Synthesis of a criss-cross overlapped tetrathiafulvalenophane and a topologically new [2]catenane

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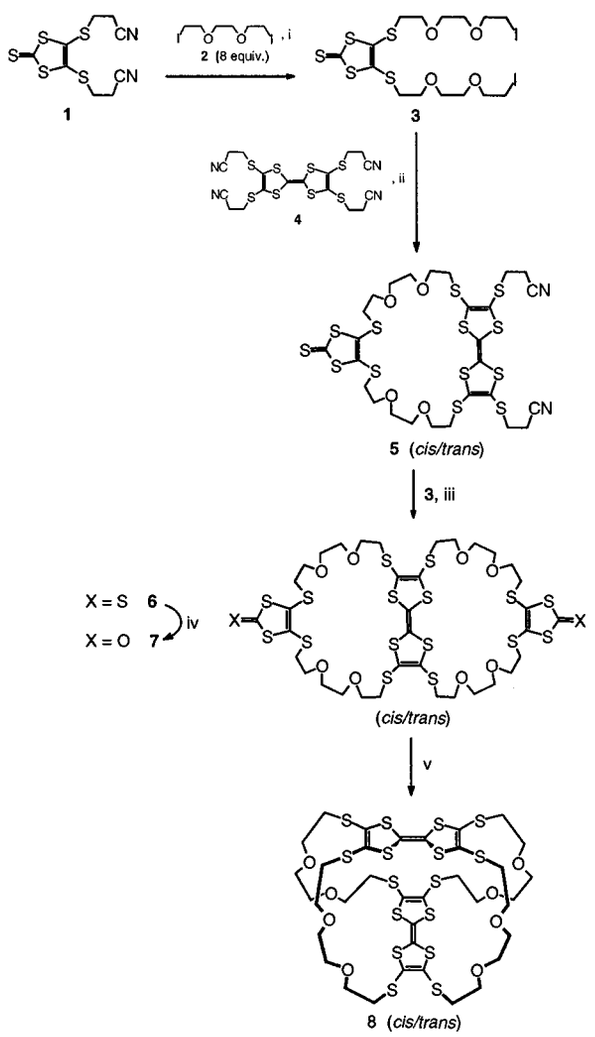
Using stepwise cyclization reactions followed by an intramolecular coupling, the criss-cross overlapped tetrathiafulvalenophane 8 was readily prepared. The structure of the *cis*,*cis* isomer was elucidated by X-ray crystallography which revealed a host–guest complex with chloroform. This electron donor was used for the synthesis of a topologically new type of [2]catenane 11-4PF$_6$, under ultra-high pressure (10 kbar).

Catenanes of different structures have been prepared from a variety of π-electron donors and acceptors utilizing the donor–acceptor self-assembly developed by Stoddart *et al.*[1] The self-assembly of tetrathiafulvalene (TTF) based supramolecular systems is strongly affected by electronic and structural features. When the cyclic acceptor cyclobis(paraquat-*p*-phenylene) is interlocked around the central TTF moiety of a bismacrocycle, it is in some cases possible to select only a single isomer in the catenation process from a *cis*/*trans* isomeric mixture of starting material.[2] This selectivity has not yet been observed for any dimeric, monocyclic TTF derivative[3] which encouraged us to use a more sterically constrained TTF donor. The quadruple-bridged tetrathiafulvalenophane **8** was chosen because a CPK model suggested that only when the two TTFs adopt a *cis*,*cis* configuration† is it possible to prepare a [2]catenane without any strain. Besides, the triethylene glycol bridges lead to a separation close to 7 Å between the TTF donors in the *cis*,*cis* geometry. This distance is optimal for the complexation of dipyridinium because it results in the preferred 3.5 Å separation between interacting rings for effective π–π charge-transfer stabilization.[4]

Results and discussion

The synthesis of **8** based on our cyanoethyl protection/deprotection method[5] is shown in Scheme 1. Bis-deprotection of **1** using two equivalents of caesium hydroxide and subsequent alkylation by an excess of **2** (8 equiv.) afforded compound **3** in 50% yield. In order to get exclusively cyclizations in the lateral direction of the TTF moiety, bismacrocycle **6** was prepared by a two-step deprotection–cyclization approach.[6] This presents a different strategy from the one recently reported for preparing quadruple-bridged tetrathiafulvalenophanes containing alkyl bridges with two to five C-atoms.[7] Thus, reaction of **3** and **4** in the presence of CsOH·H$_2$O (2 equiv.) under high-dilution conditions generated compound **5** in 62% yield as a mixture of *cis*/*trans* isomers. Compound **5** was deprotected and cyclized once more to form **6** (*cis*/*trans*) in 54% yield, whereupon transchalcogenation of **6** afforded **7** (*cis*/*trans*) in 88% yield. Subsequent treatment with triethyl phosphite in toluene gave the intramolecularly coupled criss-cross cyclophane **8** in 55% yield. The existence of two isomers of compound **6** (and **7**) is inferred from the ^{13}C NMR spectrum where two separate signals for each of the two different fulvalene carbon atoms are observed. For compound **8** two dominating peaks are observed in the fulvalene region which can be ascribed to the carbons of the *cis*,*cis* isomer. However, some smaller peaks can be assigned to the other possible isomers. The same reasoning is possible for the SCH$_2$ and OCH$_2$ carbons.‡ According to ^{1}H NMR, recrystallization seems to enrich the



Scheme 1 *Reagents and conditions*: i, CsOH·H$_2$O (2 equiv.), MeCN, room temp., 2 h, 50%; ii, CsOH·H$_2$O (2 equiv.), DMF, room temp., 20 h, 62%; iii, CsOH·H$_2$O (2 equiv.), DMF, room temp., 20 h, 54%; iv, Hg(OAc)$_2$, CHCl$_3$–AcOH, room temp., 2 h, 88%; v, P(OEt)$_3$–toluene, 120 °C, 4½ h, 55%

† The following definitions are used: *cis*,*cis* refers to a molecule containing two *cis* TTFs, whereas *cis*/*trans* means that the product contains a mixture of all possible isomers of which only one is drawn.

‡ Estimated content of *cis*,*cis* isomer: 80–85%. However, the proportion of this isomer in the crude product of reaction may be lower herefrom.

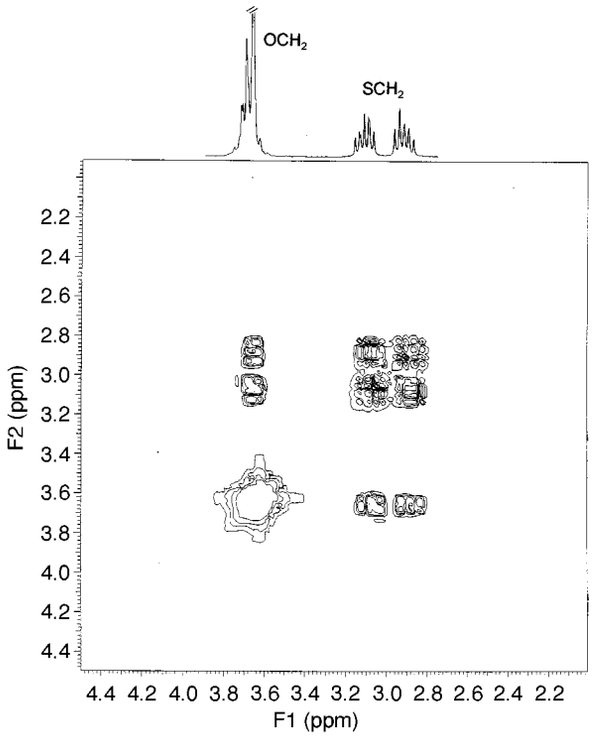


Fig. 1 ^{1}H NMR (300 MHz) 2D-COSY spectrum of **8** in $CDCl_3$ at room temp.

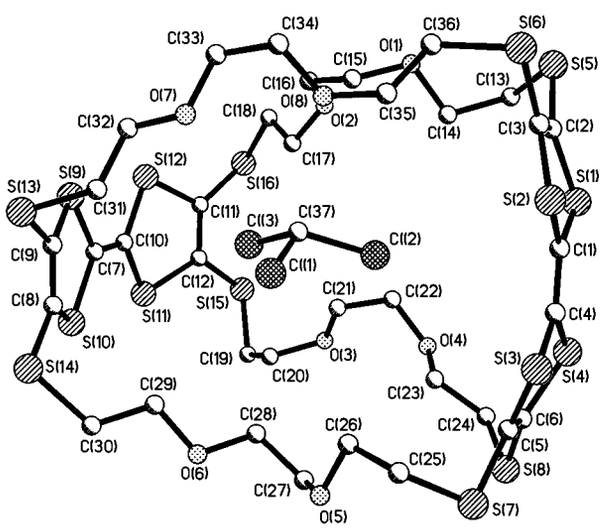


Fig. 2 Structure of *cis*,*cis* form of **8** with included chloroform molecule. Hydrogen atoms are omitted for clarity.

mixture in the *cis*,*cis* isomer showing two symmetric but complex sets of SCH_2 protons of equal intensity. As can be seen from the ^{1}H NMR 2D-COSY spectrum (Fig. 1), these two sets are coupled. Thus, in solution the criss-cross cyclophane adopts a conformation for which the two protons of each SCH_2 group become non-equivalent, $-SCH^aH^b-$.

By slow diffusion of methanol into a chloroform solution of **8**, single crystals suitable for X-ray diffraction were obtained. The crystal structure of the *cis*,*cis* isomer was determined and revealed inclusion of chloroform in the structure. The molecular structure with the atomic numbering scheme is shown in Fig. 2. The unit cell contains two formula units related by an inversion center. Each formula unit consists of one cyclophane molecule and one chloroform molecule with the latter molecule in the cavity of the cyclophane molecule. Complexations of halomethanes by cryptophanes and other cyclophane hosts are known from the literature,[8] but to our knowledge such inclusion complexes of tetrathiafulvalenophanes have only recently been

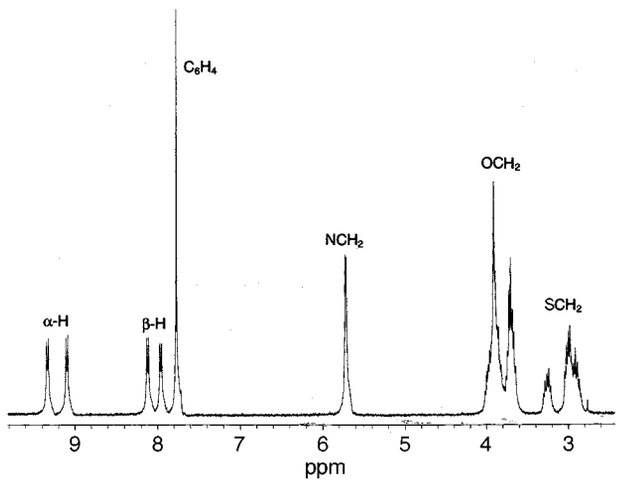
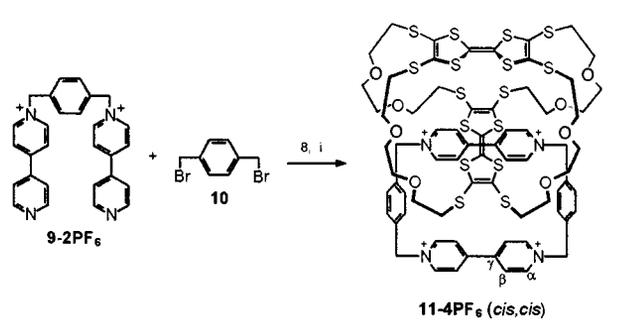


Fig. 3 ^{1}H NMR (300 MHz) spectrum of **11-4PF$_6$** in CD_3CN at room temp.

obtained for **8** and its smaller C_5 bridged counterpart.[7d] However, solution ^{1}H NMR spectroscopy ($CDCl_2CDCl_2$) revealed no detectable shift for the $CHCl_3$ proton due to complexation. The criss-cross arrangement of the fulvalene systems is clearly observed in Fig. 2 and the non-planarity of these units is also seen. The distance between the central fulvene bonds is 6.1 Å. As for the four bridging chains, the crystallographic anisotropic displacement parameters of several atoms indicate conformational disorder. This is particularly the case for the atoms O2, C21, C35 and C36. Similarly, but less pronounced, some orientational disorder of the chloroform molecule is indicated. The intermolecular interactions between neighbouring cyclophanes appear to be rather weak. The shortest intermolecular S···S distance is 3.60 Å corresponding to the normal van der Waals radius for sulfur of 1.80 Å. Hydrogen bonds of the type C–H···O may be present, but disorder of oxygen atoms prevents a detailed analysis.

Under ultra-high pressure (10 kbar), **11-4PF$_6$** was obtained as a green solid in 28% yield from **8** (*cis*/*trans*), **9-2PF$_6$** (3 equiv.) and **10** (3.5 equiv.) at room temperature after 3 days (Scheme 2).



Scheme 2 *Reagents and conditions*: i, DMF, 10 kbar, room temp., 3 d, 28%

The ^{1}H NMR spectrum of **11-4PF$_6$** is shown in Fig. 3. The inner and outer α- and β-protons of the dipyridiniums are split into two sets of doublet signals. This symmetric ^{1}H NMR spectrum clearly indicates the presence of only one isomer (*cis*/*cis*) of **11-4PF$_6$**. Four of the SCH_2 protons of the uncomplexed TTF resonate at δ 3.21–3.30 ppm, while the other four, probably pointing towards the dipyridinium, have moved upfield.

Electrochemistry

The redox behaviour of the compounds investigated by differential pulse voltammetry is shown in Table 1. The splitting of the first and second redox potentials of **8** (into E^{1a}, E^{1b} and E^{2a}, E^{2b}, respectively) when recorded in CH_2Cl_2 indicates an

Table 1 Redox potentials obtained by differential pulse voltammetry[a]

Compound	Solvent	E^{1a}/V	E^{1b}/V	E^{2a}/V	E^{2b}/V
7	CH_2Cl_2	0.56		0.87	
8	CH_2Cl_2	0.52	0.65	0.85	0.91
8	MeCN–CH_2Cl_2 (9:1)	0.49	0.60	0.85	
11-4PF$_6$[b]	MeCN	0.65		0.98	1.10

[a] Reference electrode: Ag/AgCl; working and counter electrodes: Pt, supporting electrolyte: $Bu^n_4NPF_6$ 0.1 mol dm^{-3}. [b] Conc. of **11-4PF$_6$**: 0.6 mmol dm^{-3}.

interaction between the two TTF moieties. The first potential is lowered relative to **7**, which may be explained by a stabilization of the monooxidized compound caused by delocalization of the positive charge over both TTFs. The next oxidation (E^{1b}) is thus more difficult due to Coulombic repulsion. In contrast to the related C_3 and C_4 cyclophanes, the C_5 cyclophane also showed a lowering of the first potential, but for this compound the oxidation occurred as a two-electron process.[7a,d]

The redox potentials of **11-4PF$_6$** are anodically shifted relative to **8** due to the influence of the cyclic acceptor. Differential pulse voltammetry succeeded in resolving the second oxidations, but the first oxidations could not be resolved into peaks assignable to the uncomplexed and complexed TTFs, respectively. The constrained geometry evidently causes more anodic shifts than have been observed for the catenanes derived from flexible, two-bridged, dimeric TTF macrocycles which only show a small increase of the first potential.[3]

Electrospray mass spectrometry

The catenane **11-4PF$_6$** was characterized by electrospray mass spectrometry (ESMS) showing peaks assignable to $[M - 4PF_6]^{4+}$, $[M - 4PF_6]^{3+}$, $[M - 3PF_6]^{3+}$, $[M - 3PF_6]^{2+}$ and $[M - 2PF_6]^{2+}$. The daughter ion spectrum (ESMS/MS) of the $[M - 4PF_6]^{4+}$ ion shows peaks due to fragment ions of the cyclic acceptor (*m*/*z* 104, 208) and peaks due to singly and doubly charged uncomplexed tetrathiafulvalenophane (*m*/*z* 1120 and 560, respectively). A similar fragmentation pattern has been observed for other tetrathiafulvalene containing donor–acceptor catenanes,[3] and it seems that the fragmentation of the cyclic acceptor is accompanied by one or two electron donations from the TTFs.

Conclusion

We have demonstrated the possibility of selectively obtaining a *cis*,*cis* catenane from a geometrically constrained criss-cross tetrathiafulvalene cage. This cage acts as a host for one molecule of chloroform in the solid state.

Experimental

All reactions were carried out under an atmosphere of dry N_2. Methanol was distilled from Mg. DMF was allowed to stand over molecular sieves (4 Å) for at least 3 days before use. Melting points were determined on a Büchi melting point apparatus and are uncorrected. UV experiments were performed on a Shimadzu UV160 instrument. NMR spectra were recorded on a Varian 300 spectrometer, and all chemical shifts are referenced to TMS. *J* values are given in Hz. Fast atom bombardment (FAB) and plasma desorption (PD) mass spectra were obtained on a Kratos MS 60 TC and a Bio-ion 20R, respectively. Electrospray (ES) mass spectra were recorded using a Finnigan MAT TSQ 700 triple quadrupole mass spectrometer. The compounds were electrosprayed from acetonitrile solution. ESMS/MS experiments were performed using argon, typically at a 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 analyzed by the third quadrupole. CV experiments were performed using an Autolab, PGSTAT10 potentiostat (ECO CHEMIE BV). Bu_4NPF_6 was used as supporting electrolyte. Counter and working electrodes were made of Pt and the reference electrode was Ag/AgCl. Elemental analyses were performed at the Microanalytical Laboratory, University of Copenhagen. Light petroleum refers to the fraction with bp 60–80 °C.

4,5-Bis{2-[2-(2-iodoethoxy)ethoxy]ethylthio}-1,3-dithiole-2-thione3

A solution of $CsOH·H_2O$ (4.85 g, 28.9 mmol) in methanol (15 ml) was added to a solution of **1** (4.00 g, 13.1 mmol) in acetonitrile (150 ml) over 10 min with stirring at room temp. The solution was stirred for 30 min, whereupon 1,2-bis(2-iodoethoxy)ethane **2** (38.9 g, 105 mmol) was added, and the mixture was stirred for 2 h. Then the reaction mixture was concentrated *in vacuo*. CH_2Cl_2 (200 ml) was added, and the organic phase was washed with water, and dried ($MgSO_4$). The solvent was removed and the residue purified by column chromatography (silica, i. CH_2Cl_2–light petroleum 1:1 elutes the excess of **2**, ii. CH_2Cl_2–EtOAc 10:1 elutes the product), affording **3** (4.44 g, 50%) as an orange oil (Found: C, 26.50; H, 3.16. $C_{15}H_{24}I_2O_4S_5$ requires C, 26.40; H, 3.54%); $\delta_H(CDCl_3)$ 3.11 (4 H, t, *J* 6.3, SCH_2), 3.29 (4 H, t, *J* 6.8, ICH_2), 3.67 (8 H, s, OCH_2), 3.74–3.80 (8 H, m, OCH_2); FABMS (*m*/*z*) 683 ($M + H^+$); PDMS (*m*/*z*) 682 (M^+).

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

To a solution of **4** (0.40 g, 0.73 mmol) in DMF (50 ml) was dropwise added a solution of $CsOH·H_2O$ (0.26 g, 1.5 mmol) in methanol (10 ml) over 30 min with stirring at room temp. The solution was stirred for 1 h. Then this solution and a solution of **3** (0.50 g, 0.73 mmol) in DMF (60 ml) were added simultaneously, during 20 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, whereupon the reaction mixture was concentrated *in vacuo*. CH_2Cl_2 (100 ml) was added, and the organic solution washed with water, and dried ($MgSO_4$). The solvent was removed and the residue purified by column chromatography (silica, CH_2Cl_2–EtOAc 8:1), affording **5** (0.39 g, 62%) as an orange oil (Found: C, 37.82; H, 3.83; N, 3.28. $C_{27}H_{32}N_2O_4S_{13}$ requires C, 37.48; H, 3.55; N, 3.24%); $\delta_H(CDCl_3)$ 2.76 (4 H, t, *J* 7.3, CH_2CN), 3.04–3.11 (12 H, m, SCH_2), 3.64–3.75 (16 H, m, OCH_2); PDMS (*m*/*z*) 864.1 (M^+).

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

Compound **6** was prepared in a similar way from **5** and **3** in a yield of 54% as an orange oil (Found: C, 36.86; H, 4.14. $C_{36}H_{48}O_8S_{18}$ requires C, 36.46; H, 4.08%); $\delta_H(CDCl_3)$ 2.96–3.13 (16 H, m, SCH_2), 3.62–3.78 (32 H, m, OCH_2); $\delta_C(CDCl_3)$ 35.24, 35.43, 36.31 (S*C*H$_2$), 70.00, 70.17, 70.48, 70.54, 70.61, 70.75, 70.94 (O*C*H$_2$), 109.92, 111.26 (C=C fulvene), 127.91, 128.90, 136.82 (C=C), 211.18 (*C*=S); PDMS (*m*/*z*) 1183.9 (M^+).

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

$Hg(OAc)_2$ (0.35 g, 1.1 mmol) was added to a solution of **6** (0.26 g, 0.22 mmol) in chloroform (40 ml) and glacial acetic acid (15 ml). The solution was stirred for 2 h, whereupon it was filtered on Celite and the Celite layer rinsed with $CHCl_3$ (100 ml). The filtrate was washed with $NaHCO_3$ (aq.), water, and dried ($MgSO_4$). The solvent was removed and the residue subjected to column chromatography (silica, CH_2Cl_2–EtOAc 5:1), affording **7** (0.22 g, 88%) as an orange oil (Found: C, 37.47; H, 3.97. $C_{36}H_{48}O_{10}S_{16}$ requires C, 37.48; H, 4.19%); $\delta_H(CDCl_3)$ 3.00–3.11 (16 H, m, SCH_2), 3.64–3.77 (32 H, m, OCH_2); $\delta_C(CDCl_3)$ 35.32, 35.49, 36.22, 36.28 (S*C*H$_2$), 69.98, 70.02, 70.22, 70.53, 70.56,

70.65, 70.73, 70.90 (O*C*H$_2$), 109.86, 111.14 (C=C fulvene), 127.57, 127.64, 127.82, 128.86 (C=C), 189.50, 189.64 (*C*=O). FABMS (*m*/*z*) 1153 (M + H$^+$).

2$^{\alpha}$,3$^{\beta}$,6$^{\gamma}$(7$^{\gamma}$),7$^{\delta}$(6$^{\delta}$)-[Tetrathiafulvalene-2$^{\alpha}$,3$^{\delta}$,6$^{\gamma}$(7$^{\gamma}$),7$^{\beta}$(6$^{\beta}$)-tetrayl-tetrathiotetra(ethane-1,2-diyl)tetraoxytetra(ethane-1,2-diyl)-tetraoxytetra(ethane-1,2-diyl)tetrathio]tetrathiafulvalene 8 (*cis*/*trans*) §

A solution of **7** (0.17 g, 0.15 mmol) in toluene (3 ml) and freshly distilled P(OEt)$_3$ (6 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 residue was subjected to column chromatography (silica, CH_2Cl_2–EtOAc 10 : 1), affording **8** (0.09 g, 55%) as an orange solid; mp 94.5–97.5 °C (toluene–light petroleum) (Found: C, 38.86; H, 4.08. $C_{36}H_{48}O_8S_{16}$ requires C, 38.55; H, 4.31%). δ_H(CDCl$_3$) (*cis*,*cis*) 2.86–3.00 (8 H, m, SC*H*$_2$), 3.06–3.19 (8 H, m, SC*H*$_2$), [*cis*/*trans*: 2.86–3.19 (m, SC*H*$_2$)], 3.64–3.77 (32 H, m, OC*H*$_2$); δ_C(CDCl$_3$) 34.48 (w), 35.09 (*cis*,*cis*), 35.49 (w), 35.60 (w) (S*C*H$_2$), 70.11 (*cis*,*cis*), 70.24 (w), 70.28 (w), 70.37 (*cis*,*cis*), 70.55 (w), 70.63 (w), 70.82 (w), 71.05 (w), 71.10 (w), 71.20 (w) (O*C*H$_2$), 108.78 (w), 108.87 (w), 111,14 (*cis*,*cis*) (C=C fulvene), 124.51 (w), 128.14 (*cis*,*cis*), 128.77 (w), 130.23 (w), 131.21 (w) (C=C); the weak signals correspond to the other isomers; PDMS (*m*/*z*) 1120.4 (M$^+$).

Crystallographic data for compound 8 (*cis*,*cis*)

$C_{37}H_{49}Cl_3O_8S_{16}$, $M = 1241.07$, triclinic, $a = 12.9987(4)$, $b = 14.9881(4)$, $c = 17.0644(5)$ Å, $\alpha = 100.716(1)$, $\beta = 103.570(1)$, $\gamma = 115.619(1)°$, $V = 2753.0(2)$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 1.497$ g cm^{-3}, $F(000) = 1284$, graphite monochromated Mo*K*α radiation, $\lambda = 0.710\ 73$ Å, $\mu = 0.82$ mm^{-1}, $T = 294(1)$ K. Crystal size: 0.03 × 0.15 × 0.24 mm, yellow plate. The intensities of 26 875 reflections were measured on a Siemens SMART CCD diffractometer and merged into 11 088 unique reflections ($R_{int} = 0.0701$) covering 98% of a complete hemisphere within $\theta_{max} = 26.37°$. No intensity decay was observed. For data collection and integration of frame data, the associated diffractometer software was used. Structure solution, refinement of the structure and production of crystallographic illustrations were carried out using the Siemens *SHELXTL* package[9a] and *SHELX-97*.[9b] The refinement of 580 parameters using all unique reflections converged at $R_1 = 0.0802$ [for $F_o > 4\sigma(F_o)$]. H atoms were included in calculated positions. Max/min residual electron density: 0.80/−0.46 e A^{-3}. Atomic coordinates and further crystallographic details have been deposited with the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web pages (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/193.

{2$^{\alpha}$,3$^{\beta}$,6$^{\gamma}$,7$^{\delta}$-[Tetrathiafulvalene-2$^{\alpha}$,3$^{\delta}$,6$^{\gamma}$,7$^{\beta}$-tetrayltetrathiotetra-(ethane-1,2-diyl)tetraoxytetra(ethane-1,2-diyl)tetraoxytetra-(ethane-1,2-diyl)tetrathio]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)} (11-4PF$_6$) (*cis*,*cis*)

A solution of **8** (0.18 g, 0.16 mmol), **9-2PF$_6$** (0.34 g, 0.48 mmol) and **10** (0.15 g, 0.57 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 purified by column chromatography (silica, MeOH–aqueous NH_4Cl solution (2 M)–$MeNO_2$ 7 : 2 : 1). The green fraction was concentrated and washed with water and $CHCl_3$. Then it was dissolved in $MeNO_2$ (50 ml) and washed thoroughly with water, saturated aqueous NH_4PF_6 (5 × 20 ml), and finally with water again. After removal of the solvent, **11-4PF$_6$** was obtained (0.10 g, 28%) as a green solid; mp >250 °C (Found: C, 37.96; H, 3.59; N, 2.69. $C_{72}H_{80}F_{24}N_4O_8P_4S_{16}\cdot 2.5H_2O$ requires C, 38.14; H, 3.78; N, 2.47%); δ_H(CD$_3$CN) 2.84–3.04 (12 H, m, SC*H*$_2$), 3.21–3.30 (4 H, m, SC*H*$_2$), 3.64–4.01 (32 H, m, OC*H*$_2$), 5.71 (8 H, d, *J* 3.4, NC*H*$_2$), 7.76 (8 H, s, C$_6$*H*$_4$), 7.96 (4 H, d, *J* 7.1, β-*H*), 8.12 (4 H, d, *J* 6.9, β-*H*), 9.10 (4 H, d, *J* 7.2, α-*H*), 9.33 (4 H, d, *J* 6.5, α-*H*); δ_C(CD$_3$CN) 35.18, 35.71 (S*C*H$_2$), 65.00, 65.43 (N*C*H$_2$), 69.38, 70.13, 70.24, 70.63 (O*C*H$_2$), 125.41, 125.56, 126.38, 127.02 (C=C, β-*C*), 131.35, 131.45, 136.11, 137.00 (*C*$_6$H$_4$), 144.05, 144.86, 144.95, 146.05 (α-*C*, γ-*C*), (105.06, 105.55 C=C fulvene, uncertain because of low signal to noise ratios); ESMS (*m*/*z*) 410 [M − 4PF$_6$]$^{4+}$, 546.7 [M − 4PF$_6$]$^{3+}$, 595 [M − 3PF$_6$]$^{3+}$, 892.5 [M − 3PF$_6$]$^{2+}$, 965 [M − 2PF$_6$]$^{2+}$; parent ion (*m*/*z*) 410, daughter ions (*m*/*z*) 104, 208, 560, 1120; λ_{max}(CH$_3$CN)/nm 810 (ε/dm^3 mol^{-1} cm^{-1}, 3700).

§ For naming quadruple-bridged tetrathiafulvalenophanes we have used Greek letters in order to connect the appropriate parts. Hereby it should be possible to distinguish different isomers and between the *criss-cross* cyclophane and the *face-to-face* overlapped cyclophane (belt-type).

Acknowledgements

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