Geometrically Constrained Tetrathiafulvalenophanes: Synthesis and Characterization

Jesper Lau,[†,§] Philippe Blanchard,[†,‡] Amédée Riou,[‡] Michel Jubault,[‡] Michael P. Cava,[§] and Jan Becher*[,†]

Department of Chemistry, Odense University, Campusvej 55, DK-5230, Odense M, Denmark, IMMO, CNRS, EP 66, Université d'Angers, 49045 Angers, France, and Department of Chemistry, The University of Alabama, P.O. Box 870336, Tuscaloosa, Alabama 35487-0336

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The synthesis of tetrathiafulvalenophanes **4b**, **4c**, **5**, **9**, and **10** employing two fundamentally different strategies is reported. Macrocycle **9** was obtained as a mixture of *cis* and *trans* isomers and was crystallized to afford two distinct crystals types: a red type consisting of the *cis* isomer and a yellow type consisting of the *trans* isomer. The crystal structures of *cis*-**9** and *trans*-**9**, determined by X-ray diffraction, revealed that the *cis*-form possesses a planar TTF moiety while the *trans*-form has a distorted TTF unit. The electrochemical properties of the new tetrathiafulvalenophanes are reported.

Cyclophanes are fundamentally important compounds in many aspects of macrocyclic and supramolecular chemistry, and research in this field has expanded rapidly in recent years.[1,2] Several interesting systems, like catenanes and rotaxanes, have been prepared based on self assembling of complementary electroactive units.[3] Tetrathiafulvalene (TTF) is a stable and reversible electron donor;[4] hence, the incorporation of TTF units into cyclophanes may be expected to give interesting electroactive macrocycles. Indeed a number of such tetrathiafulvalenophanes are known,[5a−l] all of which were prepared by coupling reactions in which a TTF moiety is formed in the final cyclization step. The course of these reactions, giving either inter- or intramolecular cyclization, seems to be controlled solely by the length of the linker between the two dithiole units. Very short linkers i.e. two,[5b] three,[5b] four,[5i] or five[5d,h] atoms gives intermolecular coupling whereas longer spacers[5a,d,f,g,l] tends to give intramolecular reaction. An interesting class of redox active macrocycles are the sandwich type bis-TTF macrocycles. However the easily obtainable bis-TTF derivatives of this type are those with short linkers (two to five atoms). The resulting short distance between the two TTF moieties makes it a poor candidate for donor−acceptor based host−quest chemistry. We have revisited the triethyl phosphite coupling of some bis-trithiocarbonates in the hope of gaining more information of the linkers influence on the course of the reaction.

We have previously described a versatile new methodology[6] using preformed TTF derivatives as building blocks for the modular syntheses of macrocyclic compounds.[7] In the present work we extend this approach to complement the original strategy where the TTF moiety is formed in the cyclization step. We report the syntheses of TTF building block **8a** as well as full experimental details for **8b**. Various new tetrathiafulvalenophanes were prepared employing the two different strategies. The synthesis and electrochemical properties of these new electroactive cyclophanes, as well as an X-ray crystallographic study of the two isomers of **9** will be discussed. The isolation and characterization of the pure *cis* and *trans* isomers of **9** represents a particularly novel result of this study.

Results and Discussion

The necessary cesium 1,3-dithiole-2-thione-5-thiolate **1** was obtained by the recently reported procedure.[6c,8] Alkylation of **1** proceeds cleanly and in excellent yield, and alkylation with either α,α′-dibromo-, *o*-, *m*- or *p*-xylene afforded the bis-1,3-dithiole-2-thiones **2a**−**c** in

† Odense University.
‡ Université d'Angers.
§ The University of Alabama.
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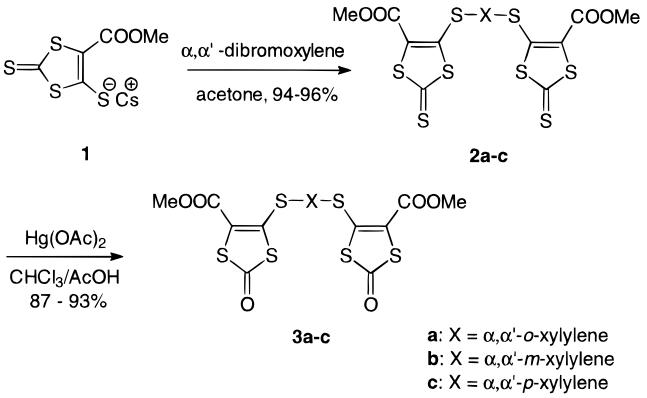
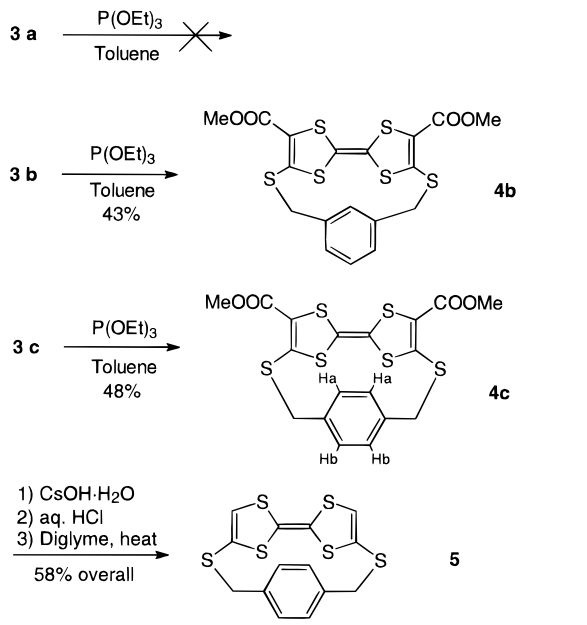
Scheme 1



Scheme 2



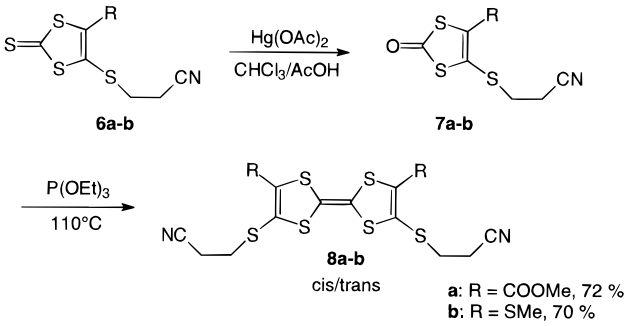
almost quantitative yields. Subsequent transchalcogenation yielded the corresponding bis-1,3-dithiole-2-ones **3a**−**c** (Scheme 1).

Triethyl phosphite treatment of **3a** gave an intractable solid. Plasma desorption mass spectrometry (PDMS) investigation of the crude material revealed a complex mixture of products. The same result was obtained in the cases of **3b** and **3c** using neat triethyl phosphite. However, an excess of triethyl phosphite in refluxing toluene resulted in fair yields of the *m*- and *p*- cyclotetrathiafulvalenophanes **4b** and **4c** (43% and 48%, Scheme 2). In order to obtain the unsubstituted TTF compound, diester **4c** was hydrolyzed to the dicarboxylic acid. Decarboxylation was achieved by heating the intermediate diacid in diglyme to give **5**. Hydrolysis and decarboxylation proceeded in an overall yield of 58%. Attempts to decarboxylate the *meta*-analog failed. It must be noted that the phosphite coupling of the present 1,3-dithiole-2-ones **3b** and **3c** yields exclusively the intramolecular coupled tetrathiafulvalenophanes. PDMS revealed that no intermolecular coupling of **3a**−**c** leading to bis-TTF macrocycles is taking place. CPK-models indicate that the new TTF-phanes **4b**, **4c**, and **5** are very compact molecules. In fact a CPK-model of neither metacyclophane **4b** nor of the corresponding orthocyclophane can be constructed due to the tremendous strain in the structure. On going from the *p*- to the *m*- to the *o*-xylylene analog, the linker gets shorter. In this approach, shortening of the linker to disfavor intramolecular reaction and hence favor intermolecular reaction does not afford the bis-TTF product.

Table 1. UV-vis Data (CH_2Cl_2)

compd	δ_{max}/nm (log ϵ)
4b	327(4.08), 414(3.53)
4c	321(4.01), 424(3.32)
5	324(3.81)
cis-**9**	236(4.29), 316(4.03), 404(3.28)
trans-**9**	232(4.37), 264(4.17), 336(4.26), 370(3.49)
10	228(4.80), 332(4.44), 379(3.79)

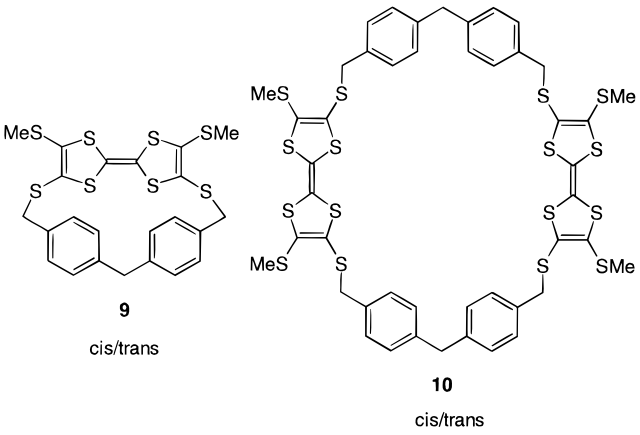
Scheme 3



Due to hindered rotation of the phenylene group, ^{1}H-NMR of the *p*-cyclophane **4c** shows two different aromatic protons H_a and H_b, indicating that the macrocycle in solution has a conformation in which part of the phenyl ring is situated over the TTF moiety.[5d] H_a appears as a mutiplet consisting of three signals between 7.480 and 7.485 ppm each separated by approximately 1 Hz. H_b likewise consists of three signals between 6.753 and 6.760 ppm each separated by 1 Hz. The multiplets are probably two unresolved doublet of doublets. Since the two H_a protons would be nonequivalent in a *trans*-isomer an *ortho*-coupling of typically 6−10 Hz would be expected for this isomer. The absence of such an *ortho*-coupling therefore indicates that the stereoisomer present is the *cis*-structure. Analogous results were obtained with the parent compound **5**. In the case of the corresponding *m*-cyclophane **4b** no upfield shift of the aromatic protons is observed. In all cases an AB-spin system was observed for the CH_2 protons with a geminal coupling J = 12.0 Hz.

The *m*-cyclophane **4b** is less colored than the *p*-cyclophane **4c**; indeed, λ_{max} for **4b** is 414 nm whereas λ_{max} for **4c** is 424 nm (Table 1). This indicates that the *m*-cyclophane has a more distorted TTF group that allows for less π-delocalization.

The building blocks **8a** and **8b** were prepared according to Scheme 3. The 1,3-dithiole-2-thiones **6a** and **6b** were treated with mercuric acetate to give the corresponding oxo compounds **7a** and **7b**. Triethyl phosphite treatment of these afforded the key TTF derivatives **8a** and **8b** in 72% and 70% yields, respectively. **8b** was treated with 2.2 equiv of cesium hydroxide in methanol to generate the TTF bis-thiolate (Scheme 4). This was reacted with bis[4-(bromomethyl)phenyl]methane under high dilution conditions, using a medical perfusor pump. Chromatography afforded **9** as an orange powder in 71% yield. No trace of the dimeric product **10** was detected in PDMS. The high yield and selectivity in this reaction is probably due to the almost perfect geometrical complementarity of the TTF bis-thiolate and the bis-bromo reagent and it nicely demonstrates the efficiency of the overall strategy.

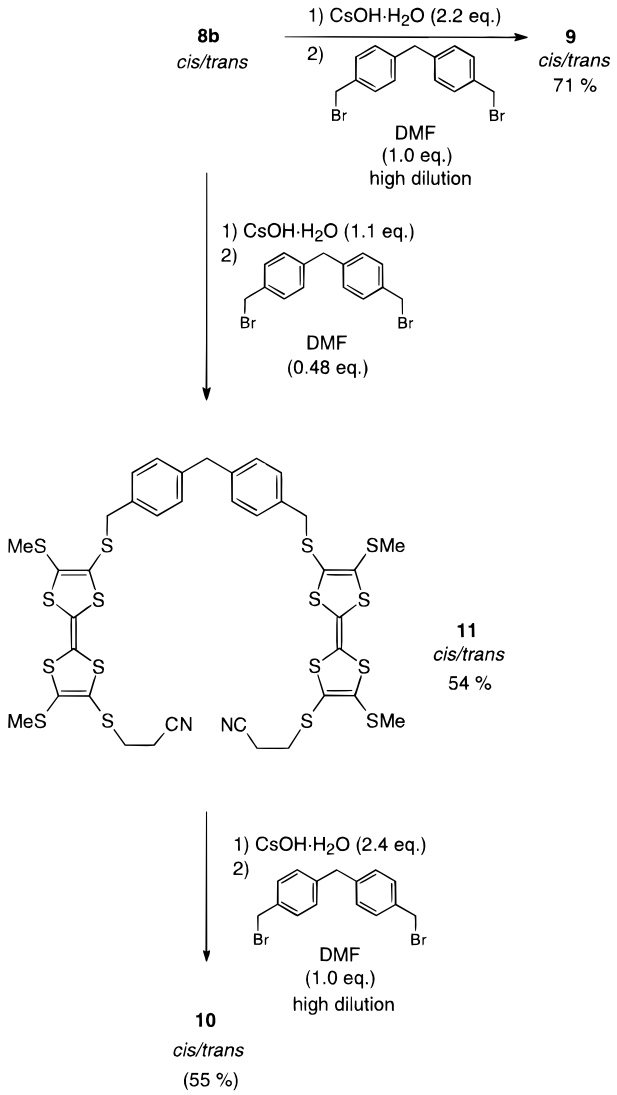


^{1}H-NMR ($CDCl_3$ stored over K_2CO_3)[9] of **9** revealed the presence of two configurational isomers, as evidenced by two well resolved singlets for the methylthio groups at 2.26 and 2.44 ppm, with the ratio of integration of 3:2, respectively. Separation of the different isomers by column chromatography was not possible. However, crystallization from a mixture of CH_2Cl_2−hexane afforded a mixture of two different crystal types: red shiny needles and yellow plates. The crystals were easily separated from each other simply by mechanical sorting. The two different types of colored crystals thus obtained exhibited identical mass and IR spectra. The red crystals melted at 192−194 °C whereas the yellow crystals melted at 210−212 °C. ^{1}H-NMR ($CDCl_3$ over K_2CO_3) of the red crystals showed a singlet at $\delta = 2.44$ ppm due to the methylthio groups, one singlet at $\delta = 3.86$ ppm from the two different methylene protons ($ArCH_2Ar$ and $ArCH_2S$), and two doublets from the para-substituted aromatic system.

On cooling below −30 °C, the methylene signal splits into two signals. In the case of the yellow compound the ^{1}H-NMR spectrum clearly corresponds to a more rigid system, since an AB spin system arises from the geminal methylenethio protons ($\delta = 3.84$ and 4.09 ppm, $J = 13.3$ Hz), equivalent to the case of **4b**, **4c**, and **5**. No *cis*−*trans* isomerization was observed in the $CDCl_3$ (previously stored over K_2CO_3) solutions of compounds *cis*-**9** and *trans*-**9**; however, addition of an excess of CF_3COOD to solutions of each isomer leads to a darkening of the solutions showing identical ^{1}H NMR spectra with broadening of signals characteristic of the presence of cation radicals in solution.[10] The ^{1}H NMR spectrum of a crude reaction product of compound **9** revealed an initial 40/60 mixture of *cis*/*trans* isomers.

The corresponding macrocycle bis-TTF **10** could be prepared via a stepwise reaction sequence: (*i*) a thiolate monodeprotection of **8b** using 1.1 equiv of cesium hydroxide, followed by alkylation with bis[4-(bromomethyl)phenyl]methane (0.48 equiv) gave **11** in 54% yield; (*ii*) subsequent deprotection of the two remaining thiolate functions, followed by ring closure reaction under high dilution conditions in the presence of bis[4-(bromomethyl)phenyl]methane (1 equiv), afforded bis-TTF **10** as an orange-brown powder 55% yield (Scheme 4). **10** shows three different methylthio protons in the ^{1}H-NMR arising from different configurational isomers. In contrast to mono-TTF **9**, the isomers of bis-TTF **10** could not be separated by neither chromatography nor crystallization.

Scheme 4



All the new tetrathiafulvalenophanes were investigated by PDMS to confirm their purity.

X-ray Analysis.[13] X-ray diffraction analysis (Figure 1) revealed that the *trans*-**9** isomer (yellow) is more strained than the corresponding *cis*-**9** isomer (red) since the *cis* isomer has a planar TTF framework, whereas the dithiole moieties are distorted out of planarity in the *trans* isomer. The central tetrathioethylene medium plane of *trans*-**9** and the two external dithioethylene medium planes of the TTF moiety formed two different angles of 28° and 16°, indicating that the TTF core is much less distorted compared to the recently described [8]tetrathiafulvalenophane[5d,11] in which the corresponding angles of 47° and 34° were observed. Furthermore, the central fulvalenic bond is significantly shorter in the *trans* isomer (1.309(5) Å) than in the *cis* isomer (1.332(8) Å). Thus, the better conjugation of the planar TTF in *cis*-**9** nicely explained the color difference between the two configurational isomers. The UV-visible spectrum (Table 1) in dichloromethane of the *cis* isomer exhibited a lower energy absorption band ($\lambda_{max} = 404$ nm) than did

(9) To avoid the slow cis/trans isomerization observed in commercial $CDCl_3$, due to the presence of traces of acid, see Souizi, A.; Robert, A.; Batail, P.; Ouahab, L. *J. Org. Chem.* **1987**, *52*, 1610.

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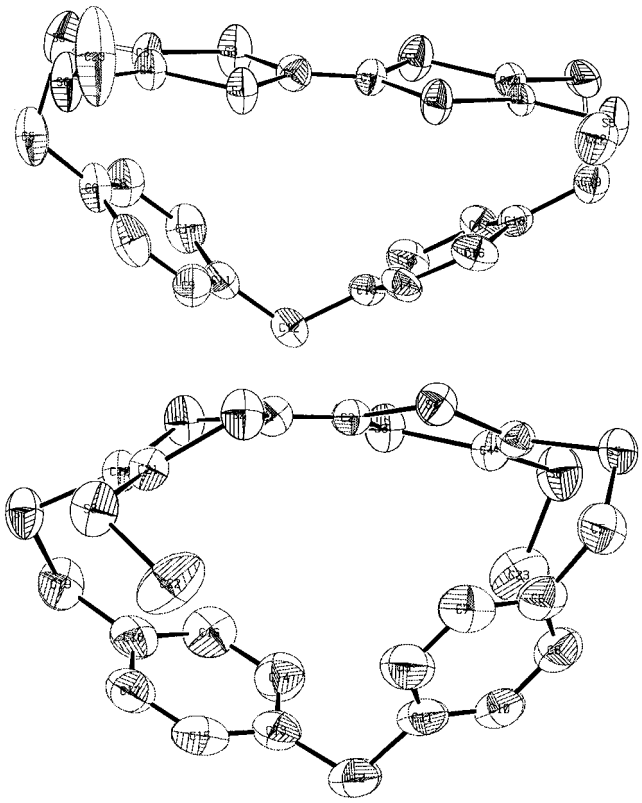

Figure 1. Crystal structures of *cis*-**9** (top) and *trans*-**9** (bottom).

Table 2. Cyclic Voltammetry Data[a]

compd (solvent)	E_{ox} or $E_{1/2}$ (V)
TTF (MeCN)	$E_{1/2}^1 = 0.32$, $E_{1/2}^2 = 0.73$
4b (MeCN)	$E_{ox} = 1.05$ (irr)
4c (MeCN)	$E_{ox} = 1.00$ (irr)
5 (CH_2Cl_2)	$E_{ox} = 0.81$ (irr)
8a (MeCN)	$E_{1/2}^1 = 0.71$, $E_{1/2}^2 = 1.05$
8b (CH_2Cl_2)	$E_{1/2}^1 = 0.65$, $E_{1/2}^2 = 1.01$
cis-**9** (CH_2Cl_2)	$E_{1/2}^1 = 0.39$, $E_{1/2}^2 = 0.83$
trans-**9** (CH_2Cl_2)	$E_{1/2}^1 = 0.44$, $E_{1/2}^2 = 0.83$
10 (CH_2Cl_2)	$E_{1/2}^1 = 0.49$, $E_{1/2}^2 = 0.87$
11 (CH_2Cl_2)	$E_{1/2}^1 = 0.54$, $E_{1/2}^2 = 0.89$

[a] NBu_4PF_6, Ag/AgCl, platinum electrode, scan speed: 100 mV s^{-1}.

the *trans* isomer ($\lambda_{max} = 370$ nm). Note that in the solid state, the benzene rings of each isomer adapt two different conformations which were not observed in a $CDCl_3$ solution on the NMR timescale at room temperature.

Cyclic Voltammetry. Cyclic voltammetry of the new cyclophanes shows that **4b**, **4c**, and **5** are irreversibly oxidized. Table 2 shows that the *m*-cyclophane **4b** has a slightly higher oxidation potential (1.05 V) than the *p*-cyclophane **4c** (1.00 V). According to previous results,[5f] the higher potential indicates that the the *m*-cyclophane has a more bent TTF unit. The oxidation potential of **5** (0.81 V) is lowered about 200 mV compared to that of **4c**, which is consistent with the disappearance of the electron withdrawing effect of the ester groups.

The cyclophanes **9** and **10** with the larger spacer groups are reversible donors, as well as all the noncyclic TTF derivatives **8a**, **8b**, **11** (Table 2). The electrochemical properties of *cis*-**9** and *trans*-**9** are somewhat different. The cyclic voltammograms of *cis*-**9** and *trans*-**9** showed two different behaviors (Figure 2, parts a and b, respectively). At a scan rate of 100 mV s^{-1}, during the first

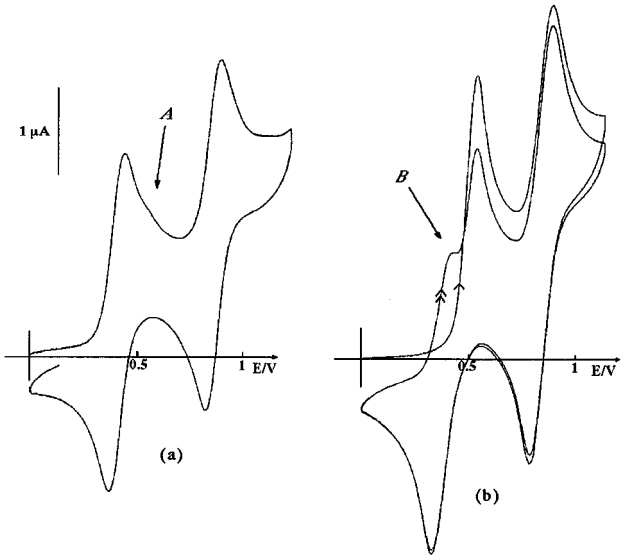

Figure 2. Cyclic voltammograms of *cis*-**9** (a) and *trans*-**9** (b).

Scheme 5

(1) $\text{Cis} \xrightarrow{-e} \text{Cis}^{+\cdot}$ (*E*)

(2) $\text{Cis}^{+\cdot} \rightleftharpoons \text{Trans}^{+\cdot}$ (*C*)

(3) $\text{Trans}^{+\cdot} + \text{Cis} \rightleftharpoons \text{Trans} + \text{Cis}^{+\cdot}$ (*C*)

(4) $\text{Trans} \xrightarrow{-e} \text{Trans}^{+\cdot}$ (*E*)

scan, *cis*-**9** revealed two reversible one-electron oxidation peaks at 0.44 and 0.88 V accompanied with a small shoulder A at 0.53 V.

The corresponding *trans*-**9** isomer showed two one-electron redox processes at 0.53 and 0.88 V during the first scan, the first one being quasireversible ($Ep_a - Ep_c = 0.185$ V) and the second being truly reversible at potentials identical to those of *cis*-**9**. These results indicated that after the electrochemical oxidation of *cis*-**9** (Scheme 5, eq 1), the resulting *cis*-$\mathbf{9}^{+\cdot}$ cation radical was subject to rapid chemical isomerization to the *trans*-$\mathbf{9}^{+\cdot}$ species (eq 2) which was reduced to the neutral *trans*-**9** by diffusing of the *cis*-**9** isomer, according to the thermodynamically allowed ($E°_{trans^{+\cdot}/trans} > E_{cis^{+\cdot}/cis}$) redox reaction (eq 3). Then the small amount of the resulting *trans* isomer was oxidized at 0.53 V (eq 4), giving rise to the small shoulder A observed in the first scan in the voltammogram of *cis*-**9**. This ECE mechanism (ECE = electron transfer with subsequent chemical reaction and further electron transfer) was seen to be independent of the scan rates since the shoulder A was always present between 200 and 10 mV s^{-1} (Figure 3a).

In the case of compound *trans*-**9**, a rapid chemical isomerization of *trans*-$\mathbf{9}^{+\cdot}$ to *cis*-$\mathbf{9}^{+\cdot}$ was also observed after the first electron transfer since a new well-resolved oxidation wave B appeared at 0.44 V during the second scan (Figure 2b). Therefore, the electrochemical behavior can be explained as followed: at the first scan, *trans*-**9** was oxidized to *trans*-$\mathbf{9}^{+\cdot}$, which then isomerized to *cis*-$\mathbf{9}^{+\cdot}$, these two species being in rapid chemical equilibrium (Scheme 5, eq 2). In the reverse scan, *trans*-$\mathbf{9}^{+\cdot}$ and *cis*-$\mathbf{9}^{+\cdot}$ were reduced to *trans*-**9** and *cis*-**9**, the presence of the latter being proved by its oxidation peak (0.44 V) at the second scan. The additional wave B can be suppressed by lowering the scan rate to 20 mV s^{-1} due to the diffusion of the electrochemically formed *cis* isomer from

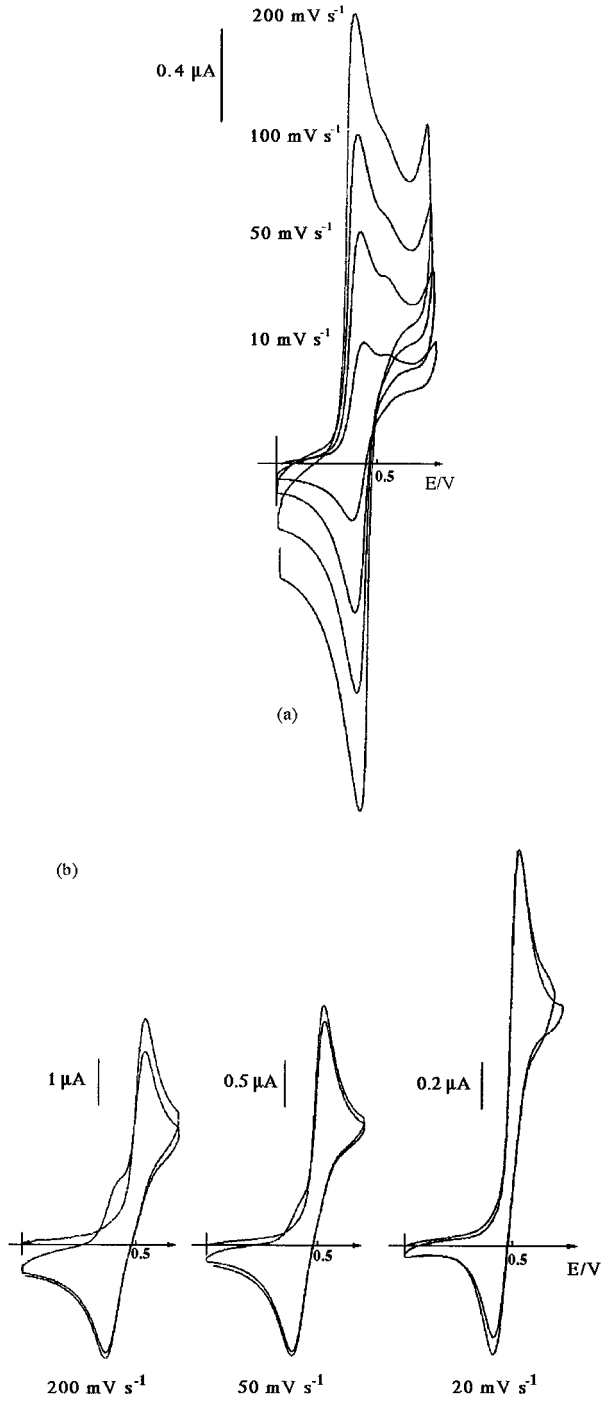

Figure 3. (a) Successive cyclic voltammograms of *cis*-**9** (5×10^{-4} mol L^{-1}) between 0 and 0.72 V *vs* scan rates: 10, 50, 100, 200 mV s^{-1}. (b) Cyclic voltammograms of *trans*-**9** (10^{-3} mol L^{-1}) between 0 and 0.70 V: first and second scan at different scan rates.

the electrode to the solution (Figure 3b). These results are in accordance with the results obtained by Robert and co-workers.[5l]

In the nonstrained macrocycle **10**, two well-resolved reversible two-electron redox systems were observed at $E_{1/2} = 0.49$ and 0.87 V. The bis-(TTF) **11** showed two well-resolved reversible peaks at $E_{1/2} = 0.54$ and 0.89 V.

The cyclic TTF derivatives *cis*-**9** ($E^1_{1/2} = 0.39$ V), *trans*-**9** ($E^1_{1/2} = 0.44$ V) and **10** ($E^1_{1/2} = 0.49$ V) have a considerably lower first halfwave potential than the TTF synthon **8b** ($E^1_{1/2} = 0.65$ V) or the noncyclic bis-TTF **11** ($E^1_{1/2} = 0.54$ V). This phenomenon is probably explained by a possible interaction between the radical cation and the π-system in the diphenylmethane moiety resulting in a stabilization of the radical cation.

Conclusion

It can be concluded that the synthetic method, using triethyl phosphite as a coupling agent for the xylylenedithio-bis-1,3-dithiol-2-ones described here, gives rise exclusively to intramolecular coupled cyclophanes in good yields. Decreasing the length of the spacer on going from the *para* to the *ortho* analog does not favor intermolecular cyclization as reported from other systems. Apparently the length of the linker as well as its geometry have a profound influence on the course of this type of coupling reaction. Therefore, a general method for preparing tetrathiafulvalenophanes with more than one TTF moiety requires a strategy involving a preformed TTF building block. In this work, we have demonstrated that the use of cyanoethyl-protected TTF-thiolate is efficient for the preparation of cyclophanes containing either one or two TTF units. An electrochemical *cis*/*trans* isomerization of **9** was observed starting either from the *cis* or from the *trans* isomer. A cyclic voltammetry study of **9** at different scan rates allowed a better understanding of chemical reactions coupled with redox processes.

Experimental Section

General.[12] X-ray structures were determined with an Enraf-Nonius MACH3 four circles diffractometer. Crystal data for *cis*-**9**: $C_{23}H_{20}S_8$, $M = 552.89$, red needles, monoclinic $P2_1/c$, $a = 5.923(6)$, $b = 17.559(11)$, $c = 23.972(12)$ Å, $\beta = 94.59(5)°$, $V = 2485(2)$ Å^3, $Z = 4$, $\rho_{calc} = 1.478$ g cm^{-3}, λ(Mo Kα) = 0.71073 Å, 7744 reflections ($2 < \theta < 30°$) were collected at 298 K, 2280 reflections with $I > 3\sigma(I)$ were used in the refinements, 280 refined parameters, $R = 0.056$, $Rw = 0.063$.

Crystal data for *trans*-**9**: $C_{23}H_{20}S_8$, $M = 552.89$, yellow plates, triclinic $P\bar{1}$, $a = 8.308(12)$, $b = 10.121(7)$, $c = 16.138(10)$ Å, $\alpha = 76.90(5)$, $\beta = 84.39(8)$, $\gamma = 73.71(7)°$, $V = 1268(1)$ Å^3, $Z = 2$, $\rho_{calc} = 1.448$ g cm^{-3}, λ(Mo Kα) = 0.71073 Å, 7354 reflections ($2 < \theta < 30°$) were collected at 298 K, 4452 reflections with $I > 3\sigma(I)$ were used in the refinements, 280 refined parameters, $R = 0.079$, $Rw = 0.096$.

Cyclic voltammetry was carried out at room temperature with platinum working (0.785 mm^2 surface) and counter electrodes and a standard calomel electrode (SCE) or a Ag/AgCl as reference: 10^{-3} mol L^{-1} of TTF derivatives in a solution of Bu_4NPF_6 (10^{-1} mol L^{-1}) in CH_2Cl_2 or MeCN (purified through basic alumina), scan rate 100 m V s^{-1} unless otherwise stated.

4,4′-(Xylylenedithio)bis(5-carbomethoxy-1,3-dithiole-2-thiones) (2a−c). General Procedure. To a stirred suspension of **1** (1.96 g, 5.50 mmol) in degassed acetone (25 mL) was added dibromoxylene (0.66 g, 2.50 mmol) in one lot. The reaction mixture was stirred at room temperature under N_2 for 45 min. The precipitate was filtered off, washed with 2×50 mL water, and dried in air. The products were all pure for practical use (NMR and TLC).

2a: 1.30 g, 95%. Yellow crystals, mp 203−204 °C (toluene). IR (KBr) (cm^{-1}) 1703, 1482, 1257, 1072. MS: m/z 550 (M$^+$, 31), 327 (16), 238 (23), 191 (100). ^{1}H-NMR ($CDCl_3$) δ 7.36 (m, 4 H), 4.37 (s, 4 H), 3.84 (s, 6 H). Anal. Calcd for $C_{18}H_{14}O_4S_8$: C, 39.25; H, 2.56. Found: C, 39.57; H, 2.68.

2b: 1.29 g, 94%. Yellow crystals, mp 168−169 °C (toluene). IR (KBr) (cm^{-1}) 1703, 1481, 1259, 1070. MS: m/z 550 (M$^+$, 53), 486 (23), 360 (7), 327 (100). ^{1}H-NMR ($CDCl_3$) δ 7.41 (s, 1

(12) See the general experimental section in ref 6d.

(13) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

H), 7.35 (s, 3 H), 4.21 (s, 4H), 3.85 (s, 6 H). Anal. Calcd for $C_{18}H_{14}O_4S_8$: C, 39.25; H, 2.56. Found: C, 39.61; H, 2.60.

2c: 1.32 g, 96%. Yellow crystals, mp 210−211 °C (toluene). IR (KBr) (cm^{-1}): 1703, 1477, 1259, 1070. MS: *m/z* 550 (M^+, 33), 486 (7), 360 (7), 327 (100). ^{1}H-NMR ($CDCl_3$) δ 7.38 (s, 4 H), 4.21 (s, 4 H), 3.85 (s, 6H). Calcd for $C_{18}H_{14}O_4S_8$: C, 39.25; H, 2.56. Found: C, 39.57; H, 2.62.

4,4′-(Xylylenedithio)bis(5-carbomethoxy-1,3-dithiol-2-ones) (3a−c). General Procedure. A solution of $Hg(OAc)_2$ (0.96 g, 3.0 mmol) in AcOH (100 mL) was added to a stirred solution of the thiones (**2a−c**) (0.55 g, 1.0 mmol) in $CHCl_3$ (100 mL). The mixture was stirred at room temperature for 30 min, and the white precipitate was filtered off using Celite. The filtrate was washed with aqueous bicarbonate (3 × 150 mL) and water (2 × 100 mL). After drying with Na_2SO_4, the solvent was removed in vacuo to give off-white crystalline products. The products were all pure for practical use (NMR and TLC).

3a: yield 0.45 g, 87%, off-white crystals, mp 188−189 °C (toluene). IR (KBr) (cm^{-1}) 1701, 1658, 1489, 1261, 1092. MS: *m/z* 518 (M^+, 14), 311 (36), 191 (43), 135 (100). ^{1}H-NMR ($CDCl_3$) δ 7.35 (m, 4 H), 4.35 (s, 4 H), 3.83 (s, 6 H). Calcd for $C_{18}8H_{14}O_6S_6$: C, 41.68; H, 2.72. Found: C, 41.82; H, 2.75.

3b: yield 0.47 g, 91%, off-white crystals, mp 168−169 °C (toluene). IR (KBr) (cm^{-1}) 1702, 1658, 1489, 1262, 1092. MS: *m/z* 518 (M^+, 38), 311 (100), 281 (43), 251 (67), 219 (95). ^{1}H-NMR ($CDCl_3$) δ 7.40 (s, 1 H), 7.33 (s, 3H), 4.20 (s, 4H), 3.84 (6H, s). Calcd for $C_{18}H_{14}O_6S_6$: C, 41.68; H, 2.72. Found: C, 41.81; H, 2.82.

3c: yield 0.48 g, 93%, off-white crystals, mp 185−186 °C (toluene). IR (KBr) (cm^{-1}) 1700, 1659, 1490, 1264, 1092. MS: *m/z* 518 (M^+, 10), 311 (100), 283 (52), 281 (48), 251 (48), 207 (43). ^{1}H-NMR ($CDCl_3$) δ 7.36 (s, 4 H), 4.19 (s, 4 H), 3.84 (s, 6 H). Calcd for $C_{18}H_{14}O_6S_6$: C, 41.68; H, 2.72. Found: C, 41.66; H, 2.72.

[2]Metacyclo-1,10-dithia[2]((3,6)-dicarbomethoxy(2,7)-tetrathiafulvaleno)phane (4b). To a stirred solution of the dione **3b** (1.96 g, 3.66 mmol) in toluene (200 mL) under N_2 was introduced freshly distilled $P(OEt)_3$ (20.0 mL, 0.12 mol). After refluxing for 10 h, the solvent was removed in vacuo . The red precipitate was subjected to column chromatography (silica, CH_2Cl_2−hexane 3:1). The pale yellow band was collected, and a crystalline product was obtained. Yield: 0.76 g, 43%. Recrystallized from glacial acetic acid for microanalysis. Yellow-orange crystals, mp 233 °C. IR (KBr) (cm^{-1}) 1698, 1495, 1433, 1251, 1075. MS: *m/z* 486 (M^+, 100), 410 (10), 382 (7), 267 (45), 105 (34). ^{1}H-NMR ($CDCl_3$) δ 7.57 (broad s, 1 H), 7.30−7.20 (m, 3 H), 4.29 (d, 2 H, J = 14.7), 4.02 (d, 2 H, J = 14.7), 3.78 (s, 6 H). ^{13}C-NMR ($CDCl_3$) δ 160.15, 142.23, 137.53, 135.17, 129.29, 128.00, 126.93, 121.62, 52.38, 40.77. Anal. Calcd for $C_{18}H_{14}O_4S_6$: C, 44.42; H, 3.00; S, 39.54. Found: C, 44.51; H, 2.87; S, 39.62.

[2]Paracyclo-1,10-dithia[2]((3,6)-dicarbomethoxy(2,7)-tetrathiafulvaleno)phane (4c). To a stirred solution of the dione **3c** (2.22 g, 4.28 mmol) in toluene (200 mL) under N_2 was introduced freshly destilled $P(OEt)_3$ (20.0 mL, 0.12 mol). After refluxing for 10 h, the solvent was removed in vacuo. The red precipitate was subjected to column chromatography (silica, CH_2Cl_2−hexane 3:1). The yellow band was collected, and a crystalline product was obtained. Yield: 1.00 g, 48%. Recrystallized once from glacial acetic acid for microanalysis. Yellow-orange crystals, mp 224 °C. IR (KBr) (cm^{-1}) 1725, 1697, 1511, 1490, 1432, 1241. MS: *m/z* 486 (M^+, 100), 382 (90), 235 (98), 218 (32). ^{1}H-NMR ($CDCl_3$) δ 7.480−7.485 (m, 2H), 6.755−6.760 (m, 2H), 4.19 (d, 2H, J = 13.2), 4.07 (d, 2H, J = 13.2), 3.87 (s, 6H). ^{13}C-NMR ($CDCl_3$) δ 160.15, 139.49, 135.82, 128.36, 128.15, 125.14, 52.62, 40.79. Anal. Calcd for $C_{18}H_{14}O_4S_6$: C, 44.42; H, 3.00; S, 39.54. Found: C, 44.46; H, 2.87; S, 39.45.

[2]Paracyclo-1,10-dithia[2](2,7)tetrathiafulvalenophane (5). A solution of **4c** (0.27 g, 0.56 mmol) and $CsOH\cdot H_2O$ (0.19 g, 1.13 mmol) in dioxane (10 mL) and water (5 mL) was stirred for 1 h. The solution was then poured into aqueous HCl to give an orange precipitate. The precipitate was filtered off, washed with water, and dried in vacuo. The intermediate acid was then heated in diglyme from 140 °C to the boiling point over a 15 min period. After the boiling point was reached the heating was continued for an additional 5 min. The light brown solution was cooled down to room temperature and poured into water (100 mL) to give a yellow suspension. In order to be able to filter off the product, a small amount of KCl was added, and the suspension was gently heated. By this treatment a pale yellow product precipitated and could be filtered off. The product was washed with water (50 mL) and dried in vacuo before it was taken up in CH_2Cl_2 and filtered through a short layer of silica. The solvent was removed in vacuo to give pale yellow needles. Yield: 0.12 g, 58%, mp >184 °C dec. IR (KBr) (cm^{-1}) 1630, 1506, 1425. MS: *m/z* 370 (M^+, 87), 306 (30), 266 (100), 177 (53). λ_{max}(log ϵ): CH_2Cl_2, 324 nm (3.81). ^{1}H-NMR ($CDCl_3$) δ 7.470−7.475 (m, 2H), 6.668−6.673 (t, 2H, J = 1.0), 3.91 (d, 2H, J = 12.0), 3.83 (d, 2H, J = 12.0). ^{13}C-NMR ($CDCl_3$) δ 135.24, 130.58, 129.28, 127.81, 127.21, 124.63, 41.32. Anal. Calcd for $C_{14}H_{10}S_6$: C, 45.37; H, 2.72; S, 51.92. Found: C, 45.52; H, 2.90; S, 51.50.

4-[(2-Cyanoethyl)thio]-5-(methoxycarbonyl)-1,3-dithiol-2-one (7a). To a solution of 4-[(2-cyanoethyl)thio]-5-(methoxycarbonyl)-1,3-dithiole-2-thione (**6a**) (5.21 g, 18.8 mmol) in a mixture of chloroform (200 mL) and glacial acetic acid (100 mL) was added $Hg(OAc)_2$ (11.97 g, 37.6 mmol). The reaction mixture was stirred for 2 h whereupon the white precipitate was filtered off using a pad of Celite. The filtrate was washed with a saturated bicarbonate solution (3 × 100 mL) and with water (2 × 100 mL). After drying ($MgSO_4$) the solvent was removed *in vacuo*. Recrystallization from ethanol afforded **7a** as colorless needles. Yield: 4.24 g (86%), mp 152 °C. IR (KBr) (cm^{-1}): 2249, 1785, 1708, 1658, 1478. MS: *m/z* 261 (M^+, 100), 130 (60), 88 (80), 59 (50). ^{1}H-NMR ($CDCl_3$) δ (t, 2H, J = 7.1), 3.25 (t, 2H, J = 7.1), 3.87 (s, 3H). Anal. Calcd for $C_8H_7NO_3S_3$: C, 36.77; H, 2.70; S, 36.80. Found: C, 36.74; H, 2.69; S, 36.60.

4-[(2-Cyanoethyl)thio]-5-(methylthio)-1,3-dithiol-2-one (7b). To a solution of 4-[(2-(cyanoethyl)thio]-5-(methylthio)-1,3-dithiole-2-thione (**6b**) (3.87 g, 14.6 mmol) in a mixture of chloroform (150 mL) and glacial acetic acid (75 mL) was added $Hg(OAc)_2$ (9.30 g, 29.2 mmol). The reaction mixture was stirred for 2 h whereupon the white precipitate was filtered off using a pad of Celite. The filtrate was washed with a saturated bicarbonate solution (3 × 100 mL) and with water (2 × 100 mL). After drying ($MgSO_4$), the solvent was removed *in vacuo*. Recrystallization from toluene−cyclohexane afforded colorless nedles of **7b**. Yield 3.00 g (82%), mp 61−62 °C. IR (KBr) (cm^{-1}): 2247, 1662, 1657, 1621, 1481, 1415. MS: *m/z* 249 (M^+, 43), 91 (100), 88 (29). ^{1}H-NMR ($CDCl_3$) δ 2.52 (s, 3H), 2.74 (t, 2H, J = 7.0), 3.07 (t, 2H, J = 7.0). Anal. Calcd for $C_7H_7ONS_4$: C, 33.71; H, 2.83; N, 5.62. Found: C, 33.71; H, 2.86; N, 5.66.

2,6(7)-Bis[(2-cyanoethyl)thio]-3,7(6)-bis(methoxycarbonyl)tetrathiafulvalene (8a). 4-[(2-Cyanoethyl)thio]-5-(methoxycarbonyl)-1,3-dithiol-2-one (**7a**) (9.72 g, 37.2 mmol) was refluxed in a mixture of benzene (150 mL) and triethylphosphite (20 mL) for 20 h. After cooling to room temperature the precipitate was filtered off, washed with methanol (3 × 100 mL), and dried *in vacuo*. Yield 6.6 g (72%), orange powder, mp >250 °C dec. IR (KBr) (cm^{-1}): 2250, 1698, 1495, 1434, 1259. MS: *m/z* 490 (M^+, 84), 451 (36), 289 (100), 88 (58). ^{1}H-NMR ($CDCl_3$) δ 2.80 (t, 2H, J = 7.3), 3.27 (m, 2H), 3.82 (s, 3H). Anal. Calcd for: $C_{16}H_{14}N_2O_4S_6$: C, 39.17; H, 2.88; N, 5.71. Found: C, 39.42; H, 2.87; N, 5.65.

2,6(7)-Bis[(2-cyanoethyl)thio]-3,7(6)-bis(methylthio)-tetrathiafulvalene (8b). 4-[(2-cyanoethyl)thio]-5-(methylthio)-1,3-dithiol-2-one (**7b**) (5.76 g, 23.1 mmol) was heated to 110 °C in triethyl phosphite (25 mL) for 45 min. During heating, an orange product started to precipitate. After cooling to room temperature, methanol (50 mL) was added and the orange precipitate was filtered off. The product was washed with methanol (3 × 100 mL) and dried. Yield 3.75 g (70%), mp 181−183 °C (MeCN). IR (KBr) (cm^{-1}): 2922, 2250, 1727, 1631, 1495, 1424, 1321. MS: *m/z* 466 (M^+, 100), 412 (39), 277 (29), 223 (32), 91 (50). ^{1}H-NMR ($CDCl_3$) δ 2.45 (s, 3H), 2.71 (t, 2H, J = 7.1), 3.03 (t, 2H, J = 7.1). Anal. Calcd for $C_{14}H_{14}N_2S_8$: C, 36.03; H, 3.02; N, 6.00. Found: C, 36.17; H, 3.09; N, 5.98.

***cis/trans*-1,7-Dithio[2.1]paracyclo[2](3,6(7))bis(methylthio)(2,7(6))tetrathiafulvalenophane (9).** To a solution of a mixture of TTF **8b** (0.466 g, 1.0 mmol) in anhydrous degassed DMF (40 mL) was added a solution of $CsOH·H_2O$ (0.376 g, 2.2 mmol) in anhydrous degassed MeOH (10 mL) over a period of 10 min. After an additional stirring of 15 min, this solution and a solution of bis[4-(bromomethyl)phenyl]methane (0.354 g, 1.0 mmol) in anhydrous degassed DMF (50 mL) were added simultaneously, during 10 h at room temperature to 50 mL of anhydrous degassed DMF, under high dilution conditions using a perfusor pump. Stirring was continued for additional 5 h, and the reaction mixture was concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2 (150 mL) and washed with water (3 × 50 mL). After drying ($MgSO_4$), the solution was concentrated *in vacuo* affording a residue which was purified by column chromatography on silica gel (CH_2Cl_2/petroleum ether 60−80 °C 1:1, $R_f = 0.62$). Yield 0.39 g (71%), an orange powder (mixture of the *cis* and *trans* isomers of paracyclotetrathiafulvalenophane **9**). Recrystallization from CH_2Cl_2/hexane gave, after one night at 4 °C, 0.27 g of a mixture of red and yellow needles. Concentration of the mother liquor followed by recrystallization from CH_2Cl_2/hexane, after one night at room temperature, afforded an additional crop of 40 mg of a mixture of red needles and yellow plates.

cis-**9** (red): mp 192−194 °C. IR (KBr) (cm^{-1}): 2918, 1616, 1508, 1422, 1110, 894, 820, 771. PDMS: $m/z = 552.9$ ($M^{+\cdot}$); calcd for $C_{23}H_{20}S_8$, 552.89. ^{1}H-NMR ($CDCl_3$) δ 2.44 (s, 6H), 3.86 (s, 4H + 2H), 7.18 (d, 4H, $J = 8.1$), 7.28 (d, 4H, $J = 8.1$).

trans-**9** (yellow): mp 210−212 °C. IR (KBr) (cm^{-1}): 2917, 1611, 1510, 1427, 1199, 1108, 968, 891, 876, 818, 774. PDMS: $m/z = 552.9$ ($M^{+\cdot}$); calcd for $C_{23}H_{20}S_8$, 552.89. ^{1}H-NMR ($CDCl_3$) δ 2.26 (s, 6H), 3.78 (s, 2H), 3.84 (d, 2H, $J = 13.3$), 4.09 (d, 2H, $J = 13.3$), 6.84 (d, 4H, $J = 8.1$), 7.27 (d, 4H, $J = 8.1$). Anal. Calcd for $C_{23}H_{20}S_8H$: C, 49.97; H, 3.65; S, 46.39. Found (mixture of *cis/trans*): C, 50.10; H, 3.63; S, 46.15.

Bis[4-[[[3′(4′)-[(2-cyanoethyl)thio]-4,4′(3′)-bis(methylthio)tetrathiafulvalen-3-yl]thio]methyl]phenyl]methane (11). To a solution of TTF **8b** (*cis/trans*) (0.979 g, 2.1 mmol) in anhydrous degassed DMF (100 mL) was added dropwise a solution of $CsOH·H_2O$ (0.390 g, 2.3 mmol) in anhydrous degassed MeOH (25 mL) over a period of 3 h. Then a solution of bis[4-(bromomethyl)phenyl]methane (0.354 g, 1.0 mmol) in anhydrous degassed DMF (20 mL) was added dropwise during 1 h. This reaction mixture was stirred at room temperature overnight. The solvent was removed *in vacuo*, and the resulting residue was dissolved in CH_2Cl_2 (200 mL), washed with water (3 × 50 mL), dried ($MgSO_4$), and concentrated *in vacuo* to afford a brown oil which was subjected to column chromatography (silica gel, CH_2Cl_2), affording 0.55 g (54%) of an orange foam of bis-TTF **11**: $R_f = 0.68$. Mp 52−54 °C. Compound **11**: IR (KBr) (cm^{-1}): 2920, 2251 (CN), 1510, 1419, 908. PDMS: $m/z = 1019.8$ ($M^{+\cdot}$); calcd for $C_{37}H_{34}N_2S_{16}$, 1019.65. ^{1}H-NMR ($CDCl_3$) δ 2.20 (s, 6H), 2.47 (s, 6H), 2.69 (t, 4H, $J = 7.2$), 3.01 (t, 4H, $J = 7.2$), 3.93 (s, 2H), 3.97 (s, 4H), 7.11 (d, 4H, $J = 8.1$), 7.22 (d, 4H, $J = 8.1$). Anal. Calcd for $C_{37}H_{34}N_2S_{16}$: C, 43.62; H, 3.37; N, 2.75; S, 50.26. Found: C, 43.72; H, 3.38; N, 2.69; S, 50.50.

***cis/trans*-1,17,28,44-Tetrathio[2.1]paracyclo[2](3,6)bis(methylthio)(2,7)tetrathiafulvaleno[2.1]paracyclo-[2](3,6)-bis(methylthio)(2,7)tetrathiafulvalenophane (10).** To a solution of TTF (*cis/trans*) **11** (0.52 g, 0.51 mmol) in anhydrous degassed DMF (25 mL) was added a solution of $CsOH·H_2O$ (0.205 g, 1.22 mmol) in anhydrous degassed MeOH (5 mL) over a period of 15 min. This solution and a solution of bis[4-(bromomethyl)phenyl]methane (0.181 g, 0.51 mmol) in anhydrous degassed DMF (30 mL) were added simultaneously, during 10 h at room temperature with stirring, to 50 mL of anhydrous degassed DMF, using a perfusor pump. Stirring was continued for additional 5 h and the reaction mixture concentrated *in vacuo*. The residue was then dissolved in CH_2Cl_2 (150 mL) and washed with water (3 × 50 mL). The organic phase was dried ($MgSO_4$) and concentrated *in vacuo* to afford a residue which was purified by column chromatography (silica gel, CH_2Cl_2/petroleum ether 60−80 °C, 1:1), affording an orange-brown powder, 0.31 g (55%) of a mixture isomers of TTF macrocycle **10**. Decomposition without melting between 163−166 °C. IR (KBr) (cm^{-1}): 2918, 1615, 1510, 1420, 889, 772. PDMS: $m/z = 1105.5$ ($M^{+\cdot}$); calcd for $C_{46}H_{40}S_{16}$, 1105.78. ^{1}H-NMR ($CDCl_3$) δ 2.04, 2.12, 2.14 (3s, 12H), 3.91, 3.92, 3.93 (3s, 12H), 7.07 (d, 8H, $J = 8$), 7.20 (d, 8H, $J = 8$). ^{13}C-NMR ($CDCl_3$) δ 19.11, 19.14, 40.29, 41.26, 110.63, 124.36, 129.07, 129.10, 129.12, 129.19, 129.25, 134.81, 135.07, 140.30, 140.35. Anal. Calcd for $C_{46}H_{40}S_{16}$: C, 49.97; H, 3.65; S, 46.39. Found: C, 50.25 H, 3.84; S, 43.45.

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