[M-2PF_6]^{+}$, 1791 $[M-PF_6]^{+}$; MS (ES): *m/z*: 561, 339 $[M-4PF_6]^{4+}$, 418 [macrocycle]$^{2+}$, 500 $[M-3PF_6]^{3+}$, 823 $[M-2PF_6]^{2+}$, 836 [macrocycle]$^{?+}$; MS/MS (ES): parent ion: *m/z*: 339, daughter ions: *m/z*: 104, 130, 208, 260, 418, 836; Found: C, 42.29; H, 3.89; N, 3.00; $C_{70}H_{76}F_{24}N_4O_8P_4S_8$,$2.5H_2O$ requires C, 42.40; H, 4.12; N, 2.83%.

{2,7(6)-Bis(methylthio)-3,6(7)-[2,7(6)-bis(methylthio)tetrathiafulvalene-3,6(7)diylbisthiobis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)bisthio]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)} (33-4PF_6)

A solution of **9** (0.200 g, 0.21 mmol), **29**–2PF_6 (0.446 g, 0.63 mmol), and **30** (0.195 g, 0.74 mmol) in DMF (12 ml) was subjected to 10 kbar at room temp. for 4 d. The solvent was then removed *in vacuo* to give a green residue, which was subjected to column chromatography on silica gel with MeOH–aqueous NH_4Cl (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 dissolved in a minimum amount of MeOH, and saturated aqueous NH_4PF_6 was added until precipitation was complete. The green solid product was removed by filtration, washed with water and pumped dry. Yield: 0.067 g (16%). Mp > 250 °C; d_H (CD_3CN) 2.38 (m, 6 H; SCH_3), 2.57 (m, 6 H; SCH_3), 2.88–3.00 (m, 4 H; SCH_2), 3.07–3.11 (m, 4 H; SCH_2), 3.68–3.87 (m, 16 H; OCH_2), 5.70–5.76 (m, 8 H; NCH_2), 7.72–7.77 (m, 8 H; C_6H_4), 8.08 (m, 8 H; b-H), 9.07–9.16 (m, 8 H; a-H); MS (ES): *m/z*: 104, 130, 208, 260, 561, 367 $[M-4PF_6]^{4+}$, 538 $[M-3PF_6]^{3+}$, 879 $[M-2PF_6]^{2+}$, 948 [macrocycle]$^{?+}$; MS/MS (ES): parent ion: *m/z*: 367, daughter ions: *m/z*: 104, 130, 208, 260, 474, 948; Found: C, 37.11; H, 3.37; N, 2.70; $C_{64}H_{68}F_{24}N_4O_4P_4S_{16}$ requires C, 37.50; H, 3.34; N, 2.73%.

{2,3-Bis(methylthio)-6,7-[2,7(6)-bis(methylthio)tetrathiafulvalene-3,6(7)-diylbisthiobis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)bisthio]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)} (34-4PF_6)

A solution of **11** (0.120 g, 0.13 mmol), **29**–2PF_6 (0.268 g, 0.38 mmol), and **30** (0.117 g, 0.44 mmol) in DMF (12 ml) was subjected to 10 kbar at room temp. for 4 d. The solvent was then removed *in vacuo* to give a green residue, which was subjected to column chromatography on silica gel with MeOH–aqueous NH_4Cl (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 the green solid filtered off. This was then dissolved in a minimum amount of MeOH–H_2O (1:1), and saturated aqueous NH_4PF_6 was added until precipitation was complete. The solid product was removed by filtration (Celite), washed with water, pumped dry, and then extracted with acetonitrile. After the solvent was removed *in vacuo*, **34**-4PF_6 (0.017 g, 7%) was obtained as a green solid. Mp > 250 °C; d_H (CD_3CN) 2.38 (s, 6 H; SCH_3), 2.58 (m, 6 H; SCH_3), 2.69–2.82 (m, 2 H; SCH_2), 2.87 (t, 4 H, *J* 5.5; SCH_2), 3.06 (t, 2 H, *J* 6.1; SCH_2), 3.53–3.88 (m, 16 H; OCH_2), 5.72–5.77 (m, 8 H; NCH_2), 7.71–7.75 (m, 8 H; C_6H_4), 7.96 (d; b-H), 8.06 [d, *J* 7.2; b-H), 8.09 [d, *J* 7.9; b-H), 8.17 (d; b-H), 8.28 (d; b-H), 7.96–8.28 (8 H), 9.08 [d, 4 H, *J* 6.9; a-H), 9.16 [d, 4 H, *J* 6.9; a-H); MS (ES): *m/z*: 104, 130, 208, 260, 561, 367 $[M-4PF_6]^{4+}$, 474 [macrocycle]$^{2+}$; 538 $[M-3PF_6]^{3+}$, 879 $[M-2PF_6]^{2+}$, 948 [macrocycle]$^{?+}$; MS/MS (ES): parent ion: *m/z*: 367, daughter ions: *m/z*: 104, 130, 208, 260, 474, 948; parent ion: *m/z*: 538, daughter ions: *m/z*: 104, 130, 208, 260, 561, 948; Found: C, 37.12; H, 3.22; N, 2.94; $C_{64}H_{68}F_{24}N_4O_4P_4S_{16}$ requires C, 37.50; H, 3.34; N, 2.73%.

{2,7(6):3,6(7)-Bis[2,7(6)-bis(methylthio)-tetrathiafulvalene-3,6(7)-diylbisthiobis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)-dioxybis(ethane-1,2-diyl)bisthio]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* peripheral TTF) tetrakis(hexafluorophosphate)} (35-4PF_6), and {2,7(6):3,6(7)-Bis[2,7(6)-bis(methylthio)-tetrathiafulvalene-3,6(7)-diylbisthiobis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)bisthio]-tetrathiafulvalene (*cis*/*trans*)}-bis{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* peripheral TTFs) tetrakis(hexafluorophosphate)} (36–8PF_6)

A solution of **13** (0.200 g, 0.13 mmol), **29**–2PF_6 (0.374 g, 0.53 mmol), and **30** (0.154 g, 0.58 mmol) in DMF (12 ml) was

subjected to 10 kbar at room temp. for 4 d. The solvent was then removed *in vacuo* to give a green residue, which was subjected to column chromatography on silica gel with MeOH–aqueous NH_4Cl (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*. Changing the eluent to MeOH–aqueous NH_4Cl (2 M)–DMF (4:5:2) afforded a second green fraction which was evaporated *in vacuo*.

The first fraction was worked up as **34**-4PF_6, affording **35**-4PF_6 (0.030 g, 9%) as a green solid. Mp > 250 °C; d_H (CD_3CN) 2.40 (m, 6 H; SCH_3), 2.58 (m, 6 H; SCH_3), 2.90–3.10 (m, 16 H; SCH_2), 3.51–3.86 (m, 32 H; OCH_2), 5.71–5.76 (m, 8 H; NCH_2), 7.71–7.77 (m, 8 H; C_6H_4), 8.07 (m, 8 H; b-H), 9.07–9.14 (m, 8 H; a-H); MS (ES): *m*/*z*: 208, 260, 507 $[M-4PF_6]^{4+}$, 724 $[M-3PF_6]^{3+}$, 1159 $[M-2PF_6]^{2+}$; MS/MS (ES): parent ion: *m*/*z*: 507, daughter ions: *m*/*z*: 104, 130, 208, 260, 754, 1508; Found: C, 37.78; H, 3.55; N, 2.25; $C_{82}H_{92}F_{24}N_4O_8P_4S_{24}$ requires C, 37.72; H, 3.55; N, 2.15%.

Second fraction: The solid was partially dissolved in methanol and filtered. The filtrate was concentrated *in vacuo*. This was then dissolved in a minimum amount water, and saturated aqueous NH_4PF_6 was added until precipitation was complete. The solid product was removed by filtration (Celite), washed with water, pumped dry, and then extracted with acetonitrile. After the solvent was removed *in vacuo*, **36**–8PF_6 (0.010 g, 3%) was obtained as an impure green solid. Mp > 250 °C; MS (ES): *m*/*z*: 319 $[M-8PF_6]^{8+}$, 473 $[M-6PF_6]^{6+}$, 597 $[M-5PF_6]^{5+}$, 782 $[M-4PF_6]^{4+}$, 1091 $[M-3PF_6]^{3+}$.

{2,3:6,7-Bis[2,7(6)-bis(methylthio)tetrathiafulvalene-3,6(7)-diylbisthiobis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)bisthio]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* peripheral TTF) tetrakis(hexafluorophosphate)} (37-4PF_6)

A solution of **22** (0.168 g, 0.11 mmol), **29**–2PF_6 (0.393 g, 0.56 mmol), and **30** (0.161 g, 0.61 mmol) in DMF (12 ml) was subjected to 10 kbar at room temp. for 4 d. The solvent was then removed *in vacuo* to give a green residue. Column chromatography on silica gel followed by preparative chromatography with MeOH–aqueous NH_4Cl (2 M)–DMF (4:5:2) as the eluent afforded a green solid after evaporation of the solvent *in vacuo*. The compound was worked up as described for **36**–8PF_6, affording **37**-4PF_6 (0.025 g, 9%) as a green solid. Mp > 250 °C; d_H (CD_3CN) 2.58 (m, 6 H; SCH_3), 2.76–3.08 (m, 16 H; SCH_2), 3.52–3.85 (m, 32 H; OCH_2), 5.72–5.77 (m, 8 H; NCH_2), 7.71–7.78 (m, 8 H; C_6H_4), 7.96 (m; b-H), 8.07 (m; b-H), 8.17 (m; b-H), 8.28 (m; b-H), 7.96–8.28 (8 H), 9.07 [d, 4 H, *J* 6.8; a-H), 9.17 [d, 4 H, *J* 6.7; a-H); d_H [$(CD_3)_2SO$] 2.44 (m, 6 H; SCH_3), 2.61 (m, 6 H; SCH_3), 2.69–3.23 (m, 16 H; SCH_2), 3.38–3.83 (m, 32 H; OCH_2), 5.82 (m, 8 H; NCH_2), 7.74–7.85 (m, 8 H; C_6H_4), 8.26 (m; b-H), 8.47 (m; b-H), 8.66 (m; b-H), 8.26–8.66 (8 H), 9.48 (m, 4 H; a-H), 9.62 (m, 4 H; a-H); MS (ES): *m*/*z*: 130, 507 $[M-4PF_6]^{4+}$, 724 $[M-3PF_6]^{3+}$, 754 [macrocycle]$^{2+}$, 1159 $[M-2PF_6]^{2+}$, 1508 [macrocycle]$^{?+}$; MS/MS (ES): parent ion: *m*/*z*: 507, daughter ions: *m*/*z*: 208, 754.

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